GELS FROM BORATE-CROSSLINKED PARTIALLY HYDROLYZED POLY(VINYL ACETATE)S: CHARACTERIZATION OF PHYSICAL AND CHEMICAL PROPERTIES AND APPLICATIONS IN ART CONSERVATION

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By

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GELS FROM BORATE-CROSSLINKED PARTIALLY HYDROLYZED POLY(VINYL ACETATE)S: CHARACTERIZATION OF PHYSICAL AND CHEMICAL PROPERTIES AND APPLICATIONS IN ART CONSERVATION

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ABSTRACT

The formation of gel-like dispersions from borate-crosslinked, partially hydrolyzed poly(vinyl acetate)s (xPVAc, where x is the percent of hydrolysis) and their application for treatment of art is explored. It is shown that gels can be prepared in organic liquid/water mixtures with organic portions up to 75 wt %; gels prepared from poly(vinyl alcohol) can form only when the organic fraction is \( \leq 25 \) wt %. Variables including the degree of hydrolysis, molecular weight, crosslink density, and the type of crosslinking agent (especially borax), as well as the proportion of organic liquid, are examined. Melting range and rheological studies of the materials show that the organic liquids confer higher thermal stability and longer relaxation times to the gel networks. These effects are explored using \(^{11}\)B NMR spectroscopy, differential scanning calorimetry, and small angle neutron scattering. It is shown that addition of an organic liquid causes an increase in the number of crosslinks in the gel network and agglomeration of the polymer chains into bundles. Modifications of the gels which are relevant to their application in art conservation, such as addition of chelating agents and short-chain glycol ethers, are explored. An alternative crosslinker, trimethyl borate, is demonstrated to form water-sensitive organogels.

xPVAc-borate gels are shown to be appropriate for conservation treatments in several case studies. The gels can be prepared with solvents used by conservators, including ethanol, 1-
propanol, 2-propanol, and acetone. Their rheological characteristics allow the gels to conform to the topography of complex artwork surfaces and to be removed with ease by being lifted from the surface. It is demonstrated that no detectable residual polymer or crosslinker is deposited on the treated surface if the softened varnish or coating is removed after treatment with the gel. Examination of the lateral and orthogonal spread of solvent in the gels shows that the liquid is constrained within the area on which the gel is applied and that diffusion into sublayers can be controlled. Studies of the materials removed from a varnished oil-painting suggest that the gels act by softening the varnish layer and facilitate its removal by a swab moistened with a mild solvent.
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Наздраве!
Lora V. Angelova
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LIST OF ABBREVIATIONS

1°, 2°, 3°  primary, secondary, tertiary

40PVAc  40% hydrolyzed poly(vinyl acetate)

45PVAc  45% hydrolyzed poly(vinyl acetate)

75PVAc  75% hydrolyzed poly(vinyl acetate)

80PVAc_l 80% hydrolyzed poly(vinyl acetate) with high molecular weight (47300 Da)

80PVAc_l 80% hydrolyzed poly(vinyl acetate) with low molecular weight (21100 Da)

80PVAc_l 80% hydrolyzed poly(vinyl acetate) with medium molecular weight (35600 Da)

AC  ammonium carbonate

AFM  atomic force microscopy

ATR  attenuated total reflectance

B, B'  boric acid, borate ion

C*  overlap concentration of a polymer solution

CA  citric acid

CA-PVAx  poly(vinyl alcohol) substituted with citric acid where x is the percent substitution

CDCl3  deuterated chloroform

CG  clear gel

C_N  concentration of network formation

CP  cross-polarized

D_2O  deuterium oxide

DB  Debye-Bueche model
DEGMBE  diethylene glycol monobutyl ether
DEGMEE  diethylene glycol monomethyl ether
DEGMME  diethylene glycol monomethyl ether
DLS     dynamic light scattering
DMF     dimethyl formamide
DMSO    dimethyl sulfoxide
DSC     differential scanning calorimetry
EDTA    ethylenediaminetetraacetic acid
EPF     3-epoxypropoxyfluorescein
F₃B-O(C₂H₅)₂ boron trifluoride diethyl etherate
FID     free-induction decay
FT      Fourier transform
FWI     free water index
G’      storage modulus
G”     loss modulus
GALDI   graphite-assisted laser desorption/ionization
GC      gas chromatography
HETCOR  heteronuclear correlation
HPLC    high pressure liquid chromatography
HVPD    high-viscosity polymeric dispersion
ICP     inductively coupled plasma
IR      infrared spectroscopy
IRUG  Infrared and Raman Users Group
L    ligand
M    metal
MALDI  matrix-assisted laser desorption/ionization
MAS  magic angle spinning
MCP  modular cleaning program
MS  mass spectrometry
M_w  weight-averaged molecular weight
N.B.  nota bene
N/M  not miscible
NaH  sodium hydride
NGA  National Gallery of Art, Washington, D.C.
NMP  N-methylpyrrolidone
NMR  nuclear magnetic resonance spectroscopy
OG  opaque gel
OZ  Ornstein-Zernicke modeling
PAFA  Pennsylvania Academy of Fine Arts
PBA  phenyl boronic acid
PVA  poly(vinyl alcohol)
PVAc  poly(vinyl acetate)
PY  Percus-Yevick approximation
Py  pyrolysis
R.I.  
refractive index

$R_G$  
radius of gyration

SAAM  
Smithsonian American Art Museum

SANS  
small angle neutron scattering

SEC  
size exclusion chromatography

SEM  
scanning electron microscopy

SIE  
secondary isotope effect

SPME  
solid phase microextraction

TAC  
triammonium citrate

TEGMEE  
triethylene glycol monomethyl ether

TG  
translucent gel

TGA  
thermogravimetric analysis

TMB  
trimethyl borate

ToF-SIMS  
time-of-flight secondary ion mass spectrometry

TSC  
trisodium citrate

UV  
ultraviolet light

Vis  
visible light

wPLMG  
windowed phase-modulated Lee-Goldberg

wt %  
weight percent

xPVAc  
partially hydrolyzed poly(vinyl acetate) where x is the percent of hydrolysis

xPVAc-EPF  
partially hydrolyzed poly(vinyl acetate) with covalently bound fluorescein
xPVA_y  alkanoate substitute poly(vinyl alcohol) where x is the percent alkanoate substitution and y is the length of the alkanoate chain

XRD  X-ray diffraction

XRF  X-ray fluorescence

$\Delta H^\dagger$  activation enthalpy
LIST OF PUBLICATIONS


CONFERENCE PROCEEDINGS


1. INTRODUCTION TO HERITAGE CONSERVATION SCIENCE

1.1. Introduction to conservation treatments.

Heritage conservation science covers a broad spectrum of research topics related to cultural heritage preservation. Scientists working in the field study the composition, properties, and historical uses of pigments and materials, their degradation pathways and the environments necessary for hindering these processes. They design new analytical and imaging techniques for the study of artists’ materials and the non-invasive probing of artworks, create novel, stable paints, varnishes, binders, and adhesives for use by artists and conservators, and examine the effects of cleaning treatments on a vastly diverse body of objects and paintings. This last field of research – conservation treatment methods and their effects – has generated much discussion in the past, leading to intense scrutiny of treatment techniques, how they act, how they can be improved, and what is the nature of their long-term consequences on the cleaned object.

Cleaning treatments for paintings, frames, and some objects may involve the partial or complete removal of the top-most surface layer from the artwork. Generally, this is a layer of spirit or oil varnish, applied to protect a paint film, gold leaf, or structural material (wood, marble, etc.) as well as to saturate the colors of a painted image and provide gloss. More recently, synthetic polymer varnishes have also been applied for the same purposes. Both traditional and modern varnishes are transparent, mechanically-flexible materials which can undergo autoxidation and crosslinking reactions that result in yellowing, cracking, and embrittlement, thus rendering useless their protective and aesthetic functions. Grime, dirt, and soot can accumulate on artwork surfaces. Nicotine layers from cigarette smoke in studios and...
galleries, animal glue from consolidations, overpaint applied by previous restorations which may age and discolor at a different pace than the original paint, as well as drying oils rubbed into the paint surface all may need to be removed. Finally, surfactants from acrylic paints tend to migrate to the surface of artworks, resulting in a powdery haze which obscures the color and texture of the paint.\textsuperscript{12-17}

Due to these processes, the stability and aesthetic quality of cultural heritage works can be impaired and restoration campaigns must be undertaken to remove aged coatings partially or completely, or to clean the surface from accumulated pollutants prior to the re-application of fresh protective coatings. The removal of these materials can be mechanical through the use of specialized cloths and erasers, dusting, or simple rubbing off of the varnish in the event that it is flaked on a structurally sound paint layer. Removal can also be achieved through chemical means by the use of wet cleaning methods such as organic liquids, aqueous solutions containing enzymes, surfactants, buffers, and chelators, microemulsions, gels, poultices, and soaps.

Organic solvents are most commonly employed to remove discolored, oxidized varnish coatings from artworks. Unlike the highly crosslinked nature of the oil binder used in many paints, natural varnishes are composed of tree resins (terpenoid and phenolic compounds)\textsuperscript{18} which remain soluble in many organic liquids.\textsuperscript{2} With age, the increase in polarity of the top-most varnish layer, due to oxidation reactions, results in a need for treatment with more polar organic solvents and even aqueous systems. Aqueous systems are also used for the removal of dirt and grime and have become increasingly popular due to the wide range of available aqueous cleaning agents, such as chelators, surfactants, and microemulsions that can be prepared for this application, and because of reduced health and environmental risks associated with such systems.
The potential of organic solvents to leach out soluble components from the paint film beneath the surface layers to be removed has been a topic of great interest. Investigations of this issue have been extensive over the past two decades and have also included studies on the changes in surface morphology due to cleaning treatment as well as the loss of original paint components (surfactants, plasticizers, etc.) during the cleaning of acrylic paints. The vast array of materials under investigation is complicated further by the changes most artists’ materials tend to undergo due to interactions with pigments, with each other and due to aging, the extent of which depend greatly on the storage environment and treatment history of the artwork. Because artists sometimes make complex mixtures of unrecorded materials to achieve a specific quality of the paint, and the compositions of many commercially sold paints are of a proprietary nature, component analysis prior to any investigation into the effects of conservation treatments is desirable. Conservation research is performed on systems with controlled variables, such as paint-outs of known composition that are artificially aged. These artificial systems do not necessarily reflect the real compositions of works of art but they shed some light, albeit limited, on the processes occurring in real systems during both aging and conservation treatments.

Understanding the complex chemical and physical properties of materials in artworks is necessary for their preservation. Investigation into the processes that occur with the use of solvents and other cleaning agents during conservation treatments require an array of instrumental techniques capable of detecting and identifying minute amounts of samples, preferably in a non-destructive manner. Techniques such as gas chromatography/mass spectrometry (GC/MS) and liquid chromatography/mass spectrometry (LC/MS) in all of their incarnations (matrix-assisted laser desorption/ionization (MALDI), time-of-flight secondary ion
MS (ToF-SIMS), graphite-assisted laser desorption/ionization (GALDI), solid phase microextraction (SPME), pyrolysis, high pressure LC (HPLC), capillary electrophoresis (CE), inductively coupled plasma (ICP), size exclusion chromatography (SEC), etc.\textsuperscript{10} have been adapted for use in the heritage science community, and methods for the identification of artists’ materials based on markers in each of the different classes of organic materials used (natural resins, proteins, glycerolipids, polysaccharides, waxes, bituminous materials, polymers, and organic dyes)\textsuperscript{18} have been developed. A growing database of infrared spectra of both fresh and aged materials has been organized,\textsuperscript{20} and attenuated total reflectance Fourier transform IR (ATR-FTIR) imaging has recently been used in the analysis of cross-sections from works of art.\textsuperscript{21} Scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction (XRD) and X-ray fluorescence (XRF), neturon scattering, Raman spectroscopy and confocal microscopy, UV/Vis and fluorescence spectroscopy, differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA), terahertz spectroscopy, fluorescence microscopy, and likely most other analytical techniques used in chemistry, physics, and biology are currently in use or being developed for heritage conservation science today. The need for non-invasive analysis in the field and the lack of laboratory instrumentation in most museums have also been driving forces for the development of many instruments into ‘hand-held’ or mobile devices. Most recently, even nuclear magnetic resonance (NMR) has found use as a non-destructive surface analytical tool in the form of the ‘NMR MOUSE’.\textsuperscript{22-25}

Alongside the need for understanding how conservation treatments work and their effects on all compositional materials in the treated artwork, another issue concerning the available treatment methods prior to the 1980’s was raised. Emerging from the debates surrounding
several high-profile conservation treatments, the question of control over the cleaning action became central to the field.\textsuperscript{1} Available conservation methods seemed to lack the potential for a controlled cleaning of the surface layers; little was known regarding which specific materials were being removed and at what rate. The concept of unpacking the surface of an artwork, layer-by-layer, was introduced by Richard Wolbers around this time to address the issue. Wolbers’s aqueous cleaning methods, which include addition of enzymes, chelators, and surfactants to the cleaning solutions, as well as variations in the pH and, more recently, the conductivity of the cleaning solutions, are intended to tune the cleaning action to the varying degrees of oxidation a conservator may encounter while uncovering different surfaces during a conservation treatment.\textsuperscript{17,26,27}

1.2. Use of gels in conservation treatments.

The aqueous cleaning toolbox introduced by Richard Wolbers included aqueous gels, which could also be prepared to contain enzymes, some additional organic solvents, and surfactants.\textsuperscript{26,28,29} Solvent poultices (prepared from cellulosic materials) and thickened pastes (from waxes) containing an organic solvent have been used in conservation treatments since the first half of the twentieth century.\textsuperscript{29} The introduction of aqueous and solvent gels by Wolbers, however, allowed for a broader spectrum of liquids and cleaning agents to be incorporated into the gels, providing access to the controlled cleaning action sought after by many conservators.

Although conservators will still use free flowing and volatile liquids for most treatments, gels have been useful for some applications. A solvent encapsulated in a gel can be delivered to a very specific location, allowing for a confined cleaning action, which is sometimes difficult
when using free liquids; the gels can also be placed on vertical surfaces for treatment of sculptures and frescos, and they can be delivered to topographically complex surfaces, such as paint impasto that may be difficult to reach with a swab. The solvent is less likely to flow into paint craquelure and will remain on the surface longer than when applied freely because it is held in place by capillary action.\textsuperscript{29} Gels do not require as much mechanical action on the surface as swab cleaning and are thus more useful for the treatment of sensitive surfaces. An example is painting frames that need to be cleared of aged varnish layers without the disruption of a thinly applied gold leaf layer beneath. Finally, gelated liquids tend to be far more efficient at softening tough layers of overpaint or mixed, aged varnishes than free solvents.\textsuperscript{29} Although this property has been attributed to the longer contact times of the solvent with the surface, recent studies tend to suggest that the gel network also aids in the cleaning action, possibly acting as a “co-solvent” in the system.

The aqueous gels introduced by Wolbers are prepared from an allyl sucrose crosslinked poly(acrylic acid) polymer, Carbopol\textsuperscript{TM}, and a non-ionic surfactant which serves as a secondary crosslinker. Carbopols are available in a range of molecular weights but tend to be highly polydisperse;\textsuperscript{30} when dissolved in aqueous solutions, the tightly coiled polymer chains unfurl as the pH is increased, resulting in a rigid microgel.\textsuperscript{31} Dissolving the polymers in non-aqueous solvents necessitates the use of a surfactant with available hydroxy groups.\textsuperscript{31} The two most commonly used surfactants in conservation are ethomeen c/12 (diethanolcocoamine) and ethomeen c/25 (polyethoxylatedcocoamine).\textsuperscript{28} In the presence of ethoxylated non-ionic surfactants, aggregation and gelation is achieved through hydrogen bonding between the carboxylate goups of the polymer and the oxygen of the ethyleneoxide chains.\textsuperscript{31} Because
Carbopol™ gels are of interest in the medical and cosmetic disciplines, their interactions with anionic, cationic, and non-ionic surfactants, the effects of these interactions, the pH and polymer concentration on their rheological and drug delivery capabilities have been thoroughly investigated.30,31

Since their introduction in the 1980s, Carbopol™ gels have found use in many conservation treatments, and have been incorporated into the Modular Cleaning Program (MCP),27,28 a software program which offers a way to combine information of the various chemical properties of cleaning solutions, buffers, surfactants, chelating agents, and gels. Carbopol™ gels have become one of the most commonly used thickened systems in conservation studios as a result of MCP workshops held worldwide. Their introduction also brought to focus several concerns regarding the use of gelated liquids on the surfaces of cultural heritage works, and has therefore been pivotal in establishing standards for other gel systems introduced to the field.

The use of cleaning agents prepared with constituents of low-volatility requires the complete clearance of these agents from the surface after the treatment. Many paintings are re-varnished shortly after the removal of the previous varnish layer, and residual materials from a gel treatment may become trapped on the surface, undergoing detrimental reactions with the paint layer or with the varnish over time. Also, the deposition of surfactants into the paint layers may increase their wettability allowing for increased atmospheric moisture penetration into the artwork.32 Controversies surrounding the clearance of gels from treatment surfaces have been described in detail.1,29 From discussions at conferences, workshops, and in publications that appeared after the introduction of Carbopol™ gels to the conservation community, several
concerns were raised. As outlined by Khandekar, the main questions regarding the use of aqueous gel systems for conservation are:\footnote{1}

1) Are there residues of the gel constituents deposited on the surface after a treatment, and what effects do they have on the materials of the composition?

2) How should the gels be cleared from the surface to avoid or minimize the deposition of gel residues?

3) Do the gels and the clearance procedures result in a leaching of material from the artwork?

4) How do the gels function? Does the gel network contribute to the cleaning mechanism?

5) What methods can be used to study the above questions?

1.3. Statement of the problem.

The body of work described in this dissertation aims to answer these questions for one type of polymeric, organo-aqueous, gel-like system which has been designed specifically for use in art conservation. The materials are not true gels, as discussed in the next chapter, but will be referred to as such throughout this dissertation for the sake of simplicity. Two parallel yet overlapping courses of research were undertaken for this project: (1) the polymeric gels were prepared and studied thoroughly through the use of analytical and physical chemistry methods and instruments in order to determine how the variables in the system affect its overall chemical
structure and physical properties; (2) simultaneously, the materials were tested by conservators and used on test panels and in complex conservation treatments to determine the qualities which were most appropriate for the application and to address the concerns raised above. The structure of the dissertation follows these two branches of research, with an in-depth description of the gel design and properties, followed by an illustration of their applications with a focus on the development of methods which can be used to answer the residue, clearance, and mode of action questions.

The gel system described is prepared through the crosslinking of partially hydrolyzed poly(vinyl acetate) (xPVAc, where x is the percent of hydrolysis) with borate ions. The degree of hydrolysis of the polymer (e.g., 75PVAc polymer has 75% hydroxyl side groups and 25% acetate side groups) affects the compositional requirements for the formation of the gels as well as their properties, and, as such, was one of the first variables explored. Polymers with differing degrees of hydrolysis were obtained from the Kuraray Co., Ltd. The crosslinking agent in the materials, borate, is commonly obtained from borax (sodium tetraborate decahydrate); a second crosslinking method with trimethyl borate will also be described. These gels have very different properties from cellulose or Carbopol™ gels and, as a result, are an additional tool available to conservators. Unlike traditional conservation gels, which are thixotropic and are applied and removed with a swab or a brush, xPVAc gels are viscoelastic and tend to have strain thickening properties, allowing for their removal from a surface by lifting the material in one piece (Figure 1-1). As a result, the potential applications for these materials are different and, in many cases, complementary to traditional gels.

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^ For a brief summary of rheological terms and definitions, see Appendix A.
Figure 1-1. Image demonstrating the difference in consistency of (left) a Carbopol™ gel which is applied to the surface of an acrylic painting with a paint brush and (right) xPVAc-borax gel which is being lifted from the surface of an acrylic painting with tweezers.

In the following sections, an introduction to soft matter, and, specifically, to polymer gels will lead into a summary and literature review of research performed on poly(vinyl alcohol)-borate (PVA-borate) gels. It will lay the foundation for our understanding of gels prepared from partially hydrolyzed poly(vinyl alcohol) and borate ions (xPVAc-borate).
2. INTRODUCTION TO SOFT MATTER AND GELS

Materials designated as “soft condensed matter” are important in many scientific and technological fields and have properties that are different from those of crystalline solids or simple fluids. They include glasses, colloidal dispersions, polymer solutions and melts, liquid crystals, and gels. The most important characteristics that all materials in this category share are: (1) structural and organizational length scales larger than atomic sizes but smaller than what is considered macroscopic; generally dimensions are on the order of tens of nanometers to less than one micrometer; (2) random fluctuations and Brownian motions which constantly affect the position and structure of the materials, and (3) self-assembly (on the molecular level as well as hierarchically to form large, complex supramolecular structures) which occurs due to a complex balance between enthalpic and entropic driving forces as the systems approach equilibrium.\(^{33}\)

Gels are materials composed of a large fraction of liquid immobilized by a macroscopic network of smaller subunits joined together through chemical or physical interactions. These materials are characterized by a discontinuous transition from a sol (a liquid state containing the network subunits in a non-crosslinked state) to a gel (a material with a non-zero shear modulus which exhibits the mechanical properties of a solid yet is highly disordered).\(^{33}\) This transition is known as the sol-gel transition, or the point of gelation. In most cases, the process of gelation (i.e., the moment of sharp transition between the sol and gel states) is not characterized by a macroscopic phase separation into crystalline and liquid phases.\(^{34}\) The process of gelation is due to a balance between the forces controlling subunit aggregation and solvent-gelator solubilization.\(^{34}\)
There are three main types of gels: materials prepared from self-assembled low molecular weight gelators,\textsuperscript{34,35} polymer gels assembled through a surfactant, and crosslinked polymer gels.\textsuperscript{34,36} Gels can be prepared in aqueous or organic media to form hydrogels or organogels, respectively. The structural units composing the gel network can be chemically or physically crosslinked.

The discussion from here forward will focus on polymer hydro- and organo-gels which can, as mentioned above, be formed by either chemical or physical bonds. In chemically crosslinked systems, the covalent bonds responsible for the formation of gels result in non-thermoreversible networks. Chemically crosslinked gels can be prepared through the reaction of small multi-functional units which react to form a three-dimensional network; gels in this category include thermosetting resins and sol-gel glasses.\textsuperscript{33} One type of chemically crosslinked polymers is vulcanized rubbers which, at very high crosslink densities, become glassy.\textsuperscript{33}

Physically crosslinked polymer gels commonly exhibit thermoreversibility (i.e., the network can be destroyed by heating). These types of gels can also be rheoreversible, or returned to the sol state through different stimuli such as pH.\textsuperscript{37} Crosslinks in physical gels can be of a microcrystalline nature, as is commonly found in biological gels where networks are composed of proteins with some regions that can assemble into ordered crystalline groups such as helices or parallel $\beta$-sheets. Alternatively, microphase separated gels are prepared through block-copolymers in which the different polymer types exist as different phases. For example, one block is in a glassy state and the other is rubbery.\textsuperscript{33} Conceptually similar are weak polyelectrolyte gels, prepared from block-copolymers containing hydrophilic, electrolyte forming side-groups, and a smaller fraction of hydrophobic side-groups which “stick” to form
crosslinks when the polymers are dissolved in aqueous media. One of the most exciting classes of physically crosslinked polymer gels is prepared through directional self-assembly, using dynamic interactions such as host-guest complex formation, ionic interactions, or metal-ligand binding, biomimetic interactions, and stereocomplex formation. Figure 2-1 shows the range of gel assembly methods discussed.

Figure 2-1. Cartoon representation of examples of gel types: (A) a chemically crosslinked gel, (B) a microcrystalline gel, (C) a dynamically crosslinked gel with host-guest interactions with polymer side-groups preferentially entering the cavity of a cucurbituril (green).

This brief summary of gels serves as a foundation for the discussion of xPVAc-borax systems, although, as mentioned in the introduction, these materials cannot be considered true
“gels”. A great deal of research has been devoted to the investigation of the properties of borate ion-crosslinked poly-ol networks because of their unique properties. In many publications, they are referred to as gels, but they are also commonly described as weak gels,\textsuperscript{39} high viscosity polymeric dispersions (HVPDs),\textsuperscript{40} organo-aqueous dispersions,\textsuperscript{41} aqueous solutions,\textsuperscript{42} associating polymer solutions,\textsuperscript{43} and, perhaps most appropriately, “slime”.\textsuperscript{44} The diverse array of terminology stems from the rheological behavior of poly-ol/borate systems which tend to exhibit a strain stiffening response to shear,\textsuperscript{39} finite crosslink lifetimes and network relaxation times, and a storage and loss moduli response to oscillatory stress that is not characteristic of gels.\textsuperscript{42} These attributes will be discussed at length in Section 3.2 for materials prepared by borate ion crosslinking of fully hydrolyzed poly(vinyl acetate) (i.e., PVA), some polymers with 80-85\% acetate hydrolysis, natural poly-ol polymers such as cellulose or guar gum,\textsuperscript{45,46} and low molecular weight diols such as 2,4-pentanediol and 2,3-butanediol.\textsuperscript{47}
3. BORATE-CROSSLINKED POLY-OL SYSTEMS

3.1. Thermodynamic and mechanistic aspects of complexation.

In the presence of borate ions, 1,2- and 1,3-diols, hydroxycarboxylic acids, and dicarboxylic acids undergo an esterification reaction to form bicyclic spiro complexes with a boron atom in the central linking position (Figure 3-1). This process involves several equilibria which are highly pH dependent and have been studied extensively using a range of analytical techniques as a result of interest in boron extraction for purification purposes.

![Figure 3-1. General scheme of the formation of a bicyclic spiro species through the esterification of two diols with one borate ion.](image)

The equilibria involved leading to the spiro species are very complex, and, based on Scheme 3-1 below, involve at least four general association constants.\(^{48}\) The first equilibrium between boric acid in the trigonal form and the borate ion in the tetrahedral form occurs with a known \(K_B^T\) of \(8.5 \times 10^4\) and \(pK_a\) 9 in water at 25 °C.\(^{47,48}\) This exchange is controlled by diffusion and depends on proton or hydroxyl transfer at low or high pH, respectively.\(^{48}\) An association constant for the reaction between BL and L to yield \(B'L_2\) has not been obtained due to the difficulty in detecting the BL species \((\text{vide infra})\). The constants will vary with pH and the type
of diol used; van Duin et al. showed that with glycol, glycolic acid, and oxalic acid, the process with the highest association constant is the esterification of the charged mono-diol to form the di-diol ($K_{B-L}^{B^-}$).\textsuperscript{48}

Based on these results, van Duin proposed “the charge rule”, stating that the “esters of boric acid and borate in aqueous medium show the highest stability at the pH where the sum of the charges of the free esterifying species is equal to the charge of the ester.”\textsuperscript{48} From their research, the authors drew several conclusions: esterification between glycol and borate will only occur when the pH\textgreater pK\textsubscript{a} of boric acid, although experimentally they find complexation occurring at pH\textgreater8 and reaching a maximum at pH 11; in the case of glycolic acid, a hydroxycarboxylic acid, the esterification can occur at a lower pH since the ligand must be present in its deprotonated form and its pK\textsubscript{a} is lower than that of boric acid. Thus, optimal complexation occurs when the pH is intermediate between the pK\textsubscript{a}s of glycolic and boric acids; with dicarboxylic acids such as oxalic acid, esterification occurs when both acid groups are deprotonated at pH $\frac{pK_1 + pK_2}{2}$.\textsuperscript{48} These results are in contrast to those found by Pizer et al. which will be discussed later.\textsuperscript{49}
Scheme 3-1. Complexation equilibria and equilibrium constants of boric acid and borate associated with the formation of mono-diol and di-diol species based on the scheme proposed by van Duin et al.48

Results from research on the substitution of the esterifying ligand show that more highly substituted diols, specifically primary, secondary (1°, 2°) and primary, tertiary (1°, 3°) combinations have a much higher propensity for boron chelation than do less substituted diols.50-52 The authors of these studies varied the substitution on the diol-bearing carbons apparently to change the solubility of the diol-borate complex in organic liquids rather than to change the affinity of the oxygen for the boron. Additional electron-donating groups on the hydroxyl-bearing carbon are known to decrease alkoxide stability, making higher order alcohols less
acidic. The oxygen atoms in these compounds should therefore be stronger bases in the protonated form, making their affinity for the electropositive boron (in the trigonal conformation) higher. Bachelier and Verchere have shown that a 1:1 monochelate complex (mono-diol) can be stable between a 1,3-diol and boric acid, and such complexes have been crystallized from solution. The species formed when a mono-diol complex is bound by only one oxygen of a second diol (Figure 3-2), although used by van Duin et al. in association-dissociation studies of boron with diols, is not considered to be a stable species. The slightly electropositive boron in the trigonal conformation is typically stabilized by a water molecule which is easily replaced during complexation by a diol; presumably, the trigonal chelated boron proposed in Figure 3-2 does not reach a significant concentration within these systems. We can therefore envision a situation in which a more highly substituted 1,3-diol would react with the boron atom. After the initial mono-diol complex is formed, full di-diol esterification with a second diol would be encouraged if the substitution of the diol-bearing carbons is higher because of the increased basicity of the oxygen atoms. The $1^\circ,2^\circ$ diol and $1^\circ,3^\circ$ diol configurations are preferred over $2^\circ,2^\circ$ and $3^\circ,3^\circ$ configurations due to steric hindrance limitations.

![Figure 3-2](image-url)  
Figure 3-2. A mono-diol complex bound by one oxygen on a second diol and stabilizing by a water molecule.
The mono-diol complex is labile and far more likely to hydrolyze in aqueous solutions than the bischelate complex, especially if the latter is stabilized by a metal cation (typically sodium in the borax-PVAc systems). The observation by Köse et al. that the bischelate complex is thermodynamically stable and nearly non-dissociable in aqueous solutions is contrasted by the commonly accepted “lability” of tetrahedral crosslinks between poly(vinyl alcohol) and borate observed by others. The differences among the expected stability of the di-diol systems are due to the ring sizes; as mentioned in several studies, six-membered rings formed through chelation with 1,3-diols are less stable than the 5-membered rings formed by chelation with vicinal diols. As summarized by Köse, the basicity of the anionic ligand or the acidity of the fully protonated ligand correlates with the stability of the complexes; the size of the ring seems to have a negative correlation with its stability; the hydrolytic instability is affected by steric and electronic factors (e.g., coplanar cis-diols have higher association constants and counterions stabilize the complexes). Henderson et al. attribute the greater degree of complexation of 1,2-diols to the inhibited rotational freedom in the 1,3-diol complexes.

It is important to recognize that many of these tenets hold only when referring to boron-diol complexes in aqueous solutions. Under such conditions, the pH of the system is of large importance to complex formation. From research performed as part of this Thesis (see Chapter 4), it is known that borax-crosslinked gels are only stable at higher than neutral pH when the diol is a part of a poly(vinyl alcohol) or poly(vinyl alcohol-co-acetate), and that the materials liquefy when the pH falls below 7. This can be partially tied to the instability of the mono-chelate trigonal 1:1 complexes, as described above, but is largely controlled by the pKₐ of the hydroxyl groups on the polymer chains.
Köse et al. point out that in aqueous solution the water molecule coordinated with the boric acid species is more easily replaced by an alcohol group than is one of the hydroxyl groups bonded to the boron of the borate ion, and that the boric acid to borate exchange is much faster than the nucleophilic substitution reaction that results in chelation.\textsuperscript{53} This observation suggests that chelation occurs more rapidly when the boron is in the trigonal state, and, the borate ion is converted into boric acid according to Le Chatelier’s principle as this species becomes depleted in reactions with diols. Köse et al. suggest that the initial substitution of the coordinated water by an OH group of the diol is the rate limiting step and the subsequent ring closure is much faster.\textsuperscript{53} Thus, although equilibria between the mono-diol and di-diol ions (B'L and B'L\textsubscript{2}) as well as between the borate and mono-diol ions (B\textsuperscript{-} and B'L) are not realistic kinetically, they are feasible thermodynamically.\textsuperscript{48,53} These observations however, do not agree with those of other researchers who have shown that complexation with the borate ion occurs orders of magnitude faster than complexation with boric acid.\textsuperscript{59}

When organic solvents are introduced into the system, at least some of the observations above must change. In aprotic organic solvents, the neutral trigonal species is likely to be more stable than the tetrahedral charged complex. As mentioned earlier, the diol used to form a complex with boron in such systems is even more efficient if it is more highly substituted on the hydroxyl-bearing carbons.\textsuperscript{50} When boric acid is dissolved in water and then extracted into a aprotic organic solvent, its partition coefficient increases when a diol is introduced as a result of the aforementioned 1:1 complexation reaction.\textsuperscript{50} In these systems, Bachelier and Verchere found that 1:1 complexes always had a higher partition into the organic phase than any other chelation configurations.\textsuperscript{50} The authors avoided the use of protic organic solvents because it was postulated
that boric acid is completely esterified by the solvent to trialkyl borate in the presence of alcohols.\textsuperscript{50} However, according to the classic text by Cotton and Wilkinson, this conversion is accomplished in the presence of a strong mineral acid, such as sulfuric acid.\textsuperscript{60} Furthermore, as will be discussed in Chapter 5, if boric acid is chelated by an alcohol, such as methanol to form trimethyl borate, the methoxy groups can be replaced by diols to form crosslinks.

Scheme 3-2. Mechanism of complexation between boric acid and diol as proposed by Köse et al.\textsuperscript{53}

The Scheme above represents Köse’s proposed mechanism for the formation of tetrahedral borate complexes from boric acid and diols. Köse’s work was performed using boron oxide as the boron source and sodium bicarbonate as a source of counterions.\textsuperscript{53} The presence of sodium bicarbonate, aside from providing counterions, also contributes to the small amount of deprotonation of the diol groups as well as to the formation of the borate ion species.
Additional information about the complexation mechanism of boric acid and borate ions with diols can be obtained from studies of boronic acids with saccharides for the purposes of recognition and detection. Boronic acids are sp\(^2\)-hybridized species (i.e., a trigonal planar arrangement of bonds to boron) that have a boron atom bonded to two hydroxyl groups and directly to the carbon of an alkyl group (Figure 3-3). Conversion from the trigonal planar to the tetrahedral form is possible for boronic acids just as it is for boric acid, and, as expected, is accompanied by changes in the oxygen-boron-oxygen bond angle and the equilibrium binding coefficients in reactions with diols. The detailed exploration of boronic acid to boronate ion conversion and diol binding below is based mainly on information in the book by James et al., on the use of these species as saccharide sensing systems.\(^{59}\)

![Figure 3-3. Boric acid (pK\(_a\) 9) and phenyl boronic acid (pK\(_a\) 8.7).\(^{59}\)](image)

Boronic acids, like boric acid, are stabilized by a coordinated water molecule when dissolved in aqueous media. The tetrahedral form of the species is referred to as a boronate ion. In these species, boron can bind to 1,2 or 1,3 diols to form 5- or 6-membered rings in the same manner as boric acid and borate ions. The thermodynamic cycle of phenyl boronic acid (PBA) complexation with a diol, shown in Scheme 3-3, includes four association constants with \(K_{tet}>K_{trig}\).\(^{59}\) Upon formation of the neutral complexed boric acid, the acidity of the molecule increases; as a result, pK\(_a\)>pK\(_a'\).\(^{59}\) To explore why this pattern in association constant strengths occurs, it is necessary to know the bond angles and hybridization of boron in these species.
As expected for a trigonal planar molecule, phenyl boronic acid has an O-B-O bond angle of ~120°; crystallographic studies have shown that in the solid state, PBA exists as a dimer with a compressed O-B-O bond angle of ~116.3°. It is difficult to elucidate the bond angle in solution because the degree of association and salvation depends on many environmental factors; however, crystallography studies of boric acid do reveal a 120° bond angle. In 5-membered phenyl boronic acid rings with fructose, the O-B-O bond angle is reduced to ~113° but the boron remains in the trigonal planar conformation. As a result, the molecule experiences a large amount of ring strain. Formation of the tetrahedral complex, where the boron is sp³ hybridized, reduces the ring strain. Because of the lower energy of the tetrahedral complex, the equilibrium favors its formation and the value of the acidity constant, Ka' is high.
Figure 3-4. Bond angles of PBA in its free and bound forms, as well as of the phenyl boronate ion and the resulting alleviation of the ring strain.\textsuperscript{59}

Boronic acid, in the trigonal planar geometry possesses one unoccupied p-orbital oriented perpendicularly to the molecular plane. During diol complexation, the lone-pair of electrons of an oxygen atom can mix with this empty orbital; as the interaction strengthens, proton dissociation is facilitated (Figure 3-5). Accordingly, the acidity constant for the equilibrium is determined by the ease of the orbital mixing process. With diol complexation, the geometry of the neutral boron is changed; on formation of a strained 5-membered ring, the p-orbital develops some s-character, resulting in hybrid orbitals that are between sp\textsuperscript{2} and sp\textsuperscript{3} in character.\textsuperscript{59}

Figure 3-5. Interaction of an oxygen atom lone-pair of electrons of an approaching diol and the unoccupied p-orbital of boronic acid.

When the empty p-orbital begins to develop some s-character, the boron nucleus is deshielded, causing an increase in the Lewis acidity of the atom. As a result, the Lewis acid-Lewis base reaction between the boron and oxygen from the approaching diol proceeds with an accompanied weakening of the adjacent H-O bond and a consequent increase in the acidity of the
hydrogen which has been computationally calculated as 64% for 5-membered ring complexation and 19% for 6-membered ring complexation (relative to the unbound boron).\textsuperscript{59}

As discussed previously, the complexation equilibria are highly dependent on pH, with association constants increasing by up to five orders of magnitude when the pH of the system is increased above the pK\textsubscript{a} of the boronic acid. The kinetics of boron-diol complexation also show increases in rate by 3 to 4 orders of magnitude when the boron atom is in the tetrahedral rather than in the trigonal state. As described above, the attack of the oxygen lone-pair on the slightly positive boron center is expected to be favorable; however, some experimental evidence shows that the attack is even faster when the p-orbital of the boron is already occupied and the boron atom is negatively charged.\textsuperscript{59} The counter-intuitive nature of this observation clearly contrasts Köse’s observations discussed earlier.

The acidity of the reacting ligand is also of importance. Boronic acid rate of complexation is small with diols but increases markedly with hydroxycarboxylic acids and dicarboxylic acids (as observed by van Duin et al. for boric acid).\textsuperscript{48} It has been observed that when boronic acid complexes with oxalic acid, the boron changes from trigonal to the tetrahedral form immediately.\textsuperscript{59} The rates of complexation (k\textsubscript{HOOC}COOH = 2000 M\textsuperscript{-1}s\textsuperscript{-1}, k\textsubscript{HOOC}COO\textsuperscript{-} = 330M\textsuperscript{-1}s\textsuperscript{-1}, and k\textsubscript{OOC}COO\textsuperscript{-} ≤ 0.1M\textsuperscript{-1}s\textsuperscript{-1}) are counterintuitive and contrast with van Duin’s “charge rule”\textsuperscript{48}; a reaction based on nucleophilic attack has a drastically lower reaction constant for the nucleophilic dianion than the fully protonated species. The results are attributed to the expelled leaving group and minimization of charge repulsion. As demonstrated above, a proton transfer is required for the complexation reaction to occur; thus, the incoming ligand must have at least one proton present. The elimination of one molecule of water during ligand binding is achieved by
the transfer of the more acidic ligand proton to one of the hydroxyl groups on the boron. There is a correlation between the rate of the acidic proton transfer in this reaction and its pKₐ.⁵⁹ In the absence of a second, less-acidic proton, the negative charge on the oxygen would decrease reaction rates due to repulsion with the leaving hydroxyl group; as a result, doubly protonated ligands have the fastest reaction rates with boronic and boric acids.⁵⁹

![Proposed transition state of dicarboxylic acid addition to a boronic acid showing the development or breaking of covalent bonds as dashed lines.](image)

Figure 3-6. Proposed transition state of dicarboxylic acid addition to a boronic acid showing the development or breaking of covalent bonds as dashed lines.⁵⁹

The proposed transition state of this reaction is shown in Figure 3-6. The initiation step is the attack of the ligating oxygen lone-pair of electrons on the empty p-orbital of the boron atom. The rate-determining step involves proton-transfer. Therefore, higher ligand acidity results in higher complexation constants. Later studies of the deuterium isotope effect, however, counter the above described mechanism. The general consensus is that the first step of the reaction of boronic acids in the formation of monoesters is associative and rate-limiting. Because the rate of reaction for the tetrahedral RB(OH)₃⁻ is much faster than that of the trigonal RB(OH)₂, ring closure is not a rate-limiting step if the tetrahedral intermediate is formed. Although different research groups agree that the proton transfer is important, there are disagreements on the nature of the transition state and the rate-determining step. When a deuterated acid is used as the ligand, a reduction of 20-30% in the reaction rate is observed (k_H/k_D < 2), confirming a secondary
isotope effect (SIE). Thus, the proton transfer, although important, may not be the rate-determining step of the reaction. Instead, the formation of the new bond between boron and the oxygen atom may be the rate-limiting step.\(^{59}\)

![Reaction coordinate](image)

Figure 3-7. Reaction coordinate for complexation of boric acid by a simplified tropolone species (shown in inset) proposed by Funahashi and Ishihara. Figure adapted from Boronic Acids in Saccharide Recognition.\(^{59,61}\)

Computational analyses of the transition states, with the formation of the new B-O bond and the elimination of a molecule of water with the trigonal state being restored, have been performed.\(^{62}\) High activation barriers were observed in vacuo, as well as in acetonitrile and methanol.\(^{62}\) The activation barrier is greatly reduced in H\(_2\)O, and in the presence of NaOH, or ammonia due to their ability to function as Lewis bases.\(^{62}\) The transition state in these simulations was found to be very dependent on the dehydration step and, thus, the proton transfer. In the absence of a protic solvent, the transition state is achieved through a strained 4-
membered ring, while in protic solvents a six-membered ring is formed (Figure 3-8).\textsuperscript{62} Computational models also showed that increasing the basicity of the solvent greatly increases the rate of proton transfer; additionally, a stabilizing interaction between the non-activated hydroxyl group on the boron and non-reacting ligand hydroxyl was also found.\textsuperscript{59,62}

\begin{center}
\includegraphics[width=0.5\textwidth]{figure3-8.png}
\end{center}

Figure 3-8. Proposed six-membered ring transition state for boron with a stabilizing hydrogen bond denoted by a mixed solid/dashed line.\textsuperscript{2}

In summary, the reaction of boric acid or a boronic acid with a diol follows a two-step reaction mechanism. In the bimolecular, rate-limiting first step, a nucleophilic attack by the diol oxygen on the $\delta^+$ trigonal boron results in a tetrahedral complex. The formation of a covalent bond between the oxygen and the boron atom is dependent on the presence of a labile proton on the diol, which can be transferred to an OH group on the boron. This step is kinetically significant and can occur directly in the absence of a protic solvent or through a solvent chain in protic solvents. This process is followed by the ring closure achieved through unimolecular elimination of the water molecule after a second attack on the boron by the unreacted diol oxygen.\textsuperscript{59}

The complexation reaction between a tetrahedral boronate ion and an acidic ligand is difficult to study due to the ambiguity concerning the location and number of protons involved.
The use of the more slowly reacting diols rather than diacids or hydroxycarboxylic acids has yielded limited information on the kinetics of boronate reactions. Instead, borate ion binding with diols has been studied. The chelation of chromotropic acid by a borate ion results in increased acidity which, in turn, increases forward and reverse rate constants. Based on the observation that the forward and reverse reaction rates are first order with respect to hydrogen ion concentration, a transition state has been proposed which involves a mechanism initiated by the protonation of the leaving hydroxyl group on the boron by the solvent (Figure 3-9). The boron-oxygen bond begins to form during the subsequent SN2 reaction, resulting in a transition state with a pentavalent boron atom. Stabilization of this complex may be achieved by a hydrogen bond between the diol and a hydroxyl group on the boron (through a solvent bridge or directly), followed by the elimination of a molecule of water and a return to tetrahedral geometry. Reaction of the second hydroxyl of the diol leads to ring closure. Because a pentavalent boron species has been isolated, this mechanism is plausible.59
Figure 3-9. Borate ion reaction with chromotropic acid through the formation of a pentavalent complex in the transition state. \(^2\)

One explanation of the observed higher rate of reaction for tetrahedral borates than trigonal boric acids is found in the difference between the bond lengths. The hydroxy groups on the tetrahedral borate ion are more basic than those on the trigonal boric acid; the tetrahedral and trigonal B—O bond lengths are 1.48 Å and 1.37 Å, respectively. \(^59\) The longer B—O bond is indicative of decreased bond strength which causes the hydroxyl group to be more basic and facilitates the proton transfer step which increases the reaction rate. Although this proposal has not been verified experimentally, it provides an explanation for the large increase in reactivity of the tetrahedral species. \(^59\)

In a paper that contradicts much of the above discussion, Bishop et al. suggested that complexation occurs through boric acid rather than the borate ion. \(^46\) This postulate has also been
put forth by Yamada and Rietjens. The extensive research by Bishop et al. employed solid-state magic angle spinning (MAS) $^{11}$B NMR and computational models to study the complexation of guar gum, simple monosaccharides, and small cyclic and linear diols. The results confirmed that five-membered rings are more stable than six-membered rings and that complexation with cis-diols is favored over that with trans-diols. Based on pH measurements, the authors report that reducing alcohols (more acidic) have higher complexation constants than non-reducing alcohols (less acidic); this observation is consistent with the higher reactivity of protonated ligands as described by Pizer et al. Bishop et al.’s research showed that if the pH of the system is increased beyond the pH maximum of 12 investigated by van Duin et al., there is a drop in the concentration of the complex and only one species, the borate ion, remains. If complexation occurs through the borate ion, then an increase in the concentration of this species due to the increase in pH is expected to promote complex formation. In their study, Bishop et al. argue that van Duin’s work, and the “charge rule”, has resulted in general confusion regarding the binding species and argue as follows.

Because interconversion of boric acid to the borate ion is mostly dependent on the pK$_a$ of water, it occurs through a hydroxide attack or a deprotonation of the coordinated water ligand as shown in Scheme 3-3 for PBA. The complexation reaction, being initiated in the same manner, is also dependent on the pK$_a$ of the ligand. Given that the pK$_a$s of simple alcohols like ethanol or methanol are close to water, the appearance of the complex as the pH is increased should commence at a pH close to that at which the borate ion begins to form. Accordingly, when studying more acidic alcohols, complexation occurs at a lower pH, thus eliminating the possibility that the complexation occurs with the borate ion. Furthermore, the researchers showed
that ligands with an alcohol and an ether group do not form complexes; it is only the chelating ability of a diol group which promotes complexation. Reaction Scheme 3-4, based upon the results and analyses of Bishop et al. suggests that in guaran and other poly-ol and borax solutions, the overwhelming presence of chelating diol groups, combined with the elimination of a water molecule during crosslink formation (contributing to the entropy), are the “saving grace” of these systems and the only driving forces for complexation.⁴⁶

Scheme 3-4. Proposed competition between borate ion formation and complexation.⁴⁶

Bishop further argues that in solution $^{11}$B NMR, the signals observed can only be those of the mono-diol and uncomplexed boron species.⁴⁶ Due to the large increase in viscosity and molecular weight of the crosslinked polymers, Bishop et al. argue that tumbling in solution would be greatly slowed and the signal from these moieties would be too broad to detect; for this reason, the authors study the systems by MAS $^{11}$B NMR.

⁴⁶ Refer to Appendix B for a brief introduction to $^{11}$B NMR, and its use for boron crosslinked small molecules and poly-ols.
Rietjens and Steenbergen put forth an argument in favor of boric acid as the complex-forming species. The authors use extensive calculations of the association constants and rate constants of both boric acid and borate ion complexation with polyhydroxylated polymers, and use experimental evidence from studies with guaran gum as a ligand and from previous publications by Pezron which employed poly(vinyl alcohol). The thermodynamic equations for both boron moieties have identical solutions, and they cannot be used to determine which species is the crosslink initiator. In the solution of the kinetic equations, the borate ion complexation rate is pH dependent, while that of the acid is pH independent allowing for the elucidation of the reacting species. Rietjens and Steenbergen further feel that $^{11}$B NMR data is unreliable because the “crosslinked” peak seen upfield of the free, exchanging boron peak contains both the mono-diol and di-diol species. Consequently, the authors use rheological measurements but take into account a model to distinguish the effects of the physical crosslinks (due to chain entanglements) from the boron crosslinks on the elastic modulus.

Using calculations derived from the rheology studies to determine the time necessary to reach the maximum viscoelasticity of the system, i.e., the gelation time, the authors find that at higher pH values, crosslinking is slower. The results of Pezron et al. are in agreement, showing that the $G'$-plateau regions extend to lower frequencies in oscillatory measurements on PVA-borax systems as the pH is increased from 8.7 to 9.2 to 11. According to Pezron et al., the $G'$ plateau region indicates that the lifetimes of the crosslinks in the higher pH systems are longer. Because the concentration of boric acid would be greatly decreased at these high pH values, the retardation of the complexation reactions can be expected if this is the reactive species. Reitjens and Steenbergen specify that due to the pK$_a$s of alcohols and diols (typically near 14) even at a
pH of 12.5, only 1% of the OH groups on poly-ols are likely to be deprotonated.\textsuperscript{64} Using a pK\textsubscript{a} value of 14, it is also possible to calculate that less than 0.4% crosslink sites on a polymer chain are occupied by mono-diol complexes at the highest poly-ol and boron concentrations tested,\textsuperscript{64} a result that is contrary to the polyelectrolyte picture presented by many authors described in the next section.

The most recent study implicating boric acid as the crosslink initiator involves the use of multinuclear solid state NMR, MAS $^{11}$B NMR, $^{11}$B Multiple-Quantum MAS, $^{11}$B stationary NMR, $^{1}$H-$^{11}$B cross-polarized (CP) NMR, heteronuclear correlation NMR (HETCOR), and $^{1}$H windowed phase-modulated Lee-Goldberg (wPMLG) NMR.\textsuperscript{63} The studies were performed on PVA films doped with boric acid and, consequently, the results may not be relevant for polymer solutions. Yamada finds that in solid state films, the trigonal species is more concentrated than the tetrahedral.\textsuperscript{63} The CP NMR spectra indicate the presence of cross peaks between the trigonal boron and the polymer OH group signals which are not present for the tetrahedral boron.\textsuperscript{63} He concludes that boric acid is the reactive species, and that the final crosslink structure is in the trigonal conformation. Although these observations may be possible in doped polymer films, they are highly unlikely to hold true in the solution state. Ring closure during di-diol reactions is a fast step and proceeds after the initial rate-determining boron-oxygen bond formation; it is unclear why one ring closure would occur and not a second. If the system contained 1,2-diol species, the ring strain argument for conversion from the trigonal to the tetrahedral state would be applicable. However, six-membered rings are not as strained and therefore this argument cannot be made. Yamada’s work, although interesting, is unlikely to be relevant to PVA-borax gels.
Throughout this discussion of boron chelation by diols several conflicting interpretations of results have been noted. All authors reviewed agree that crosslink formation with diols occurs at pH higher than 8, which is confirmed by our results. At this pH, approximately half of the boron species are in the tetrahedral, charged form, and the other half are in the trigonal neutral form.\textsuperscript{46,47} The pK\textsubscript{a} of poly(vinyl alcohol) has not been reported in the literature, though it is reasonable to assume that it is near 14 as for smaller diols. As a result it is not possible to eliminate either mechanism, although complexation through boric acid may be more likely. Results described in this dissertation (Chapter 5) seem to confirm that complexation and crosslinking occur through the trigonal boron species.

In the next section, a more global approach to understanding network formation will be presented in studies which employ rheology, \textsuperscript{11}B NMR, and dynamic light scattering (DLS). Based on the above discussion, there is a clear disagreement within the field as to how crosslink formation occurs, and which signals in the \textsuperscript{11}B NMR spectra can be assigned to the mono-diol and di-diol species in these networks. Accordingly, the validity of studies which report the complexation constants and rates of these equilibria based on \textsuperscript{11}B NMR experiments may need to be reconsidered. In support of this argument, it is relevant to note that, based on their observations, both Bishop et al. and Rietjens and Steenbergen report that approximately 1\% of the boron in guar gum systems is participating in crosslinks.\textsuperscript{46} Other authors have noted that not all of the boron in poly-ol solutions participates in crosslinks, but estimates are usually above 50\%.\textsuperscript{55} As reported in Chapter 4 of this dissertation, if the peak assignment in solution \textsuperscript{11}B NMR is valid, only 5-10\% of the boron species in the described xPVAc-borax gels are participating in crosslink reactions - a result that is closer in agreement with boric acid acting as a crosslinker.
As an aside, it may be possible to form gels crosslinked by borate species by a polymer with carboxylate side-groups, or a mixed polymer with alternating carboxylate and hydroxyl side-groups. Such gels would form at lower pH values and may be useful for expanding the range of conservation treatments possible with boron crosslinked gels.

3.2. Network formation and characterization.

The majority of mechanistic and thermodynamic considerations discussed in the previous section regarding the complexation of sp² or sp³ hybridized boron species with diols were performed through the use of small molecules such as glycol or cis- and trans-1,2-cyclohexanediols. Research on these systems, with the exception of saccharide detection using boronic acids, has been intended to shed light on the complexation of these same boron species with poly-ols such as poly(vinyl alcohol) or polysaccharides like guar. Aside from the novel properties of the materials, and some limited interest in them as drug-delivery systems due to their biocompatibility, research in this area has been driven by the applications of poly-ol-borate gels in the oil-well drilling industry as hydraulic fracturing fluids. Gels prepared from borate-crosslinked polymers provide increased viscosity in this application, yet allow for ease in the clean-up process due to their pH-dependent rheoreversibility. In the scientific literature, investigations of these systems are approached from different standpoints: rheological studies aid in better understanding the network formation and physical properties; investigations of the phases of the materials contribute to our understanding of the polyelectrolyte effects on network formation; and ¹¹B NMR studies are used to elucidate the thermodynamics and kinetics of complexation.
The addition of a polyhydroxylated polymer to an aqueous solution of borate ions (typically derived from borax decahydrate \([\text{Na}_2\text{B}_4\text{O}_7\cdot10\text{H}_2\text{O}]\) which dissolves in water to form boric acid \([\text{B(OH)}_3]\) and borate ions \([\text{B(OH)}_4^-]\) at concentrations below 0.05 M)\(^{47,70}\) can result in a significant increase in the viscosity of the solution, especially when the pH is >8 as discussed in Section 3.1.\(^{46,47,71}\) The viscosity increase has been attributed to the formation of crosslinks between vicinal diols on the polymer chains. The effect is particularly large when the hydroxy diads are in the \textit{meso} conformation.\(^{55}\) The “accepted” crosslink formation and structure, described by Deuel and Neukom in 1949 and confirmed by \(^{11}\text{B}\) NMR, is shown in Scheme 3-5.\(^{47,70}\) Although formation of the crosslinks through a pentavalent boron transition state is possible, as described in Section 3.1, it seems more likely that the reaction occurs through a two-step nucleophilic attack and proton transfer on a boric acid moiety, followed by the elimination of water. Nevertheless, as the overwhelming majority of studies on poly-ol-borate systems were performed in the latter half of the last century, before the suggestion that boric acid may be the reactive species (most of these studies were published after 2000), the following discussion will be based on the assumption that tetrahedral borate reacts during crosslink formation. Regardless of which geometric conformer of boron reacts with the two diols, the final crosslink structure should not change. The complexation reaction is very fast, and reaches a thermodynamic equilibrium within a few hours after preparation.\(^{72}\)
Several authors have noted that there is a drastic increase in the viscosity of aqueous solutions of borax when the concentration of poly(vinyl alcohol) is increased. This process is not linear, and there is a sharp inflection point at which the intrinsic viscosity changes very rapidly.\textsuperscript{73,74} Takada et al. refer to this concentration as $C_N$ (the concentration of network formation) and their studies show that it is approximately equivalent to the critical concentration, $C^*$, of polymer solutions. As is shown in Figure 3-10, $C^*$ occurs when the concentration of the polymer in solution is equal to that inside a polymer coil; $C^*$ also marks the transition of a polymer solution from the dilute regime to the semi-dilute regime.\textsuperscript{75} In the dilute regime, polymer solutions are dominated by intramolecular interactions, but once the system becomes concentrated enough to pass into the semi-dilute regime, intermolecular interactions tend to dominate.\textsuperscript{75} Accordingly, in poly-ol-borax solutions, it is expected that below $C_N$, crosslinking is
intrachain, while above $C_N$, crosslinks begin to form between polymer chains and a network can be established (vide infra). From this process, we can establish that along with polymer and borax concentration, the molecular weight of the polymer will play a large role in the onset of network formation.$^{73,74,76}$

Figure 3-10. Polymer chains in dilute solutions tend not to interact intermolecularly; above the critical concentration, $C^*$, interchain interactions begin to occur in the solution. The red dotted circles in the $C^*$ image indicate the radii of gyration $R_G$ (the root-mean-square distance of all segments with respect to the center of mass for each chain). The dashed line in the semi-dilute image indicates the correlation length, $\xi$, (the average mesh size in an entangled polymer network).$^{77}$

Tanaka proposed a model which can be used to find the elastically effective chains in such a transient gel by describing the network as a set of primary chains having $n$ repeating units and $f$ functional groups.$^{78}$ The functional groups are responsible for forming junctions (or crosslinks) between at least two primary chains, with each junction being composed of $m$ functional groups.$^{78}$ In the PVA-borax network, a diol would be considered a functional group, $f$, and $m=2$. This model indicates that $f$ is proportional to the molecular weight of the polymer. Takada et al. employed the proposed model to interpret the results of dynamic light scattering
studies on the network, with variations in the polymer concentration and molecular weight. The results indicate that the $C_N$ observed in concentration studies of the intrinsic viscosity can be taken as the overlap concentration at which the onset of intermolecular chains begins to occur, and does, therefore, correspond to the gel point.

Neutron spin-echo studies confirm the occurrence of chain entanglements in the transient network, and show the similarity of the sol-gel transition to the dilute to semi-dilute transition in polymer solutions. Calculations from these studies show that borax may not be necessary for the formation of a gel, and that not all boron species in the system participate in crosslinks (an observation confirmed through $^{11}$B NMR), allowing for the behavior of the polymer chains in the gel to be similar to that in solution even though the former is more than five orders of magnitude more viscous. However, dynamic light scattering results seem to suggest that while chain overlap is necessary for network formation, it is not sufficient to cause the drastic viscosity increase observed in borax solutions.

We may now return to the semantics of PVA-borax “systems”. The materials can be classified as gels at low temperatures and high polymer concentrations. At room temperature and polymer concentrations near or just above the $C_N$, the system may be viewed as a transient network of polymers with crosslinks of finite lifetimes. In broader terms, the materials are viscoelastic fluids with a narrow distribution of relaxation times. The relaxation time, and therefore the viscoelasticity, of the system is determined by the lifetimes of the crosslinks, which have been estimated to be on the order of 0.01 to 0.3 seconds from oscillatory experiments. According to Takada’s work, the lifetimes can vary as a result of the polymer concentration and molecular weight and also with the measurement method, because chain entanglements
contribute to rheologically measured lifetimes. Robb and Smeulders report that the relaxation times of the systems, found to be \( \sim 0.3 \) sec, are independent of the polymer concentration, degree of hydrolysis, and boron concentration.\(^{39}\) Takada et al. relate the relaxation time to the crosslink lifetime in these systems by envisioning each polymer chain in the network to be held in place by several complexes with finite lifetimes; when a complex is broken, conformational relaxation of the chain will begin.\(^{73}\) In dilute polymer solutions and low molecular weights, a chain will relax faster than the whole network, and the stress applied to the chain can be fully dissipated; thus, the relaxation time of the network depends on the lifetime of the crosslinks experiencing the applied stress.\(^{73}\) In semi-dilute polymer solutions and high molecular weights, the breaking of a complex does not allow the released chain enough time to relax to a deformed state; as a result the system relaxation time after an applied stress is longer.\(^{73}\) This observation is echoed by Robb and Smeulders who find that the relaxation process is dependent on the crosslink lifetimes and not on the chain entanglement.\(^{39}\)

Gels prepared from PVA and borax are thermoreversible due to the exothermic nature of the crosslink forming mechanism presented in Section 3.1. As temperature is increased, decomplexation increases and crosslink lifetimes become shorter. Another important process occurs with increasing temperature – the shrinking of the polymer chains.\(^{56}\) Solubilization of poly(vinyl alcohol) in water is achieved through favorable polymer-solvent interactions due to extensive hydrogen bonding: as the temperature is increased, the strength of hydrogen bonds tends to decrease,\(^ {80}\) actually making water a poor solvent for the polymer.\(^{56}\) This effect is more pronounced in polymers with high molecular weights and with lower hydrolysis due to the greater presence of less hydrophilic acetate groups. One consequence of this effect is an increase
in the $C_N$ at higher temperatures. Because dissociation of the boron moieties from the polymer chains is increased, the polyelectrolyte nature of the chains is reduced, further encouraging the chains to ‘collapse’.\textsuperscript{56} The increase in free boron species in solution contributes to a salting-out effect, causing polymer chains to aggregate and phase separation to occur.\textsuperscript{56}

An additional, important finding from the temperature, concentration, and molecular weight studies performed by Koga et al. is the decrease in the activation enthalpy, $\Delta H^\ddagger$, for network flow due to increasing concentration and the inverse relationship with acetate hydrolysis (i.e., the availability of the diol functional groups determines the activation enthalpy, $\Delta H^\ddagger$, for the crosslink breaking in the network).\textsuperscript{56} The $\Delta H^\ddagger$ for viscoelastic flow, also determined rheologically, was reported to be 40 kJ/mol by Schultz and Myers for a 100% hydrolyzed polymer system, while Koga et al. found that value to double for an 88% hydrolyzed polymer system.\textsuperscript{55,56} The $\Delta H^\ddagger$ for crosslink formation has been reported variously to be 35 kJ/mol by Sinton, and 21 kJ/mol by Schultz and Myers. Koga et al. reported 18 kJ/mol (7 wt % polymer, double $C_N$), 21 kJ/mol (4.5 wt % polymer, slightly higher than $C_N$) and 32 kJ/mol (average for all other concentrations studied).\textsuperscript{47,55,56} These values are small and confirm the ability of the crosslinks in the system to dissociate and associate spontaneously, an observation that would justify the viscid, self-healing nature of the networks.

The strain-stiffening effect observed in PVA-borax gels has also been investigated using rheological studies. When strain is applied to the systems, a marked increase in the viscosity is observed. Several authors have reported this behavior.\textsuperscript{39,42,43,43} Shear thickening in polymer systems may be due to an increase in the crosslink density, or to a switch from intra- to intermolecular crosslinking for a population of the complexes.\textsuperscript{39} The common rationalization for
the observed behavior is that in shear flow, the polymer chains are stretched and re-oriented, allowing not only for intermolecular crosslinking to occur, but also encouraging more complexation due to the alignment of the diol functional groups.\textsuperscript{39,42,43}

With the now established understanding that PVA-borax systems are strain-stiffening transient networks, with a narrow distribution of relaxation times resulting from complexes with finite lifetimes which exhibit many properties of semi-dilute polymer solutions, we will proceed to call the systems “gels”. There is one more important aspect of network formation that must be discussed for a full understanding of these materials: the polyelectrolyte nature of the chains in the presence of borate ions and the resulting re-entrant phase behavior.

PVA-borax gels tend to exhibit two phase transitions: from homogeneous sol to homogeneous gel and from homogeneous gel to a two phase system consisting of a dilute polymer solution and a concentrated polymer gel (a process sometimes referred to as “demixing”).\textsuperscript{44,72} The phase behavior is most pronounced in the presence of an additional salt such as NaCl. Pezron and Leibler’s work on the phase diagrams of poly-ol-borax materials has been extensive, and the authors have used a Flory model to account for the phase separation.\textsuperscript{44,72,81-85} Through this model, it has been established that demixing occurs as a result of competition between the energy gained during crosslink formation, the entropy lost due to increased local order, and the electrostatic repulsion from mono- and di-complexes along the polymer chain.\textsuperscript{72} The equilibrium of the network is disturbed due to a competition between the formation of crosslinks and the repulsion due to charges resulting from these crosslinks.\textsuperscript{72}

Relating these effects to the network structure, Keita et al. find that when the distance between two charges on a polymer chain ($R_X$) is longer than the correlation length of the network
(ξ, see Figure 3-10), a homogeneous gel is formed. Further increases in the crosslinker result in a
decrease of $R_X$ which results in demixing at the moment when $R_X$ becomes shorter than $\xi$.\textsuperscript{72} The
phase transition is called “re-entrant” because after this initial demixing, expansion of the gel can
occur once more when $R_X \approx$ the screening Debye length, and charge repulsion causes the chains
to swell.\textsuperscript{72,83}

DLS is used by many groups researching network dynamics in poly-ol-borax solutions,
with results typically indicating fast and slow relaxation modes which correspond to cluster
mobility (clusters of PVA molecules containing mainly intramolecular crosslinks) and network
dynamics (transient changes in the entire PVA network linked by intermolecular crosslinks),
respectively.\textsuperscript{56,86-88} Above the $C_N$, the only relevant length scale in the network is described by
the correlation length, which is dependent on the polymer concentration; below the $C_N$, both the
$R_G$ and $\xi$ length scales are relevant, with the latter being dependent on the molecular weight but
independent of the concentration of the polymer.\textsuperscript{73} As the borax concentration in the system is
increased, the slow relaxation mode fluctuates in an increasing and decreasing manner which
indicates an increase in the cluster size due to the attachment of borate ions to the polymer chains
and electrostatic repulsion, followed by a decrease in cluster size when intramolecular
crosslinking begins to occur and sodium ions screen part of the charges.\textsuperscript{86,88} The system can then
expand again because the shrinking of the clusters increases the proximity of the diol groups,
allowing for more borate attachment which results in electrostatic repulsions and another chain
expansion.\textsuperscript{86,88} The same oscillating result can be obtained by graphing the plateau storage
modulus and maximum loss modulus frequencies against borax concentration.\textsuperscript{86,88}
Shibayama et al. also studied the swelling and shrinking of PVA-borax gels, but they added sodium hydroxide with the borax, rather than a passive salt.\textsuperscript{89,90} Although the concentration of NaOH was reported, the pH of the obtained solutions was not discussed. Using DLS and monitoring the cooperative diffusive coefficient for the gels, Shibayama et al. report that during gel expansion the presence of borate ions (ensured by the addition of NaOH) accelerates the cooperative diffusion of the network, while in the shrinking mode, the presence of the same ions reduces the miscibility of the polymer chains causing phase separation.\textsuperscript{89}

Many studies of PVA-borax gels treat the systems as networks of polyelectrolytes, though at the pH of gel formation, the concentrations of borate ions and boric acid are approximately equal. At a pH of 9, the ratio of deprotonated to protonated hydroxyl groups on the polymer chains will be only $1 \times 10^{-5}$. According to Bishop’s studies, described in Section 3.1, it would be reasonable to assume that due to the sheer number of diol moieties available in these solutions, some amount of complexation will occur, and the mono-diol complexed species would continue to undergo transitions from the trigonal planar to the tetrahedral conformations while attached to the polymer chain. Sinton calculates the activation energy for the conversion of the mono-diol from trigonal to tetrahedral conformation to be only 12 kJ/mol.\textsuperscript{47} Ring strain should not be a large driving force for conversion of the trigonal mono-diol complex to the tetrahedral mono-diol complex and, as discussed above, many groups conclude that the mono-diol complex does not exist for long before the formation of a di-diol complex. Attachment of the first diol to the boron species increases the electropositive nature of the boron, making it more prone to nucleophilic attack by a second diol. Thus, the treatment of the PVA chain in a borax solution as a polyelectrolyte may not be fully appropriate unless the discussion involves mainly di-diol
complexes. The studies performed by those groups which treat the chain as a polyelectrolyte rarely mention the low number of crosslinks detected by $^{11}$B NMR or the calculations by Rietjens and Bishop discussed in the previous section. Their results are likely valid, but the electronegative complexes attached to the polymer chains which result in chain expansion should probably be treated as di-diols rather than mono-diols.

Lastly, $^{11}$B NMR studies of PVA-borax systems should be discussed to lay a foundation for much of the research described in this dissertation. Sinton showed that boric acid and the borate ion appear at two different chemical shifts in the NMR spectra (~19 ppm and ~ 1.5 ppm relative to a borontrifluoride etherate standard) when the pH of the solution is below ca. 7 or above ca. 10, respectively. In the intermediate pH range, where most gels with diols form, the interchange between the two boron species is fast on the NMR time scale and a single broad peak appears. According to the Henderson-Hasselbalch equation ($pH = \log(X) + pK_a$), the relative concentration of boric acid to borate at a given pH can be determined by equation 1 where $\delta_B$, $\delta_{B-}$, and $\delta_f$ represent the chemical shift of boric acid, the borate ion, and the exchanging mixed peak, respectively.

$$X = \frac{\delta_f - \delta_B}{\delta_B - \delta_f}$$  \hspace{1cm} (3-1)

In the presence of a small diol, at low concentrations, a peak appears for mono-diol complexes, and as the concentration of the diol is increased, a second peak, for di-diol complexation appears upfield of the mono-diol peak. The chemical shift of the former is close to 2 ppm and shifts downfield with concentration, while that of the latter is close to 1.5 ppm and remains relatively constant with increasing concentration. Furthermore, the linewidth of the
mono-diol complex signal increases with concentration, indicating a fast-exchange process from the trigonal planar uncharged state to the tetrahedral charged form. In fact, Sinton is able to confirm the increased acidity of boron in the mono-diol complexed state, finding the pK_a to be ~8.5.\textsuperscript{47}

The free borate peak, present in all of spectra of diol-borax solutions, is initially close to 10 ppm at low complexation and shifts downfield as the complexation increases, a result confirmed by our studies, described in Chapter 4.\textsuperscript{47,74} Sinton does not find two peaks for mono-diol and di-diol complexation in spectra of polymer-borax solutions. The single peak which appears at a chemical shift close to that of the borate ion contains a broad and a narrow component, which Sinton disqualifies as being due to a mixing of the mono-diol or di-diol species (as suggested by Rietjens),\textsuperscript{64} but attributes to intra- and inter-molecular di-diols.\textsuperscript{47} The lack of a mono-diol peak in the spectra is postulated to be due to two possibilities: either the mono-diol complex association and dissociation is so slow that its signal is too broad to detect (N.B. in direct contrast with Bishop’s suggestion),\textsuperscript{46} or the mono-diols formed react further to form di-diols very quickly, escaping detection.\textsuperscript{47} Thus, confusion remains as to what tetrahedral species is represented by the single upfield peak in $^{11}$B NMR spectra of poly(vinyl alcohol) and borax.
4. GELS FROM PARTIALLY HYDROLYZED POLY(VINYL ACETATE) AND BORAX

4.1. Methods and Materials.

Materials. Partially hydrolyzed poly(vinyl acetate)s, as random copolymers, were supplied by Kuraray Co., Ltd. They were washed copiously with ice-cold water to remove byproducts and residual free acetate and dried under vacuum.

Sodium tetraborate decahydrate (>99.5%; Fluka) was used as received. Methanol (Fisher, HPLC grade), ethanol (Aldrich, anhydrous, denatured), 1-propanol (Fisher, certified normal grade), 2-propanol (HPLC grade, 99.9%; Fisher), 1-pentanol (Aldrich, 99+%), methyl acetate (99.8%, Fluka), acetone (histological grade, Fisher), 1-methyl-2-pyrrolidinone (extra dry, with molecular sieves, water <50 ppm; Acros Organics), boron trifluoride etherate (Aldrich), DMSO-$d_6$, acetone-$d_6$, methanol-$d_6$, D$_2$O and CDCl$_3$ (D, 99.9%; Cambridge Isotope Laboratories, Inc.) were used as received. Water was distilled and deionized.

Instrumentation. NMR studies were performed on a Varian 400 MHz spectrometer. Data collection was made at 100.465 MHz with 128 FIDs and 399.490MHz with 2000 FIDs for $^1$H and $^{13}$C, respectively. MestReNova software was used to process the FIDs to obtain the spectra. $^{11}$B NMR spectra were obtained on the same spectrometer at 128.3 MHz with 320 FIDs in quartz NMR tubes using an external boron trifluoride etherate reference (arbitrary concentration) in a sealed capillary tube. Ratios of areas of bound and unbound borate ions remained constant as long as the delay pulse was longer than 32 μs. For that reason, a 40 μs observation pulse was used to obtain all $^{11}$B NMR spectra. Ratios of peak contributions were found by weighing
(instead of integrating electronically) the very broad peaks from paper copies of spectra; 4-7 trials were repeated and a standard deviation of the weights is shown by error-bars in the figures. DSC studies were performed on a TA DSC200 instrument using hermetically sealed aluminum pans against an empty reference cell. Samples were reweighed after thermograms were obtained to ensure that no liquid loss had occurred. Cooling and heating rates were 10° C/min. Rheological measurements were made on an Anton Paar Physica MCR 301 rheometer using a 25 mm diameter and 1° cone angle for frequency sweeps and 25 mm flat plate for extensional rheology. Angular frequency sweeps were performed in the linear viscoelastic region based on a strain sweep. In extensional rheology experiments, the initial gap between the plates was 0.5 mm; after the sample equilibration, the top plate was lifted at a constant velocity of 1μm/sec and the normal force was measured. The data were collected and analyzed using Rheoplus/32 Service V3.10 software. Flow curves were made on an Anton Paar Physica UDS 200 rheometer using a cone-plate geometry (25 mm diameter and 2° cone angle); the temperature was 25°C. The polymer and borax concentrations were varied incrementally while keeping the ratio of \([xPVAc]/[Borax]\) constant (ratios are the same as those described in Table 4-2). The intrinsic viscosity, \(\eta_0\), values were deduced from the plateau of the flow curves in the low shear rate regime (low Newtonian region). The \(\eta_0\) values were plotted versus polymer concentration to determine the concentrations of the five polymers at which 3D network formation is initiated.

*Small Angle Neutron Scattering (SANS).* Samples were prepared from 4 wt % 75PVAc and 1 wt % borax. Three gels with the following liquid compositions were prepared: 100% D_2O, 30/70 acetone-\(d_6\)/D_2O (wt/wt), and 50/50 acetone-\(d_6\)/D_2O (wt/wt). SANS measurements were conducted at the Center for Neutron Research at the National Institute of Standards and
Technology (NIST, Gaithersburg, MD, USA) using the NG7 30 m instrument\textsuperscript{91,92} over a set of 3 distances (15 m, 6 m, 1 m) at a wavelength $\lambda = 6$ Å, providing an overlap between the 3 configurations and, at the end, a range of scattering vector $Q$ from 0.004 Å\textsuperscript{-1} to 0.45 Å\textsuperscript{-1} with about 250 useful points in the range. Radial averaging of the isotropic 2D arrays was performed using the NIST software package for IGOR Pro.\textsuperscript{93} Specialized analyses were performed following the guidelines described in the field of molecular gels.\textsuperscript{94,94}

\{[204 Terech, P. 2006]\} Samples were prepared 2-3 days in advance and loaded into sealed 1 mm pathlength cells with quartz windows on the day of data collection and heated to 95°C to drive out air bubbles. They were cooled to room temperature and placed in the beam within 30 min.

*Size Exclusion Chromatography (SEC), performed by Drs. Gerald O. Brown and Patricia M. Cotts of DuPont.* The molecular weight distributions of PVAc and PVA samples were determined using SEC with a column calibration based on dextran standards. The mobile phase was aqueous phosphate buffered saline (PBS). The molecular weight data, as a function of elution volume, were fitted by a linear relation of log M versus elution volume, and this fit was used to generate a molecular weight distributions using Empower software from Waters. Analyses were performed using 2 TSKGM PW\textsubscript{XL} columns (in series) from Tosoh Biosciences and a Waters SEC-LS chromatograph consisting of a Waters Alliance 2690 (solvent delivery and auto-injector) component, a temperature-controlled column compartment and a Waters 410 differential refractive index detector.

*Sample Preparation.* A weighed sample of xPVAc was placed in a glass screw-cap vial with weighed amounts of an organic liquid and water. Organic liquid/water mixtures are reported
on a wt/wt basis. The polymers were dissolved in the liquids either by standing overnight at room temperature in a closed vessel or by gently heating and stirring. Thereafter, an aliquot of an aqueous borax solution was added drop-wise with stirring. The gels were stirred vigorously with a spatula and allowed to equilibrate at rest for several hours prior to use.

_Melting Range Studies._ A 0.3 g portion of each gel, prepared as described above, was flame-sealed in a glass tube and cooled to 4 °C. Then the tube was inverted and submerged in a water bath at 0 °C. The temperature of the bath was raised at 1.5 °C/min while the temperature ranges over which each sample first showed signs of flow and fell completely were recorded. Three trials were performed on gels prepared from 4 wt % 80PVAc with 30/70 1-propanol/water (wt/wt) and varying concentrations of borax to confirm reproducibility of the results.

_Density Studies._ Three gels were prepared from solutions of 6 wt % 75PVAc and 0.7 wt % borax with a 1/1 1-pentanol/water (wt/wt) liquid composition. Upon mixing, a two phase system was obtained consisting of an opaque gel and a separate liquid layer. The liquid layer was removed from each sample with a 50 µL syringe and weighed. The average density was calculated from the volumes and weights of the expelled liquids from the gels. The total weight of the expelled liquid after phase-separation was also measured.

4.2. _Introduction and exploration of polymer parameters._

Research on the use of PVA-borax gels for applications in art conservation was initiated as part of an ongoing collaboration with the Dei research group at the University of Florence.\textsuperscript{95,96} PVA-borax hydrogels, as described in Chapter 3, have been studied extensively. Initial work on
the system by our research group indicated that PVAc-borax gels could be prepared with a 1-propanol/water ratio as high as 25/75 wt/wt.\textsuperscript{96,97} Smaller amounts of other liquids could be incorporated into these systems as well, including 1-pentanol, 2-butanol, cyclohexanone, and propylene carbonate.\textsuperscript{96} The materials were found to be effective in removing dammar and mastic from paint-outs on glass substrates, as well as in the treatment of an oil painting from the 16\textsuperscript{th} century.\textsuperscript{96} The elastic properties of the gels made their removal from the surface being treated very easy, thus prompting more research into the possibilities for their application as an art conservation treatment system. The work described throughout this chapter has been published in Angelova et al., 2011 and Natali et al., 2011.\textsuperscript{6,7}

As described in Chapter 1, one of the important properties of a gel used for conservation treatments is its ability to gelate a variety of cleaning agents. Because of its highly polar nature, PVA is soluble in water or in water with only small amounts of polar solvents added.\textsuperscript{96,97} To expand the range of types and amounts of liquids that can be incorporated into the gels without altering their appealing physical properties, use of partially hydrolyzed poly(vinyl acetate)s as gelators was explored in place of PVA.

![Figure 4-1. Alcoholysis of poly(vinyl acetate) (PVAc) to fully hydrolyzed poly(vinyl alcohol) (PVA), and partially hydrolyzed poly(vinyl acetate) (xPVAc).](image)

Figure 4-1. Alcoholysis of poly(vinyl acetate) (PVAc) to fully hydrolyzed poly(vinyl alcohol) (PVA), and partially hydrolyzed poly(vinyl acetate) (xPVAc).
The degree of hydrolysis, or “x” in xPVAc, depends on the extent of the preparation reaction. Industrially, xPVAc is produced by alcoholysis of PVAc as shown in Figure 4-1. The polymers obtained for this study were prepared in this manner. ⁹⁸ Seven polymers with different degrees of hydrolysis and molecular weights were obtained for this research (Table 4-1). The degree of hydrolysis and “blockiness” calculations described below were performed on five of the polymers – PVA, 80PVAc_3, 75PVAc, 45PVAc, and 40PVAc. The degree of hydrolysis in the polymer designations is rounded for ease (i.e., the degree of hydrolysis of 75PVAc was established by ¹H NMR spectroscopy to be 76%; vide infra).

Table 4-1. Summary of xPVAc properties.

<table>
<thead>
<tr>
<th>Kuraray Poval® Grade</th>
<th>Exceval</th>
<th>Poval</th>
<th>Poval</th>
<th>Poval</th>
<th>Poval</th>
<th>Poval</th>
<th>Poval</th>
</tr>
</thead>
<tbody>
<tr>
<td>HR3010</td>
<td>PVA405</td>
<td>PVA420</td>
<td>PVA424</td>
<td>PVA505</td>
<td>LM-20</td>
<td>LM-10</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>&gt;99%</td>
<td>80%</td>
<td>80%</td>
<td>80%</td>
<td>75%</td>
<td>45%</td>
<td>40%</td>
</tr>
<tr>
<td>Mₜ</td>
<td>~31600</td>
<td>~21100</td>
<td>~35600</td>
<td>~47300</td>
<td>~7300</td>
<td>N/Aᵇ</td>
<td>N/Aᵇ</td>
</tr>
<tr>
<td>Blockiness</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.39</td>
<td>0.48</td>
<td>0.47</td>
<td>0.48</td>
</tr>
<tr>
<td>Viscosity (mPa·s)ᵃ</td>
<td>13.0</td>
<td>4.8</td>
<td>32.4</td>
<td>46.6</td>
<td>4.7</td>
<td>3.6</td>
<td>5.3</td>
</tr>
</tbody>
</table>

ᵃ Information provided by manufacturer. ᵇ Although Mₜ data for 45PVAc and 40PVAc were obtained by size exclusion chromatography, they are not reported here due to concerns that agglomeration (from aggregation) of these polymers may have caused erroneous results.
According to the supplier, the polymers contain < 3% residual methanol. By $^1\text{H}$ NMR spectroscopy, free acetate ions were present. All polymers for these studies were cleaned as described in the methods and materials section to remove these impurities. The hydrolysis degree and the blockiness factors of the polymers reported in Table 4-1 were obtained using $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy. Calculation of the hydrolysis of the polymers was performed using Equation 4-1. Figure 4-2 shows a labeled $^1\text{H}$ NMR spectrum of 75PVAc, while Figures 4-3 and 4-4 show the differences between five of the polymers by $^1\text{H}$ and $^{13}\text{C}$ NMR spectroscopy.

$$
\% \text{hydrolysis} = 100 - \frac{\text{acetate protons}}{3} \left( \frac{\text{methylene protons}}{2} \right) = 100 - \frac{3}{3} \left( \frac{8.46}{2} \right) = 76\% \quad (4-1)
$$

Figure 4-2. $^1\text{H}$ NMR spectrum of 75PVAc in DMSO-$d_6$ showing relevant peak assignments. Peaks at (1) encompass all methylene protons between two hydroxyl monomers (a), between a hydroxyl and an acetate monomer (b) and between two acetate monomers (c). Integrated areas of methylene and acetate hydrogens (assumed to be 3H) are labeled in red.
Figure 4-3. $^1$H NMR spectra of polymers in DMSO-$d_6$: (A) PVA, (B) $80\text{PVAc}_3$, (C) $75\text{PVAc}$, (D) $45\text{PVAc}$, and (E) $40\text{PVAc}$. 
Figure 4-4. $^{13}$C NMR spectra of polymers: (A) PVA in D$_2$O; (B) 80PVAc$_3$ in D$_2$O; (C) 75PVAc in D$_2$O; (D) 45PVAc in 1:1 methanol-$d_4$:D$_2$O; (E) 40PVAc in 1:1 methanol-$d_4$:D$_2$O.

The “blockiness” factor, $\eta$, which indicates how randomly the acetate and hydroxyl groups are distributed throughout the polymer chains, depends on the method chosen to prepare the xPVAc. The three common methods are alcoholysis, saponification, and reacetylation.
The blockiness factor of the polymers was calculated from $^{13}$C NMR spectra using the peaks highlighted in Figure 4-5 using Equations 4-5 through 4-10 discussed below. By integration of the methylene carbon peaks, the degree of hydrolysis, the mol % of methylene carbons in each of the three labeled groups, and the blockiness factor, which indicates the distribution of the two side-groups as random or blocky can be calculated. If the polymers are highly blocky, gelation may be encouraged by a mechanism similar to that for the formation of a polyelectrolyte gel described in Chapter 2.

Figure 4-5. $^{13}$C NMR spectrum of 40PVAc in 1/1 acetone-$d_6$/D$_2$O (wt/wt) and referenced to the acetone CD$_2$H signal. The inset shows the methylene carbon region - the three peaks which are attributed to the different populations of methylene carbons are those between two hydroxyl
groups (OO), those between an acetate and a hydroxyl group (AO) and those between two acetate groups (AA).

\[
PV\text{-}OAc + NaOH \rightarrow PV\text{-}OH + Na^+ OAc^- \quad (4-2)
\]

\[
PV\text{-}OAc + CH_3OH \rightarrow PV\text{-}OH + CH_3 OAc \text{ (catalyzed by NaOCH}_3) \quad (4-3)
\]

\[
PV\text{-}OH + AcOH \rightarrow PV\text{-}OAc + H_2O \quad (4-4)
\]

Saponification by acid or base results in the highest degree of blockiness. According to Moritani and Fujiwara, the direct saponification reaction has a large rate because the acid or base catalyst becomes adsorbed onto the polymer chains in the regions where the acetate groups have already been cleaved.\(^9^9\) As a result, hydrolysis of the acetate groups occurs directly adjacent to the already-formed hydroxyl groups and therefore relatively blocky co-polymer chains are generated.\(^9^9\) Moritani and Fujiwara show that samples prepared by saponification have \(\eta\) values between 0.40 and 0.53 while samples prepared by alcoholysis have \(\eta\) values between 0.49 and 0.64. Samples prepared by re-acetylation have \(\eta\) values between 0.83 and 1.10.\(^9^9\)

The values for \(\eta\) obtained for the four partially hydrolyzed polymers described in Table 4-1 are close to those obtained by Moritani and Fujiwara for their alcoholysis samples. The equations used to obtain the blockiness values are presented below, where AA, OO, and AO represent the integration of the methylene carbon peak between two acetate groups, two alcohol groups, and between one acetate and one alcohol group, respectively.\(^9^9\) When \(\eta = 1\), the polymer is considered completely random, when \(0 \leq \eta \leq 1\) the polymer has a blockier distribution, while in cases where \(\eta = 0\) the distribution is completely blocky. Figure 4-6 shows the \(^{13}\)C NMR
spectrum of 45PVAc with the appropriate integrations used to calculate the blockiness factor of this polymer. The same calculations were performed for the other three partially hydrolyzed polymers.

\[
A = 100 \frac{[AA + 0.5(AO)]}{(AA + AO + OO)} = \text{mol} \% \text{ Acetate}
\]  
\[
O = 100 \frac{[OO + 0.5(AO)]}{(AA + AO + OO)} = \text{mol} \% \text{ Hydroxide}
\]  
\[
AA/(AA + AO + OO) = \text{mol} \% \text{ AA}
\]  
\[
AO/(AA + AO + OO) = \text{mol} \% \text{ AO}
\]  
\[
OO/(AA + AO + OO) = \text{mol} \% \text{ OO}
\]  
\[
\eta^{(\text{eta})} = AO/[2(A \times O)]
\]  

Figure 4-6. $^{13}\text{C}$ NMR spectrum of 45PVAc reported in 50/50 D$_2$O/acetone-$d_6$ (wt/wt). The blockiness of this polymer is $\eta = 0.48$ which falls into the range of alcoholysis produced poly(vinyl alcohol-co-acetates) studied by Moritani and Fujiwara.$^{99}$
4.3. Formation and characterization of hydrogels and gels prepared with small fractions of organic liquids.

Initial studies on the solubilization of the polymers listed in Table 4-1 showed that the 40PVAc and 45PVAc were not fully soluble in water at concentrations of 10 to 15 wt % necessary for gel formation and required the addition of a small amount of an organic solvent such as 1- or 2-propanol. The 75% hydrolyzed polymer could be solubilized in water, although not easily. When an aqueous solution of borax was added, all of the polymer solutions were found to form gels. Establishing the minimum amounts of polymer and borax necessary to form stable, elastic gels from each polymer grade was accomplished by varying either of the components while keeping all other variables constant. Series of gels were prepared from each polymer in 30/70 (wt/wt) 1-propanol/water mixtures to ensure that all polymers could be solubilized. Thermally stable gels formed when the ratio of hydroxyl groups to borate ions in solution was in the range of 5/1 to 20/1, as shown by the falling drop measurements presented in Figure 4-7.
Figure 4-7. Melting ranges (vertical lines) for xPVAc-borax gels with 30/70 1-propanol/water (wt/wt) mixtures: (⋆) PVA, (●) 80PVA_3, (▲) 75PVAc, (▼) 45PVAc, (■) 40PVAc; (A)
varying amounts of polymer ([borax] = 2.0 wt %); (B) varying amounts of borax at 11 wt % 40PVAc, 16 wt % 45PVAc, 5 wt % 75PVAc, 4 wt % 80PVA_3, and 4 wt % PVA.

The concentration of polymer and borax necessary to form thermally stable gels is highly dependent on the polymer molecular weight and degree of hydrolysis. Due to molecular weight effects, 80PVAc_3, which has 20% fewer functional groups for crosslink formation than PVA, consistently forms more thermally stable gels. In the former, $C_N$, or the concentration of network formation (as discussed in Chapter 3), is expected to be lower because chain overlap occurs at lower concentrations. The low degree of hydrolysis polymers, 40PVAc and 45PVAc, are presumed to have molecular weights below ca. 25000 based on the reported viscosity measurements (see Table 4-1), although 40PVAc is likely to have a higher molecular weight than 45PVAc. Combined with the small amount of crosslink-forming functional groups, thermally stable gels from 40PVAc and 45PVAc require at least 10 wt % of polymer for gelation. The former shows consistently higher thermal stability due to its higher molecular weight.

Table 4-2. Parameters describing concentrations of polymer and borax found in the most thermally stable gels formed with 30/70 (wt/wt) 1-propanol/water mixtures (melting range values) or with largest observed increase in $\eta_0$ (intrinsic viscosity values) in gels prepared in pure water.
The results from falling drop experiments on gels prepared with 30/70 1-propanol/water (wt/wt) mixtures with different polymers can be seen in Table 4-2. Intrinsic viscosity measurements were performed by our collaborators at the University of Florence using the ratios of hydroxyl groups to borate ions found by the falling drop tests. The $C_N$ values determined in this manner are also presented in Table 4-2 for each polymer. The $C_N$ values are markedly different than those obtained by the falling drop method. Intrinsic viscosity measurements, as discussed in Chapter 3, reflect the transition from sol to gel, or, in a polymer solution, the transition from the dilute to the semi-dilute regime. For xPVAc-borax gels, this concentration marks the transition from predominantly intramolecular crosslinking to intermolecular crosslinking in the system. The intrinsic viscosity measurements reflect the lowest concentration at which intermolecular crosslinking occurs (the gel point), while the falling drop measurements reflect the temperature at which enough intramolecular crosslinks are broken to allow for an increase in chain motions and disentanglements, which result in viscous flow of the material.
Figure 4-8. Plots of $\eta_0$ versus xPVAc concentration in H$_2$O. The [xPVAc]/[Borax] concentration ratios are the same as those in Table 4-2. Data were obtained by Irene Natali.$^{41,74}$

The melting range results show that the thermal stability of the gel systems is affected more by the polymer concentration than by the crosslinker concentration. This observation is in
agreement with neutron spin echo results obtained for PVA/borax systems by Kanaya et al. which show that crosslinking is not necessary for gel formation while chain entanglements are crucial. Kjøniksen et al. draw similar conclusions from investigations on the viscoelasticity of PVA-glutaraldehyde systems. The gel strength of the PVA-based hydrogels increases with increasing concentrations of glutaraldehyde, an irreversible crosslinking agent. Increasing chain entanglement and more hydrogen bonding among polymer chains (from increased polymer concentrations) and more crosslinks (from higher crosslinker concentrations) also increase gel strength. These effects are more noticeable at low polymer concentrations where the network is more fragile and sensitive to perturbations. Our results are determined by, amongst other factors, the fraction of hydroxyl groups that exist as vicinal diols because they are the only ones that can effectively participate in crosslinks. Nevertheless, even when the availability of hydroxyl groups to participate in H-bonding or crosslinking is decreased due to a lower degree of hydrolysis, the polymer concentration still seems to be the dominant factor in determining the thermal stability of the borax-crosslinked system.

xPVAc-borax gels prepared with water, or water with an additional solvent at a ratio smaller than 30/70 solvent/water (wt/wt), show rheological behavior characteristic of viscous polymer fluids with a narrow distribution of relaxation times due to crosslinks with finite lifetimes. Figure 4-9-A shows the cross-over between the storage and loss moduli (G’ and G”, respectively), resulting in viscous flow at low frequencies and long observation times, and elastic behavior at high frequencies and short observation times. Figure 4-9-B shows the strain stiffening behavior of the same gel with both moduli increasing in response to the applied strain
until, at ~100% strain, there is a rapid decrease of the moduli, indicating that crosslinks and entanglements are lost.

Figure 4-9. An angular frequency sweep (A) and a strain sweep (B) of a gel prepared with 6 wt % 75PVAc and 1.4 wt % borax in 30/70 1-propanol/water (wt/wt); storage modulus, \(G'\) (■), and loss modulus, \(G''\) (■).

The angular frequency sweeps of gels prepared from two polymers with different hydrolysis degrees but similar molecular weights (based on their viscosity measurements in Table 4-1) showed nearly identical behavior, with little change in the frequency of the \(G'\) and \(G''\) cross-over. The angular frequency sweep shown in Figure 4-10 indicates that when the polymer and borax concentrations are kept constant, small changes in the degree of hydrolysis (on the order of 5%) do not change the physical properties of the system considerably. This result is consistent with observations that not all of the borax is participating in crosslinks. A reduction in crosslink functional groups on the polymer chains would be expected to produce a perceptible effect on the cross-over region if all boron moieties were forming diol complexes.
Figure 4-10. Angular frequency sweeps of gels prepared with 4 wt % polymer and 1 wt % borax in water from 80PVAc_1 (black) and 75PVAc (red) with $G'$ (■) and $G''$ (○) performed in the linear viscoelastic region with a strain of 1%. The blue dashed line indicates the cross-over frequency for both materials.

For a deeper investigation into the effects of molecular weight on the physical and chemical properties of xPVAc-borax gels, the three different polymers with 80% hydrolysis described in Table 4-1 were studied using $^{11}$B NMR spectroscopy as well as rheology. The $^1$H NMR spectra of the three polymers can be seen in Figure 4-11. The blockiness factor was not investigated. The polymers obtained from the Kuraray Co., Ltd. are expected to have $\eta$ in the range of an intermediately blocky polymer produced through alcoholysis.
Figure 4-11. $^1$H NMR spectra of 80PVAc_1 (viscosity = 4.8 Pa·s), 80PVAc_2 (viscosity = 32.4 Pa·s) and 80PVAc_3 (viscosity = 46.6 Pa·s) in DMSO-d$_6$. The bottom curve shows the 3 individual spectra normalized for peak intensity and overlaid.

Gels prepared with high molecular weight ($M_w$) PVAcs require a lower polymer concentration for formation and have higher thermal stabilities (Figures 4-7 and 4-8). When keeping the concentration of polymer and borax constant, polymers with a higher molecular weight show higher thermal stability and a more elastic behavior than gels prepared from polymers with lower molecular weights (Figures 4-12 and 4-13). These effects are to be expected, due to the higher entanglement and hydrogen bonding which can occur between polymer chains in solutions of high molecular weight species. Figure 4-13 shows the results of
extensional rheology experiments performed on gels prepared from three 80PVAc polymers with varying molecular weights. For these experiments, a sample is placed at a fixed distance between the two parallel plates of the instrument, and the top plate is moved up at a fixed velocity. The force the gel exerts on the top plate is measured. The figures show a rapid increase in the measured force as the distance between the plates is initially increased because of the entanglements and crosslinks responsible for the gel elasticity. At a critical distance these junctions are lost and the force decreases rapidly. Gels prepared from high molecular weight polymers show a larger maximum normal force than gels prepared using low molecular weight polymers. The large number of network entanglements in high $M_w$ polymer gels and the resulting enhanced elasticity causes the systems to exert a larger initial force than gels prepared from low $M_w$ polymers.

Figure 4-12. Melting ranges of hydrogels composed of 4 wt % 80PVAc and 1 wt % borax from three 80PVAc polymers with different molecular weights. On the x-axis, 80PVAc_1 has the
lowest viscosity and $M_w$ while 80PVAc_3 has the highest viscosity and $M_w$; 80PVAc_2 is intermediate.

Figure 4.13. Rheological response of hydrogels composed of 4 wt % PVA and 1 wt % borax from 80PVAc_1, 80PVAc_2, and 80PVAc_3. (A) Angular frequency sweeps; (B) storage (■) $G'$ and loss (○) $G''$ moduli cross-over frequencies (strain is 1 %, in linear viscoelastic region for all three); (C) extensional rheology; and (D) the maximum normal force found for each gel; standard deviations were calculated from three trials.
A higher degree of polymer chain entanglement does not necessarily mean that the systems have more crosslinks. $^{11}$B NMR spectra of hydrogels prepared from 80PVAc_1, 80PVAc_2, and 80PVAc_3 show a significant decrease in the amount of crosslinked boron with increasing molecular weight when the polymer and borax concentrations are kept constant at 4 wt % and 1 wt %, respectively, for each system (Figure 4-14).

![Figure 4-14](image)

Figure 4-14. Amount complexed boron species in hydrogels prepared from 4 wt % of 80PVAc and 1 wt % borax from 80PVA_1 (■), 80PVAc_2 (▲), and 80PVAc_3 (□) calculated from integration of $^{11}$B NMR spectral signals; results are shown for three hydrogel samples for each of the three polymers.

At low concentrations (1 wt % polymer and 0.25 wt % borax), the amount of cross-links in gels prepared from each polymer is relatively low and constant (Figure 4-15). The same is true of the gels prepared from 80PVAc_3 with varying concentrations of PVAc and borax (always keeping the ratio of polymer to borax at 4 to 1). Although the absolute concentration of cross-linked boron increases slightly as the total borax concentration is increased, the change is very
small (Figure 4-15). The results suggest that the longer polymer chains in 80PVAc_3 gels contribute to a decrease in crosslink-formation when the concentration of the polymer is far above the $C_N$. Because the di-diol complexes responsible for gelation in these systems have a negative charge, the decreased number of crosslinks in concentrated 80PVAc_3 gels may be a result of charge repulsion. The larger amount of chain entanglements may compensate for the gel elasticity observed rheologically.

Figure 4-15. Percentage of boron species as crosslinking borate ions in hydrogels composed of 1 wt % 80PVAc_1, 80PVAc_2 and 80PVAc_3 (points from left to right) and 0.25 wt % borax calculated from $^{11}$B NMR spectral integrations (A). Complexed borate and absolute concentration of complexed borate in hydrogels composed of different concentrations of 80PVAc_3 and borax while keeping weight ratio of PVA to borax at 4 to 1 (B).
Figure 4-16. Percentage of complexed borate ions in hydrogels composed of 4 wt % 80PVAc and 1 wt % borax as a function of time after gel preparation. (■) 80PVAc_1; (■) 80PVAc_2; (■) 80PVAc_3

In a study of the effects of aging on the xPVAc-borax hydrogels prepared with the three 80PVAc polymers, reduction of borate complexation with time was found for systems prepared with the lowest $M_W$ polymer (Figure 4-16). The percentage of complexed borate in gels prepared from the higher molecular weight 80PVAc_2 and 80PVAc_3 is similar and does not change significantly during the 24 hours post-preparation. The initial gel formed immediately upon borax addition to the xPVAc solution may not be at equilibrium, and reaching it may take several days. The reduction in the number of crosslinks observed for the low molecular weight polymer suggests a reorganization of the complexed borates throughout the system, which may cause charge repulsion, leading to a decrease in the overall number of crosslinks. Even so, the lowest molecular weight polymer gels still show a higher percentage of crosslinks than gels prepared
with the higher molecular weight polymers. This observation will be explored further in the next section, when addition of larger amounts of organic solvents to the gel system is discussed.

### 4.4. Gels prepared with large fractions of organic liquids.

As noted in Section 4.3, dissolution of xPVAc polymers where x is small was difficult in neat water. Addition of water-miscible polar organic liquids encouraged polymer solubilization. PVA and xPVAc solubilization and chain conformation in solution has been explored in the past owing to interest in the use of the polymer as a stabilizer in emulsion polymerization. On account of the hydrophobic nature of the polymer backbone and the acetate side-groups, water is not a “theta”, or ideal, solvent for partially hydrolyzed PVAc, especially if the side-group distribution is blocky. Dimethyl sulfoxide (DMSO) is among the best solvents for these polymers. N-methylpyrrolidone (NMP) is also a good solvent for PVA and xPVAc. Theta solvents solvate both the hydrophobic and the hydrophilic regions of polymers, allowing the chains to expand fully in solution. In water, the hydrophobic segments, especially in blocky co-polymers, can fold in a pseudo-micellar conformation, exposing the hydrophilic groups to the solvent and resulting in aggregation.

From the initial solubility studies of the five polymers described in Table 4-1, it was established that addition of some organic liquids to solutions of 40, 45, and 75PVAc facilitated solubilization. These liquids include methanol, ethanol, 1- and 2-propanol, acetone, DMSO and NMP. Upon addition of aqueous borax to polymer solutions of these liquids, stable gels were obtained. To find the maximum amount of organic liquid which could be gelated by these polymers, series of gels were prepared with the polymer and borax concentrations established in
Section 4.3 in which the ratio of organic liquid/water was varied. As expected, the presence of additional acetate side-groups on the polymer chains enhanced solubilization of the polymers in mixtures which contained higher fractions of organic liquids. It was possible to prepare gels from the low degree of hydrolysis polymers in which the majority of the liquid composition was organic (Table 4-3). Although some of the low degree of hydrolysis polymers were soluble in neat organic liquids, water was necessarily introduced to the systems as a delivery agent for the borax salt (N.B., borax can be solubilized in methanol and DMSO at concentrations sufficient for gel formation, and gels from neat methanol and DMSO can be obtained from 40PVAc).

Table 4-3. Maximum amounts (wt %) of organic liquid component that yield a stable gel without syneresis or flow for at least 10 s when a sample was inverted.

<table>
<thead>
<tr>
<th>Component</th>
<th>PVA</th>
<th>80PVAc_3</th>
<th>75PVAc</th>
<th>45PVAc</th>
<th>40PVAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
<td>100%</td>
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<tr>
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<td>-</td>
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<td>50%</td>
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<tr>
<td>NMP</td>
<td>30%</td>
<td>50%</td>
<td>70%</td>
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</tr>
</tbody>
</table>
The remainder of the liquid is water. \textsuperscript{b} \textit{N}-Methylpyrrolidone \textsuperscript{c} These systems are unstable and undergo syneresis shortly after preparation.

The gels prepared using organic liquids are transparent or translucent and are stable for weeks in closed containers. Some of the less polar liquids, such as 1-pentanol, can be incorporated but the resulting gels will undergo syneresis within minutes to hours. Table 4-4 shows the density of liquid expelled from a 50/50 1-pentanol/water (wt/wt) system. Based on the results, the liquid is almost exclusively 1-pentanol. Approximately 25\% of the 1-pentanol is retained by the gel resulting in an opaque appearance.

Table 4-4. Weight and density of liquid expelled (syneresis) from three gels of 6 wt \% 75PVac, 0.7 wt \% borax, and 50/50 1-pentanol/water (wt/wt). The reported density of 1-pentanol at room temperature is 0.815 g/L.\textsuperscript{104}

<table>
<thead>
<tr>
<th></th>
<th>Gel 1</th>
<th>Gel 2</th>
<th>Gel 3</th>
</tr>
</thead>
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<tr>
<td>Total liquid (g)</td>
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<td>0.3420</td>
<td>0.3531</td>
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<tr>
<td>Non-incorporated liquid (g)</td>
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<td>0.0414</td>
<td>0.0414</td>
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<tr>
<td></td>
<td>0.0412</td>
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</tr>
<tr>
<td></td>
<td>0.0401</td>
<td>0.0410</td>
<td>0.0407</td>
</tr>
<tr>
<td>Average (g)</td>
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<td>0.0410</td>
<td>0.0408</td>
</tr>
<tr>
<td>Density (g/L)</td>
<td>0.812</td>
<td>0.820</td>
<td>0.816</td>
</tr>
</tbody>
</table>
4.4.1. Rheological characterization.

As the fraction of organic liquid in the gels was increased, they were observed to become stiffer, and in some cases quite brittle. This effect was most pronounced in gels prepared from the low degree of hydrolysis polymers where the organic content could be as high as 75% of the total liquid in the system. The thermal stability of these systems was analyzed using the falling drop method (Figure 4-17). In agreement with visual observations, the melting ranges of gels prepared from 45PVAc and 75PVAc tend to increase when increasing the organic fraction of the liquid component. There are some deviations in the results shown in Figure 4-17, especially when the temperatures are close to the boiling point of the gelated liquids. A similar, although far less pronounced observation is found for gels prepared from 80PVAc_3 and PVA. For a better and more quantitative understanding of the changes occurring in these systems, rheological studies were initiated.
Figure 4-17. Melting temperature ranges (indicated by vertical lines) of gels prepared with varying amounts of methanol (■), ethanol (▲), 1-propanol (●), and NMP (■). (A) 11 wt % 40PVAc and 2 wt % borax, (B) 6 wt % 75PVAc and 1.4 wt % borax, (C) 4 wt % 80PVAc_3 and 1 wt % borax, and (D) 4 wt % PVA and 1.1 wt % borax. Data are averages from two runs.

Series of gels with constant polymer concentrations and varying amounts of 1-propanol, ethanol, or N-methylpyrrolidone were prepared from 45PVAc, 75PVAc, 80PVAc_3, and PVA. The concentrations of polymer and cross-linker which gave the most thermally stable gels have been used throughout all studies. The concentrations correspond to molar ratios of hydroxyl groups to borate ions between approximately 10:1 and 20:1.

The effect of the organic liquid on the consistency of the gels was deduced from the frequency at which the storage (G’) and loss (G’”) moduli cross over in a frequency sweep. In a true gel, no such cross-over should occur and the material should behave as a solid with infinite relaxation time (see discussion in Appendix B and Section 3.2). The behavior of xPVAc-borax gels with large fractions of organic liquids is similar to that described for a 30/70 1-propanol/water (wt/wt) gel in Section 4.3. The cross-over of the two moduli, G’ and G’”, in these
systems indicates that they are not ideal gels, rather, they are transient networks. At long observation times (low frequency) they behave as liquids and flow, while at short observation times (high frequency), the gels display solid-like behavior. The observed frequency at which $G'$ and $G''$ cross-over is approximately the inverse of the relaxation time of the network. Therefore, when the cross-over of the moduli occurs at a lower frequency, the system is closer to being ideal gel. When the cross-over of the moduli occurs at a lower frequency the network behaves elastically over a longer frequency span. As can be seen below for gels prepared from PVA, the point of $G'$ and $G''$ cross-over shifts to lower frequencies as the fraction of organic liquid in the materials is increased.
Figure 4-18. Angular frequency sweeps of gels prepared from 4 wt % PVA and 1.1 wt % borax with water, 15/85 organic/water, 30/70 organic/water (wt/wt) in which the organic components are 1-propanol (A), ethanol (B), and N-methylpyrrolidone (C). In D, the liquid composition is 30/70 1-propanol/water (wt/wt), the polymer concentration is constant at 4 wt %, and the borax concentration is varied: 1.5 wt %, 1.1 wt %, 0.9 wt %, 0.7 wt %, 0.3 wt %. $G'$ (■) and $G''$ (○) were measured in the linear viscoelastic range with strain = 1%.

The trends observed in the frequency dependence of the storage and loss moduli in these gels mirror those seen in the lower hydrolysis polymers. As the fraction of organic liquid is increased in the gels, the cross-overs of the moduli occur at lower frequencies. This is clearly shown in a plot of the cross-over frequency as a function of the organic liquid content (Figure 4-19-A). There is a rough correlation of the relaxation time and the polarity of the solvent. This trend can best be observed in the cross-over of the 15/85 1-propanol/water (wt/wt) gels seen in Figure 4-19-A. The relaxation time increases in the order N-methylpyrrolidone > ethanol > 1-propanol. The degree of cross-linking in the gels (and therefore the elasticity) depends strongly on the quantity of hydroxyl units exposed along the polymer chains. Because NMP is a good
solvent for xPVAc, the polymers are expected to be better solubilized, allowing the chains to extend further in solution. As a result, the transition from the dilute to semi-dilute regime in NMP is likely to occur at a lower concentration than in a poor solvent and intermolecular crosslinking is likely to occur to a larger degree than it does in poorer solvents. The changes in the elasticity of the system as the borax concentration is varied in gels with large 1-propanol fractions are minimal compared to those observed when the solvent composition is altered.

![Figure 4-19](image_url)

Figure 4-19. Plots of frequencies of cross-over of G’ and G” from Figure 4-18 as a function of (A) increasing organic liquid (wt %) for gel prepared from 4 wt % PVA and 1.1 wt % borax with 1-propanol, ethanol, or NMP; and (B) borax concentration in gels prepared from 4 wt % PVAc and 30/70 1-propanol/water (wt/wt).

The effect of solvent polarity on the rheologically measured elasticity of the gels is seen with the other three polymers in the series (40PVAc, 75PVAc, and 80PVAc_3) as shown in Figure 4-20. The effect is most pronounced for gels prepared from the polymer with the lowest degree of hydrolysis and least pronounced for gels prepared with the 80% hydrolyzed polymer (which also has the highest molecular weight). The large contribution of chain entanglements to
the elasticity of 80PVAc_3 gels may be the reason for the reduced effect of solvent addition on the network relaxation time. All gels prepared from 80PVAc_3 have longer relaxation times (cross-over frequencies less than 0.6 rad/s) than those composed of 40PVAc, 75PVAc, or PVA (cross-over frequencies as high as 2 rad/s). The rheology results presented above clearly show that the incorporation of organic liquids results in an increase of relaxation times, which can be further enhanced by the use of specific solvents and polymers with larger molecular weights.
Figure 4-20. Frequencies of G’ and G” cross-overs for gels composed of (A) 11 wt % 40PVAc and 2 wt % borax, (B) 6 wt % 75PVAc and 1.1 wt % borax, and (C) 4 wt % 80PVAc and 1 wt % borax with varying amounts of 1-propanol, ethanol, or N-methylpyrrolidone.

When keeping the organic liquid concentration high and varying the borax concentration, changes in the frequency of cross-over are minimal, except at very low borax concentrations (Figure 4-21). The cross-over frequency decreases rapidly as the borax concentration is increased from 0.2 wt % to 0.7 wt %. There is a slight increase in this parameter between 1.0 and 1.5 wt % borax followed by a decrease at 2.0 wt %. Although this behavior may be attributed to experimental error (the experiments have not been repeated to confirm the result), the re-entrant behavior of the gels discussed in Section 3.2 may also contribute to the results. The re-entrant behavior of the xPVAc-borax systems occurs due to charge screening and repulsion between the attached borate ions on the polymer chains (which act as electrolytes) and free sodium ions in solution. The small differences seen in Figure 4-21-C may not merit this interpretation, however.
Figure 4-21. Cross-over frequencies of gels composed of (A) 4 wt % 80PVAc and 40/60 1-propanol/water (wt/wt), (B) 6 wt % 75PVAc and 50/50 1-propanol/water (wt/wt), and (C) 11 wt % 40PVAc and 70/30 1-propanol/water (wt/wt) with varying amounts of borax.

To study the reproducibility of the angular frequency measurements of these systems, gels with different amounts of 1-propanol or different concentrations of borax were prepared from the 45PVAc and 75PVAc polymers (Figure 4-22). The trends observed in the studies described in Figures 4-18 through 4-21 were confirmed by subsequent experiments. The large increase in relaxation time observed for gels prepared with 40PVAc when the borax concentration is increased (Figure 4-21) was also found for gels prepared with 75PVAc when the
studies are extended to lower concentrations (Figure 4-22). Also included in Figure 4-22 are graphs of the storage modulus plateau as a function of 1-propanol concentration, confirming the trend of increasing elasticity with increasing organic content.
Figure 4-22. Value of G’ at the plateau reached at 80 rad/sec from frequency sweeps on gels prepared from 11 wt % 40PVAc and 2 wt % borax with varying amounts of 1-propanol (A) and frequencies of G’ and G” cross-over from the same studies (B); G’ plateau values at 80 rad/sec of gels prepared from 6 wt % 75PVAc and 1.4 wt % borax (C) and frequencies of G’ and G” cross-over from the same studies (D). G’ Plateau at 80 rad/sec of gels prepared from 6 wt % 75PVAc in 30/70 1-propanol/water (wt/wt) with varying amounts of borax (E), and frequencies of G’ and G” cross-over from the same studies (F). Experiments were performed in the linear viscoelastic region with a strain of 1%. Error bars show one standard deviation from 3-4 trials.

The trend of increased elasticity with increasing organic liquid fraction was also confirmed by extensional rheology (Figure 4-23). As noted in Section 4.3, extensional rheology can be used to measure the force on the plates of the rheometer as the gel is being stretched. In the experiments described in Section 4.3, gels were prepared with three polymers which had different molecular weights. The results of those studies showed the large impact of chain entanglements on the gel strength and their correlation with the $M_w$ of the polymers.
Figure 4-23. Extensional rheology of gels prepared from 5 wt % 75PVAc and 1 wt % borax with 0/100, 15/85, 30/70, 45/65 1-propanol/water (wt/wt) liquid compositions (A), and the maxima in the force curves as a function of 1-propanol concentration (B).

Gel strength increases as the amount of organic liquid they comprise is increased (Figure 4-23). The experiments were performed on gels prepared with the same polymer. Increasing chain entanglements are therefore not expected to be the cause of the observed results. An alternative explanation may involve the effect that organic liquid incorporation in the gels has on crosslink formation. The results of the extensional rheology experiments shown in Figure 4-23 suggest that increasing the organic liquid in the gels may force more boron crosslinks to form within the networks.

4.4.2. $^{11}$B NMR spectroscopic studies of the effects of organic liquids on xPVAc-borax gels.

$^{11}$B NMR spectroscopic studies were carried out on gels prepared with varying ratios of acetone to water. The spectra of one set of gels are shown in Figure 4-24. As discussed in Appendix B and Section 3.2, in an aqueous solution of borax one peak is evident at a chemical
shift intermediate between that of boric acid (19.6 ppm) and of the borate ion (~1.5 ppm). This peak is broad due to exchange between non-complexed boric acid and borate ion species on the experimental timescale.

Upon addition of an xPVAc polymer to the borax solution, a peak appears upfield of the exchanging borate-boric acid signal, at ~ 1.5 ppm, which has been ascribed to borate participating in crosslinks, as described in Section 3.2. Based on its chemical shift, the boron resonating near 1.5 ppm is assumed to be in the tetrahedral (i.e., tetravalent) configuration. In aqueous systems, the boron signal of the crosslinked borate is small relative to that of the exchanging borate-boric acid. It is assumed that the areas of the peaks are directly proportional to the populations of their boron-containing species; integration of the two peaks indicates that only 5 - 10% of the boron in aqueous systems is participating in crosslinks. Changing the liquid composition of the system to a 30/70 ratio of acetone/water (wt/wt) causes an enhancement of the crosslinked borate signal. A broadening and downfield shift of the exchanging borate-boric acid peak accompanies this change. Integration of the peaks reveals a significant increase in the signal from boron in crosslinks with additional changes in the liquid composition to incorporate higher ratios of acetone (Figure 4-25). The results of the NMR spectroscopy studies are in agreement with the rheological observations: the increased elasticity and strength reflected in the storage modulus and normal force measurements of gels with large fractions of organic liquids are a result of increased crosslink formation.
Figure 4-24. $^{11}$B NMR spectra of 1 wt % borax in D$_2$O (■), 4 wt % PVAc and 1 wt % borax in D$_2$O (■), 4 wt % PVAc and 1 wt % borax in 30/70 acetone-$d_6$/D$_2$O (wt/wt) (□), and 4 wt % PVAc and 1 wt % borax in 50/50 acetone-$d_6$/D$_2$O (wt/wt) (▲). Signals are referenced to F$_3$B-O(C$_2$H$_5$)$_2$ in CDCl$_3$ held in a sealed tube within the one containing the gel samples.

Figure 4-25. The percent of borate participating in crosslinks, of the total boron-containing species, determined by integration of $^{11}$B NMR signals from two trials (red and black points).
If the concentrations of the polymer and borax are increased incrementally while keeping the polymer/borax weight ratios constant, the quantity of borate species which is crosslinked remains relatively constant with only a small increase in the absolute concentration of crosslinked borate ions. Increasing the borax concentration while keeping the acetone/water content at 30/70 (wt/wt) and polymer concentration at 4 wt %, results in an apparent decrease in the fraction of boron species participating in crosslinks although the absolute concentration of crosslinks increases (Figure 4-26). The increase in the absolute number of borate ions participating in crosslinks can be correlated with the increase in the thermal stability of the gels with increasing borax concentrations (Figure 4-7).

![Graph showing concentrations and fractions of borate ion participating in crosslinking](image)

Figure 4-26. Concentrations and fractions of borate ion participating in crosslinking (of total boron-containing species) in gels composed of 4 wt % 75PVAc with a 30/70 acetone/water (wt/wt) liquid as calculated from $^{11}$B NMR spectra.
$^{11}$B NMR spectra of gels with different ratios of organic liquid/water obtained over the course of four days do not show significant changes in the amount of crosslinks present; the gels are stable and the results are reproducible over the course of several days. Increasing the temperature of the gels causes an upfield shift of the exchanging borate-boric acid peak and a decrease in the intensity of the crosslinked boron peak (Figure 4-27). As discussed in Section 3.2, a decrease in the pH of the system results from crosslink formation. The accompanying depletion of borate ions in solution due to crosslinking and reduction in the rate of boric acid to borate ion exchange causes the exchanging borate-boric acid peak to broaden and appear at a chemical shift closer to that of free boric acid. Increased crosslinking intensifies this effect, as can be seen in Figure 4-24, while increasing the temperature reverses the process (Figure 4-27).

![Figure 4-27. $^{11}$B NMR spectra of a 5 wt % 75PVAc and 1 wt % borax gel with a 30/70 acetone-$d_6$/D$_2$O (wt/wt) liquid composition at 25 °C (■), 35 °C (▲), and 45 °C (▲). Signals are referenced to F$_3$B-O(C$_2$H$_5$)$_2$ in CDCl$_3$ held in a sealed tube within the one containing the gel samples.

The molecular weight of the polymer used to prepare the organo-aqueous gels has an effect on the crosslink concentration. While there is a significant increase in the number of borate ions participating in crosslinks with increasing 1-propanol content in gels prepared with 4 wt %
of 80PVAc_1, the enhanced crosslinking is observed only in gels prepared from low concentrations of 80PVAc_3 (such as 2 wt %) (Figure 4-28). When the 1-propanol proportion in the liquid component of the gels is varied in systems of 4 wt % 80PVAc_3, there is a significant attenuation of the effect of the organic solvent on the increase in borate cross-linking.

![Figure 4-28](image)

Figure 4-28. Complexed boron from $^{11}$B NMR spectral integrations in gels composed of (■) 4 wt % 80PVAc_1 and 1 wt % borax, (●) 4 wt % 80PVAc_3 and 1 wt % borax, and (▲) 2 wt % 80PVAc_3 and 0.5 wt % borax.

The attachment of borate ions to multiple sites on a polymer chain results in a polyelectrolyte-like species in which the crosslinking is reduced. This reduction can be attributed to several factors. Two which seem probable and might work in conjunction with each other are local changes in ionic strength, especially near the crosslink points, and the increased proximity of the negatively charged borate ions which causes electrostatically unfavorable interactions. Because the three polymers are 80% hydrolyzed, their behavior should be closer to that of PVA than of PVAc, and because 1-propanol is not a good solvent for PVA, polymer-chain folding
should be favored. The ancillary increased proximity of vicinal diol groups on either the same or different polymer chains then increases the probability that borate crosslinks will form. This effect is especially noticeable when the concentration or molecular weight of the xPVAc is low, in which case chain entanglements and inter-chain hydrogen bonding interactions are limited.

Gels of 40PVAc with borax can also be prepared in neat methanol and DMSO. According to one source, borax can be solubilized in methanol with a saturation limit of 19.90 wt % at 25°C. Experimental evidence shows that borax solutions can be prepared in neat DMSO. Gels prepared in neat methanol are initially viscous liquids but become more elastic over the course of a ten-day period in a closed vial. The systems were examined using rheology and $^{11}$B NMR spectroscopy. The viscosity increase observed over time is reflected in the strain and angular frequency sweeps (Figure 4-29), while the number of crosslinks remains constant (Figure 4-30). It is possible that the enhancement in elasticity in these gels is due to a rearrangement of the crosslinks within the network.

![Graph A and B](image-url)
Figure 4-29. (A) Strain sweeps (angular frequency = 1 rad/sec), and (B) angular frequency sweeps (strain = 5%) of a gel composed of 10 wt % 40PVAc and 1 wt % borax in 100% methanol (◼) 1 day, (◻) 4 days, (◼) 6 days, and (◻) 11 days after preparation.

![Diagram of gel composition]

Figure 4-30. $^{11}$B NMR spectra of a gel composed of 10 wt % 40PVAc and 1 wt % borax in 100% methanol (◼) 1 day, (◻) 4 days, (◼) 7 days, (◼) 9 days, and (◻) 15 days after preparation. Arrow denotes the appearance of unknown signal discussed below. Signals are referenced to F$_3$B-O(C$_2$H$_5$)$_2$ in CDCl$_3$ held in a sealed tube within the one containing the gel samples.

Along with the expected signals of crosslinked borate and free, exchanging borate species, there is a third signal visible in the spectrum at $\delta \approx 7.5$ ppm in Figure 4-30 (see arrow). According to Henderson et al., the chemical shift of boron in 1,2-diol complexes appears at approximately 6 ppm. As the majority of the polymeric diols in the xPVAc-borax system are not vicinal, the 1,2-diol complexation cannot be the cause of the observed signal. In the polar protic environment of methanol, it is unlikely that the trigonal mono-diol complex discussed in Chapter 3 is present in significant concentrations. The peak at 7.5 ppm may be a result of hydroxyl and methoxy group exchange on the boron atom, resulting in partially complexed and alkoxylated boron. The peak is absent in the $^{11}$B NMR spectrum of a gel prepared using DMSO (Figure 4-
Although DMSO might coordinate with the boron atom through a lone-pair on the oxygen, it is less likely to form a covalent bond than is methanol. The gels prepared with DMSO do not show significant amounts of free boron species and the chemical shift for the crosslinked boron is 1.3 ppm, much closer than reported by Henderson et al.\(^57\)

Figure 4-31. \(^{11}\)B NMR spectra of gels composed of 10 wt % 40PVAc and 1 wt % borax in 100% DMSO (■) 1 day, (■) 4 days, (■) 7 days, (■) 9 days, and (■) 15 days after preparation. Signals are referenced to F3B-O(C2H5)2 in CDCl\(_3\) held in a sealed tube within the one containing the gel samples.

4.4.3. Differential scanning calorimetry investigation of water structuring in xPVAc-borax gels.

The changes induced by increasing weight fractions of organic liquids were examined by differential scanning calorimetry (DSC) using the free water index (FWI) (Equation 4-11), a measure of the free water (i.e., freezable at reasonably low temperatures) in a system.\(^97,108\)

\[
FWI = \frac{\Delta H_{exp}}{\Delta H_{init}}
\]  

(4-11)

In this expression, \(\Delta H_{exp}\) is the enthalpy change (in J g\(^{-1}\) of gel) determined from a DSC heating endotherm, \(A\) is the weight fraction of water in the gel, and \(\Delta H_{init}\) the specific enthalpy of fusion.
of the water in the gel if it were composed of completely freezable water at 0 °C (333.55 J·g⁻¹)⁹⁶,¹⁰⁴ As the organic content of the liquid in the gels is increased, the FWI decreases dramatically (Figure 4-32-B). This decrease is an indicator of increased structuring of the remaining water caused by the presence of the organic liquid.¹⁰⁵ Because the aqueous portion of the liquid in these gels is expected to reside closer, on average, to the polymers (bound and non-freezable water), the change of the gels can be attributed to increased crosslinking. By contrast, the concentration of borax does not have a large influence on the FWI, at least within the range investigated (Figure 4-32-D). The major changes caused by increasing the borax concentration appear to involve its influence on crosslinking density.
Figure 4-32. (A) Endotherms from DSC thermograms and (B) free water indexes derived from the normalized $\Delta H_{\text{exp}}$ of gels composed of 11 wt % 40PVAc and 1 wt % borax with (1) 75%, (2) 50%, (3) 25%, and (4) 10% 1-propanol in the liquid component; (C) DSC thermograms and (D) free water indexes derived from the $\Delta H_{\text{exp}}$ of gels composed of 11 wt % 40PVAc and 75/25 2-propanol/water (wt/wt) with varying concentrations of borax.

4.4.4. Small angle neutron scattering studies.

Small angle neutron scattering (SANS) studies were carried out on gels prepared with varying ratios of acetone to water. The majority of the data interpretation that follows was performed by a collaborator, Dr. Pierre Terech. SANS measurements were performed on gels prepared from 4 wt % 75PVAc and 1 wt % borax ($[\text{PVAc}]/[\text{borax}] = 0.25$ or $OH_{\text{PVAc}}/[\text{B(OH)}_4^-] = 11/1$). Shibayama et al. found that PVA-borate crosslinks can be characterized as crystallites with sizes on the order of tens of Ångstroms. Although partially hydrolyzed PVAc is expected form intra- and inter-molecular crosslinks in the same manner as
PVA, the presence of residual acetate groups on the polymer backbone will affect its degree of swelling.\textsuperscript{89,110}

In a polymer solution, the average distance between consecutive crosslink (or junction) sites is called the ‘network mesh size’ and is representative of the porosity of the network. When the polymer is dissolved in a good, or theta, solvent, the network swells homogeneously and the crosslinks are evenly distributed throughout. An increase in the mesh size of the polymer network is indicative of an increase in the swelling of the polymer chains.

Changes occurring in the structure of xPVAc-borax gel networks as the liquid component is altered can be evaluated by investigating the interaction parameter between the polymer chains and the solvent. The polymer-solvent interaction parameter, $\chi_{12}$ as defined by Flory-Higgins solution theory, can be found for a solvent-solute couple using vapor-pressure measurements.\textsuperscript{111-113} For PVA in water, $\chi_{12} = 0.494$ (at 30 °C); the interaction parameter for xPVAc in acetone has not been reported.\textsuperscript{114} The difficulty in solubilizing 75PVAc in neat acetone would suggest that it is a poor solvent for the polymer. Polymer chain aggregation resulting from a balance between electrostatics and short-range monomer-monomer interactions in polyelectrolyte salt-free solutions can be dismissed for these networks.\textsuperscript{115}

A change in the solvent quality with respect to polymer swelling can switch the potential of the mean force between particles from repulsive to attractive.\textsuperscript{116} The heterogeneity and time-stability of gels is greatly affected by the magnitude and sign of the potential. Because of the excess chemical potential of mixing, polymer chains extend in a good solvent since polymer-solvent interactions are energetically favorable. In a poor solvent, polymer-polymer interactions are favored and chain coiling is observed. An example is the transition from a swollen to a
shrunken gel state triggered in an acrylamide-bisacrylamide hydrogel by addition of acetone to the liquid component.\textsuperscript{36,117}

The SANS curves obtained from 75PVAc-borax gels prepared with different ratios of acetone/water show solvent-dependent changes in the intensity of the scattering vector, $Q$. The SANS curve of the hydrogel, for example, shows an intense hump at $Q \approx 0.024 \text{ Å}^{-1}$, which is shifted to lower-$Q$ in the curve of the 30/70 acetone/water (wt/wt) gel and no longer present in the curve of the 50/50 acetone/water (wt/wt) gel (Figure 4-33).
Figure 4-33. SANS of 4 wt % 75PVAc and 1 wt % borax gels. (A) Overlay of three compositions investigated with different liquids: hydrogel (0.0, green), 30/70 acetone/water (wt/wt) (0.3, blue) and 50/50 acetone/water (wt/wt) (0.5, red); (B) Percus-Yevick modeling of the correlation peak of hydrogel; (C) and (D) Ornstein-Zernicke modeling of 30/70 acetone/water and 50/50 acetone/water gels, respectively. Blue dots are experimental data and red dots are the experimental data used in the fitting procedures.

The broad peak present in the SANS curve of the hydrogel is caused by long-distance correlations in the network from crosslinked domains and 75PVAc chains and bundles. Because the concentration of polymer is kept constant, when acetone is added to the system, the polymer chains are expected to aggregate into polymer rich domains (which may or may not contain borate crosslinks), and the spacing between the network correlations is expected to increase. In the low-\(Q\) region, scattering from these polymer rich domains is absent and there is a sharp decay visible as a tail of the scattering from the crosslinked chains (curve 0.3 in Figure 4-33-A). The curve is then characterized by a smooth decay with a convex profile due to scattering from
the swollen 75PVAc chains arising from dynamic fluctuations defined by a correlations length, \( \xi \) and Eq 4-12:

\[
S(Q) = \frac{S(0)}{1 + Q^2 \xi^2}
\]

The correlation peak observed in the scattering from the hydrogel corresponds to the static part of the inhomogeneity resulting from the crosslinks, and the smooth decay represents the dynamic part of the inhomogeneity described by the Ornstein-Zernicke (OZ) function (Eq 4-12). The OZ function is used to describe equilibrated polymer solutions in a good solvent. The prefactor, \( S(0) \), can be related to the density of crosslinks and the osmotic modulus, which is a measure of the repulsive force between the solubilized particles. The OZ function can be used to fit the scattering curves of 30/70 and 50/50 acetone/water (wt/wt) gels with good agreement (Figures 4-33-C and 4-33-D). According to this fit, the increase in acetone from 30 to 50 wt % in the gels results in an increase of the prefactor from 4.80 to 49.5, reflecting the observed changes in the mechanical properties of the network. The correlation length also increases from 58.9 Å to 150 Å (a factor of 2.7). The results indicate that the crosslinks become concentrated in select regions separated by larger distances on average when the solvent quality decreases due to acetone addition.

As noted above, the characteristic feature of the hydrogel scattering curve is the correlation peak at \( Q = 0.024 \) Å\(^{-1} \) (Figure 4-33-B). This peak can be distinguished by its tail in the low-\( Q \) region of the 30/70 acetone/water gel scattering curve, but is no longer present in the 50/50 acetone/water gel scattering curve. In the latter, the scattering is defined by the swollen polymer bundles creating a network of polymer-rich domains. In such gel systems, these
domains are described as randomly dispersed heterogeneities and can be described by the Debye-Bueche (DB) model. As shown in Equation 4-13, the DB model defines spatial correlations with an average length, $\Xi$, which are attenuated by an exponential correlation function, $g(r) = \exp(-r/\Xi)$, resulting in a scattering intensity defined by:

$$ I = \frac{\Xi^3}{(1 + Q^2\Xi^2)^2} \quad (4-13) $$

A fit using the DB model should yield a decay in the scattering curve with $Q^4$ which is not present in the SANS curves of the 75PVAc-borax gels. Since the DB model cannot account for the appearance of the correlation peak in the curves, the network cannot be represented as a fractal packing of uncorrelated dense clusters. The results indicate that the heterogeneities are not randomly dispersed but posses some order. An alternative model which considers the crosslinks in the gel as polydisperse spheres interacting via a hard-sphere potential has an intensity described by Equation 4-14, where $F(Q)$ is the form-factor function for homogeneous spheres (radius $R$) and $S(Q)$ is their corresponding structure factor (Equation 4-15). A Gaussian function can be used with the intensity expressions as a convolution to account for the radial polydispersity of the spheres.

$$ I(Q) \approx S(Q) \star \left\langle |F(Q)|^2 \right\rangle \quad (4-14) $$

$$ F(Q) = \frac{3\sin(QR) - QR\cos(QR)}{(QR)^3} \quad (4-15) $$

The analytical form of the Percus-Yevick (PY) approximation for hard-sphere repulsions can be used to find $S(Q)$. The radial distribution function in interacting systems of soft matter is commonly found using the PY equation.
\[
\frac{1}{S(Q)} = 1 + \frac{24\phi}{x^3} a \left( \sin x - x \cos x \right) + \left[ \left( \frac{2}{x^2} - 1 \right) x \cos x + \frac{2}{x} \sin x \right]
\]

\[
+ \frac{\phi a}{2} \left[ \frac{24}{x^3} + 4 \left( 1 - \frac{6}{x^2} \right) \sin x - \left[ 1 - \frac{12}{x^2} + \frac{24}{u^3} \right] x \cos x \right]
\]

(4-16)

with \( x = 2QD \), \( a = (1 + 2\phi)^2 (1 - \phi)^d \) and \( b = -3/2 \phi(\phi + 2)^2 (1 - \phi)^d \)

The PY fit of the hydrogel scattering curve is shown in figure 4-33-B. From the PY model, the crosslink ‘spheres’ have radii of 50 Å, are separated by an average correlation distance of 120 Å, and have a volume fraction \( f_{\text{crosslinks}} \approx 0.05 \). The crosslink domains are highly polydisperse. The calculated center-to-center distance between the crosslinks is 220 Å, a value very close to that calculated for the correlation length by \( 2\pi / 0.024 \approx 260 \) Å.

Other refining models such as Teubner-Strey\(^{121}\) or Beaucage,\(^{122}\) have not been used to fit the data. SANS studies have been conducted previously on physically and chemically crosslinked PVA hydrogels\(^ {79,89,123-126}\) but here, the effect of solvent quality on the static and dynamic heterogeneities in the network has been demonstrated. Kanaya et al. demonstrated, by neutron spin-echo studies, that the dynamics of the polymer chains in PVA-borax gels are not affected by the gel structure and can be fitted with a classic Zimm model.\(^ {79}\) The data presented here are consistent with this observation\(^{127}\) and the smooth decay characteristic of dynamic entanglements between Gaussian chains swelled in a good solvent seen in the scatter curves can be fitted well by the OZ function.\(^ {79,89,123-126}\)

4.5. Conclusions.

It has been shown that xPVAc-borax gels can be prepared with large fractions of organic liquids. Experimental evidence suggests that increasing concentrations of xPVAc and borax, as well as increasing the molecular weights of the polymers, result in higher thermal stability and rheological behavior closer to that of true gels. Chain entanglements and hydrogen bonding among polymer hydroxyl groups are probably the greatest contributors to the increase in network strength when the polymer concentration or molecular weight is varied. As shown using $^{11}$B NMR spectroscopy, the absolute concentration of crosslinks increases when higher concentrations of borax are used in the preparation of the gels.

The increases in thermal stability and relaxation time of the gels containing large fractions of organic liquids have been shown to be related to increases in the degree of crosslinking. These effects may be a result of the interplay among several phenomena including: (1) the borate ions are insoluble in organic liquids and are in the crosslinked state or in the boric acid form; and (2) in gels prepared from polymers with high degree of hydrolysis (i.e., more PVA-like), the polymer chains tend to become increasingly folded in the presence of most organic liquids; proximity of hydroxyl groups on adjacent chains encourages crosslinking. The migration of borate ions closer to the polymer chains, accompanied by sodium counter ions, results in a decrease in the fraction of water in the system that is ‘free’. As shown by SANS measurements, the polymer chains tend to form bundles with concentrated crosslinks in ‘poor’ organic solvents.

The findings described suggest that the viscoelastic character of xPVAc-borax gels, which allows them to be effective as conservation treatment materials, is influenced by a
complex combination of factors. Addition of potential treatment agents for conservation of cultural heritage objects, such as large amounts of organic liquids and, as will be discussed next, some salts, causes significant changes in the network structure. Through these studies, methods of maintaining the viscoelasticity of the materials without compromising their stability, structure, and effectiveness can be established. For example, gels prepared with large fractions of organic liquids require a reduction in the number of crosslinks forced to form in the network. Therefore, a lower concentration of borax can be used. The resulting gel maintains a pliable character but also contains a large fraction of an organic liquid.
5. SYSTEM MODIFICATIONS

5.1. Introduction

The ability of xPVAc-borax networks to gelate liquids which have a large organic/aqueous ratio is dependent on the degree of hydrolysis of the polymer. As shown in Chapter 4, polymers with more acetate groups can be solubilized in organic liquid/water mixtures with ratios as high as 75/25 (wt/wt). The ability to prepare xPVAc-borax gels with a large range of organic liquids is crucial for their use in art conservation. Conservators tailor the composition of the solvent used in a treatment for each artwork individually. Their decisions are guided by careful analysis of the surface and bulk material compositions and how they might be affected by a cleaning agent. Consequently, a cleaning gel system must be capable of gelating a variety of solvents, preferably in a range of polarities. Ideally, other treatment agents, such as tri-basic citrate, ethylenediaminetetraacetic acid (EDTA), ammonium carbonate, and charged and neutral surfactants, should be able to be incorporated into the system.

To broaden the range of treatment applications of xPVAc-borax gels, a series of polymer modifications was initiated, including covalent attachment of a chelating agent, citrate, or long alkanoate chains directly to the poly(vinyl alcohol) polymer. Citrate-modified PVA (CA-PVA) was intended to be employed in the preparation of chelating gels which could be used to treat metal objects or to remove water-soluble dirt and grime from surfaces. It was proposed that the polymer-bound citrate would be less likely to remain on the surface than unbound citrate as a residue after the treatment was complete. Also, tri-basic citrate, EDTA, and ammonium carbonate were incorporated in the liquid portion of xPVAc-borax hydrogels.
Attaching longer alkanoates to the polymer was intended to make the chains soluble in less polar liquids. Two alkanoate moieties, butyrate and stearate, were covalently linked to PVA. Solubilization of the modified polymers in organic liquids which are not miscible with water would require an alternative crosslinking agent for the formation of a gel. Addition of an aqueous borax solution to such systems resulted in formation of translucent or opaque gels which makes surface cleaning difficult. Trimethyl borate, a trigonal boron species with three methoxy groups, was assessed for its ability to act as a crosslinker for low degree of hydrolysis poly(vinyl acetates) dissolved in pure organic liquids. Studies on the modifications of the polymer, crosslinking species, and incorporation of additives into hydrogels will be presented in the following sections.

5.2. Methods and Materials.

Partially hydrolyzed poly(vinyl acetate)s were obtained from the Kuraray Co., Ltd. The polymers were cleaned and characterized as described in Chapter 4. Trimethyl borate (TMB, Aldrich, >98%), sodium tetraborate decahydrate (borax; Fluka, >99.5%), sodium hydride (Acros, pure, anhydrous powder), sodium methoxide (Sigma-Aldrich, 95% powder), sodium hydroxide (Fisher, electrolytic pellets), EDTA disodium salt (Baker analyzed), trisodium citrate (Sigma-Aldrich, >99.0%), ammonium carbonate (Mallinckrodt, analytical grade), fluorescein (free acid, Aldrich, 95%), blonde shellac flakes (Velo Orange, http://velo-orange.com), AlCl₃ (Acros, 98.5% anhydrous), MnCl₂ (Aldrich, 99+%), CoCl₂ hexahydrate (Sigma-Aldrich, 98%), CaCl₂ (Baker Analyzed, 96%), FeCl₃ hydrate (Baker Analyzed), CuCl₂ (Aldrich, anhydrous), CuO, and CrCl₃ (Aldrich, ≥ 98%) were used as received.
Methanol (Fisher, HPLC grade), dimethyl sulfoxide, (DMSO, Alfa Aesar, 99.9+%), dimethylformamide (DMF, Fisher, analytical grade), D$_2$O, DMSO-$d_6$, CDCl$_3$, and methanol-$d_6$ (Cambridge Isotope Laboratories, Inc., all 99.9% D), boron trifluoride etherate (Aldrich, synthesis grade, pure), 2-propanol (Fisher, 99.9%), 1-octanol (Sigma Aldrich, 99+%), N-methyl-2-pyrrolidone (NMP, Acros, extra dry with molecular sieves, <50 ppm water), methyl acetate (Fluka, 99+%), ethyl acetate (Fisher, HPLC grade), n-butanol (Sigma-Aldrich, 99.5%), benzyl alcohol (Sigma-Aldrich, 99+%), xylenes (Sigma-Aldrich, isomers plus ethylbenzene, 85%), hexanes (Fisher, HPLC grade), acetone (Fisher, histological grade), thionyl chloride (Aldrich, 99%), ammonia (Sigma, 28-30% in H$_2$O), butyryl chloride (Aldrich, 99+%), and diethylene glycol monobutyl ether (DEGMBE), triethylene glycol monomethyl ether (TEGMEE), diethylene glycol monoethyl ether (DEGMEM), and diethylene glycol monomethyl ether (DEGMME) (Fisher, purified) were used as received. Pyridine (Fisher) was refluxed over sodium hydroxide pellets, distilled under normal pressure and stored over activated 4 Å molecular sieves (Aldrich).

Stearoyl chloride was prepared from stearic acid and thionyl chloride. Stearic acid (7.52 g; 0.0264 mol) was placed into a round bottom flask fitted with a drying tube and a dropping funnel. The stearic acid was heated gently until it was liquid (melting range 69 °C), and thionyl chloride (2.86 mL; 0.0394 mol) was added via a dropping funnel over the course of one hour at a temperature of 75°C. The mixture was stirred for one hour at 30°C. Unreacted SOCl$_2$ was removed by two consecutive azeotropic vacuum distillations with 10 mL of dry benzene. The liquid residue (8 g, 0.0264 mol) was confirmed to contain stearoyl chloride by melting point
analysis (M.P. = 21-22 °C)\textsuperscript{128} and by converting a portion to the methyl ester by addition of dry methanol and analyzing the product using \textsuperscript{1}H NMR spectroscopy.

\textit{Alkanoate attachment to PVA: Procedure for 10 \% OH substitution.} All glassware was dried in an oven at 80 °C prior to use. Under a dynamic N\textsubscript{2} atmosphere, PVA (0.58 g, 13 mmol) and pyridine (0.105 mL, 1.3 mmol) were dissolved in dry NMP (15 mL) by heating to 90 °C. After the polymer had dissolved completely, the system was cooled to room temperature. Stearoyl chloride (0.45 mL, 1.3 mmol) dissolved in 10 mL of NMP was added dropwise to the polymer solution via dropping funnel over the course of one hour with continuous stirring, and the reaction was continued for another hour. The product was obtained by precipitation with methanol. The fine precipitate was centrifuged to remove residual solvent, and washed several times with methanol. The product was dried over the course of four days under vacuum to yield 0.61 g (66\%). Substitution with larger ratios of stearoyl groups required precipitation of the product with water.

\textit{Citric acid attachment to PVA: Procedure for 15 \% OH substitution.} Poly(vinyl alcohol) (1.0 g, 0.022 mol) was placed in a mortar dish and citric acid (1.10 g, 0.0060 mol, dissolved in 7 mL of water) was added. The mixture was swirled until the polymer was wet, then placed in a vacuum oven for 6 hours at 60 °C followed by 3 days at room temperature. The temperature was increased to 120 °C and kept there for 6 hours. The product was stirred in distilled, deionized water for four days, with the water being changed twice per day. Hydrochloric acid was used to adjust the pH of the slurry to 2 and the polymer was dried in a vacuum oven at room temperature for 72 hours. Product structure was analyzed by ATR FT-IR, \textsuperscript{1}H NMR and \textsuperscript{13}C NMR spectroscopy; results are shown in Section 5.3.1.
Monitoring of metal chelation. CuCl₂ (0.03 g) (or another metal salt) was dissolved in water (1.89 g) in a screw-cap glass cuvette. CA-PVA or PVA (0.08 g) was added after a UV-vis absorption spectrum of the CuCl₂ solution had been recorded. UV-vis spectra of the solution were collected intermittently over the course of 96 hours. Samples for qualitative studies were prepared in 7 mL screw cap vials. CA-PVA or PVA (0.04 g) was added to each vial. To one vial containing PVA, CuO (0.036 g) was added; to another, CuCl₂ (0.078 g) was added. These concentrations were chosen to be equivalent to 50 molar % of the hydroxyl groups on the polymer. Concentrations of CuO for CA-PVAs were chosen to represent 100 molar % of the citric acid groups on the polymers (sample calculation shown below) – 0.0025 g CuO for 0.04 g CA-PVA4 and 0.0068 g for 0.04 g CA-PVA15; 0.0054 g of CuCl₂ for 0.04 g CA-PVA4 and 0.015 g for 0.04 g CA-PVA15. The weight of each vial was brought to 1.0 g with water and the vials were stirred intermittently and rested over 3 days. The supernatant was then removed and replaced with a fresh aliquot of water.

\[
\frac{0.04 \, g \, CA-PVA15}{\left(44 \, \frac{g}{mol} \times 0.85\right) + 235 \, \frac{g}{mol} \times 0.15} \times 0.15 = 8.3 \times 10^{-5} \, mol \, CA \, substituted \, monomers
\]  

(5 - 1)

where 44 g/mol is the molecular weight of a hydroxyl monomer and 235 g/mol is the molecular weight of a citrate substituted monomer

\[
8.3 \times 10^{-5} \, mol \, CA \, monomers \times 79.5 \, \frac{g \, CuO}{mol} = 0.0066 \, g \, of \, CuO
\]  

(5-2)

necessary to account for copper ion concentration equivalent to 100% of citrate derivatized monomers.
**Gel Preparation.** A weighed sample of xPVAc was placed in a glass screw-cap vial with weighed amounts of an organic liquid and water. Organic liquid/water mixtures are reported on a wt/wt basis. The polymers were dissolved in the liquids either by standing overnight at room temperature in a closed vessel or by gently heating and stirring. Thereafter, an aliquot of an aqueous borax solution was added drop-wise with stirring. The gels were stirred vigorously with a spatula and allowed to equilibrate at rest for several hours prior to use. For example, to prepare a 6 wt % 75PVAc and 1 wt % borax gel with 30/70 acetone/water liquid composition, 75PVAc (0.06 g) was dissolved in acetone (0.28 g) and water (0.45 g) by heating to 50 °C and stirring with a Teflon-coated stir-bar. In a 1.5 mL microcentrifuge tube, borax (0.01 g) was dissolved in water (0.2 g) by heating to 50 °C and vortexing periodically. The borax solution was added to the polymer solution and the mixture was stirred vigorously until it is homogeneous.

To prepare gels with trisodium citrate (TSC), the same procedure was followed but the TSC was added to the aqueous polymer solution and dissolved fully before the borax solution was added. For EDTA-containing gels, EDTA was added to the aqueous polymer solution along with 30 μL of ammonia. The pH of the solution was measured with pH indicator strips and found to be between 9 and 10. The borax solution was subsequently added and the mixture was stirred vigorously until it became homogeneous. For 40PVAc-trimethyl borate gels, the polymer was dissolved in DMSO or DMF in closed vials; solvents were not dried prior to polymer addition. Sodium hydride or sodium methoxide was added to the polymer solution at room temperature and stirred with a Teflon-coated magnetic stir bar until completely dispersed. Trimethyl borate was delivered via syringe and the mixture was stirred until homogeneous and quickly capped to avoid reversion of the gel to a sol.
Gelation studies of alkanoate polymers. In glass pipettes flame-sealed at one end, 3PVA_{18} or 15PVA_{18} (3 wt %) was combined with borax (1 wt %) in 20/80 water/organic (wt/wt) liquid mixtures. The tubes were flame-sealed and heated in a water bath to boiling continuously over the course of 8-10 hours. Each sample was stirred by vortex periodically. The samples were also vortexed periodically over the course of the following month while remaining at room temperature. Most samples were found to contain a two phase system of a dense gel and a liquid which was analyzed using a Fisher Scientific refractometer (model # 334620). One sample, 15PVA_{18}, was found to have formed a homogeneous, transparent gel. The tube contained a large piece of undissolved polymer which was found to have the same measured weight as the starting material. Further attempts to reproduce this result with < 0.1 wt % of 15PVA_{18} proved unsuccessful.

Glycol ether gels and shellac dissolution. Blonde shellac flakes (85 g) were dissolved in anhydrous ethanol (355 mL). A solution with fluorescein (1 mg/mL) was prepared. Aliquots of the shellac-fluorescein solution (0.45 g) were placed on small watch glasses which were warmed on a hot plate until no more flow was noticeable when the watch glasses were tipped from side to side, then placed in a vacuum oven to dry for 3-6 days. Gels and liquids used for the experiments were weighed prior to application; 0.4 g of each was placed on a fresh, dry shellac varnished watch glass and allowed to remain undisturbed for 3 minutes. The liquids were then placed directly into 1 mm cuvettes while the gels were placed into vials. They were then slowly transferred into 1 mm cuvettes and heated gently to expel air bubbles. UV-vis absorbance spectra and fluorescence emission spectra (λ_{ex} = 495) were collected from each sample.
**Instrumentation.** NMR studies were performed on a Varian MR-400 MHz spectrometer. Data collection was made at 100.465 MHz with 128 FIDs and 399.490MHz with 2000 FIDs for $^1$H and $^{13}$C, respectively. MestReNova software was used to process the FIDs to obtain the spectra. $^{11}$B NMR spectra were obtained on the same spectrometer at 128.3 MHz with 256-320 FIDs in quartz NMR tubes, purchased from Wilmad Lab-glass, using an external reference of boron trifluoride etherate in CDCl$_3$ (arbitrary concentration) in a sealed capillary tube. Ratios of areas of peaks remained constant as long as the delay pulse was longer than 32 μs. For that reason, a 40 μs observation pulse was used for all $^{11}$B NMR spectra. Ratios of peak contributions were found by weighing (instead of integrating electronically) the very broad peaks from paper copies of spectra; 4-7 trials were repeated and a standard deviation of the weights is shown by error-bars in the figures.

Rheological measurements were made on an Anton Paar Physica MCR 301 stress-controlled rheometer using a 25 mm diameter cone-plate (1° cone angle) for frequency sweeps and 25 mm flat plates for extensional rheology. Angular frequency sweeps were performed in the linear viscoelastic region based on strain sweeps obtained at 1 rad/sec frequency. In extensional rheology experiments, the initial gap between the plates was 0.5 mm. Data collection was not initiated until the sample had equilibrated, indicated by its exerting 0 N of force on the top plate. Equilibration typically occurred after 1-2 minute for hydrogels and 10-15 minutes for DMSO and DMF gels prepared with 50% methoxide. Weight loss was not assumed significant for these samples because of the low volatility of the liquids. The top plate was lifted at a constant velocity of 1μm/sec and the normal force was measured. Data were collected and analyzed using Rheoplus/32 Service V3.10 software.
UV/vis absorption spectroscopy studies were performed on a Varian Cary 300 Bio UV/Visible spectrophotometer. Fluorescence emission spectra of gels used to remove fluorescein-infused shellac were collected with a Photon Technology International Fluorimeter (SYS 2459) with the flattened 1 mm cuvette oriented front-face at an angle of ~ 45° with respect to the incident beam and the emission was collected at 90° with respect to the excitation source. The spectra were baseline corrected and normalized to the highest intensity. ATR FT-IR spectra with a 4 cm⁻¹ resolution were obtained on a Perkin Elmer SpectrumOne FTIR spectrometer equipped with a Pike Technologies MIRacle ATR tool.

5.3. Chelating Gels

5.3.1. Attachment of citric acid to PVA.

Chelating agents such as EDTA and triammonium citrate have been used for the conservation of cultural heritage works. Although commonly used as aqueous solutions, these agents can also be incorporated into thickened paste or gel materials when it is necessary that the application times be longer or when they are used on statues and other vertical surfaces. The removal of copper sulfate from Rodin’s The Thinker (1925) in Philadelphia was performed using EDTA in a thickened cellulose media. Conservation of iron-stained marble surfaces can also be carried out using chelating agents. The covalent attachment of a chelating agent to the polymer used to prepare such gels may make the treatment process simpler by eliminating the possibility of chelator deposition on the cleaned surface. In Chapter 6, we demonstrate, through the use of fluorophore-tagged polymers, that xPVAc-borax gel systems do not leave polymeric deposits (that are within the range of our detection limits) on acrylic and oil paintings after the
cleaning process. Assuming that the attachment of chelating agents to the polymer does not alter
the gelation mechanism, gels formed from chelating polymers are not expected to leave polymer,
and, therefore, citrate residues after treatment.

A method developed by Robert Wing for the attachment of the chelator to corn fiber
(25% starch, 27% cellulose, 32% hemicelluloses, 10% protein, 2% lipid, 2% lignin, 2% ash) was
employed to covalently bind citric acid to poly(vinyl alcohol). The reaction proceeds through a
dehydration step. An internal anhydride is initially formed, followed by attachment of the
polymer through the hydroxyl functionality (Scheme 5-1). If the reaction is allowed to
continue over a longer period of time or carried out at a higher temperature, a second internal
anhydride can form, followed by a second esterification to result in intra- or inter-molecular
chemical crosslinks.

![Scheme 5-1. Functionalization of PVA with citric acid.](image)

Citric anhydrides have been synthesized and described by Repta et al. Two
anhydrides can be formed from citric acid which contain either a five or a six membered ring.
The latter is considered the less stable and less likely to occur (Scheme 5-2).
In the citric acid molecule, the hydroxyl and the carboxylic acid groups on carbon 2 are both perpendicular to the backbone of the molecule, which aids in hydrogen bonding and metal ion chelation. To form the anhydride, this planarity must be destroyed, contributing to the difficulty in preparing this species. Zacharias et al. show, through the use of a citric anhydride derivative, that, once formed, the anhydride is extremely reactive and very difficult to isolate. Although it has been suggested by extrapolation from the formation of anhydrides of succinic acid that citric acid and its anhydride exist in equilibrium in solution, Zacharias et al. have shown that this is unlikely. Preparation of the anhydride is possible through two methods, heating or acid catalysis. During heating, several other species are formed in small quantities (Figure 5-1), but the anhydride is the dominant product.
The heating reactions can result in both crosslinking and the formation of the species described in Figure 5-1. The functionalization of PVA with citric acid (CA) was performed by suspending the polymer in an aqueous solution of CA and heating the heterogeneous mixture. Preparation by heating a homogeneous solution of PVA and CA resulted in a brown colored and completely insoluble product (vide infra). Because the heterogeneous reaction occurs only on the surface of the polymer particles, the attachment may not be evenly distributed over the polymer chains. If this is the case, gelation should not be hindered. Attachment of CA to the polymer through one of its three carboxylate groups should not hinder the chelating ability of the molecule because citrate can form monodentate, bidentate, or tridentate coordination with metal ions through any of its seven oxygen atoms. The hydroxyl and central carboxylate oxygen atoms typically participate in bidentate and tridentate coordination, and one of the terminal carboxylate oxygen atoms participates in the latter coordination type. The hydroxyl groups on the polymer may also contribute to the complexation. Citrate attachment to polymers synthesized by the suspension reaction was confirmed by ATR FT-IR and $^1$H and $^{13}$C NMR spectroscopy (Figures 5-2 to 5-4).
The infrared spectrum of citric acid shows a carbonyl peak at 1714 cm\(^{-1}\), which is lacking in the spectrum of poly(vinyl alcohol). The citric acid esterified polymer, CA-PVA, shows the characteristic carbonyl stretch at 1714 cm\(^{-1}\). The NMR spectra also confirm attachment of the chelator to the polymer. A quartet associated with the four citric acid protons can be seen in the CA-PVA \(^1\)H NMR spectrum. The PVA hydroxyl signal is not present because CA-PVA could be dissolved only in basic D\(_2\)O (resulting in rapid H-D exchange of the hydroxyl groups of the polymer). The four nonequivalent carbon atoms of citric acid can be seen in the \(^{13}\)C NMR spectrum of CA-PVA. In both the \(^1\)H and \(^{13}\)C NMR spectra, the citric acid peaks in CA-PVA appear at chemical shifts different than those of pure CA due to a change in their chemical environments after attachment. As calculated by integration of the peaks in the \(^1\)H NMR
spectrum, 15% of the molar amount of hydroxyl groups on PVA was substituted with citric acid (Figure 5-3). CA-PVA was also synthesized with a CA molar substitution of 4% of the polymer hydroxyl groups. These two polymers will be referred to as CA-PVA15 and CA-PVA4, respectively.

Figure 5-3: $^1$H NMR spectra of citric acid (■), CA-PVA15 in D$_2$O (■), and PVA (■) in DMSO-$d_6$. 
Figure 5-4: $^{13}$C NMR spectra of citric acid (■), PVA (■), and CA-PVA15 (■) in D$_2$O.

The colored CA-PVA polymer prepared in a homogeneous mixture of PVA and citric acid was tested for solubility in a range of solvents and aqueous solutions of varying pH (Table 5-1). The insolubility of these polymers not only prevents their formation into gels but also precludes determination of the degree of CA substitution.

Table 5-1. Results of trials to determine solubility in neat solvents and aqueous compositions of CA-PVA prepared by heating a homogeneous solution of polymer and citric acid. The
appearances are reported after the polymers were kept at room temperature for 48 hours, and then refluxed for 3 hours in the liquid.

<table>
<thead>
<tr>
<th>Solvent (mixtures are at 1/1 ratio)</th>
<th>Effect on CA-PVA</th>
<th>pH of water (adjusted by HCl or NaOH)</th>
<th>Effect on CA-PVA</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>brown(^c) after heating</td>
<td>3</td>
<td>no visible change</td>
</tr>
<tr>
<td>DMSO</td>
<td>swelled(^b)</td>
<td>6</td>
<td>no visible change</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>yellowed(^c)</td>
<td>7</td>
<td>no visible change</td>
</tr>
<tr>
<td>toluene</td>
<td>no visible change</td>
<td>8</td>
<td>no visible change</td>
</tr>
<tr>
<td>methanol</td>
<td>no visible change</td>
<td>10</td>
<td>no visible change</td>
</tr>
<tr>
<td>methanol/acetonitrile</td>
<td>no visible change</td>
<td>12</td>
<td>no visible change</td>
</tr>
<tr>
<td>methanol/water</td>
<td>no visible change</td>
<td>14</td>
<td>swelled(^b)</td>
</tr>
<tr>
<td>acetonitrile/water</td>
<td>no visible change</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMSO/water</td>
<td>slight swelling(^a)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The polymers, which are white solids, become \(^a\) translucent, \(^b\) transparent, or \(^c\) change color in these solvents but do not dissolve.

Both CA-PVA15 and CA-PVA4 were insoluble in water at neutral pH, although they swell, especially on heating, and dissolve completely at low concentrations in basic aqueous solutions at pH > 12. The ability of the polymer particles to absorb copper (II) ions was tested using copper oxide (a fine, black, water-insoluble powder) and copper chloride (a salt which is turquoise when dissolved in water). Both polymers were qualitatively found to take up copper ions effectively in comparison to non-functionalized PVA (Figure 5-5). The CA-PVA15 and
CA-PVA4 polymers did not visibly release the absorbed copper ions over the course one month in water; as can be seen in Figure 5 the polymers remained colored while the water remained uncolored.

Figure 5-5. (A) PVA with CuCl$_2$, (B) PVA with CuO, (C) CA-PVA4 with CuCl$_2$, (D) CA-PVA4 with CuO, (E) CA-PVA15 with CuCl$_2$ and (F) CA-PVA15 with CuO. Polymers are in aliquots of water. PVA in image (A) appears yellow due to contrast, the polymer is normally white.

The removal of the copper ions from water by CA-PVA particles can easily be monitored using UV-vis absorption spectroscopy because aqueous Cu$^{2+}$ is a turquoise solution. Figure 5-6 shows the decrease in absorption of a solution of CuCl$_2$ after the addition of CA-PVA15. The concentration of Cu$^{2+}$ in the experiment is equimolar to the concentration of citric acid groups on
the polymer. The absorbance drops consistently over 96 hours, indicating a decrease in the concentration of copper ions from 0.088 M to 0.065 M (calculated using the Beer-Lambert equation, \( A = \varepsilon \cdot C \cdot b \) where \( A \) is the absorbance of the solution above the settled polymer, \( \varepsilon \) is the molar absorptivity coefficient (L mol\(^{-1}\) cm\(^{-1}\)), \( C \) is the molar concentration, and \( b \) is the path length of the cuvette). In contrast, when non-CA-functionalized PVA is added to a solution of CuCl\(_2\) of the same concentration, the copper ion concentration is reduced from 0.088 M to 0.076 M over the course of 120 hours, and this reduction is not constant; the absorbance at 48 hrs after PVA addition is stronger than it was at 24 hours (Figure 5-7). The causes of these fluctuations were not explored but may be a result of liquid evaporation or unstable interactions between PVA and the copper ions.

Figure 5-6. UV-vis absorption spectra of a solution containing 4 wt % CA-PVA15 with 1.5 wt % CuCl\(_2\) (0.088 M, molar equivalent of Cu\(^{2+}\) to citric acid groups on polymer). (●) - aqueous
CuCl$_2$, (●) – immediately after CA-PVA15 addition, (●) – 30 min after CA-PVA15 addition, (●) – 3 hr after CA-PVA15 addition, (●) – 24 hrs after CA-PVA15 addition, (●) – 48 hrs after CA-PVA15 addition, (●) – 96 hours after CA-PVA15 addition. The UV-vis spectrometer has a linear response up to O.D. = 3.

Figure 5-7. UV-vis absorption spectra of aqueous CuCl$_2$ solution containing 4 wt % PVA with 1.5 wt % CuCl$_2$ (0.088 M, molar equivalent of Cu$^{2+}$ to citric acid groups on polymer). (●) - aqueous CuCl$_2$, (●) – immediately after PVA addition, (●) – 4 hrs after CA-PVA15 addition, (●) – 24 hrs after CA-PVA15 addition, (●) – 48 hrs after CA-PVA15 addition, (●) – 120 hrs after CA-PVA15 addition. The UV-vis spectrometer has a linear response up to O.D. = 3.

The ability of CA-PVA to take up chromium (III) chloride or cobalt (II) chloride was also tested. The ability of the polymers to take up metal ions from solution was monitored via UV-vis
absorption spectroscopy. The absorption of the metal halide aqueous solutions without any polymer, in the presence of non-derivatized PVA, and CA-PVA15 was measured.

The absorption of cobalt seems to decrease over the course of 24 hours in the presence of CA-PVA15, an effect not found in the solution of CoCl$_2$ or the solution containing CoCl$_2$ and PVA (Figure 5-8). However, the significant effect of scatter seen in the changing baseline of the spectra in Figure 5-8-C may be the cause of the perceived changes in the absorbance maxima. Scatter is likely to have been caused by undissolved polymer particles which may not have fully settled in the cuvette when the absorbance spectra were collected. Also, the reported stability constant of [CoHL]$^-$ is 4.4 while that of [CuL]$^{2-}$ is 14.2 (where L$_3^-$ is triply deprotonated citrate and L$_4^-$ is completely deprotonated citrate).$^{14}$ According to one source, copper can form an [ML]$^n$ complex with citrate because the high charge density of the metal ion causes polarization strong enough to deprotonate the hydroxyl group of the citrate, although chelation can also occur through a dimeric complex of the form [M$_2$L$_2$]$^{4+}$ which has a stability constant of 14.7.$^{142,14}$ Stability constants are likely to be lower for CA-PVA because of the inability of one carboxylate oxygen atom to participate in the complexation, with bidentate and tridentate coordinates having stability constants of $\sim$9 and $\sim$5, respectively.$^{142}$ The [CoHL]$^-$ complex may also have a reduced stability constant when citrate is attached to the polymer. Consequently, the results of these studies are inconclusive and merit future exploration.
Figure 5-8. UV-vis absorption spectra of (A) 0.063M cobalt (II) chloride in water, (B) 0.063M of CoCl₂ with 6 wt % PVA, and (C) 0.063M of CoCl₂ with 6 wt % CA-PVA15. The molar concentration of cobalt is equivalent to 50% of the molar concentration of citric acid groups on the CA-PVA15.

Interpretation of the results from the chromium (III) chloride experiment is also difficult due to the change in the absorption spectrum of the metal as chloride ligands are replaced by water to yield hexaaquo chromium ions – a process known as ionization isomerism. This transition is visible as the color of the solution changes from emerald green to grey/violet as the ligands around the metal change from $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\cdot2\text{H}_2\text{O}$ to $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}_2]\cdot\text{Cl}_2\cdot\text{H}_2\text{O}$ to
[\text{Cr(H}_2\text{O)}_6]\text{Cl}_3. These three species also have different absorption coefficients as can be seen in the decrease of the absorption intensity in the neat CrCl\textsubscript{3} solution spectrum (Figure 5-9-A). The pseudo-isosbestic points present in the spectra indicate that more than two absorbing species are present in solution over the course of the experiment. It is difficult to attribute a decrease in the intensity of the UV-vis absorption spectrum of the metal in the presence of CA-PVA15 to the chelating action of the polymer as the same trend is observed in these results as in the solution of CrCl\textsubscript{3}.

The preparation of hexaaquo chromium ion solutions prior to CA-PVA15 addition was considered in order to address the experimental difficulties. However, due to the inability of the polymers to dissolve, which necessitated the absorbance studies to be performed using swelled polymer particles, further experiments were not carried out. The inability of all CA-PVA polymers to dissolve in neutral pH or slightly basic (up to pH 9) water makes them unlikely candidates for the formation of “chelating gels” which may be used for conservation purposes. Citrate and other cleaning agents were incorporated into the liquid portion of xPVAc-borax hydrogels as an alternative.
Figure 5-9. UV-vis absorption spectra of (A) 0.063 M chromium (III) chloride in water and (B) 0.063 M CrCl₃ with 6 wt % CA-PVA15. The molar concentration of cobalt is equivalent to 50% of the molar concentration of citric acid groups on the CA-PVA15.

5.3.2. Incorporation of trisodium citrate and EDTA into xPVAc-borax gels.

Chelating agents such as citrate or EDTA are typically employed in aqueous cleaning systems at concentrations of 1-5%. Triammonium citrate solutions (TAC) are commonly used in lieu of sodium citrate because the counterion seems to affect the cleaning efficacy: ammonium is a chelator for copper, a wetting agent, and may complex with fats, oils, and proteins that contain carbonyl groups.¹⁴³ For conservation treatments, TAC solutions are typically buffered at pH of 9 and used at a concentration of 5% (~0.2 M).¹⁴³ Citrate can also be buffered at lower pHs. The Modular Cleaning Program (MCP) suggests preparation of citrate solutions (0.05 M) at pHs of 5.5, 6.5, 7.5, and 8.5.¹⁴⁴ The maximum efficiency of citrate chelation of copper occurs at ~ pH 6, with a full range of chelation occurring from pH 2 to pH 9.¹³⁴¹⁴⁵ For iron, stability constants of citrate chelation have been measured in the pH range of 2 to 6, with a maximum occurring at pH 3.¹⁴⁵ Citrate also complexes with calcium and magnesium ions in the pH range of 2-10, aluminum (III) ions at pH in the range of 2-14, zinc (II) in the pH range of 5-9 and nickel (II) in the range of 2-14.¹³⁴ For all of these metal ions, the stability constants are reported for the [MHL]⁻ complex, with the exception of Cu²⁺ and Fe³⁺ which form an [ML]ⁿ⁻ complex as described above (where HL⁻ is triply deprotonated citrate and L⁴⁻ is completely deprotonated citrate).¹⁴ The MCP suggests preparation of EDTA solutions at a concentration of 0.05 M at pHs of 5.5, 6.5, 7.5, and 8.5.¹⁴⁴ Complexation of iron by EDTA occurs in the pH range of 2-7 with a
maximum occurring at pH 4.5. The range of pH where copper is chelated by EDTA is even broader, from pH 2 to pH 12, with a maximum occurring between pH 9 – 10. For chelation to occur, the metals must be ionized.

In instances when aqueous solutions are used for varnish removal instead of organic solvents, solutions at a mildly alkaline pH have been found more effective than acidic and neutral solutions. In some cases, alkaline solutions can be ‘too effective’, causing cracking of the surface by leaching out soluble paint film components that act as plasticizers. Alkaline solutions can also leach out acidic pigment particles and destroy oil paint films by saponification. Aqueous solutions containing a chelating agent can be employed for the purposes of removing dirt and grime from paint and varnish surfaces. Their pH must be in the range where leaching and saponification do not occur but chelation can still occur. Based on the stability constants of metals with citrate and EDTA described above, EDTA is active as a chelator at the pH values used in most conservation treatments. At pH values above neutral, citric acid is likely to be fully deprotonated (pK\textsubscript{a1} = 3.1, pK\textsubscript{a2} = 4.7, and pK\textsubscript{a3} = 5.4) and capable of complex formation with a variety of metal ions.

xPVAc-borax hydrogels typically have measured pH values between 8 and 8.5. Incorporation of trisodium citrate (TSC) and EDTA into xPVAc-borax gels was performed by Emiliano Carretti and researchers at the University of Florence. Their preliminary results show that stable gels can be prepared with up to 0.3 wt % EDTA and 0.5 wt % TSC. It was shown experimentally, that the concentrations can be increased to at least 1 wt % TSC (0.04 M) and 0.5 wt % EDTA (0.01 M). Oscillatory strain and frequency studies on these gels were performed at
the University of Florence. Use of the gels on oxidized copper plates by Carretti et al. showed that the gels can remove the oxidation products with good control over the cleaning action.

Gels containing TSC and EDTA were studied by extensional rheology and $^{11}$B NMR spectroscopy. The materials were prepared with 80PVAc_3, the polymer with the highest molecular weight ($M_w = 136,000$). The pH of the gels containing sodium citrate was not adjusted and remained at ~ 8.5, while that of EDTA-containing gels was increased to 9-10 with ammonia. The extensional rheology results (Figure 5-10) show that addition of citrate results in an increase in the strength of the materials. Gels containing EDTA show little change in maximum normal force except when the concentration of ammonia is high. The materials remain stable over the course of 10 days. Syneresis occurred in gels containing large concentrations of TSC or EDTA over longer observation times.

![Graph A](image1.png)  ![Graph B](image2.png)

Figure 5-10. Extensional rheology of samples prepared from 3 wt % 80PVAc and 0.75 wt % borax with 0 wt % ( ), 0.1 wt % ( ), 0.3 wt % ( ), and 0.5 wt % ( ) of sodium citrate (A) or 0 wt % ( ), 0.1 wt % ( ) and 0.2 wt % ( ) with and 30 μL ammonia, and 0.3 wt % ( ) EDTA
with 100 μL ammonia. Plates were separated at a rate of 1 μm/sec with an initial separation of 0.5 mm. Results are shown with standard deviation from three trials.

11B NMR spectra of gels prepared with TSC have a peak at 6.5 ppm (Figure 5-11) which corresponds to a five-membered mono-diol complex with the borate ion. The complexation of the borate ion by citrate is the likely origin of the signal. To study this complexation, CuCl₂ was added to the gels and the peak at 6.5 ppm was monitored. Adding an amount of Cu²⁺ corresponding to 66% of the molar concentration of citrate in the system (0.026 mM CuCl₂) resulted in the disappearance of the cross-linked borate ion signal at 1.5 ppm and syneresis of the gel (Figure 5-12). When the concentration of Cu²⁺ was kept at 33% of the molar concentration of citrate in the gel (0.013 mM CuCl₂), the materials maintained their consistency but the peak at 6.5 ppm substantially decreased in size. The stability constant of [CuL]²⁻ is large: 14.2 in the pH range of 7.5 to 9. Other metal salts were introduced into the system to monitor whether the borate ion can be displaced from the citrate complex. Five metal salts were tested, and all were found to cause a reduction in the signal at 6.5 ppm attributed to the citric acid-borate complex with the smallest change observed following the addition of Ca²⁺, an ion for which citrate is known to have poor affinity (Figure 5-13).
Figure 5-11. $^{11}$B NMR spectra of gels from 3 wt % 80PVAc_1 with 0.75 wt % borax in D$_2$O with 0 wt % TSC (■), 0.1 wt % TSC ( ), 0.3 wt % TSC ( ), 0.5 wt % TSC ( ), and 0.75 wt % borax and 0.1 wt % TSC without 80PVAc_3 ( ). Signals are referenced to F$_3$B-O(C$_2$H$_5$)$_2$ in diethyl ether held in a sealed tube within the one containing the gel samples.
$^{11}$B NMR spectra of gels from 3 wt % 80PVAc and 0.75 wt % borax in D$_2$O with 0.04 mM TSC (■), 0.04 mM TSC and 0.013 mM CuCl$_2$ (■), 0.04 mM TSC and 0.026 mM CuCl$_2$ (■).

Figure 5-13. $^{11}$B NMR spectra of gels from 3 wt % 80PVAc and 0.75 wt % borax with 0.04 mM TSC (■) and 0.01 mM of Mn$^{2+}$ (■), Al$^{3+}$ (■), Co$^{2+}$ (■), Fe$^{3+}$ (■), Ca$^{2+}$ (■).

The results from the $^{11}$B NMR studies show that the citrate ion can preferentially bind other metals present in the gel. The amount of borate participating in crosslinks does not change substantially when sodium citrate is added (Figure 5-14), suggesting that the increased strength of the gels seen in the extensional rheology experiments must be caused by another factor. The addition of salts to PVA-borate systems is known to change their phase behavior and has been described by others as the re-entrant behavior.$^{72,86}$ The balance between negatively charged crosslink sites on the polymer chains and screening by the sodium ions in solution will be greatly affected by the introduction of other ions in the system. An increased swelling and stiffening of the system is normally followed by phase separation with an expulsion of the liquid and a
contraction of the gel.\textsuperscript{72} Re-entrant behavior is noted in gels containing amounts of metal salts higher than 25\% molar equivalent of TSC in the gels. The change in the location of the free boron peak may also be caused by changes in the screening of the polymer chains.

Figure 5-14. Percentage of boron species participating in di-diol crosslinks (■) or complexation with citrate (▲) based on integration of the $^{11}$B NMR signals from Figure 5-11.

The concentration of TSC can be increased further if the salt concentrations are carefully balanced. For example, increasing the TSC concentration in 4 wt \% 80PVAc hydrogels to 1 wt \% requires a borax concentration of 1.5 wt \% or 3 wt \% for the formation of a stable gel. When the gel is prepared with 0.75 wt \% borax, immediate phase separation is observed. At these higher borax concentrations, a new peak appears in the $^{11}$B NMR spectra at $\sim$ 2.5-3 ppm. As the citrate ion has three carboxylate groups, it is possible for the complex formed between the borate and the citrate to be a 6-membered ring, a 5-membered ring, or a tridentate interaction (Figure 5-15). The complexation may also be in a 1:1 or a 2:1 ratio. Henderson et al. find that the 2:1, 5-
membered ring complex appears at ~ 10 ppm against the BF$_3$ · O(Et)$_2$ reference and the 1:1 complex of the same nature appears at ~ 6 ppm.$^{57}$ The 2:1 and 1:1 6-membered ring complexes normally have chemical shifts between 1 and 2.$^{46,57}$ Mixed 2:1 complexes with one 5-membered and one 6-membered ring have chemical shifts close to 5 ppm.$^{46}$ The peak appearing at 3 ppm may be of such a mixed structure, or possibly the tridentate structure shown in Figure 5-15. The signal may also arise from a mixed 6-membered complex between a diol on the polymer chain and one citrate ion.

Figure 5-15. Borate ion complexation by the citrate ion. Top row: a 1:1 5-membered complex and a 2:1 5-membered complex; bottom row: a tridentate complex, a 1:1 6-membered complex, and a 2:1 6-membered complex.

Although the borate ion itself can chelate some metal ions, the stability constants for these complexes are much smaller than those between citrate and metal ions (Table 5-2).$^{148}$ The stability constants in Table 5-2 were obtained at pH < 7 where complexation is expected to
The chelation of metal ions by borate is not expected to hinder the ability of citrate or EDTA to do so to a significant extent in the gels, nor should it interfere with the integration of the peaks from the $^{11}$B NMR spectra. If borate is chelating any of the metals, a new peak is expected to be present in the spectra, especially for species that do not have paramagnetic properties. It is also possible that the peak observed at 2.5-3 ppm is a result of borate ion complexation with copper.

Table 5-2. Stability constants for unidentate monoborate-metal complex $\text{MB(OH}_4^{(n-1)+}$ obtained from the equilibrium $\text{M}^{n+} + \text{B(OH)}_4^{-} \leftrightarrow \text{MB(OH}_4^{(n-1)+} \text{ where } K_{\text{M,B}} (\text{M}^{n+}) = \{\text{MB(OH}_4^{(n-1)+}\}/\{\text{M}^{n+}\}\{\text{B(OH)}_4^{-}\}.^{148}

<table>
<thead>
<tr>
<th>Metal Ion</th>
<th>log $K_{\text{M,B}}$</th>
<th>Metal Ion</th>
<th>log $K_{\text{M,B}}$</th>
</tr>
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<tr>
<td>Fe$^{3+}$</td>
<td>5.5</td>
<td>Na$^{1+}$</td>
<td>0.22</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>4.1</td>
<td>Mg$^{1+}$</td>
<td>1.62</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>1.6</td>
<td>Ca$^{2+}$</td>
<td>1.80</td>
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<tr>
<td>Co$^{2+}$</td>
<td>1.2</td>
<td>Sr$^{2+}$</td>
<td>1.55</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>4.4</td>
<td>Ba$^{2+}$</td>
<td>1.49</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>1.6</td>
<td>Ag$^{1+}$</td>
<td>0.65</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>2.3</td>
<td>Li$^{1+}$</td>
<td>0.64</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>2.5</td>
<td>K$^{1+}$</td>
<td>-0.18</td>
</tr>
</tbody>
</table>

$^{11}$B NMR spectra obtained from gels prepared with EDTA do not show an additional peak arising from EDTA and borate complexation (Figure 5-16). A shifting of the free borate ion – boric acid exchange peak is observed in the spectra. Initially, the peaks shifts upfield on
addition of EDTA, then far downfield with increase of the EDTA concentration to 0.2 wt %, and finally to an intermediate chemical shift when the concentration is increased to 0.3 wt %. This behavior may be attributed to the re-entrant phases of the poly-ol-borax system described above for TSC-containing gels.

Integration of the crosslinked peaks and the exchanging boric acid-borate peaks reveals small changes in the amount of complexed borate ions for samples containing 30 μL of ammonia. Significant differences between the strength of the systems as measured by extensional rheology are not observed for these gels (Figure 5-10). Only with the addition of 100 μL of ammonia is a large change in the strength of the systems observed. Gels prepared with large concentrations of ammonia show drastic increases in the number of crosslinks. The large maximum normal force of EDTA-containing gels with 100 μL of ammonia is due to the enhanced crosslinked network.
Figure 5-16. $^{11}$B NMR spectra of gels prepared from 3 wt % 80PVAc, 1 wt % borax, and 30 μL NH$_3$ in D$_2$O with 0 wt % EDTA ( ), 0.1 wt % EDTA ( ), 0.2 wt % EDTA ( ), and 0.3 wt % EDTA ( ). The amount of complexed borate ion, obtained from integration of the signals from crosslinked boron and exchanging borate ion-boric acid in the NMR spectra, is shown in the inset.

5.3.3. Incorporation of ammonium carbonate and short-chain glycol ethers into xPVAc-borax gels

Addition of <0.5 wt % ammonium carbonate (AC) to xPVAc-borax gels has also been achieved. Ammonium carbonate is used for the treatment of wall paintings and frescoes. On these surfaces, the calcite (calcium carbonate) binder may be converted to gypsum (calcium sulfate dihydrate) as a result of interactions with sulfur dioxide and oxygen.$^{149,150}$ Gypsum not only causes discoloration of the surface but also disturbs the paint layers and can greatly damage the artwork.$^{149}$ Ammonium carbonate, typically applied in a poultice, can migrate into the surface of a wall painting and reconvert the gypsum to calcite. Preliminary tests by Carretti et al. have shown that ammonium carbonate incorporated into xPVAc-borax gels remains functional and can be used for the treatment of wall paintings.

Results from extensional rheology experiments on gels prepared with varying amounts of AC show increases in gel strength with AC concentration (Figure 5-17). The changes are very small, however. $^{11}$B NMR spectroscopy of gels containing up to 0.5 wt % ammonium carbonate do not show unexpected signals (Figure 5-18). The amount of crosslinked boron does not change
substantially with increasing ammonium carbonate, suggesting that the increase in strength found through extensional rheology must be due to electrostatic interactions and screening.

Figure 5-17. Extensional rheology results from gels prepared with 3 wt % 80PVAc_3, 0.75 wt % borax, and varying amounts of AC.

Figure 5-18. $^{11}$B NMR spectra gels from 3 wt % 80PVAc_3 with 0.75 wt % borax in D$_2$O with 0
wt % AC (■), 0.1 wt % AC (■), 0.3 wt % AC (■), 0.5 wt % AC (■), and of 0.75 wt % borax and 0.3 wt % AC without 80PVA_c_3 (■).

Glycol ethers contain ether, hydroxyl, and alkyl functionalities which contribute to their ability to dissolve a wide range of paints, coatings and surface pollutants. Short-chain glycol ethers such as cellosolve (ethylene glycol monoethyl ether), cellosolve acetate (ethylene glycol monoethyl ether acetate), and methyl cellosolve (ethylene glycol monomethyl ether) have been used in conservation treatments because of their good solubilization properties. Unfortunately, cellosolve and its derivatives are highly toxic and their use in conservation was phased out in the 1990s.\(^{151,152}\) Recently, longer ethylene glycol derivatives which function as nonionic surfactants have been used in the preparation of water-in-oil microemulsions for use as cleaning systems in conservation.\(^{13}\) The microemulsions were found to be very effective agents for removing dirt from acrylic paints.\(^{13}\)

Ethylene glycol moieties of intermediate chain length (ether derivatives of di- and tri-ethylene glycols) have not been explored for conservation applications. These species can be used as co-surfactants in the formation of microemulsions.\(^{153}\) When mixed with water, glycol ethers act as water structure breakers, forming a network of water-glycol hydrogen-bonded areas and completely hydrophobic environments.\(^{154}\) Diethylene glycol monobutyl ether (DEGMBE) is commonly used as an effective solvent for dyes and paints and has been deemed to have low oral, dermal, and inhalation toxicity by the European Commission committee on health and consumer protection.\(^{155}\) DEGMBE and three other glycol ether derivatives, triethylene glycol monoethyl ether (TEGMEE), diethylene glycol monoethyl ether (DEGMEE), and diethylene
glycol monomethyl ether (DEGMME) were added to xPVAc-borax hydrogels and tested as cleaning systems for removing varnish.

Stable gels from 6 wt % 75PVAc and 1 wt % borax were obtained using DEGMBE in proportions as high as 50/50 glycol ether/water. Gels did not form in the presence of DEGMEE, while TEGMEE addition resulted in the formation of gels which were stable only over the course of two days. xPVAc-borax gels prepared with DEGMME were stable but qualitatively stickier than hydrogels or gels prepared with DEGMBE. To test whether gels containing glycol ethers could be used as cleaning systems, they were compared with gels containing ethanol and 2-propanol for efficacy of dissolving shellac. The shellac was mixed with fluorescein before being painted on glass plates so that the UV/vis absorption and the fluorescence emission of gels used to remove the shellac could be monitored. Initial tests showed that DEGMBE-containing gels were capable of dissolving shellac to a similar extent as gels containing ethanol or 2-propanol. Gels containing TEGMEE and DEGMME were not as efficient as DEGMBE-containing gels and were not explored further. Comparison of 25/75 DEGMBE/water, ethanol/water, and 2-propanol/water containing xPVAc-borax gels to non-gelated liquids of the same composition revealed that the former were successful in softening shellac while the latter had very little effect on the surface (Figure 5-19). In these experiments, the liquids were applied over the same surface area, but without being rubbed with a swab. The preliminary results indicate that the encapsulation of the liquid in the xPVAc-borax gel network enhances its ability to solubilize the varnish.
Figure 5-19. UV/vis absorption spectra (A) and fluorescence emission spectra with $\lambda_{ex} = 495$ nm (B) of gels from 6 wt % 75PVAc and 1 wt % borax with (■) 25/75 ethanol/H$_2$O, (▲) 25/75 DEGMBE/H$_2$O, (■) 25/75 2-propanol/H$_2$O liquid composition and (▲) 25/75 ethanol/H$_2$O (liq), (■) 25/75 DEGMBE/H$_2$O (liq), and (▲) 25/75 2-propanol/H$_2$O (liq) used to treat shellac-fluorescein plates for 3 minutes. Emission spectra of each gel or liquid obtained before cleaning tests do not show detectable fluorescence (data not shown).

5.4. Attachment of Alkanoate groups to PVA

The ability of xPVAc-borax gels to be prepared with large fractions of organic liquids is dependent on the presence of acetate groups on the polymer chains. Based on this trend, the synthetic modification of PVA by attachment of longer alkanoate groups was undertaken to explore if these polymers could be used to gelate less polar liquids such as pentanol, octanol, and xylenes. Stearoyl chloride and butyryl chloride were used in nucleophilic acyl substitution reactions with pyridine to produce stearoyl- or butyryl-substituted PVAs.$^{156}$ Attachment of the long alkyl chains was determined by the presence of absorption at 1730 cm$^{-1}$ assigned to an ester
stretch and increased C-H stretch signals in the 2800-3000 cm\(^{-1}\) region of ATR FT-IR spectra (Figure 5-20). The percent of hydroxyl groups functionalized with alkanoate chains was determined using NMR spectroscopy (Figure 5-21).

Scheme 5-3. Reaction of stearic or butyric acid with thionyl chloride to produce the acyl chlorides and their covalent attachment to PVA.

Figure 5-20: ATR FT-IR spectra of PVA (■) and PVA with 30% butyroyl substituted hydroxyl groups (■).
Figure 5-21. $^1$H NMR spectrum of 30% stearoyl (top), and 30% butyroyl (bottom) substituted PVA in 1:1 DMSO-$d_6$:CDCl$_3$ and neat DMSO-$d_6$, respectively. The residual solvent peak of DMSO-$d_5$ is used as a reference in both spectra.

A range of stearoyl and butyroyl substituted PVAs were prepared. They are designated as $x$PVA$_y$ where “$x$” is the amount of substituted hydroxyl groups and “$y$” is the length of the
alkanoate chain. For example, a 3% stearoyl substituted polymer is designated 3PVA\textsubscript{18}. Butyroyl-substituted PVAs were synthesized and investigated by Holly Tao as a part of her undergraduate thesis. Results of dissolution, gelation, and rheological studies on butyroyl substituted PVAs indicate that the polymers are soluble in DMSO, NMP, polar alcohol/water mixtures, and benzyl alcohol. Gels can be formed in these solvents using xPVAc polymers. Stearoyl-substituted PVAs were found to be difficult to dissolve in many solvents, especially if the degree of substitution was large (≥15%). Both at room temperature over the course of 24 hours and with heating to the boiling point of the solvent, 2PVA\textsubscript{18} was not dissolved and, therefore, no gel was formed in the liquids investigated (Table 5-3).

Table 5-3. Results of attempts to dissolve 0.01 g 2PVA\textsubscript{18} in 0.5 g liquid. The polymer is a white solid before addition of solvent.

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Room Temperature</th>
<th>After Boiling</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Propanol</td>
<td>solution appeared more viscous</td>
<td>white solid</td>
</tr>
<tr>
<td>Xylene</td>
<td>swelled, polymer became transparent</td>
<td>yellow solid</td>
</tr>
<tr>
<td>Hexane</td>
<td>no visible effect</td>
<td>yellow solid</td>
</tr>
<tr>
<td>Acetone</td>
<td>no visible effect</td>
<td>swelled yellow solid</td>
</tr>
<tr>
<td>Butanol</td>
<td>no visible effect</td>
<td>white solid</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>swelled, polymer became transparent</td>
<td>swelled transparent solid</td>
</tr>
<tr>
<td>Ethyl Acetate</td>
<td>no visible effect</td>
<td>yellow solid</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>no visible effect</td>
<td>yellow solid</td>
</tr>
</tbody>
</table>
Attempts to create gels with 3PVA$_{18}$ and 15PVA$_{18}$ were unsuccessful. Mixtures were prepared from 1 wt % aqueous borax, 3 wt % polymer, and a less polar organic liquid which were heated and vortexed over the course of one month. The systems contained undissolved polymers which had swelled, possibly absorbing the aqueous portion of the liquid, but did not dissolve fully nor form gels (Figures 5-22-A and B). Several of the mixtures formed two phase systems composed of a stiff, translucent gel and liquid (Figure 5-22-C and D). However, a homogeneous, transparent gel was obtained from 15PVA$_{18}$ in acetone; as noted, homogenous gels with large fractions of acetone can be formed from 40PVAc as well. The potential differences in the cleaning efficiencies of the two gel types with acetone were not examined.
Figure 5-22. (A) 3 wt % 3PVA_{18} and 1 wt % borax in 80/20 2-propanol/hexanes, (B) 3 wt % 3PVA_{18} and 1 wt % borax in xylene, (C) 4 wt % 15PVA_{18} and 1 wt % borax in 60/15/25 DMSO/CHCl_{3}/water, and (D) 4 wt % 3PVA_{18} and 1 wt % borax in 75/25 DMSO/water.

Refractometry was used to investigate the nature of expelled liquid in the two phase systems. Many of the liquids tested for gelation were immiscible in water. In these systems, refractometry was used to elucidate whether the liquid expelled from the gel was water from the borax solution, the organic liquid, or a mixture of the two. The refractive indices of the pure liquids as well as mixtures of the liquids with water were measured. The composition of the liquid in each of the two phase systems, based on its refractive index, is listed in Table 5-4. The refractive index of aqueous borax was not measured because at salt concentrations lower than 3 wt % (NaCl), the refractive index changes < 0.005. The stiff gels retained mainly the aqueous portion of the liquid while the expelled phase was almost always the organic liquid. Because the borax is dissolved in the aqueous portion of the mixture, the results suggest that the polymers are able to swell and become crosslinked by the aqueous borax solution in the presence of water and some organic liquids, but because of the immiscibility of the organic liquid with water, phase separation occurs immediately.

Table 5-4. Composition of liquids expelled from mixtures of 3 wt % 3PVA_{18} or 15PVA_{18} and 1 wt % borax in organic liquid/aqueous solutions. Measurements were made 4 months after sample preparation; systems did not appear different from descriptions made at time of preparation.

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<table>
<thead>
<tr>
<th>Polymer</th>
<th>R.I.(^a) of Pure Liquid</th>
<th>R.I. of 25/75 wt/wt % H(_2)O/organic Liquid</th>
<th>R.I. of 50/50 wt/wt % H(_2)O/organic Liquid</th>
<th>R.I. of 75/25 wt/wt % H(_2)O/organic Liquid</th>
<th>R.I. of Expelled Liquid Composition(^c)</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>1.4929 - 1.5018</td>
<td>N/M(^d)</td>
<td>N/M</td>
<td>N/M</td>
<td>1.4985</td>
<td>Xylene OG(^e) and free liquid</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>1.3776 - 1.3785</td>
<td>1.3715</td>
<td>1.3610</td>
<td>1.3725</td>
<td>~50/50</td>
<td>2-Propanol/Water CG(^e) and free liquid</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.4941</td>
<td>N/M</td>
<td>N/M</td>
<td>N/M</td>
<td>1.4970</td>
<td>Toluene CG and free liquid</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.3727</td>
<td>N/M</td>
<td>N/M</td>
<td>N/M</td>
<td>1.3825</td>
<td>Hexane OG and free liquid</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.3588 - 1.3680</td>
<td>1.3655</td>
<td>1.3560</td>
<td>N/A</td>
<td>N/A</td>
<td>Acetone TG</td>
</tr>
<tr>
<td>Benzyl Alcohol</td>
<td>1.5396 - 1.5225</td>
<td>N/M</td>
<td>N/M</td>
<td>1.5220</td>
<td>1.5220</td>
<td>Benzyl Alcohol Solid and two phase solution</td>
</tr>
<tr>
<td>1-Butanol</td>
<td>1.3988 - 1.3925</td>
<td>N/M</td>
<td>N/M</td>
<td>1.3925</td>
<td>1-Butanol CG and free liquid</td>
<td></td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>1.3694 - 1.3650</td>
<td>N/M</td>
<td>N/M</td>
<td>1.3675</td>
<td>Methyl Acetate Solid and two phase solution</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) Refractive Index; \(^b\) Obtained from the CRC Handbook of Physics and Chemistry; \(^c\) Obtained by comparison of the R.I. value of the expelled liquid to the values of the H\(_2\)O/organic liquids; \(^d\) Not Miscible; \(^e\) OG, CG, and TG are opaque gel, clear gel, and translucent gel, respectively.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>R.I. of Pure Liquid</th>
<th>R.I. of 25/75 wt/wt % H₂O/Organic Liquid</th>
<th>R.I. of 50/50 wt/wt % H₂O/Organic Liquid</th>
<th>R.I. of 75/25 wt/wt % H₂O/Organic Liquid</th>
<th>R.I. of Expelled Liquid</th>
<th>Liquid Composition&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Sample Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>1.4929-1.5018</td>
<td>N/M&lt;sup&gt;d&lt;/sup&gt;</td>
<td>N/M</td>
<td>N/M</td>
<td>1.4990</td>
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<td>CG and free liquid</td>
</tr>
<tr>
<td>2-Propanol</td>
<td>1.3776</td>
<td>1.3785</td>
<td>1.3715</td>
<td>1.3610</td>
<td>1.3720</td>
<td>~50/50 2-Propanol/Water</td>
<td>OG and free liquid</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.4941</td>
<td>N/M</td>
<td>N/M</td>
<td>N/M</td>
<td>1.4970</td>
<td>Toluene</td>
<td>CG and free liquid</td>
</tr>
<tr>
<td>Hexane</td>
<td>1.3727</td>
<td>N/M</td>
<td>N/M</td>
<td>N/M</td>
<td>1.3815</td>
<td>Hexane</td>
<td>CG and free liquid</td>
</tr>
<tr>
<td>Acetone</td>
<td>1.3588</td>
<td>1.3680</td>
<td>1.3655</td>
<td>1.3560</td>
<td>1.3675</td>
<td>~75/25 Acetone/Water</td>
<td>OG &amp; free liquid</td>
</tr>
<tr>
<td>Benzyl Alcohol</td>
<td>1.5396</td>
<td>1.5225</td>
<td>N/M</td>
<td>N/M</td>
<td>1.5230</td>
<td>Benzyl Alcohol</td>
<td>OG and free liquid</td>
</tr>
<tr>
<td>1-Butanol</td>
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<td>1.3925</td>
<td>N/M</td>
<td>N/M</td>
<td>1.3935</td>
<td>1-Butanol</td>
<td>OG and free liquid</td>
</tr>
<tr>
<td>Methyl Acetate</td>
<td>1.3694</td>
<td>1.3650</td>
<td>N/M</td>
<td>N/M</td>
<td>1.3655</td>
<td>Methyl Acetate</td>
<td>TG and free liquid</td>
</tr>
</tbody>
</table>

<sup>a</sup> Refractive Index; <sup>b</sup> Obtained from the CRC Handbook of Physics and Chemistry; <sup>c</sup> Obtained by comparison of the R.I. value of the expelled liquid to the values of the H₂O/organic liquids; <sup>d</sup> Not Miscible; <sup>e</sup> OG, CG, and TG are opaque gel, clear gel, and translucent gel, respectively.
5.5. *Trimethyl borate as a crosslinker for xPVAc systems*

The solubility of polymers containing polar hydroxyl side-groups and randomly distributed alkanoate chains of four or eighteen carbons in neat organic liquids or mixtures with water was shown to be very poor for most of the compositions examined. However, if such polymers could be solubilized in neat organic liquids, a non-aqueous crosslinker would be required to produce transparent homogeneous gels. Trimethyl borate (TMB), a planar boron species with three methoxy groups, was explored for this purpose. Although other organic reagents, such as gluteraldehyde, can be used to crosslink PVA, the resultant gels have permanent chemical crosslinks and are expected to have different physical properties from those of xPVAc-borax gels with their mobile crosslinks. Use of TMB would allow for the study of its gels by $^{11}$B NMR spectroscopy, a tool that is very useful in understanding the properties of xPVAc-borax gel systems.

Trimethyl borate reacts quickly with water to form boric acid and methanol; the pH of the resulting solution is 4.5-5. For this reason, tests to establish whether TMB can crosslink xPVAc were conducted in aprotic solvents. In that regard, the dissolution of 40PVAc in DMSO and dimethylformamide (DMF) was accomplished at room temperature or with gentle heating. Addition of TMB to the polymer solutions resulted in gel formation. To measure the lowest concentration of polymer necessary for the formation of TMB-crosslinked gels, samples were prepared in which the polymer concentration was changed while all other variables were kept constant. Samples prepared with as little as 5 wt % of 40PVAc in DMF showed large increases in viscosity and reduced flow. However, these low-polymer concentration samples reverted to viscous solutions and lost structural characteristics within an hour of formation in closed vials;
all 40PVAc-TMB gels revert to viscous liquids when exposed to atmospheric moisture. Samples prepared with higher concentrations of polymer required a longer time or agitation for the loss of gel-like consistency to occur.

As with gels prepared with borax, $^{11}$B NMR spectra of 40PVAc-TMB gels show a cross-linked boron signal at ~2 ppm (Figure 5-23). Two coalescing peaks are present between 19 and 20 ppm. The peak centered at ~19 ppm was found to correspond to TMB while the shoulder centered at ~20 ppm corresponds to boric acid formed in the systems. Because PVA is highly hygroscopic and neither the polymer nor deuterated DMSO used in the studies were dried, the small amount of water present in the system causes the conversion of some TMB to boric acid. As the polymer concentration was increased, the amount of crosslinked boron also increased in 40PVAc-TMB gels. The relative size of the free TMB signal decreased as the amount of boron participating in crosslinks increased, suggesting that TMB rather than boric acid is the crosslinking species in these gels (Figure 5-23). Addition of boric acid to 40PVAc dissolved in methanol does not produce gels and $^{11}$B NMR spectra of these mixtures do not show a peak due to crosslinked boron.
Figure 5-23. $^{11}$B NMR spectra of gels prepared with (●) 2 wt %, (■) 5 wt %, (○) 6.5 wt %, (□) 8 wt %, (◇) 9.5 wt %, and (◆) 11 wt % 40PVAc and 3.6 wt % TMB in DMSO-$d_6$. Signals are referenced to $\text{F}_3\text{B-O(C}_2\text{H}_5\text{)}_2$ in diethyl ether held in a sealed tube within the one containing the gel samples.

Figure 5-24 shows the $^{11}$B NMR spectra of gels prepared with varying amounts of TMB. Trimethyl borate concentration was varied as a molar percentage relative to the calculated moles of hydroxyl groups on the polymer chains so that “5 mol % TMB” represents a concentration of TMB equivalent to 5 % of the molar concentration of hydroxyl groups in 10 wt % of 40PVAc. When decreasing the TMB concentration in 40PVAc-TMB gels, the free boron peak seems to disappear completely as the concentration of the TMB falls below 25 mol % (Figure 5-24). These results suggest that all of the trimethyl borate may be forced to participate in crosslinks in 40PVAc networks in DMSO. However, it is more likely that at low concentrations, the free boron peak is too broad to be detected against the baseline and background noise (see Appendix B).

Figure 5-24. $^{11}$B NMR spectra of gels prepared with 10 wt % 40PVAc and 5 mol % (●), 25 mol % (■), 50 mol % (○), and 75 mol % (◆) trimethyl borate in DMSO-$d_6$. Signals are referenced to $\text{F}_3\text{B-O(C}_2\text{H}_5\text{)}_2$ in diethyl ether held in a sealed tube within the one containing the gel samples.
As discussed in Chapter 3, crosslinks formed in PVA-borax systems are labile and dynamic. Gels formed from crosslinks by TMB are expected to have similar properties. The conversion of 40PVAc-TMB gels to the sol state when exposed to small amounts of moisture present in the open atmosphere corroborates the notion that the crosslinks are in flux. TMB not participating in crosslinks can be converted to boric acid on exposure to water, resulting in a drop in the pH of the system. When the pH of PVA-borate gels is below 7, complexation is lost and the network reverts to a solution state. The same process occurs in 40PVAc-TMB gels.

The formation of gels from TMB and xPVAc supports the claim by Bishop et al.\textsuperscript{46} and Reitjens and Steenbergen\textsuperscript{64} that attachment of the diol occurs with the trigonal form of boric acid, rather than the borate ion. In the aprotic environment of a 40PVAc-TMB gel system, the uncharged, trigonal, trimethyl borate and boric acid are more stable than a charged borate ion. However, formation of the acid results in a pH too low for hydroxide deprotonation and boron-oxygen bond formation and, thus, disfavors crosslinking. One possible interpretation of why crosslinking occurs in these mixtures is that microenvironments containing TMB in the vicinity of a diol form in the system. In these locations, where water is hydrogen-bonded to the polymer chains, the methoxy groups on boron can be replaced by hydroxyl groups through an exchange reaction. The released methoxide ion can deprotonate a proximal diol, leading to immediate reaction with the newly formed boric acid and formation of a crosslink.

To prevent conversion of the gel network to a solution and allow for more diol deprotonation, a base was added to gels prepared with TMB. Initial experiments were performed with sodium hydride (NaH), though it is not fully soluble in DMSO or DMF. Care was taken to ensure it was dispersed throughout the systems. The gels produced with NaH were a yellow to
light brown color. In the presence of a strong base, even at room temperature, some elimination reactions (involving formation of water and acetic acid) are expected to occur in 40PVAc. The unsaturation along the polymer chains is a possible cause of the coloration. The pH of the gels was tested on pre-wetted litmus paper and found to be close to 10.5.

The basified gels remained in the gel state, even when exposed to atmospheric moisture. When 0.2 gram gel samples were placed on glass plates and left exposed to the open atmosphere, the gels dried completely over the course of several hours rather than reverting to the sol state. These gels were highly elastic after the addition of base. Their stability in the presence of atmospheric moisture may be due to reduced mobility of water into the stiff, elastic gel network. The concentration of NaH incorporated into the gels was varied as a function of the percentage of molar equivalent to the hydroxyl groups on the polymers; these concentrations are reported in the same manner as the TMB concentrations (mol %).

Figure 5-25. Gels prepared from 10 wt % 40PVAc and 15 mol % TMB in DMSO with varying amounts of NaH in open atmosphere after 1 hour (left) and on wetted pH strips (right).
Basified 40PVAc-TMB gels were studied using rheology (both DMSO and DMF gels) and $^{11}$B NMR spectroscopy (DMSO gels only). As inferred from their handling properties, 40PVAc crosslinked with TMB produced viscoelastic materials which became more elastic with addition of NaH. Gels prepared from 40PVAc-TMB exhibit the accepted strain stiffening behavior of PVA-borax systems. When the concentration of NaH was high, the $G'$ modulus was larger than the $G''$ modulus over the entire range of angular frequencies measured (Figure 5-26). The frequency sweep results indicate that crosslinking with TMB in the presence of a base can produce “true gels” using 40PVAc. Evident in Figure 5-26 is the large variation in results obtained on the same gel sample. There are two reasons for the lack of reproducibility in the rheological studies: the dispersed, rather than fully dissolved, NaH causes bulk inhomogeneities within the sample, and the conversion of the gels to the liquid state occurs during the course of the experiment.

![Figure 5-26](image)

Figure 5-26. Angular frequency sweeps showing $G'$ (■) and $G''$ (○) of gels prepared from 10 wt % 40PVAc and 15 mol % TMB in DMF with 75 mol % NaH; strain = 1 %. Five experiments on different aliquots from the same gel sample are displayed.
To address these problems, sodium hydride was substituted by sodium methoxide. Although sodium methoxide was also not fully soluble in DMSO and DMF in concentrations higher than 5 mol %, it could be dispersed more homogeneously than NaH. Gels were prepared from 40PVAc and TMB in DMSO and DMF with varying amounts of methoxide. Gels containing more than 5 mol % of methoxide were found to be slightly yellow or brown despite addition of the base being performed at room temperature. Rheological investigations of the gels were carried out under continuous nitrogen gas flow to prevent liquefaction of the samples using a Peltier hood on the rheometer which covers the sample area creating a chamber into which the N₂ gas can be directed. Due to the low volatility of DMSO and DMF, solvent evaporation during the course of the experiment was considered negligible based upon the following circumstantial reasoning: the experiments required only 10-20 minutes; the boiling point of both solvents is >150 °C; gel samples were placed between two plates separated by 0.05 mm.

The results of frequency sweeps on gels prepared from 10 wt % 40PVAc and 15 mol % TMB are shown in Figures 5-27 and 5-28. The reproducibility of these results is clear from the standard deviation bars in each figure. Although the G’ and G” cross-over frequency does not show a trend (the same was found in gels prepared with NaH), the G’ plateau maxima show a consistent increase with increasing base concentration. The rheology experiments confirm visual observations: gels with higher concentrations of sodium methoxide are more elastic.
Figure 5-27. Angular frequency sweeps of gels prepared with 10 wt % 40PVAc, 15 mol % TMB and (■) 0 mol %, (▲) 5 mol %, (■) 10 mol %, (▲) 25 mol %, and (■) 50 mol % methoxide in (A) DMSO with a strain of 0.5%, and (B) DMF with a strain of 10%. Standard deviation is included from 3-5 trials on every gel except for the 50 mol % methoxide in DMSO gel which has only one trial included.

Figure 5-28. Plateau values (at 120 rad/sec) of the storage moduli, G’, from gels with different amounts of methoxide prepared with 10 wt % 40PVAc and 15 mol % TMB in (■) DMSO and (▲) DMF.
There is a tendency for the cross-over frequency of $G'$ and $G''$ to decrease and even not occur in the frequency sweeps of gels prepared with very large concentrations of methoxide. As mentioned, addition of base facilitates crosslinking in the systems. The crosslinks in 40PVAc-TMB gels are negatively charged but their electrostatic effects on nearby negative charges can be partially screened by sodium ions from the base. The $^{11}$B NMR spectra lack the expected signal from free TMB, and the results from these experiments are similar to those obtained from gels prepared with sodium hydride (Figure 5-29). An increase in the intensity of the peak for crosslinked boron is observed, but no other peaks are present in the $^{11}$B NMR spectra of the gels. The location of the crosslinked peak also shifted with increasing base concentration in both sets of gels. The increase in the signal of a crosslinked boron species is consistent with the rheological indication that the gels become more elastic with addition of more base. However, the relative amount of boron that is participating in crosslinks cannot be established because of the lack of evidence for the remaining boron in the gels. The two alternative NMR spectroscopy techniques described in Appendix B – a DEPTH pulse sequence or $^{10}$B NMR spectroscopy – have been attempted on the 40PVAc-TMB gels. The concentration of boron in these systems was too low to be detected by either method using our equipment.
Figure 5-29. $^{11}$B NMR spectra of gels prepared with 10 wt % 40PVAc and 15 mol % TMB in DMSO-$d_6$ with (top) (■) 0 mol % sodium methoxide, (■) 5 mol % sodium methoxide, (■) 10 mol % sodium methoxide, (■) 25 mol % sodium methoxide, (■) 50 mol % sodium methoxide, and (bottom) (●) – 0% NaH, (●) – 10% NaH, (●) – 50% NaH. NaH gel signals are referenced to F$_3$B-O(C$_2$H$_5$)$_2$ in diethyl ether held in a sealed tube within the one containing the gel samples.

Gels prepared by the crosslinking of PVAc with a small degree of hydrolysis by trimethyl borate present an opportunity to explore the complexation of diols with a trigonal boron species. The results presented in this section are novel, and open opportunities for further exploration of the crosslinking mechanism. The gel materials prepared with trimethyl borate are not likely to find applications in art conservation; the reversion of the gels to the sol state on exposure to water is problematic. Addition of strong bases, which allows the gels to remain solid for longer periods of time, raises the pH to values that are unsafe for most treatments. Furthermore, trimethyl borate is a volatile, flammable liquid necessitating safety precautions during its use for gel preparation that are cumbersome in a conservation studio. Preparation of viscoelastic poly-ol gels that contain liquids of low polarity will require a different approach. One possible alternative that still involves a boron species as a crosslinker is the use of diboronic acids. Materials such as benzene-1,4-diboronic acid or 4,4’-biphenylenediboronic acid may have the capacity to form crosslinks with xPVAc.
5.6. Conclusions.

Several modifications to the xPVAc-borax gel system have been investigated for the purpose of expanding its suitability for challenging conservation treatments. Because of the dynamic nature of the gel network, changes such as addition of a salt or modification of the polymers can have drastic effects on gel formation and stability. The covalent attachment of alkanoate chains or citrate groups to poly(vinyl alcohol) greatly reduces the solubility of the polymers in all of the liquids explored in this dissertation. The difficulty of solubilization of these modified polymers not only hinders their transformation into gels but also prevents elucidation of their structure and side-chain distributions. Alternative synthetic methods which ensure a random distribution of alkanoate chains and hinder chemical crosslink formation during citrate attachment may be helpful for future modifications of those polymers. Additionally, an in-depth analysis of the solubility of the modified polymers may be useful to determine possible liquids which may be appropriate for gel formation.

Gels prepared with citrate ions, EDTA, and ammonium carbonate have been successfully used in test treatments by Carretti et al. Preparation of gels with additives in the liquid portion requires a careful balance of the salt concentrations due to the polyelectrolyte nature of the xPVAc-borax networks. Gels with appropriate physical properties can only be prepared with low concentrations of citrate or EDTA. Those gels may not be effective for cleaning because higher concentrations are commonly required for the treatment of artworks. Increasing the amount of salts incorporated into a gel may result in a stiffening of the network and even phase separation. Addition of di- and tri-ethylene glycols is not likely to affect the network in the same manner and may be a good alternative for producing gels with improved cleaning capabilities. Initial tests
indicate that gels with glycol ethers are as effective at removing shellac as gels prepared with ethanol. Analysis of the cleaning action of glycol ethers incorporated into xPVAc-borax gels, their contribution to polymer solubilization, or even their formation of micelles will be explored in the future.

Research into alternative crosslinkers for xPVAc gels which produce gels with similar viscoelastic properties but with a wider range of organic liquids was initiated. Trimethyl borate, structurally one of the closest alternatives to the boric acid/borate ion species from borax has been shown to form crosslinks effectively with 40PVAc. The resulting gels are very sensitive to water due to the rapid reaction of trimethyl borate with water to produce boric acid in the system. Gels prepared from 40PVAc and trimethyl borate in aprotic liquids such as DMSO or DMF must be stabilized by a strong base, such as sodium hydride or sodium methoxide, rendering them unsuitable for most conservation treatments. Further, the liquids gelated by the system must be aprotic, which limits their applicability for conservation purposes. The dynamic crosslinks obtained by the formation of a di-diol-borate complex are crucial to the physical properties of the xPVAc gel systems. If other boron containing agents such as diboronic acids are not found to yield stable gel networks with xPVAc, alternative dynamically crosslinked polymeric gel systems may be explored.
6. ART CONSERVATION APPLICATIONS

6.1. Introduction.

The cleaning of artworks may involve complete or partial removal of surface materials that have been deemed damaging in both physical and aesthetic terms. Treatments may be carried out to remove an aged and discolored varnish layer, environmental depositions such dirt, grime, and soot accumulated over time, and non-original paint layers applied during a previous restoration. As discussed in Chapter 1, after careful consideration of the composition of the artwork and the materials to be removed, a conservator will select the appropriate methods for a treatment. If the method selected involving solvents is deemed appropriate, swabs, moistened with the cleaning agent, are rolled over the surface until the desired level of cleaning is accomplished. However, some treatments necessitate the delivery of a cleaning liquid in a thickened paste, poultice, or gel.

Several such systems are already available and in use by the conservation community. However, the gels described in this dissertation offer some advantages which make them appropriate for a variety of complex treatments. Gels prepared by the crosslinking of partially hydrolyzed poly(vinyl acetate) with borax behave both as highly viscous liquids that can conform to the topography of a surface, and as elastic solids. The gels can maintain their shapes and compositions so that their application and removal are relatively straightforward (Figure 6-1). As demonstrated in Chapters 4 and 5, the gels can be prepared with a range of organic liquids (such as ethanol, 2-propanol, n-propyl alcohol, and acetone), and with aqueous solutions of trisodium citrate, ethylenediaminetetraacetic acid (EDTA), ammonium carbonate, and short chain glycol ethers.
As will be shown in Section 6.5, the gels retain the liquid well and there is little lateral solvent spread from them, providing confined cleaning for spot treatment. As with most thickened and gelated systems, the rate of evaporation of the solvent is reduced as is the rate of solvent penetration into the surface layers. The preliminary experiments described in Section 5.3.3. suggest that the polymeric gel structure may contribute to the cleaning action of the system.

To address the concern of polymer residues, fluorescent tags were attached to the polymers used to prepare xPVAc-borax gels, and the resulting fluorescent gels were used in several case studies described in Sections 6.3 and 6.6. The deposition of boron-containing species during cleaning has been addressed in Section 6.4. In Section 6.6, analysis of the components in an xPVAc-borax gel and of the swabs used in a treatment is described in order to elucidate what was removed from the surface. This chapter also includes a summary of treatment results accompanied by remarks from the conservators who performed the tests. The work described in this chapter has been submitted for publication to Studies in Conservation.
Figure 6-1. The removal of a green-tinted xPVAc-borax gel from a textured surface with tweezers.


Gels were prepared as described in Chapters 4 and 5. Polymers: PVA (Exceval HR 3010), 80PVAc-3 (Poval PVA 424H), 75PVAc (Poval PVA 505), 45PVAc (Poval LM 20), and 40PVAc (Poval LM 10HD) (Kuraray, purified as described in Chapter 4), sodium tetraboratedecahydrate (>99.5%; Fluka), n-propyl alcohol (Fisher, certified normal grade), 2-propanol (HPLC grade, 99.9%; Fisher), ethanol (anhydrous, 200 proof ≥99.5%, Sigma-Aldrich), DMSO (HPLC grade, 99.94%, Alfa Aesar), methanol (HPLC grade, Fisher), acetone (histological grade, Fisher), fluorescein (free acid, Aldrich, 95%), NaH (Acros Organics, powder) potassium iodide (U.S.P., Fisher), epichlorohydrin (99%, Acros), potassium carbonate (ACS reagent, ≥99.0%, Sigma Aldrich), and Boron standard for ICP (Fluka, 1000 mg/L ± 3 mg/L) were used as received. Deionized water was used throughout.

The absorbance and fluorescence properties of fluorescein in xPVAc-borax gels were studied in systems prepared with 0.5 mM fluorescein: hydrogels from 3 wt % PVA, 80PVAc-3, 75PVAc, 45PVAc, or 40PVA, and 0.5 wt % borax; gels with 30/70 1-propanol/water from 6 wt% PVA, 80PVAc-3, 75PVAc, 45PVAc, or 40PVA, and 0.7 wt % borax; gels with 0/100 or 50/50 1-propanol/water from 6 wt % 75PVAc and 0.7 wt % borax; and gels with 30/70 or 80/20 1-propanol/water from 14 wt % 40PVAc and 1.3 wt % borax. The gels were transferred to flattened capillary cuvettes with a 0.4 mm path length (Vitro Com). UV-vis absorption spectra and fluorescence excitation and emission spectra of each gel were obtained. Solutions of 2.4 mM fluorescein in water, 30/70 1-propanol/water, and 50/50 1-propanol water, and in water with 0.3
wt % borax were analyzed using UV-vis absorption spectroscopy and spectrofluorimetry. A Varian Cary 300 Bio UV-visible Spectrophotometer was used for the absorbance studies. Excitation and emission spectra were obtained on a Photon Technology International Fluorimeter (SYS 2459) with the flattened cuvettes oriented front-face at an angle of ~ 45° with respect to the incident beam, and the emission was collected at 90° with respect to the excitation source. The spectra were normalized to the highest intensity and baseline corrected.

*Preparation of 3-Epoxypropoxyfluorescein (EPF) and its Attachment to xPVAc.* Potassium iodide (0.83 g, 5 mmol) was ground finely in a mortar and pestle and added to a round bottom flask along with epichlorohydrin (0.39 mL, 5 mmol) and anhydrous ethanol (10 mL). The system was stirred under a N₂ atmosphere and refluxed for 30 minutes. Potassium carbonate (0.415 g, 3 mmol) was ground in a mortar and pestle and added to the flask. Stirring was continued for 10 minutes. Fluorescein (0.17 g, 0.5 mmol) was dissolved in anhydrous ethanol (15 mL) and added to the round bottom flask through a dropping funnel. The mixture was allowed to stir for an additional 7 hours under N₂ at 50-55 °C. The heat was then removed, and stirring was continued for ~12 hours. The solvent was gently removed on a rotary evaporator and the product was dried under N₂. Flash chromatography through a Buchner funnel was used to purify the product (stationary phase - silica 43-75 μm, mobile phase – 70/30 ethyl acetate/methanol). The product (EPF) was then dried under vacuum for 48 hours.

75PVAc (3.0 g, 0.054 mol) was dissolved in DMSO (20 mL) in a round-bottom flask under N₂ and refluxed. The solution was transferred to a dry dropping funnel and allowed to cool to room temperature. NaH (0.3g) was placed in a separate flask with a Teflon-coated stir bar. The 75PVAc solution was added to the NaH slowly at room temperature under N₂ until no gas
was given off. The dropping funnel was then filled with DMSO (5 mL) containing EPF (0.010 g, 2.7 x 10^{-5} mol). This solution was added over 30 minutes. The reaction was allowed to proceed for another 2 hours. The product was precipitated with excess ethyl acetate, and centrifuged in order to collect the yellow polymer. The product was re-dissolved in water and neutralized with 0.05M hydrochloric acid. This material was reprecipitated three times by addition of acetone (until the acetone remained clear), and was dried under vacuum for 48 hours. Recovery: 71%, analysis by $^1$H NMR. Similar procedures were followed for the modification of 40PVAc, 80PVAc, and PVA.

To characterize the fluorescein-tagged polymers, each was dissolved in distilled, deionized water at pH 7 (1 wt %) and UV-vis spectra were recorded in a 1 cm glass cuvette. The percent fluorescein substitution was calculated by measuring the absorbance at 470 nm and using of the extinction coefficient of 3-O-methylfluorescein (26000 M^{-1}cm^{-1} at pH 7 and 470 nm)\textsuperscript{159} to approximate the extinction coefficient of the fluorescein bonded to the xPVAc chain. 30/70 n-propyl alcohol/water gels with the following compositions were analyzed: 4 wt % PVA-EPF and 1.1 wt % borax; 4 wt % 80PVAc_3-EPF and 1 wt % borax, 6 wt % 75PVAc-EPF and 1.4 wt % borax; and 11 wt % 40PVAc-EPF and 2 wt % borax. Fluorescence spectra of the gels were obtained front-face in 0.4 mm glass cuvettes.

Rheological measurements were made on gels prepared from 6 wt % 75PVAc or 75PVAc-EPF with 1.4 wt % borax and 0/100 or 30/70 methanol/water compositions as well as gels prepared with 6 wt % 75PVAc or 75PVAc-EPF with 1.2 wt % borax and 50/50 methanol/water compositions. An Anton Paar Physica MCR 301 stress-controlled rheometer was used with a 25 mm diameter and 1° cone angle for the frequency sweeps. Angular frequency
sweeps were performed with a strain of 1% in the linear viscoelastic region based on a strain sweep obtained with 1 rad/sec. The data were collected and analyzed using Rheoplus/32 Service V3.10 software.

Fluorescence measurements were deemed to be a sensitive method to measure the presence of xPVAc-EPF residues. Experiments to measure the detection limit were performed on a HORIBA Jobin-Yvon fluorolog-3 spectrofluorimeter with external fiber optics. A concentration gradient of fluorescein was prepared in deionized, distilled water (with the addition of 0.01 M NaOH to achieve complete dye dissolution) and 5 μL of sample were placed onto an acrylic paint test surface via a micropipette (Table 6-1 lists the concentrations tested). The emission spectrum of each sample was collected with a $\lambda_{\text{ex}} = 470$ nm with $\lambda_{\text{em}} = 490 – 600$ nm. The slit widths were 5 nm and the external optics, approximately 2 mm from the surface, were not moved throughout the process. The fluorimeter was equipped with a 450 W xenon arc lamp and a Fluorolog-3 R928P photomultiplier tube detector. Tests to determined xPVAc-EPF residue on a test acrylic painting were performed with gels prepared from the derivatized polymers containing 50/50, 30/70, and 0/100 wt % methanol/water mixtures. Spectra were obtained before, during, and after gel application. Gels were kept on the surface for approximately 13 minutes. Data were processed using Origin 8 software.
Table 6-1. List of concentrations used in the fluorescein gradient shown above for instrument detection limit experiments; highlighted is the last detectable concentration of the dye under these conditions.

<table>
<thead>
<tr>
<th>Quad</th>
<th>Concentration (M)</th>
<th>9</th>
<th>10</th>
<th>18</th>
<th>27</th>
<th>31</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.006 x 10^{-4}</td>
<td>10</td>
<td>2.257 x 10^{-5}</td>
<td>19</td>
<td>1.695E x 10^{-6}</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>2.55 x 10^{-4}</td>
<td>11</td>
<td>1.693 x 10^{-5}</td>
<td>20</td>
<td>1.271 x 10^{-6}</td>
<td>29</td>
</tr>
<tr>
<td>3</td>
<td>1.691 x 10^{-4}</td>
<td>12</td>
<td>1.27 x 10^{-5}</td>
<td>21</td>
<td>9.533 x 10^{-7}</td>
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<td>9.522 x 10^{-6}</td>
<td>22</td>
<td>7.149 x 10^{-7}</td>
<td>31</td>
</tr>
<tr>
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<td>9.511 x 10^{-5}</td>
<td>14</td>
<td>7.141 x 10^{-6}</td>
<td>23</td>
<td>5.362 x 10^{-7}</td>
<td>32</td>
</tr>
<tr>
<td>6</td>
<td>7.133 x 10^{-5}</td>
<td>15</td>
<td>5.356 x 10^{-6}</td>
<td>24</td>
<td>4.022 x 10^{-7}</td>
<td>33</td>
</tr>
<tr>
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<td>5.35 x 10^{-5}</td>
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<td>4.017 x 10^{-6}</td>
<td>25</td>
<td>3.016 x 10^{-7}</td>
<td>34</td>
</tr>
<tr>
<td>8</td>
<td>4.013 x 10^{-5}</td>
<td>17</td>
<td>3.013 x 10^{-6}</td>
<td>26</td>
<td>2.262 x 10^{-7}</td>
<td></td>
</tr>
</tbody>
</table>

An Agilent Technologies 7700x ICP-MS spectrometer in no gas mode was used in studies of the deposition of boron-containing species. Milli-Q Millipore 18.2 MΩ/cm water was used for all experiments and all samples were prepared, stored, and pipetted using plastic containers and pipette tips to avoid contact with glass. Paint-outs were treated with a 30/70 2-propanol/water gel prepared from 5 wt % 75PVAc and 1 wt % borax. Experiments to measure the minimum amount of boron on acrylic paint or dammar varnish using this technique have not
been performed. Instead, a calibration curve using boric acid was used to obtain quantitative results. All experiments were performed 4-6 times on samples obtained from different areas and standard deviation of the results was obtained. To test the concentration of boron-containing species present on the surface before gel treatment, 100 µL of water was spread over a circular area with a 1 cm diameter and collected after 3 minutes (sample name “Surface Blank”). A 0.1 g portion of gel was placed in a different location with the same dimensions and removed after a 3 minute exposure time. A 100 µL aliquot of water was immediately placed on over the gel-treated location and removed after 2 minutes (sample name “Post Gel”). In a new location of the same dimensions, a 0.1 g portion of gel was placed and removed after a 3 minute exposure time. A swab dipped in a 30/70 2-propanol/water solution was passed over the surface for 20 seconds and a 100 µL aliquot of water was immediately placed over the location. After 2 minutes, this water sample was collected (sample name “Post Gel/Swab”). Each sample was diluted to 1.5 mL and injected manually into the instrument. Agilent Technologies wash with 5% HNO₃ was injected after each sample, followed by an aliquot of Milli-Q Millipore 18.2 MΩ/cm water, represented by “Millipore Blank”.

Gels for lateral solvent spread tests were prepared with liquid compositions of 30/70, 50/50, or 70/30 acetone and 0.02 nM rhodamine B from 40PVAc, 75PVAc, 80PVAc, and PVA. The gels were placed on Winsor & Newton Finity TiO₂ 7 year old paint-out for 1 to 3 minutes. Images were obtained with a Leica DMRX optical microscope equipped with a Canon EOS camera using Canon EOS utility software. Images of the fluorescent gels and paint cross-sections were obtained using the I3 (BP 450-490, LP 590) and M2 (BP 546/14, LP 590) filter cubes.
Experiments on the penetration of gelated and non-gelated liquids orthogonal to painted surfaces were performed using the following four samples: (1) a gel from 5 wt % 75PVAc and 1 wt % borax with 24/76 acetone/water liquid containing 0.9 mM fluorescein placed on the surface for 3 minutes and removed via spatula, (2) the same gel, placed on the surface for 3 minutes, removed via spatula and cleared with 2/1 acetone/mineral spirits, (3) a liquid of 24/76 acetone/water composition, containing 0.9 mM fluorescein rolled over the surface with a cotton swab for 1 minute, and (4) a 1/1/1 acetone/2-propanol/mineral spirits liquid mixture containing 0.9 mM fluorescein, rubbed on the surface via swab for 1 minute. Cross-sections were obtained from the middle of each test site. Imaging of the cross-sections was performed on the same Leica DMRX microscope described above as well as on a Craic Technologies microspectrophotometer using both mercury and xenon lamps. Deconvolution of the emission spectra was performed using OriginPro version 8.6 software.

A Nexus 670 Spectra-Tech Continuum IR microscope/FT-IR spectrometer system was used to collect infrared spectra in the 4000 to 650 cm$^{-1}$ range with 4 cm$^{-1}$ resolution. Samples were mounted between diamond compression plates and experiments were performed at room temperature.

Cross-sections were prepared in BioPlastic (Ward). Water sensitive cross-sections were polished on dry Micro-mesh polishing cloths with grit in the range of 6000-12000. Macrographs of paint surfaces were obtained using a Leica (Wild) MZ 12.5 stereomicroscope equipped with a Q-imaging micropublisher camera at the National Gallery of Art and a HiroxKH-7700 digital microscope with image capture at the Smithsonian American Art Museum.
The three gels used for treatment of *The Fisherman’s Return* by Henry Ossawa Tanner (1917, reworked 1919) were placed into glass vials with 1 mL of ethanol and stirred until dissolution. The mixture was filtered through a 0.2 μm PTFE syringe filter and the filter was washed twice with 1 mL aliquots of pure ethanol. Alternatively, portions of the gel were placed in a glass vial and small amount of sodium hydroxide was added, causing the gels to separate into a two phase system. The liquid expelled was collected after 24 hours. The samples were concentrated and spotted onto a glass slide. After complete evaporation of the solvent, scrapings of each sample were placed into the pyrolysis pan and 2 μL of tetramethylammonium hydroxide (TMAH) were added. Samples were injected at 600 °C by a single shot method with a Frontier labs pyrolyzer; a Varian 3800 GC and Saturn 2000 GC/MS/MS system was used in EI mode with a 45-600 m/z range. A 30 m x 0.25 mm ZB5GC column was used. Three used swabs to remove softened varnish after the gel treatment were placed in vials with ethanol and vigorously stirred at 40-50 °C. The ethanol was then filtered through 0.2 μm PTFE syringe filters and the filters were washed with two more aliquots of ethanol. These samples were then processed in the same manner as the gel samples. Scrapings from the glass slides were placed between diamond transmission plates and analyzed using FTIR.

Analysis of the coating from *Multiple Views* by Stuart Davis (1918) was partially performed by Dr. Christopher Maines. For fatty acid analysis, the samples were hydrolyzed and methylated using 10 μL of trimethyl(a,a,a-trifluoro-m-tolyl)ammonium hydroxide (TMTFTTH, TCI America, 0.5M in MeOH) and incubated overnight. For protein analysis, a nucleucine solution was added to yield a final concentration of approximately 50 ppm in the final injection volume. Hydrochloric acid (50 mL, 6.0 N) was added to the vial and the sample was evacuated
using a vacuum pump. The sample was heated at 105°C for 24 hours on a heating block and allowed to cool slowly. The vial is then centrifuged, and the supernatant evaporated using a nitrogen stream while warming to 60°C. Silylating reagent (1 mL) containing MTBSTFA/TBDMCS was added per 2 mg of sample. Samples for pyrolysis were prepared as described above. Data analysis was performed on all samples using the Saturn GC/MS Workstation 6.9.2 software and the NIST 2008 spectral libraries.

6.3. Polymer residue studies.

Polymer residues left on the surface of a treated artwork after cleaning with xPVAc-borax gels were investigated by fluorescence spectroscopy. Fluorescein was covalently attached to 40PVAc, 75PVAc, 80PVAc_3, and PVA. To limit the effect of dye substitution on the properties of the gel, the amount of hydroxyl groups substituted with fluorescein was very small (< 0.01%, see Section 6.3.2). The resultant fluorescent gels were tested on an acrylic test panel and were used in two case studies described in Section 6.4. Residual polymer was not detected on the surface of the treated paintings. The detection limit of the instrument for the polymers was calculated to be < 1.5 μg of polymer per 3 mm² (Section 6.3.3).


Fluorescein was chosen as a marker for the polymer residue studies for its high quantum efficiency (Φ = 0.93 for the dianion species, vide infra)\textsuperscript{160} and stability, and because the dye has been studied extensively in PVA solutions,\textsuperscript{161,162} and hydrogels.\textsuperscript{161,163} Dibbern-Brunelli and
Atvars used fluorescein to monitor the thermal transitions of poly(vinyl alcohol) hydrogels (produced through a freeze-thaw method), showing the stability of fluorescein in a system similar to xPVAc-borax gels.\textsuperscript{163} Fluorescein was covalently bonded to the polymer chains for residue analysis. The dye was also incorporated into the liquid component of the gels in order to elucidate the structure and fluorescence properties of the dye in the presence of borax and organic liquids.

Fluorescein is known to have six different forms.\textsuperscript{163} The one which dominates is dependent on the pH of the aqueous solution or the nature of the solvent in which the dye is dissolved (Figure 6-2).\textsuperscript{163}

![Fluorescein Diagram](image reproduced by the author)

Figure 6-2. The six forms of fluorescein: (a) cation; (b) quinonoid; (c) lactone; (d) zwitterion; (e) monoanion; (f) dianion. The absorption and emission wavelengths for each species in dilute aqueous solution are noted in the Figure (image reproduced by the author).\textsuperscript{163}
Studies of the fluorescence properties of the dye were performed in solutions with different ratios of 1-propanol/water, in a pH range of 5 to 6, and in the presence of borax, as well as in gels prepared from 40PVAc, 45PVAc, 75PVAc, 80PAVc_3, and PVA. Uv-vis absorption studies of fluorescein in mixtures of 1-propanol/water at a pH of 5 show peaks due to the monoanion and neutral species, as well as a shoulder at ~ 430 nm from the cationic form of fluorescein.\textsuperscript{164} As the pH is raised to 6, the cationic species is no longer detectable. With the addition of borax, the pH increases to ~ 9, and only the dianion absorbance with a $\lambda_{\text{max}}$ ~ 490 nm and a shoulder at ~ 475 nm is present in the spectrum (Figure 6-3).\textsuperscript{164} A bathochromic shift is observed in the absorption spectrum of the di-anion when the 1-propanol concentration is increased, as would be expected as a consequence of the decrease in solvent polarity.

![Absorbance spectrum of fluorescein in different 1-propanol/water mixtures](image)

Figure 6-3. UV-vis absorption spectra of 2.4 nM fluorescein in 30/70 1-propanol/water ($\lambda_{\text{max}}$ = 496 nm), 50/50 1-propanol/water ($\lambda_{\text{max}}$ = 497 nm), and 75/25 1-propanol/water ($\lambda_{\text{max}}$ = 498 nm).

When fluorescein is incorporated into the liquid portion of xPVAc-borax gels, the spectrum of the dye indicates the presence of the dianion form. The pH of the gels is in the range of 8.1 to 8.5. In hydrogels prepared from 75PVAc, 80PVAc_3, and PVA, $\lambda_{\text{abs}} = 492$ nm and
shifts to 496 nm when the liquid in the gels is changed to 30/70 1-propanol/water. Increasing the amount of organic liquid in the gels to 50/50 1-propanol/water and 80/20 1-propanol/water shifts the λ_{abs} further to 497 nm and 500 nm, respectively (Figure 6-4). Excitation and emission spectra of xPVAc-borax gels without added fluorescein show that gels do not absorb or emit in the region of fluorescein absorption and emission. The excitation and emission spectra of the fluorescein incorporated into the gels correspond to the dianion species, with emission centered ~520 nm. Gels prepared with large fractions of 1-propanol contain some fluorescein in the monoanion and neutral forms - their excitation spectra contain a strong signal at ~475 nm.

Figure 6-4. UV-vis absorption spectra of 0.5 nM fluorescein in (A) 30/70 1-propanol/water gels prepared with 6 wt % polymer and 0.7 wt % borax from PVA (■), 80PVAc_3 (■), 75PVAc (■), 45PVAc (■), and 40PVA(■); and (B) in a gels from 6 wt % 75PVAc and 0.7 wt % borax with 0/100 1-propanol/water (■) and 50/50 1-propanol/water (■), and gels from 14 wt % 40PVAc and 1.3 wt borax in 30/70 1-propanol/water (■) and 80/20 1-propanol/water (■).

The presence of the polymer or borax in aqueous and aquo-organic liquid mixtures does not seem to affect greatly the excitation and emission properties of fluorescein. Because typically
the pH of the gels is above 7.5, the dye tends to be doubly deprotonated and emits strongly around 520 nm. Gels prepared with a large proportion of organic liquid have an environment which favors the formation of some monoionic or quininoid forms of fluorescein, both of which absorb and emit at 476 nm and 515 nm, respectively. From these studies, it was concluded that fluorescein is an appropriate dye to attach covalently to the polymer chains.

6.3.2. Covalent attachment of fluorescein to xPVAc.

Attachment of fluorescein to PVA was achieved by activation of the hydroxyl group of the dye with an epoxy group. Epichlorohydrin was chosen for the reaction which proceeds through an S\textsubscript{N}2 mechanism in which the chloride is displaced by the deprotonated hydroxyl group on the dye (Scheme 6-1).\textsuperscript{160} The product of the reaction is 3-epoxypropoxyfluorescein (EPF).\textsuperscript{160} According to Guan et al., EPF has a quantum efficiency of 0.28, although the authors do not report for which form of EPF the value was measured.\textsuperscript{160} The reduced quantum efficiency is attributed to the inability of the dye to assume the dianion form, which has the highest quantum efficiency.\textsuperscript{164} Consequently, EPF is expected to have an absorption closer to 476 nm than 496 nm.

Scheme 6-1. Preparation of 3-epoxypropoxyfluorescein (EPF) from fluorescein and epichlorohydrin.
The UV-vis absorption spectrum of the product in methanol has a peak at 490 nm (Figure 6-5), suggesting that residual fluorescein is present in the column-purified product. Attempts at further purification resulted in the loss of the epoxy functional group on EPF. As the residual fluorescein is considered unreactive in the polymer functionalization reaction, the impure product was used without further treatment.

![UV-vis absorbance spectra of EPF in methanol](image)

Figure 6-5. UV-vis absorbance spectra of EPF in methanol.

The reaction scheme for covalent attachment of EPF to PVA is depicted in Scheme 6-2. EPF was attached to 40PVAc, 75PVAc, 80PVAc_3, and PVA. The products are referred to as 40PVAc-EPF, 75PVAc-EPF, 80PVAc_3-EPF, and PVA-EPF from here on. To confirm that the dye was covalently attached to the polymers and that free fluorescein or EPF were absent in the products, a portion of each polymer was placed in acetone or methanol, chosen so that the dye would be soluble but the polymer would be insoluble for 48 hours. The emission spectra of the liquids in which the fluorescein-tagged polymers were washed were obtained. The characteristic absorbance or emission peaks of the dye was not measurable (Figure 6-6).
Scheme 6-2. Preparation of xPVAc-EPF from EPF and xPVAc.

Figure 6-6. UV-Vis absorption (left) and emission (right) spectra of acetone in which 1 wt % of 80PVAc_3-EPF (■), 75PVAc-EPF ( ), and PVA-EPF ( ) were stirred for 48 hours (1 cm glass cuvette, λ<sub>ex</sub> = 470 nm).

Uv-vis absorption of the EPF-derivatized polymers show a λ<sub>abs</sub> = 460 nm, corresponding more closely with the absorbance of the monoanion and quininoid species than with the dianion species. The spectrum also shows a shoulder at ~490 nm. The profile of the absorption spectrum
is very similar to that of the monoanion species which shows peaks with approximately the same molar absorptivity at 453 nm and 472 nm.\textsuperscript{165} It has been shown that unattached fluorescein is not present in the polymers. Therefore, it is possible that by attaching fluorescein to PVA, the new fluorescent species has a absorbance peaks that are similar to those of the free monoanion, but occurring at longer wavelengths. Emission spectra of gels prepared from each polymer in 30/70 1-propanol/water show emission maxima at ~520 nm with a shoulder above 550 nm which can increase in intensity if the substitution of EPF on the chains is increased. The results suggest that some aggregation of the fluorescein species on the polymer chains is occurring. It is possible that the dye molecules are not distributed completely randomly on the chains.

Figure 6-7. UV-vis absorption (left) and excitation and emission (right) spectra of 30/70 1-propanol/water gels prepared from 4 wt% PVA-EPF and 1.1 wt% borax (■); 4 wt% 80PVAc_3-EPF and 1 wt% borax (□), 6 wt% 75PVAc-EPF and 1.4 wt% borax (■); and 11 wt% 40PVAc-EPF and 2 wt% borax (▲).

To calculate the number of hydroxyl groups on the polymers substituted with EPF, the molar extinction coefficient of 3-\textit{O}-methylfluorescein was used (Figure 6-8). The dye,
commonly used in biological systems, has a methoxy group in place of the hydroxyl group on the fused benzene moiety of fluorescein. Because the dianion form is prevented from forming in 3-\textit{O}-methylflourscein, the molar extinction coefficient should be similar to that of epoxy-prooxy-fluorescein (EPF).

![Structure of 3-\textit{O}-methylfluorescein](image)

Figure 6-8. Structure of 3-\textit{O}-methylfluorescein.

Using the extinction coefficient of 3-\textit{O}-methylfluorescein, $26000 \text{ M}^{-1} \text{ cm}^{-1}$ at pH 7 and 470 nm, the percent molar substitution of the dye was back calculated from the absorption spectrum of each polymer dissolved in distilled deionized water at pH 7. The amount of fluorescein substitution was found to be less than 0.01\% of OH monomers for each of the four polymers (Table 6-2). A sample calculation for obtaining the mol \% substitution of EPF in 40PVAc is shown below where $\varepsilon = 26000 \text{ M}^{-1} \text{ cm}^{-1}$, $b = 1 \text{ cm}$, and $A = 0.0721$ in the UV-vis spectrum of 0.0104 g of 40PVAc-EPF dissolved in 1.9899 mL of H$_2$O.

\[
\frac{0.0104 \text{ g PVA}}{44 \frac{g}{\text{mol OH}} (0.46) + 86 \frac{g}{\text{mol Ac}} (0.54)} = 1.56 \times 10^{-4} \times (0.46) = 7.17 \times 10^{-5} \text{ mol OH groups} \quad (6-1)
\]

\[
\frac{7.17 \times 10^{-5} \text{ mol OH monomer}}{1.9899 \times 10^{-3} \text{ L}} = 0.036 \text{ M OH monomer} \quad (6-2)
\]

\[
c = \frac{A}{\varepsilon b} = \frac{0.0721}{26000 \text{ M}^{-1} \text{ cm}^{-1} \times 1 \text{ cm}} = 2.77 \times 10^{-6} \text{ M EPF} \quad (6-3)
\]

\[
\frac{2.77 \times 10^{-6} \text{ M}}{0.036 \text{ M}} \times 100 = 0.0077\% \text{ of OH monomers are substituted} \quad (6-4)
\]
Table 6-2. Percent of hydroxyl monomers substituted with fluorescein calculated from UV-vis absorption spectra of each polymer in distilled deionized water at pH 7.

<table>
<thead>
<tr>
<th>Polymer Hydrolysis (%)</th>
<th>Hydroxyl Monomers Substituted with Fluorescein (%)</th>
<th>% of all Monomers Substituted with Fluorescein</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>80</td>
<td>0.003</td>
<td>0.002</td>
</tr>
<tr>
<td>75</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>40</td>
<td>0.008</td>
<td>0.004</td>
</tr>
</tbody>
</table>

A series of gels prepared using EPF-substituted polymers and varying proportions of methanol was studied by rheology to assess whether attaching the dye to the polymer had an effect on the elasticity of the gels. The xPVAc-EPF-borax gels were compared to similar PVAc-borax gels in which the dye was dissolved in the liquid portion. The frequencies at which $G'$ and $G''$ cross over in both sets of gels become lower with increasing methanol concentration. This behavior is the same as that described for xPVAc-borax gels in Chapter 4. There is good agreement between the frequency at which the cross-over occurs for both the gels with fluorescein in the liquid portion and the gels with fluorescein attached to the xPVAc chains. The experimental evidence suggests that substitution of EPF on the polymer chains does not affect the physical properties of the materials to a significant degree. The highly fluorescent xPVAc-
borax gels were used on an acrylic painting to determine the amount of residual polymer on the surface after cleaning.

![Angular frequency sweeps showing G' (■) and G" (●) of gels prepared with 0/100 methanol/water (■), 30/50 methanol/water (■), and 50/50 methanol/water (■) from 6 wt % 75PVAc (left) or 6 wt % 75PVAc-EPF (right) and 1.4 wt % borax (or 1.2 wt % borax when the liquid was 50/50 methanol/water. Experiments performed in the linear viscoelastic region with strain = 1%.

Figure 6-9. Angular frequency sweeps showing G’ (■) and G” (●) of gels prepared with 0/100 methanol/water (■), 30/50 methanol/water (■), and 50/50 methanol/water (■) from 6 wt % 75PVAc (left) or 6 wt % 75PVAc-EPF (right) and 1.4 wt % borax (or 1.2 wt % borax when the liquid was 50/50 methanol/water. Experiments performed in the linear viscoelastic region with strain = 1%.

6.3.3. Polymer residue detection on an acrylic test panel.

Gels were prepared with xPVAc-EPF for initial tests on a sample acrylic painting, *Untitled*, by Michael Dotson (Figure 6-10). The unfinished artwork was covered in grime and organic waste because it had been used in the place of a lid on a kitchen waste bin for approximately 6 months. A 30/70 methanol/water gel was prepared using fluorescein-tagged 75PVAc (6 wt %) and 1 wt % borax. An excitation-emission profile was collected of the acrylic ground or paint prior to treatment. Then the gel was placed over an area approximately 1 cm in
diameter and allowed to remain in contact for 13 minutes, the time required to collect the excitation-emission profile of the gel on the surface. The gel was removed simply by lifting from the surface with a spatula—the inset of Figure 6-10 shows this process—and the excitation-emission profile of the same area on the surface was immediately recorded.

Figure 6-11 shows the three spectra obtained during this test as well as the compressed 2D images. Although there is a change in the intensity of the excitation and emission spectra of the surface after the gel treatment (probably due to inability to interrogate exactly the same surface area), the actual profile has not changed. This result, which is in agreement with four other tests performed on this painting (results not shown), suggests that no detectable polymeric residue is present on the acrylic painting as a result of gel application for a significant amount of time.
Figure 6-10. Michael Dotson, *Untitled*, 2008. Acrylic on canvas, 51 x 41 cm. Unfinished acrylic painting on which xPVAc-EPF residue studies were performed. The red square shows the area tested in Figure 6-11; the inset shows removal of an applied gel by lifting it with tweezers.

Figure 6-11. Excitation-emission plots of the acrylic ground of the painting defined by the red square in Figure 6-10 (A), of the gel on the surface (B), and of the surface immediately after gel removal without any clearing (C). The z-axis indicates the intensity (a.u.) with red indicating the highest intensity and blue indicating the lowest. D shows the excitation (dotted lines) and
emission (solid lines) profiles of the surface before treatment (■), with the gel during treatment (■), and after gel removal (■) obtained as a ‘slice’ from the 3-D spectra using data from \( \lambda_{\text{ex}} = 470 \text{ nm} \) and \( \lambda_{\text{em}} = 520 \text{ nm} \).

The detection limit for each polymer, back-calculated for the instrument using a gradient of fluorescein solutions dropped on an acrylic test strip, is less than 0.5 μg per 3 mm\(^2\) area (Figure 6-12 and calculations below). Aliquots of solution of aqueous fluorescein were pipetted onto an acrylic paint test surface and spectra were collected immediately. The emission spectrum of the acrylic paint was obtained both dry (i.e., directly) and “wet” – with 5 μL of distilled deionized water on the surface - as a control for any distortions in the emission spectra caused by the presence of the small droplet of fluorescent liquid on the surface. As can be seen in Figure 6-12, both the wet and dry blank surface emissions show the same profile, with the wet sample having a slightly lower intensity.
Figure 6-12. Gradient of aqueous fluorescein on acrylic paint out used for detection limit experiments (top) and emission spectra of fluorescein concentration gradient. The gradient starts with a concentration of $3.006 \times 10^{-4}$ M fluorescein and decreases by 25% in each subsequent sample; inset is a magnification of the emission spectra from aliquots with the lowest fluorescein concentrations, and the wet and dry paint blanks. A calibration curve is shown with $R^2 = 0.992$;
the aliquot with the lowest fluorescein concentration which still shows the characteristic emission with $\lambda_{\text{max, em}} = 515$ nm has a concentration of $4.026 \times 10^{-8}$ M (Table 6-1).

Using the lowest fluorescein concentration which still shows the characteristic emission of the dye, $4.026 \times 10^{-8}$ M (Table 6-1) and the known amount of hydroxyl groups substituted with EPF on each polymer (Table 6-2), the minimum amount of polymer residue detectable on the acrylic surface can be calculated (Equations 6-5 through 6-7 below). Assuming that the quantum efficiency of the covalently bound fluorescein is 0.28, as reported by Guan et al., which is approximately 1/3 of the quantum efficiency of the dianion species detected in these experiments, the minimum amount of polymer which can be detected by this method is three times larger than calculated. With the instrument used, 1.32 µg of PVA-EPF, 1.05 µg of 80PVAc_3-EPF, 1.44 µg of 75PVAc-EPF and 0.57 µg of 40PVAc-EPF can be detected on an unvarnished, fresh acrylic surface.

\[
\frac{4.026 \times 10^{-8} \text{ mol FL}}{1 \text{ L}} \times \frac{1 \text{ L}}{1 \times 10^6 \mu \text{L}} \times \frac{5.0 \mu \text{L}}{1} \times \frac{1 \text{ mol EPF}}{1 \text{ mol FL}} \times \frac{389 \text{ g EPF}}{1 \text{ mol EPF}} = \]

\[
7.8 \times 10^{-11} \text{ g fluorescein or } 2.0 \times 10^{-13} \text{ or mol EPF} \quad (6-5)
\]

\[
\frac{X g \text{ PVA}}{44 g/mol} \times 0.00002 = 2.0 \times 10^{-13} \text{ mol EPF} \quad (6-6)
\]

\[
X = 4.4 \times 10^{-7} \text{ g PVA} = 0.44 \mu \text{g PVA – EPF} \times 3 = 1.32 \mu \text{g PVA – EPF} \quad (6-7)
\]
6.4. **Residues of boron-containing species.**

Investigation of borate residues on gel-treated surfaces was conducted by quantitative inductively coupled plasma mass spectrometry (ICP-MS) on test paint outs. Sample introduction to the instrument could only be achieved by a nebulizing gas rather than by laser ablation, preventing direct analysis of the treated surfaces for change in boron concentration. Instead, the boron-containing species present on acrylic and dammar paint-outs were quantified by exposing the surfaces to milli-Q purified water prior to and after a 3 minute xPVAc-borax application with and without swab clearance. The water aliquots were then introduced to the instrument. Detailed description of the experimental set-up can be found in the methods and materials section.

Tests were carried out on a 3 year old acrylic paint out and a 25 year old dammar paint out. The gel used, composed of 5 wt % 75PVAc and 1 wt % borax with a liquid content of 30/70 2-propanol/water softened the dammar coating within the 3 minute application time. Exposure and dissolution of the softened dammar into the water aliquot to be analyzed by ICP-MS resulted a significant increase in the boron species detected (Figure 6-13). Removal of the softened dammar by a 20 second clearance with a swab dipped in the same liquid mixture as that in the gel, resulted in a reduction of surface boron species to nearly pre-gel treatment levels.
Figure 6-13. Concentration of boron-containing species obtained by quantitative-ICP-MS from an acrylic paint-out (left) or a dammar paint-out (right) treated with a 30/70 2-propanol/water gel (5 wt % 75PVAc and 1 wt % borax) for 3 minutes without a swab clearing of the surface (“Post Gel”) and with a swab pass (“Post Gel/Swab”). “Millipore Blank” samples represent milli-Q purified water tested between samples showing that boron is present to the same extent as on the paint-out surface before gel treatment, “Surface Blank”.

Results from $^{11}$B NMR spectroscopy experiments show that more than half of the boron-species in xPVAc-borax does not participate in crosslinks (Chapter 4). Consequently, a fraction of free boron species can migrate with the liquid encapsulated by the gel network. During treatment of surfaces which can be solubilized by the gelated solvent, the free boron species travel with the solvent into the softened coating. As long as the softened material is removed completely by a swab, boron species should not remain on the surface after treatment. On surfaces that are not softened by the gelated liquids or do not absorb large fractions of the liquid through capillary forces, boron-containing residues are not apparent. Similar results are expected with other cleaning agents, such as citrate, EDTA, solvents (which can also volatilize from the
surface), and surfactants, regardless of their being used in a gel or as part of aqueous solutions. The use of xPVAc-borax gels with higher organic fractions may decrease the boron species residue because $^{11}$B NMR spectroscopy results show that in such systems, larger numbers of the borates participate in crosslinks. The same is true of very basic systems. Unfortunately, such gels are often too stiff or too aggressive, respectively, for use in conservation treatments.

6.5. Lateral and orthogonal spread of gelated liquid.

The ability of the xPVAc-borax gels to deliver the solvent to the surface in a confined area was explored on acrylic paint. Solvent spread beyond the gel boundary was shown to be minimal using gels prepared with 0.02 mM rhodamine B in the liquid portion (not covalently linked to the polymer). The gels were placed on a 7 year-old Winsor & Newton Finity titanium dioxide paint-out. The boundary between the gel and the untreated surface of the paint film was examined by fluorescence microscopy. A green filter cube (M2) was used because, under these conditions, the rhodamine in the gel fluoresces while the paint does not. It can be seen that a detectable amount of the dye dissolved in the liquid portion of the gel diffused into the paint film, and it can be detected after the gel was lifted from the surface (Figure 6-14). The gels were placed on the acrylic paint surface for 1-3 minutes, removed with a spatula, and the surface was not cleared with a swab. Images were obtained immediately after gel removal: on the micrometer scale, there is no visible solvent spread beyond the gels on sample acrylic paint surfaces (Figure 6-14).

These experiments have been performed with a series of gels with varying amounts of acetone (30/70, 50/50, and 70/30 acetone/water) as well as with gels prepared with polymers of
differing hydrolysis degrees but constant solvent composition. The results in each study show that the solvent penetrated the surface of the paint directly beneath the gel without lateral spread unless the gel was moved to another location during the removal process. Visual observations of the areas cleaned on *Multiple Views* by Stuart Davis (Section 6.6.1.), *The Fisherman’s Return* by Henry Ossawa Tanner (Section 6.6.2), and a shellac-varnished frame (Section 6.6.3) show very good confinement of cleaning action.

Figure 6-14. Gel prepared with a solution of rhodamine on top of Winsor & Newton Finity white paint under daylight (A), the paint surface using a green M2 filter cube (B), the gel-paint boundary under the green M2 filter cube (shutter speed 0.4 second) (C), and the surface of the
paint after gel removal without the use of additional solvents or swabbing, (1.6 second shutter speed) (D). Please disregard the black scale label in C and D, the yellow scale bar = 100 μm.

Liquids delivered to the surface of artworks during a cleaning treatment should, ideally, be confined only to the uppermost surface layer. Penetration of the liquid into the paint layers beneath may result in leaching of paint film components which may accelerate the degradation of the artwork.166,167 One proposed advantage of using gelated liquids for conservation treatments is the reduced penetration of the solvent into the paint layers.29 Although the solvent in gels seems to have a greatly reduced diffusion on the macroscopic scale, the majority of solvent molecules are free to diffuse normally at the microscopic level. It is, therefore, important to test if xPVAc-borax gels diminish solvent penetration into the surface layers relative to using a free solvent delivered with a swab.

To explore the migration of liquid from xPVAc-borax gels into an oil paint film, fluorescein was incorporated into the liquid component of gels used to treat the surface of an oil test painting. The age of the artwork is unknown, but is likely to have been painted during the 19th century. Cross-sections were obtained from areas treated with a gel and from areas treated by cleaning with a swab only. Analyses of cross-sections obtained from the painting revealed a layer of shellac varnish on top of the original paint film, a layer of overpaint followed by a second natural varnish layer which was dry and oxidized. Examination of the surface under UV light showed that the entire surface had been re-varnished with a synthetic resin (Figure 6-15).
Figure 6-15. Top corner of test oil painting used in solvent diffusion tests under visible light (left) and under UV light (right).

The experimental set-up and the locations treated and sampled for cross-sections are shown in Figure 6-16. Because the aqueous-based 75PVAc/borax gel was not capable of solubilizing the relatively fresh synthetic varnish, the surface was first swab-cleaned with toluene. Four experiments were performed: (1) a fluorescein-containing ~ 25/75 acetone/water gel was placed on the surface for three minutes and removed without clearing with a swab, (2) a ~ 25/75 acetone/water fluorescein-containing gel was placed on the surface for three minutes; after three minutes the gel was removed and the area was cleared with a 2/1 mixture of acetone/mineral spirits chosen by the conservator, (3) the area was cleaned with a swab dipped in 25/75 acetone/water for one minute, and (4) the area was cleaned with a swab dipped in a standard solvent for an overpainted, aged painting – 1/1/1 acetone/2-propanol/mineral spirits for one minute.
Figure 6-16. (A) A gel prepared with fluorescein (0.9 mM) from 5 wt % 75PVAc and 1 wt % borax gel with liquid composition of 24/76 acetone/water on the surface, covered with mylar; (B) conservator clearing an area with 1/1/1 acetone/2-propanol/mineral spirits for one minute; (C)
finished test surface; (D) cleaning test sites labeled as described. Cross-sections were obtained from each area.

Application of 25/75 acetone/water by swab for 1 minute caused the complete dissolution and removal of the oxidized layer of natural varnish. In contrast, application of the same liquid in a 75PVAc-borax gel for 3 minutes caused the surface to blanch and softened only the topmost layer of the varnish. To remove the oxidized varnish layer, a second or third gel application or a longer exposure would be necessary. On this surface, the 75PVAc-borax gel seems to retard the cleaning action of the liquid. Cross-sections from area 1 and 3 (gel treatment without a clearance with a swab and swab treatment only, respectively), do not show fluorescein emission (Figure 6-17).

Figure 6-17. (A) Cross-section from area 1 in Figure 6-16, where fluorescent gel was applied but not cleared with a swab (20 x magnification). When viewed with a blue filter cube, I3 (B),
autofluorescence is present, but no fluorescein layer is visible. (C) Cross section from area 3 in Figure 6-16 where swab cleaning with 24/76 acetone/water liquid and 0.9 mM fluorescein was carried out viewed under visible light (C, magnification 10 x), and viewed through blue filter cube, I3, (D, magnification 20 x), showing autofluorescence but no fluorescein layer.

Because there is a possibility that fluorescein delivered to the paint layer via the gel or swab was washed away during the wet work-up of the cross-sections, a second set of cross-sections were obtained and prepared using a dry method. One cross-section was obtained from an area on the painting that had been treated with a ~25/75 acetone/water gel containing fluorescein and had visible gel residue remaining on the surface. A second cross-section was obtained from a test site that was cleaned with a swab dipped in 25/75 acetone/water and fluorescein. The fluorescein-doped 75PVAc-borax gel is clearly visible on the surface of the cross-section (Figure 6-18-A). Fluorescein was not visible in the paint layers of the cross-section cleaned with a swab.
Figure 6-18. (A) Cross-section from area treated with fluorescein doped 25/75 acetone/water gel prepared from 5 wt % 75PVAc and 1 wt % borax, with dry gel clearly fluorescing on surface and visible layer of varnish beneath the overpaint; (B) cross-section from area swab-treated with fluorescein doped 25/75 acetone/water with layer of varnish visible beneath overpaint. Both cross-sections are shown viewed through an I3 blue filter cube and a D filter cube.

Visible in the cross-section obtained from the area treated with a swab in Figure 6-18 are a thick priming layer, an original pigment layer, a faintly fluorescing varnish, and an overpaint layer. Emission spectra of the varnish in the cross-section of area cleaned with a swab and of the dried 75PVAc-borax gel residue from the gel-treated cross-section were obtained by fluorescence microscopy (Figure 6-19). Although the two spectra are similar, the gel has an emission maximum at 521 nm, while the varnish layer has an emission maximum at 510 nm. The
emission peaks have been deconvoluted. The fluorescein emission seems to suggest the presence of dimers and trimers. The varnish emission is far more complex due the presence of multiple unknown and aged components. There is no overlap between the deconvoluted peaks of the gel residue and those of the varnish layer. If solvent carrying fluorescein has migrated into the varnish layer during the swab cleaning, the observed emission signals may be due to the new environment surrounding the dye.

Figure 6-19. (A) Fluorescence of varnish beneath overpaint (■) and of the dried 75PVAc-borax gel on surface of cross-section (□) from the two different cross-sections shown in Figure 6-18.
obtained using a 436 nm cube by fluorescence microscopy. The two emission signals are
deconvoluted using Origin 8.5 software in B and C with good agreement between the predicted
and real spectra.

It is difficult to draw conclusions regarding liquid diffusion into the paint layers from
these experiments. The hindered ability of the same liquid mixture, 25/75 acetone/water, to
dissolve the oxidized varnish when gelated in an xPVAc-borax network would suggest that
solvent penetration is diminished relative to the use of the non-gelated liquid delivered with a
swab. The fluorescence tests show inconclusive results but may suggest that the solvent did not
penetrate beneath the overpaint layer in either cleaning protocol. As will be described in Section
6.6.1, use of xPVAc-borax gels on a different aged, complex coating allowed for a more
successful and faster treatment than use of the same non-gelated liquid mixture. Therefore,
depending on the composition and age of the material being removed, xPVAc-borax gels may
deliver the gelated liquid more or less effectively than a swab.


The detailed investigation of xPVAc-borax gels during several cleaning trials on test
panels and frame fragments showed that the materials have desirable qualities such as efficacy
and removability, therefore, they are appropriate for use in case studies. Through the initial
testing stages of the materials, it was shown that the range of liquids incorporable into the
network can be extended greatly while maintaining the physical properties of the gels intact. The
ability of the system to limit the cleaning action to an area defined by the gel, the ease of
application and conformation to the surface topography, and the simplicity of the removal
process, combined with the lack of detectable residues, make xPVAc-gels an appropriate tool for some treatment applications.

As will be discussed in the following sections, the gels were effective in softening several complex coatings and, allowed the conservator to remove the materials with a swab dipped in a milder solvent than would have been necessary without the gel treatment. Analyses of the gels and swabs used in one of these case studies suggest that the gels act primarily by delivering solvent to the surface, and that little surface material seems to be absorbed back into the network. It is important to note that depending on the nature of the coating and the gel application time, xPVAc-borax gels used in some treatments may have the capacity to uptake more materials from the surface than was observed in the studies described below.

Use of the gels on a frame with gold leaf for the removal of a shellac coating reduced the need for swabbing the surface and, therefore, the possibility of abrading the gold leaf. The ability of the gels to conform to shapes proved useful to treat crevices and curved features on carved frames. The confined cleaning action was appropriate for these applications. However, during some cleaning trials conducted with xPVAc-borax gels, the hard edge present between the cleaned and untreated areas was found to be too crisp by the conservator. Recently, the xPVAc-borax gel system was found suitable for the treatment of a boulle marquetry object precisely because the gels could be shaped to fit the brass metal inlays. Several other applications of xPVAc-borax gels in conservation treatments are described in the following sections which include both successful and unsuccessful treatment attempts.
6.6.1. **Stuart Davis, Multiple Views (1918).**

Figure 6-20. *Multiple Views* by Stuart Davis, 1918, oil on canvas, 120 x 89.5 cm at the National Gallery of Art in Washington, D.C. viewed under daylight (left) and UV light (right) Art © Estate of Stuart Davis/Licensed by VAGA, New York, NY.

*Multiple Views* (Figure 6-20) was acquired by the NGA in 2008. This early work is very different from Davis’s jazz-influenced proto pop-art paintings and was created during his time at the Whitney Club Studio in New York City. Davis exhibited *Multiple Views* at the “Exhibition of Indigenous Painting” in 1918, a small show that initially began as a contest held by the creator of the studio, Mrs. Gertrude Vanderbilt Whitney. In Davis’ own words,

“Club members were invited into the two galleries and confronted with blank canvases of varying sizes that hung on the walls. A table in the center of the room was filled with paints and brushes, whiskey bottles, cigars, and cigarettes. The artists had three days to
paint a picture in that atmosphere of drinking and conviviality during which a tipsy George Luks threatened to overpaint everyone’s canvases.”

One stipulation of the contest was that the artists were not allowed to use visual aids of any kind; Davis relied on his memory, recreating a series of images that he had painted in Gloucester, Massachusetts the previous year.

Examination revealed that the painting had gone through an extensive restoration campaign before arriving at the NGA. It had been inexpertly lined, evidenced by the excessive amount of wax (contaminated by animal hair) along the tacking margins. In addition to a complex coating layer consisting of a mixture of varnish, dirt and other components (vide infra), wax was detected on the surface of the painting along all four edges. Cross-sections revealed that this wax layer was as thick as the paint and ground layers combined in some regions of the painting. Figure 6-22-A shows a detail from the house in the lower right quadrant illustrating the poor appearance of the surface.

Examination of cross-sections revealed that wax was present on top of the complex coating system which is visible in some of the cross-sections but completely absent in others. This suggests that the painting may have been partially cleaned previously. Ultraviolet illumination was not helpful in characterizing the nature of the coating. Samples of the coating were analyzed using gas chromatography/mass spectrometry (GC/MS) and a substantial amount of fatty acids, as well as a natural triterpenoid resin such as dammar, were detected. Although most samples were found to contain only oil and resin, one sample seemed to contain polysaccharides and protein-containing materials. It is likely that these materials were remnants from a facing applied during lining or local consolidation (Figure 6-21).
Figure 6-21. GC chromatograms of scrapings from the coating on *Multiple Views* by Stuart Davis (1918), showing the presence of drying oil residues, dammar resin, amino acid residues from proteins, and sugars as well as a small amount of nicotine.

The complex make-up of the surface coating called for a complex systematic cleaning treatment protocol. The Modular Cleaning Program was employed to aid in experimenting with a wide range of cleaning solvents and systems. Testing suggested the need for a multi-step cleaning process in order to remove all of the disparate components. The layer of wax was removed first using a combination of xylene and mineral spirits. Combinations of free solvents (e.g., acetone, mineral spirits, alcohols, and toluene) proved ineffective at removing the coating exposed on removal of the wax. A two-step approach of using free solvents as described above, followed by the application of an aqueous 0.5 wt % citrate solution at pH 7.5 also proved ineffective. Approximately 15 Carbopol solvent gels were tested. The coating was slightly disturbed by a benzyl alcohol/xylene gel. This multi-step approach was not satisfactory because it would have necessitated the painting being subjected to a number of cleaning passes.

An aqueous emulsion, comprising the acrylic-based polymer Pemulen TR-2, was also tried in an effort to remove the deteriorated surface coating. First introduced to art conservation at the Winterthur/University of Delaware Program in 2007, these polymers have been adopted by conservators to treat a variety of artworks and, in 2009, were incorporated into the Modular Cleaning Program. Pemulen is a block co-polymer of poly(acrylic acid) and poly(C15-C30 acrylic acid esters) that is used in industry for cleansing lotions and make-up removers. A Pemulen emulsion with 5 vol % xylene was used initially, but eventually addition of 5 vol % benzyl alcohol proved necessary to remove the surface coating. Although much of the
painting could be successfully cleaned, a few places remained dark and discolored. In these areas the coating was particularly intractable. Figure 6-22-A shows such an area cleaned twice with the benzyl alcohol/Pemulen emulsion.

Figure 6-22. *Multiple Views*, Stuart Davis (1918). (A) Detail of an area unsuccessfully treated using Pemulen 5% benzyl alcohol/emulsion; (B) after 30/70 acetone/water gel (5 wt % 75PVAc and 1 wt % borax) was removed from an area in the center after a four-minute treatment; (C) after removal of the softened surface coating by swabbing with 1/1 acetone/mineral spirits.

Areas that proved difficult to clean using the Pemulen emulsions were treated with xPVAc-borax gels. Gels were applied with a melinex cover to reduce the rate of solvent evaporation and allow unobstructed viewing. A gel containing 30/70 acetone/water was successful at removing the solvent-resistant residual material. Although initial tests with a one minute contact time were unsuccessful, the coating became softened with increased times (four minutes) and could be cleared with 1/3 acetone/mineral spirits. For comparison, a swab moistened with 30/70 acetone/water was rolled on the surface for a reasonable amount of time and was found to have no effect on the coating. It appears that the xPVAc-borax gel softened or broke down the oxidized surface of the coating, making it possible to remove it using
combinations of free solvents that had initially been ineffective. The gels conform well to the surface in paint impasto and effectively soften the hard-to-reach residues that were entrenched within the folds of the paint strokes (Figure 6-23). The crisp boundary between treated and untreated areas shows that the coating remains undisturbed up to the border of the gel. This attribute makes these gels optimal for situations that require local cleaning.

Figure 6-23. *Multiple Views*, Stuart Davis (1918). Detail of the varnished surface with large impasted paint stroke (top left), gel placed on top of surface (top right), surface after gel removal and clearing (bottom left), and after second gel cleaning (bottom right), where removal of the coating has been achieved.
Figure 6-24. Excitation (left) and emission (right) spectra of the paint surface of the blue house in *Multiple Views*, by Stuart Davis (1918) before treatment (■), with the gel on the surface (■), and after gel removal and clearing of the softened surface coating with 2/1 acetone/mineral spirits (■).

To test for gel residue on the surface, a 30/70 acetone/water gel was prepared using 1 wt % 75PVAc-EPF, 4 wt % 75PVAc and 1 wt % borax. Excitation and emission spectra were collected from the surface during the treatment of two areas with the fluorescein-tagged gels. Locations for the tests were chosen on uncleaned areas near the edges of the work. Figure 6-24 shows the normalized emission and absorption spectra of one region tested on the painting – a light blue area on the house in the lower right quadrant; brown area on the ground in front of the house was also treated and showed similar results. The spectrum of the surface after cleaning (i.e., after gel removal and clearing with 2/1 acetone/mineral spirits) has no detectable fluorescein residue.

Henry Ossawa Tanner’s work is characterized by his use of complex binding mixtures, vibrant colors, and layering of the paint to achieve highly textured surfaces. Unfortunately, these same properties of the paint films – experimental paint binder mixtures and interlayering of tempera paints with glue and resins – may have had a negative impact on their current condition. A collaborative study between the SAAM and the Pennsylvania Academy of Fine Arts (PAFA) on the artist’s use of materials has been launched to obtain a thorough understanding of Tanner's layering techniques and the current state of preservation of his works.\textsuperscript{170}

*The Fisherman’s Return* (Figure 6-25), one of Tanner’s paintings being treated at SAAM has undergone extensive analysis using cross-sectional samples. A detailed account of the composition of this painting is available in the study cited above. Notations found in Tanner’s journals suggest that the binder in the paint layers may consist of a mixture of flax seed syrup, parchment glue, mastic varnish, linseed and poppy oils, and lanolin. A discolored coating which is unlikely to be artist-applied covers the majority of the painting. The coating covers exposed canvas fibers in areas of loss (Figure 6-25). A layer of grime is also present on the surface.
Figure 6-25. Henry Ossawa Tanner, *The Fisherman’s Return*, 1917 (reworked 1919). Oil on canvas, 64.8 x 48.9 cm, Smithsonian American Art Museum. To the right are details of an area of loss before (top) and after (bottom) a two-minute treatment with a 30/70 2-propanol/water gel with 6 wt % 75PVAc and 1 wt % borax and clearance of the softened coating with a swab moistened with 1/3 2-propanol/mineral spirits.

PVAc-borax gels were considered for the removal of parts of the discolored surface coating from *The Fisherman’s Return* because of their ability to conform to the topographically uneven surfaces and to be applied and removed with minimal mechanical action. Several tests
were undertaken using 30/70 ethanol/water and 30/70 2-propanol/water mixtures in gels prepared from 6 wt % 75PVAc and 1 wt % borax. Initial cleaning tests were carried out on the white paint of the lantern in the lower center of the painting. After a two-minute application, the 30/70 ethanol/water gel was removed and its appearance was found to have become slightly yellow. As with the treatment of *Multiple Views*, the surface did not seem affected until a pass with a wetted swab was performed. The area treated with the xPVAc-borax gel was well defined. Using a similar protocol to that used on the Stuart Davis painting, a 1/3 ethanol/mineral spirits mixture was chosen to remove the softened surface layer. The rinsing mixture was ineffective in removing the aged surface coating and grime without pretreatment with the gel.

The 30/70 2-propanol/water gel proved to be effective and the conservator chose to use this gel to treat several other areas on the painting. A two-minute application of the gel followed by a pass with a swab wetted with 1/3 2-propanol/mineral spirits mixture seemed to remove the majority of the coating and grime without disturbing the complex paint layers below. The gels conformed to the surface well and small pieces which adhered to areas of impasto after gel removal were easily picked up by the swab.

A gel prepared with 3 wt % 75PVAc-EPF, 3 wt % 75PVAc and 1 wt % borax was used on two locations near the areas cleaned in the tests mentioned above to ascertain whether polymeric residues remained on the surface. After gel removal and clearing by swab of the softened coating, cross-sections were obtained from the treated areas, cut with a microtome, and dry-polished in order to avoid dissolution and loss of any fluorescein-tagged polymer. Imaging under a fluorescence microscope using a blue I3 filter cube did not reveal fluorescence that could
be ascribed to traces of fluorescein-tagged polymer on any of the four cross-sections analyzed (Figure 6-26).

Figure 6-26. *The Fisherman’s Return*, Henry Ossawa Tanner (1917, reworked 1919). A cross-section obtained from an area treated with a 30/70 2-propanol/water xPVAc-75-borax gel, under visible light (left) and with an I3 filter cube (right).

To gain insight into how the gels function and to confirm that they are acting mainly on the surface, rather than aggressively breaking through the paint layers underneath, gels and swabs used during the treatment of *The Fisherman’s Return* were analyzed by pyrolysis GC/MS (Py-GC/MS). Several scrapings of the surface coating were also analyzed by this technique and showed the presence of resin and drying oil (dehydroabietic, and azelaic acids). Analyses of the gel contents by two methods – dissolution and filtration of the gel, or forced expulsion of the liquid from the gel structure – did not show the presence of either of these components (Figure 6-27). If the gels are absorbing any components from the treated surface or the paint binder, their concentration is too low to be detected by these methods. The swabs used to remove the softened surface coating after gel treatment show the presence of azelaic acid and several other diacids. xPVAc-borax gels of the same formulation as those used on *The Fisherman’s Return* have been applied to paint-outs simulating Tanner’s own recipes with a mastic resin coating. Analysis by
Py-GCMS of gels after two minute application times on these paint-outs did not show the presence of oils or resins although the surface appeared blanched.

Because the gel and swab analyses as performed would not reveal the presence of other components which might be extracted from the paint binder, such as proteins or sugars, the extracts were also analyzed by transmission Fourier-transform infrared spectroscopy (FTIR). The characteristic amide bond bending and stretching signals for proteins were not found in either the gel and swab sample spectra. The spectra obtained from the swabs most closely match those of aged oil and resins from the Infrared and Raman Users Group (IRUG) database. If binder leaching were occurring, proteinaceous residues from the glue in the binder would likely be found in the gel extracts due to their aqueous nature.
Figure 6-27. Top – Pyrograms of the contents of three swabs used to remove the softened coating after gel treatment of *The Fisherman’s Return*, by Henry Ossawa Tanner (1917, reworked 1919). Bottom - Pyrograms of the contents of three 30/70 2-propanol/water gels with 6 wt % 75PVAc and 1 wt % borax that had been applied for two minutes to the surface of the painting. The relevant oil peaks are labeled, showing diacids present in the swab samples but absent from the gel samples; stearic and palmitic acids are found as contaminants in the pyrograms of unused gels as well.
6.6.3. Frames.

Because the xPVAc-borax gels conform well to surface topography, they are excellent candidates for cleaning frames with complex carved patterns. Initial tests were performed on a fragment of a 19\textsuperscript{th}-century Italian wooden frame which was prepared with a gesso layer and yellow bole followed by silver leaf. A thick coating of shellac was used to make the silver leaf look golden. An 80/20 ethanol/water gel with 16 wt \% 45PVAc and 2 wt \% borax was applied to the surface for different periods of time. A 15 minute application was found to remove the shellac completely without disturbing the silver leaf. Shellac removal was confirmed by ultraviolet illumination as well as by excitation emission spectrofluorimetry of the surface (Figure 6-28).¹⁰⁹
Figure 6-28. The surface of a 19th century Italian frame with silver leaf and an unbleached shellac varnish that was treated with a 80/20 ethanol/water gel containing 16 wt % 45PVAc and 2 wt % borax for (A) 5 minutes, (B) 10 minutes, and (C) 15 minutes. The softened shellac was removed from the surface with a dry swab after gel removal. The excitation-emission spectra of the surface before (bottom left) and after (bottom right) gel application show the complete removal of the shellac as a result of the treatment. In these spectra, only data within the central delineated regions are meaningful.

At the J. Paul Getty Museum in Los Angeles, the xPVAc-borax gels were tested on a frame undergoing treatment. A 10/90 ethanol/water gel was applied to the carved features of the frame, allowing the conservator to treat selected areas that were difficult to access using a swab. A thick layer of grime was softened by the xPVAc-borax gel after a 5 minute application and could be removed with a swab moistened in water (Figure 6-29). The material removed from the surface, when dissolved in water, showed fluorescence excitation and emission bands of 320-350 nm and 420-450 nm respectively. These results are inconclusive, as a number of artist’s materials including some resins and proteinaceous materials show excitation and emission in the same region.\textsuperscript{171} Further analysis by Py-GC/MS and ATR-FTIR of the liquid expelled from the gel used during the treatment as well as the swabs used to remove the softened material from the frame did not reveal the composition of the surface coating. Nonetheless, the use of an xPVAc-borax gel proved effective in difficult to reach areas and allowed for a reduction in the number of swab passes necessary to remove the grime from the surface, without disturbing the underlying gilded surface.
Figure 6-29. Frame partially treated with 10/90 ethanol/water gel containing 4 wt % 80PVAc and 1 wt % borax for 5 minutes. In image A, the gel is in the carved recess. Image B shows the surface immediately after the gel was removed. Image C shows the surface after the softened grime was removed with a swab dipped in deionized water.


xPVAc-borax gels have been used in an attempt to remove stains that may be metal soap formations from the surface of an alkyd painting – Sacramento Mall Proposal #4 by Frank Stella (1978). The treatment of the work involved the removal of dried ketchup stains (Figure 6-30). During a previous conservation treatment, the stains had been partially removed and many were concealed with blue or purple pastels. Although the brown, dried stains were not difficult to remove from the surface using a methyl cellulose poultice with water, the conservator found identically shaped white stains on the paint beneath the cleared stains.
The white areas were augmented in some locations by the exposure of the canvas fibers (the painting is not primed). The conservator treating the artwork believed that the white crystals causing the discoloration of the surface after the ketchup removal were a result of a residual ingredient in the ketchup. Analysis by FTIR of scrapings from the white material suggested the presence of gums. GCMS analyses were inconclusive. A range of pure and mixed solvents of both high and low polarity, as well as aqueous solutions including chelators, surfactants, and pH buffers, were used to try to remove the crystals without success.

Alkyd paint is prepared by the polymerization of polyols, polybasic acids and fatty acids, resulting in an ‘oil modified alkyd polyester’. The large concentrations of unsaturated fatty acids - linoleic acid and linoleinic acid - in alkyd paint are known to undergo auto-oxidation reactions and can be hydrolyzed easily from their triglyceride source. The lycopene and other UV-vis absorbing species found in ketchup can also act as sensitizers for these oxidation
reactions. In the presence of alkaline earth or heavy metals, fatty acids form metal soaps which
can have some beneficial properties such as increasing the physical strength of the film and
generating anti-corrosive properties. However, in alkyd paints, metal soaps can accumulate on
the surface and produce a loss of gloss and a hazing effect due to an appearance of
‘protuberances’.

The high acidity of ketchup (pH = 3.6) can be implicated in the hydrolysis of fatty
acids from the triglycerides in alkyd paint. Di- or tri-valent metal soaps are insoluble in water.
For example, the metal soap zinc stearate, is not soluble in highly polar alcohols and ethers, has a
0.3 wt % solubility in benzene, and, therefore, a low solubility in commonly used conservation
solvents such as mineral spirits, xylene and toluene, but may be decomposed by dilute
acids. The appearance and location of the crystals on the surface, and the difficulty in
finding a liquid suitable for their dissolution, may indicate the formation of metal soap crystals
on the surface of Sacramento Mall Proposal # 4, although further analyses on the crystals have
not been performed to confirm this possibility.

Figure 6-31. Stella detail. Magnified purple paint area showing white hazy surface material in
crevices of canvas (A); Application of a 50/50 acetone/water gel containing 6 wt % 75PVAc and
1 wt % borax on the surface of the paint (B); The area after cleaning; the hazy white material is
still visible (C).
Several xPVAc-borax gels with 50/50 2-propanol/water, ethanol/water, and acetone/water liquid compositions were applied over the areas affected by the white stains for two minutes. After their removal from the surface with a dry swab or a spatula, a 70/30 mixture of mineral spirits and 2-propanol was used to swab clear the treated area. Upon wetting the areas treated by the gel, the white crystals nearly disappeared, but their presence was once again noted when the surface dried. If the stains are caused by metal soaps, the largely aqueous and basic nature of xPVAc-borax gels is unsuitable for the removal of the stains. Although the xPVAc-borax gels were not effective in the removal of possible metal soaps from the painting, they did not disturb the paint surface and may be useful in the treatment of alkyd paintings with other surface contaminants.
6.6.5. Objects.

Figure 6-32. Table Fountain, c. 1320-1340. France, Paris, 14th century. 33.8 x 25.4 x 26.0 cm. The Cleveland Museum of Art, Gift of J. H. Wade 1924.859. Gilt-silver and translucent enamel.

The Cleveland Museum of Art requested a sample of PVAc-borax gels prepared with high percent volumes of acetone, ethanol, or both for the treatment of a medieval table fountain (Figure 6-32). The French fountain is composed of gilt-silver and translucent enamel. The silver had been coated with Agateen (cellulose nitrate) which, due to aging, no longer protected the
metal, resulting in the development of tarnish. The enamel had been consolidated with Paraloid B72. The typical method of cleaning Agateen from a metal object – submerging the object in acetone or coating it with acetone soaked cotton – was not possible in this case due to the solubility of B72 in acetone. The fountain was being treated by application of acetone-soaked cotton balls to small locations for approximately 20 minutes followed by clearance of the softened coating with swabs dipped in acetone. The process was tedious and difficult, especially in the crevices of the worked metal.

Gels with 80/20 acetone/water, 80/20 ethanol/water, and 40/40/20 ethanol/acetone/water containing 10 wt % 40PVAc and 1.5 wt % borax were prepared for the conservator. The gels were brittle, due to the large proportions of acetone and ethanol, but workable. Small pieces of the 80/20 acetone/water gels were placed on the metal surface, covered with Parafilm (a pliable polyethylene film which retards evaporation of the liquid in the gels), for 3-4 minutes. After the gel was removed, a conservator used a cotton swab dipped in acetone to clear the surface. Initial observations were not encouraging; the Agateen coating has a very weak yellow color and the surface under daylight did not look altered. It was nearly impossible, even for those working on the project, to distinguish areas that had been cleaned and those still coated with Agateen. However, a satisfactory working method was established when an area of blanched Agateen (from a previous acetone drip) was effectively cleared with the 80/20 acetone/water gel without any swabbing (Figure 6-33).
Figure 6-33. *Table Fountain* (c. 1320-1340). Detail showing blanched Agateen spot on the basin and completely cleared area over which the xPVAc-borax gel was placed for three minutes (indicated by arrow), and the same area after gel removal under UV light. The inset shows the yellowed gel after cleaning.

Further tests and viewing the object under UV light confirmed the success of the 80/20 acetone/water gel in removing the aged Agateen (Figure 6-33). Because the concentration of acetone in the gels was high, conservators at the Museum were encouraged to reduce the polymer concentration to 9 wt % or the borax concentration to 0.7 wt % in order to obtain more malleable gels. These gels were used in localized areas for the treatment of the fountain, and occasionally applied through a Japanese paper barrier because it was established that removing the gel from the surface was easier with a barrier tissue.

A tissue barrier was also used at the Cleveland Museum of Art in an attempt to treat a low-temperature fired earthenware bowl. According to the conservator treating the piece, placing the gel on the ceramic with a tissue barrier seemed to reduce solvent penetration and to decrease the efficacy of the cleaning process. When applied directly to the ceramic, the xPVAc-borax gels appeared to clean more effectively, but were more difficult to remove, likely as a result of
adhesion of the gels to the porous ceramic surface. The conservator felt that the xPVAc-borax gels may work better on ceramics for removing on-surface accretions and for removing stains from stoneware or porcelain rather than for removing in-body stains. The ability of the gels to act as a poultice has not been studied.

The work of Carretti et al. in Florence has shown the effectiveness of xPVAc-borax gels in the removal of Paraloid B-72 coatings, shellac, and other polymeric consolidants from tempera on wood paintings as well as from frescos. As described in Chapter 5, ammonium carbonate has been successfully loaded into xPVAc-borax gels, making them useful not only for the removal of aged synthetic coatings on the surfaces of frescos, but also in the reversion of gypsum to calcite.

6.7. Conclusions.

The studies presented here involving controlled sample systems and a limited number of case studies offer insight into the cleaning action of xPVAc-borax gels. Additional use of the gels by conservators will further test the utility of the gels. This research demonstrates that xPVAc-borax gels can be easily prepared and can be formulated in a wide range of properties desirable for different applications. In addition, a range of liquids may be gelated and inclusion of other cleaning agents and salts is possible. Treatments performed on both test surfaces and paintings treated with the xPVAc-borax gels indicate a lack of polymer residue after gel treatment. Experiments that traced lateral solvent diffusion using fluorescence illustrate the localized cleaning action of the gels. Lastly, analyses of a gel used in a treatment indicate that the
action can be restricted to the surface with which they are in contact; evidence thus far suggests there is no leaching of material from paint layers beneath.

The gels have been used to treat works of art where other systems proved ineffective. Because they can be applied onto a surface gently and removed with minimal mechanical action, xPVAc-borax gels are useful on sensitive surfaces such as metal-leaf frames. Use of the gels on more porous surfaces, such as ceramics or paper, may not be as appropriate. On such materials, xPVAc-borax gels are more difficult to remove and a barrier tissue must be used, which further limits the diffusion of the solvent and contact of the polymer with the surface, and, in some cases, interferes with the efficacy of the cleaning action. Studies on the nature of the gel network and its interaction with the gelated liquid and the surface undergoing treatment are necessary in order to understand the reduction in cleaning efficacy when the gels are applied through a barrier tissue.
APPENDIX A: RHEOLOGY

Rheological measurements allow us to understand the flow and deformation of matter. Rather than an extensive review, this section will give a short description of the forces involved in such measurements which are relevant to the research discussed in this dissertation. Unless otherwise indicated, the summary of terms in this section is referenced from the *Soft Condensed Matter* primer by Dr. Richard A. L. Jones.\textsuperscript{33}

Ideal solids and liquids respond to applied stress in a well-defined manner. To measure their elastic or viscous behavior, a shear stress ($\sigma$) is applied which can be defined as the force ($F$) applied over an area ($A$) (Equation A-1). Figure A-1 describes this process.

\[
\sigma = \frac{F}{A} \quad \text{(A-1)}
\]

![Figure A-1](image-url)

Figure A-1. Schematic representation of shearing process adapted from *Soft Condensed Matter*.\textsuperscript{33}
When applying a shear stress to a Hookean solid, the material responds with a sustained shear strain \( e \) that is proportional to the stress by a constant called the shear modulus, \( G \). The shear strain is defined in equation A-2, but if the strain is very small, it is equivalent to \( \theta \).

\[
G = \frac{\sigma}{e}
\]  

(A-2)

In Newtonian liquids, application of a shear stress results in flow, characterized by a constant shear strain rate proportional to the applied shear stress by the viscosity of the liquid. To describe this using the schematic representation of a material in Figure A-1, the cube will be representative of a liquid between a top and a bottom plate, with the top plate moving in one direction at a specific velocity, \( u \). Thus, the force of resistance exerted by the liquid is described by equation A-3, with the coefficient \( \eta \) being the viscosity of the liquid.

\[
F = A\eta \frac{u}{y}
\]  

(A-3)

As the top plate moves forward, a gradient will develop in the velocity, defined by \( u/y \), which is equal to the time derivative of the shear strain (i.e. the shear strain rate, \( \dot{e} \)). Thus the shear stress in a Newtonian liquid is defined in equation A-4.

\[
\sigma = \eta \dot{e}
\]  

(A-4)

The materials commonly studied in rheology display both of these behaviors, on a time-dependent scale. Simply put, a viscoelastic material can act as a liquid with a measurable viscosity on very long time scales (slow observation times), or an elastic solid at short time scales (fast observation times). Viscoelastic behavior can be graphically represented by the shear strain curve in Figure A-2. A material with this kind of shear response acts as an elastic solid with a constant strain response for a finite amount of time after a constant stress has been
applied; at a certain time, $\tau$, the response of the material changes to that of a liquid with a time-dependent strain response. This time is termed the *relaxation time*. The modulus $G_o$ describes the elastic behavior of the materials at time shorter than the relaxation time. At longer times, the response of the material is also characterized by its viscosity, so that $\eta \sim G_o \tau$.

Figure A-2. Strain response of a viscoelastic material under constant stress. Figure adapted from Soft Condensed Matter.\textsuperscript{33}

Non-Newtonian liquids diverge from the ideal response described above by having a shear-rate dependent viscosity, $\eta(\dot{\varepsilon})$, described in equation A-5. Several types of non-Newtonian fluids are shown in Figure A-3. We can also define a thixotropic material as shear thinning so that as the shear rate is increased, its viscosity decreases but additionally, these materials show a shear thinning response with time if the shear rate is kept constant.\textsuperscript{178}
The majority of experiments used to study xPVAc-borax gels described in this work involve the application of an oscillatory deformation with a frequency $\omega$. To measure the response of the materials under this kind of stress, the gel is placed between the two plates of a rheometer, and the top plate is moved with an increasing oscillation frequency. This oscillatory strain is defined in equation A-6, while the stress response is defined in equation A-7.

\[ e(t) = e_o \cos(\omega t) \] \hspace{1cm} (A-6)

\[ \sigma(t) = e_o \left[ G'(\omega) \cos(\omega t) - G''(\omega) \sin(\omega t) \right] \] \hspace{1cm} (A-7)

From the above equation, we can define a complex modulus, $G^*(\omega) = G'(\omega) + G''(\omega)$. This modulus contains information about both the elastic and viscous responses of the material at the
measured frequencies. The storage modulus, $G'$, is also called the elastic modulus and represents the solid-like behavior of the material, while loss modulus, $G''$, can be called the viscosity modulus and describes the liquid-like behavior of the material. The response also has a characteristic phase angle, $\delta$, described by $\tan \delta = G'/G''$. The loss factor, $\tan \delta$, can also be used to define the viscoelastic behavior. When $\delta = 0^\circ$ and $\tan \delta = 0$, $G'$ dominates $G''$ entirely, and the material behaves as an ideal elastic solid.\textsuperscript{179} When $\delta = 90^\circ$ and $\tan \delta = \infty$, $G''$ dominates $G'$ entirely and the material displays ideal viscous behavior.\textsuperscript{179} For an ideal balance between the viscous and elastic behavior, when $G' = G''$, $\tan \delta = 1$ and $\delta = 45^\circ$; this value is considered as the gel point of a material.\textsuperscript{179} However, $\tan \delta$ does not consider the absolute magnitudes of $G'$ and $G''$ which are important considerations as well in defining a material.

For a true gel, a frequency sweep experiment (i.e., where the oscillation frequency is changed and the $G'$ and $G''$ moduli are being measured), performed in the linear viscoelastic region will show a response similar to that schematically represented in Figure A-4. The storage modulus should remain larger and parallel to the loss modulus over the entire frequency range studied; in general $G':G''$ should be in the range of 10:1 to 100:1.\textsuperscript{179} In the event that the two moduli show a cross-over, also shown in Figure A-4, the material cannot be considered a true gel and the response is characteristic of unlinked polymers (as opposed to crosslinked polymers).\textsuperscript{179} This response is similar to that of the non-Newtonian fluids described earlier, with the elastic response predominating at high frequencies (corresponding to short observation times), and the viscous response predominating at low frequencies (corresponding to long observation times). The dynamic nature of the crosslinks in xPVAc-borax gels is likely responsible for the observed response in these kinds of experiments as discussed in Chapter 3.
Figure A-4. (Left) Angular frequency sweep response of a true gel with $G'$ (■) consistently having a higher value than $G''$ (■); (right) typical angular frequency response of high viscosity polymeric dispersions from xPVAc and borax, with $G''$ (■) > $G'$ (■) at low frequency and $G'$ (■) > $G''$ (■) at high frequency. Both measurements are made in the linear viscoelastic region where the strain response is independent and linear when measured at a constant frequency.

In Figure A-4, the cross-over point of the two moduli, where $G'$ = $G''$, is defined as being approximately equal to the inverse of the relaxation time of the system (the time when the strain behavior changes from that of an elastic solid to that of a viscous liquid). As an ideal solid or true gel would display a linear response between the two moduli, lacking such a cross-over point, it follows that true gels have an infinite relaxation time. Although the relaxation time was briefly described earlier, an additional explanation is included here, which may be helpful for understanding this value.

During a shear flow experiment, isotropically arranged particles in the material under examination experience an anisotropic reorganization. This process is characterized by elastic
(recoverable) energy used in the structuring of the material components, and a lost energy which is dissipated during the flow of the material related to its viscosity. There is a finite amount of time associated with the formation and loss of anisotropy in a material due to shear flow. The amount of anisotropy is thus dependent on both the speed and the duration of the shear. When the applied force is stopped, the material will relax to an isotropic state due to Brownian motion and internal spring forces. The relaxation time necessary to return to this state is proportional to the size of the local structures, with larger local structures requiring longer relaxation times. The decrease in anisotropy is expressed as an exponential function in Figure A-5, with the relaxation time commonly defined as the time necessary for the anisotropy to decrease by a factor of $1/e$. In oscillatory experiments, the global induced anisotropy varies with the size and period of the oscillation and the relaxation time.

![Figure A-5. Decay of initial anisotropy (A) at $t_0$ to the isotropic state, with the relaxation time, $\tau$, indicated.](image)
APPENDIX B: $^{11}$B NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Both $^{10}$B and $^{11}$B nuclei can be probed by NMR spectroscopy due to their high natural abundance and the magnetic moments. The two nuclei have spins of $I > 1$, and as a result allow for quadrupolar relaxation which shortens the relaxation time of the nucleus to the ground state and thus results in line broadening. Due to this property, fine line structure and coupling with other nuclei is usually not detectable in the spectra. Table B-1 shows some of the properties of boron nuclei, as well as those of hydrogen and carbon for comparison.\(^{106}\)

Table B-2. Properties of boron nuclei compared to hydrogen and carbon.\(^{106}\)

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>Natural Abundance</th>
<th>$I$</th>
<th>Magnetogyric ratio (radians s(^{-1}) T(^{-1}))</th>
<th>Electric Quadrupole Moment $Q$ ($10^{-28}$ m(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{1}$H</td>
<td>99.98%</td>
<td>1/2</td>
<td>$2.676 \times 10^{8}$</td>
<td>—</td>
</tr>
<tr>
<td>$^{10}$B</td>
<td>18.83%</td>
<td>3</td>
<td>$2.875 \times 10^{7}$</td>
<td>0.111</td>
</tr>
<tr>
<td>$^{11}$B</td>
<td>81.17%</td>
<td>3/2</td>
<td>$8.582 \times 10^{7}$</td>
<td>0.0355</td>
</tr>
<tr>
<td>$^{13}$C</td>
<td>1.11%</td>
<td>1/2</td>
<td>$6.725 \times 10^{7}$</td>
<td>—</td>
</tr>
</tbody>
</table>

$^{11}$B has a smaller quadrupole moment than $^{10}$B, which results in a slightly narrowed linewidth; combined with its higher natural abundance, $^{11}$B is the more appealing nucleus for spectroscopy.\(^{106}\) Typically, both nuclei are referenced against boron trifluoride diethyl etherate [F$_3$B-O(C$_2$H$_5$)$_2$] but this has not been the case for all studies, and some authors choose to use boric acid or other boron containing compounds as reference signals. The spectral range of boron compounds can cover 250 ppm, and the location of the signal will be affected by the environment of the boron atom, including its charge and coordination number, and the type of
substituents it is bound to.\textsuperscript{106} As in $^1$H NMR, integration of the signals gives information on the relative abundance of the species detected in the spectrum.

Of importance for interpreting spectra in this research are tri- and tetra-(organyloxo)boranes, boric acid, and the borate ion. Along with the six-membered cyclic structures obtained through monodiol and didiol complexation described throughout the work, chapter X also focuses on trimethylborate (TMB), a compound with three methoxy substituents. Organyloxy substituents are strong π-donors, shifting the signal of the boron atom upfield.\textsuperscript{105} For example, boric acid is detected at 19.6 ppm in water, while the signal for trimethylborate is found closer to 18 ppm (measured in methanol, as trimethylborate is rapidly converted to boric acid in the presence of water).\textsuperscript{105} Tetrahedral, negatively charged tetra(organyloxo)boranes are detected further upfield, between 0 and 3 ppm. Based on the work by Bishop at al. the relevant shifts for cyclic trigonal and tetrahedral mono and di-diols are presented in figure B-1.\textsuperscript{46}

![Figure B-1. $^{11}$B NMR shifts of relevant cyclic compounds and trimethylborate.\textsuperscript{46}](image)

A sample spectrum of an xPVAc-borax gel with a trisodium citrate additive is shown in figure B-2 with the relevant peaks labeled. As mentioned in section 3.1 the trigonal and tetrahedral species of boric acid are in equilibrium, with a broad peak appearing between their
individual shifts, its shift being dependent on the pH and therefore the concentration of each species.

Figure B-2. $^{11}$B NMR spectrum of a gel prepared with 3 wt % 80PVAc, 0.75 wt % borax, and 0.1 wt % trisodium citrate in D$_2$O.

A critical aspect of $^{11}$B NMR spectroscopy is the background signal present in most spectra. An example of a typical spectrum that has not been background corrected can be seen in figure B-3. There are two causes for background signal in $^{11}$B NMR; the first is easily corrected through the use of quartz NMR tubes instead of standard borosilicate glass tubes which contain boron. The second cause, which is the major contributor to background resulting in an 80 ppm-wide signal as seen in figure B-3 is due to parts of the NMR probe in proximity to the coil which are made of glass.$^{181,182}$ Consequently, this signal will differ from one instrument to another.
There are two methods of suppressing the background signal arising from the NMR probe. One technique, introduced by Cory and Ritchey in the 1980s, uses a composite pulse sequence of a 90° pulse followed by two 180° pulses for spins inside and outside the coil respectively.\textsuperscript{182,183} This sequence is known as DEPTH. The second technique, introduced by Király in 2012, involves the monitoring of $^{10}\text{B}$ rather than $^{11}\text{B}$.\textsuperscript{184} In NMR spectra of the $^{10}\text{B}$ nucleus, the background signal is essentially undetectable. $^{10}\text{B}$ has a spin of $I=3$, and consequently very fast relaxation in solids, such as the probe components, resulting in extremely broad, and undetectable, peaks in the NMR spectrum.\textsuperscript{184} Unfortunately, the far smaller natural abundance and magnetogyric ratio of $^{10}\text{B}$ lower the sensitivity of these spectra and very long collection times may be necessary.

Spectra presented in this work have been background corrected by software modulation. Each spectrum typically undergoes three correction steps. First, a Gaussian apodization of 5 Hz is applied which reduces noise (this step is periodically omitted for high resolution spectra); next, a backward linear prediction (LP) is performed, and finally, a Whittaker-smoother baseline correction is applied to the signal. The backward LP is a method for predicting data that is missing or distorted, backward, to time zero; such distortions may be a result of receiver dead time or acoustic ringing and typically result in loss of broad features in the spectrum and baseline.
modulation. With these corrections, the signal can generally be recovered as is shown in figure B-4. However, if a signal from a species in the sample decays completely before the collection of meaningful data, backward LP would not be able to recover its signal. In some cases, backward LP was not applied, and only a baseline correction was enough to remove the background noise. Throughout the dissertation, treatment of the spectra has been noted in the figure captions.

Figure B-4. $^{11}$B NMR spectrum of boric acid in D$_2$O with Gaussian apodization, backward LP, and Whittaker-smoother baseline correction.
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APPENDIX D: AUTOBIOGRAPHY

Lora Angelova (Лора Ангелова) was born in Sofia, Bulgaria in 1984. She moved with her family to Buffalo, New York, in 1994, and then to Cleveland, Ohio, in 1999, where she obtained her B.A. degree in Chemistry from Case Western Reserve University in 2007. In 2008, Lora joined the Department of Chemistry at Georgetown University. She obtained her Ph.D. in July 2013.
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