

Soft, Peelable Organogels from Partially Hydrolyzed Poly(vinyl acetate) and Benzene-1,4-diboronic Acid: Applications to Clean Works of Art

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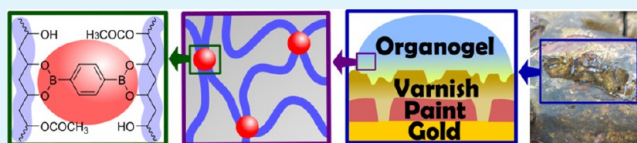
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S Supporting Information

ABSTRACT: We have developed soft, peelable organogels from 40% hydrolyzed poly(vinyl acetate) (40PVAc) and benzene-1,4-diboronic acid (BDBA). The organic liquids gelled include dimethyl sulfoxide, dimethylformamide, tetrahydrofuran, 2-ethoxyethanol, and methanol. The rheology of these soft materials can be tuned by altering the concentration of the polymer and/or crosslinker. Insights into the mechanisms leading to gelation were obtained from ¹H NMR experiments, fluorescence measurements, and studies comparing properties of materials made from BDBA and phenylboronic acid, a molecule incapable of forming covalent crosslinks between the polymer chains. These organogels can be easily peeled off a surface, leaving no residue detectable by UV–vis spectroscopy. They are demonstrated to be effective at softening and removing deteriorated coatings from water-sensitive works of art and delicate surfaces. They have the needed characteristics to clean topographically complex surfaces: good contact with the surface, easy removal, and little to no residue after removal. A 2-ethoxyethanol organogel was used to remove oxidized varnish from a 16th century reliquary decorated with painted gold leaf, and an ethanol gel was used to remove solvent-resistant coatings from 16th and 18th century oil paintings.

KEYWORDS: polymer, organogel, boron chemistry, cleaning, cultural heritage



INTRODUCTION

Preserving cultural heritage objects often involves cleaning their surfaces to remove not only accumulated dirt and soil but also deteriorated coatings that had been applied for aesthetic and protective purposes. Their removal from delicate surfaces (e.g., paints, plastics, or metals) can be achieved with a range of methodologies, including dry cleaning methods, such as laser ablation,^{1,2} microfiber cloths,³ and polymeric micropillars,⁴ as well as wet cleaning methods employing solvents, surfactants,⁵ microemulsions,⁶ and gels.⁷ When wet methods are necessary, gel matrixes can attenuate the migration of solvents into subsurface layers, where they may cause permanent changes.^{8,9} Although aqueous gels are useful for cleaning a range of types of surfaces,^{10,11} organogels are preferred for applications in which the presence of water is undesirable or ineffective. Organogels, gels in which the solvent system comprises organic liquids, are capable of promoting selective removal of organic components while leaving water-soluble and water-sensitive components unaffected. A few types of organogels for cleaning cultural heritage have been reported in the literature, but they are either rigid^{12,13} (and best suited to cleaning flat surfaces) or soft^{14,15} (and require addition of a weak acid for their efficient removal).

Efforts have recently turned to designing soft, peelable organogels that can conform to delicate, textured surfaces, and yet be easily removed from them after treatment by peeling.

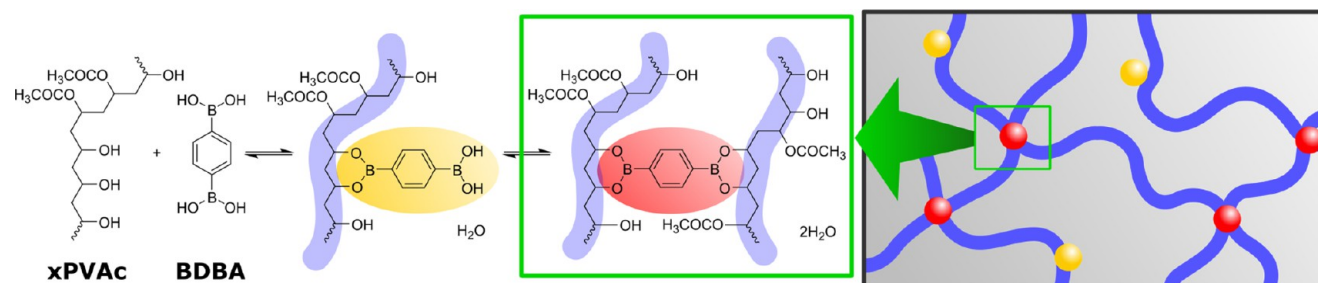
The use of a peelable organogel would reduce physical (e.g., rubbing) and chemical (e.g., addition of other solutions) manipulations while also reducing the likelihood of gel residue being left behind. Peelable, gel-like materials comprising aqueous solutions of poly(vinyl alcohol) (PVA) and borax as a crosslinker (after its dissociation to boric acid and borate ion)^{16,17} with small amounts of added organic solvent have been used for cleaning painted surfaces.¹⁸ By using partially hydrolyzed poly(vinyl acetate) (x PVAc, where x denotes the percent hydrolysis of the acetate groups) in place of PVA (i.e., 100PVAc), more organic solvent could be incorporated,¹⁹ but a significant amount of water is necessary to dissolve the borax. Although some “dry” gels with borate ester crosslinks have been made in very high-polarity organic solvents, such as methanol and dimethyl sulfoxide (DMSO), in which borax is sparingly soluble, they are very difficult to prepare reproducibly and contain residual solid borax.²⁰ Water-free gels have been made with crosslinkers such as trimethyl borate (TMB) and x PVAc, but they are problematic as well—they are extremely water-sensitive and, thus, unstable under normal atmospheric conditions.²⁰

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Scheme 1. Reactions of BDBA with Hydroxyl Groups on x PVAc Form Mono- (Yellow) and Diesterified (Red) Boronate Species, of which Only the Diesterified Species Lead to Intra- and Interchain Crosslinks between Polymer Chains (Blue)



Here, to make gels that combine the stability of the aqueous x PVAc–borax materials and the organic nature of the x PVAc–TMB ones, we have employed benzene-1,4-diboronic acid (BDBA) as a crosslinker: it is soluble and stable in many organic liquids and combines with hydroxyl groups of x PVAc in esterification reactions to form inter- and intrachain crosslinks. Previously, PVA has been mixed in aqueous media with small boronic acid molecules to form microspheres²¹ and fibers,²² and with boronic acid-functionalized polymers to produce hydrogels^{23–25} and films^{26,27} that disassemble with the addition of a sugar or a decrease in pH. However, the use of organic solvents in x PVAc-based gels has been limited to those from PVA in DMSO/water mixtures²⁸ and from PVA and BDBA in DMSO.²⁹ To the best of our knowledge, organogels from x PVAc with $x < 100$ have not been reported in the literature, and they are expected to have the qualities sought by conservators to clean several types of works of art in which aqueous gels cannot be employed.

We describe here the syntheses and characterizations of the structural and viscoelastic properties of gelled systems in which the solvent consists of organic liquids and only the water molecules (one per esterification reaction) produced as side products in the crosslinking reactions between an x PVAc and BDBA (Scheme 1). Furthermore, we demonstrate their utility in cleaning applications for works of art that require nonaqueous solvents, including aprotic ones and alcohols. Because the rheological properties of the organogels depend on the concentrations of the polymer and crosslinker, the viscoelastic properties of the organogels can be tuned to suit specific applications.

MATERIALS AND METHODS

Materials. 40PVAc (Kuraray Co., Ltd.; poly(vinyl acetate); 40% hydrolyzed, molecular weight unknown) was purified by rinsing with ice-cold deionized water, filtering, and vacuum drying (~125 mmHg) at room temperature. The organic solvents used include dimethyl sulfoxide (Sigma-Aldrich, >99.5%), 2-ethoxyethanol (Sigma-Aldrich, 99%), dimethylformamide (DMF; EMD, ACS grade), methanol (Sigma-Aldrich, ACS grade, >99.8%), 1-methyl-2-pyrrolidinone (Alfa Aesar, ACS grade, 99.0%), tetrahydrofuran (Sigma-Aldrich, anhydrous, >99.9%), dichloromethane (Fisher Scientific, ACS grade), acetone (Fisher Scientific, histological grade), ethanol (Sigma-Aldrich, 200 proof, anhydrous, >99.5%), 95:5 ethanol/water (ethanol, Warner Graham Co., 190 proof), 1-propanol (Fisher Scientific, Certified grade), 2-propanol (Fisher Scientific, HPLC grade), ethyl acetate (Fisher, ACS grade), acetonitrile (Fisher Scientific, HPLC grade), *n*-butyl acetate (Alfa Aesar, 99%, semiconductor grade), and cyclohexanone (Sigma-Aldrich, 99.8%). The deuterated NMR solvents used were DMSO-*d*₆ (Cambridge Isotope Laboratory, 99.9% D) and methanol-*d*₄ (Sigma-Aldrich, 99 atom % D). Benzene-1,4-diboronic acid (Sigma-Aldrich, ≥95.0%) and phenylboronic acid (BBA; Alfa

Aesar, >98%) were used as received. Acrylic paint (Grumbacher, Academy Acrylic, thalo green—a chlorinated copper phthalocyanine pigment), canvas sheet primed with acrylic primer (Fredrix, canvas pad, medium texture real artists canvas), and a boar bristle brush (Winsor & Newton, Rathbone Filbert #3) were used to create acrylic paint samples for residue studies.

Preparation and Characterization of Organogels. Organogel samples were prepared by dissolving 40PVAc and BDBA separately in an appropriate organic solvent. The BDBA solution was transferred with a pipette into the 40PVAc solution, and the mixture was stirred vigorously with a spatula for approximately 30 s.

¹H NMR Spectroscopy. ¹H NMR spectra were acquired at 25 °C, unless otherwise noted, on a Varian-MR 400 MHz NMR spectrometer. For these measurements, gels were prepared using a syringe to disperse a BDBA/DMSO-*d*₆ solution throughout a 40PVAc/DMSO-*d*₆ solution in an NMR tube, stirring with the syringe needle. For NMR temperature studies, samples were allowed to equilibrate at each temperature for 5 min before beginning an experiment.

Rheological Measurements. Rheological measurements were made on samples 2 days after their preparation on a stress-controlled Anton Paar Physica MCR 302 rheometer with a 25 mm diameter cone (angle of 2.0°) and plate. Strain sweeps were measured at 0.08–300% at a constant angular frequency of 1 rad/s. In linear viscoelastic regions, frequency sweeps were recorded in the range of 0.01–100 rad/s.

Fluorescence Measurements. A Photon Technology International fluorimeter was used to collect excitation and emission spectra of samples in a front-face geometry in a 1 cm triangular quartz cuvette. N₂ was bubbled through the 40PVAc and BDBA solutions before mixing them; all other experiments were conducted in air.

Residue Study. One coat of acrylic paint (~0.05 mm thick after drying) was brushed onto a primed canvas sheet and dried for 5 months under ambient conditions. A 1 cm² square was cut from the prepared canvas sheet and placed into a vial with 5 mL of acetonitrile for 60 s, after which the solvent was placed in a 1 cm quartz cuvette, and a UV–vis spectrum was acquired using an Agilent 8453 spectrophotometer. This procedure was repeated for a second paint sample, except before placing the sample into an acetonitrile-filled vial, a 6 wt % 40PVAc/0.2 wt % BDBA in 95:5 ethanol/water organogel was placed directly on the surface of the paint for 2 min, the bulk of the organogel was removed, and a paper towel was gently pressed to the surface of the paint to remove any remaining pieces of organogel. Because acetonitrile extracted UV-absorbing components from the paint sample, this procedure was repeated on paint samples that were “prewashed”—they were first soaked for 60 s each in three sequential 5 mL aliquots of acetonitrile.

Cleaning a Painted and Gilded Reliquary. A spatula was used to place an aliquot of 6 wt % 40PVAc/0.2 wt % BDBA 2-ethoxyethanol gel onto the object’s surface. After 10 min, the bulk of the gel was removed by lifting it off using a spatula, and small residual pieces were removed by gently pressing a paper towel to the surface. Finally, an ethanol-moistened swab was rolled over the surface where the gel had been placed.

Removing a Shellac Varnish from an Oil Painting. A spatula was used to place an aliquot of 6 wt % 40PVAc/0.2 wt % BDBA in

95:5 ethanol/H₂O gel onto the surface of the painting by Sir Joshua Reynolds, *Miss Beatrix Lister* (1765). A piece of Mylar sheet was used to press the gel gently onto the surface to increase contact between the gel and varnish and to slow the evaporation of the solvent. After 5 min, the bulk of the gel was removed with a cotton swab and tweezers. The gel caused the aged shellac to swell, but not to dissolve, and an ethanol-moistened swab rolled over the surface where the gel had been placed had little effect. Instead, a sharpened bamboo skewer was used to gently lift the softened varnish away from the underlying paint surface, and the pieces of varnish were brushed off the surface. The surface during cleaning was recorded with a Hirox digital microscope (KH-7700), and stillshots from the video are presented herein.

RESULTS AND DISCUSSION

On mixing 6 wt % 40PVAc and 0.2 wt % BDBA, clear homogeneous gels were formed in DMSO, dimethylformamide (DMF), tetrahydrofuran (THF), 2-ethoxyethanol (Cellosolve), and *N*-methyl-2-pyrrolidone (NMP) (Table 1). Mixing the

Table 1. Formation and Temporal Stability of 6 wt % 40PVAc/0.3 wt % BDBA Organogels^a

solvent	40PVAc solubilized?	nature of material	stability ^b
dimethyl sulfoxide	yes	gel	>6 months
dimethylformamide	yes	gel	5 days
tetrahydrofuran	yes ^c	gel	7 days
2-ethoxyethanol	yes ^c	gel	>6 months
<i>N</i> -methyl-2-pyrrolidone	yes	gel	4 h: returned to sol
methanol	yes ^c	gel after incubating at 25 °C overnight	7 days
ethanol	yes ^c	phase separated	
95:5 ethanol/water	yes ^c	gel	30 days
2-propanol	yes ^c	phase separated	
1-propanol	yes ^c	phase separated	
<i>n</i> -butyl acetate	no		
cyclohexanone	no		
acetonitrile	no		
acetone	no		
dichloromethane	yes	no gel; BDBA not soluble	
ethyl acetate	no		

^aRatio of OH_{40PVAc} groups to BDBA molecules (OH/BDBA) is 19:1, where "OH_{40PVAc}" refers to the hydroxyl groups on the *x*PVAc chains. ^bUnless stated otherwise, the stability is the length of time before syneresis could be detected visibly. ^cWith heating at ~55 °C.

solutions resulted in a marked increase in viscosity in less than 1 min. Although an inhomogeneous mixture was formed upon combining 40PVAc and BDBA methanol solutions, the mixture became homogeneous after standing for several hours. Upon mixing 40PVAc and BDBA in ethanol, permanent phase separation occurred; however, a 95:5 ethanol/water solvent system produced a clear, stable gel. The organogels were stable at room temperature in closed vials for various periods: an NMP organogel returned to a sol after approximately 4 h, whereas those organogels that were formed in DMSO, DMF, THF, 2-ethoxyethanol, and methanol exhibited syneresis (visually noted) after longer time periods, ranging from 5 days to several months (Table 1). Photographs of three organogels are shown in Figure 1. Although these gels are listed as "stable" in Table 1 because they did not undergo syneresis, the organogels with DMSO, THF, DMF, *N*-methyl-2-pyrrolidone, and methanol as a liquid became orange over



Figure 1. Gels of 6 wt % 40PVAc/0.3 wt % BDBA in methanol, DMSO, and THF (left to right) 7 days after preparation.

several days. See for example the UV–vis spectra in Figure S1 for a DMSO organogel.

To determine whether the formation of an organogel is due to crosslinking of 40PVAc polymer chains by BDBA, strain (Figure S2) and frequency (Figure 2) sweeps of systems

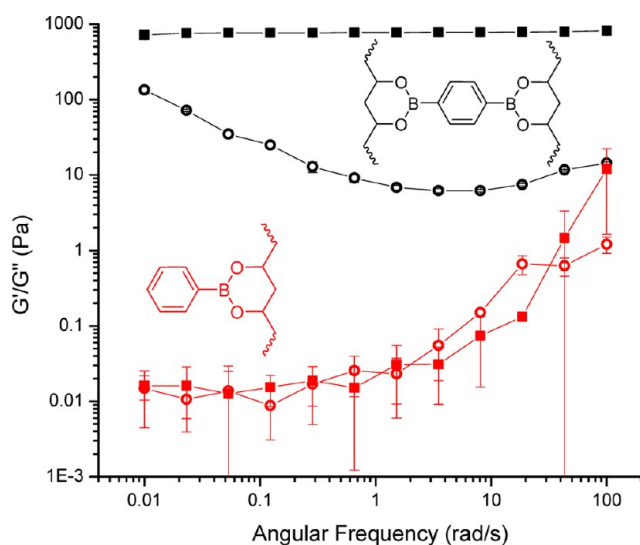


Figure 2. Frequency sweeps (strain of 1%) of 6 wt % 40PVAc and 0.3 wt % BDBA (black) or 0.45 wt % BBA (red) in DMSO. Closed squares and open circles represent G' and G'' , respectively. The OH/BDBA ratio is 19:1 (black), and the ratio for OH_{40PVAc} groups to BBA molecules is 9:1 (red).

consisting of 40PVAc and either BDBA or phenylboronic acid (BBA) were compared. BBA, with only one boronic acid group, can react with the hydroxyl groups of 40PVAc but cannot form crosslinks between polymer chains. The frequency sweep of the 40PVAc/BDBA mixture exhibited a storage modulus, G' , near 1000 Pa and a G' greater than loss modulus, G'' , at all angular frequencies studied. In contrast, a 40PVAc/BBA mixture (with a BBA molar ratio twice that of the 40PVAc/BDBA molar ratio) exhibited small G' and G'' values, a behavior characteristic of a liquid. These results demonstrate the necessity of crosslinking by BDBA to induce gelation.

The frequency sweep of the 40PVAc/BDBA mixture in DMSO (Figure 2) demonstrated that the material was a soft gel with a long relaxation time, as indicated by the approach (without crossing) of G' and G'' at the lowest frequency examined, 0.01 rad/s. Rheology was used to monitor the physical changes that arose from varying the concentrations of 40PVAc and BDBA in DMSO (strain sweeps in Figure S3;

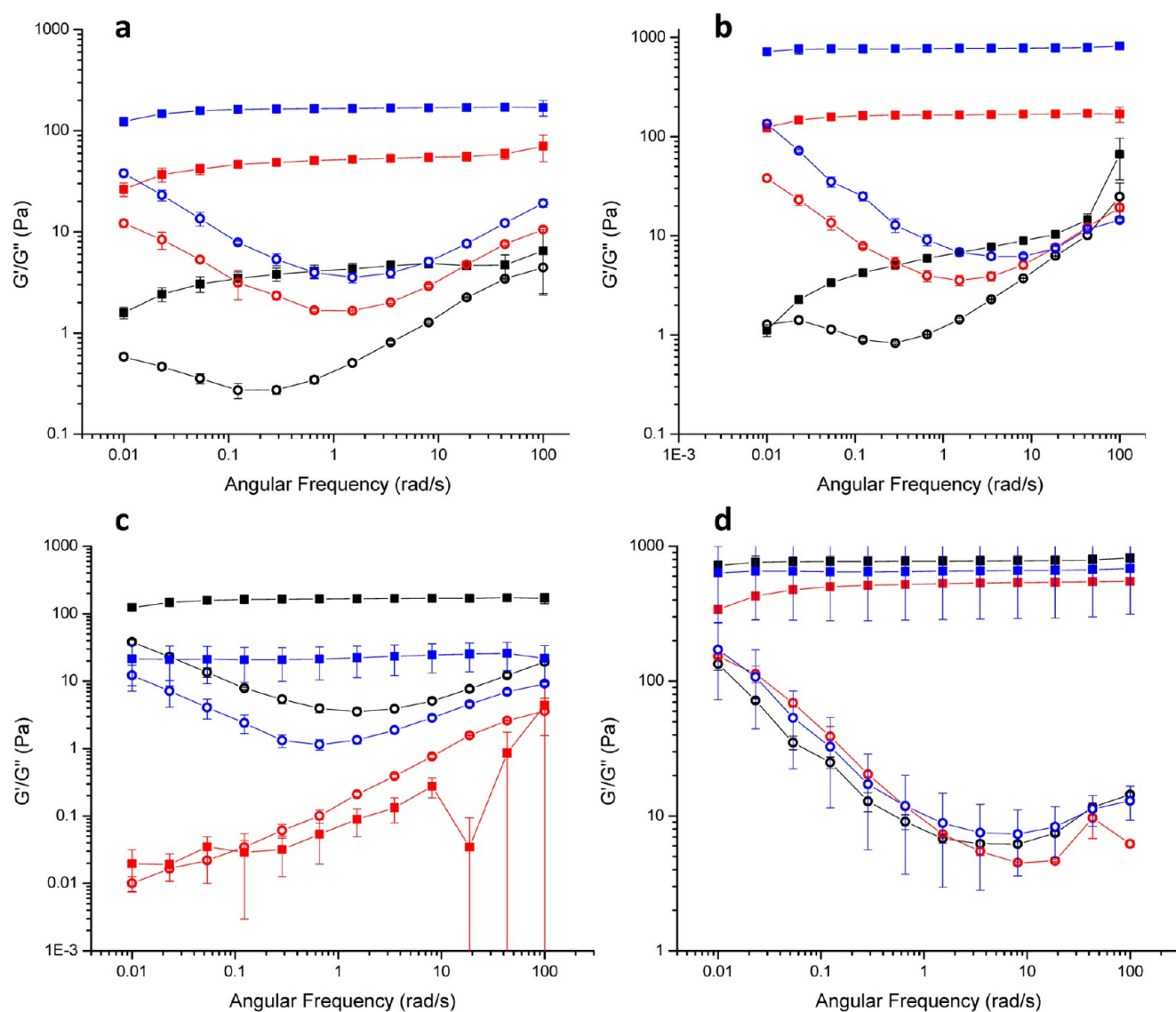


Figure 3. Frequency sweeps (strain of 1%) of (a) 3 wt % (black), 4.5 wt % (red), or 6 wt % (blue) 40PVAc and 0.2 wt % BDBA in DMSO; (b) 6 wt % 40PVAc and 0.15 wt % (black), 0.2 wt % (red), or 0.3 wt % (blue) BDBA in DMSO; (c) 6 wt % 40PVAc and 0.2 wt % BDBA in either DMSO (black), DMF (red), or 2-ethoxyethanol (blue); and (d) 6 wt % 40PVAc and 0.3 wt % BDBA in either DMSO (black), DMF (red), or 2-ethoxyethanol (blue). Closed squares and open circles represent G' and G'' , respectively. The OH/BDBA ratios for each figure are (a) 14:1, 22:1, and 29:1; (b) 38:1, 29:1, and 19:1; (c) 29:1; and (d) 19:1.

frequency sweeps in Figure 3). Increasing the concentration of 40PVAc while maintaining a constant BDBA concentration (Figure 3a) caused an increase in both G' and G'' , and the shape of the curves underwent no significant changes. Increasing the concentration of BDBA while maintaining a constant 40PVAc concentration (Figure 3b) not only caused an increase in G' and G'' , but also appeared to decrease the crossover frequency: the 0.15 wt % BDBA sample exhibited a crossover frequency near 0.01 rad/s, and extrapolation of the moduli to lower angular frequencies for the 0.2 and 0.3 wt % BDBA samples suggested still lower crossover frequencies. These results demonstrate that the viscoelastic properties of the organogels can be tuned easily by varying the concentrations of the polymer and/or crosslinker.

Strain (Figure S3c,d) and frequency sweeps (Figure 3c,d) were performed to compare the rheological properties of organogels in DMSO, DMF, and 2-ethoxyethanol. Figure 3c shows that, although 6 wt % 40PVAc and 0.2 wt % BDBA

mixtures formed viscoelastic materials in DMSO and 2-ethoxyethanol, the DMF sample was a liquid. As expected, the properties of the solvent play an important role in the equilibrium between mono- and diesterified BDBA. By increasing the concentration of BDBA to 0.3 wt %, viscoelastic materials with comparable strain and frequency sweeps were formed in the three solvents (Figures 3d and S3d).

^1H NMR spectroscopy was used to determine the extent of reaction between BDBA and 40PVAc. BDBA in DMSO- d_6 exhibited two signals: one at 8.09 ppm due to the hydroxyl groups and one at 7.71 ppm from the aromatic protons (Figure 4a). Upon addition of a molar excess of $\text{OH}_{40\text{PVAc}}$ groups, the BDBA signals disappeared entirely and were replaced by two broad signals at 7.64 and 7.76 ppm, as well as at least one shoulder at 7.88 ppm (Figure 4b). A similar increase in line width and decrease in signal resolution was apparent through a comparison of a BBA spectrum before (Figure 4c) and after (Figure 4d) addition of a molar excess of $\text{OH}_{40\text{PVAc}}$ groups. To

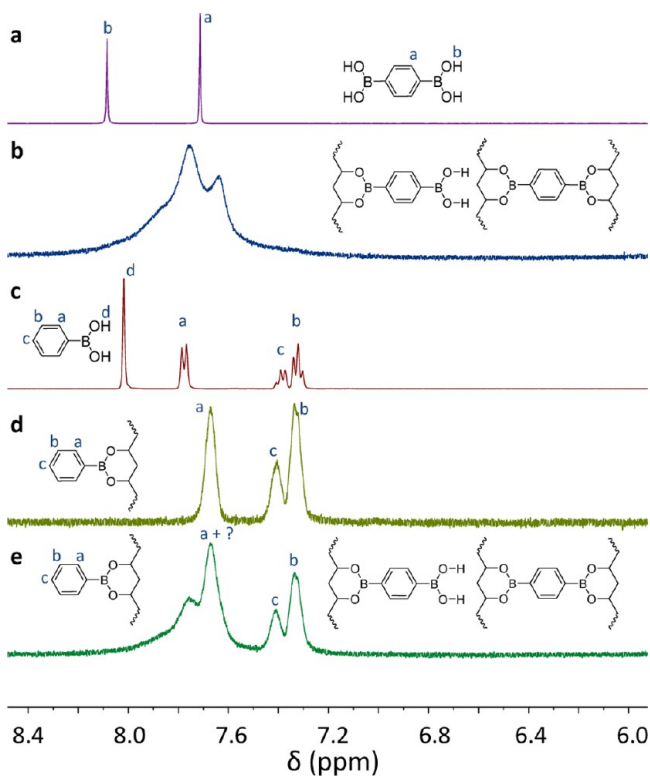


Figure 4. ^1H NMR spectra in $\text{DMSO-}d_6$ of (a) 0.3 wt % BDBA, (b) 8 wt % 40PVAc and 0.2 wt % BDBA, (c) 0.45 wt % BBA, (d) 8 wt % 40PVAc and 0.04 wt % BBA, and (e) 8 wt % 40PVAc, 0.16 wt % BDBA, and 0.04 wt % BBA. All spectra were acquired 24 h after sample preparation, and the signals with the largest intensities in the displayed ppm range were normalized to each other for comparison.

determine whether the viscosity of the medium played a major role in increasing the line width, the differences between the physical properties of gel-state 40PVAc/BDBA (Figure 4b) and solution-state 40PVAc/BBA (Figure 4d) were probed. Specifically, the effect of viscosity on the line widths of BBA was examined by combining BDBA, BBA, and 40PVAc (Figure 4e), so BBA was effectively “trapped” in a viscous medium. The BBA line widths were almost unchanged after the addition of BDBA, suggesting that bulk gelation was not a large contributor to the increase in signal broadness.

The spectral changes were studied further by monitoring the effects of changing concentration (Figures 5 and S5) and temperature (Figure 6). ^1H NMR spectra recorded as a function of 40PVAc concentration (Figure 5) show that the broad signals at 7.64 and 7.76 ppm were independent of each other, as their intensities changed relative to each other, and may represent the mono- and diesterified BDBA species. The presence of both species was not unexpected; mono- and diesterified BDBA species were also detected after reaction with ethylene glycol (Figure S4 and Tables S1 and S2). In some samples, two small doublets at 6.7 and 7.6 ppm increased in intensity with aging; a study tracking the appearance of these peaks (Figure S6) suggests that both the acetate groups and BDBA are necessary for the efficient formation of this species.

In addition, ^1H NMR spectra were recorded at different temperatures to investigate the cause of line width changes noted in the signals associated with BDBA in the presence of 40PVAc. For that purpose, samples of 6 wt % 40PVAc/0.2 wt % BDBA in $\text{DMSO-}d_6$ (for working at temperatures above 25

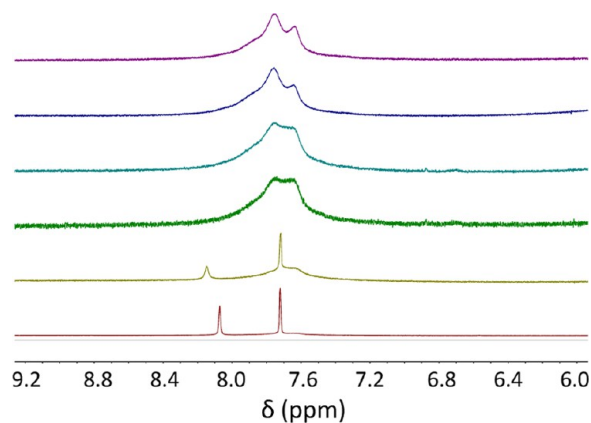


Figure 5. ^1H NMR spectra of 40PVAc/BDBA in $\text{DMSO-}d_6$ at varying amounts and ratios of the gel components at 25 °C: 8.0 wt % (purple), 6.0 wt % (blue), 2.0 wt % (teal), 1.2 wt % (green), 1.1 wt % (yellow), 1.0 wt % (red) 40PVAc and 0.2 wt % BDBA in $\text{DMSO-}d_6$. The OH/BDBA ratios (top to bottom) are 38:1, 29:1, 10:1, 5.7:1, 5.3:1, and 4.8:1.

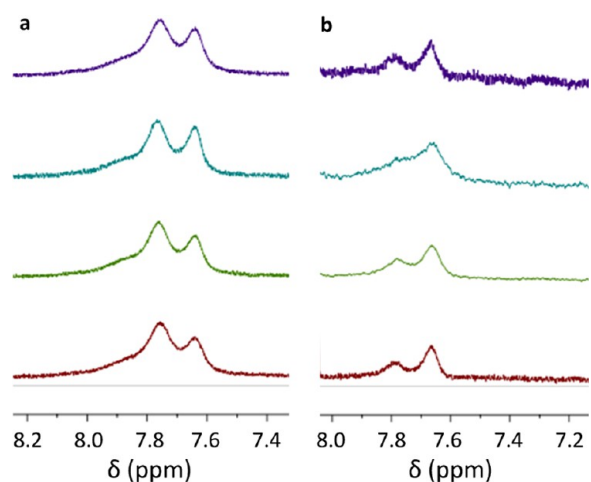


Figure 6. ^1H NMR spectra of 6 wt % 40PVAc/0.2 wt % BDBA organogels as a function of temperature: (a) in $\text{DMSO-}d_6$ at 25 °C (red), 40 °C (green), 55 °C (blue), and returning to 25 °C after heating (purple) and (b) in $\text{methanol-}d_4$ at 25 °C (red), -10 °C (green), -30 °C (blue), and returning to 25 °C after cooling (purple).

°C) and in $\text{methanol-}d_4$ (for working at temperatures below 25 °C) were employed (Figure 6a,b). Because the signals did not narrow as the temperature was lowered and there was no evidence for coalescence at higher temperatures, we infer that the broad line width of BDBA is due primarily to the immobilization of the mono- and diesterified boronate species associated with crosslinking. However, the temperature range explored was relatively small, and different results might be obtained in a different temperature regime or in different solvents.

Changes that occur in the fluorescence of BDBA when it reacts with 40PVAc were also monitored. Upon addition of 40PVAc to a BDBA solution (Figure 7), the wavelength maximum in the excitation spectrum was red-shifted by 4 nm and the emission was blue-shifted very slightly, by ~1 nm. This decrease in the Stokes shift of BDBA can be attributed to the increase in ground-state energy of BDBA upon reaction with 40PVAc. When BDBA reacts with 40PVAc to form boronate esters, it becomes conformationally constrained.

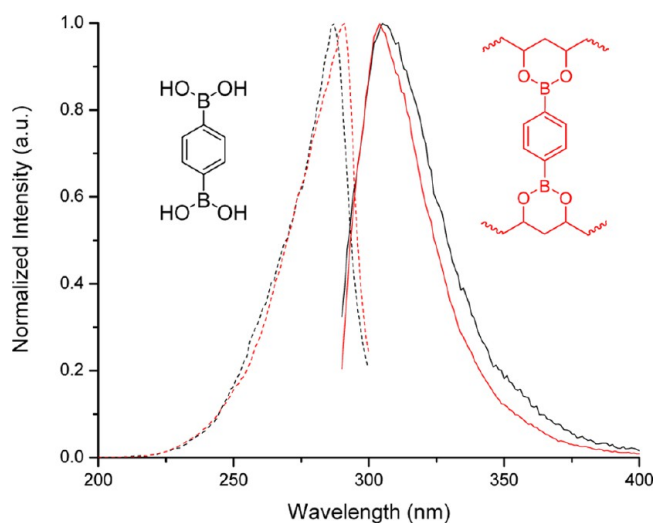


Figure 7. Excitation (dashed; λ_{em} 320 nm) and emission (solid; λ_{exc} 270 nm) spectra of a 0.2 wt % BDBA in methanol solution (black) and a 6 wt % 40PVAc/0.2 wt % BDBA in methanol organogel 2 days after preparation (red).

UV-vis spectroscopy was used to determine whether any BDBA residue remained on an acrylic paint surface after treatment with an organogel. A 6 wt % 40PVAc/0.2 wt % BDBA in 95:5 ethanol/water organogel was placed on a primed canvas coated with acrylic paint. After soaking a sample of the acrylic paint-out in 5 mL of acetonitrile, a UV-vis spectrum of the acetonitrile wash showed no discernible BDBA when compared with the spectrum of an acetonitrile wash from another piece of the acrylic paint sample that had not been treated with the gel (Figure 8). However, the analyses are difficult because the 230 nm peak of BDBA overlaps with a 224 nm peak from the material extracted from the paint-out. In an effort to reduce the size of the 225 nm peak, this residue experiment was repeated on two acrylic paint-outs that had

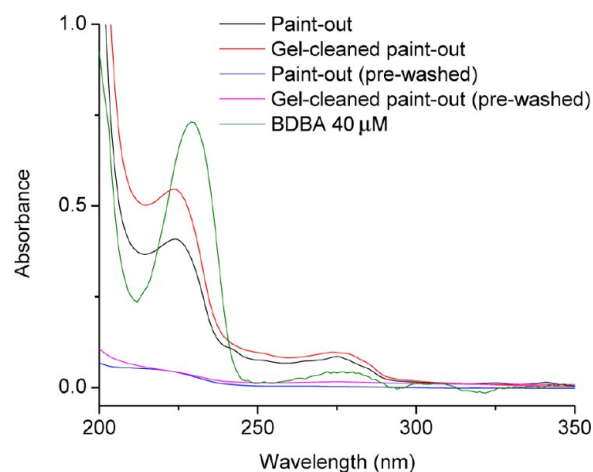


Figure 8. UV-vis spectra of acetonitrile after soaking either an acrylic paint-out (black) or acrylic paint cleaned for 2 min with a 6 wt % 40PVAc/0.2 wt % BDBA in 95:5 ethanol/water organogel (red). A 40 μ M BDBA in acetonitrile solution (green). Because absorbance from components in the paint-out overlap with where BDBA absorbs (λ_{max} of 230 nm), the experiment was repeated on paint-outs that were prewashed with acetonitrile with (pink) and without (blue) gel cleaning.

been prewashed with acetonitrile. BDBA was still not detected on the surface. On the basis of a detection limit study (Figure S7), this method is capable of detecting as little as 3 μ g on a 1 cm^2 area of paint. Note that this study pertains to only one type of painted surface, and different results may be expected when other types of paints and backing materials are employed. Even so, the results presented here indicate that the organogels with BDBA offer important advantages over other methods for limiting residue after gel cleaning: they are peelable and adhere strongly to cellulosic materials, allowing gel residue to be removed efficiently using a tissue or cotton swab.

Selective removal of a surface layer from an object without disturbing the layers below, either chemically or physically, has been and continues to be a challenge for art conservators. Gold and silver leaf-covered objects are especially difficult to treat in this regard: they consist of very thin (micrometer range), delicate sheets of metal foil applied onto surfaces with adhesives. The foil is sometimes coated with varnish, which oxidizes, darkens, and loses transparency with time.

Previously, different types of organo-aqueous gels have been employed to soften and remove varnish when the object was amenable to contact with water.³⁰ Here, we extend the range of surfaces that may be treated to ones with water-sensitive components that lie below the surface coating by using an organogel with no added water. Specifically, a 6 wt % 40PVAc/0.2 wt % BDBA in 2-ethoxyethanol organogel was used to remove aged varnish from a gold leaf surface of a 16th century Italian, gold leaf-gilded reliquary (Figure 9).³¹ The artist adhered the gold leaf with a water-soluble adhesive and then applied a red paint layer that was scratched off (in a technique termed *sgraffito*) to reveal the gold.³² In addition, the surface had been coated with varnish that had oxidized and darkened over time. An ethanol-moistened swab with no gel pretreatment did not remove any of the varnish. To remove the varnish while leaving the red paint and gold leaf unaffected, the 2-ethoxyethanol organogel was placed on the surface for 10 min. After lifting the gel from the surface, the varnish had been softened sufficiently to allow removal of some of it using an ethanol-moistened swab that was rolled gently over the surface. The organogel aided swelling and subsequent removal of varnish and made the linear *sgraffito* pattern visible. Importantly, the red paint and gold were revealed on the surface during the cleaning process (Figure 9f), and there was no evidence of pigment or gold being removed by the gel or the swab.

These 40PVAc/BDBA gels are also useful for cleaning applications in which a high proportion of organic solvent is required for solubilization. A shellac-based varnish layer on the edge of a portrait by Sir Joshua Reynolds (Figure 10) was a challenge to remove using free solvent. However, it could be successfully and safely removed using a gel to soften the varnish. The edge of the painting had been overpainted with a mixture of shellac, drying oils, and pigment (identified using pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS); Figure S8) to match the original background of the portrait.³³ Thus, a 6 wt % 40PVAc/0.3 wt % BDBA in 95:5 ethanol/water gel, covered with a Mylar sheet to slow the evaporation of the solvent, was placed on this layer for 5 min. During that time, the varnish began to soften and swell (Figure 10e-g). After pushing the gel together with a cotton swab (Figure 10h) and carefully using tweezers to remove the bulk of it (without touching the painted surface) (Figure 10i), an ethanol-moistened swab was rolled over the surface. Although



Figure 9. Sixteenth century Italian reliquary coated with gold leaf, paint, and oxidized varnish. (a, b) Object before cleaning. Details of the steps in the treatment procedure using a 6 wt % 40PVAc/0.2 wt % BDBA in 2-ethoxyethanol organogel: (c) before cleaning, (d) organogel placed on surface for 10 min, (e) ethanol-moistened swab rolled across the surface, and (f) after treatment. The blue ovals show the area before and after treatment.

swab cleaning removed only a small portion of the swelled layer (Figure 10j), it was removed effectively with a bamboo skewer to lift the softened varnish from the underlying paint surface (Figure 10k) and brushing the pieces away (Figure 10l) to reveal the paint layer below (Figure 10m).

In a third example, it was found that the x PVAc/borax gel-like materials (i.e., containing added water)^{18,30,34,35} were more efficient than the dry x PVAc/BDBA ones at removing an oil-based layer. During treatment, a conservator found that a nonoriginal drying oil layer on *Portrait of an Old Woman* by Maarten de Vos (1556) (Figure S9) could not be removed with solvents. However, gels were effective. Also, a gelled 50:50 wt %

mixture of ethanol/H₂O (using 80PVAc/borax) was more efficient than a 95:5 wt % mixture of ethanol/H₂O (using 40PVAc/BDBA). This result highlights the importance of developing an extensive repertoire of peelable gels for conservation of objects of cultural heritage and, potentially, other purposes.

CONCLUSIONS

A 40PVAc/BDBA network successfully gelled DMSO, DMF, THF, 2-ethoxyethanol, *N*-methyl-2-pyrrolidone, and methanol in the absence of added water. Generally, the gels were stable for long periods—all except the one incorporating *N*-methyl-2-

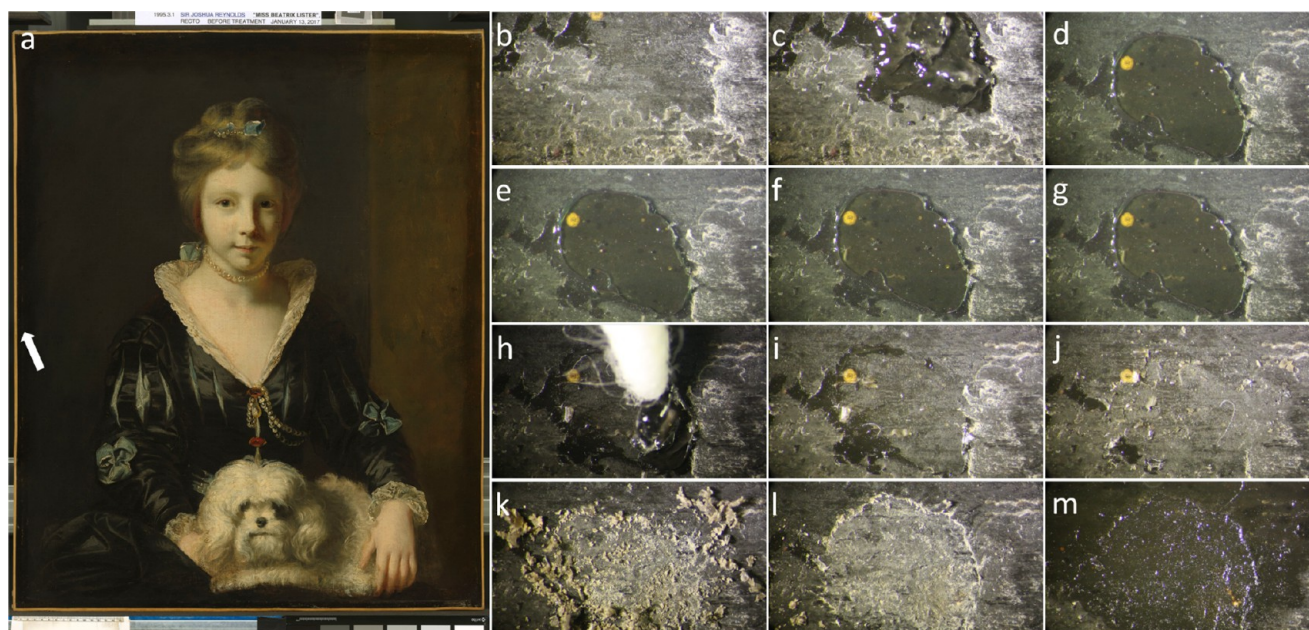


Figure 10. Sir Joshua Reynolds, *Miss Beatrix Lister*, 1765, National Gallery of Art, Washington, DC (a), with a white arrow showing the approximate location to be cleaned using a 6 wt % 40PVAc/0.3 wt % BDBA in 95:5 ethanol/water gel. Stillshots from a video of the cleaning process: (b) before removal of the coating, (c) during gel application, and (d) gel with Mylar cover to prevent solvent evaporation and improve contact. Surface changes can be seen after 3 min (e), 4 min (f), and 4.5 min (g) of gel contact time. The gel was rolled off the surface with a swab (h); before (i) and after (j) rolling an ethanol-moistened swab across the surface. At this point, the shellac had softened sufficiently to scrape it away with a wooden stick (k). The surface below (l) was coated with mineral spirits (m) to mimic how the surface is expected to look after application of fresh varnish.

pyrrolidone were stable for at least 5 days. The 40PVAc/BDBA systems were shown to be soft gels whose stiffness could be tuned by changing the concentrations of the polymer and crosslinker. We hypothesize that the bulk physical properties of the material can also be altered by using x PVAc of a different percent hydrolysis and/or different molecular weight. ^1H NMR spectra showed that BDBA reacted completely if an excess of 40PVAc hydroxyl groups were present, forming both mono- and diesterified boronate species. Fluorescence data indicated that BDBA became more conformationally constrained following its transformation into boronate esters.

The peelability of these materials allowed them to be removed from a surface quickly and easily. This property, in combination with the adhesiveness of the gels to cotton and paper, reduces the probability of leaving detectable residue on a paint surface after treatment. However, the potential for leaving residue must be explored further with a variety of surfaces. Of significant importance is the ability to combine properties of neat solvents, structural characterization techniques (e.g., NMR and fluorescence) at the molecular level, and measurements of viscoelasticity and adhesion on the bulk level to catalog the appropriateness of a gel for a specific cleaning application. Although we have demonstrated already that the x PVAc/BDBA organogels can remove oxidized coatings from delicate surfaces that other cleaning formulations commonly used by conservators did not, additional data to complete the aforementioned “catalog” must be collected and analyzed in future studies. The greater efficacy of gelled solvents than free solvents, demonstrated by the three applications included here, suggests that the gelator may play a chemical role in the mechanism of the cleaning processes in addition to serving as a macroscopic immobilizing matrix for the solvents. The success of the case studies reported here illustrates the potential of these gels to remove a range of materials on delicate surfaces of

objects of value in historical and cultural heritage and, by extension, other types of objects (such as soft plastics). Although in this study gels made using only one x PVAc were investigated, other polymers with diol groups and/or different aromatic boronic acids may yield viscoelastic materials for a range of uses, and such experiments will be conducted. We suspect that these peelable gels may be useful in fields such as drug delivery,³⁶ sensing,³⁷ coatings,³⁸ or consumer goods.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09473.

UV–vis spectra with time, strain sweeps of 40PVAc/BBA and 40PVAc/BDBA in DMSO, strain sweeps of 40PVAc/BDBA in DMSO, DMF, and 2-ethoxyethanol, ^1H NMR spectra of ethylene glycol and BDBA in DMSO- d_6 , ^1H NMR spectra of 40PVAc/BDBA as a function of time and concentration, UV–vis from BDBA residue study, pyro-GC/MS of varnish from *Miss Beatrix Lister* by Sir Joshua Reynolds, cleaning of *Portrait of an Old Woman* by Maarten de Vos (PDF)

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Notes

The authors declare no competing financial interest.

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(32) The reliquary bust was water-gilded over gesso (calcium sulfate dihydrate) and red Armenian bole (hydrated aluminum silicate) with an animal hide glue binder to adhere the gold leaf. Damage to the piece has exposed many of these layers, but the area selected for cleaning appeared to consist of only exposed varnish, red paint, and gold leaf. The goal of the (successful) cleaning test was to remove varnish while leaving the red paint and gold leaf intact.

(33) At some point after its creation, the painting was lined and its original tacking margins (i.e., the portion of canvas that wraps around the stretcher) were flattened and incorporated onto the front of the painting, resulting in an increase in dimensions by approximately 4–5 cm on each side.

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