Soft Matter

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Selective Formation of Organo, Organo-aqueous, and Hydro Gel-like Materials from Partially Hydrolysed Poly(vinyl acetate)s Based on Different Boron-containing Crosslinkers.

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Viscoelastic, gel-like, polymeric dispersions (HVPDs) can be prepared by crosslinking poly-ols with borax or boric acid in water under alkaline conditions. Rheologically similar HVPDs have been prepared in organic liquids containing no water or hydroxylic groups through crosslinking partially or fully hydrolysed poly(vinyl acetate)s with trimethyl borate, boric acid, or borax. The organo-HVPDs are water-sensitive and rheoreversible on exposure to water. They were characterised rheologically and by solution and solid-state ^{11}B NMR spectroscopy. Spectroscopic analyses show the presence of mono- and di-diol crosslinks, as well as non-crosslinked boron species in HVPDs prepared with trimethyl borate or boric acid. The number of crosslinks in organo-HVPDs prepared with borax increased over the course of several days. Results from solution and solid-state ^{11}B NMR spectroscopy are comparable; no solid-like component was detectable. We demonstrate that hydro, organo, or organo-aqueous HVPDs can be obtained from partially hydrolysed poly(vinyl acetate)s by 'tuning' the structure of the boron-based crosslinker.

Introduction

The formation of gel-like[†] highly viscous polymeric dispersions, HVPDs, from crosslinking poly-ols, such as poly(vinyl alcohol) (PVA) or naturally occurring polysaccharides, by boric acid/borate in aqueous media is well documented. Their interesting properties have been exploited for a diverse range of applications, including hydraulic fracturing fluids,[1-4] drug delivery,[5] and surface cleaning

agents for cultural heritage conservation.[6, 7] These viscoelastic materials can be prepared with as much as 97 wt % water content, are pH- and temperature-reversible, self-healing, and environmentally benign. The crosslinks in PVA-borate HVPDs are formed through the intermolecular interaction of two diol moieties with one boron center. Both borate ion and boric acid have been implicated in the crosslink formation step when borax is the added crosslinker;[8] the two scenarios are shown in Scheme 1.

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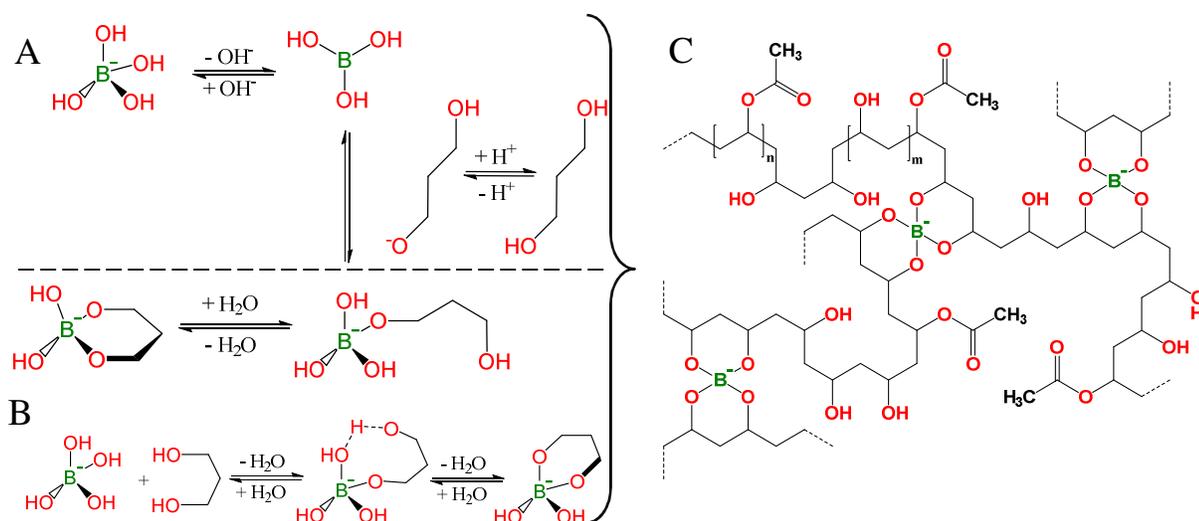
Scheme 1. (A) Monodiol/borate formation proposed by Bishop *et al.*[3] Nucleophilic attack occurs on boric acid only after initial deprotonation of a diol. (B) Scheme proposed by Yamamato *et al.*.[9] The highest reaction rates occur when the diol is fully protonated and borate is the active crosslinking form. (C) Representation of a partially hydrolysed poly(vinyl acetate)/borate HVPD network.

Recently, we demonstrated that poly-ol/borate HVPDs can be prepared in organo-aqueous liquid mixtures from partially hydrolysed poly(vinyl acetate)s (xPVAc where x is the percent of acetate groups that has been hydrolysed).[10] The residual acetate groups on the polymer backbone aid the solubilisation of the polymer in polar organic liquids such as methanol, ethanol, 1- or 2-propanol, methyl pyrrolidone, and dimethyl sulfoxide (DMSO). Because the crosslinking agent, borax, is insoluble in higher alcohols and many other organic solvents, and only sparingly soluble in methanol, approximately 20 wt % of the liquid composition in the HVPDs must be aqueous. These organo-aqueous xPVAc-borax HVPDs have been shown to be effective solvent delivery systems in cultural heritage surface cleaning treatments.[6, 7, 11]

In order to create xPVAc HVPDs with completely non-aqueous liquid components, we explored different formulations, including borax dissolved in methanol and DMSO and other boron-containing molecules as the crosslinking agent. Borax is sufficiently soluble in methanol and DMSO to form organo-HVPDs using partially or fully hydrolysed polymers.[12] Trimethyl borate (TMB), the tri-methyl ester of boric acid, can crosslink partially or fully hydrolysed

poly(vinyl acetate) in aprotic organic liquids. Thus, the liquid component need not contain water. The resulting materials have viscoelastic properties similar to those of borax-crosslinked poly-ols in both aqueous and organo-aqueous mixtures. Unlike typical borax-crosslinked HVPDs, TMB-crosslinked HVPDs revert with time to the solution/sol state upon exposure to small quantities of water or humid air; this liquefaction seems to be non-reversible. The elasticity of the materials can be modulated by the addition of sodium hydride or sodium methoxide, which slows the reversion of the HVPDs to their solution/sol states upon exposure to moisture.

Both the mono-diol and di-diol crosslink signals of the poly-ol borate organo-HVPDs described in this work were detected by ^{11}B NMR spectroscopy. To the best of our knowledge, both types of crosslink peaks have rarely been detected simultaneously in ^{11}B NMR spectra of poly(vinyl alcohol)-borate systems;[13] some reports maintain that the mono-diol species are too short-lived to be observed by NMR spectroscopy, while others have suggested that only the mono-diol and free borate species can be detected in solution state ^{11}B NMR spectroscopy because the di-diol crosslinked boron species are involved in the formation of an extensive, solid-

like, crosslinked network.[1, 3, 8, 13] Here, we report that no solid-like component is detected by solid-state ^{11}B NMR spectroscopy in xPVAc-borate systems.

Results and Discussion

Viscoelastic organo-HVPDs from partially and fully hydrolysed poly(vinyl acetate) in DMSO or DMF can be prepared with borax (BX), boric acid (BA), and trimethyl borate (TMB). HVPDs using BA or TMB crosslinkers are rheoreverisble on exposure to moisture. Non-water-reversible, stable organo-HVPDs were prepared from low-hydrolysis xPVAc and borax in protic organic solvents such as methanol or mixtures of benzyl alcohol and methanol.[6] Trimethyl borate reacts quickly with water to form boric acid and methanol; the pH of the resulting solution, 4.5-5, is typically too acidic for the formation of crosslinks with diols.[18] For this reason, experiments were conducted in aprotic solvents to establish whether TMB can crosslink xPVAc. Although it was initially postulated that the conversion of TMB to BA in these systems causes their rheoreversion, we show that BA can also act as a crosslinker to form moisture-sensitive xPVAx-borate HVPDs. Consequently, the exact cause for the moisture-induced reversion of the HVPDs to solutions/sols is yet to be elucidated.

Poly-ol/borate aqueous systems consist of strain-stiffening transient networks. They exhibit a narrow distribution of relaxation times as a result of complexes with finite lifetimes that exhibit many of the properties of semi-dilute polymer solutions.[19-22] Their response to oscillatory deformation is typical of viscoelastic materials: the loss modulus (G'') is higher than the storage modulus (G') at low-frequency oscillations, and $G' > G''$ at higher frequencies. Thus, the materials display viscous, liquid behaviour and they flow during long observation periods, but behave as gels at short observation times.

HVPDs prepared with 40PVAc and TMB in DMSO or DMF also have finite relaxation times: there is a cross-over of the G' and G'' moduli in oscillatory deformation experiments; the inverse of the frequency at which this cross-over occurs is approximately equal to the relaxation time of the system. Addition of a base, sodium hydride or sodium methoxide, to these materials noticeably slows their reversion to the solution/sol state and enhances their elasticity. The responses of HVPDs prepared from 10 wt % 40PVAc and 15 mol % TMB to oscillatory deformation are shown in Fig. 1. Although the frequencies at which G' and G'' cross do not follow a consistent

trend, the calculated relaxation time tends to become longer as more base is added to the samples. In addition, the plateau values of the G' modulus increase by amounts proportional to the concentration of base (Fig. 2). Both of these observations indicate an increase in the elasticity of the materials caused by the addition of base; the cross-over of G' and G'' is completely absent when 50 mol % methoxide was present (Fig. 1B).
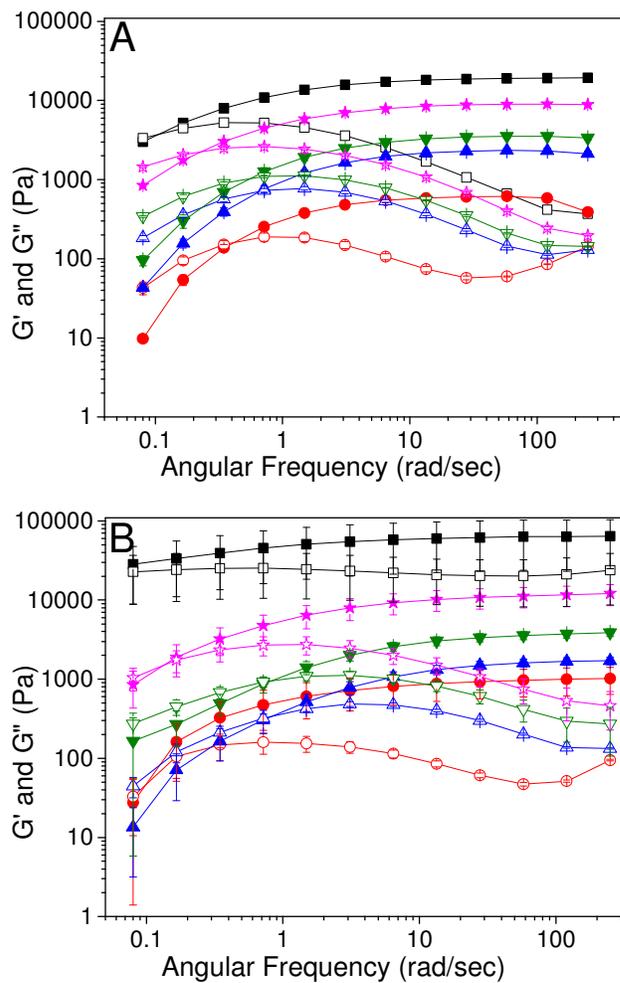

Fig. 1. Angular frequency sweeps of HVPDs prepared with 10 wt % 40PVAc, 15 mol % TMB and (●) 0 mol %, (▲) 5 mol %, (▼) 10 mol %, (★) 25 mol %, and (■) 50 mol % sodium methoxide in (A) DMSO with strain 0.5%, and (B) DMF with strain 10%. G' and G'' are represented by solid squares and open circles, respectively. The vertical bars are standard deviations from 3-5 samples of each HVPD except for the 50 mol % sodium methoxide in DMSO HVPD (for which one trial was made, with strain 0.05%). Addition of sodium methoxide results in HVPDs with higher elasticity.
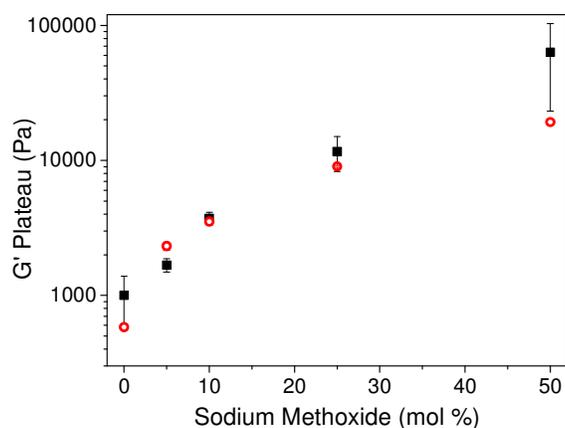
Fig. 2. Plateau values (at 120 rad/sec) of the storage modulus, *G'*, of HVPDs with different amounts of sodium methoxide prepared from 10 wt % 40PVAc and 15 mol % TMB in (○) DMSO or (■) DMF.

If both the polymer and the borax are solubilised, borax can be used as an effective crosslinker of xPVAc or PVA in both aprotic and protic liquids. Because it is sparingly soluble in most organic solvents in which the polymers are soluble, limited amounts of borax can be incorporated into such systems. The small number of immediately formed crosslinks is sufficient to create the HVPD; more crosslinks can form over the course of several days when solid borax is present as demonstrated by the increase in elasticity of HVPDs prepared in methanol (Fig. 3), and the enhancement of the crosslinked boron signal in ^{11}B NMR spectra of an HVPD prepared in DMSO (Fig. 4).
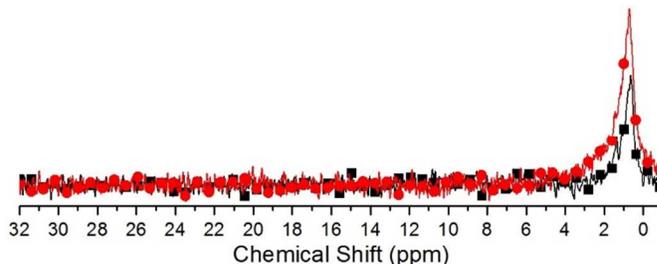

Fig. 4. ^{11}B NMR spectra (recorded under the same instrumental conditions) of 4 wt % poly(vinyl alcohol) and 0.5 wt % borax in DMSO-d_6 shortly after preparation (■) and one day later (●). No free boron peak is detectable in the ~10-17 ppm region.

^{11}B NMR spectroscopy is commonly used to study networks of polyols crosslinked by borate. Of importance for interpreting spectra in this research are tri- and tetra-(alkyloxo)boranes, boric acid, and the borate ion. Along with the six-membered cyclic structures obtained through mono-diol and di-diol complexation with borax, we also consider trimethylborate. Alkyloxy substituents are strong π-donors, shifting the signal of the boron atom upfield.[23] Boric acid is detected at 19.6 ppm in water, while the signal for trimethylborate is found closer to 18 ppm in methanol (*N.B.* trimethylborate is rapidly converted to boric acid in the presence of water).[23] Tetrahedral, negatively charged tetra(alkoxo)boranes are detected further upfield, between 0 and 3 ppm. Based on the work by Bishop *et al.*, the relevant shifts for cyclic trigonal and tetrahedral mono and di-diols are presented in Fig. SI1.[3]
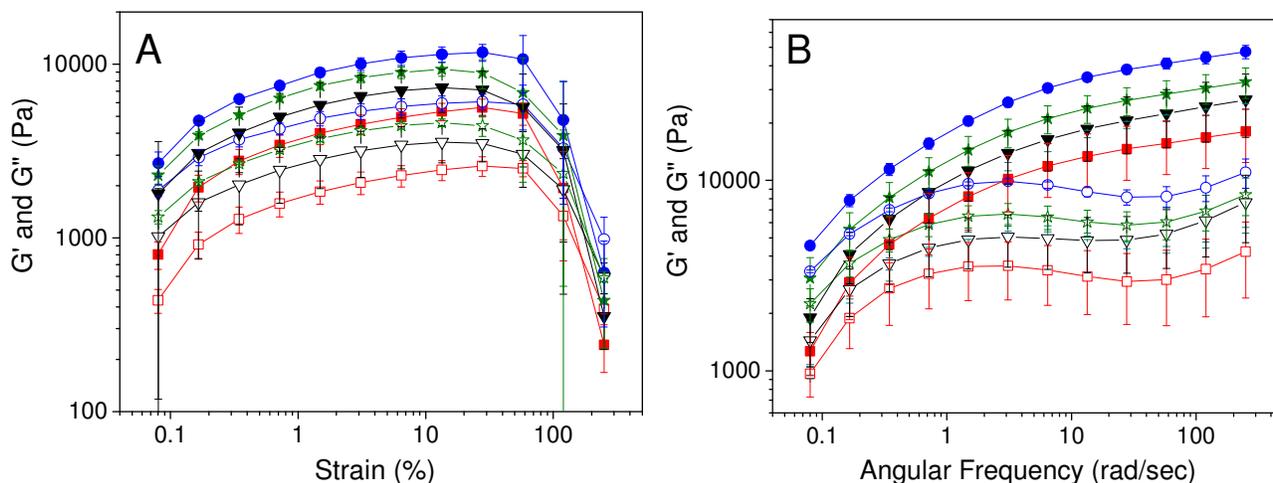

Fig. 3. (A) Log-log strain sweeps (angular frequency = 1 rad/sec), and (B) angular frequency sweeps (strain = 5%) of HVPDs composed of 10 wt % 40PVAc and 1 wt % borax in methanol (■) 1 day, (▼) 4 days, (☆) 6 days, and (●) 11 days after preparation. *G'* and *G"* are represented by solid squares and open circles, respectively.

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As has been extensively reported in the literature, not all of the boron species in aqueous polyol/borax systems participate in crosslinks. The signal from boron not participating in crosslinks appears as a broad peak in the ^{11}B NMR spectra of the materials, typically between 10 and 17 ppm. Its width and position depend on the pH and concentration-dependent averaging of the signals due to chemical exchange between the boric acid (ca. 19 ppm) and borate ions (ca. 1 ppm) signals.[1] Addition of organic liquids to the HVPDs increases the relative number of boron-mediated crosslinks;[10] as the ratio of organic solvent to water in the HVPDs becomes larger, increased crosslinking is favoured. As exemplified by the ^{11}B NMR spectrum in Fig. 4, polyol/borax HVPDs in neat DMSO do not include a detectable peak attributable to free boron; dissolution of borax is limited by the number of crosslinks that can occur. A comparison of the ^{11}B NMR spectra of HVPDs prepared by crosslinking PVA in DMSO with each of the three crosslinkers used in this study reveals that free, non-crosslinked boron is present in the TMB and boric acid systems at the concentrations examined (Fig. 5).
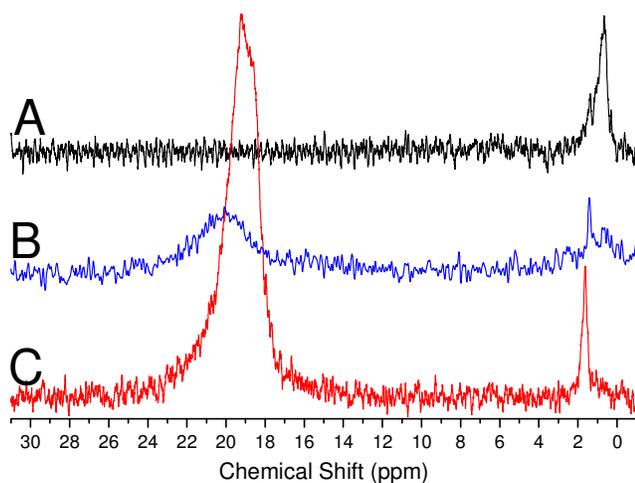

Fig. 5. ^{11}B NMR spectra of 4 wt % poly(vinyl alcohol) in DMSO-d_6 with 0.5 wt % borax (●/A), 1 wt % boric acid (●/B), or 25 mol % TMB (equivalent to 2 wt %) (●/C).

Because the three HVPDs represented in Fig. 5 are formed with different concentrations of the crosslinker, these data are only qualitative. As mentioned, borax is minimally soluble in DMSO;

reducing the concentration of boric acid and TMB to 0.5 wt % does not result in HVPD formation. The crosslinker concentrations chosen were the lowest necessary for HVPD formation and ^{11}B NMR detection.

Two distinct peaks in the 'crosslinked boron' region are present in the spectra, at 0-1 ppm and at 1-2 ppm, corresponding to the di-diol- and mono-diol/borate moieties, respectively. Although the chemical shifts for the borate esterfied mono-diol and di-diol species have been assigned and reported for low molecular weight diols[1] and some naturally occurring polymers, we have found only one report of these two species being observed in the ^{11}B NMR spectra of an xPVAc- or PVA-borate system.[13]

The spectrum of PVA crosslinked with TMB in Fig. 5 shows only what appears to be mono-diol crosslinks, though this is not necessarily representative of all HVPDs prepared with TMB. Both di-diol and mono-diol crosslinks can be observed in the ^{11}B NMR spectrum of a 40PVAc HVPD prepared with different concentrations of TMB (Fig. 6). To confirm that this signal is not the result of an interaction between TMB and the residual acetate groups on 40PVAc, the spectra of poly(vinyl acetate) mixed with each of the three crosslinkers in DMSO were recorded (Fig. 7). No increase in the viscosity of these mixtures was noted, and the signal from a crosslinked boron species is apparent in the spectra.
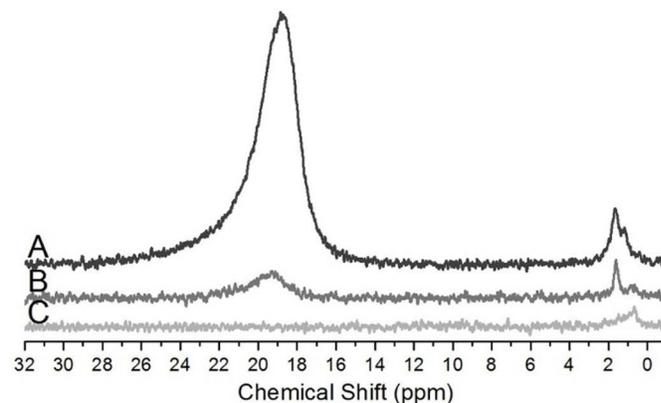

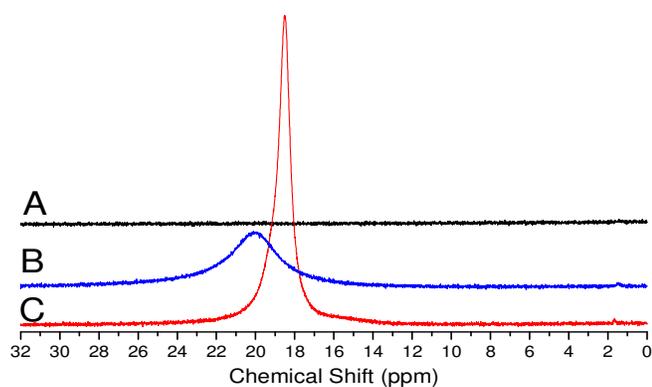Fig. 6. ^{11}B NMR spectra of 10 wt % 40PVAc in DMSO-d_6 with 10 (●/C), 25 (●/B), and 50 mol % TMB (●/A).

Fig. 7. ^{11}B NMR spectra of 5 wt % poly(vinyl acetate) in DMSO-d_6 with 0.5 wt % borax (A), 1 wt % boric acid (B), or 50 mol % TMB (C).Very small peaks can be seen in the crosslinked boron region, likely from a small amount of hydroxyl groups on the polymer side chains.

Solid-state ^{11}B NMR spectra of HVPDs prepared with TMB were recorded after rheoreversion (due to exposure to atmospheric moisture) and in the HVPD state with added sodium hydride. As confirmed by oscillatory deformation experiments and visual observations, HVPDs prepared with sodium methoxide (Fig. 1) or sodium hydride were much more elastic than those without, due largely to increased crosslinking (Fig. 8). The spectra of HVPDs prepared with TMB and sodium hydride base show broad peaks between 1-3 ppm which probably include both the mono-diol and di-diol borate species. A TMB-crosslinked HVPD prepared without base and examined by solid state NMR in the process of rheoreversion appears to have a predominance of mono-diol borate interactions, as well as both boric acid and TMB. In this sample, the typical 'free' and 'crosslinked' boron peaks are noted, with chemical shifts and integration ratios similar to those found in the NMR spectra that probe the 'liquid' components. These studies confirm the dynamic nature of the polyol/borate networks, and also demonstrate that NMR spectra from solution state studies provide an accurate picture of the boron populations.
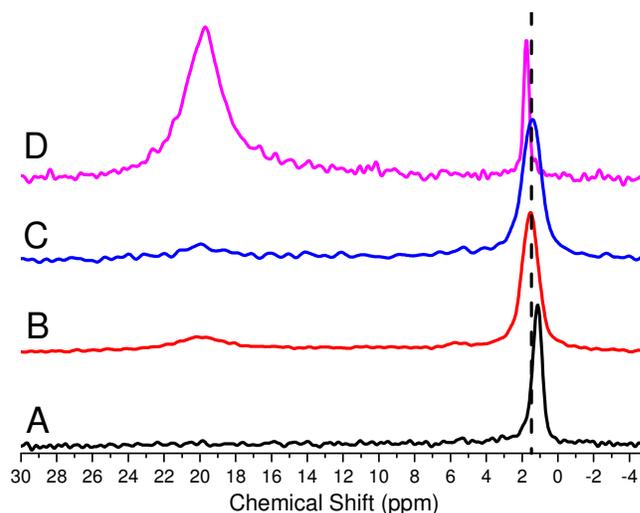

Fig. 8. Solid-state MAS ^{11}B NMR spectra of HVPDs in DMSO prepared from 10 wt % 40PVAc with 0.5 wt % (~10 mol %) borax (A), 10 wt % 40PVAc with 50 mol % TMB with 25 mol % NaH (B), 10 wt % 40PVAc with 50 mol % TMB with 50 mol % NaH (C), and 10 wt % 40PVAc with 50 mol % TMB in the process of liquefaction (D). Spectra are referenced against 0.1 M boric acid in water.

Materials and Methods

Partially hydrolysed poly(vinyl acetate)s were obtained from the Kuraray Co., Ltd. The polymers were cleaned and characterised as described elsewhere.[14] Poly(vinyl acetate) (Aldrich, MW 100,000, beads), trimethyl borate (TMB, Aldrich, >98%), sodium tetraborate decahydrate (borax; Fluka, >99.5%), sodium hydride (Acros, pure, anhydrous powder), sodium methoxide (Sigma-Aldrich, 95% powder), methanol (Fisher, HPLC grade), dimethyl sulfoxide, (DMSO, Alfa Aesar, 99.9+%), dimethylformamide (DMF, Fisher, analytical grade), DMSO-d_6, methanol-d_6 (Cambridge Isotope Laboratories, Inc., all 99.9% D), and boron trifluoride etherate (Aldrich, synthesis grade) were used as received. Boric acid was prepared by adding excess water to trimethyl borate; the resulting white precipitate was filtered and dried under nitrogen.[15]

To prepare trimethyl borate-crosslinked HVPDs, the polymer (concentrations are listed in figure captions) was dissolved in DMSO or DMF in a closed glass vial; solvents were not dried prior to polymer addition. Sodium hydride or sodium methoxide was added to the polymer solution at room temperature, and it was 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 the vial was quickly capped to avoid reversion of the HVPD to a solution/sol. Trimethyl borate and base concentrations were varied as a molar percentage relative to the calculated moles of hydroxyl groups on the polymer chains; for example, "5 mol % TMB" represents a concentration equivalent to 5 % of the molar concentration of hydroxyl groups in 10 wt % of 40PVAc. Although >5 mol % sodium methoxide could not be dissolved completely in DMSO and DMF, it could be dispersed more homogeneously than NaH. HVPDs containing more than 5 mol % of sodium methoxide were slightly yellow, despite the base being added at room temperature. Systems crosslinked with boric acid or borax were prepared by dissolving the crosslinker in 20 wt % of the liquid composition in a separate vial, and dissolving the polymer in the remaining 80 wt % of liquid. The two solutions were then mixed together vigorously with a spatula until a HVPD or viscous liquid formed.

Rheological measurements were made on an Anton Paar Physica MCR 301 stress-controlled rheometer using a 25 mm diameter cone-plate (1° cone angle) tool. Angular frequency sweeps were performed in the linear viscoelastic region based on strain sweeps obtained at 1 rad/sec frequency. Data collection was not initiated until the sample had equilibrated, as indicated by its exerting 0 N of force on the top plate. Equilibration typically occurred after 10-15 minutes for DMSO and DMF HVPDs prepared with 50 % sodium methoxide. Data were collected and analysed using Rheoplus/32 Service V3.10 software. To prevent liquefaction of the samples due to exposure to atmospheric moisture, rheological investigations of the HVPDs were carried out under continuous nitrogen gas flow using a Peltier hood on the rheometer which covers the sample area and creates a chamber into which the N_2 gas can be directed. DMSO and DMF were assumed to have negligible evaporation during the course of the experiments because the experiments required only 10-20 minutes, the boiling point of both solvents is >150 ℃, and the samples were between plates separated by only 0.05 mm.

Liquid-phase ^{11}B NMR spectroscopy was carried out on a Bruker 400 UltraShield Avance III HD spectrometer at 128.3 MHz in 5 mm diameter glass NMR tubes; using quartz tubes did not decrease substantially the background signal. The DEPTH composite pulse sequence (a 90° pulse followed by two 180° pulses)[16] was used for all samples; 64 FIDs were averaged and analysed with MestReNova software to obtain the spectra.

Solid state ^{11}B NMR spectroscopy was carried out on a 9.4 T Bruker Avance 400 spectrometer using a 4 mm double resonance magic angle spinning (MAS) probe. Samples were sealed in HR MAS Kel-F inserts and placed inside 4 mm zirconium rotors that were spun at 5 kHz. Spectra were acquired using a rotor synchronised Hahn echo with a radio frequency (RF) amplitude of 135 kHz and a relaxation delay of 0.5 s. All spectra were acquired with hard (non-scaled) RF pulses. To verify that no solid components are present in the samples, spectra were also acquired with the pulse length scaled by a factor of $I+1/2$, with spin of $I=3/2$ for [11]B (for better excitation of species with non-negligible quadrupolar couplings), as well as ^{1}H decoupling using a SPINAL-64 decoupling sequence[17] with an RF amplitude of 70 kHz. No additional components were detected. Furthermore, Hahn echo measurements performed on static samples with a short echo delay of 10 μs did not result in significant signal broadening when compared with the MAS measurements, indicating that the signals are not broadened by anisotropic interactions.

Conclusions

The addition of any of the three boron-based crosslinkers, borax, boric acid, or trimethyl borate, to solutions of fully or partially hydrolysed poly(vinyl acetate)s in aprotic solvents results in the formation of gel-like materials whose rheological properties are like those of the corresponding hydro-HVPDs. Borax-crosslinked organo-HVPDs in protic organic solvents can be prepared in those cases where the polymer is solubilised. Regardless of the crosslinker or the solvent composition employed, the same crosslink structure, a negatively charged, tetrahedral boron center bonded to one or two diols, is indicated by ^{11}B NMR spectroscopic studies.

In the presence of small amounts of added water (and it should be noted that all xPVAc polymers contain a small amount of water), HVPDs prepared with boric acid or trimethyl borate revert to their solution/sol states. As a consequence of the labile and dynamic nature of all of the crosslinks in boron-xPVAc HVPDs, it is likely that trimethyl borate is converted to boric acid, which preferentially remains unbound to the diols in the presence of water. Addition of a base, sodium hydride or sodium methoxide, to these materials aids the retention of the HVPD state in the presence of water, and also enhances HVPD elasticity by encouraging boron-diol interactions and crosslink formation. Regardless, no 'solid-like' network containing boron was detected by solid-state MAS ^{11}B NMR. Boron-crosslinked poly-ol organo-HVPDs remain dynamic, malleable, and self-healing even when highly crosslinked. Their dynamic nature is

further evidenced by their eventual reversion to the solution/sol state when exposed to moisture.

In summary, the results reported here provide new insights into the manner by which partially hydrolysed poly(vinyl acetate)s are crosslinked by boron-containing species and the properties of the materials so produced. They also suggest possible future research, perhaps with different trialkyl borates as crosslinkers, to produce organo-HVPDs of partially hydrolysed poly(vinyl acetate)s with greater resistance to hydrolysis.

Acknowledgements

Notes and references

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† xPVAc-borate materials are not 'true gels' in the rheological sense, i.e., their G' and G" moduli cross-over during the course of an angular frequency sweep. Although the systems are commonly referred to as 'gels' in the literature, we feel that the materials are better defined as highly viscous polymeric dispersions, HVPDs.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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+ POLY(VINYL ALCOHOL)

ORGANOGEL
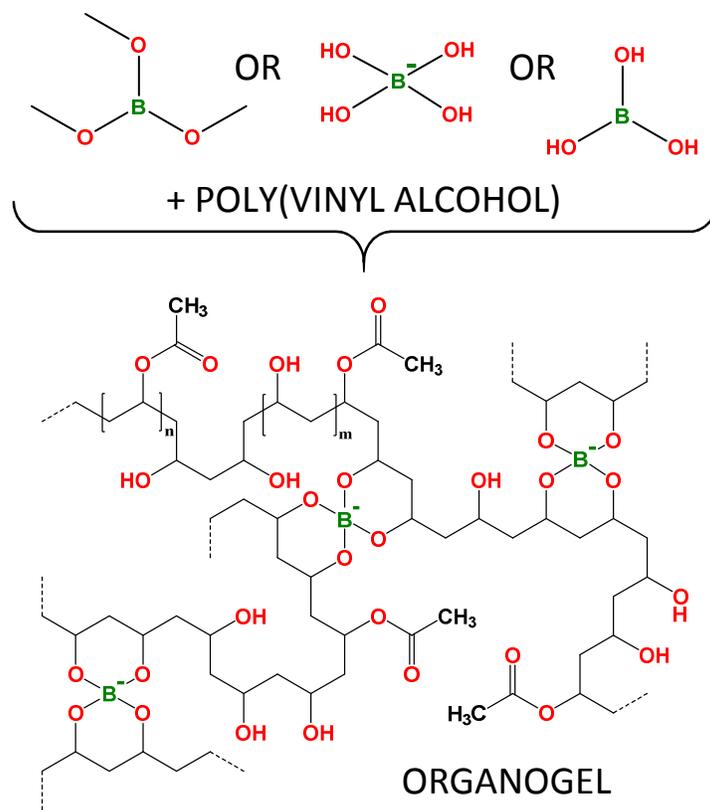
Gel-like, highly viscous polymeric dispersions from borate-crosslinked poly-ols can be prepared entirely with organic liquids and have viscoelastic properties similar to the equivalent materials prepared in aqueous or organo-aqueous solutions.