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Thermoreversible Supramacromolecular Ion Gels via Hydrogen Bonding

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ABSTRACT: We report the thermoreversible viscoelastic properties of a supramolecular ion gel. Two building blocks were used to form “supramacromolecules”. An ABA triblock copolymer ($M_n = 50\,000$, poly(2-vinylpyridine)-*b*-poly(ethyl acrylate)-*b*-poly(2-vinylpyridine)) (P2VP−PEA−P2VP), with a mole ratio of 0.1/0.8/0.1 as a telechelic polymer, and a poly(4-hydroxystyrene) (PHS) homopolymer, with $M_n = 6600$ as a connector, form a physical gel via hydrogen bonding between P2VP and PHS. The thermally stable, hydrophobic ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI) provided a good solvent medium for PEA from room temperature up to at least 160 °C. A solution containing 10 wt % P2VP−PEA−P2VP and 4% PHS was a liquid at elevated temperatures but on cooling formed a network at 141.5 °C. Dynamic shear moduli obtained as a function of frequency at various temperatures from 30 to 160 °C could be superposed to form excellent master curves, with a distinct plateau modulus extending over more than 11 orders of magnitude in frequency. The longest relaxation time inferred from the time−temperature superposition shift factors showed a similar 11 order of magnitude increase on cooling. This remarkable temperature sensitivity of the supramacromolecular ion gel is attributed to the formation of multiple hydrogen bonds between a given P2VP block and PHS cross-linker. A hydrogen bond energy of 13 kJ/mol was estimated from temperature-dependent FTIR measurements, and a straightforward analysis yielded an estimate of the number of hydrogen bonds per P2VP block as a function of temperature. This system is distinct from other supramolecular hydrogen-bonded polymers, and from hydrophobically modified associating polymers, in that below the gelation temperature the number of physical cross-links is independent of temperature, but the strength of each association, namely, the number of active hydrogen bonds within a particular cross-link site, increases strongly on cooling.

Introduction

The supramolecular concept has attracted increasing attention in macromolecular science, as one can design new supramolecular architectures with interesting morphologies or physical properties derived from noncovalent bonding, such as nanostructure switching with temperature and strongly temperature-dependent viscoelasticity. There are many illustrations of the formation of supramolecular polymers via hydrogen bonding or metal coordination.[1−10] For example, Stadler et al. studied hydrogen-bonded telechelic polyisobutylene, which showed temperature-dependent viscoelastic properties.[1] More recently, Meijer and Sijbesma et al. have studied supramolecular polymers from telechelic polymers with quadruple hydrogen-bonding units.[2]

Supramolecular polymers composed of telechelic polymers are simple model systems that can show markedly different behavior from nonmodified polymers. However, there are some limitations to construct thermosensitive supramolecular polymers in this manner. One limitation is the choice of media for supramolecular polymers. Since normal organic solvents are volatile and have relatively low boiling points, thermosensitive supramolecular polymers have mainly been prepared in bulk. Hence, component polymers with low glass transition temperatures and relatively low molecular weights (usually less than 5000) have been used.[1,2,5] Another limitation is the need for carefully controlled end-functionality,[2,4−6,8,10] which can present a synthetic challenge. More fundamentally, end-to-end association of telechelic polymers is a step-growth process, and thus high degree of polymerization supramolecular polymers are very hard to achieve.

Here we present the temperature-controlled formation of supramolecular polymers in an ionic liquid. Two polymer building blocks were used: an ABA triblock copolymer, with poly(2-vinylpyridine) (P2VP) end blocks and poly(ethyl acrylate) (PEA) as the fully ionic-liquid-soluble midblock, and a poly(4-hydroxystyrene) (PHS) homopolymer. The P2VP and PHS could interact via hydrogen bonding in an ionic liquid,[9,11−14] leading to the formation of a “supramacromolecule”. This term is an appropriate description[10,15] because the supramolecular polymers are constructed exclusively by macromolecules (molecular weight >6000). The ionic liquid medium is chosen, in part, because it remains liquid over a much wider temperature range than either water or common organic solvents. Ionic liquids (ILs) display a combination of attractive properties such as nonvolatility, nonflammability, and thermal stability.[16−21] Ionic liquids have been studied as useful media for polymerization in macromolecular science.[22,23] More recently, ionic liquids have been studied as solvents for micellization and gelation by using block copolymers.[24−28] The term “ion gel” has been employed to describe a polymeric network swollen with an ionic liquid.[29] Ion gels are solids, but they can retain the high ionic conductivity of the ionic liquid and as such are appealing in a number of applications, including actuators, gas separation membranes, polymer electrolytes, and gate dielectrics in organic thin film transistors.[30−33] The work reported here also provides a new route to thermoreversible ion gels, which we term supramacromolecular ion gels, chemical composites composed of supramacromolecules in an ionic liquid.

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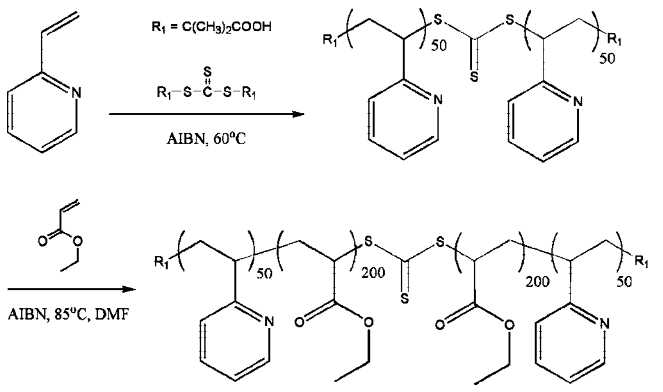
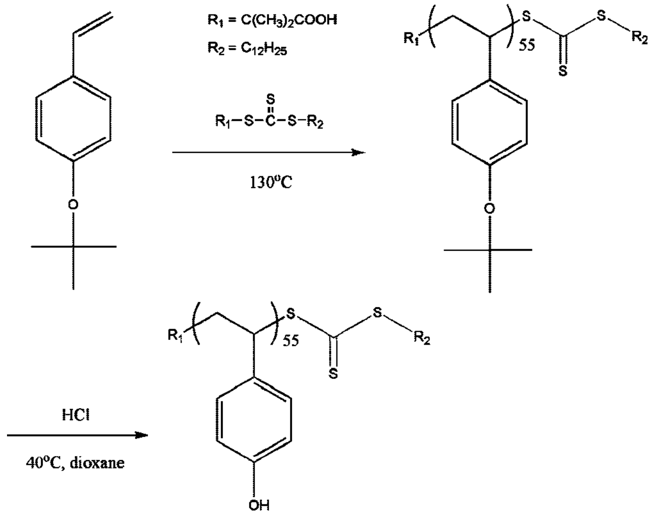
Scheme 1



Scheme 2



Experimental Section

Synthesis of Poly(2-vinylpyridine)-*b*-poly(ethyl acrylate)-*b*-poly(2-vinylpyridine) (P2VP–PEA–P2VP) Triblock Copolymer. P2VP–PEA–P2VP was synthesized via reversible addition–fragmentation chain transfer (RAFT) polymerization (Scheme 1).[34–36] The bifunctional chain transfer agent (CTA) (*S*,*S*′-bis(α,α″-dimethyl-α″-acetic acid) trithiocarbonate) was synthesized as in ref 35. Monomers were purified by passing through an aluminum oxide column before use. Purified 2-vinylpyridine (9.75 g, 0.0928 mol) was polymerized in bulk at 60 °C for 6 h with AIBN (26 mg, 0.155 mmol) and a bifunctional CTA (0.219 g, 0.775 mmol) as the first step. After termination with liquid nitrogen, P2VP-macro-CTA was purified with three reprecipitations into hexanes (M_n = 10 000, PDI = 1.09). The monomer conversion was determined to be 85 mol % by ^{1}H NMR spectroscopy on the crude solution. Then, purified ethyl acrylate (8.19 g, 0.0819 mol) was polymerized at 85 °C in DMF (9 mL) for 39 h with AIBN (2.4 mg, 0.014 mmol) from the P2VP-macro-CTA (1.5 g, 0.15 mmol). Since the macro-CTA has a CTA unit in the middle of the P2VP polymer chain, ethyl acrylate was polymerized from the middle of the P2VP polymer chain. After termination with liquid nitrogen, P2VP–PEA–P2VP was obtained and purified with multiple reprecipitations into hexanes. The monomer conversion was determined to be 70 mol % by ^{1}H NMR spectroscopy on the crude solution.

Synthesis of Poly(4-hydroxystyrene) (PHS) Homopolymer. 4-*tert*-Butoxystyrene used in polymerization was purified by passing through an aluminum oxide column before use. This purified 4-*tert*-butoxystyrene (tBOS, 18.7 g, 0.106 mol) was polymerized in bulk at 130 °C for 9 h with a monofunctional CTA[35] (*S*-1-dodecyl-*S*′-(α,α′-dimethyl-α″-acetic acid) trithiocarbonate, 0.485 g, 1.33 mmol) via RAFT polymerization. After termination with liquid nitrogen and the following reprecipitation of PtBOS homopolymer into MeOH with a small quantity of water, the deprotection of the *tert*-butyl group was performed by adding an excess of hydrochloric acid to a 1,4-dioxane solution of PtBOS at 40 °C for 12 h. PHS homopolymer was collected and dried in vacuo after precipitating the solution into a mixture of water and methanol. The conversion was estimated by ^{1}H NMR and found to be almost 100%.

Characterization. The obtained polymers were characterized by size exclusion chromatography (SEC) and ^{1}H NMR spectroscopy. SEC was performed to determine the polydispersity indices (PDIs) of the polymers by using an Alltech 426 HPLC pump combined with three Phenogel columns (Phenomenex) and DAWN DSP interferometric reflectometer (Wyatt Technology Corp.). Tetrahydrofuran (THF) with 1 vol % tetramethylethylenediamine was used as the eluent. The flow rate was 1 mL/min. PDIs of polymers were estimated by using calibration curves based on polystyrene standards. Molecular weights of PHS and P2VP homopolymers were determined by ^{1}H NMR spectroscopy (Varian), by comparing the integrals of peaks at 4.5–4.9 ppm from one proton or two protons at the end of the polymer adjacent to the CTA residue (S–C(=S)–S) with the integral of the peaks for the backbone. ^{1}H NMR was also used to measure the mole fractions in the P2VP–PEA–P2VP triblock copolymer. The solvent used for the measurements of P2VP homopolymer, P2VP–PEA–P2VP triblock copolymer, and PtBOS homopolymer was deuterated chloroform ($CDCl_3$), while the solvent for PHS was a 1:1 mixture of $CDCl_3$ and DMSO-d_6 to confirm the proton of hydroxyl group. The total number-average molecular weight, polydispersity index, and mole ratio of P2VP–PEA–P2VP were determined to be 50 000, 1.6, and 0.10/0.80/0.10, respectively (see Figures S1 and S3). For the poly(4-hydroxystyrene) (PHS) homopolymer the number-average molecular weight and PDI were determined to be 6600 and 1.09, respectively (see Figures S2 and S4). Although the PDI of the triblock copolymer is comparatively large, it was established that there is very little P2VP precursor in the triblock copolymer sample, as judged from SEC (Figure S1). The precursor of the triblock copolymer, P2VP, had a small PDI (1.09) as well; therefore, the comparatively broad PDI of the whole triblock copolymer resides in the PEA block and does not substantially affect the association by hydrogen bonding.

Preparation of a Supramacromolecular Ion Gel. The IL used in this study is 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMITFSI), one of the more promising ILs for applications; it is hydrophobic and stable at high temperatures.[16] The synthesis of EMITFSI was achieved following earlier reports.[16,18] An IL solution of the blend of P2VP–PEA–P2VP/PHS was prepared with a weight ratio of P2VP–PEA–P2VP/PHS/IL as 10/4/90 (the mole ratio of P2VP–PEA–P2VP:PHS is 1:3) using THF as a cosolvent. After the complete removal of THF by drying in vacuo at 110 °C, the IL solution appeared transparent, homogeneous, and gel-like at room temperature.

Rheology and Spectroscopy. Oscillatory shear measurements were performed on an ARES rheometer (TA Instruments). Dynamic temperature ramp tests were run from 160 to 30 °C at a ramp rate of 1 °C/min, a strain of 3%, and a frequency of 0.3 rad/s. Dynamic frequency sweeps were also obtained at 10 deg intervals from 160 to 30 °C at a strain of 3%. To confirm hydrogen bonding between P2VP–PEA–P2VP and PHS, infrared absorption spectra were taken on a Nicolet Series II Magna-IR System 750 FTIR with Nic-Plan IR microscope with transmitted, reflected, and attenuated total reflectance (ATR) objectives. Spectra were measured at 25 deg intervals from 200 to 25 °C.

Results

Oscillatory Shear Measurements of a Supramacromolecular Ion Gel. Figure 1 shows a dynamic temperature ramp test. At high temperatures, the storage modulus G' is less than the loss modulus G'', and the solution shows liquidlike behavior. Then, G' and G'' intersect at 141.5 °C, and at all lower temperatures $G' > G''$, with G' remarkably constant. Therefore, the gel point is taken to be 141.5 °C. Dynamic frequency sweeps were also obtained at 10 deg intervals from 160 to 30 °C.

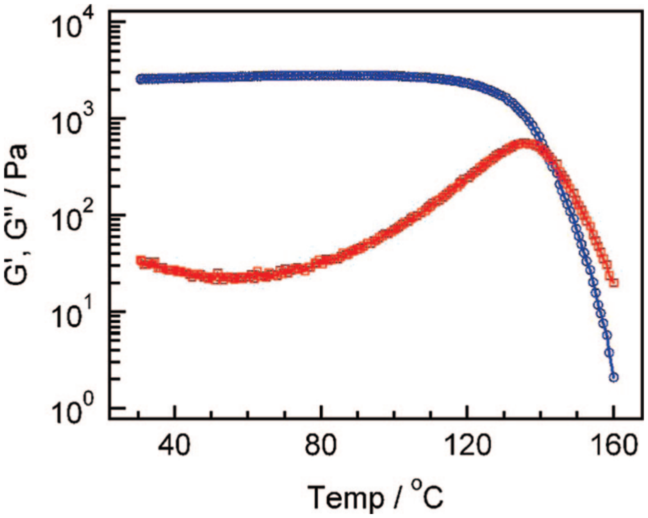


Figure 1. Dynamic moduli G' (blue circles) and G'' (red squares) at 0.3 rad/s and a cooling rate of 1 °C/min and a strain of 3%.

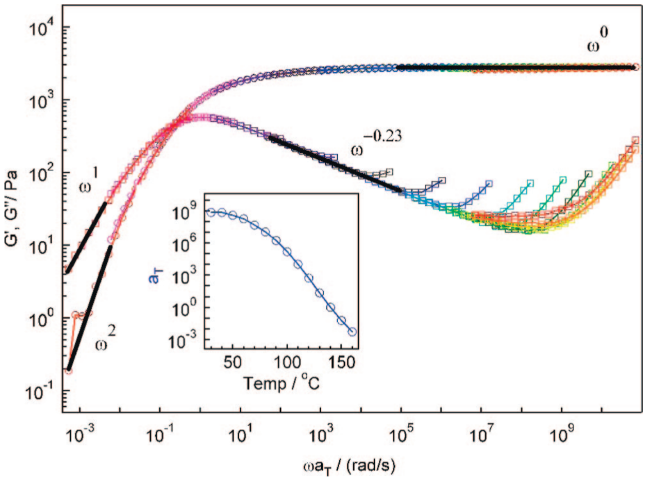


Figure 2. Time−temperature superposition master curves of G' and G'' obtained every 10 °C from 160 to 30 °C, with a reference temperature of 140 °C. The circles are G' and the squares are G''. The color for each plot is as follows: The right red plots are at 30 °C, orange for 40 °C, yellow for 50 °C, yellow-green for 60 °C, dark green for 70 °C, light green for 80 °C, light blue for 90 °C, blue for 100 °C, dark blue for 110 °C, gray for 120 °C, purple for 130 °C, red-purple for 140 °C, pink for 150 °C, and light red for 160 °C. The shift factors are plotted in the inset. The solid line in the inset is just a guide for the eye.

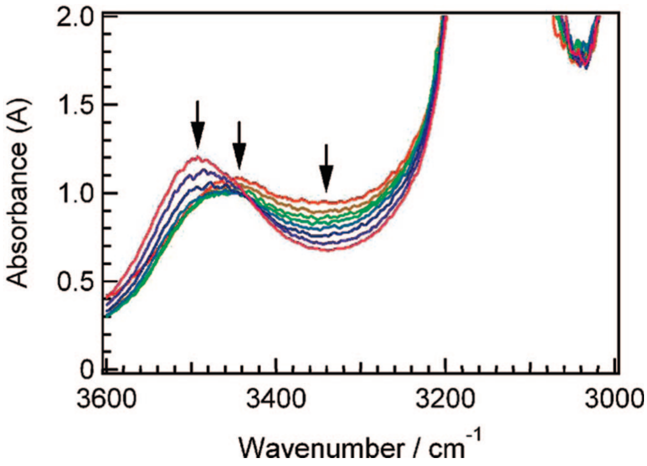


Figure 3. FTIR absorption spectra of the IL solution (P2VP−PEA−P2VP/PHS/IL = 10/4/90). Spectra were recorded at 25 °C (red), 50 °C (yellow), 75 °C (yellow-green), 100 °C (light green), 125 °C (light blue), 150 °C (blue), 175 °C (bluish-purple), and 200 °C (purple). Arrows indicate 3492, 3446, and 3334 cm^{-1} from left to right.

Time−temperature superposition was attempted, and Figure 2 shows double-logarithmic master curves for G' and G'' vs reduced frequency ωa_T with a reference temperature of 140 °C. Remarkably, all these data can be superposed very well, although there are systematic deviations at higher frequencies at each temperature (see also Figure S5).[37] The inset to the figure shows the resulting shift factor a_T vs temperature, where a_T means the ratio of any relaxation time at one temperature to its value at the chosen reference temperature. At low reduced frequencies, log G' has a slope of 2 and log G'' has a slope of 1, indicating liquid (terminal) behavior. The intersection of G' and G'' at a reduced frequency of 0.24 rad/s gives a estimated longest relaxation time τ of 4.2 s at 140 °C. Above the crossover, G' is constant and shows a remarkably wide plateau, extending over at least 11 orders of magnitude in reduced frequency. This implies that the viscosity of this associating polymer solution increases by the same factor over this temperature range, as does the shift factor. On the other hand, G'' also shows a clear power law, decreasing with a slope of −0.23 with increasing ωa_T.

FT-IR Measurements. Figure 3 shows the spectra obtained at 25 deg intervals from 200 to 25 °C. The absorption peaks of the ionic liquid appear in the region from 2800 to 3200 cm^{-1},[38] but these peaks were saturated. A peak at 3492 cm^{-1} was found in the curve at 200 °C and is attributed to the absorption of free hydroxyl groups of PHS (3525 cm^{-1}), according to the literature.[13,39] This peak shifted to lower wavenumbers as temperature decreased, as does the peak located at 3446 cm^{-1} at 25 °C, which is related to the self-association of hydroxyl groups.[13] On the other hand, the absorption distributed around 3334 cm^{-1} increased as temperature decreased. The absorption in this region is attributed to the hydroxyl group associated with pyridine via hydrogen bonding.[13] Hence, complexes between P2VP−PEA−P2VP and PHS are formed preferentially at lower temperatures.

Discussion

Molecular Model of Supramacromolecules in an Ionic Liquid. We propose the following model to explain these remarkable results. First, the association between PHS "cross-linkers" and two or more P2VP blocks leads to a transient network, where the value of the plateau modulus is dictated by the network of swollen PEA strands. Second, the longest relaxation time is determined by the average lifetime of a PHS/P2VP block association, which is generally not a single hydrogen bond. Third, the adherence to time−temperature superposition suggests a network topology that does not evolve appreciably with temperature. Fourth, the visible upturns in G'' at the high-frequency end of the measurements for each temperature reflect the relaxation of the PEA strands. Evidence for this picture includes the following. Clearly, some kind of a network structure is formed, given the viscoelastic results, and neither the triblock nor the PHS by itself in the IL gives any kind of significant rheological features. In fact, we prepared an IL solution of the blend composed of PEA homopolymer and PHS with a weight ratio of PEA/PHS/IL of 10/4/90 and an IL solution of P2VP−PEA−P2VP triblock copolymer with a weight ratio of P2VP-PEAP2VP/IL of 10/90, but no gelation occurred for these two solutions even at room temperature. The presence of H-bonding between P2VP and PHS was confirmed by FT-IR, and so the source of the transient network is clear. From the experimental plateau modulus $G_N \approx 2570$ Pa at 30 °C, we can estimate the average mesh size of the gel, ξ:

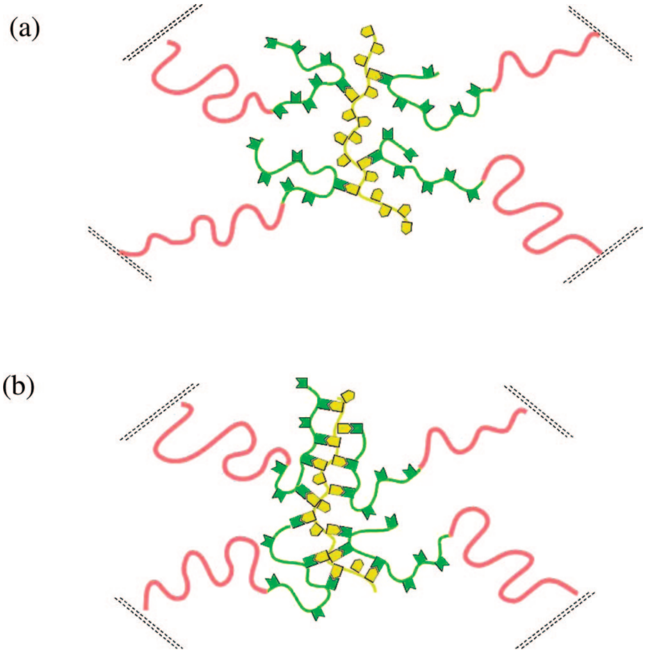


Figure 4. Cartoon of the association between P2VP blocks (green) and a PHS chain (yellow) at (a) high T, near the gel point, and (b) lower T, where more hydrogen bonds form between the same polymers. The red chains denote the PEA blocks connecting to the macroscopic network. The effective cross-link functionality as shown is four.

$$G_N \approx \frac{kT}{\xi^3} \tag{1}$$

where k is the Boltzmann constant and T is temperature. Thus, estimated, ξ is about 12 nm, which is comparable to the expected end-to-end distance of a swollen PEA block.

Temperature Dependence of the Number of Active Hydrogen Bonds. The second hypothesis, that the more than 11 order of magnitude increase in relaxation time is due to the lifetime of the PHS/P2VP association, is the most important and, as will be discussed below, is reasonable on the basis of some simple calculations. The adherence to time−temperature superposition requires that the main relaxation process or processes have the same temperature dependence, which implies that the structure underlying the relaxation spectrum is invariant. Note that if the H-bonding sites (i.e., 2VP units) were randomly distributed along the PEA block, rather than gathered at the ends, an increasing fraction of H-bonds on cooling would lead to a tighter mesh and an increase in G_N, which is not observed. The location of the upturn in G'' at high frequencies scales as the solvent viscosity, supporting our hypothesis that its origin in local chain motion; an obvious interpretation is the onset of chain relaxation modes within the PEA network strands (see Figures S5 and S6).

In the picture we propose the crucial feature is that the network structure is locked in place at relatively high temperature, near or just below the gel point which we take as 141.5 °C. Subsequent cooling increases the number of hydrogen bonds, $n(T)$, between a given P2VP block and given PHS chain, but no substantial rearrangements of network connectivity take place. The unique feature of this system, therefore, is that the net *strength* of the association between a P2VP block and its PHS partner increases with decreasing T, as n increases, but not the *number* of cross-links, which is more or less fixed at the gel point. This is illustrated in cartoon form in Figure 4. This feature is a fundamental distinction between this reversibly associating system and other supramolecular systems based on hydrogen bonds[2,5,40,41] or reversible networks formed by associations between hydrophobic "stickers" in aqueous solution.[42]

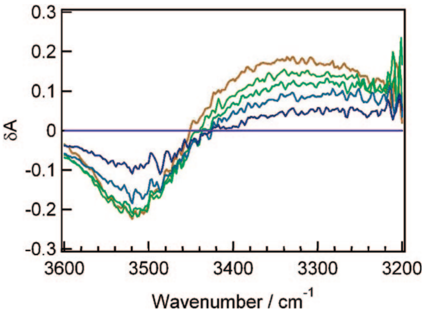


Figure 5. Corrected FT-IR spectra. The spectrum at 175 °C (bluish-purple) was used as a baseline and subtracted from all spectra. The corrected spectra are displayed in the order of the magnitude of temperature, that is, 50 °C (yellow), 75 °C (yellow-green), 100 °C (light green), 125 °C (light blue), 150 °C (blue), and 175 °C (bluish-purple).

The structure of the network is presumably very similar to that formed by thermoplastic elastomers of the ABA triblock type,[43] but again the key distinction is the fact that in thermoplastic elastomers the penalty to extract an A block from its micelle has an activation energy that does not depend on temperature. On the other hand, it is possible to access many orders of variation in network relaxation time, as recently shown by Shull and co-workers.[44]

To pursue this argument further, we propose a simple model for the longest relaxation time, τ_1, which we equate with the time for complete dissociation of a given P2VP block and its PHS partner, i.e., the simultaneous breaking of n hydrogen bonds. (We therefore neglect the possibility of a cooperative "unzipping" of a particular cross-link.) If we take ΔE as the energy of a single hydrogen bond, then τ_1 involves an Arrhenius factor

$$\tau_1 \propto \exp(n\Delta E/RT) \tag{2}$$

The unspecified proportionality factor in eq 2 likely includes the solvent viscosity, but as this changes by about an order of magnitude over the relevant temperature range (see Supporting Information), whereas a_T changes by more than 11 orders of magnitude, we can neglect this. From the T dependence of the FT-IR absorptivity at 3334 cm^{-1} attributed to the associated hydroxyl groups, we can extract ΔE. To estimate the absorbance just from the hydroxyl group, we subtracted a reference from all the spectra to obtain the corrected FT-IR spectra shown in Figure 5. We used the spectrum at 175 °C as a baseline since there is almost no hydrogen bonding between P2VP and PHS at 175 °C.

Although the corrected absorbance is negative in the wavenumber range higher than 3450 cm^{-1} because of self-association of hydroxyl groups, this is not a serious issue when we consider only the change in hydrogen bonding between the hydroxyl groups and the pyridine groups. We assume that the population of hydrogen bonds is given by a Boltzmann factor, that is, going to 0% at T = infinity and 100% at T = 0 K. Therefore, if we plot logarithmic absorbance (ln A) vs 1/T, we can extract an estimate of $\Delta E \approx 13 \pm 2.5$ kJ/mol from the slope in Figure 6. This is a very reasonable value for one hydrogen bond in a polar environment. Then, if we take $n = 1$ at the gel point, we can invert eq 2 to obtain $n(T)$:

$$n(T) = \frac{T}{T_{\text{ref}}} + \frac{RT}{\Delta E} \ln a_T \tag{3}$$

The result of this analysis is shown in Figure 7. As T is reduced, n increases before saturating at about 5. A given PHS chain has, on average, about 55 possible H-bond donors (i.e., the degree of polymerization), whereas a P2VP block has about

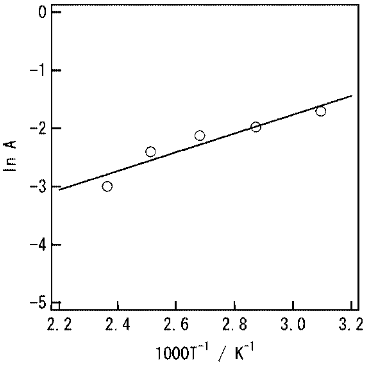


Figure 6. Arrhenius plot of corrected absorbance vs inverse temperature. The slope of the regression line is 1600 ± 310 K.

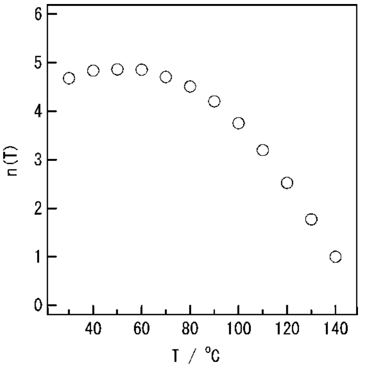


Figure 7. Estimated number of hydrogen bonds per P2VP block as a function of temperature.

50 H-bond acceptors. These results imply that, if all PHS repeat units were involved in hydrogen bonding at low temperature, there could be as many as 11 P2VP blocks connected to one PHS chain. However, stoichiometrically, there are about three PHS chains for every two PVP blocks, so it is more likely that there are remaining PHS sites that are unused. This could reflect a combination of steric effects between repeating units of P2VP and PHS, which impede full utilization of hydrogen-bonding sites and self-associations of the hydroxyl groups plus the stoichiometric excess of hydrogen bond donors.

Further Discussion of the Viscoelastic Properties. Five other points are worth noting. First, the frequency dependence of G' and G'' actually appears remarkably similar to an extremely high molecular weight linear polymer, where the slope of −0.23 for G'' is consistent with the reptation model[45,46] augmented by contour length fluctuations.[47,48] But, as shown by Groot and Agterof,[41] simulations of the dynamics of associating polymers can yield exactly the same frequency dependence of the dynamic moduli (see, for example, Figures 8 and 12 of ref 41). Thus, there is no reason to interpret our results as suggesting a linear association of polymers to prepare one extremely long supramacromolecule. Second, appealing similarities have been drawn between the dynamics of glass formation and the gelation of "sticky" polymers.[49] The fact that a_T varies by so many orders of magnitude in our system is also strikingly reminiscent of a glass-transition-like phenomenon. However, we feel there is a crucial difference, evident in the inset to Figure 2 and in Figure 7; both a_T and $n(T)$ show a *saturation* with decreasing temperature, not a *divergence* at a Vogel temperature. This saturation is consistent with our model, as it simply reflects the formation of the maximum number of H-bonds. Third, one might ask whether the solidification transition we observe could actually reflect an underlying block copolymer order−disorder transition. This would not be consistent with the observed time−temperature superposition, however; order−disorder transitions in block copolymer liquids are almost always accompanied by significant changes in the frequency dependence of the dynamic moduli. Furthermore, preliminary X-ray scattering experiments on this solution show no sign of Bragg peaks, or any noticeable change in scattering, near the gel point (see Figure S7). At room temperature there is some evidence of a hexagonal packing emerging, which we tentatively ascribe to a microphase separation between PHS + P2VP associations,[9,12] perhaps cylindrical in shape, and a well-solvated PEA-rich phase. Fourth, the viscoelastic properties of this material differ in important ways from typical solvated thermoplastic elastomers. A good example for comparison was recently presented, for a poly(styrene-*b*-ethylene oxide-*b*-styrene) triblock dispersed in an ionic liquid at 10%.[27] Thermoplastic elastomer dynamics are are dominated by the glass transition of the (usually polystyrene) end blocks and the order−disorder transition. Consequently, time−temperature superposition is not followed; furthermore, the 11 order of magnitude variation in the transient gel relaxation time observed in our system is very unusual. Lastly, it is worth noting the crucial role of the ionic liquid in this material: namely, it remains a liquid over the entire temperature range. As this range is much broader than can be accessed in water, or in most organic solvents, the IL can enable a much more detailed examination of the dynamics of model associating polymer systems. Furthermore, as gelation of ionic liquids is of considerable interest in many applications, including actuators, polymer electrolytes, membranes, and dielectrics for organic transistors, this thermoreversible gelation may be an attractive route to readily processable materials.

Summary

In this report we have demonstrated strikingly thermosensitive viscoelastic properties of supramacromolecules in an ionic liquid, which we term a supramacromolecular ion gel, due to hydrogen bonding between the end blocks of an ABA triblock, and an added homopolymer as "cross-linker". The longest relaxation time of the system increases by more than 11 orders of magnitude on cooling from above the gel point (141.5 °C) down to 30 °C. At the same time, time−temperature superposition yields an excellent master curve. The results are interpreted in terms of a simple model in which the number of cross-links is essentially fixed below the gel point, but the number of hydrogen bonds per end block increases on cooling. The primary role of the ionic liquid is to maintain good solvent conditions over a very wide temperature range, allowing the network dynamics to be exposed. However, the importance of supramolecular ion gels in a variety of applications suggests that this kind of supramacromolecular assembly may be of practical use.

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Supporting Information Available: Details of characterization of the polymers and synthesis of the ionic liquid, additional rheology data, and small-angle X-ray scattering data. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Muller, M.; Dardin, A.; Seidel, U.; Balsamo, V.; Ivan, B.; Spiess, H. W.; Stadler, R. *Macromolecules* **1996**, *29*, 2577–2583.

(2) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071–4097.

(3) ten Brinke, G.; Ruokolainen, J.; Ikkala, O. *Hydrogen-Bonded Polym.* **2007**, *207*, 113–177.

(4) Hofmeier, H.; Schubert, U. S. *Chem. Soc. Rev.* **2004**, *33*, 373–399.

(5) Sivakova, S.; Rowan, S. J. *Chem. Soc. Rev.* **2005**, *34*, 9–21.

(6) Yang, X. W.; Hua, F. J.; Yamato, K.; Ruckenstein, E.; Gong, B.; Kim, W.; Ryu, C. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 6471–6474.

(7) Mather, B. D.; Baker, M. B.; Beyer, F. L.; Berg, M. A. G.; Green, M. D.; Long, T. E. *Macromolecules* **2007**, *40*, 6834–6845.

(8) Binder, W. H.; Zirbs, R. *Hydrogen-Bonded Polym.* **2007**, *207*, 1–78.

(9) Matsushita, Y. *Macromolecules* **2007**, *40*, 771–776.

(10) Noro, A.; Nagata, Y.; Takano, A.; Matsushita, Y. *Biomacromolecules* **2006**, *7*, 1696–1699.

(11) Ruokolainen, J.; Makinen, R.; Torkkeli, M.; Makela, T.; Serimaa, R.; ten Brinke, G.; Ikkala, O. *Science* **1998**, *280*, 557–560.

(12) Asari, T.; Matsuo, S.; Takano, A.; Matsushita, Y. *Macromolecules* **2005**, *38*, 8811–8815.

(13) Dai, J.; Goh, S. H.; Lee, S. Y.; Siow, K. S. *Polym. J.* **1994**, *26*, 905–911.

(14) Mullens, J.; Yperman, J.; Francois, J. P.; Vanpoucke, L. C. *J. Phys. Chem.* **1985**, *89*, 2937–2941.

(15) Chun, D.; Wudl, F.; Nelson, A. *Macromolecules* **2007**, *40*, 1782–1785.

(16) Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.* **1996**, *35*, 1168–1178.

(17) Welton, T. *Chem. Rev.* **1999**, *99*, 2071–2083.

(18) Noda, A.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2001**, *105*, 4603–4610.

(19) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. *Green Chem.* **2001**, *3*, 156–164.

(20) Sheldon, R. *Chem. Commun.* **2001**, 2399–2407.

(21) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3691.

(22) Carmichael, A. J.; Haddleton, D. M.; Bon, S. A. F.; Seddon, K. R. *Chem. Commun.* **2000**, 1237–1238.

(23) Harrison, S.; Mackenzie, S. R.; Haddleton, D. M. *Chem. Commun.* **2002**, 2850–2851.

(24) He, Y. Y.; Li, Z. B.; Simone, P.; Lodge, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 2745–2750.

(25) He, Y. Y.; Lodge, T. P. *J. Am. Chem. Soc.* **2006**, *128*, 12666–12667.

(26) Simone, P. M.; Lodge, T. P. *Macromol. Chem. Phys.* **2007**, *208*, 339–348.

(27) He, Y. Y.; Boswell, P. G.; Buhlmann, P.; Lodge, T. P. *J. Phys. Chem. B* **2007**, *111*, 4645–4652.

(28) He, Y. Y.; Lodge, T. P. *Chem. Commun.* **2007**, 2732–2734.

(29) Susan, M. A.; Kaneko, T.; Noda, A.; Watanabe, M. *J. Am. Chem. Soc.* **2005**, *127*, 4976–4983.

(30) Ding, J.; Zhou, D. Z.; Spinks, G.; Wallace, G.; Forsyth, S.; Forsyth, M.; MacFarlane, D. *Chem. Mater.* **2003**, *15*, 2392–2398.

(31) Jiang, Y. Y.; Zhou, Z.; Jiao, Z.; Li, L.; Wu, Y. T.; Zhang, Z. B. *J. Phys. Chem. B* **2007**, *111*, 5058–5061.

(32) Zhou, M. J.; Kidd, T. J.; Noble, R. D.; Gin, D. L. *Adv. Mater.* **2005**, *17*, 1850.

(33) Lee, J.; Panzer, M. J.; He, Y. Y.; Lodge, T. P.; Frisbie, C. D. *J. Am. Chem. Soc.* **2007**, *129*, 4532–4533.

(34) Moad, G.; Rizzardo, E.; Thang, S. H. *Aust. J. Chem.* **2005**, *58*, 379–410.

(35) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754–6756.

(36) Convertine, A. J.; Sumerlin, B. S.; Thomas, D. B.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 4679–4681.

(37) Eisenberg, A. D. I.; Saito, S. *J. Macromol. Sci., Chem. A2* **1968**, *4*, 799–820.

(38) Talaty, E. R.; Raja, S.; Storhaug, V. J.; Dolle, A.; Carper, W. R. *J. Phys. Chem. B* **2004**, *108*, 13177–13184.

(39) Moskala, E. J.; Varnell, D. F.; Coleman, M. M. *Polymer* **1985**, *26*, 228–234.

(40) Tanaka, F.; Edwards, S. F. *Macromolecules* **1992**, *25*, 1516–1523.

(41) Groot, R. D.; Agterof, W. G. M. *Macromolecules* **1995**, *28*, 6284–6295.

(42) See, for example: Yoshida, T.; Taribagil, R.; Hillmyer, M. A.; Lodge, T. P. *Macromolecules* **2007**, *40*, 1615–1623, and references therein.

(43) *Thermoplastic Elastomers*, 2nd ed.; Holden, G., Legge, N. R., Quirk, R., Schroeder, H. E., Eds.; Hanser: Cincinnati, OH, 1996.

(44) Seitz, M. E.; Burghardt, W. R.; Faber, K. T.; Shull, K. R. *Macromolecules* **2007**, *40*, 1218–1226.

(45) De Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572–579.

(46) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789–1801.

(47) Milner, S. T.; McLeish, T. C. B. *Phys. Rev. Lett.* **1998**, *81*, 725–728.

(48) Watanabe, H. *Prog. Polym. Sci.* **1999**, *24*, 1253–1403.

(49) Kumar, S. K.; Douglas, J. F. *Phys. Rev. Lett.* **2001**, *8718*, 188301.

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