Macromolecules
ARTICLE

Macromolecules **2010**, *43*, 9529–9533 **9529**
DOI: 10.1021/ma101506p

Synthesis and Creep-Recovery Behavior of a Neat Viscoelastic Polymeric Network Formed through Electrostatic Interactions

Michel Wathier and Mark W. Grinstaff*

Departments of Biomedical Engineering and Chemistry, Metcalf Center for Science and Engineering, Boston University, Boston, Massachusetts 02215, United States

Received July 6, 2010; Revised Manuscript Received October 18, 2010

ABSTRACT: The preparation of a supramolecular polymer ionic network and its rheological properties are described. The polymer ionic network is formed between a dicationic phosphonium ionic liquid and the carboxylate residues of poly(acrylic acid). Upon substituting the dicationic phosphonium for a monocationic phosphonium or polyacrylate for poly(vinyl alcohol), the network is lost. The viscosities of the materials are highly dependent on the composition of this ionic network. Creep-recovery experiments show the polymer ionic network exhibits viscoelasticity.

Introduction

Noncovalent synthesis is a versatile, diverse, and programmable approach to new supramolecular compositions where the properties of these resulting assemblies are dependent and unique to the specific bonding interaction (e.g., hydrogen bonding vs $\pi-\pi$ stacking interactions).[1,2] Of the various supramolecular assemblies known, polymer networks are particularly interesting as their properties can be dramatically different from the properties of their covalently bonded counterparts or the individual macromers.[3−11] For example, hydrogen[12,13] and metal−ligand[14−16] bonding are used to prepare reversible polymer networks. Ionic or Coulombic forces can also be used. The cross-linking of polysaccharides in aqueous solution, such as calcium cross-linked alginate, is well-known.[17] Likewise ionomers, hydrophobic polymers sparsely populated with ionic functional groups within the main chain, have been cross-linked with metal cations.[18] Polyelectrolytes have also been coordinated with surfactants to give interesting materials in the solid state.[19−23] This latter approach, using ion pairs, provides exciting opportunities for synthesizing and evaluating new supramolecular materials through manipulation of the type and strength of the ion pair as well as the number of interactions.[24,25] Herein, we report the preparation of a neat polymer network using noncovalent electrostatic interactions, the processing of the material into a defined shape, and its creep-recovery behavior as a viscoelastic polymeric salt.

Supramolecular networks are usually synthesized by reacting two different chemical species whereby one structure possesses at least two and the other three or more complementary molecular recognition groups. Examples include the use of a large molecular weight polymer and a small molecule cross-linker or two macromers of similar molecular weight. We will use the former approach. We formed the polymer network by mixing an alkylphosphonium dication and polyacrylate/poly(acrylic acid). The specific chemical structures under investigation and the proposed coordination between the phosphonium dication (P^{2+}) and polyacrylate (PAA) responsible for network formation are shown in Figure 1. A geminal phosphonium dication was chosen because this symmetric compound possesses two positive charges,[24,26] cannot participate in H-bonding, and belongs to a family of compounds known as ionic liquids. Ionic liquids are of widespread interest as new battery electrolytes, solvents, thermal fluids, separation media, and protein crystallization matrices.[27−29]

*Corresponding author. E-mail: mgrin@bu.edu.

Experimental Section

General. All chemicals were purchased from Aldrich or Acros as highest purity grade and used without further purification. All reactions were performed under a nitrogen atmosphere. NMR spectra were recorded on a Varian INOVA spectrometer (for ^{1}H, ^{13}C, and ^{31}P at 400, 100.6, and 161 MHz, respectively). Electrospray mass spectra were obtained on an Agilent 1100 LC/MSD trap with ESI and APCI sources. Elemental analysis was obtained from Atlantic Microlab, Inc. A TA Instruments AR 1000 was used for the rheological measurements. Poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) were purchased from Aldrich. Poly(vinyl alcohol) had an average M_w of 160 000 g/mol. The poly(acrylic acid) (0.3% sodium salt) in water had an average M_w of 240 000 g/mol.

Synthesis of Phosphonium 1,1′-(1,10-Decanediyl)bis(1,1,1-trihexyl) Chloride (P^{2+}:2Cl^{-}). Trihexylphosphine (19.14 g, 94.7 mmol) and 1,10-dichlorodecane (10 g, 47.4 mmol) were mixed together and heated to 140 °C for 24 h. Next, the mixture was placed under vacuum at 140 °C to remove any volatile components. A clear colorless liquid was obtained in 99% yield. ^{1}H NMR ($CDCl_3$): δ 0.89 (m, 18, CH_3); 1.30−1.72 (br, 64, CH_2-CH_2); 2.38−2.52 (br, 16, CH_2-P). ^{13}C NMR ($CDCl_3$): δ 14.52−14.60 (CH_3); 19.48−22.99 (CH_2); 30.98−31.89 (CH_2-P). ^{31}P NMR ($CDCl_3$): δ 33.92 (P^{+}). ES MS: 747.68 m/z $[MCl]^{-}$ (theory: 784.12 m/z $[M]^{+}$). Elemental analysis: (theory: C, 70.46; H, 12.60) found C, 70.34; H, 12.40.

Synthesis of Phosphonium 1-(1-Decanediyl)-1,1,1-trihexyl Chloride (P^{+}:Cl^{-}). Trihexylphosphine (8.3 g, 29 mmol) and 1-chlorodecane (5.22 g, 29.6 mmol) were mixed together and heated to 140 °C for 24 h. Next, the mixture was placed under vacuum at 140 °C to remove any volatile components. A clear colorless liquid was obtained in 99% yield. ^{1}H NMR ($CDCl_3$): δ 0.78 and 0.797 (t, 12, CH_3); 1.12−1.26 (br, 24, CH_2); 1.35−1.50 (br, 16, CH_2-CH_2-P); 2.30−2.38 (br, 8, CH_2-P). ^{13}C NMR ($CDCl_3$): δ 13.71 and 13.87 (CH_3); 19.27 and 18.80 (CH_2-CH_3); 21−22 (CH_2); 28.75−31.60 (CH_2-P). ^{31}P NMR ($CDCl_3$): δ 35.46 (P^{+}). ES MS: 427.44 m/z $[MCl]^{-}$ (theory: 463.20 m/z $[M]^{+}$). Elemental analysis: (theory: C, 72.60; H, 13.20) found C, 72.53; H, 13.18.

General Procedure for Network Formation. 1 g of phosphonium in the minimum of water was mixed with the PAA

Published on Web 10/28/2010

(solution in water) such that there was one phosphonium for each monomer. For the PVA control, the right amount (one monomer per positive charge) of PVA was directly added to 1 g of phosphonium. The solutions were warmed (80 °C) and vortexed several times to obtain a homogeneous solution. For the PAA solution, the water was pulled off under vacuum at 110 °C. Both networks were dried for an additional 24 h at 100 °C under vacuum.

General Procedure for Rheological Measurement. Rheological characterization of the synthetic polymers was performed as follows. 1 mL of each sample was placed on a AR 1000 controlled strain rheometer from TA Instruments equipped with a Peltier temperature control using a 20 mm diameter aluminum plate. The experiments were performed under nitrogen gas. An oscillatory strain sweep (strain amplitude from 0.01 to 10%) at fixed frequency (1 Hz) was applied to the sample to determine the pseudo-linear viscoelastic region (LVR). Steady-state flow (shear stress amplitude from 0.01 to 60 Pa) was applied to the sample to determine the dynamic viscosity of the samples. The measurements were performed at 25 °C to obtain the dynamic viscosity. The viscosity of the PAA and PVA has been measured in solution in water with their concentrations (wt %) matching the concentrations at which they have been used to form the network with the ionic liquid.

First an oscillatory stress sweep (OSS) was used to determine the pseudo-linear viscoelastic region (LVR) using a stress sweep from 0.1 to 10 000 Pa at constant frequency (1 Hz). Then a pseudo-viscosity profile was determined using a continuous flow test (CF) with a broad torque range (shear stress from 0.01 to 100 Pa). Once the LVR and the first Newtonian plateau were known (from the CF experiment), an oscillation time sweep (OTS) was performed to determine whether the properties of the material change over time. A steady-state flow (SSF) experiment using the data collected from the CF, OTS was then performed to select the shear stress within the first Newtonian plateau. Finally, a creep-recovery experiment was performed using the data collected in the CF, OTS, and SSF experiments.

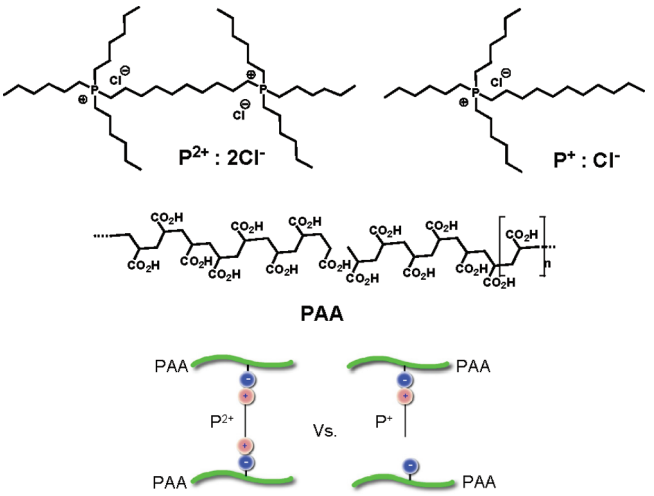

Figure 1. Chemical structures of the ionic liquids under investigation and poly(acrylic acid) (top) and illustration of the supramolecular polymer network formed by the ion pairs (bottom) (not to scale).

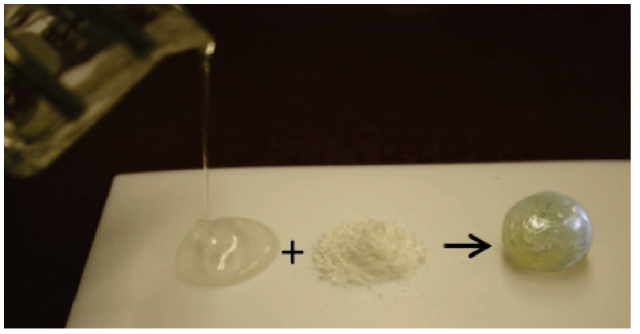

Figure 2. Photograph of a P^{2+}:PAA network in the form of a ball (right) made from the liquid P^{2+}:$2Cl^-$ (left) and the solid PAA (middle).

Results and Discussion

We synthesized the dicationic phosphonium ionic liquid (P^{2+}:$2Cl^-$) by reacting 2 equiv of trihexylphosphine with 1 equiv

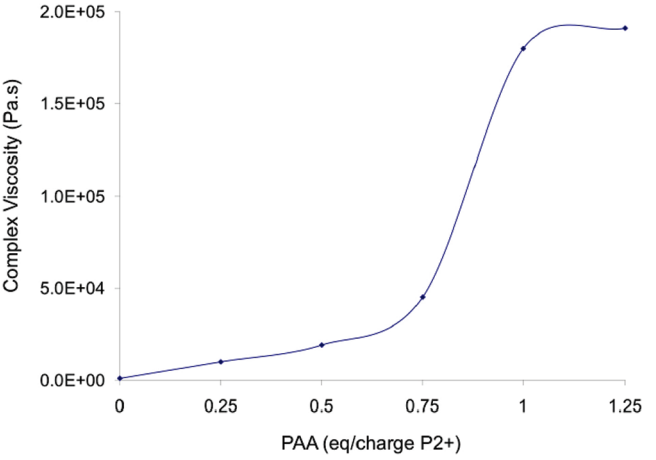

Figure 4. Viscosity curve for P^{2+}:PAA as the function of the PAA equivalency (data collected at 1 Hz and 25 °C).

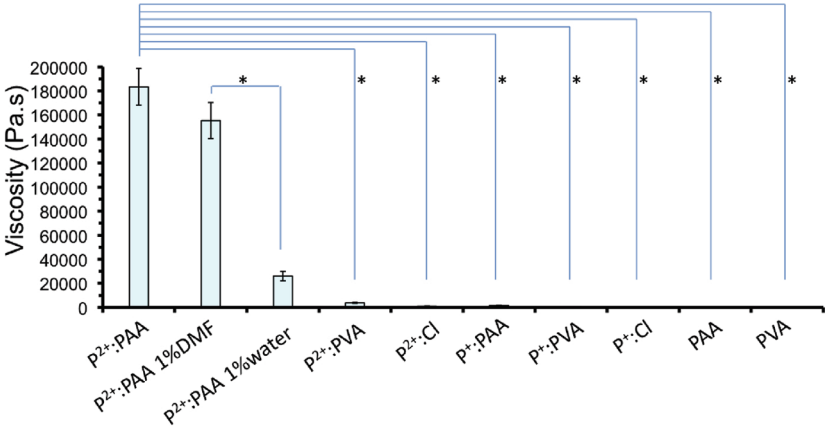

Figure 3. Viscosity data for the various ionic liquids and network ionic liquids at 25 °C ($N = 3$; mean ± SD; $*p < 0.004$).

Table 1. Storage (G'), Loss (G'') Moduli, Delta, and Compressive Modulus (E) of the Different Ionic Liquids and Ionic Networks

composition	G' (Pa)	G'' (Pa)	E (Pa)
P^{2+}:PAA	$7.1 \times 10^5 \pm 15000$	$2.0 \times 10^6 \pm 50000$	$5.0 \times 10^6 \pm 5000$
P^{+}:PAA	$5.5 \times 10^3 \pm 100$	$7.8 \times 10^3 \pm 100$	$2.0 \times 10^3 \pm 300$
P^{2+}:PVA	$1.4 \times 10^3 \pm 25$	$3.0 \times 10^3 \pm 40$	< 500
P^{+}:PVA	$1.0 \times 10^3 \pm 30$	$3.0 \times 10^3 \pm 20$	< 500
P^{2+}:PAA + 1% water	$8.8 \times 10^3 \pm 120$	$1.5 \times 10^4 \pm 250$	$3.0 \times 10^4 \pm 1000$
P^{2+}:PAA + 1% DMF	$2.3 \times 10^5 \pm 80$	$5.5 \times 10^5 \pm 400$	$1.0 \times 10^6 \pm 4000$
P^{2+}:2Cl^-	200 ± 20	$2.0 \times 10^3 \pm 15$	< 500
P^{+}:Cl^-	0.7 ± 1	14 ± 5	< 500

of 1,10-dichlorodecane for 24 h at 140 °C, following our published procedure.[24,25] The monocationic phosphonium ionic liquid (1-(1-decanediyl)-1,1,1-trihexyl chloride); P^{+}:Cl^-) was prepared in a similar manner. Both of these liquids flow (viscosity ≤1000 Pa·s) and are colorless. Upon mixing the dicationic phosphonium with poly(acrylic acid), PAA (M_w 240 000 g/mol; 0.3% sodium salt), a neat highly viscous liquid was obtained as a consequence of the attractive electrostatic forces (Figure 2). PAA is soluble in the dicationic phosphonium ionic liquid, and no precipitation was observed upon addition of a 25% excess. Attempts to prepare a sample with 100% or 10% $PAANa^+$ failed as a heterogeneous mixture was obtained. The exact number of cross-linking sites between the polymer and P^{2+} has not been determined. We did not observe any phase transitions for the P^{2+}:PAA material in the DSC trace over a range from −80 to 250 °C.

The viscosities of the supramolecular polymer networks were measured. The P^{2+}:PAA ionic network, prepared with a ratio of 1:1, possessed a viscosity of 180 000 Pa·s, a significant increase over P^{2+}:2Cl^- itself (Figure 3). The viscosity increased as the amount of PAA was added to the P^{2+} with a significant increase occurring at the ratio of 1:1 (Figure 4). To confirm that no precipitations were formed, we performed a DLS and a light microscopy experiment on the P^{2+}:PAA network. No micrometer- or larger-sized particles or aggregates were detected or observed, indicating the mixture to be homogeneous using these techniques. For reference, honey has a viscosity of about 2.5 Pa·s. The viscosity of PAA (3 Pa·s) at the same concentration in water was significantly lower than the P^{2+}:PAA. The enhanced viscosity in P^{2+}:PAA is a consequence of the network formed between the dication and the polyanion. To confirm this ionic network formation, we performed several control experiments (Figure 3). First, a mixture was prepared where P^{2+} was substituted with the monocation P^{+}, while still maintaining a 1:1 charge ratio with PAA. This mixture cannot form a network due to the insufficient number of ionic interactions required to form a bridge between the carboxylic acids on the PAA chains (Figure 1). The P^{+}:PAA mixture had a significantly lower viscosity (≈1500 Pa·s; $p < 0.002$). Second, to determine the importance and requirement of carboxylate residues to form these ionic liquid networks, poly(vinyl alcohol), PVA (M_w 160 000 g/mol), was substituted for PAA to afford the P^{2+}:PVA composition. This resulting liquid had a significantly lower viscosity compared to P^{2+}:PAA (≈3700 Pa·s; $p < 0.002$). As an additional control, we measured the viscosity of the P^{+}:PVA mixture, and again a low viscous material similar to P^{+}:PAA was obtained (≈500 Pa·s). As attractive electrostatic forces hold these networks together, the viscosities of the networks should be sensitive to water since this will disrupt that interaction. Addition of 1 wt % water to P^{2+}:PAA afforded a significant decrease in viscosity ≈20 000 Pa·s. To confirm that this observed effect was not a dilution phenomenon, we performed an analogous experiment with the addition of 1 wt % DMF to the P^{2+}:PAA network. As shown in Figure 3, the viscosity of the water added P^{2+}:PAA sample was significantly less than the DMF added sample ($p < 0.004$).

Table 2. Viscosity (η) and δ of P^{2+}:PAA, P^{2+}:PAA plus NaCl, CH_3CO_2Na, or Glucose, and P^{+}:PAA plus NaCl

composition[a]	η (Pa·s)	δ
P^{2+}:PAA	$1.8 \times 10^5 \pm 1.5 \times 10^4$	72 ± 3
P^{2+}:PAA + 1 equiv NaCl	$3.1 \times 10^5 \pm 1.4 \times 10^4$	75 ± 4
P^{2+}:PAA + 1 equiv CH_3CO_2Na	$2.5 \times 10^5 \pm 1.5 \times 10^4$	5 ± 3
P^{2+}:PAA + 1 equiv glucose	$2.7 \times 10^5 \pm 1.1 \times 10^4$	70 ± 3
P^{+}:PAA + 1 equiv NaCl	$2.7 \times 10^4 \pm 4 \times 10^3$	53 ± 3

[a] Equiv per monomer of PAA.

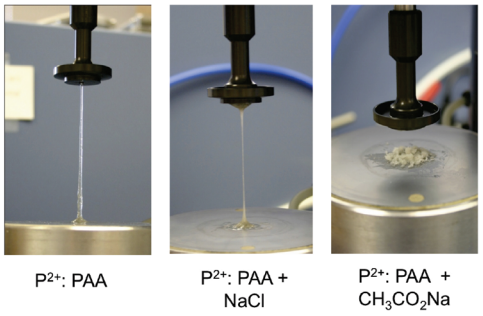

Figure 5. Photograph of P^{2+}:PAA (right), P^{2+}:PAA with 1 equiv of NaCl (middle), and P^{2+}:PAA with 1 equiv of CH_3CO_2Na (left).

The storage (G') and loss (G'') moduli as well as the equilibrium compressive modulus of the different ionic liquids and ionic networks were also measured. The data shown in Table 1 were collected at 25 °C, and as observed with the viscosity data, a strong dependence on the composition was noted. For example, the P^{2+}:PAA ionic network sample had a G' and a G'' of 0.7 and 2.1 MPa, whereas the P^{+}:PAA sample had a G' and a G'' of 5.5 and 7.8 kPa, respectively. The E also decreased from 5 MPa for the P^{2+}:PAA sample to 2 kPa for P^{+}:PAA sample. Likewise, substitution of the PAA for PVA to create the P^{2+}:PVA gave a significantly lower G', G'', and E of 1.4 kPa, 3 kPa, and < 500 Pa, respectively. The rheological properties of the P^{+}:PVA sample are similar to the P^{2+}:PVA sample. The significant decrease in modulus values is the consequence of the lack of network with P^{+}:PAA or P^{2+}:PVA sample. As observed with the viscosity data, introduction of water to the ionic network P^{2+}:PAA afforded a significant decrease in materials properties as the G', G'', and E decreased by roughly 2 orders of magnitude relative to the DMF added control. Finally, relatively low G, G'', and E values were observed for ionic liquid mixtures of P^{2+}:2Cl^- and P^{+}:Cl^-.

We then added NaCl to the P^{2+}:PAA composition to determine its effect on the rheological properties. Upon addition of an extra 0.1 equiv of NaCl, based on charge of the P^{2+}, no significant change in viscosity was observed (Table 2). Increasing the concentration of NaCl up to 1 equiv increased the viscosity by less than 2 times. Under light microscopy, we do observe some small crystals, indicating that we are at or exceeding the NaCl solubility limit. The increase in viscosity is likely a result of the increase in mass of the sample due to the added NaCl. To examine the effect of addition of a noninteracting solid on the P^{2+}:PAA, we added 1 equiv of glucose. Glucose will not cross-link or alter

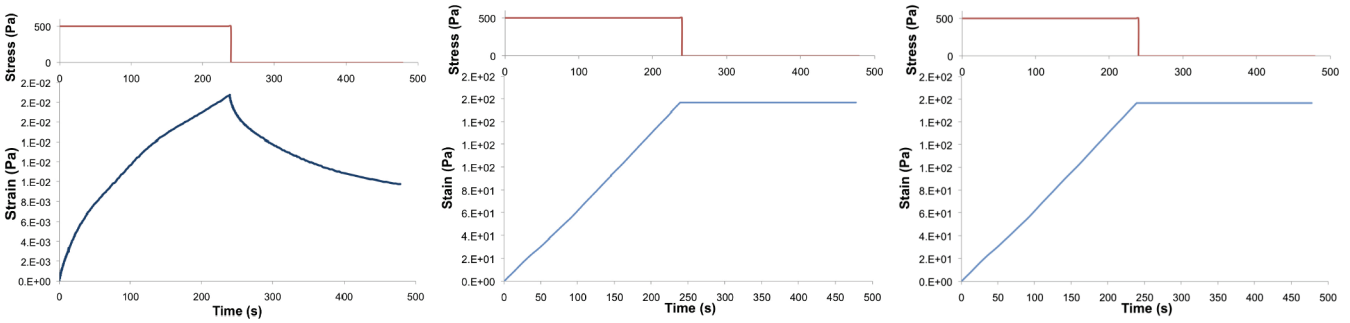

Figure 6. Creep-recovery curves for P^{2+}:PAA at 5 °C (left), for the P^{2+}:PVA at 5 °C (middle), and for P^{+}:PAA at 5 °C (right). A similar response to P^{+}:PAA was observed for P^{+}:PVA (data not shown).

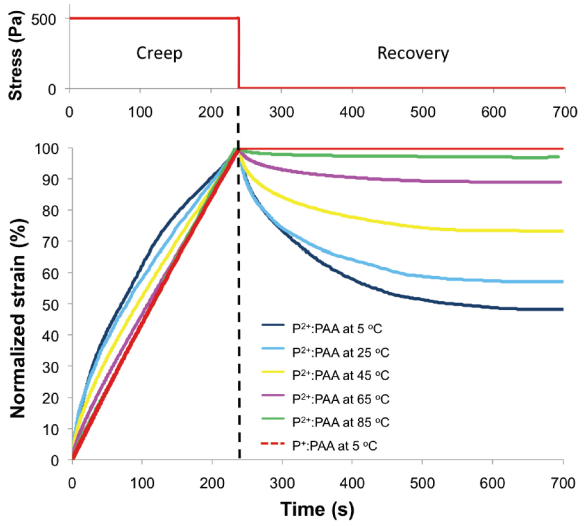

Figure 7. Creep-recovery curves for P^{2+}:PAA and P^{+}:PAA at 5 °C and for the P^{2+}:PAA at several temperatures from 5 to 85 °C.

the protonation state of the PAA. Experimentally, we found that the P^{2+}:PAA + glucose sample had a slightly higher viscosity than P^{2+}:PAA (2.7×10^5 vs 1.8×10^5). This increase in viscosity is like that observed for the addition of 1 equiv of NaCl. With the addition of more NaCl a heterogeneous mixture is formed, with no apparent viscoelasticity, and the network appears broken. This is in contrast to the decrease in viscosity of several orders of magnitude observed with the addition of a small amount of water. To further support this conclusion, we added 1 equiv of NaCl to the P^{+}:PAA network and saw an increase in the viscosity (1.5×10^3 vs 2.7×10^4 Pa·s). In contrast, the addition of 1 equiv of CH_3CO_2Na has a drastic effect. This is evident when examining the material itself. As shown in Figure 5, P^{2+}:PAA with 1 equiv of NaCl is still a viscoelastic fiber, whereas P^{2+}:PAA with 1 equiv of CH_3CO_2Na is a more like a coarse powder. The acetate anion is able to coordinate with the P^{2+} replacing the interaction with the carboxylic acid groups of the PAA, affording a material that has loss the supramolecular network. The difference in the material properties is highlighted in the difference in the phase angle ($\tan \delta = G''/G'$) for the two materials. As shown in Table 2, the P^{2+}:PAA with or without 1 equiv of NaCl (or glucose) has a δ in the low 70's and is a viscoelastic material with more viscous character. However, the P^{2+}:PAA sample with 1 equiv of CH_3CO_2Na has a δ value of 5 and is a solid.

To further characterize and quantify the viscoelastic behavior of these new materials, we performed creep-recovery experiments with the P^{2+}:PAA network as well as the control samples, P^{2+}:PVA, P^{+}:PAA, and P^{+}:PVA. The materials were first placed under a constant stress (500 Pa). As shown in Figure 6, the creep curve for the P^{2+}:PAA network increased and bowed, characteristic

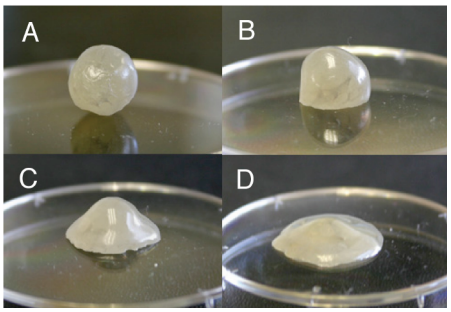

Figure 8. Photograph of a P^{2+}:PAA sample when rolled into a ball (A). Upon standing, the polymer network flows and ball loses shape as shown on day 1 (B), day 2 (C), and day 3 (D).

of network chains reorganizing under the stress. In contrast, the strain response for the P^{2+}:PVA and P^{+}:PAA samples were linear and over a smaller strain range (see Figure 6); the P^{2+}:PVA and P^{+}:PAA samples are viscous liquids. The same response was observed with P^{+}:PVA as this mixture is also a liquid. When the applied stress was removed from the P^{2+}:PAA sample at 250 s, the viscoelastic behavior of the material became evident. For the P^{2+}:PAA sample, a 50% recovery of deformation was observed, while no recovery was observed for the P^{2+}:PVA and P^{+}:PAA samples at 5 °C: P^{2+}:PVA and P^{+}:PAA are liquids while P^{2+}:PAA is a viscoelastic ionic network. This pattern of response is characteristic of viscoelastic behavior.[30] We next varied the temperature from 5 to 85 °C. As shown in Figure 7, the percent recovery decreased with increasing temperature, consistent with the increased thermal energy breaking the electrostatic interactions between the cations and anions.

The P^{2+}:PAA supramolecular ionic network can be processed into specific macroscopic sizes and shapes. To illustrate this feature, we rolled the P^{2+}:PAA mixture to form a ball of ≈1 cm diameter. A photograph of the ball is shown in Figure 8. The shape is not permanent, and over a 3-day period the ball begins to spread and flatten out. Likewise, the P^{2+}:PAA network can be stretched to form an elongated structure between two surfaces as shown in Figure 5.

Conclusion

In summary, a neat supramolecular polymer network was synthesized using ionic bonds between a dicationic phosphonium and the carboxylates of PAA. Rheological measurements show that when the phosphonium dication is replaced by a phosphonium monocation or when the carboxylate functionality of the polymer is substituted by an alcohol, the properties dramatically decrease as a result of the lost network. Likewise, the addition of water or a competing carboxylate anion (e.g., sodium acetate) affords a disruption in the assembled network. The multiple electrostatic interactions between the small molecule phosphonium

and the polymer are sufficient to give macroscopic properties such as viscoelasticity. This strategy of using complementary electrostatic interactions, like H-bonding and metal−ligand bonds, offers a wealth of opportunities to synthesize supramolecular polymer networks.

Acknowledgment. This work was supported by BU and by the Advanced Energy Consortium. Discussions with Reimi Yonekura and Xinrong Lin were appreciated.

Supporting Information Available: Rheological data and TGA procedure. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Lehn, J. M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995.
(2) Atwood, J. L.; Davies, J. E. D.; MacNicol, D. D.; Vögtle, F.; Lehn, J. M. *Comprehensive Supramolecular Chemistry*; Pergamon: Oxford, 1996.
(3) Ciferri, A. *Supramolecular Polymers*; Marcel Dekker: New York, 1998.
(4) Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. *Chem. Rev.* **2001**, *101*, 4071.
(5) Serpe, M. J.; Craig, S. L. *Langmuir* **2007**, *23*, 1626–1634.
(6) Lehn, J. M. *Chem. Soc. Rev.* **2007**, *36*, 151–160.
(7) Corbin, P. S.; Zimmerman, S. C. Linear Supramolecular Polymers and Networks. In *Supramolecular Polymers*; Cifferi, A., Ed.; CRC Press: New York, 2005.
(8) Fouquey, C.; Lehn, J. M.; Levelut, A. M. *Adv. Mater.* **1990**, *2*, 254–257.
(9) Kato, T.; Kihara, H.; Kumar, U.; Uryu, T.; Fréchet, J. M. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1644–1645.
(10) Zimmerman, N.; Moore, J. S.; Zimmerman, S. C. *Chem. Ind.* **1998**, *15*, 604–610.
(11) Pollino, J. M.; Weck, M. *Chem. Soc. Rev.* **2005**, *34*, 193.
(12) Sijbesma, R. P.; Beijer, F. H.; Brunsveld, L.; Folmer, B. J. B.; Hirschberg, J.; Lange, R. F. M.; Lowe, J. K. L.; Meijer, E. W. *Science* **1997**, *278*, 1601–1604.
(13) Thibault, R. J.; Hotchkiss, P. J.; Gray, M.; Rotello, V. M. *J. Am. Chem. Soc.* **2003**, *125*, 11249–11252.
(14) Yount, W. C.; Loveless, D. M.; Craig, S. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 2746–2748.
(15) Weng, W.; Beck, J. B.; Jamieson, A. M.; Rowan, S. J. *J. Am. Chem. Soc.* **2006**, *128*, 11663–11672.
(16) Zhao, Y.; Beck, J. B.; Rowan, S. J.; Jamieson, A. M. *Macromolecules* **2004**, *37*, 3529–3531.
(17) Braccini, I.; Perez, S. *Biomacromolecules* **2001**, *2*, 1089–1096.
(18) Eisenberg, A.; Kim, J. S. *Introduction to Ionomers*; Wiley-Interscience: New York, 1998.
(19) Faul, C. F. J.; Antonietti, M. *Adv. Mater.* **2003**, *15*, 673–683.
(20) Goddard, E. D.; Ananthapadmanabhan, K. P. *Interactions of Surfactants with Polymers and Proteins*; CRC Press: Boca Raton, FL, 1993.
(21) Antonietti, M.; Conrad, J.; Thunemann, A. *Macromolecules* **1994**, *27*, 6007–6011.
(22) Antonietti, M.; Conrad, J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1869–1870.
(23) MacKnight, W. J.; Ponomarenko, E. A.; Tirrell, D. A. *Acc. Chem. Res.* **1998**, *31*, 781–788.
(24) Wathier, M.; Grinstaff, M. W. *J. Am. Chem. Soc.* **2008**, *130*, 9648–9649.
(25) Craig, S. L. *Angew. Chem., Int. Ed.* **2009**, *48*, 2645–2647.
(26) Payagala, T.; Huang, J.; Breitbach, Z. S.; Sharma, P. S.; Armstrong, D. W. *Chem. Mater.* **2007**, *19*, 5848–5850.
(27) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792–793.
(28) Wasserscheid, P.; Welton, T. *Ionic Liquids in Synthesis*; Wiley-VCH: Weinheim, Germany, 2003.
(29) Ohno, H. *Ionic Liquids: The Front and Future of Material Developments*; CMC: Tokyo, 2003.
(30) Ward, I. M.; Sweeney, J. *An Introduction to The Mechanical Properties of Solid Polymers*, 2nd ed.; Wiley: New York, 2004.