JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

High Toughness, High Conductivity Ion Gels by Sequential Triblock Copolymer Self-Assembly and Chemical Cross-Linking

Yuanyan Gu,[†] Sipei Zhang,[‡] Luca Martinetti,[‡] Keun Hyung Lee,[‡] Lucas D. McIntosh,[‡]
C. Daniel Frisbie,*[,‡] and Timothy P. Lodge*[,†,‡]

[†]Department of Chemistry and [‡]Department of Chemical Engineering & Materials Science, University of Minnesota, Minneapolis, Minnesota 55414-0431, United States

Supporting Information

ABSTRACT: Self-assembly of ABA triblocks in ionic liquids provides a versatile route to highly functional physical ion gels, with promise in applications ranging from plastic electronics to gas separation. However, the reversibility of network formation, so favorable for processing, restricts the ultimate mechanical strength of the material. Here, we describe a novel ABA system that can be chemically cross-linked in a second annealing step, thereby providing greatly enhanced toughness. The ABA triblock is a poly(styrene-*b*-ethylene oxide-*b*-styrene) polymer in which about 25 mol % of the styrene units have a pendant azide functionality. After self-assembly of 10 wt % triblock in the ionic liquid [EMI][TFSA], the styrene domains are cross-linked by annealing at elevated temperature for ca. 20 min. The high ionic conductivity (ca. 10 mS/cm) of the physical ion gels is preserved in the final product, while the tensile strength is increased by a factor of 5.

Ion gels—polymeric networks swollen with a substantial amount of ionic liquid (IL)—have recently received a great deal of attention for diverse applications, including solid electrolytes, gate dielectrics for organic electronics, actuators, and gas separation membranes.[1−11] Key attributes of these soft materials include facile ion or solute transport, chemical and thermal robustness, tunable modulus, and negligible vapor pressure.[12−14] Among the various routes to ion gels, including direct polymerization of monomer/cross-linker combinations and swelling of elastomeric films,[15−21] the self-assembly of ABA triblock copolymers has proven to be particularly versatile.[22−24] For example, by simply adjusting the lengths of the IL-philic B and IL-phobic A blocks and the concentration of polymer, properties such as minimum gel concentration, gel modulus and ionic conductivity may be tuned over broad ranges.[25] Importantly, the noncovalent network structure, or physical gel, can be made reversible upon application of an external stimulus, such as temperature and light.[26−32] These reversible ion gels can be processed as liquids, and then solidified *in situ*, enabling rapid, cost-efficient processing steps such as aerosol jet printing and transfer printing.[33,34] A possible disadvantage of physical gels, however, is a lack of toughness when subjected to large strains, due to chain pull-out of the A blocks.[23,28,35−37] Herein, we describe a simple strategy to prepare thermoreversible, physical ion gels from an ABA copolymer that can subsequently be chemically cross-linked to form mechanically superior materials. We envision that the enhanced toughness will confer significant advantages when the gels are used as gate dielectrics in flexible electronics, or as thin membranes in CO_2 separations.[38,39] Crucially, we demonstrate the act of chemical cross-linking, being confined to the nonconducting A domains, has no deleterious effect on the ionic transport in the conducting B + IL majority phase.

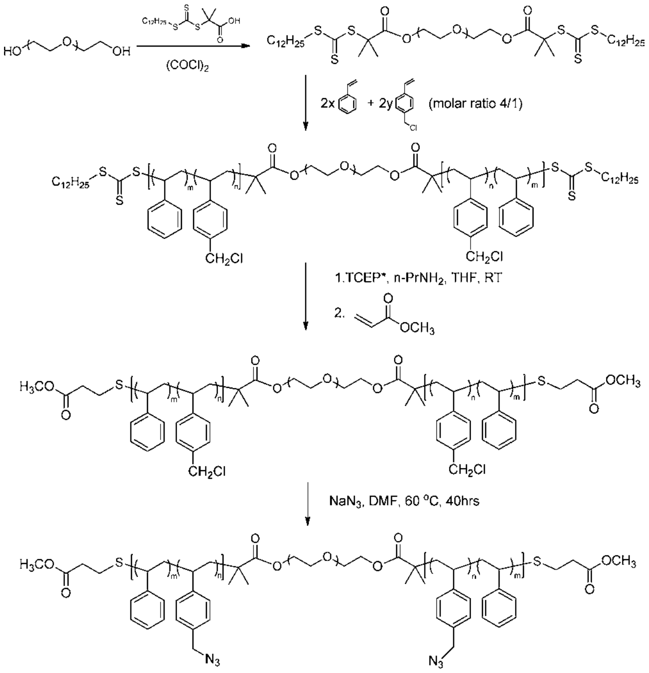
We have previously characterized in detail the mechanical and electrical impedance properties of ion gels prepared from poly(styrene-*b*-ethylene oxide-*b*-styrene) (SOS) triblock copolymers swollen with 1-ethyl-3-methylimidazolium bis(trifluoromethyl)sulfonyl amide ([EMI][TFSA]).[25] Remarkably, gels prepared with only modest amounts of copolymer (10−20% by weight) were able to achieve combinations of permselectivity and flux for CO_2/N_2 and CO_2/CH_4 gas separations that matched or exceeded the famous Robeson's Upper Bound.[40−42] The same ion gels were also able to gate organic thin film transistors at switching rates near 100 kHz, with very modest gate voltages (ca. 1 V), in fully printed circuits on plastic substrates.[38] Herein, we modify this triblock by introducing 28 mol % of vinylbenzyl azide into the styrene end blocks, as shown in Scheme 1. The triblock is prepared by RAFT polymerization from a telechelic poly(ethylene oxide) precursor, using styrene and 4-vinylbenzyl chloride as co-monomers in a 4:1 ratio. After removal of the RAFT agents at each chain end, reaction with NaN_3 installed the desired azide functionality in place of the chloride (see Supporting Information for more details).[36]

The resulting polymer is designated SOS-N_3(3.8-35-3.8), where the numbers in parentheses indicate the block molar masses in kDa, as determined by a combination of size exclusion chromatography (SEC) and ^1H NMR spectroscopy; the dispersity is 1.12 (see Table S1 for details). Ion gels with 10 wt % SOS-N_3(3.8-35-3.8) in [EMI][TFSA] were prepared gravimetrically, with the aid of CH_2Cl_2 as a co-solvent. The co-solvent was removed with a N_2 purge, followed by annealing in a vacuum oven at 45 °C for 2 days. Ion gels were also prepared with unfunctionalized SOS(2.8-35-2.8) and SOS(3.4-35-3.4) copolymers, for comparison.

Shear viscoelastic properties of gels were examined with an ARES rheometer (TA Instruments) using parallel plates (see Supporting Information for details). The dynamic moduli, G'

Received: May 24, 2013
Published: June 18, 2013

Scheme 1. Synthetic Route to SOS-N_3 Triblock Copolymer



*TCEP: tris(2-carboxylethyl)phosphine hydrochloride

and G'', were determined as a function of frequency at temperatures from 30 to 100 °C, a range where no azide cross-linking takes place. Time–temperature superposition was used to generate master curves following a previously described procedure, as shown in Figure 1.[25] The important features of these data are that (i) the two samples are nearly equivalent; (ii) the slight increase in longest relaxation time for 10 wt % SOS-N_3(3.8-35-3.8) compared to SOS(2.8-35-2.8) is attributable to the slightly longer end blocks in the former, which suppresses chain pull-out; (iii) neither sample is strictly a gel, in the sense that terminal behavior (i.e., flow) is achieved at long times (>10^3 s at 40 °C). However, it is this feature that enables thermoreversibility and liquid-state processing. The lifetime of the physical cross-links at a given temperature can easily be tuned by varying the end-block molecular weight.

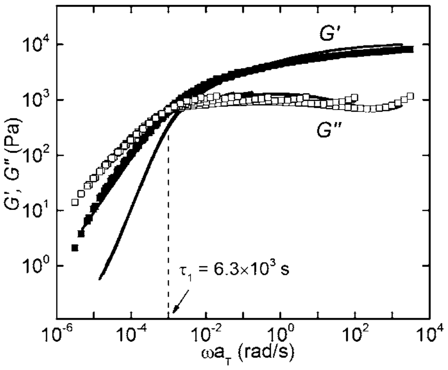


Figure 1. tTS master curves of dynamic storage and loss moduli referenced to 40 °C for ion gels with 10 wt % SOS-N_3(3.8-35-3.8) and 10 wt % SOS(2.8-35-2.8) measured over 30–100 °C. Symbols and lines represent moduli for the SOS-N_3(3.8-35-3.8) and SOS(2.8-35-2.8) gel, respectively.

Chemical cross-linking of the azide groups can be achieved at elevated temperature, or by UV irradiation.[43−46] In this case, we annealed samples at 200 °C in the rheometer, before cooling the sample to 100 °C to run a frequency sweep. The results are shown in Figure 2. After 20 min at 200 °C, G' becomes fully independent of frequency, with a value of ca. 8 kPa that corresponds closely to the high frequency value in Figure 1. Concomitantly, the loss tangent (tan $\delta = G''/G'$) drops to values below 0.01, consistent with formation of a highly elastic solid (see Figure S4). The enhanced mechanical toughness of the chemically cross-linked ion gels was revealed by large amplitude extensional tests performed on an ARES-G2 (TA Instruments) at 40 °C, using an extensional fixture. Figure 3 displays replicate stress–strain measurements for cross-linked 10 wt % SOS-N_3(3.8-35-3.8) gels, and uncross-linked 10 wt % SOS (3.4-35-3.4) gels. The strain-to-break more than doubles in the cross-linked case, and the tensile strength increases by a factor of about 5. The average toughness of the cross-linked ion gel was 4×10^5 J/m^3, compared to 5×10^4 J/m^3 for the non-cross-linkable comparison. (Interestingly, the 10 wt % SOS-N_3(3.8-35-3.8) gels before chemical cross-linking were too deformable to be reproducibly mounted in the extensional fixture.)

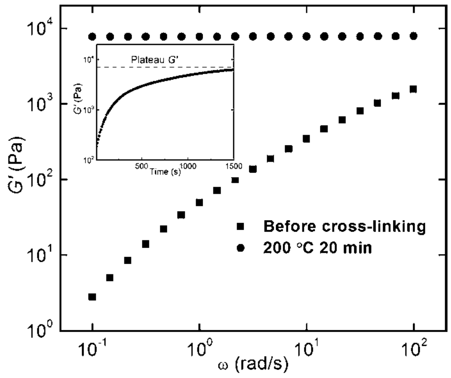


Figure 2. Dynamic storage moduli of ion gels with 10 wt % SOS-N_3(3.8-35-3.8) before chemical cross-linking, and after holding at the 200 °C for 20 min. Inset shows the dynamic storage modulus as a function of time at 200 °C (see Supporting Information).

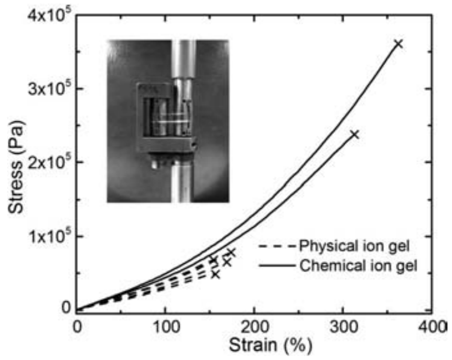


Figure 3. Stress–strain relationships for ion gels with 10 wt% SOS(3.4-35-3.4) (dashed lines) and 10 wt % SOS-N_3 (3.8-35-3.8) after chemical cross-linking (solid lines) measured at 40 °C. Inset photo is an ion gel sample loaded on the extensional fixture.

The ionic conductivity, σ, was determined as a function of temperature for the 10 wt % SOS-N_3(3.8-35-3.8) gels both before and after chemical cross-linking, using impedance analysis (see Supporting Information). The results are shown in Figure 4, along with data for pure [EMI][TFSA], and for 10 wt % SOS(2.8-35-2.8). Neither the presence of the azide functionality, nor the subsequent chemical cross-linking, has a significant effect on σ, and all three ion gels show a conductivity as high as 2/3 of that of the pure ionic liquid. This result is fully consistent with a previous study, in which it was shown that in this concentration regime the reduction in σ can be attributed almost entirely to the obstruction provided by the non-conductive styrene domains.[23,25]

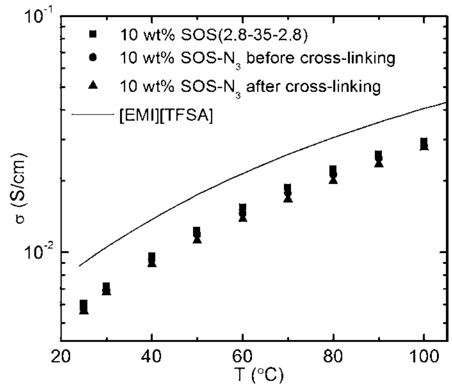


Figure 4. Temperature dependence of ionic conductivity for [EMI][TFSA] and ion gels with 10 wt % SOS(2.8-35-2.8) and 10 wt % SOS-N_3(3.8-35-3.8) before and after cross-linking.

In summary, we have developed a straightforward route to prepare highly conductive, high toughness ion gels by a sequential self-assembly and chemical cross-linking strategy. This approach marries the key advantages of physical gelation, namely, thermoreversibility and liquid state processing, with the enhanced mechanical strength of chemical gels. These materials are anticipated to be of advantage in diverse applications where ion gels have already shown promise, such as printable plastic electronics and membrane-based CO_2 separation.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details for polymer synthesis, characterization, sample preparation, rheological measurements and impedance analysis. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

lodge@umn.edu; frisbie@umn.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the Air Force Office of Scientific Research, the National Science Foundation through Award DMR-1206459 (TPL), and the MRSEC program of the National Science Foundation under Award DMR-0819885 at the University of Minnesota and Abu Dhabi Minnesota Institute for Research Excellence (ADMIRE), a partnership between the Petroleum Institute of Abu Dhabi and the Department of Chemical Engineering and Materials Science of the University of Minnesota. Y.G. and S.Z. were also partly supported by University of Minnesota Doctoral Dissertation Fellowships. The authors acknowledge Wenxin Fu, Yu Liu and Dr. Zhibo Li (ICCAS, China) for helpful discussions. We also thank Prof. Philippe Buhlmann for access to his impedance spectroscopy equipment, and Dr. David Giles, Dr. Jae-Hong Choi, Can Zhou and Tim Gillard for assistance.

■ REFERENCES

(1) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621−629.

(2) Ueki, T.; Watanabe, M. *Macromolecules* **2008**, *41*, 3739−3749.

(3) Imaizumi, S.; Kokubo, H.; Watanabe, M. *Macromolecules* **2012**, *45*, 401−409.

(4) Lu, J.; Yan, F.; Texter, J. *Prog. Polym. Sci.* **2009**, *34*, 431−448.

(5) Gin, D. L.; Noble, R. D. *Science* **2011**, *332*, 674−676.

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

(7) Le Bideau, J.; Ducros, J.-B.; Soudan, P.; Guyomard, D. *Adv. Funct. Mater.* **2011**, *21*, 4073−4078.

(8) Gwee, L.; Choi, J.-H.; Winey, K. I.; Elabd, Y. A. *Polymer* **2010**, *51*, 5516−5524.

(9) Virgili, J. M.; Nedoma, A. J.; Segalman, R. A.; Balsara, N. P. *Macromolecules* **2010**, *43*, 3750−3756.

(10) Hoarfrost, M. L.; Segalman, R. A. *Macromolecules* **2011**, *44*, 5281−5288.

(11) Thiemann, S.; Sachnov, S.; Porscha, S.; Wasserscheid, P.; Zaumseil, J. *J. Phys. Chem. C* **2012**, *116*, 13536−13544.

(12) Wilkes, J. S. *Green Chem.* **2002**, *4*, 73−80.

(13) Welton, T. *Chem. Rev.* **1999**, *99*, 2071−2084.

(14) Rogers, R. D.; Seddon, K. R. *Science* **2003**, *302*, 792−793.

(15) Susan, M. A. B. H.; Kaneko, T.; Noda, A.; Watanabe, M. *J. Am. Chem. Soc.* **2005**, *127*, 4976−4983.

(16) Fujii, K.; Asai, H.; Ueki, T.; Sakai, T.; Imaizumi, S.; Chung, U.; Watanabe, M.; Shibayama, M. *Soft Matter* **2012**, *8*, 1756−1759.

(17) Matsumoto, K.; Endo, T. *Macromolecules* **2008**, *41*, 6981−6986.

(18) Seki, S.; Susan, M. A. B. H.; Kaneko, T.; Tokuda, H.; Noda, A.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 3886−3892.

(19) Klingshirn, M. A.; Spear, S. K.; Subramanian, R.; Holbrey, J. D.; Huddleston, J. G.; Rogers, R. D. *Chem. Mater.* **2004**, *16*, 3091−3097.

(20) Jansen, J. C.; Friess, K.; Clarizia, G.; Schauer, J.; Izak, P. *Macromolecules* **2011**, *44*, 39−45.

(21) Harner, J. M.; Hoagland, D. A. *J. Phys. Chem. B* **2010**, *114*, 3411−3418.

(22) Lodge, T. P. *Science* **2008**, *321*, 50−51.

(23) He, Y.; Boswell, P. G.; Bühlmann, P.; Lodge, T. P. *J. Phys. Chem. B* **2007**, *111*, 4645−4652.

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

(25) Zhang, S.; Lee, K. H.; Sun, J.; Frisbie, C. D.; Lodge, T. P. *Macromolecules* **2011**, *44*, 8981−8989.

(26) Castelletto, V.; Hamley, I. W.; Ma, Y.; Bories-Azeau, X.; Armes, S. P.; Lewis, A. L. *Langmuir* **2004**, *20*, 4306−4309.

(27) Li, C.; Tang, Y.; Armes, S. P.; Morris, C. J.; Rose, S. F.; Lloyd, A. W.; Lewis, A. L. *Biomacromolecules* **2005**, *6*, 994−999.

(28) Tanaka, F.; Edwards, S. F. *Macromolecules* **1992**, *25*, 1516−1523.

(29) Ueki, T.; Nakamura, Y.; Yamaguchi, A.; Niitsuma, K.; Lodge, T. P.; Watanabe, M. *Macromolecules* **2011**, *44*, 6908−6914.

(30) Ueki, T.; Watanabe, M. *Langmuir* **2007**, *23*, 988−990.

(31) Aamer, K. A.; Sardinha, H.; Bhatia, S. R.; Tew, G. N. *Biomaterials* **2003**, *25*, 1087−1093.

(32) Sanabria-DeLong, N.; Crosby, A. J.; Tew, G. N. *Biomacromolecules* **2008**, *9*, 2784−2791.

(33) Cho, J. H.; Lee, J.; Xia, Y.; Kim, B.; He, Y.; Renn, M. J.; Lodge, T. P.; Frisbie, C. D. *Nat. Mater.* **2008**, *7*, 900−906.

(34) Lee, K. H.; Zhang, S.; Gu, Y.; Lodge, T. P.; Frisbie, C. D., submitted for publication, 2013.

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

(36) Tae, G.; Kornfield, J. A.; Hubbell, J. A.; Lal, J. *Macromolecules* **2002**, *35*, 4448−4457.
(37) Annable, T.; Buscall, R.; Ettelaie, R.; Whittlestone, D. *J. Rheol.* **1993**, *37*, 695−726.
(38) Cho, J. H.; Lee, J.; He, Y.; Kim, B. S.; Lodge, T. P.; Frisbie, C. D. *Adv. Mater.* **2008**, *20*, 686−690.
(39) Gu, Y.; Lodge, T. P. *Macromolecules* **2011**, *44*, 1732−1736.
(40) Gu, Y.; Cussler, E. L.; Lodge, T. P. *J. Membr. Sci.* **2012**, *423*−*424*, 20−26.
(41) Robeson, L. M. *J. Membr. Sci.* **1991**, *62*, 165−185.
(42) Robeson, L. M. *J. Membr. Sci.* **2008**, *320*, 390−400.
(43) Bang, J.; Bae, J.; Lowenhielm, P.; Spiessberger, C.; Given-Beck, S. A.; Russell, T. P.; Hawker, C. J. *Adv. Mater.* **2007**, *19*, 4552−4557.
(44) Yoo, M.; Kim, S.; Lim, J.; Kramer, E. J.; Hawker, C. J.; Kim, B. J.; Bang, J. *Macromolecules* **2010**, *43*, 3570−3575.
(45) Lee, S.; Lee, B.; Kim, B. J.; Park, J.; Yoo, M.; Bae, W. K.; Char, K.; Hawker, C. J.; Bang, J.; Cho, J. *J. Am. Chem. Soc.* **2009**, *131*, 2579−2587.
(46) Bates, C. M.; Strahan, J. R.; Santos, L. J.; Mueller, B. K.; Bamgbade, B. O.; Lee, J. A.; Katzenstein, J. M.; Ellison, C. J.; Willson, C. G. *Langmuir* **2011**, *27*, 2000−2006.