Macromolecules

Article

Cite This: *Macromolecules* 2019, 52, 1389−1399

pubs.acs.org/Macromolecules

Studies of Ion Conductance in Polymers Derived from Norbornene Imidazolium Salts Containing Ethyleneoxy Moieties

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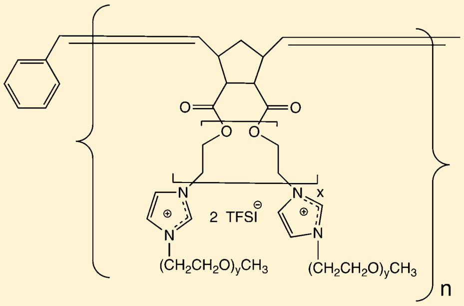
Supporting Information



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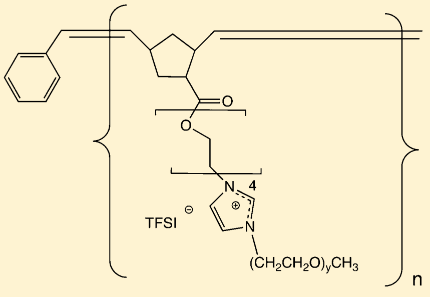

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ABSTRACT: "Two-armed" imidazolium polymers **2a−2f**, most of which contain oxyethylene moieties as linkers and ethyleneoxy terminal units, were prepared via ROMP. These polymers were thermally stable, with 5% weight losses occurring at 350 ± 5 °C under nitrogen. Their glass transitions were −22 to −51 °C, mostly ~3 °C higher than those of the respective monomers. The conductivities of the polymers were 4−30-fold lower than those of the respective monomers. The maximum room temperature (RT) conductivity, $\sigma_{25} = 2.27 \times 10^{-5}$ S/cm, was observed with the polymer **2f** with a tetra(oxyethylene) linker ($X = 4$) and a terminal di(ethyleneoxy) unit ($Y = 2$). Reduction of the double bonds in polymers **2** resulted in only small changes in T_g of the resultant **3** but 2.4-fold loss in RT conductivities. Four "one-armed" norbornene imidazolium TFSI monomers via ROMP produced polymers **5**, whose T_gs were generally low (−50 to −65 °C) and very close to those of the monomers. Although the RT conductivities were reduced by about an order of magnitude from the monomers, the polymers with tetra(oxyethylene) linkers ($X = 4$) and di- and triethyleneoxy terminal units ($Y = 2$ or 3) (**5c** and **5d**) had $\sigma_{25} \sim 3 \times 10^{-5}$ S/cm, similar to the best two-armed polymer. Two ABA triblock copolymers **8** were successfully synthesized from norbornene-*N*-phenylimide and two-armed monomers with different terminal ethyleneoxy units (**1d** and **1e**); these polymers demonstrated single direction actuation, but their performance was mediocre because of phase mixing that prevented the formation of the required bicontinuous phase morphology.

■ INTRODUCTION

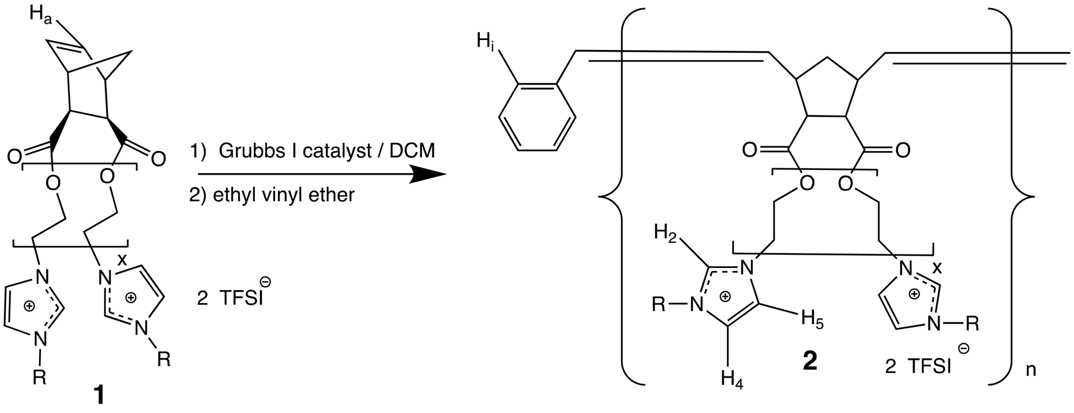
The investigation of ionic liquids for use in mechanical actuators has steadily attracted attention over recent years.[1−6] At the forefront of this work have been imidazolium ionic liquids[1−26] because of their easy functionalization, electrochemical stability, and excellent conductivities. Work toward mechanical actuators has ranged from simply swelling a polymer with an ionic liquid[9,15,16,18,20−23] to incorporation of the ionic liquid structures into high-conductivity polymers.[8,10−13,19,24−26] Swelling a polymer with an ionic liquid offers an easy approach, but since both the cation and anion are free to move, actuation occurs in both directions sequentially. Incorporation of either the cation or anion into the polymeric system restricts ion movement to a single component, thereby limiting actuation to a single direction, a desirable trait.

In the accompanying publication[27] norbornene-based imidazolium TFSI monomers containing oxyethylene linkers and terminal ethyleneoxy moieties were demonstrated to posssess high RT ionic conductivity. The present paper focuses on polymers made from those monomers for evaluation as polyelectrolytes suitable for incorporation into the soft phases of block copolymers for electromechanical actuator applications. Ring-opening metathesis polymerization (ROMP) was chosen over other methods due to its livingness and mild

Received: October 26, 2018
Revised: January 14, 2019
Published: February 11, 2019

DOI: 10.1021/acs.macromol.8b02303
Macromolecules 2019, 52, 1389−1399

Scheme 1. Synthesis of Two-Armed Norbornene Imidazolium TFSI Polymers 2a−2f[a]



a.	X = 1, R = $(CH_2)_4H$	poly{NB[C(O)OEIm$^+$Bu]$_2$ (TFSI$^-$)$_2$}
b.	X = 1, R = $CH_2CH_2OCH_3$	poly{NB[C(O)OEIm$^+$EOMe]$_2$ (TFSI$^-$)$_2$}
c.	X = 1, R = $(CH_2CH_2O)_3CH_3$	poly{NB[C(O)OEIm$^+$EO$_3$Me]$_2$ (TFSI$^-$)$_2$}
d.	X = 2, R = $(CH_2CH_2O)_3CH_3$	poly{NB[C(O)OE$_2$Im$^+$EO$_3$Me]$_2$ (TFSI$^-$)$_2$}
e.	X = 2, R = $(CH_2CH_2O)_4CH_3$	poly{NB[C(O)OE$_2$Im$^+$EO$_4$Me]$_2$ (TFSI$^-$)$_2$}
f.	X = 4, R = $(CH_2CH_2O)_2CH_3$	poly{NB[C(O)OE$_4$Im$^+$EO$_2$Me]$_2$ (TFSI$^-$)$_2$}

[a] Abbreviations: NB = norbornene, OE = oxyethylene = OCH_2CH_2, Im = imidazolium, Bu = *n*-butyl, EO = ethyleneoxy = CH_2CH_2O, Me = CH_3, TFSI = $N(SO_2CF_3)_2$.

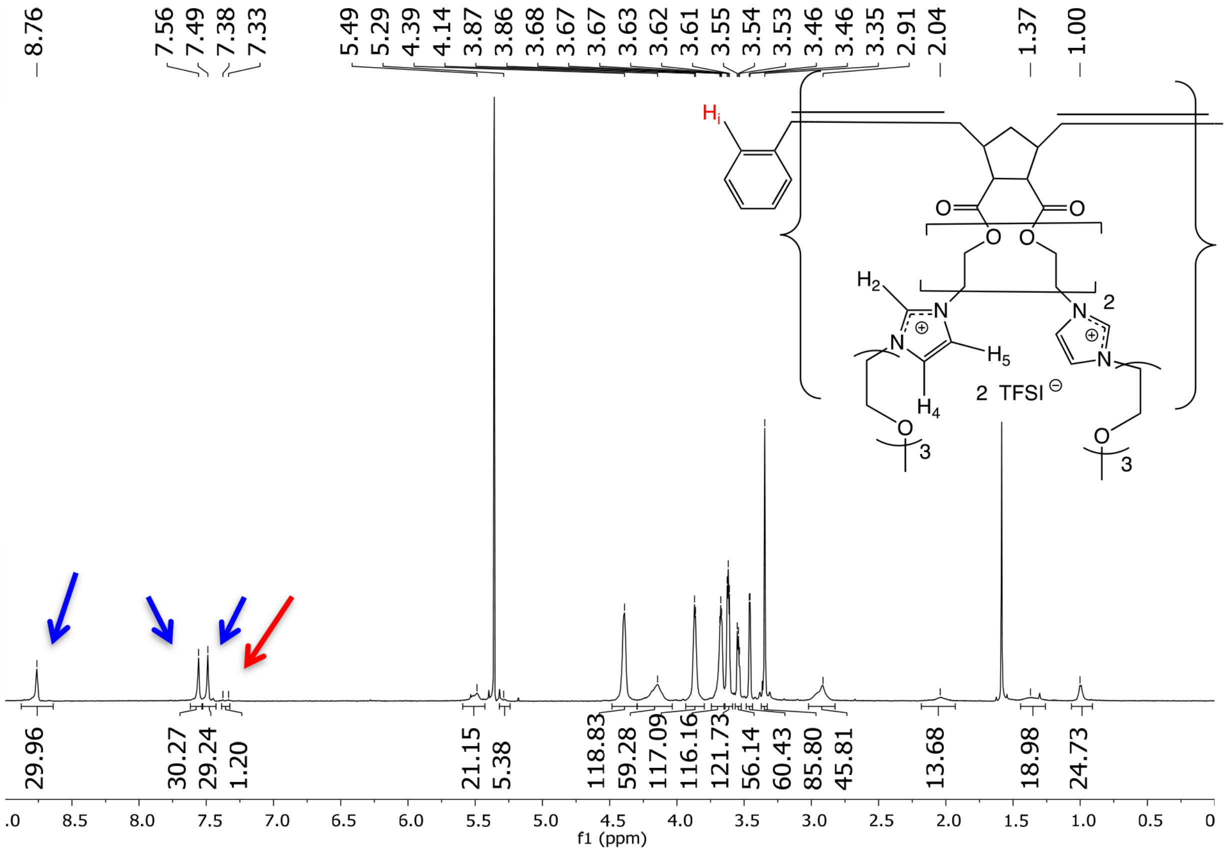


Figure 1. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, room temperature) of poly{NB[C(O)OE$_2$Im$^+$EO$_3$Me]$_2$ (TFSI$^-$)$_2$} (**2d**) indicating DP = 25. Initiator hydrogens H_i are indicated in red (integral 1.20), and imidazolium hydrogens (H_2, H_4, H_5) are indicated in blue (integrals 29.96, 30.27, and 29.24; average 29.8/H).

reaction conditions.[28,29] The living nature of ROMP makes it attractive for producing block copolymers.[30,31] The monomers employed here in the presence of mild bases at temperatures just above 70 °C can undergo an inversion of stereochemistry from *exo* to *endo*. ROMP generally employs mild reaction conditions, quenching compounds, and isolation techniques,

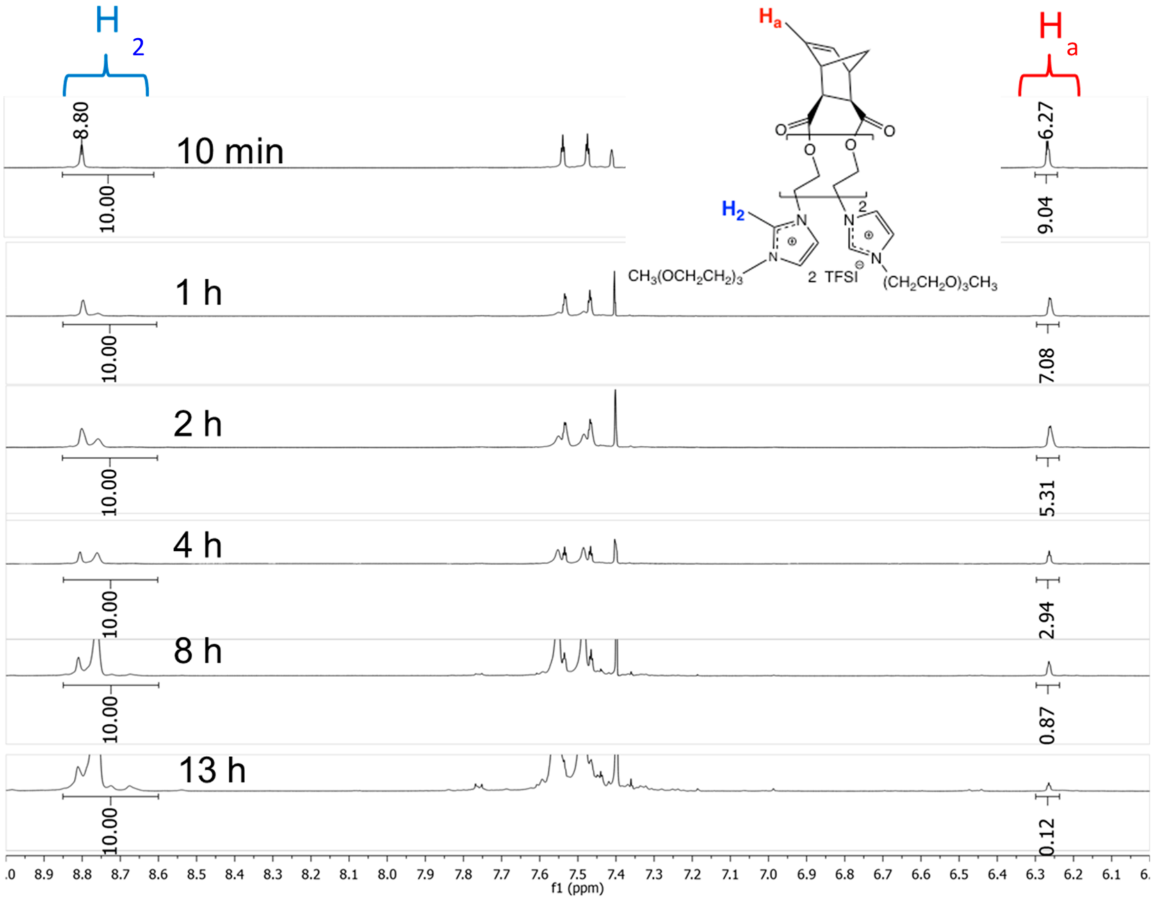


Figure 2. Partial ^{1}H NMR spectra (500 MHz) taken during the polymerization of monomer NB[C(O)OE$_2$Im$^+$EO$_3$Me]$_2$ (TFSI$^-$)$_2$ (**1d**) (275 mM) at 25 °C in CD_2Cl_2 with Grubbs catalyst 1 (9.4 mM). Signals for H_2 (blue) of the imidazolium moiety and olefinic proton H_a (red) of the monomer were used to monitor the kinetics.

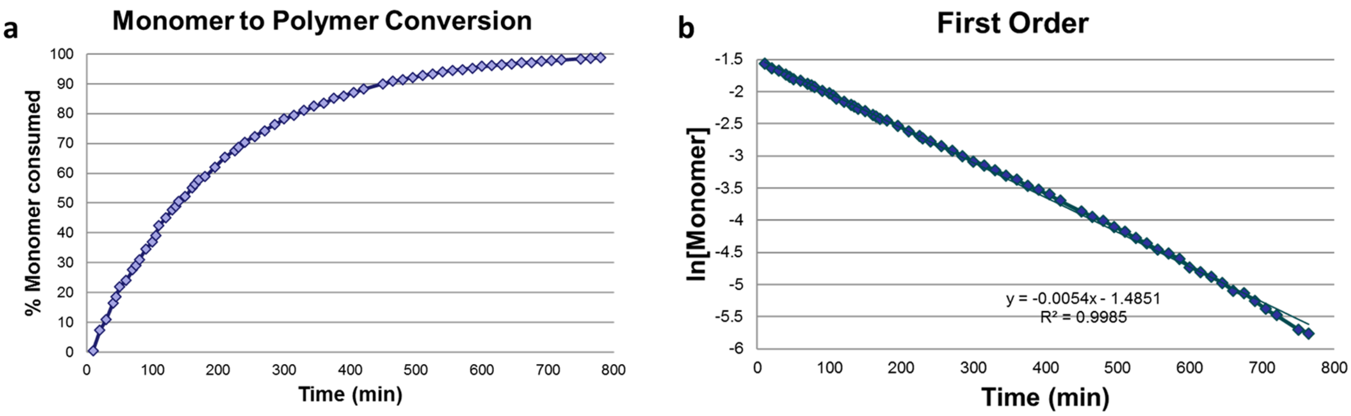


Figure 3. (a) Consumption of monomer NB[C(O)OE$_2$Im$^+$EO$_3$Me]$_2$ (TFSI$^-$)$_2$ (**1d**) in the ROMP experiment of Figure 2 as determined by ^{1}H NMR. (b) Graph of ln[monomer] vs time (pseudo-first-order plot).

making it the obvious choice for avoiding this isomerization and maintaining the stereochemistry of the monomers. Zheng et al. optimized ROMP conditions for a norbornene monomer containing imidazolium ethyleneoxy pendant groups, similar to our monomers.[7] Their work focused on a single-armed monomer containing a PF_6 counterion. Shaplov et al.[8] and Gin et al.[14] have employed ROMP for synthesis of imidazolium polymers as well. The goal of the present work was to produce polymers with high conductivities based on one mobile ion, the anion, a requirement for single direction actuation.

In this report only RT conductivities are discussed; elsewhere, full analyses of the dielectric relaxation spectra will be presented.

RESULTS AND DISCUSSION

Synthesis of Two-Armed Norbornene-Based Imidazolium TFSI Polymers. Scheme 1 shows the syntheses of polymers **2a**−**2f** from monomers **1** using ROMP via Grubbs first-generation initiator in dichloromethane (DCM) at room temperature. The entire monomer set was not employed for the production of homopolymers, since their conductivities were all within the same order of magnitude (10^{-5}−10^{-4} S/cm). Molecular weights were controlled via the monomer-to-initiator ratio. Targeted degrees of polymerizations ranged from 29 to 50, while targeted molecular weights ranged from 38 to 61 kDa. Reaction termination was achieved by quenching with ethyl vinyl ether. Isolations of **2a**−**2f** were achieved by precipitations of the reaction mixtures into mixtures of ether and methanol at −70 °C; subsequent precipitations were performed identically after dissolving the polymers in DCM. Molecular weight analyses were accomplished through ^{1}H NMR end-group analysis of initiator and imidazolium signals. As an example, Figure 1 shows the end-group analysis of **2d** as others have done;[32,33] the initiator *o*-phenyl signal (doublet) for H_i located at ∼7.3 ppm indicated by the red arrow was compared to imidazolium H_2, H_4, and H_5 signals shown in blue. For **2d** the observed DP of 25 gives an M_n of 33 kDa.

The polymerization of **1d** was performed in DCM in an NMR tube, and reaction progress at 25 °C was monitored via disappearance of the monomer's olefinic signals (Figure 2). At a monomer concentration of 275 mM with 9.4 mM Grubbs catalyst in DCM 99% conversion was achieved in 13 h. A spectrum was taken every 10 min for the first hour and every 15 min until 99% of the monomer had been consumed. The monomer's olefinic proton signals, shown in red, were compared to the imidazolium protons, shown in blue, to determine the level of monomer consumption. Figure 3 contains a plot of these results and a first-order kinetic treatment of the data, demonstrating the living nature of the reaction. Before quenching, each polymerization was usually monitored for 99+% conversion via ^{1}H NMR. The olefinic proton peaks were used to determine the *cis*:*trans* ratio via peaks at ∼5.3 and ∼5.5 ppm, respectively, as reported by others.[34−37] Although in some cases these peaks were unresolved, in others they could be individually integrated and indicated a predominance of *trans* double bonds, on average 74 ± 6% for polymer series **2**; this is similar to other reports for polynorbornenes made with Grubbs 1 catalyst.[34]

Table 1 lists molecular weights determined via ^{1}H NMR for polymers **2a**−**2f** and their T_g values compared to their monomeric counterparts. The target and experimental molecular weights generally agree well with one another, except in cases where the reactions were quenched prematurely for one reason or another.

Table 1. Molecular Weights and Glass Transition Temperatures for Two-Armed Norbornene Imidazolium TFSI Polymers 2a−2f in Comparison to Monomers 1a−1f

			monomer	polymer		
structures	*X*	*Y*	T_g[a] (°C)	target M_n (kDa)	obsd M_n (kDa)	T_g[a] (°C)
1a/**2a**	1	*n*-Bu	−44	44	35	−22
1b/**2b**	1	1	−39	47	44	−34
1c/**2c**	1	3	−50	61	17	−47
1d/**2d**	2	3	−54	39	33	−51
1d/**2d′**	2	3	−54	66	60	−49
1e/**2e**	2	4	−57	56	26	−42
1f/**2f**	4	2	−46	45	45	−39

[a] Determined from the second heating scan at a rate of 10 °C/min. T_g was taken as the midpoint in the change of heat capacity.

These polymers are surprisingly thermally stable, displaying 5% weight losses only at 350 ± 5 °C under nitrogen. The T_gs of most of the polymers are only 3−7 °C higher than those of the corresponding monomers. The major exceptions to this trend are **2a**, which contains a butyl tail with an increase of 22 °C, and **2e**, which is 15 °C higher than its corresponding monomer. For the previously developed acrylate and methacrylate monomers containing similar pendant groups and TFSI counterions, the differences in polymer and monomer T_gs ranged between 14 and 29 °C.[10,17,19] Interestingly, these ROMP polymers narrow the gap between monomer and polymer T_g values, giving an additional advantage to the ROMP approach to ion conducting polymers.

Polymers **2d** and **2d′** with M_n of 33 and 60 kDa, respectively, display T_gs within experimental error of each other, indicating that these molecular weights are above that at which the glass transition temperature (and other properties) is (are) molecular weight dependent.

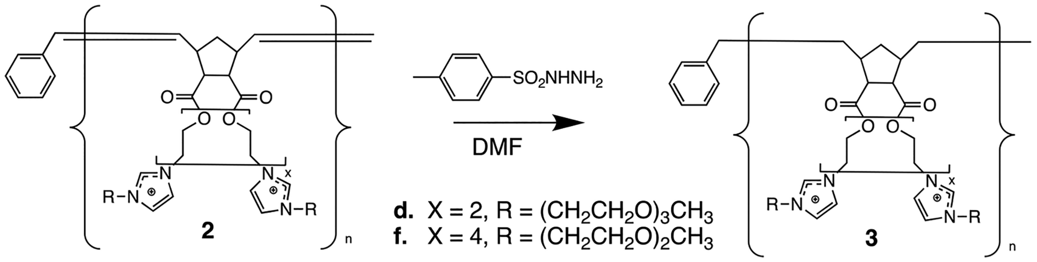
Ionic Conductivity of Two-Armed Norbornene-Based Imidazolium TFSI Polymers. Table 2 includes RT conductivity values for polymers **2a**−**2f** along with their corresponding monomers. For the *X* = 1 systems the RT conductivities of the polymers are more than an order of magnitude lower than their monomeric counterparts. However, for *X* ≥ 2, RT conductivities of the polymers drop only ∼4-fold in comparison to the monomers. Thus, we conclude that for optimal conductivities, a spacer of at least two ethyleneoxy units between the backbone of the polymer and imidazolium group must be used and that the N-terminal unit should be an oligo(ethyleneoxy) moiety. Of the polymers examined, the best system is **2f**, which has an OE_4 spacer and an EO_2 terminal group. This is consistent with the results for the 22 monomers examined; its monomer **1f** displayed the highest RT conductivity in the group. These results are attributed to complexation of the imidazolium cations by the oxyethylene and ethyleneoxy groups,[27] freeing the TFSI counterions for transport. There is no obvious relationship between the RT conductivity and the glass transition temperature.

Table 2. Ionic Conductivities of Two-Armed Norbornene Imidazolium TFSI Polymers 2a−2f in Comparison to Monomers 1a−1f

structures	*X*	*Y*	monomer *σ* (S/cm) at 25 °C	polymer *σ* (S/cm) at 25 °C
1a/**2a**	1	*n*-Bu	3.07×10^{-5}	1.03×10^{-6}
1b/**2b**	1	1	2.42×10^{-5}	8.10×10^{-7}
1c/**2c**	1	3	7.10×10^{-5}	1.38×10^{-6}
1d/**2d**	2	3	5.39×10^{-5}	1.71×10^{-5}
1e/**2e**	2	4	6.26×10^{-5}	1.49×10^{-5}
1f/**2f**	4	2	9.57×10^{-5}	2.27×10^{-5}

Reduced Two-Armed Norbornene-Based Imidazolium TFSI Polymers. In an attempt to further lower the T_gs and thus perhaps increase conductivities, the olefinic backbones of representative polymers were reduced using *p*-toluenesulfonyl hydrazide (Scheme 2). According to the literature, by conversion of the double bonds to aliphatic units, the T_g should be reduced by up to 30 °C.[38,39] The polymer with the highest conductivity, **2f**, was chosen for

Scheme 2. Reduction of Two-Armed Norbornene Imidazolium TFSI Polymers 2d and 2f to 3d and 3f



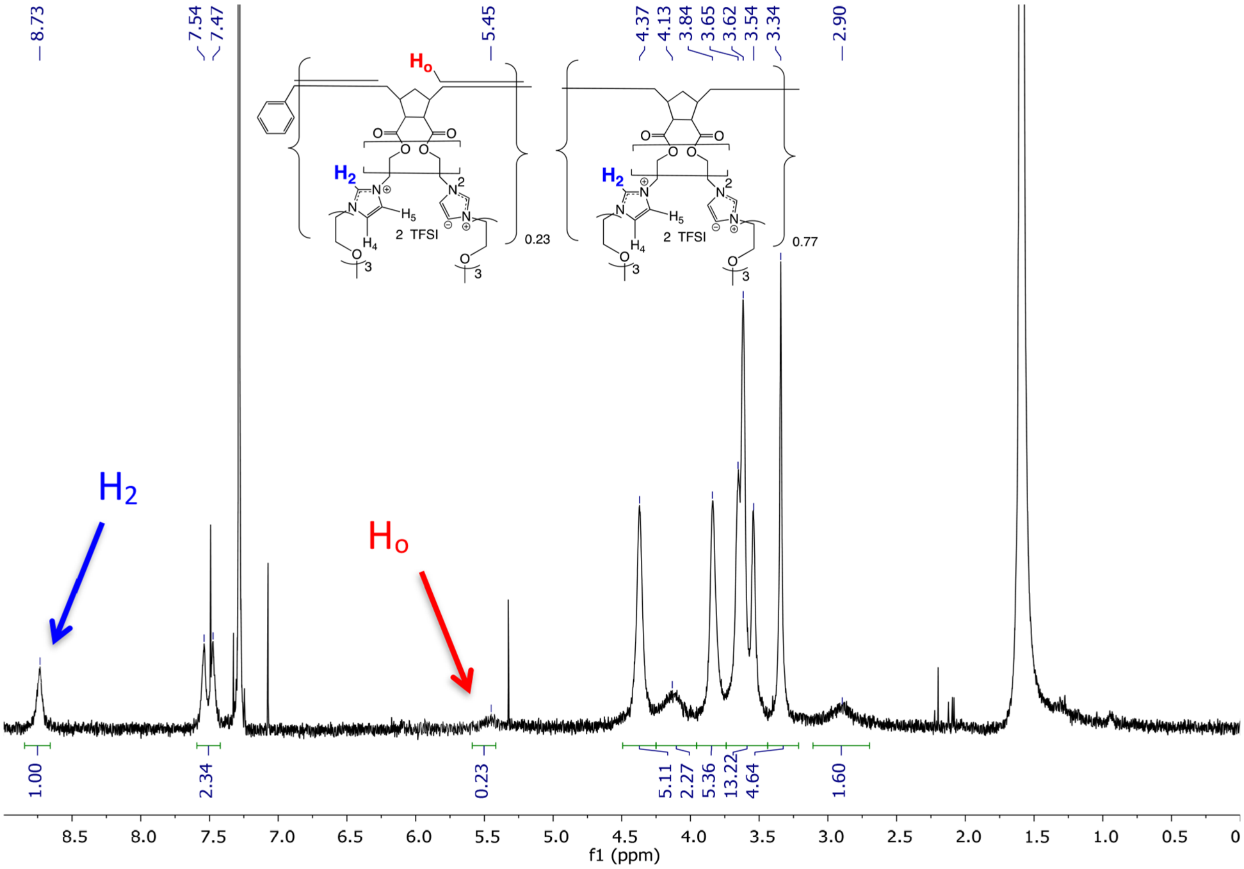


Figure 4. ^1H NMR spectrum (500 MHz, $CDCl_3$, room temperature) of polymer **3d**, indicating the loss of the olefinic backbone hydrogens of **2d**. Olefinic hydrogens H_o are indicated by the red arrow (integral 0.23), and imidazolium hydrogens H_2 are indicated by the blue arrow (integral 1.00).

reduction as well as polymer **2d**. Although a literature procedure[38] was used, complete conversion could not be achieved by moderately increasing reaction times or through the addition of excess *p*-toluenesulfonyl hydrazide. By increasing reaction times to 24 h, it was possible to achieve a conversion of 77% for **2d** and 83% for **2f**. Olefin reduction was monitored and determined by ^1H NMR as shown in Figure 4. The integral of the olefinic backbone hydrogens H_o (red arrow) in the starting material was compared to the integral of the imidazolium hydrogens H_2 (blue arrow) found in both the starting material and product.

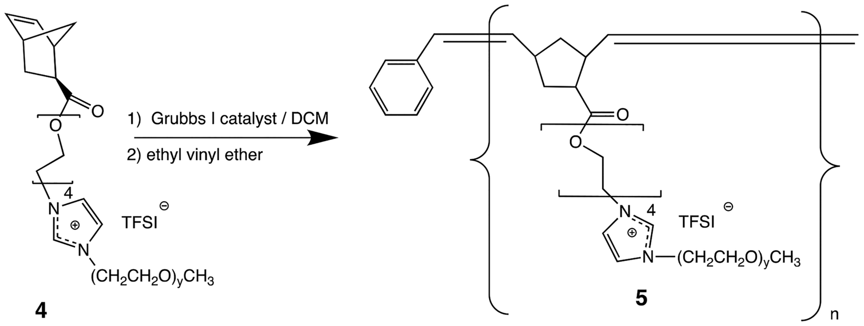
Table 3 offers a comparison of the T_g and conductivity values of the reduced polymers versus the unsaturated counterparts. Although a slight drop in T_g was observed for polymer **3f**, none was observed for polymer **3d** after hydrogenation. Furthermore, an increase in RT conductivity was not observed; in fact, the RT conductivities of both polymers **3d** and **3f** decreased ~2.4-fold upon reduction. These unexpected results suggest that the olefinic backbone is important in terms of conductivity, perhaps via conformational effects. It is reasonable to suspect from work performed on other ROMP norbornene polymers[40,41] that the unsaturated

Table 3. Glass Transition Temperatures and Ionic Conductivities of Hydrogenated Two-Armed Norbornene Imidazolium TFSI Polymers 3 Compared to Their Unsaturated Precursors 2

polymer	T_g[a] (°C)	conductivity (S/cm) $\sigma_{25°C}$
2d	−51	1.71×10^{-5}
3d	−51	5.66×10^{-6}
2f	−39	2.27×10^{-5}
3f	−46	9.66×10^{-6}

[a] Determined from the second heating scan at a rate of 10 °C/min. T_g was taken as the midpoint in the change of heat capacity.

Scheme 3. Synthesis of One-Armed Norbornene Imidazolium TFSI Polymers 5a−5d



a. Y = 0 poly[NBC(O)EO$_4$Im$^+$Me TFSI$^-$]
b. Y = 1 poly[NBC(O)EO$_4$Im$^+$EOMe TFSI$^-$]
c. Y = 2 poly[NBC(O)EO$_4$Im$^+$EO$_2$Me TFSI$^{-]}$
d. Y = 3 poly[NBC(O)EO$_4$Im$^+$EO$_3$Me TFSI$^-$]

polymers **2a**−**2f** adopt a helical structure due to the olefinic backbone. Hydrogenation of the olefinic backbone presumably destroys any stereoregularity and leads to a random coil conformation. The helical conformation may allow for better interactions between the ethyleneoxy units and imidazolium cations, thus providing more free TFSI anions for charge transport.

Synthesis and Properties of One-Armed Norbornene-Based Imidazolium TFSI Polymers. Syntheses of polymers **5** from the four monomers **4**[27] were accomplished using Grubbs first-generation catalyst (Scheme 3). The monomers were dissolved in DCM and degassed, and the catalyst was added in DCM solution. After polymerization, the reaction was quenched using ethyl vinyl ether. All of the resulting polymers were liquids; they were isolated by washing repeatedly with DCM. The polymers were characterized by DSC to determine their T_g values (Table 4). It is noteworthy and unusual that with one exception the polymers had glass transition temperatures within 2 °C of their parent monomers. The number-average molecular weights for the polymers were calculated from the ^{1}H NMR spectra as outlined above and, although generally higher than targeted, were close to the theoretical values. ^{1}H NMR spectra, via the olefinic signals at 5.45 and 5.26 ppm[34−37] in a ratio of 3:1, indicated that polymers **5** all had 75% cis linkages.

Table 4. Molecular Weights and Glass Transition Temperatures for One-Armed Norbornene Imidazolium TFSI Polymers 5a−5d in Comparison to Monomers 4a−4d

			monomer	polymer		
structures	X	Y	T_g[a] (°C)	target M_n (kDa)	obsd M_n (kDa)	T_g[a] (°C)
4a/**5a**	4	0	−55	50	45	−57
4b/**5b**	4	1	−66	49	54	−65
4c/**5c**	4	2	−69	50	55	−50
4d/**5d**	4	3	−56	51	63	−56

[a] Determined from the second heating scan at a rate of 10 °C/min. T_g was taken as the midpoint in the change of heat capacity.

The RT ionic conductivities of the one-armed polymers are summarized and compared to those of the monomeric precursors in Table 5. Generally the RT conductivities are all in the 10^{-5} S/cm range—about an order of magnitude (9−23-fold) less than those of the respective monomeric presursors.

Table 5. Ionic Conductivities of One-Armed Norbornene Imidazolium TFSI Polymers 5a−5d in Comparison to Monomers 4a−4d

structures	X	Y	monomer σ (S/cm) at 25 °C	polymer σ (S/cm) at 25 °C
4a/**5a**	4	0	2.80×10^{-4}	1.23×10^{-5}
4b/**5b**	4	1	2.07×10^{-4}	2.12×10^{-5}
4c/**5c**	4	2	4.39×10^{-4}	2.87×10^{-5}
4d/**5d**	4	3	2.79×10^{-4}	3.05×10^{-5}

Nonetheless, the one-armed norbornene imidazolium TFSI polymers **5**, like their monomeric precursors **4**, display RT conductivities generally higher than their two-armed analogues **2** and **1**, respectively (Table 2). Note that the linkers in the one-armed series **5a**−**5d** are all tetra(ethyleneoxy), and only the terminal unit was varied. Comparison with the equivalent member of the two-armed series, namely **2f**, which has a tetra(ethyleneoxy) linker and a di(ethyleneoxy) terminal unit, like **5c**, reveals similar RT conductivities: 2.27×10^{-5} vs 2.87×10^{-5} S/cm, respectively, but not as high as that of **5d**. One distinguishing feature of the polymers versus the corresponding monomers is that for polymer series **5** the maximum RT conductivity was observed at $Y = 3$, while in the monomer series the maximum was observed at $Y = 2$.[27] This may arise from the more sterically hindered situation in the polymers and/or the possibility of interactions between moieties in different repeat units.

Synthesis and Properties of ABA Block Copolymers of Two-Armed Norbornene-Based Imidazolium TFSI. To function in an effective mechanical actuator, the polymer must possess, in addition to ionic conductivity, a reasonably high modulus to do work. Because ionic conduction is maximized in low-T_g soft phases, bicontinuous phase-separated block copolymers are targets in which the second hard phase provides the necessary mechanical integrity. The ABA triblock design was chosen to be "hard−soft−hard" with imidazolium moieties as the soft B segment.

The homopolymer **7**, synthesized from monomer **6** (Scheme 4a) using Grubbs first-generation catalyst at a molecular weight of 44 kDa (DP = 184), formed brittle, nearly colorless, translucent films having T_g = 234 °C, in reasonable agreement with the literature.[39]

Monomer feed ratios were chosen in an attempt to obtain the gyroid phase, a bicontinuous morphology that is deemed optimal for ion transport.[42,43] From literature precedent the

Scheme 4. (a, top) Synthesis of Homopolymer 7 from Oxanorbornene Imide Monomer 6; (b, bottom) ABA Triblock Copolymers 8a and 8b Prepared from Monomers 6 and 1d and 6 and 1e, Respectively, by ROMP Using Sequential Addition of the Monomers

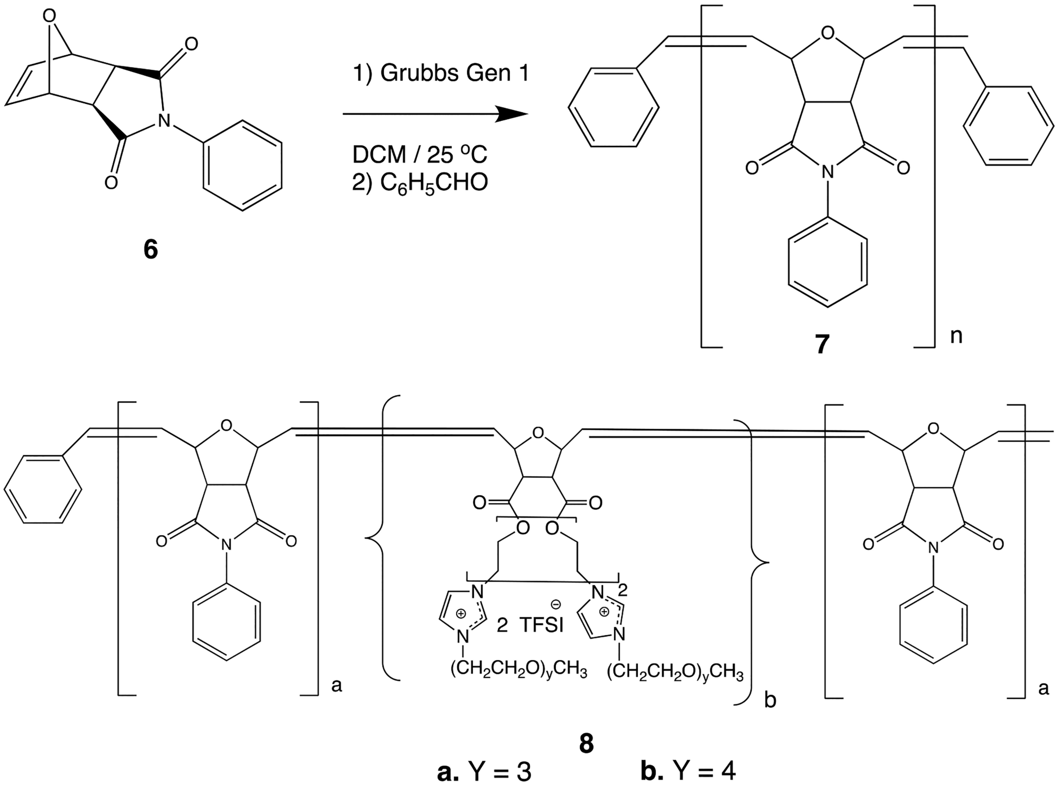


Table 6. Properties of ABA Triblock Copolymers 8a and 8b

polymer	A:B:A wt ratio	target M_n (total)	5% wt loss[a] (°C)	T_g[b] (°C)	$\sigma_{25°C}$ (S/cm)	actuation time to 63% curvature (s)
8a	21:58:21	65.3	353	−25, 154	1.2 × 10^{-8}	20
8b	19.5:61.0:19.5	58.4	346	−11		50

[a]By TGA under N_2 at 10 °C/min. [b]By DSC at 10 °C/min. Determined from the second heating scan as the midpoint in the change of heat capacity.

gyroid phases of ABA triblocks are expected to fall within the mole fraction constraints of an AB diblock copolymer, whose volume fraction of B block is twice that of the A blocks, in the A:B:A region of 16:68:16 to 19:62:19.[44] Using **6**, two ABA triblock copolymers, **8a** and **8b**, were synthesized from monomers **1d** and **1e**, respectively (Scheme 4b). Conversions were monitored via ^{1}H NMR, and sequential additions were not made until the previous monomer had been ≥99% consumed. Quenching of the reactions was achieved with ethyl vinyl ether.

Compositions, molecular weights, glass transition temperatures, thermal stabilities, conductivities, and actuation parameters for block copolymers **8a** and **8b** are listed in Table 6. Films of **8a** cast from chloroform were tough and creasable. The drastic increase in the soft segment T_g (+22 °C) from −47 °C for **2d** to −25 °C for polymer **8a** and the decrease in that of the hard segment (−80 °C) indicate significant phase mixing, most likely by interaction of the imidazolium cation with the phenyl moieties of the hard segment, a cation−π interaction.[45−47]

Confirming this, SAXS measurements revealed very little ordering.[48] Annealing the material at 170 °C/12 h and 202 °C/24 h resulted in embrittlement and discoloration of the film, indicating decomposition, presumably by oxidation in view of the polymer's excellent thermal stability; the T_g of the hard phase is believed to be too high to anneal without oxidative degradation (see Supporting Information). Gin et al. showed that 16 compositions of an AB diblock copolymer of poly(norbornene dodecyl ester) and poly(norbornene imidazolium) displayed a range of morphologies from disordered to lamellar.[49] Indeed, these workers found no evidence of formation of the required bicontinuous gyroidal morphology even after annealing for 2 months and concluded that the charged−uncharged architecture resulted in the strongly segregated regime, making formation of the bicontinuous morphology very difficult.

In an actuation test triblock copolymer **8a**, being a single-ion conducting material, provided modest single direction actuation (Figure 5), while **8b** provided slower and less actuation. Films of **8a** reached a maximum curvature of 0.14 mm^{-1} in 60 s with a characteristic curvature time of 20 s. **8b**, on the other hand, reached a maximum curvature of 0.10 mm^{-1} in 176 s with a characteristic time of 50 s. For comparison, Nafion swollen with 30 wt % *N*-ethyl-*N*′-methylimidazolium TFSI reached a maximum curvature of 0.6 mm^{-1} in 20 s.[20]

Figure 5. Overlay of photographs of electromechanical activation of a thin film of ABA block copolymer **8a** before (left) and after (right) application of a field of 4 V dc.

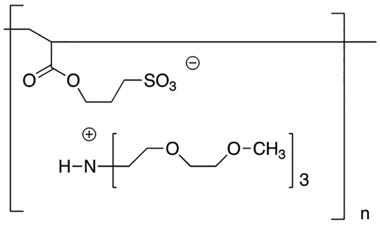
We conclude that the actuation of the block copolymers **8** was hindered by the phase mixing of the A and B segments, which resulted in the observed T_g increase of the soft phase and drop in conductivity. However, it is clear that these polynorbornene systems are capable of producing single direction actuation. Future efforts should focus on a redesigned hard segment monomer with a lower T_g and lower miscibility with the soft block to promote separation into bicontinuous phases.

CONCLUSIONS

In conclusion, six two-armed norbornene imidazolium TFSI monomers were converted to polymers **2a**−**2f** via ROMP. Most of the glass transitions of the polymers are ∼3 °C higher than those of the monomers, the lowest being −51 °C. The RT conductivities of the polymers are 4−30-fold lower than those of the monomers. The maximum RT conductivity, 2.27×10^{-5} S/cm, was observed with the polymer (**2f**) with a tetra(oxyethylene) linker and a terminal di(ethyleneoxy) unit. Partial (77 and 83%, respectively) reduction of the double bonds in polymers **2d** and **2f** resulted in only small changes in T_g but 2.4-fold loss in RT conductivities of the resulting **3d** and **3f**.

Four one-armed norbornene imidazolium TFSI monomers **4** were subjected to ROMP to produce polymers **5a**−**5d**, whose T_gs were generally low (−50 to −65 °C) and very close to those of the respective monomers. Although the RT conductivities were reduced by about an order of magnitude from the monomers, the polymers, all of which had tetra(ethyleneoxy) linkers, with di- and tri(ethyleneoxy) terminal units (**5c** and **5d**) had $\sigma_{25} \sim 3 \times 10^{-5}$ S/cm, similar to the best two-armed polymer, **2f**.

To put this work in perspective, polymers **9** with sulfonate pendant groups and tris{2-[2′-methoxyethoxy]ethyl}-ammonium counterions were recently reported to display glass transition temperatures from −48 to −57 °C and ionic conductivities ranging from 3.2×10^{-6} to 6.3×10^{-6} S/cm at 27 °C; these were claimed to be "the highest dc-conductivity values observed for this class of materials below 100 °C so far".[50] The ROMP polymers in the present work possess RT conductivities up to 4-fold higher (reaching 3×10^{-5} S/cm) as can be seen from Tables 2 and 5. And it should be noted that the Oak Ridge/U Tennessee group reported conductivities as high as 5×10^{-5} S/cm for some polysiloxanes with pendant imidazolium TFSI moieties.[25]



9

In this work two ABA triblock copolymers were successfully synthesized and shown to be capable of single direction actuation, but challenges in material design and processing remain if such triblock copolymers are to be optimized for functional electromechanical actuators.

A superfast (10^{-2} s) actuator consisting of a block copolymer doped with a low molecular weight imidazolium zwitterion was recently reported by one of us;[23] this appears to be the current state-of-the-art for electromechanical actuators.

EXPERIMENTAL SECTION

General. Reagents were purchased and used as received unless otherwise noted. Monomer **6** was prepared by a literature method.[51] ^{1}H NMR spectra were obtained on JEOL ECLIPSE-500, BRUKER 500, and AGILENT NMR vnmrs400 spectrometers. ^{13}C NMR spectra were collected on these instruments at 125, 125, and 101 MHz, respectively. ^{1}H NMR splitting abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet), h (heptet), b (broad), br u (broad, unresolved). High-resolution mass spectrometry (HR MS) was performed using an Agilent LC-ESI-TOF system. TGA data were obtained on a TA Instruments under N_2: TGA Q500; heating was performed at a rate of 20 °C/min. DSC data were obtained on a TA Instruments Q2000 differential scanning calorimeter under N_2; heating and cooling were performed at a rate of 10 °C/min; T_g values were recorded on second heating scans as the midpoint of the change in heat capacity. The ionic conductivity measurements were performed by dielectric relaxation spectroscopy. Samples were prepared by allowing them to flow to cover a 30 mm diameter freshly polished brass electrode at 100 °C *in vacuo*. To control the sample thickness at 100 μm, silica spacers were placed on top of the sample after it flowed to cover the electrode. Then a 15 mm diameter freshly polished brass electrode was placed on top to make a parallel plate capacitor cell which was squeezed to a gap of 100 μm in the instrument (with precise thickness checked after dielectric measurements were complete). The samples sandwiched between two electrodes were positioned in a Novocontrol GmbH Concept 40 broadband dielectric spectrometer, after being in a vacuum oven at 100 °C for 24 h. Each sample was then annealed in the Novocontrol at 120 °C in a heated stream of nitrogen for 1 h prior to measurements. The conductivity was measured using a sinusoidal voltage with amplitude 0.1 V and 10^{-1}−10^7 Hz frequency range for all experiments. Data were collected in isothermal frequency sweeps every 5 K from 120 °C to −100 °C. The actuation experiments were done as previously reported.[22]

General Procedure 1: Two-Armed Poly(nobornene imidazolium)s. Poly(NB[C(O)OEIm$^+$BuTFSI$^-$]$_2$ (2a). Monomer **1a** (1.89 g, 1.80 mmol) was added to a reaction tube with dry DCM (4 mL) under nitrogen. Grubbs first-generation catalyst (35.3 mg, 0.0429 mmol) was dissolved in a minimum amount of DCM (0.5 mL) and added. The solution was stirred at room temperature until ≥99% consumption of the monomer as determined by ^{1}H NMR. Ethyl vinyl ether (1.0 mL, 10 mmol) was added to quench the reaction. Volatile compounds were removed under vacuum. The crude polymer was washed with ether (5 mL × 3), dissolved in methanol (40 mL), and added to 15% diethyl ether in methanol (6 mL), and the solution was cooled to dry ice temperature for 4 h to allow the polymer to "oil out". Solvent was decanted and the process was repeated 2×. The polymer was dried under vacuum for 12 h; 1.04 g (55%). ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.10 (s, 33.70H), 7.72 (m, 67H), 7.34 (br u, 1.00H), 5.23 (m, 20H), 4.27 (m, 185H), 2.86 (br s, 23H), 2.69 (br s, 18H), 1.78 (br s, 74H), 1.26 (br s, 74H), 1.07 (m, 11H), 0.88 (br s, 99H). Target DP = 42; target M_n = 44 kDa. Measured by ^{1}H NMR DP = 33.7 and M_n = 35 kDa by end-group analysis of the imidazolium H_2 signal compared to the initiator *o*-phenyl proton signal. Integral 9.10 ppm = 33.70; integral 7.34 ppm = 1.00 H. DP = (33.70/2)/(1.00/2) = 33.7. T_g (DSC) = −22 °C. Conductivity at 25 °C = 1.03 × 10^{-6} S/cm.

General Procedure 2: Reduced Two-Armed Poly(norbornene imidazolium)s (3d). Unsaturated polymer **2d** (1.02 g, 0.0262 mmol), *p*-toluenesulfonyl hydrazide (0.42 g, 2.3 mmol), and DMF (20 mL) were stirred at 140 °C for 24 h. Most of the DMF was removed by rotary evaporation, and the material was precipitated into water. The polymer was washed with water (15 mL × 5), toluene (15 mL × 5), and water (15 mL × 3) and dried under vacuum for 1 day to give 1.01 g (99%) of reduced polymer. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.73 (br s, 1H), 7.54−7.47 (m, 2H), 5.45 (br s, 0.23H), 4.37 (br s, 5H), 4.13 (br s, 2H), 3.84 (br s, 5H), 3.74−3.44 (m, 13H), 3.34 (br s, 5H), 2.90 (br s, 2H). ^{1}H NMR indicated reduction of 77% of the olefinic units using the imidazolium H_2 signal at 8.73 ppm (1.00 H) compared to the residual olefinic H_o signal at 5.45 ppm (0.23 H). T_g (DSC) = −51 °C. Conductivity at 25 °C = 5.66 × 10^{-6} S/cm.

General Procedure 3. One-Armed Poly(norbornene imidazolium)s. Poly[NBC(O)OE$_4$Im$^+$MeTFSI$^-$] (5a). Monomer **4a** (1.0985 g, 1.667 mmol) was dissolved in dry DCM (2.0 mL). Grubbs first-generation catalyst (18.5 mg, 21.9 μmol) was dissolved in 2.0 mL of dry DCM. The catalyst solution was added quickly to the monomer solution, and the resulting solution was allowed to stir for 3 h at room temperature. After stirring, the solution separated into two phases. Ethyl vinyl ether (1.0 mL, 10 mmol) was added to quench the reaction. The two phases were separated, and the resulting polymer was washed 5× with DCM. Residual solvents and ethyl vinyl ether were removed under vacuum. The polymeric product was a dark brown viscous liquid (0.90 g, 82%). ^{1}H NMR (400 MHz, acetone-d_6): δ 9.01 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 5.45 (bm, 1.5H, 75% *cis*), 5.26 (bm, 0.5H, 25% *trans*), 4.52 (t, *J* = 4, 2H), 4.19 (bs, 2H), 4.07 (s, 3H), 3.93 (t, *J* = 4, 2H), 3.75−3.55 (m, 10H), 3.14 (bs, 0.25H), 3.00 (bs, 0.25H), 2.8−2.5 (m, 2.5H), 1.92 (bs, 1H), 1.69 (bm, 1H), 1.20 (bm, 2H). ^{13}C NMR (101 MHz, acetone-d_6): δ 175.07, 137.00, 124.86, 123.47, 123.20, 120.07 (q, *J* = 323 Hz), 70.22, 70.14, 70.08, 70.04, 68.82, 68.47, 63.11, 54.06, 49.60, 47.54, 42.14, 40.99, 35.81 (19 peaks, theory 21). DP = 68, M_n = 45 kDa (^{1}H NMR as above). Target DP = 76, M_n = 50 kDa. T_g −57 °C (DSC). Conductivity at 25 °C = 1.23 × 10^{-5} S/cm.

General Procedure 4. ABA Triblock Copolymer: A = Poly((3*aR*,7*aS*)-2-phenyl-3*a*,4,7,7*a*-tetrahydro-1*H*-4,7-epoxyisoindole-1,3(2*H*)-dione), B = Poly[NBC(O)OE$_2$Im$^+$EO$_3$MeTFSI$^-$] (8a). Monomer **6** (0.3126 g, 1.296 mmol) was added to a reaction tube with dry DCM (4 mL) under nitrogen. Grubbs first-generation catalyst (18.5 mg, 0.0225 mmol) in a minimum amount of DCM (0.5 mL) was added. The solution was stirred at room temperature and monitored by ^{1}H NMR until complete consumption of the monomer was observed. Monomer **1d** (0.8428 g, 0.6418 mmol) was added to the reaction mixture and monitored via ^{1}H NMR until complete consumption, at which time monomer **6** (0.3126 g, 1.296 mmol) was added. After consumption of the last monomer, ethyl vinyl ether (0.50 mL, 5.2 mmol) was added to quench the reaction. Volatile compounds were removed by vacuum. The crude polymer was washed with ether (5 mL × 3) and dissolved in a minimum amount of DCM (2 mL) and precipitated into a mixture of ether/DCM (v/v 85/15) (15 mL × 3) at dry ice temperature; this was repeated 2×. The polymer was collected and dried under vacuum for 12 h: 1.38 g (94%). Target DPs: initial A block 58, center block 29, terminal A block 58. Total target M_n: 65.3K: initial A block 13.9K (21 wt %), center B block 37.5K (58 wt %), terminal A block 13.9K (21 wt %). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 8.77 (br s, 1H), 7.61−7.36 (m, 10H), 7.29 (br s, 5H), 6.15 (br s, 3H), 5.90 (m, 1H), 5.48 (m, 0.65H), 5.32 (m, 0.25H), 5.19−5.11 (m, 1.32H), 4.69−4.64 (m, 3H), 4.39 (br s, 4H), 4.26−4.14 (m, 3H), 3.87 (br s, 4H), 3.67 (m, 4H), 3.62 (m, 5H), 3.56−3.41 (m, 7H), 3.35 (s, 3H), 2.91 (m, 2H), 2.03 (br s, 0.50H), 1.37 (br s, 0.68H). TGA (N_2) 5% wt loss = 353 °C. T_g = −25 and +154 °C. Conductivity at 25 °C = 1.1 × 10^{-8} S/cm.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.8b02303.

> Syntheses of polymers, representative NMR spectra, thermogravimetric analyses (TGA), and differential scanning calorimetric (DSC) determinations of glass transition temperatures (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are very appreciative of financial support from the U.S. Army Research Office under Grant W911NF-07-1-0452 Ionic Liquids in Electroactive Devices (ILEAD) MURI. We are also grateful to Prof. James McGrath (deceased, VT) and Tim Long (VT) for use of their thermal analysis equipment and Prof. James Runt (Penn State) for use of his dielectric spectrometer.

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DOI: 10.1021/acs.macromol.8b02303
Macromolecules 2019, 52, 1389−1399