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# **RAFT Polymerization: Ion Conductivity and Assembled Structures**



Synthesis of 1,2,4-Triazolium Salt-Based Polymers and Block Copolymers by RAFT Polymerization: Ion Conductivity and Assembled Structures

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**Abstract:** Well-defined 1,2,4-triazolium-based polymers were synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization of N-vinyl-1,2,4-triazolium salts, i.e., N-vinyl-4-ethyl-1,2,4-triazolium bromide (NVETri-Br) and N-vinyl-(4-ethoxyethyl)-1,2,4-triazolium bromide (NVEtOETri-Br). Reasonable control of the polymerization of these monomers was attained using a trithiocarbonate-type chain transfer agent (CTA), producing poly(N-vinyl-1,2,4-triazolium bromide)s with controlled molecular weights ( $M_{n,SEC} > 20000$ ) and low D values ( $M_w/M_n < 1.1$ ). Nonionic (water-soluble)-ionic (solubility tunable) block copolymers were achieved by RAFT polymerization of N-vinyl-1,2,4-triazolium salts using hydrophilic macro-CTAs derived from N-vinyl pyrrolidone (NVP) and N-vinyl-1,2,4-triazole (NVTri). The anion exchange reaction of the poly(NVETri-Br) segment in the block copolymers with lithium bis(trifluoromethanesulfonyl)imide (LiNTf<sub>2</sub>) proceeded selectively to afford amphiphilic block copolymers composed of hydrophobic poly(NVETri-NTf<sub>2</sub>) and hydrophilic nonionic segment, poly(NVP) or poly(NVTri). The ionic conductivity of poly(NVP)<sub>33</sub>-*b*-poly(NVETri-NTf<sub>2</sub>)<sub>67</sub> was  $4.3 \times 10^{-5}$  S/cm at 25 °C, which was remarkably higher than that of poly(NVETri-NTf<sub>2</sub>)  $(1.7 \times 10^{-5} \text{ S/cm})$ . At 90 °C, poly(NVP)-*b*-poly(NVETri-NTf<sub>2</sub>) exhibited high ionic conductivities of  $3.1-2.3 \times 10^{-4}$  S/cm under the ambient humidity conditions, depending on the comonomer composition (NVP content = 12-33 %). We believe that this represents the first report on controlled synthesis of 1,2,4-triazolium-based polymers and block copolymers that exhibit high characteristic ion-conducting properties, depending on the structure of the substituent group, counter anion, comonomer structure, and composition.

### 1. INTRODUCTION

The field of polymeric ionic liquids, which are macromolecules obtained by polymerizing ionic liquid monomers, has considerably extended in the past few decades, owing to their great interest in polymer science as well as in practical applications.[1-4] Many researchers have focused on the manipulation of their attractive properties, such as ionic conductivity and CO<sub>2</sub>-absorbing property, by adjusting the structures of the cation (e.g., imidazolium, pyridinium, and tetraalkylammonium) and the anion (e.g., halide, tetrafluoroborate, hexafluorophosphate), in addition to the structure of the polymer backbone. Among the various polymeric ionic liquids, imidazolium salt-based polymers are the most popular cationic components, which include polymers having imidazolium moieties in the side chains, such as poly(*N*-vinylimidazolium salt) derivatives.[5-8]

Recently, growing attention has been paid to triazolium-based polymers as a new member of the polymeric ionic liquids family.[4, 9] Triazole belongs to a versatile class of five-membered heterocyclic azole compounds having three isomers, including 1,2,3-triazole, 1,2,4-triazole, and 1,3,4-triazole derivatives, depending on the relative positions of the three nitrogen atoms. Among then, 1,2,3-triazole derivatives and their viny monomers, which can be utilized as precursors for 1,2,3-triazolium units, have gained great interest, driven by the remarkable development of the copper-catalyzed azide-alkyne cycloaddition as a representative click reaction.[10, 11] Based on the versatility of the click reaction, various 1,2,3-triazolium-based polymers have been prepared via post-quaternization of 1,2,3-triazole units in the polymers[12, 13] or direct polymerization of 1,2,3-triazolium-containing monomers[14] originating from the 1,2,3-triazole derivatives. In addition to main-chain type polymers, [15-17] a variety 1,2,3-triazolium of polymers having side chains have developed from been C-vinyl-1,2,3-triazolium,[14] vinyl ester,[12] and acrylate[13, 18] derivatives. 1,2,3-Triazolium-based ion conducting networks comprise an intriguing subclass of such triazolium-based polymers.[19] Other interesting systems involve antimicrobial polymethacrylates and their copolymers based on quaternized thiazole and 1,2,3-triazole side-chains.[20-22] However, to the best of our knowledge, the direct

controlled radical polymerization of *N*-vinyltriazolium salt monomers (e.g., *N*-vinyl-1,2,3-triazolium salts and *N*-vinyl-1,2,4-triazolium salts) has never been reported.

The 1,2,4-triazolium ring, another nitrogen-rich heterocyclic ionic liquid, has also gained increased interest due to its various attractive physicochemical and thermal properties, [23-26] as well as its potential electrochemical and energetic applications.[27-30] For example, Luo et al. demonstrated high ionic conductivity, wide electrochemical window, and good thermal stability of 1,2,4-triazolium methanesulfonate, which would be a suitable candidate for high temperature proton exchange membrane fuel cell electrolytes.[31] Vestergaard et al. also reported the availability of molten mixtures of 1,2,4-triazolium chloride-aluminum chloride, exhibiting high conductivity in a wide range of temperature range, as secondary battery electrolytes.[27] Despite the many characteristic functions and properties of 1,2,4-triazolium-containing ionic liquids, research on 1,2,4-triazolium-based polymers has been rather limited. Shreeve et al. developed 1,2,4-triazolium-based energetic polymers via free radical polymerization of N-vinyl-1,2,4-triazolium salts or by protonation of poly(N-vinyl-1,2,4-triazole), respectively.[32] Very recently, Yuan's group demonstrated that poly(N-vinyl-1,2,4-triazolium) obtained by free radical polymerization exhibited unique behavior in loading metal ions.[33] Miller et al. reported the synthesis of 1,2,4-triazolium-based covalently crosslinked polyester networks by Michael addition polymerization.[34] Another example is the preparation of proton-conducting membranes based on incorporating a proton conductor, 1,2,4-triazolium methanesulfonate, into the Nafion membrane.[35]

To further exploit the intriguing properties of 1,2,4-triazolium units for the development of advanced polymeric materials, in this study, we focus on *N*-vinyl-1,2,4-triazolium salts (NVTri-X) as a new family of triazolium-based monomers (Scheme 1). Two monomers, *N*-vinyl-4-ethyl-1,2,4-triazolium bromide (NVETri-Br) and *N*-vinyl-(4-ethoxyethyl)-1,2,4-triazolium bromide (NVEtOETri-Br), were selected, which were prepared by quaternization of *N*-vinyl-1,2,4-triazole (NVTri), as shown in Scheme 2. Similar to *N*-vinylimidazolium salts (NVIm-X), 1,2,4-triazolium-containing monomers belong to the class of non-conjugated *N*-vinyl monomers having a cationic heterocyclic ring. The reactivity of the

monomers and the various properties of the resulting polymers can be tuned as a function of the structure of the substituted group at the 4-position and the nature of the counteranion. Both NVTri-X and NVIm-X are ionic and azolium-based monomers, whereas NVTri and NVIm can be recognized as nonionic precursors and azole-based monomers (Scheme 1). Triazole, possessing an electron-rich aromatic ring, undergoes a proton-transfer mechanism similar to that of imidazole.[36] It was reported that the proton in 1,2,4-triazole is more readily transferred than that in imidazole due to the alternating single-double bond structure and the three nitrogens in the triazole.[35, 37] Electrochemical stability of 1,2,4-triazole and efficient promotion of proton conductivity were also demonstrated,[37] which are crucial for fuel cell applications. Poly(NVTri) composed of the 1,2,4-triazole unit is a water-soluble polymer possessing a pyridine-type isolated nitrogen atom that tends to form hydrogen bonds with water molecules, and its solubility is distinctly different from that of other water-insoluble poly(vinylazole)s containing sequences of two or more nitrogen atoms in heterocycle, the such as poly(N-vinyl-1,2,3-triazole) and poly(N-vinyl-1,3,4-triazole).[38, 39] Hence, 1,2,4-triazolium-based polymers may offer many attractive functions and properties compared to imidazolium- and 1,2,3-triazolium analogues.



**Scheme 1.** Structures of *N*-vinyl azoles (NVIm: *N*-vinylimidazole, NVTri: *N*-vinyl-1,2,4-triazole) and *N*-vinyl azolium salts (NVIm-X: *N*-vinylimidazolium salt, NVTri-X: *N*-vinyl-1,2,4-triazolium salt).

Ionic liquid-based block copolymers have continued to attract widespread interest because of their characteristic ionic conductivity and the ability to self-assemble into hierarchical structures. A variety of block copolymers with imidazolium salts having various substituent groups and counterions have been developed as promising candidates for diverse applications.[40-42] For example, atom transfer radical polymerization,[43, 44] reversible addition-fragmentation chain transfer (RAFT) polymerization,[45-48] and cobalt-mediated radical polymerization[49, 50] of imidazolium-containing monomers have been utilized to synthesize block copolymers having imidazolium-containing segments. In particular, much effort has been devoted to exploring the structure-morphology-property correlation, including the ionic conductivity and nanostructured morphologies of self-assembled architectures.[51-54] In some systems, the block copolymers exhibited increased ionic conductivity relative to statistical copolymer analogues or homopolymers; this is attributed to the confinement blocks within the ordered nanodomains.



**Scheme 2.** RAFT Polymerization of *N*-vinyl-4-ethyl-1,2,4-triazolium bromide (NVETri-Br) and *N*-vinyl-(4-ethoxyethyl)-1,2,4-triazolium bromide (NVEtOETri-Br) using different chain transfer agents (CTAs).

In this study, we initially investigated the RAFT polymerization of two 1,2,4-triazolium-based monomers (NVETri-Br and NVEtOETri-Br), which were prepared from NVTri (Scheme 2). In previous studies, we reported RAFT polymerization of NVTri, which is a nonionic *N*-vinyl monomer having a basic aromatic heterocycle.[38] RAFT polymerization of NVTri afforded well-defined amphiphilic block copolymers[38] and star block copolymers[55] comprising poly(NVTri) as a hydrophilic segment and poly(*N*-vinylcarbazole) as a hydrophobic segment with characteristic optoelectronic properties. We also developed controlled RAFT polymerization of NVIm-X, which were prepared by quaternization of NVIm, using xanthate-type chain transfer agents (CTAs).[45] The RAFT polymerization of NVIm-X afforded various imidazolium-based polymers.[45, 56] As a distinction from previous related studies using imidazolium-based and 1,2,4-triazole-based *N*-vinyl monomers (NVIm-X [45, 56] and NVTri [38, 55]), this contribution represents the first report of the controlled radical polymerization of *N*-vinyl-1,2,4-triazolium salts (NVTri-X), leading to the production of a new class of functional polymer electrolyte having characteristic ion conductivity.

We also describe the synthesis of well-defined block copolymers composed of two different *N*-vinyl monomers, in which the ionic segment was obtained by RAFT polymerization of NVETri-Br, as shown in Scheme 3. Poly(*N*-vinyl pyrrolidone) and poly(NVTri) were selected as non-ionic water-soluble segments. The solubility of the poly(NVTri-X) segment in the block copolymers can be tuned by changing the structure of the counteranion (Br<sup>-</sup> and bis(trifluoromethanesulfonyl)imide ((SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>N<sup>-</sup> = Tf<sub>2</sub>N<sup>-</sup>) to hydrophilic and hydrophobic ions, respectively) via anion exchange reactions. Hence, the resulting block copolymers are regarded as nonionic (water-soluble)-ionic (solubility tunable) block

copolymers that can be transformed from double hydrophilic block copolymers into amphiphilic block copolymers via anion exchange. Herein, we evaluate the ion conductivity and assembled structures of the resulting block copolymers.

#### 2. EXPERIMENTAL SECTION

#### 2.1.Materials

2,2-Azobis(isobutyronitrile) (AIBN, Kanto Chemical, 97%) was purified by recrystallization from methanol. *N*-vinyl pyrrolidone (NVP, Wako Pure Chemical, > 98 %) was purified by distillation under vacuum. *N*-Vinyl-1,2,4-triazole (NVTri) was obtained by the reaction of 1*H*-1,2,4-triazole with a excess of vinyl acetate in the presence of trifluoroacetic acid, hydroquinone, and mercury(II) acetate.[38, 57] Bromoethane (Kanto Chemical, > 98 %), 2-bromoethyl ethyl ether (Tokyo Chemical Industry, > 95 %), lithium bis(trifluoromethanesulfonyl)imide (LiNTf<sub>2</sub>, Tokyo Chemical Industry, > 98 %), and methanol (anhydrous MeOH, Kanto Chemical, 99.8%) were used as received. Other materials were used without further purification.

Eight different chain transfer agents (CTAs) were employed in this study, as shown in Scheme 2. O-Ethyl-S-(1-phenylethyl) dithiocarbonate (CTA 1),[58-60] O-ethyl-S-propionic acid dithiocarbonate (CTA 2),[61] O-ethyl-S-(1-ethoxy carbonyl) ethyl dithiocarbonate (CTA 3),[62, 63] and O-ethyl-S-(cyanomethyl) dithiocarbonate (CTA 4),[64] were synthesized by the reaction of potassium ethyl xanthogenate with corresponding bromide (1-bromoethyl benzene for CTA 1, 2-bromopropionic acid for CTA 2, ethyl 2-bromopropionate for CTA 3, bromoacetonitrile for CTA 4, respectively), according to a procedure reported in the literature. Benzyl 1-pyrrolecarbodithioate (CTA 5) was also synthesized according procedure reported previously.[65, to the 66] 2-(Dodecylthiocarbonothioylthio)-2-methylpropanoic acid (CTA 6, Aldrich, >98%), 2-cyano-2-propyl 7. trithiocarbonate (CTA Aldrich, >97%), dodecyl and 4-cyano-4-[(dodecyl-sulfanylthiocarbonyl)sulfanyl]pentanoic acid (CTA 8, Aldrich, >98%) were used as received.

#### 2.2.Synthesis of N-Vinyl-1,2,4-triazolium Salts

Two *N*-viny-1,2,4-triazolium salts having different substituent groups, NVETri-Br and NVEtOETri-Br, were synthesized by the reaction of NVTri with corresponding alkyl bromides according to the method used for the synthesis of *N*-vinylimidazolium salts, with slight modifications (Scheme 1).[6] In a typical experiment, NVTri (2.50 g, 26.3 mmol) and 3-bromoethane (14.1 g, 0.13 mol) were placed in a flask equipped with a magnetic stirring bar, and the mixture was refluxed at 50 °C for five days. During the reaction, the product precipitated from the reaction mixture. After washing the resulting precipitate several times with ethyl acetate by decantation, the product was isolated by filtration and dried under vacuum overnight at room temperature to afford NVETri-Br as a white solid (2.9 g, 54%).  $T_m = 85$  °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.49 (t, 3H, -CH<sub>2</sub>-CH<sub>3</sub>), 4.29 (q, 2H, -CH<sub>2</sub>-CH<sub>3</sub>), 5.58 (d, 1H, CH<sub>2</sub>=CH-), 6.07 (d, 1H, CH<sub>2</sub>=CH-), 7.50 (dd, 1H, CH<sub>2</sub>=CH-), 9.35 (s, 1H, N-CH-N), 10.37 (s, 1H, N-CH-N) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  14.20 (-CH<sub>2</sub>-CH<sub>3</sub>), 43.36 (-CH<sub>2</sub>-CH<sub>3</sub>), 110.01 (CH<sub>2</sub>=CH-), 129.24 (CH<sub>2</sub>=CH-), 141.60 (N-CH-N), 144.69 (N-CH-N) ppm. Anal. Calcd for C<sub>6</sub>H<sub>10</sub>BrN<sub>3</sub>: C, 35.3; H, 4.9; N, 20.6. Found: C, 35.3; H, 5.0; N, 20.5.

The same procedure was employed for the synthesis of NVEtOETri-Br. The mixture of NVTri (2.50 g, 26.3 mmol) and 2-bromoethylethyl ether (12.1 g, 78.9 mmol) was refluxed at 70 °C for 5 days, followed by the decantation with ethyl acetate, NVEtOETri-Br was obtained as a white solid (9.3g, 71%).  $T_{\rm m} =$  72 °C. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  1.11 (t, 3H, -CH<sub>2</sub>-CH<sub>3</sub>), 3.49 (q, 2H, -CH<sub>2</sub>-CH<sub>3</sub>), 3.77 (t, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 4.46 (t, 2H, -CH<sub>2</sub>-CH<sub>2</sub>-), 5.58 (d, 1H, CH<sub>2</sub>=CH-), 6.07 (d, 1H, CH<sub>2</sub>=CH-), 7.57 (dd, 1H, CH<sub>2</sub>=CH-), 9.29 (s, 1H, N-CH-N), 10.28 (s, 1H, N-CH-N) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  14.51 (-CH<sub>2</sub>-CH<sub>3</sub>), 47.86 (-N-CH<sub>2</sub>-), 65.54 (-O-CH<sub>2</sub>-), 66.51 (-O-CH<sub>2</sub>-), 110.04 (CH<sub>2</sub>=CH), 129.17 (CH<sub>2</sub>=CH), 141.88 (N-CH-N), 145.16 (N-CH-N) ppm. Anal. Calcd for C<sub>8</sub>H<sub>14</sub>BrN<sub>3</sub>O: C, 38.7; H, 5.7; N, 16.9. Found: C, 38.3; H, 5.84; N, 16.9.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of NVETri, NVETri-Br, and NVEtOETri-Br are shown in Figures S1-S5 (Supporting Information).

#### 2.3. General Polymerization Procedure

All polymerizations were carried out with AIBN as the initiator in a degassed sealed tube. A representative example is as follows: NVETri-Br (0.20 g, 1.00 mmol), CTA 7 (6.9 mg, 0.02 mmol), AIBN (1.6 mg, 0.01 mmol), and methanol (0.5 mL,  $[M]_0 = 2.0 \text{ mol/L}$ ) were placed in a dry glass ampule equipped with a magnetic stirring bar, and then the solution was degassed by three freeze-evacuate-thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 24 h. The reaction was stopped by rapid cooling with liquid nitrogen. For the determination of the monomer conversion, the <sup>1</sup>H NMR spectrum of the polymerization mixture collected just after the polymerization was measured in DMSO- $d_6$  at room temperature, and the integration of the monomer C=C-H resonance at around 6.1 ppm was compared with the sum of N-CH-N peak intensity of the triazolium ring in the polymer and the monomer at around 10.4-11.3 ppm. Conversion determined by this method was >99%. The crude polymer was purified by reprecipitation into a large excess of acetone/chloroform (7/3 vol%), and the resulting product was dried under vacuum at 60 °C to afford poly(NVETri-Br) as a pale yellow solid: yield 0.195 g, 95 %. <sup>1</sup>H NMR (DMSO- $d_6$ ):  $\delta$  1.2-1.9 (br, 3H, CH<sub>3</sub> in the side chain), 1.9-3.1 (br, 2H, CH<sub>2</sub> in the polymer main chain), 3.9-4.5 (br, 2H, CH<sub>2</sub>-CH<sub>3</sub> in the side chain), 4.5-5.4 (br, 1H, CH in the polymer main chain), 9.2-9.8 (br, 1H, N-CH-N), 10.4-11.3 (br, 1H, N-CH-N) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>): δ 12.5-15.2 (CH<sub>3</sub>), 35.3-38.9 (CH<sub>2</sub>-CH), 42.6-45.9 (CH2-CH3), 53.6-57.5 (CH2-CH), 141.8-144.7 (N-CH-N), 144.7-146.9 (N-CH-N) ppm. Anal. Calcd for C<sub>6</sub>H<sub>10</sub>BrN<sub>3</sub> • 1/2H<sub>2</sub>O: C, 33.8; H, 5.2; N, 19.7. Found: C, 34.0; H, 5.3; N, 19.3.

Similar procedure was applied for the polymerization of NVEtOETri-Br. In the case, monomer conversion was determined by the <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ) by comparing the peak integration of the monomer C=C-*H* resonance at around 6.1 ppm to the sum of N-C*H*-N peak intensity of the triazolium ring in the polymer and the monomer at around 10.1-11.0 ppm. After the polymerization, the crude polymer was purified by dialysis (Spectra Pore; MWCO 1000Da) with methanol. After 2 days, the solution was concentrated, and dried under vacuum at 60 °C to afford poly(NVEtOETri) as a pale

yellow solid. <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>):  $\delta$  0.9-1.4 (br, 3H, C*H*<sub>3</sub> in the side chain), 1.8-3.0 (br, 2H, C*H*<sub>2</sub> in the polymer main chain), 3.4-3.7 (br, 2H, C*H*<sub>2</sub>-CH<sub>3</sub> in the side chain), 3.7-4.1 (br, 2H, -CH<sub>2</sub>-C*H*<sub>2</sub>-), 4.2-4.6 (br, 2H, -C*H*<sub>2</sub>-CH<sub>2</sub>-), 4.7-5.5 (br, 1H, C*H* in the polymer main chain), 8.8-9.5 (br, 1H, N-C*H*-N), 10.1-11.0 (br, 1H, N-C*H*-N) ppm. <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>):  $\delta$  15.0-16.7 (*C*H<sub>3</sub>), 36.4-38.7 (*C*H<sub>2</sub>-CH), 47.3-50.1 (N-CH<sub>2</sub>-CH<sub>2</sub>), 54.1-57.8 (CH<sub>2</sub>-CH), 65.6-66.3 (-O-CH<sub>2</sub>-), 66.3-67.3 (-O-CH<sub>2</sub>-), 140.3-144.8 (N-CH-N), 144.8-147.7 (N-CH-N) ppm. Anal. Calcd for C<sub>8</sub>H<sub>14</sub>BrN<sub>3</sub>O • 1H<sub>2</sub>O: C, 36.1; H, 6.1; N, 15.8. Found: C, 36.7; H, 6.1; N, 16.1.

<sup>1</sup>H and <sup>13</sup>C NMR spectra of poly(NVETri-Br) and poly(NVEtOETri-Br) are shown in Figures S2-5 (see Supporting Information). Both poly(NVETri-Br) and poly(NVEtOETri-Br) were soluble in water, methanol, DMSO, and insoluble in acetone, ethyl acetate, THF, diethyl ether, hexane. Additionally, poly(NVEtOETri-Br) was soluble in DMF and chloroform. The solubilities of these polymers in various solvents are summarized in Table S1 (Supporting Information).

#### 2.4.Synthesis of Block Copolymers

A representative example of the synthesis of the block copolymer composed of NVP and NVETri-Br is as follows: NVP (5.3 mL, 5.6 g, 50 mmol), CTA 3 (0.22 g, 1.0 mmol), and AIBN (0.08 g, 0.5 mmol) were placed in a dry ampule, and then the solution was degassed by three freeze-evacuate-thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 50 min. After the product was purified by precipitation into diethyl ether, the product was dried under vacuum to afford poly(NVP) as a pale yellow solid (5.5 g, yield = 99%,  $M_{n,NMR}$  = 7000 g/mol,  $M_w/M_n$  = 1.07), which was employed as a macro-CTA. The xanthate-terminated poly(NVP) (0.14 g, 0.02 mmol), AIBN (1.6 mg, 0.01 mmol), NVETri-Br (0.20 g, 1.0 mmol), and methanol (0.7 mL) were placed in a dry ampule. After the solution was degassed by three freeze-evacuate-thaw cycles, the polymerization was conducted at 60 °C for 24 h (conversion determined by <sup>1</sup>H NMR spectroscopy = 97%). The reaction mixture was purified by reprecipitation into a large excess of acetone/chloroform (7/3 vol%), and isolated by filtration to give a block copolymer, poly(NVP)-*b*-poly(NVETri-Br) as a pale yellow solid (0.206 g,

60%). The block copolymer was soluble in water, methanol, DMSO, and insoluble in DMF, acetone, ethyl acetate, THF, chloroform, diethyl ether, hexane. The copolymer composition was determined using <sup>1</sup>H NMR spectroscopy (CD<sub>3</sub>OD) by a comparison of peaks associated with the two comonomers; the peak at 4.8-5.4 ppm attributed to the methine proton (1H) of the main chain in NVETri-Br unit and the peak at 1.9-2.1 ppm corresponded to the methylene proton (2H) of the NVP units.

In the case of the block copolymer obtained at  $[NVP]_0/[macro-CTA]_0/[AIBN]_0 = 25/2/1$ , the product was purified by dialysis (Spectra Pore; MWCO 1000Da) with methanol and then by reprecipitation into a large excess of acetone/diethylether (6/4 vol%).

For the synthesis of the block copolymer composed of NVTri and NVETri-Br, initially NVTri (3.8 g, 40 mmol), CTA 7 (0.14 g, 0.4 mmol), and AIBN (0.03 g, 0.2 mmol), and methanol (20 mL) were placed in a dry ampule, and then the solution was degassed by three freeze-evacuate-thaw cycles. After the ampule was flame-sealed under vacuum, it was stirred at 60 °C for 6 h. After the product was purified by precipitation into diethyl ether, the product was dried under vacuum to afford poly(NVTri) as a pale yellw solid (1.4 g, yield = 41%,  $M_{n,NMR}$  = 5100 g/mol,  $M_w/M_n$  = 1.09), which was employed as a macro-CTA. The trithiocarbonate-terminated poly(NVTri) (0.10 g, 0.02 mmol), AIBN (1.6 mg, 0.01 mmol), NVETri-Br (0.20 g, 1.0 mmol), and methanol (0.8 mL) were placed in a dry ampule. After the solution was degassed by three freeze-evacuate-thaw cycles, the polymerization was conducted at 60 °C for 24 h (conversion determined by <sup>1</sup>H NMR spectroscopy = 97%). The reaction mixture was purified by reprecipitation into a large excess of acetone/chloroform (7/3 vol%), and isolated by filtration to give a block copolymer, poly(NVTri)-b-poly(NVETri-Br) as a pale yellow solid (0.304 g, 99%). The block copolymer was soluble in water, methanol, DMSO, and insoluble in DMF, ethyl acetate, THF, chloroform, diethyl ether, hexane. The copolymer composition was determined using <sup>1</sup>H NMR spectroscopy (DMSO- $d_6$ ) by a comparison of peaks associated with the two comonomers: the peak at 9.0-9.7 ppm attributed to the N-CH-N proton (1H) of the triazolium ring in NVETri-Br unit and the peak at 7.4-8.2 ppm corresponded to the N=CH-N protons (2H) of the NVTri units.

<sup>1</sup>H NMR spectra and the solubilities of the block copolymers are shown in Figures S6-8 and Table S2, respectively (Supporting Information).

#### 2.5. Anion Exchange Reactions

The anion exchange to replace Br with NTf<sub>2</sub> was carried out according to the method used for the exchange poly(*N*-vinylimidazolium bromide), modifications.[6] reaction of with slight Poly(NVETri-NTf<sub>2</sub>) was synthesized by adding an aqueous solution (1.2 mL) of lithium bis(trifluoromethanesulfonyl)imide (LiNTf<sub>2</sub>, 0.6 g, 2.1 mmol) dropwise to a solution of poly(NVETri-Br) (0.1 g, 0.5 monomer unit mmol) dissolved in distilled water (2.0 mL). The mixture was then stirred at room temperature for 30 min. The precipitate was isolated by filtration, and the residual solid was washed with distilled water. Subsequently, the product was dried under vacuum at 60 <sup>o</sup>C overnight to afford poly(NVETri-NTf<sub>2</sub>) as a pale yellow solid (0.19g, 94%). Anal. Calcd for C<sub>8</sub>H<sub>10</sub>F<sub>6</sub>N<sub>4</sub>O<sub>4</sub>S<sub>2</sub>: C, 23.8; H, 2.5; N, 13.9; S, 15.9. Found: C, 24.3; H, 2.7; N, 13.9; S, 15.3.

The anion exchange reaction of poly(NVEtOETri-Br) was conducted using the same procedure to afford poly(NVEtOETri-NTf<sub>2</sub>) as a pale yellow solid (95%). Anal. Calcd for  $C_{10}H_{14}F_6N_4O_5S_2$ : C, 26.8; H, 3.2; N, 12.5; S, 14.3. Found: C, 26.3; H, 3.2; N, 12.2; S, 14.8.

The same method was employed for anion exchange to replace Br<sup>-</sup> with NTf<sub>2</sub><sup>-</sup> in the block copolymers, poly(NVP)-*b*-poly(NVETri-Br) and poly(NVTri)-*b*-poly(NVETri-Br).

### 2.6.Instrumentation

<sup>1</sup>H (400 MHz) and <sup>13</sup>C NMR (100 MHz) spectra were recorded with a JEOL JNM-ECX400. Elemental analysis was carried out on a Perkin-Elmer 2400 II CHNS/O analyzer. For the determination of the number-average molecular weight ( $M_n$ ) and molecular weight distribution ( $M_w/M_n$ ) of the 1,2,4-triazolium-based polymers, the SEC measurement was conducted using special SEC columns applicable for cationic polymers in acetonitrile/water (50/50 vol%) containing 0.05 M NaNO<sub>3</sub> as an eluent, similar to the case of poly(N-vinylimidazolium bromide)s.[45, 56] The SEC was performed on a

system consisting of a Tosoh DP-8020 pump, a Viscotek TDA model-301 triple detector array (RI, Viscosity, and RALLS; wavelength = 670 nm) at a flow rate of 1.0 mL/min. The column set was as follows: two consecutive columns [Tosoh TSK-GELs (exclusion limited molecular weight): G5000PW<sub>XL</sub>-CP (1 x  $10^6$ ), G3000PW<sub>XL</sub>-CP (9 x  $10^4$ ), 30 cm each] and a guard column [TSK-guardcolumn PW<sub>XL</sub>-CP, 4.0 cm]. Poly(ethylene oxide) standards were employed for calibration. Dynamic Light Scattering (DLS) was performed using a Zetasizer Nano (Sysmex) with a He-Ne laser. Thermogravimetric analysis (TGA) was performed on a SEIKO TGA/6200 at a heating rate of 10 °C/min under nitrogen atmosphere. Differential scanning calorimetry (DSC) analysis was conducted using a Seiko EXSTAR 6000 DSC 6200 at a heating rate of 10 °C /min under a nitrogen atomsphere. Tapping mode scanning force microscopy (SFM) observation was performed with an Agilent AFM 5500, using micro-fabricated cantilevers with a force constant of approximately 34 N/m. The samples were prepared by the drop casting of polymer methanol solutions onto mica substrates.

Ionic conductivity in plane direction of a membrane was determined using an electrochemical impedance spectroscopy technique over the frequency from 5 to  $10^5$  Hz (Hioki 3532-80) at 25, 55, and 90 °C under the ambient humidity conditions. A two-point-probe conductivity cell with two platinum plate electrodes was fabricated. The cell was placed under a thermo-controlled chamber. Ionic conductivity ( $\sigma$ ) was calculated from:

### $\sigma = d/(L_{\rm s}w_{\rm s}R)$

where *d* is the distance between the two electrodes,  $L_s$  and  $w_s$  are the thickness and width of the membrane, and *R* is the resistance value measured.

#### 3. RESULTS AND DISCUSSION

#### 3.1.RAFT Polymerization of N-Vinyl-1,2,4-triazolium Salts

Driven by our interest to probe the effects of the structures of the azolium component and the substituent group on the polymerization behavior and resulting polymer properties, we synthesized two *N*-viny-1,2,4-triazolium salts having different substituent groups, NVETri-Br and NVEtOETri-Br, by

the reaction of NVTri with corresponding alkyl bromides (Scheme 2). Compared to the synthesis of *N*-vinylimidazolium bromides,[6] a higher reaction temperature and a longer reaction time (50 and 70 °C for 5 days) were employed for the synthesis of the 4-substituted *N*-vinyl-1,2,4-triazolium bromides. Both NVETri-Br and NVEtOETri-Br can be regarded as nonconjugated *N*-vinyl monomers with cationic units, in which the nature of triazolium moiety, the counter ion, and the structure of the alkyl chain may affect the polymerization behavior.

Initially, various CTAs for conducting RAFT polymerization of NVETri-Br were tested with AIBN as an initiator at [M]<sub>0</sub>/[CTA]<sub>0</sub>/[AIBN]<sub>0</sub> = 100/2/1 at 60 °C for 24 h. Methanol was selected as a polymerization solvent due to its good solvency for the monomers and the resulting polymers. The results are summarized in Table 1. Under the conditions, suitable systems could be identified. The polymerization of NVETri-Br with the trithiocarbonate-type CTAs (CTA 6, CTA 7, and CTA 8) proceeded homogeneously to afford polymers having low D values ( $M_w/M_n = 1.09-1.10$ ) with almost quantitative conversions (>95%, as determined by <sup>1</sup>H NMR spectroscopy). The SEC traces of poly(NVETri-Br)s prepared with the trithiocarbonate-type CTAs were unimodal with no evidence of high and low molecular weight species (Figure S9, Supporting Information), and observed molecular weights were comparable to the theoretical values. In contrast, the molecular weights distributions were somewhat broader for poly(NVETri-Br)s obtained via polymerization with the xanthate-type mediating agents (CTA 1, CTA 3, and CTA 4,  $M_w/M_n > 1.4$ ). Relatively low monomer conversions (<30%) were obtained when using CTA 2 and CTA 5. We also investigated RAFT polymerization of NVETri-Br at a higher CTA-to-initiator ratio ( $[CTA]_0/[AIBN]_0 = 4$ ), but no significant effect was detected (Figure S9, Table S3, Supporting Information). Similarly, RAFT polymerization of NVEtOETri-Br with the trithiocarbonate-type CTAs (CTA 6, CTA 7, and CTA 8) showed well-controlled molecular weights and low *D* values ( $M_w/M_n = 1.09-1.10$ , Figure S10, Supporting Information) with quantitative conversions, as shown in Table 1.

Table 2 summarizes the results of the polymerization of two 1,2,4-triazolium-based monomers, NVETri-Br and NVEtOETri-Br, using the trithiocarbonate-type CTA 7 at different  $[M]_0/[CTA]_0$  ratios between 25 and 200. The polymerizations of NVETri-Br reached more than 95% conversion after 24 h at 60 °C in all cases, and the molecular weights increased with the  $[M]_0/[CTA]_0$  ratio while low D values ( $M_w/M_n = 1.07-1.34$ ) were maintained up to a  $[M]_0/[CTA]_0$  ratio of 200 (Figure 1a). Figure 2 shows the <sup>1</sup>H NMR spectra of poly(NVETri-Br) and poly(NVEtOETri-Br) obtained with CTA 7. The molecular weights of poly(NVETri-Br) could be estimated from relative integration of the <sup>1</sup>H NMR signal of the polymer backbone proton (triazolium ring at around 10.7 ppm) to the end group proton (methylene group in the trithiocarbonate group at around 1.2 ppm), as shown in Figure 2a. The values matched reasonably well with the theoretical molecular weights, which were apparently higher than the observed values determined by the SEC measurements. The end groups of the poly(NVETri-Br)s obtained at different  $[M]_0/[CTA 7]_0$  ratios and with other CTAs (CTA 1, 5, 6, and 8) were also detected by <sup>1</sup>H NMR spectroscopy (Figures S11 and S12, Supporting Information).

<insert Table 2>



**Figure 1.** SEC traces of (a) poly(NVETri-Br) and (b) poly(NVEtOETri-Br) obtained by RAFT polymerization with CTA 7 at different monomer-to-CTA ratios.

Similarly, the control exhibited by the polymerization of NVEtOETri-Br with CTA 7 was satisfactory, in terms of the molecular weight controlled by the monomer/CTA molar ratio with low D values (Table 2). The unimodal SEC trace shifts toward the higher molecular weight region with an increase in the  $[M]_0/[CTA]_0$  ratio, as shown in Figure 1b. Reasonable agreement between the theoretical and experimental molecular weights determined by SEC analysis and <sup>1</sup>H NMR measurement (Figure 2b) is seen until  $[M]_0/[CTA]_0$  ratio of 50. In this system, the conversion decreased markedly at a high monomer-to-CTA ratio ( $[M]_0/[CTA]_0 = 200$ ), which may be due to relatively slow polymerization rate

of NVEtOETri-Br. Nevertheless, efficient control of the molecular weights of the 1,2,4-triazolium-based polymers, poly(NVETri-Br) and poly(NVEtOETri-Br), could be achieved, regardless of the structure of the substituent group, by adjusting the [M]<sub>0</sub>/[CTA]<sub>0</sub> ratio.



**Figure 2.** <sup>1</sup>H NMR spectra (DMSO- $d_6$ ) of (a) poly(NVETri-Br) and (b) poly(NVEtOETri-Br) obtained by RAFT polymerization with CTA 7 at [M]<sub>0</sub>/[CTA 7]<sub>0</sub>/[AIBN]<sub>0</sub> = 100/2/1.

Kinetic studies of the polymerization of NVETri-Br and NVEtOETri-Br were carried out in the presence of the trithiocarbonate-type CTA 7 with AIBN in methanol at 60 °C. As illustrated in Figure 3a and d, the rate of polymerization of NVETri-Br was notably faster than that of NVEtOETri-Br. In both cases, after the short induction period of less than 4 h, the kinetic plots followed a pseudo-first-order profile up to high conversions. A similar induction period is often observed during

RAFT polymerization of *N*-vinylimidazolium bromides[45] and several *N*-vinyl monomers.[60, 63, 67-71] Nevertheless, a controlled polymerization process is indicated by the linear increase in the number-average molecular weights,  $M_n$ , vs the monomer conversion and low D values ( $M_w/M_n < 1.1$ , Figure 3b and e). In both cases, the SEC traces of the 1,2,4-triazolium-based polymers are unimodal and clearly shift toward the higher region with time, and no shoulder peak is apparent in the high molecular weight region, even in the last stage of the polymerization (Figure 3c and f). The structure of the substituent group in the 1,2,4-triazolium unit did not affect the controlled behavior of the polymerization, whereas the polymerization rate was influenced by the substituent group, presumably steric reason. All these results verified the controlled nature of the polymerization of *N*-vinyl-1,2,4-triazolium bromides with CTA 7 under the conditions.



**Figure 3.** (a, d) Time-conversion and first-order-kinetic plots for RAFT polymerization of (a-c) NVETri-Br and (d-f) NVEtOETri-Br at  $[M]_0/[CTA]_0/[AIBN]_0 = 100/2/1$  in methanol at 60 °C. (b, e) Conversion vs  $M_n$  and  $M_w/M_n$  plots. SEC traces of (c) poly(NVETri-Br) and (f) poly(NVEtOETri-Br).

#### 3.2.Synthesis of Triazolium-based Block Copolymers

We synthesized two series of block copolymers composed of two different *N*-vinyl monomers, in which one segment is composed of the 1,2,4-triazolium-based polymer formed by controlled RAFT polymerization of NVETri-Br (Scheme 3). As another component, a representative *N*-vinyl monomer, NVP, was initially selected, which afforded an important water-soluble polymer. Owing to the many desirable properties, such as low toxicity, chemical stability, and good biocompatibility, poly(NVP) has been employed in various fields, such as biomedical and cosmetic applications. Recently, much attention has been paid to controlled radical polymerization of NVP, as it offers the possibility to produce various functional polymers with specific architectures, such as block and graft copolymers, star and branched polymers, and hybrids.[40, 42, 72] Since xanthate-type CTAs have proven for controlling the polymerization of NVP and other nonconjugated *N*-vinyl monomers,[40, 42, 72] in this study we selected the xanthate-type CTA 3 for the synthesis of poly(NVP) macro-CTA. Then, the xanthate-terminated poly(NVP) was employed as a macro-CTA for the synthesis of a nonionic-ionic block copolymer (Scheme 3a).



**Scheme 3.** Synthesis of block copolymers by RAFT polymerization of NVETri-Br using (a) poly(NVP) macro-CTA prepared with CTA 3 and (b) poly(NVTri) macro-CTA prepared with CTA 7.

Polymerization of NVETri-Br was initially conducted in the presence of the xanthate-terminated poly(NVP) ( $M_{n,NMR} = 7000$ ,  $M_w/M_n = 1.07$ ) in methanol at 60 °C for 24 h. The polymerization conditions and results are presented in Table 3. When the polymerization was carried out with an [NVETri-Br]<sub>0</sub>/[macro-CTA]<sub>0</sub> of 25, the conversion determined by <sup>1</sup>H NMR spectroscopy was 93%, whereas the polymer was recovered in moderate yield (42%) by precipitation in acetone/chloroform (7/3)vol%). During the purification process, unreacted poly(NVP) macro-CTA and the monomer (and some oligomers) could be removed, which may contribute relatively lower polymer yield. As shown in Figure 4a, formation of the block copolymer was evidenced by the SEC chromatograms of the starting poly(NVP) macro-CTA and resulting block copolymer, illustrating a clear increase in the molecular weight, while the *D* value remained at  $M_w/M_n \approx 1.4$ . No significant macro-CTA impurity was detected in the block copolymer. The <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ) of the product exhibits peaks corresponding to the triazolium units at 9.2-9.8 and 10.4-11.3 ppm (Figure 5b), suggesting that chain extension proceeds with consequent formation of the block copolymer, poly(NVP)-b-poly(NVETri-Br). <sup>1</sup>H NMR analysis of the block copolymer in CD<sub>3</sub>OD permitted evaluation of the comonomer composition via comparison of the peaks associated with the two comonomers (Figure S7, Supporting Information). As Table 3, the comonomer composition could be tuned by adjusting shown in the [NVETri-Br]<sub>0</sub>/[macro-CTA]<sub>0</sub> ratio and the molecular weights of the poly(NVP) macro-CTAs. However, the molecular weights determined from the comonomer composition and the molecular weights of the macro-CTA were inconsistent with the theoretical and experimental molecular weights determined by SEC measurement. Note that SEC analysis of these ionic-nonionic block copolymers was challenging since these species are prone to hydrophilic and electrostatic interactions with the stationary phase. In this study, the use of special SEC columns applicable to cationic polymers and SEC measurement in acetonitrile/water (50/50 vol%) containing 0.1 M NaNO3 as an eluent facilitated estimation of the molecular weights and the D value of the cationic block copolymers by SEC. However, the presence of nonionic poly(NVP) in the block copolymers may lead to difficulty in accurate determination of the molecular weights. Another possible reason for the discrepancy between  $M_{n,NMR}$  and  $M_{n,SEC}$  as well as

the theoretical values is partial chain extension from the xanthate-terminated poly(NVP) to NVETri-Br, suggesting that this process is not perfectly controlled. Synthesis of the block copolymer by RAFT polymerization using an opposite order, i.e., polymerization of NVP using xanthate-terminated poly(NVETri-Br), was also unsuccessful (Figure S13, Supporting Information). Nevertheless, the nonionic-ionic (pyrrolidone/1,2,4-triazolium)-based block copolymers with tunable comonomer compositions were successfully produced by the polymerization of NVETri-Br with the xanthate-functionalized poly(NVP) and subsequent purification process.



**Figure 4.** SEC traces of (a) poly(NVP)-*b*-poly(NVETri-Br) and poly(NVP) macro-CTA ( $M_{n,NMR} = 7000$ ,  $M_{n,SEC} = 1100$ ,  $M_w/M_n = 1.07$ , and (b) poly(NVTri)-*b*-poly(NVETri-Br) and poly(NVTri) macro-CTA ( $M_{n,NMR} = 5100$ ,  $M_{n,SEC} = 1300$ ,  $M_w/M_n = 1.09$ ). In both cases, the block copolymers were synthesized by the polymerization at [NVETri-Br]<sub>0</sub>/[macro-CTA]<sub>0</sub>/[AIBN]<sub>0</sub> = 50/2/1.

Novel 1,2,4-triazole/1,2,4-triazolium-based block copolymers comprising poly(NVTri) as a water-soluble segment and poly(NVETri-Br) as an ionic segment were synthesized by RAFT polymerization (Scheme 3b). Note that water-solubility of non-ionic poly(NVTri) is ascribed to the presence of a pyridine-type isolated nitrogen atom in the heterocycle, which is in accord with the tendency nonionogenic poly(vinyl azole)s, including poly(vinylimidazole)s of and poly(vinyltriazole)s.[38, 39] In this case, RAFT polymerization of NVETri-Br was conducted in the presence of the trithiocarbonate-terminated poly(NVTri) macro-CTA (Figure S14, Supporting Information) in methanol at 60 °C for 24 h. For preparation of block copolymers having pre-determined comonomer compositions and molecular weights, the monomer to CTA ratio was varied in the range of  $[NVETri-Br]_0/[macro-CTA]_0 = 25-100$ . Under the given conditions, the conversions determined by <sup>1</sup>H NMR spectroscopy were more than 95%, and the polymers were recovered in high yields (78–99%) after precipitation in acetone/chloroform mixed solvent (Table 3). The structure of the resulting block copolymer was confirmed by <sup>1</sup>H NMR measurement (Figure 5c). Peaks corresponding to poly(NVTri) and poly(NVETri-Br) were clearly observed in the spectrum acquired in DMSO- $d_6$ . Integration of the appropriate peaks facilitated elucidation of the compositions of NVTri and NVETri-Br, and the molecular weights calculated from <sup>1</sup>H NMR were comparable to the theoretical compositions, as shown in Table 3. Figure 4b shows a complete shift of the SEC trace of the parent poly(NVTri) to the higher molecular mass region without residual macro-CTA impurity, indicating successful chain extension from the trithiocarbonate-terminated poly(NVTri) macro-CTA to NVETri-Br. With an increase of the [NVETri-Br]/[macro-CTA] ratio, the molecular weight increased with maintaining unimodal SEC peaks  $(M_w/M_n < 1.2)$ , Figure S14, Supporting Information), which is indicative of the formation of the 1,2,4-triazole/1,2,4-triazolium-based block copolymers with controlled comonomer compositions.

#### 3.3.Anion Exchange Reactions

Anion exchange to replace Br with NTf<sub>2</sub> was carried out according to the method used for the synthesis of poly(N-vinylimidiazolium salt)s with slight modifications (Scheme 4).[6] Poly(NVETri-NTf<sub>2</sub>) was synthesized by initially dissolving poly(NVETri-Br) in distilled water, after which an aqueous solution of  $LiN(SO_2CF_3)_2$  (LiNTf<sub>2</sub>) was added dropwise to the polymer solution at room temperature. After stirring the mixture at room temperature for 30 min, the precipitate, which was formed by the anion exchange reaction, was isolated by filtration, and the residual solid was washed with distilled water. As expected, the resulting poly(NVETri-NTf<sub>2</sub>) was insoluble in H<sub>2</sub>O but soluble in methanol, DMSO, DMF, acetone, ethyl acetate, and THF (Table S1, Supporting Information). As shown in Figure 5a, the <sup>1</sup>H NMR spectrum of poly(NVETri-NTf<sub>2</sub>) exhibits peaks at 9.0–9.4 and 9.8–10.2 ppm attributed to the triazolium ring, which were notably shifted from the peaks at 9.2–9.8 and 10.4–11.3 ppm corresponding to the original poly(NVETri-Br). In the case of poly(NVEtOETri-Br), similar chemical shifts of the peaks at 8.8–9.5 and 10.1–11.0 ppm were observed for the NVEtOETri-Br repeating unit to 8.7–9.4 and 9.8–10.2 ppm in the NVEtOETri-NTf<sub>2</sub> repeating unit (Figure S16a, Supporting Information). The  $^{13}$ C NMR spectrum of poly(NVETri-NTf<sub>2</sub>) clearly shows four peaks in the range of 114-125 ppm, attributed to the trifluoromethyl group in the NTf<sub>2</sub> unit, whereas these peaks were not apparent in the profile of poly(NVETri-Br) (Figure S17a, Supporting Information). The <sup>13</sup>C NMR spectrum of poly(NVEtOETri-NTf<sub>2</sub>) also exhibited four new peaks at 115–125 ppm (Figure S16b, Supporting Information), indicating successful incorporation of the NTf<sub>2</sub> unit. The elemental analyses of the products, poly(NVETri-NTf<sub>2</sub>) and poly(NVEtOETri-NTf<sub>2</sub>), obtained after the anion exchange reaction also indicated that the observed values including sulfur content were well agreement with the theoretical values (see experimental section). The <sup>1</sup>H and <sup>13</sup>C NMR results and elemental analyses suggested quantitative anion exchange to generate the targeted hydrophobic 1,2,4-triazolium-based polymers, poly(NVTri-NTf<sub>2</sub>)s.



Scheme 4. Anion exchange of (a) poly(NVETri-Br), (b) poly(NVP)-*b*-poly(NVETri-Br), and (c) poly(NVTri)-*b*-poly(NVETri-Br).

The thermal stability of poly(NVTri-Br) and poly(NVTri-NTf<sub>2</sub>) was investigated under nitrogen atmosphere by TG analysis. Figure 6 illustrates initiation of rapid decomposition around 220 °C for pristine poly(NVETri-Br) and poly(NVEtOETri-Br) ( $T_{d10} = 221$  and 230 °C, respectively), and the residual weight at 300 °C was less than 30%. In contrast, the poly(NVETri-NTf<sub>2</sub>) and poly(NVEtOETri-NTf<sub>2</sub>) species obtained after the anion exchange reaction exhibited higher stability ( $T_{d10} > 320$  °C). Thus, anion exchange to generate the NTf<sub>2</sub> form led to improve thermal stability at elevated temperature in both cases. Glass transition temperature ( $T_g$ ) of poly(NVETri-Br) and poly(NVETri-NTf<sub>2</sub>) were evaluated by DSC analysis (Figure S18, Supporting Information). The  $T_g$ s of poly(NVETri-Br) and poly(NVETri-NTf<sub>2</sub>) were observed at 70 and 13 °C, respectively. The lower  $T_g$  of poly(NVETri-NTf<sub>2</sub>) might result from an increase of the free volume by the larger NTf<sub>2</sub> anions.



**Figure 5.** <sup>1</sup>H NMR spectra (DMSO- $d_6$ ) of (a) poly(NVETri-Br) and poly(NVETri-NTf<sub>2</sub>), (b) poly(NVP)-*b*-poly(NVETri-Br) and poly(NVP)-*b*-poly(NVETri-NTf<sub>2</sub>), and (c) poly(NVTri)-*b*-poly(NVETri-Br) and poly(NVTri)-*b*-poly(NVETri-NTf<sub>2</sub>).



Figure 6. TG analysis of (a) poly(NVETri-X) and (b) poly(NVEtOETri-X); X = Br and NTf<sub>2</sub>.

Anion exchange was also conducted for the block copolymers, poly(NVP)-b-poly(NVETri-Br) and poly(NVTri)-b-poly(NVETri-Br), under the same conditions used for the homopolymer, poly(NVETri-Br). The <sup>1</sup>H NMR spectrum of the exchanged pyrrolidone/1,2,4-triazolium-based block copolymer measured in DMSO- $d_6$  clearly shows peaks corresponding to  $poly(NVETri-NTf_2)$  (Figure 5b), which were evidently shifted relative to the peaks of the original poly(NVETri-Br), in addition to the unchanged peaks attributed to the poly(NVP) segment. Successful incorporation of the NTf<sub>2</sub> unit into the pyrrolidone/1,2,4-triazolium-based block copolymer was also confirmed by the presence of the four peaks at 115–125 ppm in <sup>13</sup>C NMR spectrum of poly(NVP)-b- $poly(NVETri-NTf_2)$ , corresponding

to the trifluoromethyl group (Figure S17b, Supporting Information). In the case of the 1,2,4-triazole/1,2,4-triazolium-based block copolymer, poly(NVTri)-*b*-poly(NVETri-X), the product obtained after the anion exchange reaction exhibited <sup>1</sup>H NMR peaks corresponding to poly(NVETri-NTf<sub>2</sub>) and poly(NVTri) segments (Figure 5c) and four new <sup>13</sup>C NMR peaks at 115–125 ppm, attributed to the NTf<sub>2</sub> unit (Figure S17c, Supporting Information). In both cases, the exchanged block copolymers having the NTf<sub>2</sub> counter anion were difficult to dissolve in water (Table S2, Supporting Information), indicating successful transformation of the double hydrophilic block copolymers into amphiphilic block copolymers by the anion exchange reaction. In other words, these results indicate that anion exchange of the poly(NVETri-Br) segment in the block copolymers proceeds selectively to afford amphiphilic block copolymers composed of hydrophobic poly(NVETri-NTf<sub>2</sub>) and a hydrophilic nonionic segment, poly(NVP) or poly(NVTri).

#### 3.4.Ionic Conductivity

The temperature-dependent ionic conductivities of the polymers were investigated under the ambient humidity conditions. Methanol solutions of the polymers were casted onto a platinum electrode and dried at 40 °C. As shown in Figure 7a, poly(NVETri-Br) exhibited ionic conductivities of  $9.3 \times 10^{-4}$ ,  $3.4 \times 10^{-4}$ , and  $1.4 \times 10^{-4}$  S/cm at 90, 55, and 25 °C, respectively. Poly(NVETri-NTf<sub>2</sub>) exhibited ionic conductivities of  $1.6 \times 10^{-4}$ ,  $7.1 \times 10^{-5}$ , and  $1.7 \times 10^{-5}$  S/cm at 90, 55, and 25 °C, respectively; the ionic conductivity of poly(NVETri-X) was strongly dependent on the counter anions, as in the case of various previously reported polymers containing ionic liquid moieties.[13, 73-76] Furthermore, the ionic conductivity of poly(NVETri-NTf<sub>2</sub>) was affected by the molecular weight. Poly(NVETri-NTf<sub>2</sub>) with  $M_n$ = 22400 exhibited 2–4 fold higher ionic conductivity in the range of 90 to 25 °C, in comparison with that of the  $M_n$  = 45200 polymer, which may result from the difference in the polymer dynamics due to the molecular weights (Figure S19). As a control experiment, the ionic conductivities of poly(NVIm-NTf<sub>2</sub>) prepared independently by RAFT polymerization of NVIm-Br and a subsequent anion exchange reaction, was evaluated at three different temperatures under the same conditions. As

shown in Figure S20 (Supporting Information), poly(NVETri-NTf<sub>2</sub>), developed in this study, exhibited higher ion conductivity than the control sample, poly(NVIm-NTf<sub>2</sub>), suggesting that use of the 1,2,4-triazole-containing polymers was advantageous. The ionic conductivity of poly(NVEtOETri-X) was also investigated in the range of 90 to 25 °C (Figure 7b). No significant difference in the ionic conductivity of poly(NVEtOETri-Br) and poly(NVETri-Br) was observed. On the other hand, the ionic conductivity of poly(NVEtOETri-NTf<sub>2</sub>) was 1.4-3.7 times higher than that of poly(NVEtOETri-NTf<sub>2</sub>), which was due to the higher hydrophilicity and/or flexible substituent group of poly(NVEtOETri-NTf<sub>2</sub>). Note that the measurements of ionic conductivities were carried out under the ambient humidity conditions. Hence, the hydrophilic polymers with Br counter anion might absorb the moisture under the conditions, which could affect the ionic conductivity behaviors in some degree.

The ionic conductivity of poly(NVP)-b-poly(NVETri-X) was also investigated (Figure 8). The ionic conductivity of poly(NVP)<sub>33</sub>-*b*-poly(NVETri-Br)<sub>67</sub> tended to be lower than that of poly(NVETri-Br). On the other hand, poly(NVP)-b-poly(NVETri-NTf<sub>2</sub>) exhibited higher ionic conductivity than poly(NVETri-NTf<sub>2</sub>). In particular, the ionic conductivity of poly(NVP)<sub>33</sub>-*b*-poly(NVETri-NTf<sub>2</sub>)<sub>67</sub> was  $4.3 \times 10^{-5}$  S/cm at 25 °C, which was 2.5 times higher than that of poly(NVETri-NTf<sub>2</sub>) ( $1.7 \times 10^{-5}$  S/cm). In the case of poly(NVP)-*b*-poly(NVETri-NTf<sub>2</sub>), the poly(NVP) and poly(NVETri-NTf<sub>2</sub>) blocks behave as hydrophilic and hydrophobic blocks, respectively; the poly(NVP) and poly(NVETri-NTf<sub>2</sub>) blocks may undergo phase separation on the nano scale, and continuous poly(NVETri-NTf<sub>2</sub>) blocks would function as the ionic conductive path. Such phase separation contributed to the improvement of the ionic conductivity.[77-79] In the case of poly(NVP)-b-poly(NVETri-Br) (i.e., the hydrophilic-hydrophilic structure), there was no capacity for phase separation between the respective blocks; furthermore, the less ionic sites might lead to a decrease in ionic conductivity of poly(NVP)-b-poly(NVETri-Br) compared to poly(NVETri-Br). Figure 8b shows the relationship between the ionic conductivity and poly(NVP)/poly(NVETri-NTf<sub>2</sub>) block ratios in poly(NVP)-*b*-poly(NVETri-NTf<sub>2</sub>). The observed result demonstrated that the poly(NVP)/poly(NVETri-NTf<sub>2</sub>) block ratios clearly affected the ionic conducting behaviors, which might result from the difference in the phase separation. High ionic conductivities of

 $3.1 \times 10^{-4}$ ,  $1.1 \times 10^{-4}$ , and  $3.4 \times 10^{-5}$  S/cm were achieved with poly(NVP)<sub>12</sub>-*b*-poly(NVETri-NTf<sub>2</sub>)<sub>88</sub> at 90, 55, and 25 °C, respectively. The control of the polymer structure in block copolymers, such as hydrophilic/hydrophobic feature and block lenghts, contributed to the formation of adjusted phase separation, which led to the enhancement of ionic conductivities. The ionic conductivity of polymers containing ionic liquid moieties ranged from *ca*.  $10^{-7}$  to  $10^{-4}$  S/cm below 90 °C in most reported examples.[13, 73-76] In that regard, the 1,2,4-triazolium salt-containing polymers developed herein were classified as high ionic conducting materials based on ionic liquid moieties.



**Figure 7.** Temperature-dependent ionic conductivity of (a) poly(NVETri-X) ( $M_n = 22800$ ,  $M_w/M_n = 1.53$  at X = Br) and (b) poly(NVEtOETri-X) ( $M_n = 16100$ ,  $M_w/M_n = 1.42$  at X = Br), X = Br and NTf<sub>2</sub>.



**Figure 8.** Ionic conductivity of (a)  $poly(NVP)_{33}$ -*b*-poly(NVETri-X)<sub>67</sub>, X = Br and NTf<sub>2</sub>, and (b) poly(NVP)-*b*-poly(NVETri-NTf<sub>2</sub>) with different compositions.

In the cases of the 1,2,4-triazole/1,2,4-triazolium-based block copolymers, poly(NVTri)-*b*-poly(NVETri-X), the ionic conductivity was in the range of  $7.2 \times 10^{-5} - 8.9 \times 10^{-7}$  S/cm at 90–25 °C (Figure S21, Supporting Information), which are clearly lower than those of the pyrrolidone/1,2,4-triazolium-based block copolymers, poly(NVP)-*b*-poly(NVETri-X). Similar to other systems mentioned above, poly(NVTri)-*b*-poly(NVETri-Br) exhibited higher ionic conductivity than poly(NVTri)-*b*-poly(NVETri-NTf<sub>2</sub>). These results suggest that the ionic conducting behavior is affected by the comonomer structure, in addition to other factors, such as the structure of the counter ions and comonomer composition in the 1,2,4-triazolium-based block copolymers.

#### 3.5.SFM Observation

The tapping mode phase image of the surface of the  $poly(NVP)_{12}$ -*b*- $poly(NVETri-NTf_2)_{88}$  membrane, as a representative sample, was recorded under ambient conditions on the 3 × 3  $\mu$ m<sup>2</sup> scale to investigate the phase separation between the hydrophilic and hydrophobic domains (Figure 9). The dark and bright regions were assigned to the soft structure corresponding to the hydrophilic poly(NVP) domains and the hard structure corresponding to the hydrophobic  $poly(NVETri-NTf_2)$  domains, respectively. As seen in Figure 9, the bright  $poly(NVETri-NTf_2)$  domains were well dispersed and connected to each other. On the other hand, no phase separation was observed on the surface of the  $poly(NVETri-NTf_2)$ homopolymer membrane (Figure S22). These results demonstrated that the phase separation of poly(NVP)-*b*- $poly(NVETri-NTf_2)$  indeed contributed to the enhancement of the ionic conductivity, and that block copolymers with the hydrophilic-hydrophobic structure are potentially promising polymer architectures for achieving high ionic conductivity.



Figure 9. SFM tapping mode phase image of  $poly(NVP)_{12}$ -*b*-poly(NVETri-NTf<sub>2</sub>)<sub>88</sub> membrane: scan size is  $3 \times 3 \ \mu m^2$ .

### 4. CONCLUSION

In summary, RAFT polymerization of a new family of triazolium-based monomers, NVETri-Br and NVEtOETri-Br, was successfully exploited in the preparation of novel 1,2,4-triazolium-based homopolymers and block copolymers having well-defined structures. Poly(N-vinyl-1,2,4-triazolium bromide)s with a molar mass of more than 20000 and low D values ( $M_w/M_n < 1.1$ ) were obtained by RAFT polymerization with a trithiocarbonate-type chain transfer agent (CTA 7). Two series of 1,2,4-triazolium-based amphiphilic block copolymers were obtained by RAFT polymerization of NVETri-Br using hydrophilic macro-CTAs, followed by the quantitative anion exchange reaction of the ionic segment. The xanthate-type mediating agent, CTA 3, was found to be effective for the synthesis of well-defined ionic-nonionic block copolymers based on two nonconjugated N-vinyl monomers, NVP and NVETri-Br. Chain extension of NVETri-Br from the trithiocarbonate-terminated poly(NVTri) also afforded the novel triazole/triazoluim-based block copolymer, poly(NVTri)-b-poly(NVETri-Br). We have demonstrated first report on controlled synthesis of 1,2,4-triazolim-based polymers and block copolymers, in which characteristic ion-conducting properties could be tuned by the counter anions, and comonomer structures of the substituent group, structure and composition.  $Poly(NVP)_{12}$ -*b*-poly(NVETri-NTf<sub>2</sub>)<sub>88</sub> exhibited high ionic conductivities of  $3.1 \times 10^{-4}$ ,  $1.1 \times 10^{-4}$ , and  $3.4 \times 10^{-5}$  S/cm at 90, 55, and 25 °C, respectively, which resulted from the clear phase separation between the hydrophilic poly(NVP) domains and hydrophobic poly(NVETri-NTf<sub>2</sub>) domains. The assembled structures of the 1,2,4-triazolium-based block copolymers obtained in this study can provide tailored materials with unique ion-conducting properties for various applications.

#### **Supporting Information**

Supplementary data associated with this article can be found in the online version; Figures showing <sup>1</sup>H NMR spectra of the monomers and polymers, GPC traces of the polymers, DSC analysis, ion-conductivity, SFM image, and table summarizing solubility of the products and polymerization results.

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Table	1.	RAFT	Polymerization	of	<i>N</i> -vinyl-1,2,4-triazolium	salts	with	AIBN	and	various	CTAs	in
metha	nol	at 60 °C	C for 24 h <sup>a)</sup>									

	Monomor	CTA	conv. <sup>b)</sup>	$M_{\rm n}^{\rm c)}$	$M_{\rm n}{}^{\rm b)}$	$M_{\rm n}{}^{\rm d)}$	$M_{ m w}/M_{ m n}{}^{ m d)}$
run	wonomer	UIA	(%)	(theory)	(NMR)	(SEC)	(SEC)
1		-	98	-	-	36900	2.73
2		1	64	6800	9500	11100	1.47
3		2	< 5	-	-	- 0	<u> </u>
4		3	97	10100	-	15500	1.44
5	NVETri-Br	4	83	8600	-	20200	1.83
6		5	24	2700	8800	9400	1.39
7		6	> 99	10500	12200	11200	1.10
8		7	99	10400	10500	11100	1.09
9		8	96	10200	10000	10100	1.09
10		-	96	-	-	30900	2.67
11		1	93	11800	14600	12700	1.32
12		2	94	11900	-	14400	1.55
13		3	61	7800	-	13400	1.37
14	NVEtOETri-Br	4	95	11900	-	19100	1.75
15		5	21	2800	7200	9500	1.21
16		6	98	12500	20500	10000	1.09
17		7	98	12500	17000	10500	1.09
18		8	98	12600	17900	10200	1.10

<sup>a)</sup>  $[I]_0/[CTA]_0/[M]_0 = 1/2/100$ . [M] = 2.0 mol/L. <sup>b)</sup> Calculated by <sup>1</sup>H NMR in DMSO-*d*<sub>6</sub>. <sup>c</sup> The theoretical molecular weight ( $M_{n, \text{ theory}}$ ) = (MW of M) ×  $[M]_0/[CTA]_0 \times \text{conv.} + (MW \text{ of CTA})$ . <sup>d)</sup> Measured by SEC using poly(ethylene oxide) standards in H<sub>2</sub>O/acetonitrile (50/50 vol% containing 0.05 M NaNO<sub>3</sub>).

Table	2.	Effect	of	[M] <sub>0</sub> /[ <b>(</b>	$CTA]_0$	ratio	on	RAFT	polymerizati	on	of N-vinyl-1	,2,4-triazoliun	ı salts	with
AIBN	anc	l CTA	7 iı	n metha	unol at	60 °C	for	· 24 h <sup>a)</sup>						

		[M] <sub>0</sub> /	conv. <sup>b)</sup>	$M_{\rm n}^{\rm c)}$	M <sub>n</sub>	$M_{ m w}/M_{ m n}^{ m d)}$
run	Monomer	[CTA7] <sub>0</sub>	(%)	(theory)	(SEC <sup>d)</sup> /NMR <sup>b)</sup> )	(SEC)
1		25	> 99	5400	6600/4900	1.07
2	NVFTri_Br	50	99	10400	11100/10500	1.09
3		100	99	20500	17600/29800	1.16
4		200	98	40300	26400/34800	1.34
5		25	96	6300	6800/7700	1.06
6	NVFtOFTri-Br	50	98	12500	10500/17000	1.09
7		100	> 99	24900	13700/29700	1.19
8		200		31100	21000/51700	1.29

<sup>a)</sup> [CTA 7]<sub>0</sub>/[I]<sub>0</sub> = 2. [M] = 2.0 mol/L. <sup>b)</sup> Calculated by <sup>1</sup>H NMR in DMSO- $d_6$ . <sup>c)</sup> The theoretical molecular weight ( $M_{n, \text{ theory}}$ ) = (MW of M) × [M]<sub>0</sub>/[CTA 7]<sub>0</sub> × conv. + (MW of CTA). <sup>d)</sup> Measured by SEC using poly(ethylene oxide) standards in H<sub>2</sub>O/acetonitrile (50/50 vol% containing 0.05 M NaNO<sub>3</sub>).

Table 3.	Synthesis	of poly(NVP	)- <i>b</i> -poly(NVETr	i-Br) and j	poly(NVTri)-	<i>b</i> -poly(NVE	Tri-Br) by	RAFT
polymeri	zation of N	VETri-Br wit	th AIBN in meth	anol at 60 $^{\circ}$	C for 24 h $^{a)}$			

Magra CTA	[M] <sub>0</sub> /	Conv. <sup>b)</sup> /Yield <sup>c)</sup>	$M_{\rm n}{}^{\rm d)}$	$M_{\rm n}^{\rm b)}$	$M_{\rm n}^{\rm e)}$	$M_{\rm w}/M_{\rm n}^{\rm e)}$	n · m <sup>b)</sup>	
Macio-CIA	[macro-CTA] <sub>0</sub>	(%)	(theory)	(NMR)	(SEC)	(SEC)	11 . 111	
	12.5	91/26 <sup>f)</sup>	9300	11000	8500	1.46	62:38	
poly(NVP) 1	25	93/42	11700	35300	11000	1.42	33 : 67	
	50	97/60	16900	35500	7900	1.17	16 : 84	
poly(NVP) 2	50	99/76	13300	45500	15800	1.61	12:88	
	25	95/78	9900	9600	6600	1.05	70:30	
poly(NVTri)	50	97/99	15000	16200	10000	1.07	48 : 52	
	100	97/96	24900	24600	16900	1.16	34 : 66	

<sup>a)</sup> [macro-CTA]<sub>0</sub>/[I]<sub>0</sub> = 2. [M]<sub>0</sub> = 2.0 mol/L. macro-CTA : poly(NVP) 1;  $M_{n, NMR}$  = 7000,  $M_w/M_n$  = 1.07. poly(NVP) 2;  $M_{n, NMR}$  = 3200,  $M_w/M_n$  = 1.06. poly(NVTri);  $M_{n, NMR}$  = 5100,  $M_w/M_n$  = 1.09. <sup>b)</sup> Calculated by <sup>1</sup>H NMR in CD<sub>3</sub>OD or DMSO- $d_6$ . <sup>c)</sup> Insoluble part for acetone/chlorofolm (7/3 vol%). <sup>d)</sup> The theoretical molecular weight ( $M_{n, theory}$ ) = (MW of M) × [M]<sub>0</sub>/[macro-CTA]<sub>0</sub> × conv. + (MW of macro-CTA). <sup>e)</sup> Measured by SEC using poly(ethylene oxide) standards in H<sub>2</sub>O/acetonitrile (50/50 vol% containing 0.05 M NaNO<sub>3</sub>). <sup>f)</sup> Insoluble part for acetone/diethyl ether (6/4 vol%) after purification by dialysis with methanol.

#### Reference

[1] Lu J, Yan F, Texter J. 2009;34:431-48.

[2] Mecerreyes D. Progress in Polymer Science. 2011;36:1629-48.

[3] Green O, Grubjesic S, Lee S, Firestone MA. Polymer Reviews. 2009;49:339-60.

[4] Shaplov AS, Marcilla R, Mecerreyes D. Electrochemica Acta. 2015;175:18-34.

[5] Leddet C, Fischer A, Brembilla A, Lochon P. Polymer Bulletin. 2001;46:75-82.

[6] Marcilla R, Blazquez JA, Rodriguez J, Pomposo JA, Mecerreyes D. Journal of Polymer Science: Part A: Polymer Chemistry. 2004;42:208-12.

[7] Amajjahe S, Ritter H. Macromolecular Rapid Communications. 2009;30:94-8.

[8] Marcilla R, Blazquez JA, Fernandez R, Grande H, Rodriguez J, Pomposo JA, et al. Macromolecular Chemistry and Physics. 2005;206:299-304.

[9] Obadia MM, Drockenmuller E. Chemical Communications. 2016;52:2433-50.

[10] Thibault RJ, Takizawa K, Lowenheilm P, Helms B, Mynar JL, Frechet JMJ, et al. Journal of American Chemical Society. 2006;128:12084-5.

[11] Beghdadi S, Miladi IA, Addis D, Ben Romdhane H, Bernard J, Drockenmuller E. Polymer Chemistry. 2012;3:1680-92.

[12] Obadia MM, Colliat-Dangus G, Debuigne A, Serghei A, Detrembleur C, Drockenmuller E. Chemical Communications. 2015;51:3332-5

[13] Sood R, Obadia MM, Mudraboyina BP, Zhang B, Serghei A, Bernard J, et al. Polymer. 2014;55:3314-9.

[14] Adzima BJ, Taylor SC, He H, Luebke DR, Matyjaszewski K, Nulwala HB. Journal of Polymer Science: Part A: Polymer Chemistry. 2014;52:417-23.

[15] Mudraboyina BP, Obadia MM, Abdelhedi-Miladi I, Allaoua I, Drockenmuller E. European Polymer Journal. 2015;62:331-7.

[16] Obadia MM, Mudraboyina BP, Allaoua I, Haddane A, Montarnal D, Serghei A, et al. Macromolecular Rapid Communications. 2014;35:794-800.

[17] Mudraboyina BP, Obadia MM, Allaoua I, Sood R, Serghei A, Drockenmuller E. Chemistry of Materials. 2014;26:1720-6.

[18] Sood R, Zhang B, Serghei A, Bernard J, Drockenmuller E. Polymer Chemistry. 2015;6:3521-8.

[19] Obadia MM, Mudraboyina BP, Serghei A, Montarnal D, Drockenmuller E. Journal of the American Chemical Society. 2015;137:6078-83.

[20] Tejero R, Lopez D, Lopez-Fabal F, Gomez-Garces JL, Fernandez-Garcia M. Polymer Chemistry. 2015;6:3449-59.

[21] Tejero R, Gutierrez B, Lopez D, Lopez-Fabal F, Gomez-Garces JL, Fernandez-Garcia M. Acta Biomaterialia. 2015:86-96.

[22] Tejero R, Arbe A, Fernandez-Garcia M, Lopez D. Macromolecules. 2015;48:7180-93.

[23] Mirzaei Y, Twamley B, Shreeve J. Journal of Organic Chemistry. 2002;67:9340-5.

[24] Meyer D, Strassner T. Journal of Organic Chemistry. 2011;76:305-8.

[25] De La Hoz AT, Brauer UG, Miller KM. Journal of Physical Chemistry B. 2014;118:9944-51.

[26] Daily LA, Miller KM. Journal of Organic Chemistry. 2013;78:4196-201.

[27] Vestergaard B, Bjerrum N, Petrushina I, Hjuler H, Berg R, Begtrup M. Journal of the Electrochemical Society. 1993;140:3108-13.

[28] Swain PK, Singh H, Tewari SP. Journal of Molecular Liquids. 2010;151:87-96.

[29] Singh R, Verma R, Meshri D, Shreeve J. Angewandte Chemie-International Edition. 2006;45:3584-601.

[30] Xue H, Gao Y, Twamley B, Shreeve J. Chemistry of Materials. 2005;17:191-8.

[31] Luo J, Hu J, Saak W, Beckhaus R, Wittstock G, Vankelecom IFJ, et al. Journal of Materials Chemistry. 2011;21:10426-36.

[32] Xue H, Gao H, Shreeve JnM. Journal of Polymer Science: Part A: Polymer Chemistry. 2008;46:2414-21.

[33] Zhang W, Yuan J. Macromolecular Rapid Communications. 2016:DOI: 10.1002/marc. 201600001.

[34] De La Hoz AT, Miller KM. Polymer. 2015;72:1-9.

[35] Hao J, Li X, Yu S, Jiang Y, Luo J, Shao Z, et al. Journal of Energy Chemistry. 2015;24:199-206.

[36] Zhou Z, Liu R, Wang J, Li S, Liu M, Bredas J. Journal of Physical Chemistry A. 2006;110:2322-4.

[37] Li S, Zhou Z, Zhang Y, Liu M, Li W. Chemistry of Materials. 2005;24:5884-6.

[38] Mori H, Ishikawa K, Abiko Y, Maki Y, Onuma A, Morishima M. Macromolecular Chemistry and Physics. 2012;213:1803-14.

[39] Kizhnyaev VN, Pokatilov FA, Vereshchagin LI. Polymer Science Series C. 2008;50:1-21.

[40] Green MD, Allen MH, Jr., Dennis JM, Salas-de la Cruz D, Gao R, Winey KI, et al. European Polymer Journal. 2011;47:486-96.

[41] Yuan J, Antonietti M. Polymer. 2011;52:1469–82.

[42] Nakabayashi K, Mori H. Polymer International. 2013;49:2808-38.

[43] Texter J, Vasantha VA, Crombez R, Maniglia R, Slater L, Mourey T. Macromolecular Rapid Communications. 2012;33:69-74.

[44] He H, Luebke D, Nuwala H, Matyjaszewski K. Macromolecules. 2014;47:6601-9.

[45] Mori H, Yahagi M, Endo T. Macromolecules. 2009;42:8082-92.

[46] Yang J, Sun W, Lin W, Shen Z. Journal of Polymer Science, Part A: Polymer Chemistry. 2008;46:5123-32.

[47] Yuan J, Schlaad H, Giordano C, Antonietti M. European Polymer Journal. 2011;47:772-81.

[48] Vijayakrishna K, Jewrajka SK, Ruiz A, Marcilla R, Pomposo JA, Mecerreyes D, et al. Macromolecules. 2008;41:6299–308.

[49] Detrembleur C, Debuigne A, Hurtgen M, Jerome C, Pinaud J, Fevre M, et al. Macromolecules. 2011;44:6397-404.

[50] Cordella D, Kermagoret A, Debuigne A, Jerome C, Mecerreyes D, Isik M, et al. Macromolecules. 2015;48:5230-43.

[51] Choi J-H, Ye Y, Elabd YA, Winey KI. Macromolecules. 2013;46:5290-300.

[52] Schneider Y, Modestino MA, McCulloch BL, Hoarfrost ML, Hess RW, Segalman RA. Macromolecules. 2013;46:1543-8.

[53] Ye Y, Choi J-H, Winey KI, Elabd YA. Macromolecules. 2012;45:7027-35.

[54] Green MD, Choi J-H, Winey KI, Long TE. Macromolecules. 2012;45:4749-57.

[55] Mori H, Ishikawa K, Abiko Y, Nakabayashi K, Onuma A, Morishima M. Polymer. 2013;54:2001-10.

[56] Mori H, Ebina Y, Kambara R, Nakabayashi K. Polymer Journal 2012;44:550-60.

[57] Kizhnyaev VN, Pokatilov FA, Tsypina NA, Ratovskii GV, Vereshchagin LI, Smirnov AI. Russian Journal of Organic Chemistry. 2002;38:1056-9.

[58] Ladaviere C, Dörr N, Claverie JP. Macromolecules. 2001;34:5370-2.

[59] Gaillard N, Guyot A, Claverie J. Journal of Polymer Science: Part A: Polymer Chemistry. 2003;41:684-98.

[60] Mori H, Ookuma H, Nakano S, Endo T. Macromolecular Chemistry and Physics. 2006;207:1005-17.

[61] Nese A, Kwak Y, Nicolay R, Barrett M, Sheiko SS, Matyjaszewski K. Macromolecules. 2010;43:4016-9.

[62] Destarac M, Brochon C, Catala JM, Wilczewska A, Zard SZ. Macromolecular Chemistry and Physics. 2002;203:2281-9.

[63] Maki Y, Mori H, Endo T. Macromolecular Chemistry and Physics. 2007;208:2589-99.

[64] Liautard V, Robert F, Landais Y. Org Lett. 2011;13:2658-61.

[65] Chiefari J, Mayadunne RTA, Moad CL, Moad G, Rizzardo E, Postma A, et al. Macromolecules. 2003;36:2273-83.

[66] Mori H, Nakano S, Endo T. Macromolecules. 2005;38:8192-201.

[67] Pound G, McLeary JB, McKenzie JM, Lange RFM, Klumperman B. Macromolecules. 2006;39:7796–7.

[68] Maki Y, Mori H, Endo T. Macromolecules. 2007;40:6119-30.

[69] Nguyen UTL, Eagles K, Davis TP, Barner-Kowollik C, Stenzel MH. Journal of Polymer Science: Part A: Polymer Chemistry. 2006;44:4372-83.

[70] Wan D, Satoh K, Kamigaito M, Okamoto Y. Macromolecules. 2005;38:10397-405.

[71] Barner-Kowollik C, Buback M, Charleux B, Coote ML, Drache M, Fukuda T, et al. Journal of Polymer Science: Part A: Polymer Chemistry. 2006;44:5809-31.

[72] Lowe AB, McCormick CL. Progress in Polymer Science. 2007;32:283-351.

[73] Green MD, Salas-de la Cruz D, Ye Y, Layman JM, Elabd YA, Winey KI, et al. Macromolecular Chemistry and Physics. 2011;212:2522-8.

[74] Ogihara W, Suzuki N, Nakamura N, Ohno H. Polymer Journal. 2006;38:117-21.

[75] Dimitrov-Raytchev P, Beghdadi S, Serghei A, Drockenmuller E. Journal of Polymer Science: Part A: Polymer Chemistry. 2013;51:34-8.

[76] Obadia MM, Mudraboyina BP, Serghei A, Phan TNT, Gigmes D, Drockenmuller E. ACS Macro Letters. 2014;3:658-62.

[77] Nakabayashi K, Higashihara T, Ueda M. Journal of Polymer Science: Part A: Polymer Chemistry. 2010;48:2757-64.

[78] Yang Y, Shi Z, Holdcroft S. Macromolecules. 2004;37:1678-81.

[79] Ding J, Chuy C, Holdcroft S. Advanced Functional Materials. 2002;12:389-94.

Synthesis of 1,2,4-Triazolium Salt-Based Polymers and Block Copolymers by RAFT Polymerization: Ion Conductivity and Assembled Structures

### Highlights

- This contribution represents the first report of the controlled radical polymerization of *N*-vinyl-1,2,4-triazolium salts, leading to the production of a new member of the polymeric ionic liquids having characteristic ion conductivity.
- Poly(*N*-vinyl-1,2,4-triazolium bromide)s with cotrolled molecular weighst ( $M_n > 20000$ ) and low polydispersities ( $M_w/M_n < 1.1$ ) were obtained by RAFT polymerization with a trithiocarbonate-type chain transfer agent
- Nonionic (water-soluble)-ionic (solubility tunable) block copolymers were obtained by RAFT polymerization, followed by the quantitative anion exchange reaction.