

# Synthesis of 1,2,4-triazolium salt-based polymers and block copolymers by RAFT polymerization: Ion conductivity and assembled structures



Kazuhiro Nakabayashi<sup>a</sup>, Akiko Umeda<sup>a</sup>, Yu Sato<sup>a</sup>, Hideharu Mori<sup>a, b, \*</sup>

<sup>a</sup> Department of Polymer Science and Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan

<sup>b</sup> Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan

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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 (NVtOETri-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  $\bar{D}$  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>) ( $1.7 \times 10^{-5}$  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.

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## 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 them, 1,2,3-triazole derivatives and their vinyl 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-

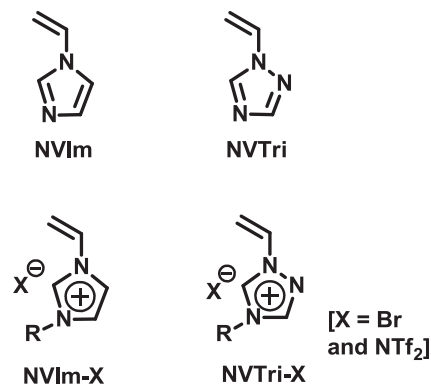
\* Corresponding author. Department of Organic Device Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16, Jonan, Yonezawa, 992-8510, Japan.

E-mail address: [h.mori@yz.yamagata-u.ac.jp](mailto:h.mori@yz.yamagata-u.ac.jp) (H. Mori).

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 of polymers having 1,2,3-triazolium side chains have been developed from 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 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



**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).

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 the heterocycle, 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.

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.

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 involving thermoresponsive-ionic liquid block copolymers, star, and star-block copolymers [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

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