Design ofClickable Ionic Liquid Monomers to Enhance Ionic Conductivity for Main-Chain 1,2,3-Triazolium-Based Poly(ionic Liquid)s

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ABSTRACT: A series of clickable α-azide-ω-alkyne ionic liquid (IL) monomers with an ethylene oxide spacer were developed and applied to the synthesis of 1,2,3-triazolium-based poly(ionic liquid)s (TPILs) with high ionic conductivities via one-step thermal azide–alkyne cycloaddition click chemistry. Subsequently, the number of IL moieties in the resultant TPILs was further increased by N-alkylation of the 1,2,3-triazole-based backbones of the TPILs with a quaternizing reagent. This strategy afforded the preparation of TPILs having either one or two 1,2,3-triazolium cations with bis(trifluoromethylsulfonyl)imide anions in a monomer unit. Synthesis of the TPILs was confirmed by H and 13C NMR spectroscopy and gel permeation chromatography. The effects of the length of the ethylene oxide spacer and the number of IL moieties in the IL monomer unit on the physicochemical properties of the TPILs were characterized by differential scanning calorimetry, thermogravimetric analysis, and impedance spectroscopy. The introduction of a longer ethylene oxide spacer or an increase in the number of IL moieties in the monomer unit resulted in TPILs with lower glass-transition temperatures and higher ionic conductivities. The highest ionic conductivity achieved in this study was 2.0 × 10−5 S cm−1 at 30 °C. These results suggest that the design of the IL monomer provides the resultant polymer with high chain flexibility and a high IL density, and so it is effective for preparing TPILs with high ionic conductivities.

1. INTRODUCTION

Poly(ionic liquid)s (PILs) are an emerging class of polyelectrolytes composed of ionic liquid (IL) units. Recently, they have attracted substantial attention in the field of polymer chemistry and materials science due to their ability to combine the favorable attributes of ILs (e.g., enhanced thermal, chemical, electrochemical, and ion-conducting properties) and polymer materials (e.g., processability, viscoelasticity, adhesion, film-forming properties, and microstructural design).1−3 A wide library of PILs with tunable properties could therefore be obtained through unlimited combinations of cations (e.g., ammonium, pyridinium, imidazolium, phosphonium, and more recently 1,2,3-triazolium) and anions (e.g., halides, phosphates, inorganic fluorides, and perfluorinated sulfonimides, among others). Such a structural variety makes PILs potential candidates for applications such as catalysis, dye-sensitized solar cells, electrochromic devices, membranes, sensors and actuators, electrolyte-gated transistors, batteries, and supercapacitors.4−11

Among the various PILs reported to date, 1,2,3-triazolium-based PILs (TPILs) have been developed as a structurally rich family of PILs.12,13 Their synthesis combines step-growth or chain-growth polymerization methods with copper-catalyzed azide–alkyne cycloaddition click chemistry using diazide and dialkyne or α-azide-ω-alkyne monomers, followed by a 1,2,3-triazole N-alkylation reaction. To date, a rich library of TPILs with tailored structures and properties (e.g., ionenes, poly(acrylate)s, poly(vinyl ester)s, poly(styrene)s, and poly(siloxanes)) have been developed using efficient and orthogonal synthetic approaches.14−20 Recently, Drockenmüller et al. proposed to combine the thermal azide–alkyne cycloaddition of α-azide-ω-alkyne monomers with in situ N-alkylation of the generated poly(1,2,3-triazole)s using methyl iodide or N-methyl bis(trifluoromethylsulfonylimide) as quaternizing agents.19,20 Inspired by these studies, we developed clickable α-azide-ω-alkyne IL monomers with 1,2,3-triazolium cation and iodide(I) or bis(trifluoromethanesulfonylimide) (Tf2N) counteranions and demonstrated the one-pot synthesis of backbone TPILs via click chemistry using clickable IL monomers.21 Unlike the previous synthetic processes employed for TPIL preparation, our process is a one-step process for the synthesis of TPILs from the monomer, and the polymerization does not require solvents, polymerization mediators, or catalysts. However, the TPILs obtained using clickable IL monomers showed low ionic

Received: December 18, 2020
Accepted: February 5, 2021
Published: April 9, 2021

http://pubs.acs.org/doi/10.1021/acsomega.0c06173
ACS Omega 2021, 6, 10030−10038

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conductivities in the order of $10^{-8}$ S cm$^{-1}$ at 30 °C. To realize the application of TPILs in solid electrolytes for electronics, it is therefore essential to enhance their ionic conductivities.

Thus, to impart PILs with superior ionic conductivities, various polymer backbones and spacers have been examined that vary in their chemical nature and structure. A range of cationic/anionic moieties have also been studied, and some trends between the macromolecular design of PILs and the resulting ionic conductivity have been reported. For example, the chemical nature and structure of both the cations and anions greatly affect the ionic conductivities of PILs. More specifically, in the case of polycations based on imidazolium cations, the ionic conductivity can be influenced by factors including the size and symmetry of the anion and the dissociation energy of the ion pair. It is also well known that the ionic conductivities of PILs correlate with their glass-transition temperatures ($T_g$), whereby a decrease in $T_g$ accelerates the segmental dynamics and leads to a higher ionic conductivity at an ambient temperature. To enhance the segmental dynamics of polymer chains, the introduction of longer flexible spacers into the PILs is also effective. For example, Puguan et al. recently reported that the insertion of ethylene oxide fragment spacers into a monomer unit of the TPIL leads to high ionic conductivities.

Thus, we herein report the development of a new series of clickable $\alpha$-azide-$\omega$-alkyne IL monomers with one or four ethylene oxide fragments and the preparation of a new series of main-chain TPILs via polyaddition of the monomers. These IL monomers allow the synthesis of monocationic main-chain TPILs in a one-step thermal azide–alkyne cycloaddition (TAAC) and introduce ethylene oxide spacers into the monomer repeating unit of main-chain TPILs, which can lead to a lower $T_g$ value and a higher ionic conductivity. Moreover, this strategy affords the preparation of dicationic TPILs having 1,2,3-triazolium-based backbone by N-alkylation of the 1,2,3-triazole-based backbones of the resultant monocationic TPILs using N-methyl bis-(trifluoromethylsulfonyl)imide as a quarternizing reagent. To the best of our knowledge, there are few studies on the synthesis and physicochemical evaluation of dicationic PILs. We expect that the ionic conductivity of dicationic TPILs could show a higher value than that of the monocationic ones since the dicationic TPILs have increased number of IL moieties in the monomer unit than monocationic TPILs.

Following our account of the aforementioned synthetic methodology to obtain TPILs from clickable IL monomers bearing different numbers of ethylene oxides via a click chemistry approach, we describe our investigation of the effects of the monomer structure and the number of IL moieties in the polymer backbone on the $T_g$ thermal decomposition temperature, and ionic conductivity of the resultant TPILs.
2. RESULTS AND DISCUSSION

2.1. Synthesis of the TPILs. The first goal of our study was the design of novel ethylene glycol-based (EG-)α-azide-ω-alkyne IL monomers 2 and 3 (Scheme S1). The successful synthesis of each compound was confirmed by 1H and 13C NMR spectroscopy (Figures S1−S4). In addition, the 1H and 13C NMR spectra of the EG-IL monomers clearly confirmed the preparation of α-azide-ω-alkyne IL monomers bearing a 1,2,3-triazolium cation (Figures S5 and S6), and the purities of EG-IL monomers were evaluated by elemental analysis. Indeed, besides the disappearance of the signal at 8.2 ppm attributed to the 1,2,3-triazole moiety, new signals were confirmed at 9.0 ppm, corresponding to the 1,2,3-triazolium proton, and at 2.9 and 3.4 ppm, corresponding to the propargyl and azidomethylene chain ends, respectively. It was also found that the 13C NMR spectra of the EG-IL monomers contain many nonassigned peaks. These peaks could be derived from various side products including cyclic species via intramolecular click reaction with the produced monomers.

Subsequently, using the TAAC polyaddition strategy (Scheme 1), α-azide-ω-alkyne IL monomers 1−3 were polymerized in bulk at 110 °C over 24 h. The resulting TPILs 4−6 were obtained as brown sticky materials in 90−93% yields after precipitation in ethyl acetate and further drying under vacuum. TPILs 4−6 were characterized by 1H and 13C NMR spectroscopy (Figures 1 and S7−S9), elemental analysis, and gel permeation chromatography (GPC) (Figure S13). In all cases, the 1H NMR spectra confirmed polymerization of the IL monomers by the appearance of proton signals corresponding to the 1,2,3-triazole ring at 7.6−7.9 ppm, as well as the absence of signals corresponding to the propargyl and azidomethylene chain ends. TPILs 4−7 were found to be mixtures of 1,4- and 1,5-substituted 1,2,3-triazole groups, and the ratio of mixtures were determined from the appearance of two separate signals for the C-4 and C-5 1,2,3-triazole protons (Table S1). It was also found that the 13C NMR spectra of TPILs contain many nonassigned peaks, indicating the presence of some impurities in the polymers. The molecular weight and molecular weight dispersity of TPILs 4−6 were evaluated by GPC using a 60 mM solution of LiTf2N in N,N-dimethylformamide (DMF) as an eluent. For all samples, the GPC traces were monomodal and a number-average molecular weight of 13−28 kg mol−1 was determined. The molecular weight dispersities (Mw/Mn) were large, ranging from 1.7 to 3.3, and this was attributed to the step-growth polymerization process.

TPILs 7−9 were then obtained by N-alkylation of the 1,2,3-triazole groups of TPILs 4−6 using CH3Tf2N in DMF at 110 °C over 24 h (Scheme 1). After precipitation in ethyl acetate and further drying under vacuum, their structures and purities of TPILs 7−9 were confirmed by 1H and 13C NMR spectroscopy (Figures 2 and S10−S12) and elemental analysis. Indeed, the 1H NMR spectra of TPILs 7−9 confirmed the quantitative N-alkylation of the 1,2,3-triazole groups by the appearance of signals corresponding to the N-3 methyl groups at 4.2−4.3 ppm, as well as the disappearance of the 1,2,3-triazole ring signal at 7.6−7.9 ppm, which is characteristic of the precursor TPILs 4−6. The solubilities of TPILs 7−9 in...
DMF allowed for their characterization by GPC using a 60 mM solution of LiTf2N in DMF as the eluent. However, the molecular weight and the molecular weight dispersity of TPILs 7 and 8 could not be obtained by GPC. This could be due to higher basic conditions upon increasing the number of charged groups in TPILs 7 and 8 compared to the precursor TPILs 4 and 5. GPC analysis showed that TPIL 9 exhibits a number-average molecular weight of 24 kg mol\(^{-1}\) with a molecular weight dispersity of 2.5. It was also confirmed that there was no significant difference in molecular weight between TPIL 9 (the sample after N-alkylation) and TPIL 6 (the sample before N-alkylation). This result suggests that TPILs 7 and 8 would exhibit approximately the same number-average molecular weights as TPILs 4 and 6, respectively, although we could not obtain the molecular weight and molecular weight dispersity of TPILs 7 and 8 by GPC.

### 2.2. Thermal Properties of the TPILs

The thermal properties of the TPILs were then characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), as outlined in Table 1. In addition, Figure 3 summarizes the glass-transition temperatures (\(T_g\)) of TPILs 4–9 as a function of the number of ethylene oxide groups in an IL monomer unit. It should be noted here that alkyl-based TPILs (i.e., TPILs 4 and 7) are represented by zero ethylene oxide groups. When comparing TPILs with the same number of IL moieties in a monomer unit, TPILs with longer ethylene oxide spacers exhibited lower \(T_g\) values, in the following order: TEG-based TPILs 6 (or 9) < MEG-based TPILs 5 (or 8) < alkyl-based TPILs 4 (or 7). This result indicates that the \(T_g\) values of PILs containing the same IL moieties could depend on the spacer length. The differences in \(T_g\) values between the TPILs with alkyl spacers and those with ethylene oxide spacers can be attributed to the more rigid nature of the alkyl spacer.
2.3. Ion Conducting Properties of the TPILs. The temperature dependence of the DC conductivity ($\sigma_{DC}$) of TPILs 4–9 was evaluated by impedance spectroscopy analysis over the range of 40–10$^7$ Hz. The data were collected at temperatures ranging from −40 to 130 °C in steps of 10 °C. It should be noted that the ionic conductivity measurement was not performed under anhydrous condition. The $\sigma_{DC}$ values of the TPILs were plotted as a function of inverse temperature (Figure 5). As generally observed for polymeric materials, the temperature evolution of the $\sigma_{DC}$ followed the Vogel–Fulcher–Tamann (VFT) relationship, which describes the correlation between the charge transport capability of the ionic moiety and the molecular mobility of the polymer chain. Thus, the experimental data were fitted to the VFT equation

\[
\sigma_{DC} = \sigma_\infty \exp\left(-B/(T-\Theta)\right)
\]

where $\sigma_\infty$ is the ionic conductivity in the limit of high temperature, $B$ is a fitting parameter related to the activation energy of ionic conduction, and $\Theta$ is the Vogel temperature. The fitted values are summarized in Table 1.

For monocationic TPILs 4–6, as the number of ethylene oxide fragments in the monomer unit increased, the values of $\sigma_{DC}$ at 30 °C were remarkably increased. This difference was consistent with the change in $T_g$ values measured by DSC, i.e., $T_g$ decreases from 7 to −14 °C between 4 and 6, respectively. Moreover, the values of $\sigma_{DC}$ at 30 °C for dicaticonic TPILs 7–9 were higher than those of monocationic TPILs 4–6, and TPILs 9 exhibited the highest ionic conductivity of 2.0 × 10$^{-5}$ S cm$^{-1}$ at 30 °C. Thus, if we assume a density of TPILs 4 and 7 of 1.4 g cm$^{-3}$, the number densities of Tf$_2$N anions in TPILs 4 and 7 would be 1.40 × 10$^{21}$ and 1.88 × 10$^{21}$ cm$^{-3}$, respectively. Although there is no significant difference in the number density between TPILs 4 and 7, the ionic conductivity of TPIL 7 is significantly higher than that of TPIL 4. This result indicates that the higher $\sigma_{DC}$ values of the dicaticonic TPILs compared to the monocationic TPILs cannot be solely attributed to a higher anion concentration for the dicaticonic TPILs. We then considered that the main factor related to the difference in ionic conductivity among the TPILs could be the $T_g$ value, since the ionic conductivity is inversely proportional to the $T_g$ as indicated in Table 1. Thus, to eliminate the effect of $T_g$ on the ionic conductivity of TPILs, we plotted the normalized temperature $(T_g/\Theta)$ versus the ionic conductivity and found that all data overlapped onto a single curve. This result strongly suggests that $T_g$ plays a dominant role in ion transport in both monocationic and dicaticonic TPILs, especially with charge placement in the polymer backbone. Based on these results, we concluded that the introduction of a long ethylene oxide spacer or an increase in the IL moiety in the monomer unit contributes to a decreasing $T_g$ value for the resultant TPILs, which results in enhanced polymer chain relaxation, and ultimately, a higher ionic conductivity.
3. CONCLUSIONS

We herein reported the development of a new series of clickable α-azido-ω-alkyne ionic liquid (IL) monomers containing one or four ethylene oxide fragments, and the successful synthesis of a new series of main-chain 1,2,3-triazolium-based poly(ionic liquid)s (TPILs) exhibiting high ionic conductivities. We believe that these findings will be helpful in the future design of monomer structures to develop TPILs with high ionic conductivities.

4. EXPERIMENTAL SECTION

4.1. Materials. Diisopropylethylamine (DIPEA, 97%), benzy1 azide (94%), copper(II) acetate (Cu(OAc)2, 97%), super-dehydrated acetonitrile (99.8%), N,N-dimethylformamide (99.5%), sodium azide (98%), sodium hydride (NaH in oil, 72%), triphenyl phosphine (97%), and dichloromethane (99%) were purchased from FUJIFILM Wako Pure Chemical Corp. (Japan). 5-Chloro-1-pentyne (96%), lithium bis(trifluoromethanesulfonyl)imide (LiTf2N, 98%), iodine (99.5%), sodium azide (98%), sodium hydride (NaH in oil, 72%), triphenyl phosphine (97%), and dichloromethane (99%) were purchased from TOKYO CHEMICAL INDUSTRIAL Co., Ltd. (Japan). 6-Iodo-1-hexyne (97%) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). 8-iodo-1-hexyne (97%) was purchased from Tokyo Chemical Industry Co., Ltd. (Japan). All chemicals were used as received. Propargyl-TEG-OH, propargyl-MEG-iodide, and benzyl azide (2.62 mL, 20 mmol) under stirring. The reaction mixture was stirred in the dark at 25 °C for 24 h, after which the solvent was evaporated. The crude product was purified by column chromatography (hexane/ethyl acetate = 5:4) to give MEG-iodized 1,2,3-triazole as a yellow oil (6.25 g, 18.2 mmol, 91%). H NMR (400 MHz, DMSO-d6, δ): 8.16 (s, 1H), 7.40–7.29 (m, 5H), 5.59 (s, 2H), 4.56 (s, 2H), 3.68 (t, J = 6.4 Hz, 2H), 3.33 (t, J = 6.5 Hz, 2H). 13C NMR (100 MHz, DMSO-d6, δ): 144.0, 136.0, 128.7, 128.1, 127.9, 124.1, 70.0, 62.8, 52.7, 5.10.

4.3.2. Synthesis of TEG-Azido-1,2,3-triazole. A similar procedure was performed using propargyl-TEG-iodide (6.84 g, 20 mmol), with the exception that the crude product was purified by column chromatography using ethyl acetate. The purified TEG-iodized 1,2,3-triazole was obtained as a yellow oil (7.58 g, 16.0 mmol, 76%). H NMR (400 MHz, DMSO-d6, δ): 8.16 (s, 1H), 7.41–7.30 (m, 5H), 4.53 (s, 2H), 3.66 (t, J = 6.4 Hz, 2H), 3.59–3.49 (m, 12H), 3.32 (t, J = 6.5 Hz, 2H). 13C NMR (100 MHz, DMSO-d6, δ): 144.3, 136.0, 128.7, 128.1, 127.8, 124.0, 70.9–68.9, 63.5, 52.7, 5.4.

4.3.2.1. Synthesis of MEG-Iodized 1,2,3-Triazole. A solution of MEG-iodized 1,2,3-triazole (6.88 g, 20.0 mmol) and sodium azide (1.56 g, 24.0 mmol) in DMF (25 mL) was stirred at 50 °C for 24 h. After this, the crude reaction mixture was quenched with saturated NH4Cl aq. and then extracted with ethyl acetate (3 × 100 mL). The resulting organic layer was washed with water (2 × 100 mL) and saturated brine (2 × 100 mL) and dried over anhydrous MgSO4. After filtration, the solvent was evaporated to give MEG-iodized 1,2,3-triazole as a yellow liquid (5.05 g, 19.6 mmol, 98%). H NMR (400 MHz, DMSO-d6, δ): 8.15 (s, 1H), 7.40–7.28 (m, 5H), 5.59 (s, 1H), 4.56 (s, 1H), 3.62 (t, J = 5.0 Hz, 2H), 3.40 (t, J = 4.9 Hz, 2H). 13C NMR (100 MHz, DMSO-d6, δ): 144.1, 136.1, 128.7, 128.1, 127.9, 124.0, 68.4, 63.4, 52.7, 5.00.

4.3.2.2. Synthesis of TEG-Azido-1,2,3-triazole. A similar procedure was performed using TEG-iodized 1,2,3-triazole (9.52 g, 20.0 mmol) to give TEG-iodized 1,2,3-triazole as a yellow oil (7.26 g, 18.6 mmol, 93%). H NMR (400 MHz, DMSO-d6, δ): 8.14 (s, 1H), 7.39–7.28 (m, 5H), 5.58 (s, 1H), 4.50 (s, 1H), 3.59–3.48 (m, 14H), 3.37 (t, J = 4.9 Hz, 2H).
the MEG-IL monomer as a slightly yellow viscous liquid after reaction mixture was precipitated

\[ \text{M} \] MHz DMSO-

\( ^{13} \text{C} \) NMR (100 MHz, DMSO-

\( ^{1} \text{H} \) NMR (400 MHz, DMSO-

\( ^{13} \text{C} \) NMR (100 MHz, DMSO-

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c06173.
Synthesis of propargyl-TEG-OH; synthesis of propargyl-TEG-iodide; synthesis of propargyl-TEG-iodide; synthesis of EG-α-azide-α-alkyne ionic liquid monomers; ratio of 1,2- and 1,3-substituted derivatives for TPILs; 1H and 13C NMR spectra of MEG-iodized 1,2,3-triazole, TEG-iodized 1,2,3-triazole, MEG-azido-1,2,3-triazole, TEG-azido-1,2,3-triazole, MEG-IL monomer, and TEG-IL monomer; and GPC traces of TPILs 4–6, and 9 at 40 °C (eluent: 60 mM LiTf2N in DMF) (PDF)

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This work was financially supported by the JSPS KAKENHI (grant nos. JP18H03854 and JP19K15340). The authors thank Associate Professor Takashi Teranishi (Okayama University) for his invaluable advice. They also thank Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan for supporting this research. The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was financially supported by the JSPS KAKENHI (grant nos. JP18H03854 and JP19K15340). The authors thank Associate Professor Takashi Teranishi (Okayama University) for his invaluable advice. They also thank Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, Okayama 700-8530, Japan for supporting this research. The authors declare no competing financial interest.

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**Author Contributions**

R.H., T.W., and T.O. designed the experiments. R.H. performed the experiments and analyzed the data. R.H., T.W., and T.O. interpreted the results and wrote the manuscript. T.W. and T.O. designed the research.

**Notes**

The authors declare no competing financial interest.

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