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Synthesis of polysiloxane-based quaternized imidazolium salts with a hydroxy group at the end of alkyl groups

Tsukasa Ichikawa, Tsuyoshi Wako, Nobukatsu Nemoto *

Department of Chemical Biology and Applied Chemistry, College of Engineering, Nihon University, Tamura-machi, Koriyama, Fukushima 963-8642, Japan

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ABSTRACT

A series of polysiloxane derivatives having quaternized imidazolium moieties with hydroxyalkyl groups (**[HPIm*n*OH]X**s) (where ***n*** is the number of methylene group and **X** is counter anion) were prepared by quaternization of poly(3-chloropropylmethylsiloxane) (**P1**) using 1-(ω-hydroxyalkyl)imidazole derivatives (**Im*n*OH**s) and anion-exchange reaction using lithium bis(trifluoromethanesulfonyl)imide. Polysiloxane-based quaternized imidazolium salts having hydroxyalkyl groups with chloride anion (**[HPIm*n*OH]Cl**s) were obtained with high quaternization ratio of approximately 100 mol%. The glass transition temperatures (T_gs) of **[HPIm*n*OH]X**s were reduced by introducing a hydroxy group at the end of alkyl groups; however, no significant reduction in T_gs was observed by anion exchange from chloride anion to bis(trifluoromethanesulfonyl)imide one (Tf_2N^-).

1. Introduction

Ionic liquids (ILs) are well-known organic salts with melting point <100 °C that exhibit nonvolatility [1], flame retardation [2], relatively high heat resistance, and high ionic conductivity [3]. Thus, ILs would be expected to be materials for various ionic devices. Poly(ionic liquid)s (PILs) obtained by polymerization of IL monomers with polymerizable group, such as vinyl group, have been attracting attention as polymer electrolytes [4–12] and CO_2 absorbents [13–15]. It has been reported that the properties of PILs are influenced by the introduction of a substituent and/or functional group [7]. Furthermore, it has been reported that the morphological changes induced by the introduction of hydroxy groups into the PILs based on imidazolium salt reduce the glass transition temperature (T_g), and the distances among main chains have been also reported to be extended due to the increase of free volume around the main chains [16]. In addition, the introduction of hydroxy group at the end of alkyl moiety of IL based on imidazolium salt has been reported to reduce cation–anion electrostatic interactions because of the extended distances between the proton of 2-position of imidazolium moiety and an anion as deduced from the density functional theory calculations [17]. Thus, the introduction of hydroxy group at the end of alkyl moiety on imidazolium salt would effectively reduce the T_g. It has been also reported that anion exchange of halogen anions to bis(trifluoromethanesulfonyl)imide ones (Tf_2N^-) significantly reduces the T_g and improves thermal stability [18–21]. In addition, PILs based on polyacrylate with phosphate anion ($H_2PO_4^-$) have been reported to exhibit proton conductivity of 10^{-2} S cm^{-1} at 120 °C by doping phosphoric acid [6]. In particular, the change of substituent and/or functional groups as well as the anion exchange would be remarkably effective for the enhancement of PIL properties.

Polydimethylsiloxane (PDMS) is the most common and a representative polysiloxane derivative that is well known to exhibit flexibility, hydrophobicity, thermal stability, surface activity, high gas permeability, physiology, and chemical inactivity [22,23]. In addition, polysiloxane derivatives having various pendant groups have been applied in various fields for their favorable properties. For example, polysiloxane copolymers having quaternary ammonium salt have been studied as amphiphilic or antimicrobial polymers [24,25]. Polysiloxanes containing fluoroalkyl groups have been studied as highly hydrophobic materials [26]. In addition, polysiloxane derivatives having ionic as well as mesogenic moieties have been studied as liquid crystalline polymers, which are applied in electro-optic displays [27].

On the contrary, quaternized imidazolium salts based on polysiloxane are expected to be in liquid state in a low-temperature range, because polysiloxanes are known to render flexibility to the main chain because of the large free volume around main chains and fluidity at such low temperatures [22,23]. We have investigated the properties of quaternized imidazolium salts based on polysiloxane (**[HPIm*n*]Cl**) (where ***n*** is the number of methylene group) and reported [28] that the incorporation of long alkyl chains reduces the T_g and increases solubility in organic solvents. It has been revealed [28] that the T_gs of quaternized imidazolium salts based on polysiloxane with a relatively strongly basic anion (Cl^-) are lower than those of poly[1-alkyl-3-vinylimidazolium] derivatives with a relatively weakly basic anion (Tf_2N^-) [7] because of the flexibility of the polysiloxane main chain. On the contrary, the influences of the introduction of functional groups as well as the counter anion of

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* Corresponding author.
E-mail address: nemoto.nobukatsu@nihon-u.ac.jp (N. Nemoto).

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polysiloxane-based quaternized imidazolium salts on their thermal behavior have not been clarified.

From these viewpoints, the synthesis and properties of novel polysiloxane-based quaternized imidazolium salts (**[HPIm*n*OH]X**s) bearing a hydroxyalkyl group at 1-position of imidazolium moieties (**Im*n*OH**s) have been investigated. It will be revealed in the following section that the introduction of hydroxy group at the end of alkyl groups on imidazolium moieties as well as the long alkyl chains reduces the T_g because of the increase of free volume around main chains and reduction of electrostatic interactions between the cation and anion.

2. Experimental

2.1. Materials

Poly(3-chloropropylmethylsiloxane) (**P1**) was prepared by the method reported in the literature using 3-chloropropyldichloromethylsilane as the raw material [29]. The number average molecular weight (M_n) and molecular weight dispersity (M_w/M_n) of the **P1** used, as estimated by size-exclusion chromatography (SEC) using polystyrene standards, were 21,000 and 1.10, respectively. Tetrahydrofuran (THF, Tokyo Chemical Industry Co., Ltd) and diethyl ether (Kanto Chemical Co., Inc.) were used after distillation over sodium. *N*,*N*-dimethylformamide (DMF, Kanto Chemical Co., Inc.) was used after distillation over calcium hydride. Tetramethylammonium hydroxide (TMAH, 10% in methanol, Tokyo Chemical Industry Co., Ltd), potassium *tert*-butoxide (*t*-BuOK), ethyl bromoacetate, γ-butyrolactone, ε-caprolactone (Tokyo Chemical Industry Co., Ltd), hydrobromic acid (48% aqueous solution), lithium aluminum hydride ($LiAlH_4$), sodium hydroxide (Kanto Chemical Co., Inc.), lithium bis(trifluoromethanesulfonyl)imide ($LiTf_2N$, Kanto Chemical Co., Inc.), and imidazole (Nacalai Tesque, Inc.) were used as received. 4-Bromobutanoic acid (**4a**) and 6-bromohexanoic acid (**4b**) were prepared by the method reported earlier [30].

2.2. Measurements

^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE 400F spectrometer or JEOL ECX-400 spectrometer in deuterated chloroform ($CDCl_3$) or dimethylsulfoxide (DMSO-d_6) at ambient temperature. ^{19}F NMR spectra were recorded on a JEOL ECX-400 spectrometer in deuterated DMSO-d_6 at ambient temperature. Infrared (IR) spectra were measured on a Perkin-Elmer Spectrum One Fourier transform infrared (FTIR) spectrometer. The glass transition temperature (T_g) was determined by differential scanning calorimetry (DSC) on a RIGAKU ThermoPlus DSC 8230 at a heating or cooling rate of 10 °C/min under a nitrogen flow rate of 10 mL/min. The number average (M_n) and weight average (M_w) molecular weights were determined by SEC on a SHOWA DENKO Shodex GPC-101 system with polystyrene gel columns (a pair of Shodex GPC LF-804) eluted with THF using a calibration curve of polystyrene standards.

2.3. Synthesis of 1-(ethoxycarbonylmethyl)imidazole (*2*)

Under a dry argon atmosphere, a solution of imidazole (**Im**, 4.10 g, 60.2 mmol) in dry THF (15 mL) was added dropwise to a solution of potassium *tert*-butoxide (6.73 g, 60.0 mmol) in dry THF (150 mL) at 0 °C, and the resulting mixture was stirred for 2 h at the same temperature. Ethyl bromoacetate (10.0 g, 59.9 mmol) was added dropwise to this reaction mixture and stirred for 18 h at room temperature. It was then filtered and the filtrate was concentrated under reduced pressure. The residual liquid was dissolved in dichloromethane, and the resulting solution was washed with water and brine several times, dried over anhydrous sodium sulfate, and filtered. The filtrate was again concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with a mixed solvent of chloroform/methanol (10/1 v/v). The fraction with an R_f value of 0.58 was collected and dried under reduced pressure to afford 1-(ethoxycarbonylmethyl)imidazole (**2**) as yellow oil (6.702 g, 72%).

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.63 (t, J = 5.3 Hz, 2H, NCH_2), 3.98 (q, J = 5.5 Hz, 2H, CH_2OH), 4.94 (t, J = 3.9 Hz, 1H, OH), 6.85 (s, 1H, $CHNCH_2$), 7.13 (s, 1H, $NCHCH$), and 7.57 (s, 1H, $NCHN$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 49.00 (NCH_2), 60.95 (CH_2OH), 32.38 (CH_2COOH), 119.90 ($NCHCH$), 128.22 ($CHNCH_2$), and 137.71 ($NCHN$). IR (NaCl, cm^{-1}): 1747 ($C{=}O$).

2.4. Synthesis of 1-(2-hydroxyethyl)imidazole (*Im2OH*)

Under a dry argon atmosphere, a solution of **2** (6.05 g, 39.2 mmol) in dry THF (20 mL) was added dropwise to the mixture of lithium aluminum hydride (3.00 g, 79.1 mmol) and dry THF (60 mL) at 0 °C. The reaction mixture was stirred for 5 min at 0 °C and for 4 h at room temperature. Then, water (3 mL), 15% sodium hydroxide aqueous solution (3 mL), and water (9 mL) were separately added dropwise to the reaction mixture at 0 °C. The resulting reaction mixture was stirred at room temperature for 12 h and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with a mixed solvent of chloroform/methanol (10/1 v/v). The fraction with an R_f value of 0.22 was collected and purified by distillation under reduced pressure twice to afford 1-(2-hydroxyethyl)imidazole (**Im2OH**) as colorless oil (2.386 g, 54%).

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.62 (t, J = 5.3 Hz, 2H, NCH_2), 3.97 (t, J = 7.2 Hz, 2H, NCH_2CH_2), 4.96 (t, J = 5.1 Hz, 1H, OH), 6.85 (s, 1H, $CHNCH_2$), 7.14 (s, 1H, $NCHCH$), and 7.57 (s, 1H, $NCHN$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 48.96 (NCH_2), 60.93 (CH_2OH), 119.85 ($NCHCH$), 128.20 ($CHNCH_2$), and 137.66 ($NCHN$). IR (NaCl, cm^{-1}): 3363 (—OH).

2.5. Synthesis of 4-bromobutanoic acid (*4a*) and 6-bromohexanoic acid (*4b*) [30]

Typical procedure: Under a dry argon atmosphere, 48% HBr aqueous solution (41.0 mL, 360 mmol) and conc. sulfuric acid (9.6 mL) were added dropwise to γ-butyrolactone (**3a**) (6.10 g, 70.9 mmol), and the resulting mixture was left undisturbed at room temperature for 2 h. Then, after refluxing for 12 h, the reaction mixture was cooled to room temperature. To this reaction mixture, 192 mL of water was added, and the crude product was extracted with diethyl ether. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and filtered. The filtrate was concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with a mixed solvent of ethyl acetate/hexane (1/2 v/v). The fraction with an R_f value of 0.44 was collected and dried under reduced pressure to afford 4-bromobutanoic acid (**4a**) as yellow oil (7.638 g, 65%).

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 2.19 (quint, J = 6.4 Hz, 2 H, $BrCH_2CH_2$), 2.58 (t, J = 4.2 Hz, 2H, CH_2COOH), and 3.48 (t, J = 3.2 Hz, 2H, $BrCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 27.36 ($BrCH_2CH_2$), 32.11 ($BrCH_2$), 32.38 ($Br(CH_2)_2CH_2$), and 178.58 ($COOH$). IR (NaCl, cm^{-1}): 1711 ($C{=}O$), 3046 (—OH).

6-Bromohexanoic acid (**4b**) was obtained by a method similar to the preparation of **4a** using ε-caprolactone (**3b**) as the raw material. The spectroscopic data of the obtained **4b** are as follows:

6-Bromohexanoic acid (**4b**)

Yield: 92% as yellow oil. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 1.51 (quint, J = 4.0 Hz, 2H, $Br(CH_2)_2CH_2$), 1.68 (quint, J = 7.7 Hz, 2H, $Br(CH_2)_3CH_2$), 1.89 (quint, J = 7.1 Hz, 2H, $BrCH_2CH_2$), 2.39 (t, J = 7.3 Hz, 2H, $Br(CH_2)_4CH$), and 3.42 (t, J = 6.9 Hz, 2H, $BrCH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 23.80 ($Br(CH_2)_3CH_2$), 27.54 ($Br(CH_2)_2CH_2$), 32.33 ($BrCH_2$), 33.39 ($Br(CH_2)_4CH_2$), and 179.64 ($COOH$). IR (NaCl, cm^{-1}): 1709 ($C{=}O$), 3046 (—OH).