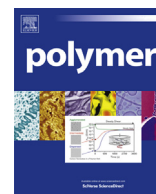




Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Polymerized ionic liquid diblock copolymers with long alkyl side-chain length

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ARTICLE INFO

Article history:

Received 4 January 2014

Received in revised form

11 March 2014

Accepted 3 April 2014

Available online xxx

Keywords:

Ionic liquid

Block copolymer

Conductivity

ABSTRACT

A polymerized ionic liquid (PIL) diblock copolymer with a long alkyl side-chain, poly(MMA-*b*-MUBIm-Br), was synthesized at various compositions from an ionic liquid monomer, (1-[(2-methacryloyloxy)undecyl]-3-butylimidazolium bromide) (MUBIm-Br), and a non-ionic monomer, methyl methacrylate (MMA). The PIL diblock copolymer was synthesized *via* post-functionalization from its non-ionic precursor PIL diblock copolymer, poly(MMA-*b*-BrUMA) (BrUMA = 11-bromoundecyl methacrylate), which was synthesized *via* the reverse addition fragmentation chain transfer (RAFT) polymerization technique. Differential scanning calorimetry reveals two distinct constant glass transition temperatures (T_g s) with a low PIL segment T_g . These PIL block copolymers result in easily processable, flexible, transparent films with high mechanical strength. A high bromide ion conductivity of 64.85 mS cm^{-1} at 80°C and 90% RH was measured for the PIL diblock copolymer with an ion exchange capacity (IEC) of 1.44 meq/g (23.3 mol % MUBIm-Br). Interestingly, this result was three times higher than its analogous PIL homopolymer (2.75 meq/g ; 100 mol% MUBIm-Br) and an order of magnitude higher than a PIL block copolymer from a previous study with similar chemistry, similar IEC, higher water content, but shorter alkyl side-chain length. Ion conductivity did not scale as expected with water content, which is unusual for water-assisted ion transport (e.g., protons, hydroxide, chloride) in ion-containing polymers, and therefore suggests other mechanisms that impact ion transport in PIL block copolymers.

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1. Introduction

Polymerized ionic liquid (PIL) block copolymers are a distinct set of block copolymers that combine the properties of both PILs and block copolymers [1–5]. More specifically, the unique physicochemical properties of PILs include high solid-state ionic conductivity, high chemical, thermal and electrochemical stability, and widely tunable physical properties (e.g., *via* anion exchange), while block copolymers are known to self-assemble into a range of nanostructures (e.g., body-centered cubic spheres, hexagonal cylinders, bicontinuous gyroid, lamellae). In the solid-state, this self-assembly results in materials that can accelerate the transport of ions and small molecules within continuous nanostructured channels, where the PIL chemistry within these channels offer unique property advantages, such as high electrochemical stability for hydroxide or lithium ions or high preferential sorption affinity for carbon dioxide. These features have led to a recent exploration

of PIL block copolymers for a number of applications, including gas separations [6,7], electrochemical transducers [8], and fuel cells [9].

Transport in PIL block copolymers differs from other work on ion transport (conductivity)–morphology studies in block copolymers, where previous studies typically involve a mixture of either a solid salt (e.g., Li salt) or molten salt (e.g., ionic liquid (IL)) with a neutral block copolymer [10–15]. In these mixtures, the cations and anions migrate simultaneously to provide ion conduction. Contrastingly, PIL block copolymers are single-ion conductors, where one ion is covalently attached to the polymer chain (e.g., cation) and the counterion is mobile (e.g., anion). Typical counterions in PILs are fluorinated (e.g., bis(trifluoromethanesulfonyl)imide; TFSI) resulting in a hydrophobic polymer, where ion transport in the anhydrous polymer is dictated by the segmental dynamics of the polymer chains (Vogel–Fulcher–Tammann behavior with temperature) [16]. However, when these counterions are exchanged with other anions (e.g., hydroxide), the PIL becomes hydrophilic and ion transport is dictated by a water-mediated mechanism (Arrhenius behavior with temperature) [17]. Understanding how nanostructured morphology in PIL block copolymers impacts the transport of both types of ions is of

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importance for applications, such as gas separations and energy storage for the former type and fuel cells and water purification for the latter type. Recently, there have been several fundamental investigations on conductivity–morphology relationships in PIL block copolymers [1–5]. For fluorinated counterions (e.g., TFSI), morphology type [1,3], the extent of long-range order [1,4], the strength of micro-phase separation [2,3], and the glass transition temperature of the PIL microdomain [3,5] have all shown to have a significant impact on ion conductivity in PIL block copolymers.

More recently, the transport of other counterions, which are of interest for this present investigation, such as bromide and hydroxide, in PIL block copolymers has been explored, where these counterions are facilitated by a water-mediated transport mechanism. The conductivity of these counterions is of interest for alkaline exchange membrane (AEM) fuel cells and water purification applications [9]. Recent work in our laboratory [9] synthesized and investigated the bromide and hydroxide conductivity in a PIL diblock copolymer poly(MMA-*b*-MEBIm-Br) or poly(methyl methacrylate-*b*-1-[(2-methacryloyloxy)ethyl]-3-butylimidazolium bromide). In this previous work, the PIL block copolymer with 17.3 mol% MEBIm-Br composition or 1.4 meq/g ion exchange capacity (IEC) showed a high bromide conductivity of 5.67 mS cm⁻¹ at 80 °C and 90% RH. The bromide conductivity of this PIL block copolymer was over an order of magnitude higher than its analogous PIL random copolymer (at the same IEC and water content) over a temperature range of 30–80 °C at high humidity (90% RH). This was a product of the strong micro-phase separation (lamellae) in the PIL block copolymer, where no microphase separation was evident in the PIL random copolymer. Surprisingly, the bromide ion conductivity in this PIL block copolymer was higher than its analogous PIL homopolymer, which had a higher IEC (3-fold) and water content (2-fold) than the block copolymer. It is not clear why the bromide ion conductivity was higher in the block copolymer compared to the homopolymer as this has not been evidenced before in water-assisted ion transport in block copolymers to the authors' knowledge [18]. Similar conductivity trends were also observed for hydroxide ion conductivity in these PIL polymers as well, where the PIL block copolymer had a hydroxide conductivity of 25.46 mS cm⁻¹ at 80 °C and 90% RH at a low water content.

To date, there are only few reports of water-assisted ion conductivity in PIL block copolymers. However, several recent reports have investigated water-assisted ion transport in block copolymers for alkaline fuel cells [9,19–21]. Watanabe and coworkers [19] investigated hydroxide ion conductivity in aromatic multiblock copolymers of poly(arylene ether)s containing covalently attached quaternary ammonium cations. A high hydroxide ion conductivity of 144 mS cm⁻¹ at 80 °C in liquid water for the block copolymer with an IEC of 1.93 meq/g was measured, which was ~3 times higher than its analogous random copolymer at an IEC of 1.88 meq/g. The higher conductivity in the block copolymer compared to the random copolymer was attributed to a strong micro-phase separation observed in the block copolymer *via* electron microscopy. Coughlin and co-workers [20] synthesized and investigated the morphology and conductivity of the block copolymer poly(styrene-*b*-vinyl benzyl trimethylammonium hydroxide), PS-*b*-[PVBtMA][OH]. A hydroxide conductivity of 12.55 mS cm⁻¹ at 80 °C and 90% RH was measured for the block copolymer with an IEC of 1.36 meq/g. Differences in hydroxide conductivity were observed between block copolymers of varying IEC, which was attributed to differences in morphology type and d-spacing observed with small-angle X-ray scattering. Knauss and coworkers [21] synthesized bromide and hydroxide conducting poly(phenylene oxide) block and random copolymers and measured a bromide and hydroxide conductivity of 26 mS cm⁻¹ (90 °C; 95% RH) and 84 mS cm⁻¹ (80 °C; 95% RH), respectively, for the block copolymer with an IEC of

1.27 meq/g. Similar to the work of Elabd and coworkers [9], the block copolymer showed a higher conductivity compared to its analogous random copolymer.

Several of the recent observations in water-assisted ion transport in anion exchange block copolymers, such as ion conductivity higher in a block copolymer compared to its random copolymer, has previously been observed in cation exchange block copolymers (e.g., sulfonated block copolymers) [18]. However, the recent observation of ion transport higher in a block copolymer compared to its analogous homopolymer is unique and is of interest to explore further [9]. In this study, a PIL block copolymer was synthesized with a similar chemistry to a former study, poly(MMA-*b*-MEBIm-Br), however, the PIL chemistry was modified to incorporate a longer alkyl side-chain length (from C = 2 to C = 11). This should lower the glass transition temperature of the PIL domain and therefore produce more flexible films under dry conditions at room temperature. We are interested in the properties and conductivity of these new materials, particularly the conductivity of the block copolymer compared to its homopolymer.

In this paper, a PIL diblock copolymer with a long alkyl side-chain was synthesized, poly(MMA-*b*-MUBIm-Br), at various compositions comprising of a PIL component (1-[(2-methacryloyloxy)undecyl]-3-butylimidazolium bromide) (MUBIm-Br) and a non-ionic component (MMA). Poly(MMA-*b*-MUBIm-Br) was synthesized *via* post-functionalization from its non-ionic precursor PIL diblock copolymer, poly(MMA-*b*-BrUMA) (BrUMA = 11-bromoundecyl methacrylate), which was synthesized *via* the reverse addition fragmentation chain transfer (RAFT) polymerization technique. An analogous PIL homopolymer, poly(MUBIm-Br), was synthesized by conventional free radical polymerization for comparison. The thermal, mechanical, and conductivity properties of these PILs were investigated in this study.

2. Experimental

2.1. Materials

4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (chain transfer agent (CTA), >97%, HPLC), tetrahydrofuran (THF, ≥99.9%), *N,N*-dimethylformamide (DMF, 99.9%, HPLC), methanol (99.9%, HPLC), acetonitrile (anhydrous, 99.8%), calcium hydride (CaH₂, 95%), lithium bromide (LiBr, ≥99%), 11-bromo-1-undecanol (98%), 1-butylimidazole (98%), magnesium sulfate (anhydrous, ReagentPlus®, 99%), triethylamine (≥99.5%), methacryloyl chloride (97%, stabilized with 200 ppm monomethyl ether hydroquinone (MEHQ)), dichloromethane (ACS reagent, ≥99.5%, contains 50 ppm amylene stabilizer), dimethyl sulfoxide-*d*₆ (DMSO-*d*₆, 99.9% atom % D, contains 0.03% v/v TMS) and chloroform-*d* (CDCl₃, 99.96 atom % D, contains 0.03% v/v TMS) were used as received from Sigma–Aldrich. Azobisisobutyronitrile (AIBN, 98%, Sigma–Aldrich) was purified by recrystallization twice from methanol. Methyl methacrylate (MMA, 99%, Sigma–Aldrich) was purified by distillation over CaH₂ at a reduced pressure. Ultrapure deionized (DI) water with resistivity ca. 16 MΩ cm was used as appropriate.

2.2. Synthesis of 11-bromoundecyl methacrylate monomer

A typical synthesis method for the bromine terminated monomer, 11-bromoundecyl methacrylate (BrUMA), which has been synthesized in a previous publication [22], is shown in Scheme 1(1) and includes adding 37.4 g (148.89 mmol) of 11-bromo-1-undecanol and 80 mL of dichloromethane to a three-neck 500 mL flask in an ice bath. Under nitrogen, a mixture of 15.24 g (150.61 mmol) of triethylamine and 40 mL of dichloromethane was slowly added to the flask, followed by a slow addition of a mixture of 15.75 g

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