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Synthesis of polymeric ionic liquids with unidirectional chain topology by AB step growth polymerization

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ABSTRACT

Poly(ionic liquid)s with alkyl imidazolium moieties in the main chain were synthesized by step growth addition polymerization of the AB monomers 1-(4-chlorobutyl)-1*H*-imidazole, 1-(6-chlorohexyl)-1*H*-imidazole, and 1-(6-bromohexyl)-1*H*-imidazole in the melt. The molar masses of the polymers were controlled by adding 1-butyl-1*H*-imidazole as monofunctional chain stopper. The bromine containing monomer polymerized spontaneously at room temperature whereas the chlorine containing monomers were sufficiently stable up to 40 °C. This could be evidenced by DSC measurements which showed a broad exothermal peak above 40 °C caused by the polymerization. MALDI-TOF investigations proved that dissociation of the alkyl imidazolium groups which might disturb the expected directional chain topology (AB-AB-AB…) did not occur. This is an important precondition for the intended cross-linking free grafting reactions of the AB monomers on halide containing polymers without any danger of gelation. Additionally, the results of the MALDI-TOF investigations indicated partial complexation of the polymer with the matrix and structural rearrangements during the measurements which converted the ionic imidazolium moieties into neutral moieties. The thermal behavior of the poly(ionic liquid)s has proved to be dependent on the length of the alkyl linking group between the imidazolium moieties and the type of counter ion.

1. Introduction

After the enormous progress in the field of low molar mass ionic liquids, nowadays a growing interest in polymeric ionic liquids (PIL) is evident. A comprehensive overview about this topic has been given in a number of recently published reviews [1,2]. PILs comprise a group of polymers containing the typical structural units of common ionic liquids. Most frequently, such polymers are synthesized by chain growth polymerization of polymerizable ionic liquids. Derived from this, the term “polymerized ionic liquid” has been established. A further alternative term used in publications is “poly(ionic liquid)” which is also preferred by us since it also comprises polymers obtained by step growth polymerization and polymer analogous reactions.

Beside the large number of PILs synthesized by chain growth polymerization, several examples are known which were obtained by step growth polymerization. In the latter, the ionic groups are located in the main chain which can either be formed during the polymerization [3–9] or after polymerization by subsequent quaternization of respective nitrogen containing functional groups [10–12]. This also includes the broad class of ionenes synthesized by a Menshutkin reaction of ditertiary amines and alkyl dihalides [13]. Furthermore, the introduction by using ionic group containing monomers is also possible [14]. For imidazolium containing PILs, the most obvious method is the conversion of bis-imidazoles with bifunctional alkylhalogenides (AA, BB monomers) [3–6,8] or the conversion of asymmetric halogen alkylimidazoles (AB monomers) [6,12]. Both methods directly lead to the formation of polyalkylimiazolium PILs and may result in the same repetition unit in the polymer backbone [6]. However, one important difference exists in the kind of terminal groups. Provided that no exchange reactions occur, the polymerization of an AB monomer forms a polymer chain with two different terminal groups (halogen and imidazole) which might be important if grafting of such a PIL to other halogen group containing polymers is intended. In this case, the directional chain build up with the AB monomer would

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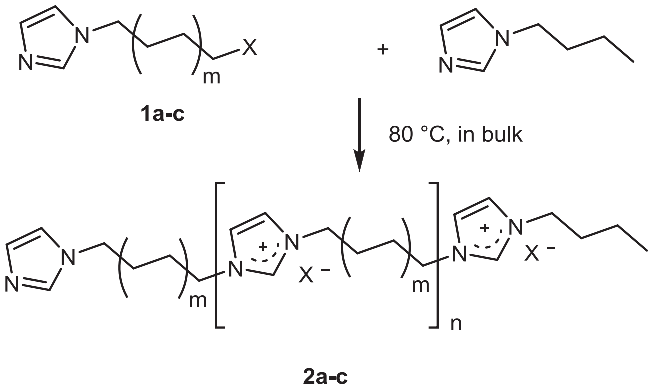
promote the formation of free dangling grafts whereas the alternate linking of AA and BB monomers in presence of the polymer to be grafted would result in cross-linking.

In this article, our focus is on the synthesis of PILs by step growth polymerization using asymmetric AB monomers of type **1** (see Scheme 1). Although this approach of synthesizing PILs is in principle known [6,7], we faced a couple of questions related to our final intention to graft PIL chains to other polymers. Recently, we published about the self-healing behavior of ionically modified bromobutyl rubber (BIIR) [15]. For this the bromine groups of BIIR were converted with butylimidazole. It was shown that the imidazolium groups obtained by this reaction formed ionic associates, the rearrangements of which were assumed to be responsible for the self-healing effects observed. Since the concentration of bromine groups in BIIR is relatively small (1–2 mol%), only a limited number ionic groups can be introduced by this way. One promising alternative to increase the number of ionic groups in BIIR is a directional grafting with AB monomers mentioned above, whereby cross-linking reactions should be prevented. From that point of view, our major concern was to prove the assumption whether the polymerization of AB monomers according to Scheme 1 would result in the formation of directed polymer chains with two different terminal groups (halogen and imidazole). Theoretically, polymer chains with two imidazole terminal groups or two alkyl halide groups might be formed by dissociation of the alkyl imidazolium groups formed during the polymerization as shown for the trimer of polymer **2a** in Scheme 2. If such reactions occurred during grafting of BIIR, cross-linking would be inevitable.

2. Experimental

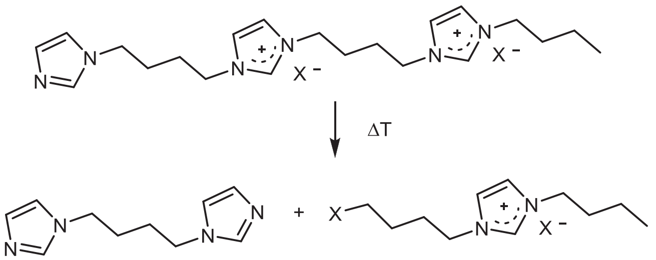
2.1. Materials

Imidazole (puriss p.a., ≥99.5%), 1-bromo-6-chlorohexane (95%), 1,6-dibromohexane (96%), 1-bromo-4-chlorobutane (99%), 1-butylimidazole (98%), and sodium amide (98%) from Sigma-Aldrich, methylene chloride (p.a.) and THF (p.a.) from Acros Organics and DMSO-d_6 (water < 0.02%),D_2O (≥99,9%), and $CDCl_3$ (≥99,8%) from Euriso-top were used as received.



	1/2a	1/2b	1/2c
m	1	2	2
X	Cl	Cl	Br

Scheme 1. Synthesis of poly(ionic liquids) (**2a-c**) starting with AB monomers (**1a-c**).



Scheme 2. Hypothetical dissociation of alkyl imidazolium groups. This reaction may disturb the unidirectional chain topology.

2.2. Monomer synthesis (*1a-c*)

The procedure is described for 1-chlorohexylimidazole (**1b**) as an example.

In a 50 ml Schlenk flask equipped with a stir bar and a septum, imidazole (73.4 mmol, 5 g) and sodium amide (90 mmol, 3.5 g) were consecutively dissolved in 25 ml of dry THF under nitrogen as protective gas. After 1.5 h stirring at room temperature, the mixture was cooled down with ice water and 1-chloro-6-bromohexane (73.4 mmol, 14.64 g) was added carefully. The cooling was continued for another 3 h under steady nitrogen flow. After keeping the mixture overnight at room temperature, 100 ml water was added. Then, the reaction mixture was extracted three times with methylene chloride and dried with Na_2SO_4. After evaporation of the solvent a yellow oily liquid was obtained. The purification was performed by flash chromatography with a graduated mixture of *n*-hexane and acetone, starting with 100% *n*-hexane. The resulting colorless oily liquid was stored in a freezer at −20 °C.

The monomers **1a** and **1c** were synthesized accordingly using 1-chloro-4-bromobutane and 1,6-dibromohexane, respectively, instead of 1-chloro-6-bromohexane. To prevent polymerization, **1c** was stored in a solution of methylene chloride in a freezer at −20 °C.

1a: Yield: 51%, ^1H NMR ($CDCl_3$) δH ppm: 7.48 (1H, s, Im), 7.06 (1H, s, Im), 6.91 (1H, s, Im), 3.98 (2H, t, $J = 7.1$ Hz, N-CH_2), 3.53 (2H, t, $J = 6.5$ Hz, CH_2-Cl), 1.96 (2H, m, N-CH_2-*CH_2*), 1.46 (2H, m, *CH_2*-CH_2-Cl).

1b: Yield: 67%, ^1H NMR ($CDCl_3$) δH ppm: 7.44 (1H, s, Im), 7.04 (1H, s, Im), 6.89 (1H, s, Im), 3.93 (2H, t, $J = 7.1$ Hz, N-CH_2), 3.51 (2H, t, $J = 6.6$ Hz, CH_2-Cl), 1.82–172 (4H, m, N-CH_2-*CH_2*, *CH_2*-CH_2-Cl), 1.46 (2H, m, CH_2), 1.31 (2H, m, CH_2).

1c: Yield: 10% (polymerization during flash chromatography), ^1H NMR ($CDCl_3$) δH ppm: 7.44 (1H, s, Im), 7.03 (1H, s, Im), 6.88 (1H, s, Im), 3,92 (2H, t, $J = 7.1$ Hz, N-CH_2), 3.37 (2H, t, $J = 6.8$ Hz, CH_2-Br), 1.86–1.75 (4H, m, N-CH_2-*CH_2*, *CH_2*-CH_2-Br), 1.46 (2H, m, CH_2), 1.30 (2H, m, CH_2).

2.3. Polymer synthesis (*2a-c*)

The polymerization of **1** was performed in bulk. In order to limit the degree of polymerization, 1-butylimidazole was added as mono-functional chain stopper. In a typical approach a mixture of 6.3 mmol (1 g) of **1b** and 0.63 mmol (78 mg) of 1-butylimidazole were stirred for 16 h at 80 °C. The resulting yellowish solid **2b** was washed with acetone and dried under vacuum at 80 °C for several hours. **1c** polymerized spontaneously at room temperature after removal of the solvent. A sample overview is given in Table 1. The polymers were soluble in water, ethylacetate (except **2c**), and methanol and insoluble in ethanol, THF, acetone, chloroform, dichloromethane, DMSO, and DMAc. NMR spectra were recorded in D_2O.