



New reactive poly(ionic liquid)s synthesized by polymer analogous conversion of maleic anhydride containing polymers



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ABSTRACT

New poly(ionic liquids) were synthesized by a two stage polymer analogous reaction. In the first stage, the reactive maleic anhydride groups of the starting polymer were converted with 1-(3-aminopropyl)-imidazole. The second stage comprises an alkylation reaction of the imidazole groups with various alkylbromides. This approach allowed tailoring of the polymer properties to a large extent. With the degree of conversion, the number of reactive groups remaining in the polymer could be adjusted. The possibility to preserve reactive groups opens new applications of the poly(ionic liquid)s as reactive blend components. As an example, reactive mixtures with bromobutyl rubber were prepared which exhibited pronounced self-healing properties.

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1. Introduction

After rapid developments in the field of ionic liquids in the last decades, nowadays poly(ionic liquid)s have gained more and more interest in material research. This is owed to the fact that poly(ionic liquid)s combine favorable properties of ionic liquids and polymers. Ionic conductivity, strong interactions, and fluidity on the one hand and mechanical strength and processability on the other hand enable new developments in various fields of material research. Examples for this are the utilization of poly(ionic liquid)s as materials in sorption and separation processes [1–11], as catalysts [12–18], as ion conductive materials in batteries [19–23], as precursors for the production of carbon [24,25], and as component in biologically active materials [26,27]. The utilization of poly(ionic liquid)s as components in blends or composites has hardly been considered so far. This is due to the fact that poly(ionic liquid)s are highly incompatible with most of the common polymers. Chemical reactions between the components might contribute to an improved miscibility which demands poly(ionic liquid)s with reactive groups.

Different synthetic strategies have been described for the

preparation of poly(ionic liquid)s. Comprehensive overviews were published recently [28–30]. The classical way of synthesis is the free radical polymerization of respective ionic liquids monomers. Among them acrylate, methacrylate, styrene and vinyl monomers are mentioned. The most prominent ones are monomers of the vinylimidazolium type which are easily available by quaternization of vinylimidazole with alkyl halides and subsequent anion exchange. Their polymerization directly leads to the formation of poly(ionic liquid)s.

In some examples step-grow polymerization was utilized in the course of which the ionic structures were formed during the polymerization.

Alternatively, poly(ionic liquid)s are also available by polymer analogous reactions. Here five different methods can be distinguished. (1) Ion exchange of halide anions of already existing ionic groups in the polymer [13,15,21,23,25,26,31–35]. This procedure was applied on poly(ionic liquid)s based on vinylimidazole [15,25] and vinylpyridine [26,36] with the aim to tailor material properties according to the demands. (2) Quaternization of functional groups covalently bond to the polymer backbone [24,36,37]. Examples for this are conversions of imidazole, pyridine, or tertiary amino groups with alkyl halides. This step is usually followed by an ion exchange reaction as mentioned before. (3) Introduction of a quaternizable functional group with subsequent quaternization

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[38,39]. (4) Introduction of a quaternizable functional group with simultaneous quaternization [34,35,40–44]. (5) Introduction of an already quaternized functional group.

In comparison to the polymerization of ionic liquid monomers, polymer analogous reactions are less commonly used. The reasons for this might be difficulties in achieving complete conversions and in removal of unreacted modifiers. Nevertheless, some advantages are apparent, which consist of the fact that structure and molar mass of the prepolymers are mostly easier to be tailored than that of poly(ionic liquid)s synthesized by polymerization [35]. Furthermore, polymer analogous reactions offer the possibility to synthesize reactive poly(ionic liquid)s, in which the number of reactive groups can easily be tailored by the degree of conversion. This idea has been taken up by us and is object of this study.

This article describes a new method to synthesize poly(ionic liquid)s by polymer analogous conversion of alternating maleic anhydride copolymers with 1-(3-aminopropyl)imidazole and subsequent quaternization of the imidazole moiety. Co-conversion of the polymer with aliphatic amines and the optional partial quaternization enables tailoring of properties in a wide range. Depending on the degree of conversion, this approach provides polymers with reactive groups (anhydride or imidazole) which can be used for post-cross-linking reactions or compatibilization of polymer blends and composites. As an example, a reactive mixture with bromobutyl rubber (BIIR) was prepared which showed distinct self-healing effects. According to the best of our knowledge, this is the first poly(ionic liquid) with succinic anhydride units in the main chain.

2. Experimental

2.1. Materials

1-(3-aminopropyl) imidazole (Aldrich, 98%), N,N-dimethylacetamide (Roth, $\geq 99\%$), 1-bromobutane (Aldrich, RegentPlus[®] 99%), 1-bromononane (Aldrich, 98%), hexylamine (Merck, for synthesis), diethyl ether (Merck, p. a.), n-hexane (Merck, p. a.), tetrahydrofuran (Acros Organics, p. a.) and dimethylsulfoxid-d6 (water < 0.02%) were used as received. The bromobutyl rubber (BIIR) is a commercial product of Lanxess with a bromine content of 1.13 wt% (0.80 mol% brominated isoprene units) determined by ¹H NMR.

2.2. Starting polymer 1

1: A 25% solution of poly(butadiene-*alt*-maleic anhydride) (Polysciences, Mn = 10,000–15,000 g/mol) in acetone, was precipitated in n-hexane. The precipitate was dried under reduced pressure for 10 h. ¹H NMR (DMSO-d6) δ_{H} ppm: 5.54 (2H, –CH=CH–), 3.09 (2H, –CH–CH–), 2.31 (4H, –CH₂–CH=CH–CH₂–), 1.89 (2H, –CH₂–).

2.3. Polymers of structure 2

The synthesis of polymers of common structure **2** by polymer analogous conversion of the anhydride groups with primary amines is demonstrated using **2b** as an example. In a 25 ml two-necked round flask equipped with a stir bar, an amount of 208.9 mg of polymer **1** (1.316 mmol anhydride groups) was dissolved in 10 ml of N,N-dimethylacetamide and heated under nitrogen up to 100 °C. Then, an amount of 82.4 mg (0.658 mmol) of 1-(3-aminopropyl)-imidazole and 66.6 mg (0.658 mmol) of hexylamine was added drop wise. After 24 h stirring, the reaction mixture was cooled down to room temperature and precipitated in diethyl ether. The precipitate was filtered off, washed several times

with n-hexane and tetrahydrofuran, and dried for several hours at 70 °C under reduced pressure. The obtained raw product was purified by dialysis in water (ZelluTrans/Roth dialysis membranes w 46 mm, ϕ 29.3 mm, MWCO 3500). **2a**: ¹H NMR (DMSO-d6) δ_{H} ppm: 5.29 (2H, –CH=CH–), 3.31 (2H, –NCH₂–), 2.99 (2H, –NCH₂–), 2.55 (2H, –CH–CH–), 2.50–1.80 (6H, –CH₂–CH=CH–CH₂–; –NCH₂–CH₂–), 1.51–1.10 (6H, –(CH₂)₃–), 0.85 (3H, –CH₃). **2b**: ¹H NMR (DMSO-d6) δ_{H} ppm: 7.64 (1H, Im-H2), 7.17 (1H, Im-H5), 6.90 (1H, Im-H4), 5.70–5.15 (4H, –CH=CH–), 3.92 (2H, –CH₂–Im), 3.32 (2H, –NCH₂–), 2.98 (2H, –NCH₂–), 2.55 (4H, –CH–CH–), 2.30 (8H, –CH₂–CH=CH–CH₂–), 1.90 (2H, –CH₂–), 1.41 (2H, –NCH₂–CH₂–), 1.30–1.05 (6H, –(CH₂)₃–), 0.83 (3H, –CH₃). **2c**: ¹H NMR (DMSO-d6) δ_{H} ppm: 7.65 (1H, Im-H2), 7.16 (1H, Im-H5), 6.90 (1H, Im-H4), 3.92 (2H, –CH₂–Im), 3.31 (2H, –NCH₂–), 2.54 (2H, –CH–CH–), 1.89 (2H, –CH₂–), 1.8–1.45 (4H, –CH₂–CH₂–).

2.4. Polymers of structure 3

The alkylation reaction was performed according to Pinaut et al. [15]. The synthesis is demonstrated using **3f** as an example. An amount of 518 mg of polymer **2c** (2 mmol imidazole groups) was dissolved in 15 ml N,N-dimethylacetamide and heated up to 100 °C. Then, an amount of 548.2 mg (4 mmol) of 1-bromobutane was added. After 24 h heating under nitrogen, the product was precipitated drop wise in diethyl ether. The precipitate was filtered off, washed with n-hexane and tetrahydrofuran, and then dried for several hours at 70 °C under reduced pressure. **3f**: ¹H NMR (DMSO-d6) δ_{H} ppm: 9.44 (1H, Im-H2), 7.87 (2H, Im-H4, Im-H5), 5.47 (2H, –CH=CH–) 4.21 (4H, –CH₂–Im, Im–CH₂–), 3.32 (2H, –NCH₂–), 2.65 (2H, –CH–CH–), 2.36 (2H, –CH₂–CH₂–Im), 2.04 (2H, Im–CH₂–CH₂–), 1.76 (4H, –CH₂–CH=CH–CH₂–), 1.26 (2H, –CH₂–CH₃), 0.89 (3H, –CH₃).

2.5. Instruments

DSC curves were recorded on a DSC Q1000 (TA Instruments). The samples were scanned (heating-cooling-heating) from –80 to +230 °C with a heating and cooling rate of 10 K/min.

¹H NMR (500.13 MHz) spectra were recorded on an Avance III 500 NMR spectrometer (Bruker). DMSO-d₆ ($\delta(^1\text{H}) = 2.50$ ppm, $\delta(^{13}\text{C}) = 39.6$ ppm) was used as solvent, lock, and internal standard.

Tensile tests were carried out on a Zwick 1456 tensile tester with a rate of elongation of 200 mm/min according to DIN EN ISO 527–2/S2/20.

Rheological measurements were carried out with a moving die rheometer (Scarabeus VIS-V50). For this 5 g of the premixed rubber samples were punched out with a volume cutter to get round test specimens for the measurements. The measurements were performed at 170 °C at a frequency of 1.67 Hz for 1 h.

2.6. Mixtures of polymers 2 and 3 with BIIR

BIIR (50 g) and polymers **2** or **3** (2.5 g) were premixed in an internal mixer (Thermo Haake Rheocord PolyLab 300p) for 10 min with a rotor speed of 60 rpm at 40 °C. Subsequently, the mixtures were pressed (Fontijne Holland Table Press TP 1000) with a force of 150 kN for 4 h at 140 °C. From the obtained sheets (2 mm), dumbbell test bars with the dimensions of 2 × 12.5 × 75 mm (DIN 53504-S2) or 1 × 6 × 35 mm (DIN 53504-S3) were punched out.

2.7. Self-healing tests

Immediately after cutting, the two parts of the test specimen were linked together under slight pressure. Then, the test specimen was allowed to heal for 16 h at 70 °C and then stored at room

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