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NEW METHOD FOR SYNTHESIS OF METHACRYLATE-TYPE POLYMERIZABLE IONIC LIQUIDS

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GRAPHICAL ABSTRACT



Abstract A new method for the synthesis of polymerizable ionic liquids bearing a methacrylate moiety was developed with the aim to avoid premature polymerization of synthesized compounds. Spacer length between the imidazolium cation and the polymerizable functional group varied from 2 to 10 carbon atoms. Different 1-(n-hydroxyalkyl)-3-methylimidazolium bromides and 1-[n-(methacryloyloxy)-alkyl]-3-methylimidazolium bromides were obtained with very good yields (more than 90%).

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications[®] for the following free supplemental resource: Full experimental and spectral details.]

Keywords Imidazolium salts; ionic liquids; methacrylate; polymerizable ionic liquids

INTRODUCTION

Ionic liquids (ILs) are a diverse group of salts that are liquid at ambient temperature. The formation of a stable crystal lattice is prevented by poorly coordinated ions. Cation is generally an organic structure with low symmetry, and the anion can be either organic or inorganic. ILs are the focus of intense research because of their extraordinary chemical and physical properties.^[1,2]

Recently, polymeric forms of ILs (PILs) have attracted attention. Typical characteristics of ILs combined with mechanical durability of polymers make PILs a key material for development of a wide range of emerging technologies, for

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example, electrochemical devices, such as batteries and fuel cells.^[3–4] Another major area of PIL research is the use of the material as gas absorber.^[6] The extraordinary solvation properties inherent to ILs make PILs attractive for the preparation of composite materials such as "bucky plastic"^[7] or PIL-cellulose composites.^[8,9]

PILs can be prepared either from polymerizable cations or anions.^[10] To date, research has been focused more on the introduction of polymerizable groups (acrylate, methacrylate, or vinyl) to the IL cation. Several papers have been published addressing electrical and mechanical properties of PILs and their potential applications. However, at the same time the synthesis of PIL monomers has received relatively little attention. The general approach for the preparation of acrylate- or methacrylate-containing PIL monomers is accomplished in a two-step synthesis. In the first step haloalcoholis treated with (meth) acryloyl chloride, resulting in formation of the corresponding ester. In the second step N-alkylimidazole is quaternized with ester from the previous step.^[11,12] A variety of anions can serve as the counteranion and are introduced by anion exchange.^[2]

Contrary to the conventional synthetic route, we decided to introduce the methacrylate function into the IL structure in the last step (Scheme 1). This helps to avoid the premature polymerization of synthesized PIL monomers, which is the main drawback of the published method.^[11,12] Previously the idea has been noted in the literature,^[13] but to the best of our knowledge it has not been studied further. With this work we aim to investigate its scope and limitations. Alkyl chain lengths between imidazolium cation and polymerizable moiety were also varied because it



Scheme 1. Synthesis of PIL monomers.

has been shown earlier that increasing the spacer length leads to greater electrical conductivity of the polymerized material.^[14] It is worthwhile to mention that intermediates of the synthesis, 1-(n-hydroxyalkyl)-3-methylimidazolium salts, have been applied in tribology^[15] and in organic synthesis because of their catalytic activity in a coupling reaction to obtain cyclic carbonates.^[16,17]

DISCUSSION

In the current study different PIL monomers containing methacrylate groups as polymerizable moieties were synthesized (3a-e). ω -Bromo alcohols with alkyl chain of different lengths (1a-d) were used for quaternization of N-methylimidazole. The obtained 1-(n-hydroxyalkyl)-3-methylimidazolium salts (2a-d) were acylated with methacryloyl chloride for introducing the polymerizable functional group. The polymerizable ionic liquid monomers (3a-e) were obtained with good yields. The structures of compounds 2a-d and 3a-e were confirmed by spectral techniques [Infrared (IR), ¹H and ¹³C NMR]. Compounds 2c, 2d, 3c, and 3d are new, and their molecular structures were additionally confirmed by high-resolution mass spectroscopy.

For synthesis of ω -bromo alcohols, a well-known method starting from corresponding α, ω -diols was used.^[18,19] The reaction resulted in a mixture from the desired product, unreacted diol, and corresponding dibromide. To separate the product, a liquid–liquid extraction method, innovative for the particular synthesis, was developed.

The following step, quaternization of N-methylimidazole, occurs smoothly at a reasonable temperature and results in different 1-(n-hydroxyalkyl)-3-methylimidazolium bromides (**2a–d**) with quantitative yields (Scheme 1, Table 1). The reaction can be carried out without any solvent, as the reagents are liquids and mutually miscible. The reaction time depends on the particular ω -bromo alcohol. The reactivity of alkyl halides in substitution reactions generally decreases with increasing alkyl chain length.^[2] In the case of 2-bromoethanol it is about 24 h but with other applied ω -bromo alcohols a reaction time up to 48 h is necessary to complete the reaction. The reaction can be accelerated with moderate heating but the temperature should not exceed 40–50 °C to avoid darkening the product, supposedly caused by chromophores formed in side reactions.^[20] The physical state of obtained 1-(n-hydroxyalkyl)-3-methylimidazolium bromides depends on the length of the alkyl chain (Table 1).

As the last step of the synthesis, the polymerizable moiety was introduced to the IL cation (Scheme 1, Table 2). 1-(n-Hydroxyalkyl)-3-methylimidazolium bromides obtained in the previous step were acylated with methacryloyl chloride. The

Compound	Yield (%)	Physical state
2a	99	Solid
2b	99	Viscous liquid
2c	89	Viscous liquid
2d	94	Solid

Table 1. Yields of 1-(n-hydroxyalkyl)-3-methylimidazolium bromides 2a-d

Yield (%)
95
97
93
92

 Table 2. Yields of 1-[n-(methacryloyloxy)-alkyl]-3-methylimidazolium

 bromides 3a-d

reactions were carried out at room temperature to avoid polymerization of the synthesized products. To force the reaction run completely, excess reagent was used. Washing with dichloromethane was effective for removing any residue of hydroxyl functionalized ionic liquid from the final product.

To conclude, a new method for synthesis of PIL monomerswith methacrylate as the polymerizable functional group was developed. Unlike conventional methods, the new method does not suffer from premature polymerization of the product—a drawback that would significantly limit its practical applications. As a result, different 1-[n-(methacryloyloxy)-alkyl]-3-methylimidazolium bromides were obtained with very good yields (more than 90%).

EXPERIMENTAL

Materials

N-methylimidazole (Aldrich), methacryloyl chloride (Fluka), 2,6-di-*tert*-butyl-4-methylphenol (BHT; Fluka), HBr (40% aqueous solution), and all solvents except acetonitrile (ACN) were used as received. ACN (Rathburn) was distilled over CaH₂. 2-Bromoethanol (Fluka) was distilled prior to use, collecting a fraction with boiling point 149–150 °C at atmospheric pressure.

Characterization

¹H and ¹³C NMR spectra were recorded at ambient temperature on a Bruker Avance II 200 spectrometer, using dimethylsulfoxide (d_6 -DMSO) or CDCl₃ as a solvent. The ¹H NMR spectra were measured at 200 MHz and the ¹³C NMR spectra were determined at 50 MHz. The chemical shifts were internally referenced by the residual solvent signals relative to tetramethylsilane. The IR spectra were obtained on a Perkin-Elmer Spectrum BXII FT-IR instrument. Gas chromatography-mass Spectrometry (GC-MS) was performed on Agilent Technologies 7890A GC System MSD 5975C (column HP-5 ms 30 m × 0.25 mm). The spectra of high-resolution mass spectrometry (HRMS) were measured on a Thermo Electron LTQ Orbitrap ESI spectrometer, and the sample was dissolved in ACN.

General Procedure for Synthesis of ω -Bromo Alcohols (1b–d^[18])

In a typical experiment α,ω -diol (0.33 mol) was mixed with 1.2 eq of concentrated HBr (40% aqueous solution) and toluene. The reaction mixture was refluxed

in Dean–Stark equipment until water separation was completed. While the reaction mixture cooled down to room temperature, two layers were formed. The layers were separated. Toluene was removed by evaporation and the product was separated from the evaporation residue using the following extraction: 100 mL of mixture of ethylene glycol and methanol (1:1) were added to the evaporation residue and extracted with 3×50 mL of hexane, which removed the dibromide side product. Methanol was removed by evaporation and 100 mL of toluene was added to ethylene glycol. Ethylene glycol was washed out with water, and a solution of ω -bromo alcohol in toluene was obtained. After drying the solution with MgSO₄ and removing toluene by evaporation, ω -bromo alcohol was obtained with the purity of more than 98% according to GC-MS. The yield varied between 40 and 60% depending on the starting material.

General Procedure for Synthesis of 1-(n-Hydroxyalkyl)-3methylimidazolium Bromides (2a-d^[21,22])

n-Bromoalcohol (0.1 mol) was dropwise added to 1 eq N-methylimidazole at room temperature under an inert atmosphere. The reaction mixture was stirred for 24–48 h. Depending on the alkyl chain length of n-bromoalcohol used, a white solid or colorless viscous liquid was formed with quantitative yield. The obtained product was vacuumed (<1 mm Hg) at room temperature for 12 h.

Compound 2a: 1-(2-Hydroxyethyl)-3-methylimidazolium bromide^[21]

¹H NMR (200 MHz, DMSO): δ 9.10 (s, 1H, -N-CH-N-), 7.74 (s, 1H, -N-CH=CH-N-), 7.70 (s, 1H, -N-CH=CH-N-), 5.52 (s, 1H, -OH), 4.23 (t, 2H, J = 5.2 Hz, -N-CH₂-), 3.87 (s, 3H, -N-CH₃), 3.72 (t, 2H, J = 5.2 Hz, -CH₂-OH). ¹³C NMR (50 MHz, DMSO): δ 137.21, 123.80, 123.11, 59.79, 52.08, 36.19. IR (cm⁻¹): 3239 (O-H), 3057 (C-H_{arom}-), 2928 (C-H), 2856 (C-H), 1571 (C=C), 1427 (C⁺ = N-), 1231 (C-N), 1168 (C-N), 1069 (C-O).

General Procedure for Synthesis of 1-[n-(Methacryloyloxy)-alkyl]-3methylimidazolium Bromide (3a–d^[23,24])

1-(n-Hydroxyalkyl)-3-methylimidazolium bromide (0.1 mol) was suspended in 150 mL of acetonitrile and 5 mg of BHT was added. The obtained suspension was stirred in an argon atmosphere and cooled on an ice bath to 0 °C. Methacryloyl chloride (2 eq) diluted with 20 mL of acetonitrile was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred 48 h in an argon atmosphere. Acetonitrile was removed by evaporation. After that the residue was extracted with 3×25 mL of diethyl ether to remove the unreacted methacryloyl chloride. After extraction, a new amount of BHT was added. The obtained viscous liquid was vacuumed (<1 mm Hg) 12 h on an ice bath. The product was obtained as yellowish oil with yield 93–97%.

Compound 3a: 1-[2-(Methacryloyloxy)-alkyl]-3-methylimidazolium bromide^[24]

¹H NMR (200 MHz, DMSO): δ 9.39 (s, 1H, -N-C*H*-N-), 7.89 (s, 1H, -N-C*H*=CH-N-), 7.81 (s, 1H, -N-CH=C*H*-N-), 6.06 (s, 1H, $CH_2 = C$ -), 5.73 (s, 1H, $CH_2 = C$ -), 4.60 (t, 2H, J = 5.4 Hz, -N-C H_2 -), 4.46 (t, 2H, J = 5.2 Hz, -C H_2 -O-), 3.91 (s, 3H, -N-C H_3), 1.86 (s, 3H, C $H_2 = C$ -C H_3). ¹³C NMR (50 MHz, DMSO) δ 166.53, 137.57, 135.70, 127.09, 124.12, 123.22, 63.18, 48.44, 36.38, 18.34. IR (cm⁻¹): 3024 (C-H_{arom}-), 2961 (C-H), 2949 (C-H), 1718 (C=O), 1635 (C=C H_2), 1575 (C=C), 1452 (C⁺ = N-), 1317, 1295 (C-O), 1161 (C-O, C-N overlapped) 945 (C=H₂).

SUPPORTING INFORMATION

Full experimental detail and ¹H and ¹³C NMR spectra can be found via the "Supplementary Content" section of this article's Web page.

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