



Synthesis, polymerization and conducting properties of an ionic liquid-type anionic monomer

Jonathan Juger, Franck Meyer, Frédéric Vidal*, Claude Chevrot, Dominique Teyssié

Laboratoire de Physicochimie des Polymères et des Interfaces, Université de Cergy-Pontoise, 5 mail Gay-Lussac, F-95031 Cergy-Pontoise Cedex, France

ARTICLE INFO

Article history:

Received 25 September 2008

Accepted 21 October 2008

Available online 25 October 2008

ABSTRACT

The synthesis of a new ionic liquid-type monomer has been performed by association of a methacrylate polymerizable group, a polar tri(ethylene oxide) (TEO) spacer, a trifluoromethane sulfonic (TFSI⁻) anion and a free imidazolium (EMIm⁺) cation. The ionic liquid monomer (ILM) has demonstrated a good thermal stability and a high ionic conductivity around $2.1 \times 10^{-3} \text{ S cm}^{-1}$ at 20 °C. The corresponding homopolymer has shown an ionic conductivity closely related to the monomer ($6.5 \times 10^{-4} \text{ S cm}^{-1}$ at 20 °C), which confirms the ILM as a valuable monomer for the formation of polymeric ionic liquid (PIL) materials.

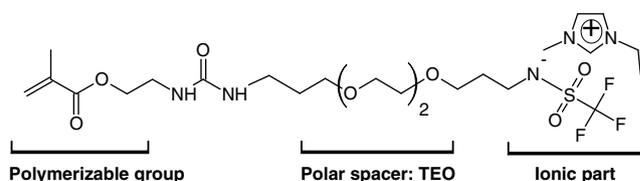
© 2008 Elsevier Ltd. All rights reserved.

During the last decade, the field of ionic liquids (ILs) has attracted much attention due to their beneficial properties and their low impact on environment. Many investigations have been dedicated to their use as new media for synthetic chemistry supported by their peculiar physical properties such as chemical stability, non-volatility and non-flammability.¹ Moreover, their intrinsic behaviour has also been highlighted in materials' sciences through structural modifications.²

The ionic liquids are also characterized by a high ionic conductivity, which has broadened their field of applications as electrolyte.³ Thus, their contribution is frequently encountered in the development of new functional materials, such as solar cells, lithium batteries, conductive polymer supercondensators and artificial muscles.⁴ The design of new advanced materials with high-ionic conductivity has been explored by the formation of monomers incorporating an ionic liquid part. The main feature of these compounds lies in the combination of different active functions, namely a polymerizable group, a polar poly(ethylene oxide) (PEO) spacer and a terminal ionic liquid moiety.⁵ As concern the IL segments, the elaboration of monomers containing imidazolium rings has attracted much attention since measurement of one of the highest ionic conductive values was observed with 1,3-ethylmethylimidazolium (EMIm⁺) ((bis) trifluoromethane) sulfonimide (TFSI⁻).^{3a-e} In general, the rational design of ionic liquid monomers (ILMs) based on imidazolium derivatives is studied according to two pathways: the imidazolium ring belongs to the matrix backbone and the anionic partner allows the ionic conductivity within the polymeric ionic liquid (PIL) materials.⁶ By reversing the roles, a second approach has consisted in the elaboration of polymeric compounds with a free non-symmetric imidazolium cation as mobile entity. This strategy was mainly developed by formation

of protic ILs,⁷ namely a proton transfer from the acid end chain group to the base.⁸ However, the conductivity of the resulting macromolecules remains at a low level, probably due to the presence of several hydrogen bond acceptor sites which decrease the cation movement by competitive interactions. Keen to explore a new conducting system based on the imidazolium cation mobility, we figure that the incorporation of ionic pairs without available proton (i.e., monoalkylated imidazolium cation) should enhance dramatically the conductivity. Thus, we investigated the design of the purpose-built monomer **1** which is, comprised three parts: a methacrylate end group, a tri(ethylene oxide) (TEO) spacer and a trifluoromethanesulfonimide anion with 1,3-ethylmethylimidazolium counterion (Scheme 1).

This structure was motivated by the role played by the three blocks, as reported by several authors.³ First, the double bond end chain should afford the synthesis of PIL materials by free radical polymerization. As concerns the polar TEO spacer, the segment length is directly involved in the ion motion, and should confer a good ionic conductivity to the resulting polymer. Some research works have demonstrated that polymeric materials exhibit a good ionic conductivity with pendant chains composed of three to eight ethylene oxide units.⁸ Finally, it was shown that a non-symmetric imidazolium cation should induce a high-ionic conductivity with respect to a mobile anion.³



Scheme 1. Structure of the ionic liquid ILM1.

* Corresponding author. Tel.: +33 1 34 25 70 52; fax: +33 1 34 25 70 70.
E-mail address: frederic.vidal@u-cergy.fr (F. Vidal).

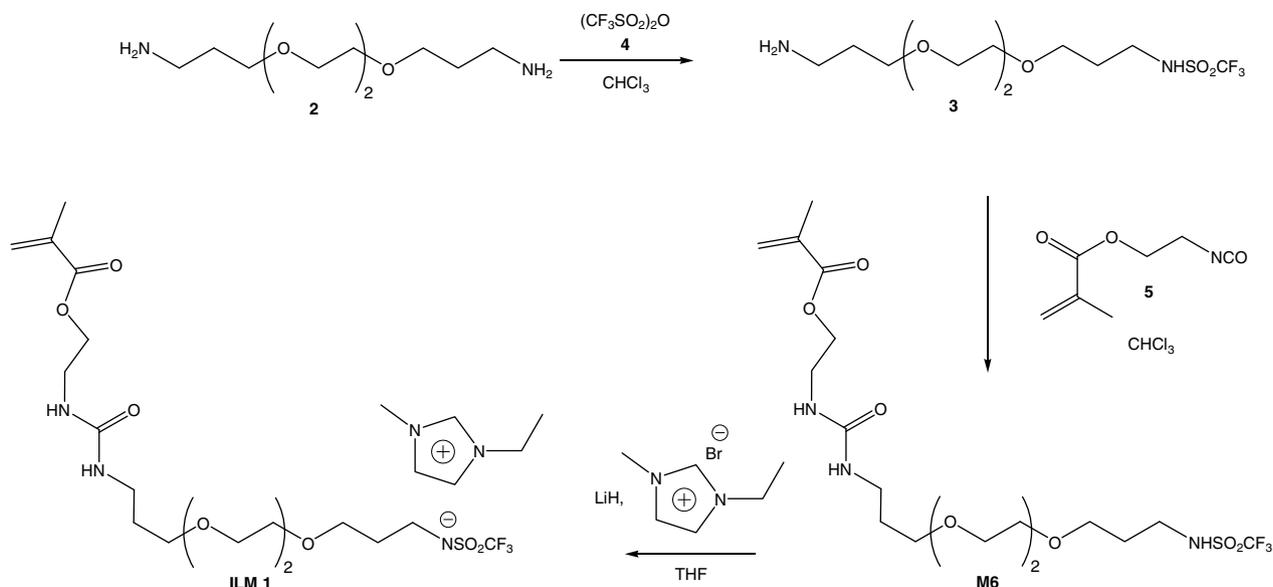


Figure 1. Synthesis of the ionic liquid ILM1.

The preparation of ionic liquid monomer **1** (ILM1) was performed according to a three-step synthesis, as illustrated in Figure 1. First, the amino derivative **3** was obtained by reaction of 4,7,10-trioxa-1,13-tridecanediamine **2** with trifluoromethanesulfonyl anhydride **4**.⁹ Thus, the mono substituted product **3** was quantitatively recovered in pure form, when 1 equiv of anhydride has reacted with 2.1 equiv of diamine **2** in chloroform. The NMR spectroscopic studies gave us more informations about this result and confirmed its high purity. The remarkable selectivity was attributed to intramolecular hydrogen bonds which may lock the second N terminal end of **3** and induce a cyclic conformation.

This hypothesis was supported by the ^{19}F NMR spectrum that shows two peaks at -78.0 and -79.0 ppm in a ratio 1:1.5, respectively (see Fig. 2). The same observation was done by analysis of the ^1H NMR data, in agreement with the presence of a mixture of two conformations. The CH_2N methylenes of starting diamine **2** have shifted from 2.75 ppm to 3.30 and 2.96 ppm in a ratio 2:8, which is respectively, consistent with an amount 1:1.5 of conformational isomers: the CH_2N methylenes of the isomer in excess remained equivalent at 2.96 ppm while a variation of chemical was observed with the second isomer, that is, 2 hydrogens at 2.96 ppm and 2 hydrogens at 3.30 ppm (see Fig. 3). Finally, a variation of chemical shift was also observed by ^{13}C NMR in the regions assigned to $\text{CH}_2\text{-CH}_2\text{N}$ (30.6 and 28.1 ppm) and CH_2N methylenes (42.2 and 38.9 ppm) (see Fig. 1. in Supplementary data); the $^1\text{H}\text{-}^{13}\text{C}$ heteronuclear NMR spectra has also revealed univocally the correlation between the peaks at 3.30 ppm and 42.2 ppm (see Figs. 1 and 2 in Supplementary data). However, further investigations are proceeding in our laboratory concerning the fully elucidation of this reaction.

Subsequently, the methacrylate group was appended to the fluorinated compound **3** by reaction of the free N-terminal end chain of **3** with the isocyanate **5**. The resulting difunctionalized amine monomer **6** (M6) was isolated in 79% yields by precipitation in ether; the protocol has required a catalytic amount of hydroquinone in order to prevent the polymerization process. Finally, the formation of the ionic pair was done by deprotonation of the trifluorosulfonimide group with lithium hydride in THF. Then, an excess of imidazolium bromide was added to the mixture allowing the $\text{Li}^+/\text{EMIm}^+$ cation exchange. After filtration of the residual salts, the evaporation of the solvent has provided the ILM1 in 90% yields.

The ^1H and ^{13}C NMR analysis have revealed an equimolar amount of both ionic entities ($\text{EMIm}^+ \text{-methacrylate TFSI}^-$), consistent with a total conversion into the ILM1. The ionic liquid profile of ILM1 was confirmed by a Newtonian fluid behaviour and a dynamic viscosity around 1 Pa s measured on a cone/plane geometry rheometer in the rotary mode. The coulometric Karl Fisher titration with iodide reactant has indicated an average water content of about 2%, which allowed a reliable ionic conductivity measurement (see the experimental conditions in Supplementary data).

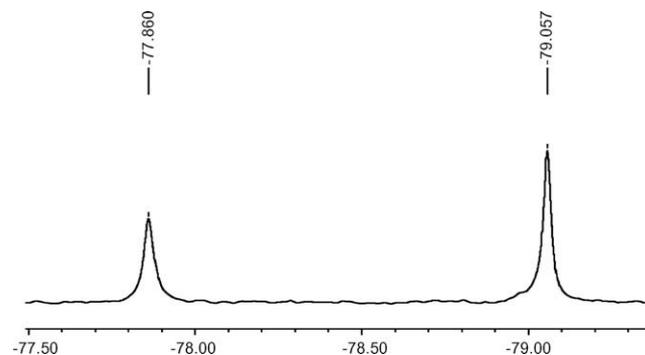


Figure 2. ^{19}F NMR of compound **3** showing two peaks at -78.0 and -79.0 ppm.

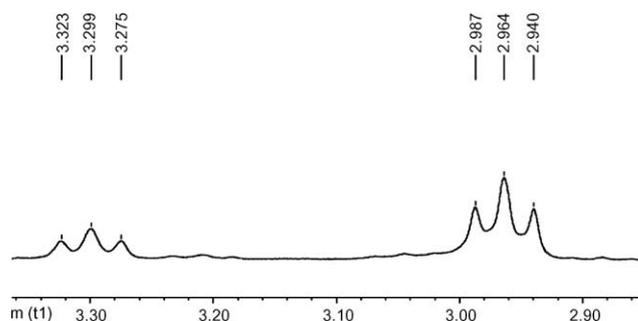


Figure 3. ^1H NMR corresponding to the CH_2N -terminal methylenes of the mono-substituted amine **3**.

Download English Version:

<https://daneshyari.com/en/article/5276291>

Download Persian Version:

<https://daneshyari.com/article/5276291>

[Daneshyari.com](https://daneshyari.com)