Macromolecules **2008**, *41*, 3389−3392

Polymerization of Ionic Liquid-Based Microemulsions: A Versatile Method for the Synthesis of Polymer Electrolytes

Shaomei Yu,[†] Feng Yan,*[,†,‡] Xingwang Zhang,[§] Jingbi You,[§] Peiyi Wu,[‡] Jianmei Lu,*[,†] Qingfeng Xu,[†] Xuewei Xia,[†] and Guilin Ma[†]

Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, P.R. China; Key Laboratory of Molecular Engineering of Polymers, Fudan University, P.R. China; and Key Lab of Semiconductor Materials Science, Institute of Semiconductors, CAS, Beijing, 100083, P.R. China

Received February 19, 2008
Revised Manuscript Received April 3, 2008

Ionic liquids (ILs) are attracting significant attention in many fields of chemistry and industry because of their unique physicochemical properties, such as negligible vapor pressure, low volatility, high thermal stability, and ionic conductivity.[1,2] Among these properties, excellent ionic conductivity up to their decomposition temperature enables ILs to play an important role in polymer electrolytes. In principle, there are mainly two methods to prepare IL-based polymer electrolytes: one is doping of polymers with a selected IL, and another approach is via in situ polymerization of vinyl monomers in an IL solvent.[3] In both cases, however, the successful preparation of IL-based polymer electrolytes is critically dependent on the compatibility between the IL and polymeric matrix. For example, Snedden et al. have investigated the solubility of a range of polymers in the selected ILs for the design of IL/polymer composites.[3d] However, phase separation was observed in several IL−polymer solutions. In a recent study, Watanabe et al. reported the preparation of ion gels by in situ radical polymerization of vinyl monomers in an IL, 1-ethyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (EMITFSI).[3e] Although the chosen vinyl monomers such as styrene, acrylonitrile, and acrylamide are compatible with EMITFSI, phase separation occurred as well due to the incompatibility between the resulting vinyl polymers and EMITFSI solvent. Since the factors responsible for the polymer solubility in an IL are complex, it is still difficult to predict the compatibility of an IL with the polymers. As an alternative approach to prepare ionic conductive polymer electrolytes, polymerization of the IL-based micromeulsions, therefore, is investigated in this work.

Microemulsions are thermodynamically stable dispersions containing two immiscible liquids stabilized by surfactants at the liquid−liquid interface. Compared with "classic" water-in-oil microemulsions, IL-in-oil microemulsions, in which an IL dispersed in an oil-continuous phase by suitable surfactants, are of great interest due to the unique features of both IL and microemulsion system.[4–9] Microemulsions composed of a room temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF_4]), cyclohexane, and a surfactant, Triton X-100, have been recently studied by Han[8] and Eastoe.[4] Small-angle neutron scattering data clearly demonstrated the formation of IL nanodroplets dispersed in cyclohexane.[4] More recently, microemulsions composed of an IL dispersed in a variety of organic oils, such as toluene,[9a,b] xylene,[9c] and benzene,[9d] have been investigated by several groups. These microemulsions behaviors are consistent with water-in-oil microemulsions and provide nanosized IL domains as reaction or extraction media which should avoid contacting with water. However, potential uses of these IL-based microemulsions have not been intensively studied so far.

Here, we report the preparation and polymerization of microemulsions that contain IL polar cores dispersed in a polymerizable oil. We expect that the IL nanostructures formed in these microemulsions could be preserved in the resultant polymeric matrix through the polymerization of an oil-continuous phase. To the best of our knowledge, this is the first report of polymerization of microemulsions with an IL as the polar core. We expect that the resulting IL/polymer composites should have potential as polymer electrolytes.

As the first demonstration of this approach, styrene and [Bmim][BF_4] (Scheme 1) were chosen as the polymerizable oil and model IL, respectively, because [Bmim][BF_4] and polystyrene are incompatible with each other. A polymerizable surfactant, 1-(2-methyl acryloyloxyundecyl)-3-methylimidazolium bromide (MAUM-Br) (Scheme 1), was synthesized and used to stabilize the [Bmim][BF_4]/styrene microemulsions.

MAUM-Br was synthesized as described in the Supporting Information. [Bmim][BF_4] was freshly synthesized and further dehydrated as documented in the literature.[10] For phase behavior studies, the single-phase microemulsion domains were determined visually on the basis of transparency and absence of phase separation. A phase diagram of the pseudoternary [Bmim][BF_4]/styrene/MAUM-Br system at 28 and 60 °C is illustrated in Figure 1. Samples within the one-phase microemulsion region were transparent and stable. It is interesting to note that the area of the single-phase microemulsion region at 60 °C is smaller than that at 28 °C, indicating that the amount of solubilized [Bmim][BF_4]/styrene/MAUM-Br decreased when the temperature was increased to 60 °C. On the contrary, the amount of solubilized styrene increased remarkably with temperature increasing in the "classic" styrene−water microemulsion systems.[11] The factors that govern this lower critical solution temperature (LCST) phase behavior in these IL-based microemulsions are not yet clearly understood. Our understanding is that it might be caused by the interactions (such as hydrogen bonding or van der Waals interaction) between the styrene and the π-system of IL cations (imidazolium rings), as also observed inthe1-alkyl-3-methylimidazoliumbis{(trifluoromethyl)sulfonyl}-amide ([$C_n$mim][NTf_2])/trichloromethane[12a] and [$C_n$mim][NTf_2]/poly(benzyl methacrylate) systems.[12b] However, this phase behavior might as well be simply due to the lower solubility of monomers in the [Bmim][BF_4] at higher temperature.

A microemulsion consisting of [Bmim][BF_4] (30 wt %), styrene (47 wt %), and MAUM-Br (23 wt %) was initiated with 2,2-azobis(isobutyronitrile) (AIBN) at 60 °C. Divinylbenzene was added as a cross-linker (2−4 wt %) based on the weight of styrene and surfactant MAUM-Br to the formulation. No apparent visible phase separation could be observed during and after the polymerization process. Figure 2 shows a photograph of the resulting [Bmim][BF_4]/polystyrene membrane. The free-

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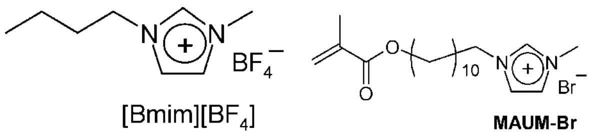
* Corresponding authors. E-mail: fyan@suda.edu.cn or lujm@suda.edu.cn.
[†] Suzhou University.
[‡] Fudan University.
[§] Institute of Semiconductors, CAS.

10.1021/ma8003696 CCC: $40.75

Scheme 1. Molecular Structures of Ionic Liquid, [Bmim][BF$_4$], and Surfactant, MAUM-Br, Investigated in This Work



standing membrane with the thickness of 80 μm is transparent and flexible.

The microstructures of the resultant [Bmim][BF$_4$]/polystyrene composite membranes were characterized by phase-lag atomic force microscopy (AFM) images on a NT-MDT Solver P47 AFM in semicontact mode. The oscillation frequency was set to ~255 kHz with a Si cantilever which had a spring constant of about 11.5 N/m. Changes in the phase lag reflect changes in the mechanical properties of the sample surface such as composition, hardness, friction, and viscoelasticity. Parts A and B of Figure 3 show the AFM phase images of the fracture cross section of the [Bmim][BF$_4$]/polystyrene composites containing 5 and 30 wt % of [Bmim][BF$_4$], respectively. In both two images, the brighter regions correspond to hard polymer domains, while the dark regions correspond to the soft IL domains. Minimal correlation of AFM height images (Figure 3A1,B1) indicates that phase-lag images (Figure 3A,B) are unlikely to be an artifact of surface roughness.

In Figure 3A, one can observe that [Bmim][BF$_4$] droplets with the diameter of ~20 nm (dark areas) are dispersed in a "continuous" polymeric matrix (bright areas). Since polymerizable surfactants have been demonstrated to be the most effective method to preserve the nanostructures of parent microemulsions during polymerization,[13] this result may indicate that the expected surfactant stabilized IL-in-oil nanostructures in microemulsion are preserved on fixation during the polymerization process, without macroscopic phase separation. In the case of a membrane containing 30 wt % of [Bmim][BF$_4$], 15–25 nm size domains with long and winding channels of the IL and polymer bicontinuous networks can be obtained (Figure 3B). It is noteworthy that at the bottom of some IL domains one can observe smaller inner openings with the diameter of ~10 nm (inset of Figure 3B). These pores might be derived from the interconnected IL-filled domains or channels. The formation of IL-based nanostructures preserved in the resulting polymers can explain why the obtained [Bmim][BF$_4$]/polystyrene membranes are transparent even though they are incompatible with each other.

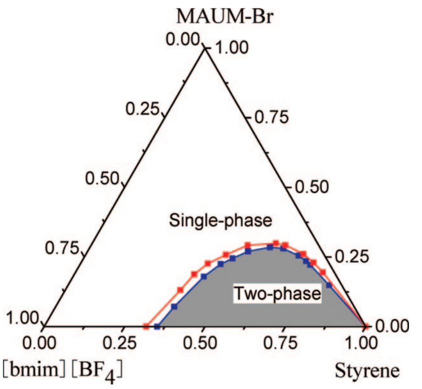


Figure 1. Partial phase diagrams (weight fraction) of MAUM-Br/[Bmim][BF$_4$]/styrene systems at 28 °C (blue line) and 60 °C (red line). The single-phase microemulsion domains were determined visually on the basis of transparency and absence of phase separation (in PTFE-lined, screw-capped culture tubes). The partial phase diagrams at 60 °C were determined by titration with styrene containing a few parts per million of 1,4-dihydroxybenzene in order to inhibit thermal polymerization.

Figure 2. Photograph of [Bmim][BF$_4$]/polystyrene membrane produced from microemulsion polymerization of [Bmim][BF$_4$]/styrene/MAUM-Br (0.30/0.47/0.23), initiated by AIBN at 60 °C.

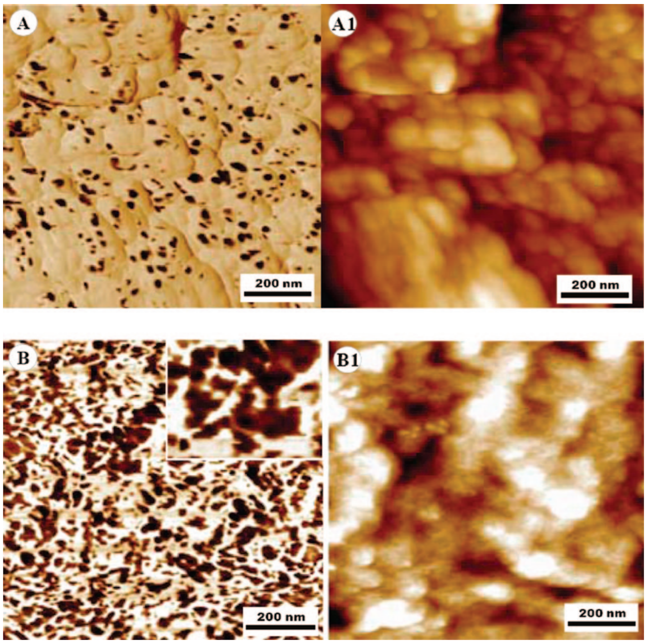


Figure 3. AFM phase (A and B) and height (A1 and B1) images of the fracture cross section of the [Bmim][BF$_4$]/polystyrene membrane containing (A and A1) 5 wt % and (B and B1) 30 wt % of [Bmim][BF$_4$], respectively. For (A) and (B), brighter regions correspond to hard polymer domains. Dark regions correspond to soft ionic liquid domains. Each image frame is 1 μm × 1 μm.

The electrical conductivity of the [Bmim][BF$_4$]/polystyrene membranes was measured with an alternating current impedance spectroscopy at ambient temperature. For a membrane containing 5 wt % of [Bmim][BF$_4$], the conductivity is about 5.5×10^{-6} S/cm in dry air. Under the same experimental conditions, for comparison, [Bmim][BF$_4$] alone has a conductivity of 3.9×10^{-3} S/cm, which is similar to the value (3.5×10^{-3} S/cm) reported by Hanabusa et al.[14] In addition, a copolymer membrane of styrene/MAUM-Br (2:1 by weight) shows a conductivity of 1.28×10^{-8} S/cm. Thus, it is believed that [Bmim][BF$_4$] is the only active group that promotes ionic conduction through the polymeric membrane. The conductivity of the [Bmim][BF$_4$]/polystyrene membranes increases with an increase in weight fraction of ILs (Figure 4A). In the presence of 30 wt % of

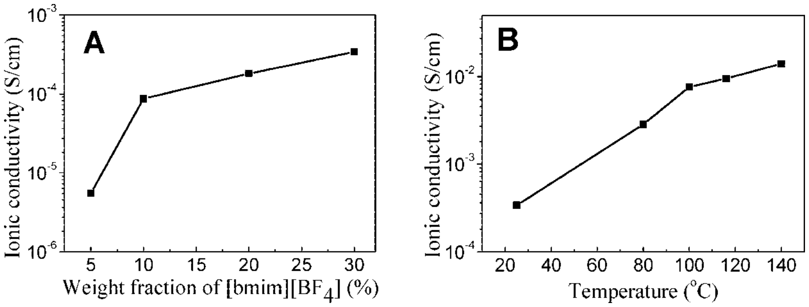


Figure 4. Ionic conductivity as a function of (A) the weight fraction of [Bmim][BF$_4$] at 28 °C and (B) temperature for the polymer membrane which containing 30 wt % of [Bmim][BF$_4$].

[Bmim][BF$_4$], the conductivity of the membrane reaches to 3.4 × 10^{-4} S/cm at room temperature. We believe that this relatively higher ionic conductivity is mainly due to the interconnected IL nanochannels formed in the [Bmim][BF$_4$]/polystyrene membrane.

The conductivity of the resulting composite membranes also increases with temperature increasing. Figure 4B shows the temperature dependence of the ionic conductivity of a polystyrene membrane containing 30 wt % of [Bmim][BF$_4$]. At 120 °C, the membrane shows the conductivity of 9.5 × 10^{-3} S/cm, and the value is increased to 1.4 × 10^{-2} S/cm at 140 °C. The conductivity of this membrane is comparable to most reported IL-based polymer electrolytes at the same temperature region.[15] Therefore, the resulting [Bmim][BF$_4$]/polystyrene composites prepared in this way may have potentials to be used as an ionic conductor at temperatures above 100 °C.

To demonstrate the effectiveness of this method, we chose methyl methacrylate, vinyl acetate, and *N*,*N*-dimethylacrylamide instead of styrene as a polymerizable oil to prepare the microemulsions containing IL polar cores. Phase diagrams show that all of these [Bmim][BF$_4$]/vinyl monomer systems can form transparent and stable microemulsions when MAUM-Br was used as surfactants (see Supporting Information). An LCST phase behavior was as well observed in [Bmim][BF$_4$]/methyl methacrylate and [Bmim][BF$_4$]/*N*,*N*-dimethylacrylamide microemulsion systems. This result further supports the solubilization behavior observed in [Bmim][BF$_4$]/styrene microemulsions. Polymerization of these IL-based microemulsions yielded transparent polymer membranes with high conductivity as well as a rubbery property, even though all of these resulting vinyl polymers are incompatible with [Bmim][BF$_4$] cores. In addition, the mechanical strength of resultant polymer electrolytes can be easily tuned by varying of monomer(s) and the amount of cross-linker added.

In conclusion, we present here the first example of polymerization of microemulsions comprising surfactant-stabilized IL nanodomains. Polymerization of these IL-based microemulsions yielded free-standing, flexible, and transparent polymer electrolytes even though the resulting vinyl polymers are incompatible with IL cores. The obtained IL/polymer composites show high conductivity at both room temperature and elevated temperature. This facile yet and effective method provides a versatile platform for the preparation of semisolid polymer electrolytes containing ILs. Although we only demonstrated this method with vinyl monomers of styrene, methyl methacrylate, vinyl acetate, and *N*,*N*-dimethylacrylamide and only one surfactant as examples, we believe that this method should be extendable to other liquid monomers with similar polarity and ionic liquids with desirable properties. The elucidation of interaction between the polymeric matrix and ionic liquids need to be further explored in future work.

Acknowledgment. This work was supported by Natural Science Foundation of China (No. 20774063, 20571054), the Program for New Century Excellent Talents in University (Grant NCET-07-0593), and Fok Ying Tung Education Foundation (No. 114022).

Supporting Information Available: Experimental details of syntheses, characterization of surfactants, and conductivity measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA8003696