Characterizations of nano-structures of Polyurea synthesized in Soft Ionic Liquids

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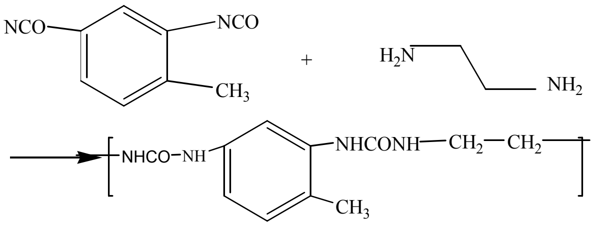
1. Introduction

Room temperature ionic liquids (ILs) are molten organic salts with melting temperature normally below 100°C. This class of soft materials exhibits very complicated molecular interactions such as ionic interactions, hydrogen bonding, - interactions, and amphiphilic polarization, rendering various molecular structures from merely local orderness up to macroscopic thermotropic or lyotropic liquid crystalline phases.[1-3]

Recent reports on nano-size morphological features such as flower-like or shuttle-like crystals or interconnected nano-porous structures of inorganic compounds synthesized in ILs, including ZnO, TiO_2, and silica, have received increasing attentions. Nevertheless, the origin of the molecular interactions mediated by the ILs during the synthetic reactions is still unknown.[4-6] Some explanations based on hydrogen-bonding/ - ring stacking were given to interpret the observed porous structures for a length scale below 3nm. On the organic counterpart, we first report exotic nano-porous structures sizing 50~300nm in polyurea synthesized by interfacial polymerization between n-hexane (with 2,4-toluene diisocyanate, TDI) and a series of 1-alkyl-3-methylimidazolium tetrafluoroborates and 1-alkyl-3-methylimidazolium hexafluorophosphates (with ethylene diamine or 1,4 diaminobutane). These nanostructures were observed under scanning electron microscopy (SEM). Small angle x-ray scattering (SAXS) and wide angle x-ray scattering (WAXS) were used for characterizing the polyurea synthesized under ILs. Clear distinction in the WAXS patterns of the polyurea synthesized between hexane/water interface and hexane/IL interface was observed. The crystallinity of polyurea seems suppressed with the presence of ILs.

2. Material Preparation

Polyurea was synthesized by using 2,4-toluene diisocyanate (TDI) and ethylene diamine (EDA) or 1,4-diaminobutane (BDA), with n-hexane acting as the upper organic phase with TDI dissolved in it. A series of pure ILs were used as the lower organic phase with diamine in it. A typical reaction between TDI and EDA can be simply expressed as follow:



For the comparison purpose, polyurea was also synthesized at the regular hexane/water interface. Most common ionic liquids are insoluble in n-hexane. Therefore, two series of ILs, 1-alkyl-3-methylimidazolium tetrafluoroborates, ($[C_n\text{mim}][BF_4]$, n=2,4,6,8) and 1-alkyl-3-methylimidazolium hexafluorophosphates, ($[C_n\text{mim}][PF_6]$, n=4,6) were studied by dissolving EDA in the pure IL to form the lower organic phase.

In a typical experiment, the two solutions were mixed together in a 50ml beaker at room temperature. The reaction occurred immediately and formed a white film at the interfacial layer. After 1 hour, the white polymer film was was collected in a Buchner funnel, washed repeatedly with 1:1 ethanol/water volumetric mixture and dried under vacuum for 24 hours at 50°C.

3. Characterization Results and Discussion

Fourier Transform Infrared (FTIR) spectra of the synthesized polymers were recorded by Perkin Elmer SpectrumOne® FTIR spectrometer. Leo 1530VP Scanning Electron Microscopy (SEM) was employed to examine the surface morphology and microstructure of the polyurea. Small and Wide angle X-ray Scattering (S-WAXS) was performed in Beamline 27C in Brookhaven National Laboratory.

The FTIR analysis implied the success of the interfacial polymerization of polyurea at the hexane-ionic liquid interface by exhibiting main –NH- peaks at 3280~3300 cm^{-1} and the carbonyl bonding peak at ~1600cm^{-1}, indicating the existence of strong linkages of –CO-NH- in the samples, which denotes the polyurea structure. (See Figure 1) No significant difference was found for the composition of polyurea due to the addition of ionic liquids.

These polymeric materials exhibit volcano-like, coral-like, sphere (~100nm), or polymer fibrils of sizes around 50 nm forming porous structures with pore size ranging from 50~ 300 nm (See Figure 2)- depending on the ionic liquids and diamines. The polyurea synthesized from EDA in short carbon-chain ionic liquids exhibit either porous (C_n=2) or nanofibric (C_n=4) structure with sizes as small as 50~100nm. When the carbon number on alkyl chain of ILs increases to 8, alveolate structure with pore size from 200~500nm was revealed. A network structure with open pores of 100~200 nm and volcano-like structure with the domain diameter of 50~100 nm was observed at the surface of polyureas synthesized in $[\text{bmim}][PF_6]$ and $[\text{hmim}][PF_6]$, respectively. Polyureas prepared from BDA in $[C_n\text{mim}]$[BF4] ILs display consistent alveolate nanostructures sizing about 100~200nm, regardless of the different alkyl chain length in cation part.

Results from small angle x-ray scattering (SAXS, synchrotron source, Brookhaven Laboratories) depict characteristic lengths around 22 nm, (Figure 3) which may reflect the crystalline lamellar layers or may come from the existence of polyurea nanostructures. Figure 4 has compared the WAXS data of regular polyurea and the one synthesized in ionic liquid. It is found that the multi-peak pattern exhibited by regular polyurea was suppressed in the IL-prepared polyurea except the two peaks indicating characteristic distance of 4.35• and 3.5•, which represent π–π stacking planes and intermolecular N…H hydrogen bonding, respectively.

The physical origin of the morphological features of polyurea could come from molecular interactions, particularly, hydrogen bonding, π–π interactions, and molecular orientations due to ionic interactions and polarity that may extend to a quasi long range. These speculations are yet verified and the relative importance of the above interactions is still not known. More information in the structures and chemicophysical properties of ILs must be acquired before the scenario can be addressed.

4. Summary

Polyurea with exotic nanostructures were synthesized by interfacial polymerization at the interfaces between n-hexane and a series of 1-alkyl-3-imidazolium based ILs. The FTIR results revealed no significant change in chemical composition for the polyurea synthesized with ionic liquids compared to the polyurea synthesized with water.

Distinct nanostructures with size varied from 50~300nm were observed by SEM on the surface of polyurea synthesized with ILs. WAXS patterns revealed the intermolecular π–π stacking distance of 4.35Å and intermolecular N…H hydrogen bonding of 3.5 Å. Factors affecting the morphology may include the local molecular structure and ordering of ionic liquids, alkyl chain length of ionic liquids, cations of ILs and the reactivity of the reagents. Further study on the mechanism of the nanostructure formation of polyurea synthesized with ILs is still in progress.

References

1. Robin D. Rogers, Kenneth R. Seddon, *Ionic Liquids: Industrial Applications to Green Chemistry*, ACS Symposium Series 818, **2002**.

2. C.M. Gordon, J.D.Holbrey, A.R. Kennedy and K.R. Seddon, *Journal of Materials Chemistry*, **1998**, 8, 2627-2636.

3. J.D. Holbrey and K.R. Seddon, J. Chem. Soc., *Dalton Trans.*, 2133-2139, 1999.

4. Y.Zhou, J.H. Schattka and M. Antonietti, *Nanoletters*, 4(3), 477-481, 2004.

5. M. Antonietti, D. Kuang, B. Smarsly, Y. Zhou, *Angewandte Chemie,* International Edition 43(38), 4988-4992, 2004.

6. J. Cao, J.Wang, B.Fang, X.Chang, M. Zheng, H.Wang, *Chemistry Letters,* 33(10), 1332-1333, 2004.

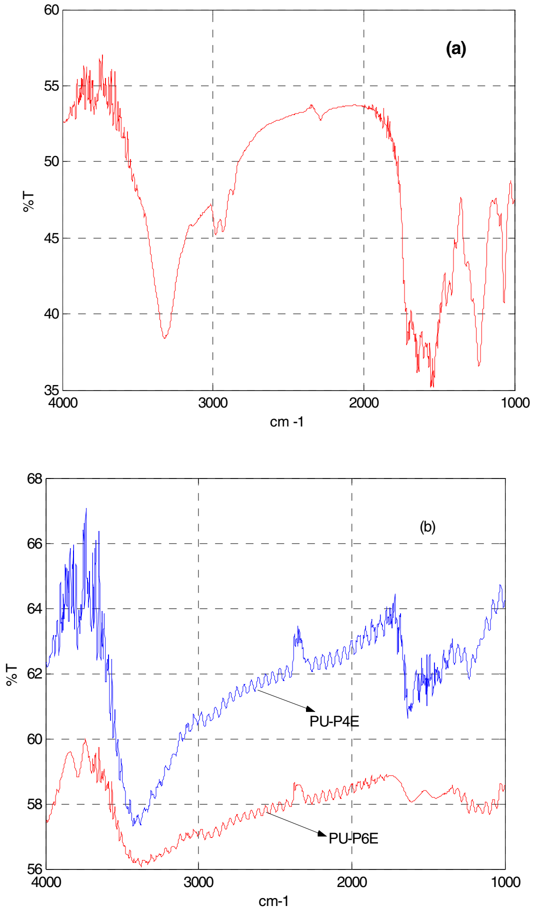


Figure 1 FTIR spectra of typical polyurea samples synthesized via interfacial polymerization in (a) hexane-water; (b) hexane-ILs interfaces.

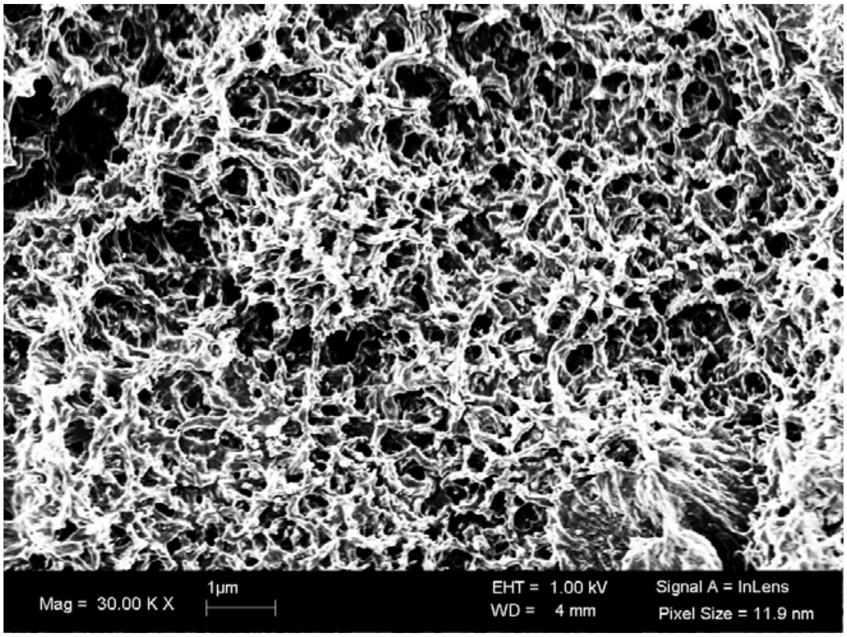


Figure 2 SEM pictures of polyurea nanoporous structure by IP in ILs.

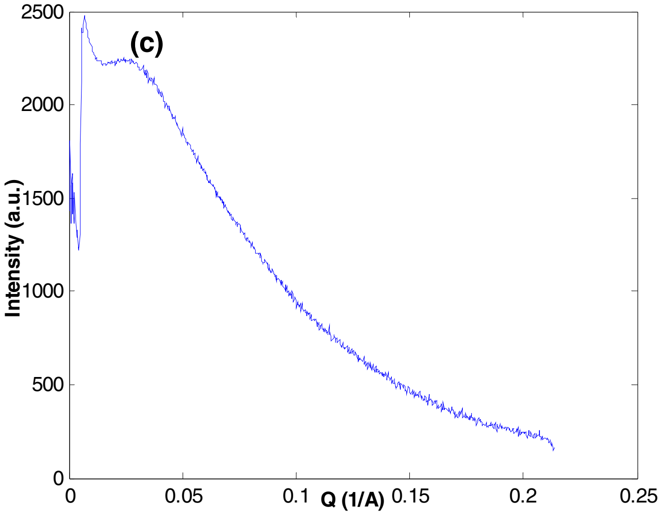


Figure 3 SAXS pattern of polyurea prepared by IP in ILs: Peak at 0.028•$^{-1}$ indicative of a characteristic length of 22nm.

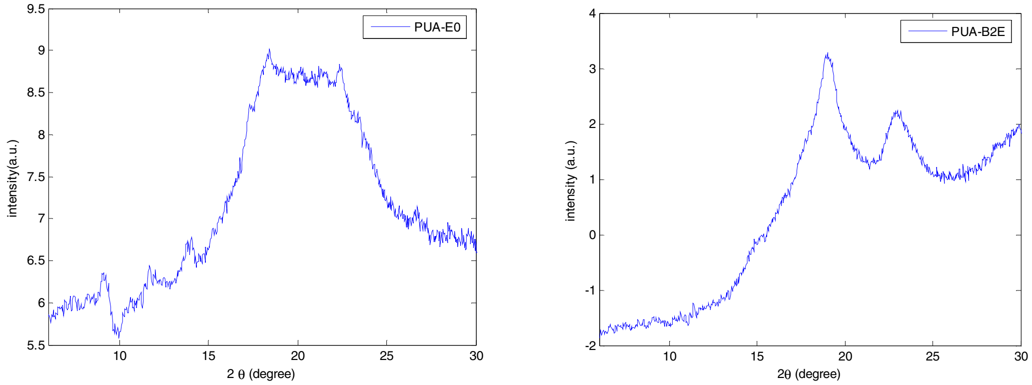


Figure 4 WAXS patterns of polyurea synthesized by regular IP (left) and IP in ionic liquids. (right)