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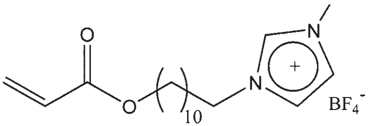
Porous Materials

Solvent-Reversible Poration in Ionic Liquid Copolymers**

Feng Yan and John Texter*

Herein we present a synthetic strategy for obtaining reversible solvent-induced porous polymers. The approach is based on the polymerization of microemulsions using a surfactant based on a polymerizable ionic liquid (IL). An IL comprising a polar imidazolium group and a hydrophobic tail was chosen as the surfactant. The resulting copolymer structure can be tuned between a hydrogel and a porous structure by changing the anions in the IL moiety of the copolymer. This concept combines the advantages of both the polymerization of microemulsions and the properties of methylimidazolium-based ILs. The production of porous polymer membranes by inversion of the nonsolvent phase (for example, of poly(methyl methacrylate) (PMMA)) has been very thoroughly reported.[1]

The polymerizable surfactant IL 1-(2-acryloyloxyundecyl)-3-methylimidazolium tetrafluoroborate (IL-BF_4, m.p. 31.8 °C; Scheme 1) was synthesized as described in the Supporting Information.



Scheme 1. Structure of the ionic liquid surfactant IL-BF_4.

The IL-BF_4/H_2O/1-propanol/methyl methacrylate (MMA) system forms transparent and stable microemulsions at room temperature, with 1-propanol acting as a cosurfactant. A phase diagram of the pseudoternary IL-BF_4/aqueous 1-propanol/MMA system at 24 °C is illustrated in the Supporting Information. A microemulsion consisting of IL-BF_4 (15 wt %), MMA (15 wt %), 1-propanol (35 wt %), and H_2O (35 wt %) was initiated with 2,2-azobisisobutyronitrile (AIBN) at 60 °C. Ethylene glycol dimethacrylate (EGDMA) was added as a cross-linker (1–10 wt % based on the weight of MMA and surfactant IL) to the formulation. All the transparent microemulsions were transformed into transparent or semitransparent copolymer gels (depending on the cross-linker content) after thermally initiated polymerization. Gravimetric analysis of the 2 % and 10 % EGDMA cross-linked samples indicated that essentially complete conversion was obtained (see the Supporting Information). Thermal decomposition (TGA) data (see the Supporting Information) indicate an elevated narrow decomposition regime centered around 380 °C, about 100 °C higher than that of PMMA. The absence of significant decomposition at lower temperature suggests an essentially random copolymer in the present case.

Figure 1 A shows a transparent copolymer gel, polymerized with 2 % EGDMA in an NMR tube. Such a transparent gel rod becomes opaque after being immersed in a 0.1 M solution of KPF_6 (Figure 1 B). This opaque material can be converted into a semitransparent polymer gel by immersion in a 1:4 (v/v) mixture of water and dimethylsulfoxide (aqueous DMSO; Figure 1 C). Such a recovered semitransparent gel rod can be converted back to an opaque rod by simply immersing it in water (Figure 1 D).

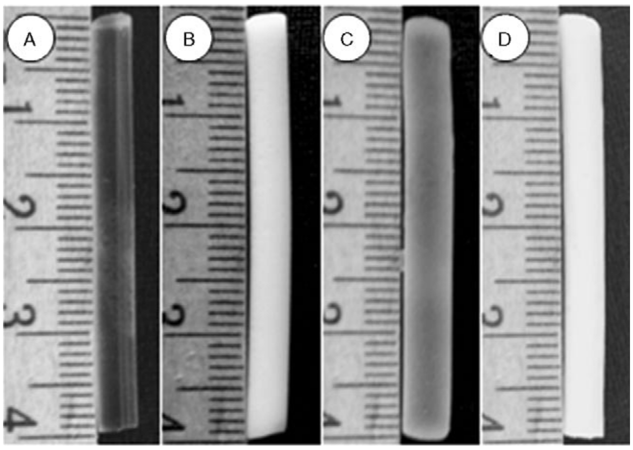


Figure 1. Photographs of polymer rods: A) after polymerization of the microemulsion (IL-BF_4, MMA, 1-propanol, H_2O at 15:15:35:35 weight ratio plus EGDMA at 2 wt% with respect to the other components); B) gel in (A) treated with aqueous 0.1 M KPF_6; C) gel in (B) treated with water/DMSO solution (1:4 v/v); D) recovered polymer gel in (C) treated with water.

Figure 2 A shows the scanning electron microscopy (SEM) images of these polymer rods. The original transparent polymer gel shows some isolated pores with a pore diameter of about 3 μm on the fractured surface (Figure 2 A). These pores may be formed during the polymerization as a consequence of an earlier onset of phase separation, but most likely form by solvent evaporation under the vacuum used during the SEM examination. However, as shown in

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[*] Dr. F. Yan, Prof. Dr. J. Texter
School of Engineering Technology
Eastern Michigan University
Ypsilanti, MI, 48197 (USA)
Fax: (+1) 734-483-0085
E-mail: jtexter@emich.edu

Dr. F. Yan
Key Laboratory of Organic Synthesis of Jiangsu Province
School of Chemistry and Chemical Engineering
Suzhou University, Suzhou 215123 (P.R. China)

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

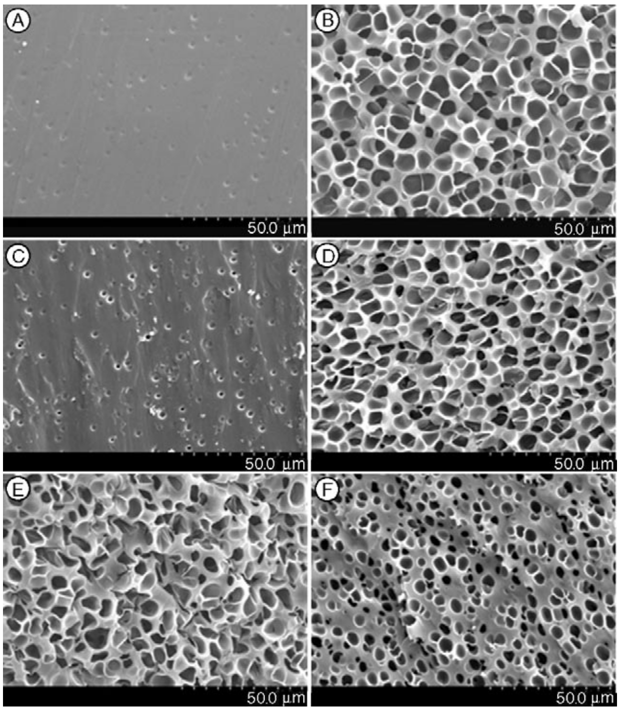

Figure 2. SEM images of polymers: A) after polymerization of the microemulsion (IL-BF$_4$, MMA, 1-propanol, H$_2$O at 15:15:35:35 weight ratio plus EGDMA at 2 wt% with respect to other components); B) gel in (A) treated with aqueous 0.1 M KPF$_6$; C) gel in (B) treated with aqueous DMSO; D) gel in (C) treated with water; E) after three cyclic treatments of aqueous DMSO/water; F) after seven cyclic treatments of aqueous DMSO/water.

Figure 2B, close-packed pores (both closed- and open-cell pores) with diameters of 3–8 µm are observed in the opaque gel shown in Figure 1B. The formation of these pores is due to the shrinkage of the copolymer at the interfaces between the aqueous and copolymer domains. Prior to the polymerization, the molecules of the polymerizable surfactant IL-BF$_4$ are situated along these interfaces between the aqueous and liquid MMA nanodomains, with the hydrophilic imidazolium portions protruding into the aqueous domains or channels. Solvent exchange between the aqueous 1-propanol solution contained in the polymer gel and the KPF$_6$ solution facilitates the anion exchange from BF$_4^-$ to PF$_6^-$ in the IL moiety. It is well-known that methylimidazolium-based ionic liquids containing PF$_6^-$ ions are hydrophobic and immiscible with water.[2] Therefore, the anion exchange from BF$_4^-$ to PF$_6^-$ changes the copolymer from being hydrophilic (a hydrogel) to being hydrophobic. This change causes the shrinkage at the interface to make pores (see below).

The formation and distribution of closed-cell and open-cell pores are probably linked to how the net curvature evolves locally during polymerization and ion exchange. Open-cell volumes have lower net curvature.

The shrunken polymer domains at the interface can be swollen in some organic solvents, such as aqueous DMSO, which partially heals or closes the pores. Figure 2C shows the SEM image of a polymer gel recovered from a DMSO solution. Most of the polymer pores have been closed. DMSO is a poor solvent for PMMA, thus the pore healing is due to the swelling of the IL surfactant containing the copolymer blocks. In addition to DMSO solutions, these porous polymers have also been exposed to a representative range of organic solvents, such as dimethylformamide (DMF), tetrahydrofuran (THF), acetonitrile, methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1,2-butanediol, hexane, benzene, toluene, and cyclohexane. Interestingly, these polymer pores show a high selectivity, and can only be self-healed or closed after immersion in water-miscible solvents, such as DMF, THF, acetonitrile, or alcohols (all of these are good solvents for IL-PF$_6$). THF and acetonitrile are noteworthy since they are also good solvents for PMMA.

The most striking property of these copolymers is that the recovered gel can reform a porous polymer (with pore diameters of 3–7 µm) by immersion in water (Figure 2D). The semitransparent polymer gels are converted back into opaque and microporous materials as shown in Figure 1D. This transformation is due to solvent exchange between the aqueous DMSO solution and water, which causes the surfactant IL chains to condense again and form pores.

The reversibility in the formation of the pores has been verified by several cyclic treatments with aqueous DMSO and water. Figure 2E shows the pore structure of the same polymer after three cycles of treatment with aqueous DMSO and water. Similar to the structures shown in Figure 2B and D, most of the pores are close-packed, with diameters of 3–7 µm retained. However, some of the circular pores are deformed. Figure 2F suggests some loss of porosity after numerous cycles. We believe the reversibility of such a gel/pore formation can be improved by modification of the microemulsion formulations. Since DMSO, DMF, and alcohols are widely used as drug solvents,[3] these porous polymers have potential for controlled release applications in chemical delivery.

The pore size of the porous polymer can be tuned by adjusting the content of the cross-linker. Figure 3A and B show SEM images of the polymer prepared from a microemulsion containing 1 wt% of cross-linker EGDMA. A

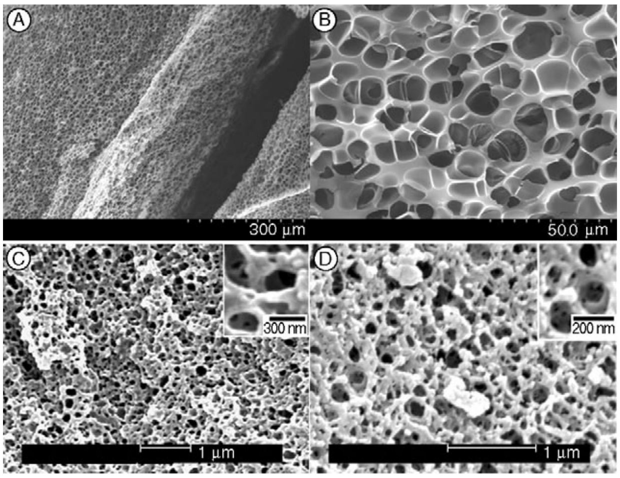

Figure 3. SEM images of porous polymers synthesized with different cross-linker contents: A) and B) EGDMA 1 wt%; C) EGDMA 7 wt%; D) EGDMA 10 wt%.

honeycomb-structured polymer is observed with pores of 5–10 μm. The pore size decreased to about 200 nm while the number of pores increased as the cross-linker content was increased from 1 to 7 wt% (Figure 3C). Most of these pores connect to others through small circular "windows" with diameters of approximately 50 nm (see inset in Figure 3C). The size of the open-cell pores decreased to about 100 nm when the cross-linker content was increased to 10 wt% (Figure 3D). Similarly, most of these pores are interconnected through "windows" with diameters of about 20 nm. This porous polymer exhibits a BET surface area of 36.6 $m^2 g^{-1}$. These results indicate that increasing the proportion of the cross-linking agent present in the microemulsion not only affects the composition of the final monoliths but also decreases their average pore size as a result of the early formation of highly cross-linked polymer domains that have a reduced tendency to coalesce.

It appears that a physical explanation for this reversible solvogel–porous material transition may be expressed in terms of: 1) a three-dimensional phase space for the cross-linked copolymer, a polymer swelling solvent (for example, DMSO), and a nonsolvent (water), and 2) a spinodal decomposition of this three-component unstable solvogel phase, after addition of excess nonsolvent, to give a small-pore condensed copolymer membrane in equilibrium with the nonsolvent mixture. The monomer sequences in the resulting copolymer strands (Figure 4A, left) have not yet been identified, and detailed molecular-weight and sequence analyses will be reported subsequently. However, from the cross-linking results presented below, it appears the final cell dimensions are controlled by the expanded chain length of the strands modeled in Figure 4A (left). A solvogel phase exists when there is excess swelling solvent. The swelling solvent induces charge separation between the hexafluorphosphate anions and the imidazolium cations (Figure 4A, right) and thereby solvates the IL-surfactant blocks thus causing the copolymer to swell, and causing a significant decrease in the light scattering, as the solvogel becomes translucent (Figure 1C and Figure 4B, left) or transparent. Immersion of the solvogel into excess nonsolvent (water) induces "nonsolvent phase inversion" to a totally collapsed and deswollen polymer having an open-cell porosity in equilibrium with the nonsolvent/swelling solvent mixture (Figures 1D and 4B, right). The inversion process of the nonsolvent phase to produce microporous membranes from PMMA solutions put in contact with nonsolvents has been very well analyzed in terms of the dynamics of the spinodal decompositions.[4,5]

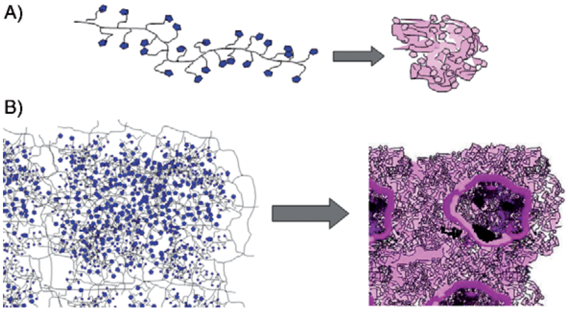

Figure 4. Schematic representation illustrating: A) collapse of an ionic liquid surfactant copolymer brush upon exposure to a poor solvent and B) the corresponding spinodal decomposition of a cross-linked bicontinuous gel to form open-cell porous material upon exposure to a poor solvent. In (A) the individual brush hairs on the left represent the undecylimidazolium hexafluorophosphate species, with substantively dissociated hexafluorophosphate ions; these ions condense onto the imidazolium rings upon exposure to a poor solvent (water), thus causing individual and proximal copolymeric chains to condense upon themselves (A, right). The extended chain length in (A, left) is of the order of 10 nm and in (B) the dimensions of a given cell are of the order of 100 nm.

The spinodal nature and the reversibility of this transition is supported by the necessarily bicontinuous nature of the starting solvogel and resulting porous systems (Figure 4B).[6,7] The solvogel comprises the swollen copolymer in equilibrium with a preponderance of a good solvent. The porous polymer comprises an open-cell highly scattering and condensed polymer in a locally phase-separated equilibrium with a preponderance of a poor solvent. The solvogel is bicontinuous in terms of the cross-linked copolymer and the solvent, and derives from the starting and opaque porous (random) block copolymer system, continuous in the copolymer, and continuous in the nonsolvent. As the open-cell porous material is solvated by the swelling solvent, the IL surfactant blocks then solvate, and the condensed copolymer film expands and becomes much less scattering because of its local solvation. The resulting solvogel, still inherently bicontinuous in the cross-linked copolymer and solvent, then recondenses reversibly to a highly light scattering bicontinuous system comprising an open-cell porous structure in equilibrium with the pore-filling solvent. The cross-linked nature of the copolymer necessarily precludes the possibility of this system from undergoing a binodal decomposition, since macroscopic phase separation is precluded by the cross-linking. This lack of access to binodal transitions tends to preserve the reversibility of the system, as demonstrated experimentally. The spinodal decompositional nature of this transition from solvogel to a porous material is "pinned due to elasticity arising from the crosslinkage".[6]

We have synthesized cross-linked polymer gels by polymerization of microemulsions stabilized by surfactants based on ionic liquids. The resulting polymer gels can be transformed into porous polymers by anion exchange of the IL moiety. These porous polymers can be converted back into polymer gels by immersion in organic solvents, such as DMSO and DMF, and these polymer gels can be reconverted into porous polymers by immersion in water. These striking properties present a new class of microporous polymers suitable for diverse applications, including tissue scaffolding, bicontinuous materials templating, antimicrobial filtration, and fire-resistant foams, in addition to controlled-release chemical- and drug-delivery applications. Reversible poration in cell membranes has reported as being induced chemically[8] and physically.[9] Reversible poration in synthetic systems has been recently reported in electrochemically active inorganic membranes[10] and in thermoreversibly porous systems.[11]

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