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Capturing Nanoscale Structure in Network Gels by Microemulsion Polymerization

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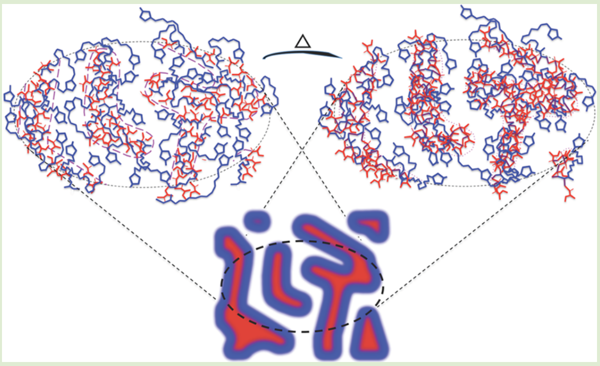
Supporting Information

ABSTRACT: Small-angle neutron scattering and turbidity were used to probe nanoscale structure in bicontinuous microemulsions before and after polymerization. Difficulties in capturing nanoscale structure by polymerizing microemulsions have persisted with the use of thermal initiation. Bicontinuous microemulsion polymerization with a reactive surfactant monomer and cross-linker was done with only a 20% increase in repeat distance. This small increase represents better than an order of magnitude advance over previous attempts, exhibiting hundreds to thousands percent increases. Both the network gel and the precursor microemulsion were transparent and devoid of microphase separation.

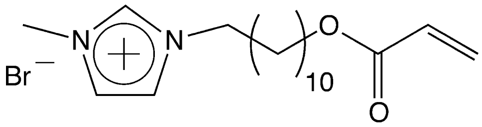


Microemulsion and mesophase polymerization have been pursued for over 30 years, and a continuing challenge has been to capture the nanostructure that exists in microemulsions and mesophases prior to polymerization.[1−5] An examination of polymerization in and of microemulsions and mesophases as well as precipitation of nanoparticles in microemulsions and the associated prereaction and post-reaction length scales has led to our postulating several empirical principles for capturing nanoscopic length scales in microemulsions: (1) use a polymerizable surfactant or surfmer; (2) provide sufficient degrees of freedom so that surfactants can polymerize without destroying interfacial packing; (3) increase the ratio of polymerization rate to the microemulsion/mesophase structural reorganization rate. Various studies addressing and exemplifying these principles have been reviewed.[4,5]

The first principle (1) to use polymerizable surfactants or surfmers derives from the work of Gan and co-workers,[6] O'Brien and co-workers,[7−9] and others.[10−14] The second principle (2) comes from the life work[7−9] of David F. O'Brien and his co-workers who learned how to polymerize surfactants and amphiphiles in two-dimensional films and interfaces and is more easily implemented by including cross-linking agents. Principle (3) comes mainly from the work of Gan and co-workers[6] who demonstrated the use of UV-driven polymerization in producing nanoporous membranes from bicontinuous microemulsions. Successful demonstrations of this principle have also been presented by Co and co-workers[12] where water-free microemulsions with sugar-based surfactants were polymerized. In addition to using UV-initiated polymerization that provides rapid polymerization, decreasing the reorganization time scale[13,14] of the polymerizable assemblies also promotes this principle. However, UV-driven polymerization does not always suffice to capture nanoscale structure.[15] The use of cross-linking agents in these systems also contributes to increasing the rate ratio in (3) above by decreasing the microemulsion reorganization rate.

Here we report further on the creation of new hydrogels and stimuli-responsive materials following Yan and Texter[16] using the reactive ionic liquid surfactant acrylate, ILBr (Scheme 1).

Scheme 1. 1-(11-Acryloyloxyundecyl)-3-methyl Imidazolium Bromide (ILBr)



This monomer yields materials that are stimuli responsive to various anions as well as materials that are stimuli responsive to solvents.[17−20] In this study we focus on the thermally initiated polymerization of bicontinuous microemulsions without inducing microphase separation. The quaternization step induces the formation of IL_2Br (1,3-bis(11-acryloyloxy undecyl) imidazolium bromide) at about 4−5 mol %. This

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moiety provides cross-linking (see Supporting Information (SI)) and may form as a result of alkyl group scrambling.[21] We focus further on using thermally initiated polymerization for the practical application reasons articulated by Cheung and coworkers.[22]

Partial ternary phase diagrams at 25 and 60 °C of water, ILBr, and methylmethacrylate (MMA) are illustrated in Figure 1. There is a large multiphase domain that is nearly the same at 25 and 60 °C, and the single-phase microemulsion domain extends beyond compositions of 75% in ILBr. The extension of the microemulsion domain to the water corner has previously been exploited to develop stimuli-responsive nanolatexes[16,23] that form stimuli-responsive thin films[16,23] as well as forming high concentration waterborne dispersions of nanocarbons, including nanotubes and graphene.[24−26] Electrical conductivity data (see SI) indicate a transition region from reverse microemulsion to bicontinuous nanostructure over the (10/60) to (20/50) water/MMA compositional interval.

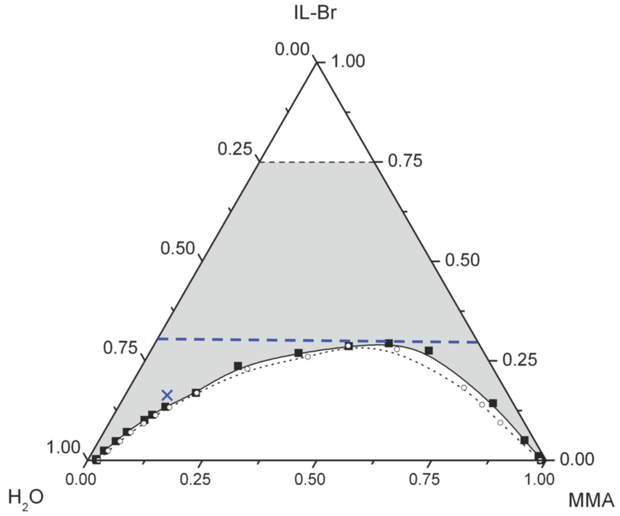

Figure 1. Ternary phase diagrams of the water/ILBr/MMA system at 25 and 60 °C. The shaded area above the curves represents the single-phase microemulsion region. The black squares and solid line represent the boundary points and curve at 25 °C, with points at 60 °C represented by open circles and a dotted line. At 60 °C, the shaded region extends to the dotted curve. The dashed line at 75% ILBr concentration (w/w) represents the upper limit verified as single-phase microemulsion. The dashed line at 30% ILBr represents the range of some of the compositions examined in this study. The composition (substituting D_2O for H_2O) examined by small-angle neutron scattering (SANS) is indicated by the cross (×).

The compositions polymerized in this study include that marked by the × in Figure 1 at 15% ILBr, 10% MMA, and 75% water (D_2O) and along the 30% ILBr compositional (dashed) line at water/MMA ratios of 70/0, 60/10, 50/20, 40/30, 30/40, 20/50, 10/60, and 0/70. All of these microemulsion compositions were optically transparent to the eye after gentle mixing of all of the components. The series of eight compositions of 30% in ILBr and spanning the aqueous to MMA extremes after polymerization are illustrated in Figure 2.

No light scattering indicative of nanophase or microphase separation is visually detectable after polymerization in the (70/0), (60/10), (50/20), (10/60), or (0/70) water/MMA compositions. This transparency is supportive qualitative evidence (not proof) of capturing the microemulsion nanostructure and is understandable in view of the high water solubility of the polyILBr homopolymers[27] as well as the solubility of random and partially cross-linked poly(ILBr-*co*-MMA).[28] This transparency is proof of the absence of significant microphase separation. The very slight turbidity generated in the (40/30) and (30/40) compositions suggests only minor nanophase separation has occurred, and for the (20/50) composition where we see moderate turbidity, the nanophase separation appears to be greater, but much, much less than seen in micro- or macrophase separation.

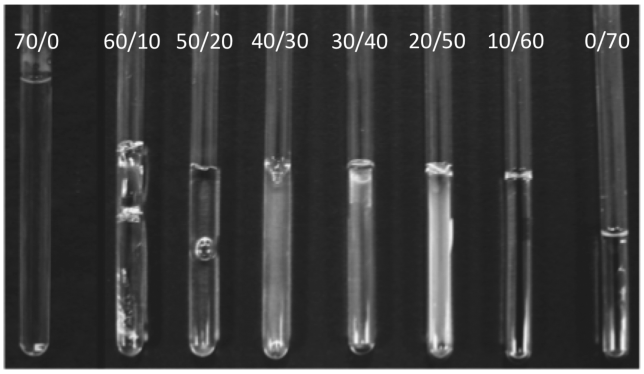

Figure 2. Network gels from polymerized compositions (left to right) of (water/MMA weight ratio): (70/0); (60/10); (50/20); (40/30); (30/40); (20/50); (10/60); (0/70). ILBr is constant at 30% (w/w), and decreasing % ratios of water to MMA are illustrated from left to right (photographed against a black background to highlight the turbidity).

None of the polymers produced could be analyzed meaningfully by size exclusion chromatography because of light cross-linking; our samples were effectively microgels or nanogels. Had the cross-linker not been present, we believe a much bigger increase in repeat distance would have been observed, but at least molecular weight measurements should then have been feasible. Had we used a nonpolymerizable homologue of ILBr, we believe microphase separation would have been obtained. This cross-linking provides a physical basis for an interesting stimuli responsiveness for these gels that can be reversibly transformed into porous materials by spinodal decomposition.[16,29,30]

A quantitative approach to investigating nanostructure is to use an appropriate scattering technique such as SANS. SANS is a well-accepted technique for examining nanostructure in microemulsions,[31−33] so we examined its application in this system. SANS data for a microemulsion composed similarly to one earlier reported[7] wherein scattering intensity as a function of scattering vector is illustrated in Figure 3. The intensity for Q < 0.003 Å (not shown) is attenuated by the beam stop. These SANS data bear significant similarity to those of Kaler and coworkers[34] where D_2O/DTAB (dodecyltrimethyl ammonium bromide)/styrene microemulsions were thermally initiated but produced turbid suspensions comprising 25−30 nm diameter latex particles (low Q peak) in addition to empty micelles (high Q peak), rather than the optically clear gel obtained in our experiment.

The ILBr/MMA/D_2O microemulsion scattering agreed well with the Teubner−Strey model[32] for a bicontinuous microemulsion. The nonlinear least-squares fitted line can be seen passing through the open circles in Figure 3 to low and high Q on both sides of the scattering peak. The polymerized wafer showed deviations at lower Q values that merit further study.

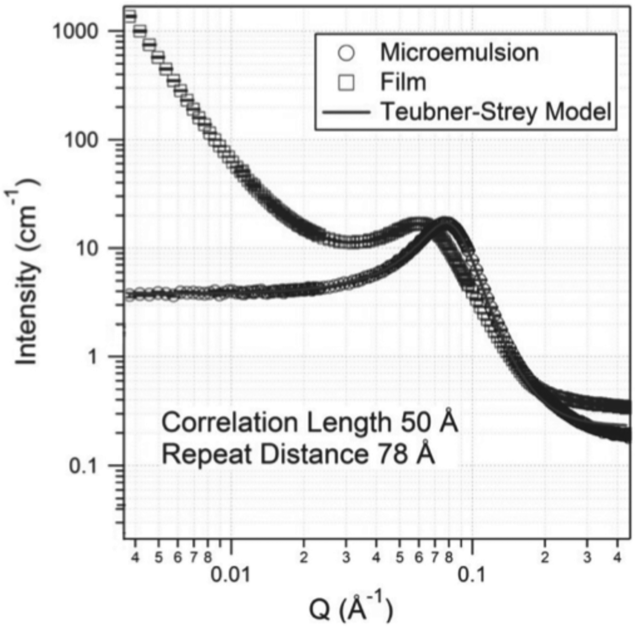

Figure 3. SANS data for D_2O/ILBr/MMA (0.15/0.10/0.75) microemulsion (○) and polymerized microemulsion (□); fit (——) to Teubner–Strey[33] model.

The correlation length (ξ) of 50 Å represents the average distance over which the local structural order is preserved in this irregularly shaped bicontinuous microemulsion or, more precisely, the distance over which the spatial correlation function decays from unity to $(1/e)(\sin(2\pi\xi/d)/[2\pi\xi/d])$[33] or −0.071. The repeat distance (d) of 78 Å denotes the average distance between two continuous oil or two water pseudophase domains in the microemulsion. A key result is the similarity in the scattering peak positions before and after polymerization, 0.75 and 0.6 Å $^{-1}$, respectively. This decrease of only 20% appears to be the smallest structural change ever reported for a thermally initiated polymerized bicontinuous microemulsion. As a practical matter, the polymerized product appeared clear and transparent to the eye, and this transparency indicates that any structural growth features do not perceptibly scatter visible light.

In the case of macroscopic phase separation, these repeat distances would diverge. In microphase separation, they increase from tens/hundreds of nanometers to micrometers and larger. In the present case where the increase is only of the order of 20% and nanophase separation is not present, this small increase may be assigned to the greater localization of the interfacial surfactant in the continuous polymer phase with a concomitant slight increase in repeat distance.

While the turbidity is a sensitive qualitative measure, small-angle light scattering (SALS) and small-angle X-ray scattering (SAXS) may have provided alternative views of structural preservation and transformation during these polymerization processes. Co and Kaler[35] showed that SANS could also be used to see how micellar dimensions shrink as a function of conversion when nonreactive surfactants are used, in spite of intense lower Q scattering developing from the 25–50 nm latex particles being generated. Similarly, Burban et al.[36] showed by SAXS that surfactant association structures were preserved during microemulsion polymerization, even though significant microphase separation and otherwise loss of microemulsion structure were obtained in cross-linked styrene, MMA, and butyl methacrylate systems. Recently, Peng et al.[37] used SAXS to monitor microemulsion structural evolution in a methacrylate dimethylsiloxane macromonomer microemulsion stabilized by nonionic surfactant. Polymerization was driven by X-ray exposure, and significant structure generation with conversion was identified. The resulting solids ranged from near-transparent to opaque, and SEM demonstrated micrometer-scale structures present after polymerization in all cases.

Stubenrauch et al.[38] presented an interesting polymerizable microemulsion that could be made to gel in the dodecane pseudophase by addition of a cosurfactant like molecule apparently without dramatically changing the bicontinuous structure (a few percent shift in peak Q upon addition of a few percent by weight of the cosurfactants). This system was too complex, however, to avoid significant phase separation upon polymerization.

The apparent peak associated with the increasing intensity for $Q < 0.012$ Å $^{-1}$ from the polymerized microemulsion is interesting and suggests scattering emanating from longer-range structures than those related to the basic correlation length. These data fit the power law $I(Q) \sim Q^{-3}$ and may be tentatively assigned to a de facto pore structure having a mass fractal dimension of 3.[39] These pores are the volume elements bounded by the lightly cross-linked polymer chains. This assignment is plausible in view of the fact that this polymer gel is dense in its pores. Using the estimate of $R > 3.5/Q_{\min}$ for average pore radius,[40] we have the estimate $R > 120$ nm. We stress this inequality is limited by the beam stop occlusion of scattered intensity at lower Q, and the apparent porosity observed after spinodal decomposition after stimuli response (ion exchange) to PF_6^{-1} suggests this estimate is conservative.

Similar medium-Q SANS scattering approximately following a log $I(Q) \sim Q^{-3}$, $Q \in (10^{-3}, 3 \times 10^{-2})$, has been reported for polyisoprene solutions and gels,[41] for lightly cross-linked sliding ring gels and aqueous polyethylene oxide and tetra-PEG gels,[42] for swollen hydrogels of poly(HEMA) (hydroxyethyl methacrylate),[43] for aqueous gels of *N*-acyl-L-aspartic acids and *N*-dodecanoyl-β-alanine,[44] for marine mussel protein gels,[45] and for cross-linked PVA (polyvinyl alcohol) gels.[46] A cogent assignment of this phenomenological scattering at moderate Q for other than a dense pore structure has not yet been made, and more work is needed to better understand this apparently new scattering law.

The longer range order (>100 nm) implied by the $I(Q) \sim Q^{-3}$ scattering suggests the need for further theoretical development in scattering from gels and cross-linked systems. Porod's law with Q^{-4} dependence of the scattered intensity is well illustrated for high Q. The open cell pore structure (see SI) and associated distribution created by spinodal decomposition represent an upper bound to the distribution associated with dense "pores" in the hydrated gel state. This medium Q behavior is being investigated further.

Comprehensive studies of thermal polymerization of bicontinuous aqueous microemulsions of MMA/methylacrylic acid (MAA) and of MMA/acrylic acid (AA) stabilized by SDS and cross-linked with ethyleneglycol dimethacrylate (EGDMA) showed that microporous polymeric solids were obtained with characteristic length scales growing from nanometers to micrometers (accompanied by transitions from optical transparency to high turbidity) upon polymerization.[21,47,48] Molecular reorganization of cetyltrimethylammonium bromide (CTAB) stabilized bicontinuous microemulsions of aqueous AA/styrene (S) undergoing thermally initiated polymerization with phase separation producing 50−1000 nm structures with similar transitions from transparency to opacity was studied.[1] Polarized light microscopy demonstrated (vesicular) lamellar mesophase formation of the surfactant during and after the polymerization,[1] as has been previously demonstrated for AOT by cryo-TEM.[49] Increases in the length scale characteristic of the monomers and polymers of hundreds to thousands of percent were realized in these systems.

The lack of turbidity in the 15% ILBr formulation and in the 30% ILBr formulations with water/MMA ratios greater than 40/30 supports the nanoscale capture of microemulsion structure. This conclusion is unequivocally supported by SANS data for the 15% ILBr case. We ascribe the formation of polymer gels without significant microphase separation in this system to the combination of having a polymerizable surfactant and a small amount of cross-linker present. This condition is similar to that derived in the work of O'Brien and co-workers.[7−9]

We believe our result of a 20% increase in repeat distance, supported by SANS, is the most structure-preserving to date obtained by thermal initiation in polymerizable bicontinuous microemulsions. This process is depicted schematically in Figure 4.

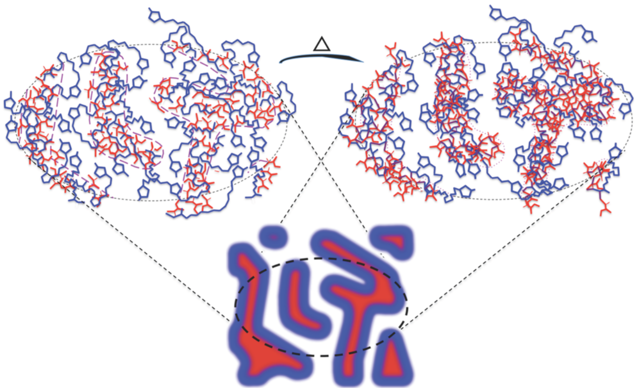

Figure 4. Cartoon of two-dimensional bicontinuous microemulsion (center, lower) wherein water (white), ILBr (blue), and MMA (red) occupy interdigitated pseudodomains of oil (red) and water (white) stabilized by interfacial surfactant (blue). These pseudodomains are also depicted by molecular models for ILBr and MMA in an oval nanodomain before (upper left) and after (upper right) thermally initiated polymerization, wherein (upper right) nanoscale structure is essentially captured during and after polymerization.

We believe the key contribution enabling this result is the pronounced amphilicity imparted to the polymer by the hygroscopic imidazolium bromide ion pairs that appear to maintain high solvation (hydration) of the resulting polymeric network. The images (turbidity) of Figure 2 suggest this solvation effect can be driven to ILBr/water ratios between 1.5 and 1.0 and suggest a hypothesis for further evaluation. A solvated and partially swollen aqueous network gel, poly(A-*co*-B-*co*-C), can be derived by microemulsion polymerization of water-immiscible monomer B when stabilized by reactive surfactant A and lightly cross-linked by monomer C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental methods describing phase diagram generation; polymerization details and the reactor used for creating SANS sample; electrical conductivity data; SEM of freeze fracture; SEM of polymerized D_2O gel after soaking in stimuli responsive KPF_6 solution and undergoing spinodal decomposition to open cell porous material. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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