

## Self-Assembly and Polymerization of Epoxy Resin-Amphiphilic Block Copolymer Nanocomposites

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A variety of methods for the preparation of nanostructured materials for applications in catalysis, separations, and as hosts for the templated synthesis of other nanoscopic materials have been reported.<sup>1–3</sup> Of particular interest are the new generation of mesoporous ceramics prepared in surfactant solutions of suitable ceramic precursors.<sup>3–7</sup> In these systems there is a subtle interplay between the kinetics of gel formation and self-assembly, and these two coupled processes dictate the final ordered state symmetry of the ceramic.<sup>3</sup> Ceramics with pore sizes ranging from 2 to 10 nm have been routinely prepared employing a variety of surfactant systems.<sup>7,8</sup>

As part of a more general program aimed at understanding the thermodynamics of block copolymer self-assembly, we have developed a fundamentally different method for the preparation of composite materials with nanoscopic features. Our synthesis relies on the formation of a well-ordered nanostructure from a two-component mixture of a low-molecular-weight thermosetting epoxy resin and a diblock copolymer.<sup>9</sup> These mixtures form ordered morphologies with compositional heterogeneities on 10–20 nm length scales. Cross-linking of the epoxy matrix without macroscopic phase separation of the block copolymer leads to stable structures with nanoscopic features. Unlike the mesoporous ceramic syntheses, the ordered state symmetry of these thermoset composites is fixed by the overall composition of the mixture before curing of the epoxy. Self-assembly and polymerization are sufficiently uncoupled that once an ordered state symmetry has been prepared, the cross-linking of the epoxy resins does not significantly affect the morphology.

Recently we reported the preparation<sup>10</sup> and bulk phase behavior<sup>11</sup> of a new set of amphiphilic poly(ethylene oxide)–poly(ethyl ethylene) (PEO–PEE) and poly(ethylene oxide)–poly(ethylene-*alt*-propylene) (PEO–PEP) block copolymers.

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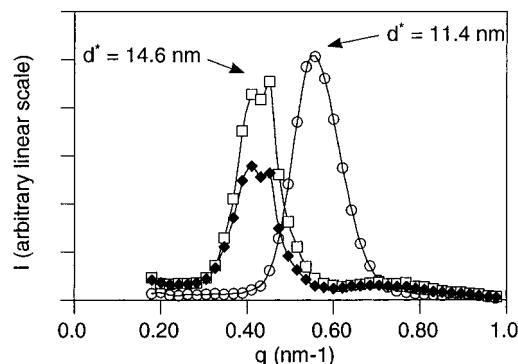
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(9) There have been reports on the preparation, morphology, and mechanical properties of block copolymer modified epoxy resins. However, the control of the morphology, the long-range order, and the microstructure formation have not been addressed. For example, see: Buchholz, U.; Mühlaupt R. *ACS Polym. Prepr.* **1992**, *33*, 205–206. Könczöl, L.; Döll W.; Buchholz U.; Mühlaupt R. *J. Appl. Polym. Sci.* **1994**, *54*, 815–826. Ochi, M.; Uno M.; Mimura K.; Kamoto T.; Tagami T.; Kiyohara O. *Kobunshi Ronbunshu* **1992**, *49*, 953–960.

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**Figure 1.** SANS profiles from pure OE-9 (open circles, 75 °C) and a mixture of an OE-9-BPA480/phthalic anhydride epoxy mixture containing 30 wt % OE-9: before curing (open squares, 75 °C) and cured (filled diamonds, 200 °C).

The amphiphilic nature of these molecules allows the selective partitioning of added components to one of the blocks. For our initial studies, a low-molecular-weight bisphenol-A/epichlorohydrin epoxy resin (BPA480) was employed as the thermosetting precursor.<sup>12</sup> The miscibility of PEO and this type of epoxy resin has been confirmed, and it was speculated that the mixture is characterized by a negative Flory–Huggins interaction parameter,  $\chi$ .<sup>13</sup> We anticipated that the epoxy resin (and an appropriate hardener) would swell the PEO domains in these block copolymers without dissolving the polyalkane blocks and thus lead to an ordered composite material. Here we describe the preparation and characterization of three samples that highlight the experimental methods and salient features of this system.

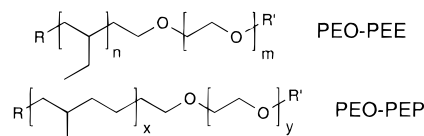


Figure 1 shows the one-dimensional small-angle neutron scattering (SANS)<sup>14</sup> profile for a pure sample of PEO–PEE at 75 °C (OE-9:  $n = 34$ ,  $m = 50$ ;  $f_{\text{PEO}} = 0.46$ ). The principal reflection at  $q^* = 0.55 \text{ nm}^{-1}$  yields an interplanar spacing of 11.4 nm. A sample of OE-9 and a precured BPA480/phthalic anhydride epoxy resin (30 wt % OE-9) were codissolved in THF.<sup>15</sup> After evaporation of the THF, the sample was dried at  $\approx 65 \text{ °C}$  to yield an optically homogeneous material. A nanostructure spacing of 14.6 nm was extracted from the principal SANS reflection (Figure 1). The epoxy resin has swollen the structure of the block copolymer and produced a material that has scattering density correlations on the order of 15 nm with no sign of macrophase separation. A hexagonally packed cylinder morphology is supported by the higher order

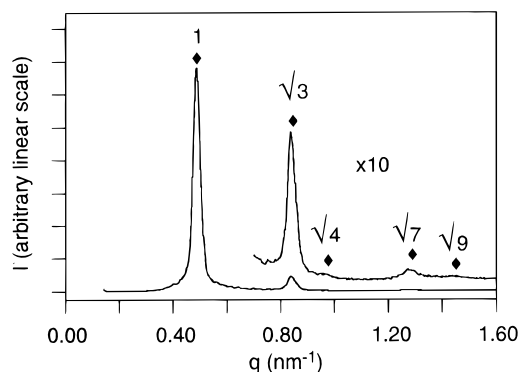
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(12) BPA480: Poly(bisphenol A-co-epichlorohydrin), glycidyl end-capped, ( $M_n \approx 480$  (Aldrich Chemical Co.)). This resin can be cured by the addition of a variety of hardeners. See: *Epoxy Resins. Chemistry and Technology*; May, C. A., Ed.; Marcel Dekker, Inc.: New York, 1988.

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(14) SANS experiments were conducted at the Risø National Laboratory, Denmark, using 5.6 Å wavelength neutrons. The principal interplanar spacing  $d^*$  is equal to  $2\pi/q^*$ , where  $q^*$  is the principal scattering wave vector.

(15) The precured BPA480/phthalic anhydride resin was prepared as described: *Practical Macromolecular Organic Chemistry*; Braun, D., Chedron, H., Kern, W., Eds.; Harwood Academic Publishers: New York, 1984. This precured resin is completely soluble in THF at room temperature. The block copolymer/epoxy mixtures can also be mixed in the melt state. Care was taken during the mixing of these samples to avoid premature gelation of the epoxy.



**Figure 2.** One-dimensional SAXS profiles of a cured sample of epoxy containing 36 wt % OP-2 that was shear aligned (radially averaged pattern taken down the shear gradient axis).

reflection in the SANS profile. This composite material was shear aligned<sup>16</sup> and heated to 200 °C stepwise over 90 min. This treatment cured the epoxy in the mixture and led to a hard thermoset material. The alignment and the nanostructure spacing were relatively unaffected during heating (Figure 1). An array of PEE domains, tentatively identified as cylinders, dispersed at a nanoscopic scale in an epoxy matrix was observed by TEM.

In a second experiment we simultaneously examined the rheological and structural properties of a sample before, during, and after curing, using a rheometer that was designed for in-situ SANS measurements.<sup>17</sup> A sample of a precured BPA480/phthalic anhydride epoxy resin and a PEO-PEP block copolymer (36 wt % OP-2:  $x = 19$ ,  $y = 43$ ;  $f_{\text{PEO}} = 0.52$ ) mixture was loaded into a shear sandwich tool. The linear dynamic elastic and loss modulus ( $G'$  and  $G''$ ) were probed as a function of frequency at 100 °C (2% strain) before significant curing had taken place. The sample was then shear aligned at 1 rad/s and 160% strain at 100 °C, cooled to 30 °C and sheared to improve the alignment, reheated to 100 °C, and then ramped to 200 °C at 2 °C/min.  $G'$  ( $\omega = 1$  rad/s) increased by more than two orders of magnitude as the sample cured, and both the alignment of the material and the first-order reflection were relatively unchanged. However, unlike the precursor material,  $G'$  was frequency independent in the cured material at 200 °C. The increase in modulus and solid-like frequency response is consistent with a cured network state. Well-aligned hexagonally packed cylinders of PEE in a matrix of PEO and epoxy were observed with TEM. The hexagonal symmetry and the principal interplanar spacing was confirmed by high resolution small-angle X-ray scattering (SAXS)<sup>18</sup> (Figure 2).

Stabilization of ordered morphologies in our two-component system is fundamentally different than in polymerizable surfactants,<sup>19</sup> surfactant/ceramic precursor mixtures,<sup>3-7</sup> or surfactant/monomer/water mixtures.<sup>20</sup> The surfactants employed in all of the above cases are typically low-molecular-weight

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(17) A Rheometrics Solids Analyzer RSA2 equipped with an aluminum shear sandwich sample holder was used for the simultaneous SANS/rheology measurements. Details to be published.

(18) SAXS images were obtained on a custom-built small-angle system utilizing a rotating anode generator, Franks mirror optics tuned to  $\lambda = 1.54$  Å, and an area detector.

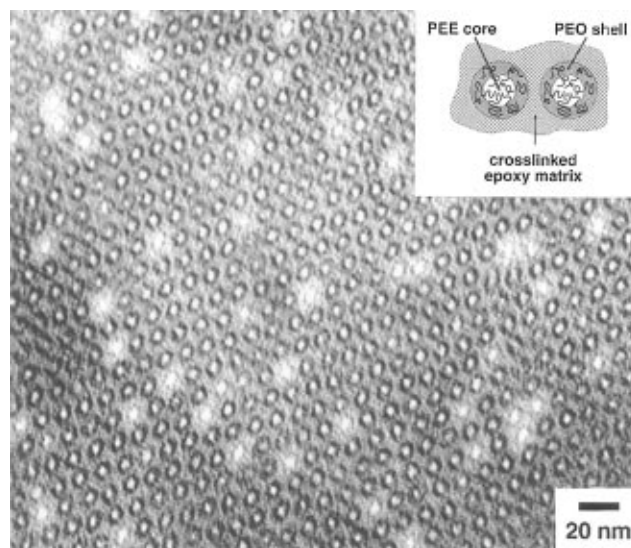
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**Figure 3.** TEM of a cured OE-7/epoxy mixture (25 wt % OE-7). The sample was microtomed at RT and stained with RuO<sub>4</sub>. The inset depicts the idealized nanostructure.

materials, and additives (reactive or unreactive) are necessary to induce self-assembly. Subtle changes in the chemical nature of the systems upon polymerization can significantly affect the resultant morphologies. Conversely, the polyalkane-PEO block copolymers self-assemble in the absence of solvents. These “super surfactants” are therefore less susceptible to chemical changes of the reactive additives due to their relatively large molecular weights. However, in our systems the matrix epoxy undergoes a dramatic change during the gelation reaction in which its molecular weight diverges. This should lead to a significant decrease in the compatibility of the PEO in the epoxy matrix. In fact, similar PEO/BPA480 mixtures have been shown to be miscible over the entire composition range in the uncured state, but adding a hardener to these mixtures results in macrophase separation during cross-linking and the generation of opaque samples in one example.<sup>13,21,22</sup> The miscibility of PEO with these types of epoxy resins is an important mechanistic feature of the block copolymer templating scheme described above.

Figure 3 is a TEM image of a cured PEO-PEE block copolymer/epoxy mixture (25 wt % OE-7:  $n = 36$ ,  $m = 39$ ;  $f_{\text{PEO}} = 0.39$ ) that was shear aligned and cured at 180 °C. SAXS results indicate that the sample morphology is hexagonally packed cylinders. This image was obtained by slicing the specimen perpendicular to the shear axis of the cylinders followed by staining with RuO<sub>4</sub> vapors. A clear core/shell morphology is evident from this picture. The dark circular regions are predominately PEO shells, the white regions are the PEE cylinder cores, and the epoxy matrix is gray.<sup>23</sup> Variations in the slice thickness and nonuniform staining are presumably responsible for the large bleached areas in the photograph, although in those regions the general core/shell morphology can still be observed. Adding a PEO compatible precured epoxy resin to an ordered polyalkane-PEO block copolymer leads to an ordered morphology swollen with a reactive diluent. Gelation of the epoxy resin forces an expulsion of the PEO from the matrix. We believe the curing also impedes the mobility of the block copolymer in the matrix, and thus macrophase separation of the block copolymer is kinetically hindered. This process yields optically homogeneous materials containing nanoscopic core/shell-like morphologies.

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