Macromolecules **2000,** *33,* 9522−9534

Reactive Block Copolymers for Modification of Thermosetting Epoxy

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Received August 11, 2000; Revised Manuscript Received October 30, 2000

ABSTRACT: Block copolymers incorporating epoxy-reactive functionality in one block have been studied as modifiers for model epoxy resins. As observed previously with nonreactive poly(ethylethylene)-*b*-poly(ethylene oxide) (OP) copolymers, reactive poly(epoxyisoprene)-*b*-polybutadiene (BIx*n*) copolymers and poly(methyl acrylate-*co*-glycidyl methacrylate)-*b*-polyisoprene (MG-I) copolymers form ordered microstructures in blends with epoxy precursors as evidenced by small-angle X-ray scattering and transmission electron microscopy. Like OP copolymers, both types of reactive copolymer remain well-dispersed within the epoxy matrix during cure. Additionally, DSC and solubility studies suggest that these copolymers can react with the curing epoxy resin to form covalent linkages between the copolymeric microstructures and the cross-linked epoxy resin. The capability of these types of copolymers to template epoxy resin is proposed to arise from a combination of (1) the miscibility of one block with the epoxy components well into the curing process and (2) the energetic barriers to nucleation and growth of copolymer-rich regions in the epoxy matrix as network formation occurs and the epoxy molecular weight diverges.

Introduction

Epoxy-based thermosets play an important role as modern polymeric materials.[1,2] However, the effective range of use of these highly cross-linked materials is limited by their inherent brittleness. Much research has been devoted to the improvement of their physical properties, chiefly through the incorporation of flexible elastomeric domains within the brittle epoxy network.[3−5] Typical rubbery modifiers phase-separate during the epoxy curing process to result in an irregular distribution of micron-scale rubbery inclusions throughout the resin.[6] Control over the scale and homogeneity of these inclusions would facilitate the understanding of epoxy-toughening mechanisms and could enable the preparation of useful new thermosetting materials.

The polymers typically used for epoxy modification are homopolymers or random copolymers and do not form microphase-separated structures. Block copolymers, however, are known to self-assemble on polymeric length scales (tens of nanometers) into well-defined ordered phases both in the undiluted state and in blends.[7] In high molecular weight polymers, these equilibrium morphologies primarily emerge from the balance between the enthalpic penalties arising from contact between dissimilar copolymer blocks and the incompressibility constraints which result from the covalent linkage between the blocks. The ultimate morphology selected by a given polymer is governed by polymer length, block symmetry, and interblock repulsion strength. In blends and solutions, solvent−block interaction parameters and blend composition further dictate morphology. Block copolymers have been studied extensively for stabilization of interfaces between incompatible phases, including those in modified epoxy systems.[8−10]

The discovery that amphiphilic block copolymers of poly(ethylene-*alt*-propylene) (PEP) and poly(ethylene oxide) (PEO) are not only dispersible in a model epoxy system but also capable of ordering epoxy networks on the nanometer scale in both the uncured and cured states has important implications for the homogeneous modification of epoxy-based materials.[11,12] In these systems, macrophase separation of PEP−PEO copolymers (OP, Figure 1) is not observed during cure, but the initially epoxy-miscible PEO chains are expelled from the epoxy resin within nanometer-sized ordered domains of the growing epoxy network. This nanometer-scale phase separation results in structuring of the block copolymer domains such that PEP domains are shielded from unfavorable interactions with the polar epoxy network by coronae of PEO blocks.

To further fix these ordered morphologies in the rigid thermoset matrices, we have explored the incorporation of reactive sites into the epoxy-miscible block. Covalent linkage of block copolymeric inclusions to the epoxy resin provides opportunities for greater improvement in fracture toughness at low copolymer concentration[3] and allows for the possible preparation of functional epoxy resins at higher copolymer concentrations. Initially, we have examined the modification of a model epoxy system consisting of the diglycidyl ether of bisphenol A (BPA348) and 4,4′-methylenedianiline (MDA) (Figure 1). While the physical properties of the resins arising from the cure of these specific components are often inferior to those of other systems, the components are readily available, and their cure kinetics are well understood.[13,14]

The miscibility of polymers with uncured epoxy tends to increase with increasing polarity of the polymer repeat unit—monomers including acrylonitrile, methyl methacrylate, and caprolactone have been incorporated to enhance the miscibility of a given polymer with epoxy.[15−17] Likewise, epoxidized natural rubber has been used as a more miscible rubbery modifier.[18−20] A related new class of block copolymers designed to exhibit amphiphilicity toward epoxy resins has been prepared in order to simultaneously examine the generality of the epoxy templating effect observed with PEP−PEO copolymers and the effect of the incorporation of reactive sites in the epoxy-miscible block of similar copolymers upon the observed phase behavior. BIx*n* block copolymers (Figure 1) of poly(1,2-butadiene) (1,2PB) and poly(epoxy-1,4-isoprene-*ran*-1,4-isoprene) (PIOx*n*) can be

10.1021/ma001414f CCC: $19.00

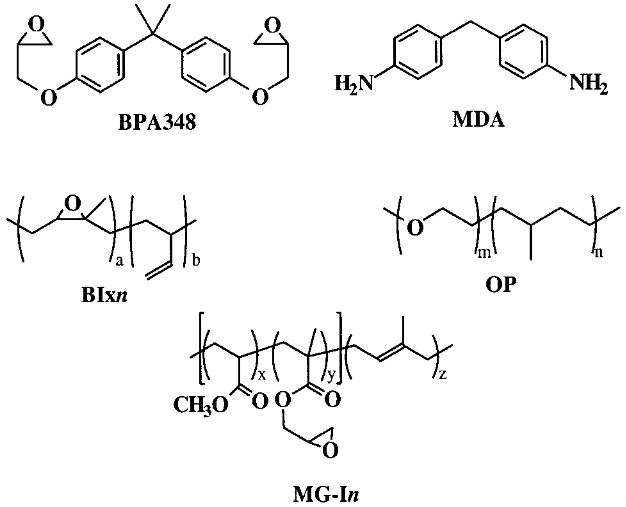


Figure 1. Epoxy components and representative structures of copolymers used in this study. See experimental text for full description of polymer characteristics.

prepared in one step from poly(1,2-butadiene)-*block*-poly(1,4-isoprene) and exhibit molecular order at room temperature over a range of epoxide contents.[21] The 1,2PB block, much like the aliphatic PEP block of PEP−PEO, is immiscible with the epoxy resin while the epoxidized PIOx*n* block not only provides miscibility with the uncured resin but also presents numerous reactive sites for chemical reaction with the curing epoxy resin. The potential for covalent stitching of the copolymer to the epoxy network additionally provides the opportunity to examine the effects of such linkages upon the ultimate properties of the resulting resin.

Asymmetric amphiphiles, including surfactants, lipids, and block copolymers, are known to form interesting micellar and vesicular structures in blends and in solution,[22,23] but the formation of such inclusions in rigid thermosets is heretofore unreported.[24] Structural similarities between block copolymers and the smaller classes of amphiphiles suggest that asymmetric copolymers should self-assemble in epoxy blends into similar interesting morphologies at low concentrations and into ordered morphologies at higher concentrations. Asymmetric, nonreactive PEP−PEO copolymers can be readily prepared through the standard anionic polymerization/hydrogenation sequence.[25] Likewise, asymmetric, reactive BIx*n* copolymers can be prepared by the selective epoxidation of asymmetric 1,2PB-1,4PI copolymers.

In addition to anionic polymerization, nitroxide-mediated living free radical polymerization can be used to prepare block copolymers with characteristics suitable for modification of epoxy resins.[26] The recent development of the unimolecular initiator 2,2,5-trimethyl-3-(1′-phenylethoxy)-4-phenyl-3-azahexane (**1**) by Hawker and co-workers has enabled the controlled polymerization of both acrylic and diene monomers (Scheme 1).[27,28] By utilizing this alternate polymerization chemistry in conjunction with the knowledge drawn from the study of more conventional polymers in epoxy, specific shortcomings of the above anionically prepared copolymers can be targeted. Specifically, initiator **1** has enabled the preparation of diblock copolymers wherein one block (epoxy-reactive/epoxy-miscible) is a random copolymer of methyl acrylate (MA) and glycidyl methacrylate (GMA) and the other block (epoxy-immiscible) is PI with predominantly 1,4-addition (Scheme 1).

The ordering effects and reactivity of these copolymers in epoxy resins have been studied through a combination of small-angle X-ray scattering (SAXS) measurements, transmission electron microscopy (TEM), differential scanning calorimetry (DSC), and solubility studies. The goals of this study are twofold: (1) to demonstrate the universality of the ability of amphiphilic block copolymers to template thermosetting materials and (2) to demonstrate that the incorporation of epoxy-reactive sites in these block copolymers does not significantly alter this ordering behavior so that the effect of chemical stitching on the physical properties of the ordered resins can be examined.

Experimental Section

Materials. Symmetric poly(1,2-butadiene)-*block*-poly(epoxy-1,4-isoprene-*ran*-1,4-isoprene) (1,2PB-1,4PIOx: BIx*n*, where *n* represents the percentage of isoprene repeat units epoxidized) copolymers were prepared from poly(1,2-butadiene)-*block*-poly(1,4-isoprene) (M_n = 21 000; 50 wt % PI; I block: 94% 4,1-addition; B block: 83% 1,2-addition; $M_w/M_n < 1.05$) as described previously.[21] Asymmetric poly(1,2-butadiene)-*block*-poly(epoxy-1,4-isoprene-*ran*-1,4-isoprene) (**$B_{0.8}$Ix87**: M_n = 15 600 g/mol; $\phi_I \approx 0.8$; 75 wt % PI; precursor PI block: 94% 4,1-addition; precursor B block: 97% 1,2-addition; $M_w/M_n < 1.05$) and poly(epoxy-1,4-isoprene) (Ix100) were prepared from the appropriate parent copolymer by the same route.[21] Poly(ethylene oxide)-*block*-poly(ethylene-*alt*-propylene) (PEO−PEP: **OP4**: M_n = 2100, f_{PEO} = 0.26, wt % PEO = 32.1, M_w/M_n = 1.14) was prepared according to a previously described anionic polymerization−hydrogenation−anionic reinitiation scheme.[25] ^1H NMR peak integration values were used to calculate block mole fractions. Volume fractions, *f*, were determined from published densities for PEP (ρ = 0.790 g/cm^3) and PEO (ρ = 1.064 g/cm^3) at 140 °C[29] or, for PIOx*n*, approximated from group additivities ($\rho \approx$ 1.07 g/cm^3).[30]

Poly(bisphenol A-*co*-epichlorohydrin), epichlorohydrin end-capped, MW = 348 g/mol (BPA348, Aldrich), and 4,4′-methylenedianiline, (MDA, Aldrich) were used as received.

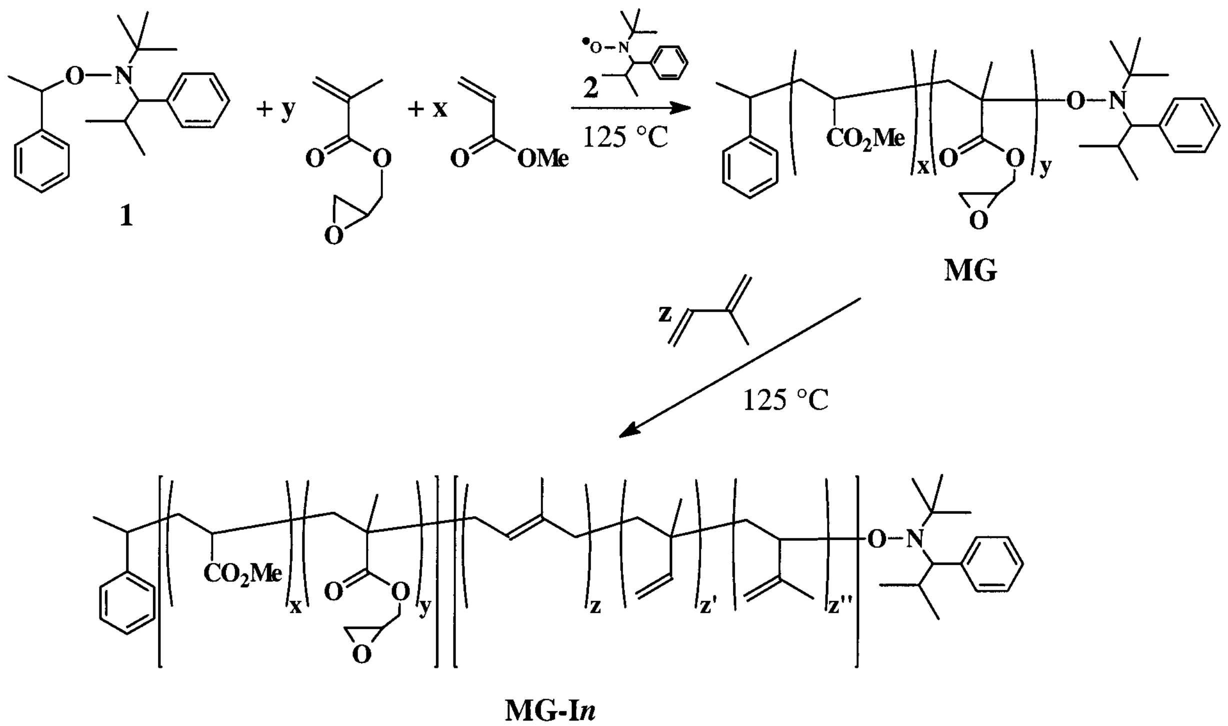
2,2,5-Trimethyl-4-phenyl-3-azahexane-3-nitroxide (**2**) and 2,2,5-trimethyl-3-(1′-phenylethoxy)-4-phenyl-3-azahexane (**1**) were prepared as described by Benoit et al.[27] Methyl acrylate (MA) and glycidyl methacrylate (GMA, Aldrich) were eluted through basic alumina prior to use. Isoprene (Acros) for free-radical polymerizations was distilled under reduced pressure over CaH_2 before use.

Preparation of Poly(methyl acrylate-*co*-glycidyl methacrylate)-*b*-polyisoprene (MG-I*n*). Nitroxide-mediated free radical polymerizations were carried out according to literature procedures.[26−28] These copolymers are referred to as MG-I*n*, where *n* represents the approximate volume fraction of polyisoprene in the final copolymer.

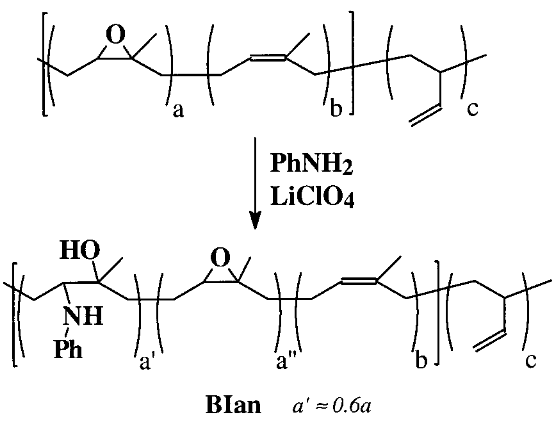
For the preparation of **MG**, a solution of nitroxide **2** (19 mg, 0.09 mmol) and alkoxyamine initiator **1** (0.55 g, 1.7 mmol) in methyl acrylate (10.25 g, 119 mmol) and glycidyl methacrylate (4.2 g, 29.5 mmol) was degassed with three "freeze−pump−thaw" cycles and sealed under argon. The sealed tube was immersed in an oil bath preheated to 125 °C for 20 h and allowed to cool. ^1H NMR of the crude polymerization mixture showed about 71 mol % of MA and 93 mol % of GMA were converted to polymer in this time to yield a product with about 70 mol % MA. The solid polymer was dissolved in CH_2Cl_2 (10 mL) and precipitated into excess hexanes (800 mL). The white solid (10.6 g, 71%, 93% based on conversion) was collected, washed with MeOH, and dried in vacuo. ^1H NMR: M_n = 6600, mol GMA/mol polymer = 17.3; SEC (PS stds): M_n = 6340, M_w/M_n = 1.25; MALDI-TOF MS (indoleacrylic acid matrix): M_n = 6700, M_w/M_n = 1.24.

For the preparation of **MG-I70**, isoprene (8.4 g, 0.123 mol) was added to **MG** (1.0 g, 0.15 mmol), and the mixture was degassed with three "freeze−pump−thaw" cycles, sealed under argon, and heated at 125 °C for 86 h. The copolymer was dissolved in CH_2Cl_2 and precipitated into excess MeOH, then

Scheme 1



Scheme 2



redissolved in CH_2Cl_2, and precipitated into 8:2 MeOH/acetone. ^{1}H NMR: $M_n = 20\,150$; wt % PI = 67; SEC (PS stds.): M_n = 42 000, $M_w/M_n = 1.22$.

Sample Preparation. OP blends were degassed and melt-blended as described previously.[11] BPA348 and MDA were blended at a molar ratio of 2:1 to provide a stoichiometric balance between amine protons and epoxy groups. Cured samples were heated at 55 °C for 48 h and at 220 °C for 6 h.

BIx*n* and MG-I*n* blends (0.5 g total mass) were solvent cast from well-dissolved 10−15 wt % solutions in CH_2Cl_2 at room temperature overnight and then dried under vacuum for at least 16 h. Unless otherwise noted, the stoichiometry of reactive copolymer blends was calculated to give a 1:1 ratio between amine protons and total (BPA348 and BIx*n* or MG) epoxy groups. BIx*n* blends were cured through a two-stage process: at 55 °C for at least 48 h (low-*T* cure) and at 200 °C for 1 h (high-*T* cure). MG-I blends were cured at 100 °C for 24 h and 210 °C for 1 h.

Aniline Ring-Opening of BIx87.[31] Copolymer **BIx87** (0.50 g, 21.4 μmol, 2.83 mmol of epoxyisoprene), aniline (2.64 g, 28.3 mmol), and lithium perchlorate (0.30 g, 2.83 mmol) were dissolved in THF and heated at reflux for 27 h (see Scheme 2). Precipitation into MeOH afforded a glassy yellowish solid **BIan** (0.4 g). Approximately 61% of the copolymer epoxy groups were opened (^{1}H NMR). A small sample of the polymer was dissolved in CH_2Cl_2 and stirred with excess acetyl chloride and triethylamine for several hours, precipitated into methanol, and then analyzed by GPC, which showed a single unimodal peak. M_n (^{1}H NMR) ≈ 31 500. ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.4−7.4 (broad, C_6H_5N-), 3.0−4.2 (broad, C*H*OH and N*H*).

Small-Angle X-ray Scattering. Scattering patterns of Cu Kα X-rays from these samples were measured at the University of Minnesota on a custom-built system utilizing Franks mirror optics and a Rigaku RU-200BVH rotating anode generator. Two-dimensional diffraction patterns were collected on a multiwire detector at room temperature, corrected for response characteristics, and converted to one-dimensional format (intensity vs *q*, where $q = (4\pi/\lambda)\sin(\theta/2)$ is the scattering wavevector) by azimuthally averaging the data. The principal domain spacing (d^*) was determined by the relationship $d^* = 2\pi/q^*$, where q^* is the maximum of the primary order peak. Peak spacings and intensity ratios were compared with established parameters for given morphologies and used in combination with TEM images to determine blend morphologies. PEO/PIOx and epoxy are essentially contrast matched, and scattering arises between PEP or PB domains and PEO/epoxy or PIOx/epoxy domains.

Transmission Electron Microscopy (TEM). Real-space images of epoxy composite morphologies were obtained with TEM. Representative pieces of each sample were microtomed at room temperature with a diamond-knife equipped Reichert Ultra-microtome S. Thin (~90 nm) sections were floated on water and recovered on copper grids. PB domains of BIx*n* samples and PI domains of MG-I samples were stained with OsO_4. Stained samples were then imaged with a JEOL 1210 TEM at an accelerating voltage of 120 kV.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed at a heating rate of 10 K/min under nitrogen with a Perkin-Elmer DSC-7 calibrated with indium. Reaction exotherms were measured on the first heating scan, and glass-transition temperatures were measured on subsequent heating scans.

Results

Symmetric Reactive Block Copolymers. To enable an understanding of the behavior of BIx*n* copolymers in blends, the neat copolymers were first characterized by SAXS and DSC. Both **BIx87** and **BIx75** show lamellar scattering patterns at room temperature with primary spacings of 23.1 and 22.0 nm, respectively.[21] These lamellar morphologies are maintained up to 180 °C, but upon cooling the polymers are no longer soluble in typical good solvents (CH_2Cl_2, THF, toluene) as a result of thermal cross-linking. DSC analysis of copolymer **BIx87** shows a small exothermic transition (T_{onset} = 105 °C, $\Delta H \approx 42$ J/g of **BIx87**) at elevated temperature which is not apparent in a second heating scan of the same sample. Thermal analysis of homopoly(epoxy-1,4-isoprene) and homo-1,2PB suggests that the **BIx87** exotherm arises from thermal cross-linking of the 1,2PB block.[32,33] At higher temperatures (>200 °C), thermal cross-linking of epoxidized block is evident in the DSC trace. No order–disorder transition (ODT) is apparent below 180 °C by SAXS measurements for either **BIx87** or **BIx76**, well above temperatures at which cross-linking sets in. Plots of d^* vs $1/T$ for both polymers change slope in the same temperature range where the DSC exotherm appears. Copolymer **BIx46**, in which the blocks are only weakly segregated, shows an ODT (SAXS) between 30 and 40 °C.

(i) Miscibility. As the miscibility of the polar block of the templating copolymer with the uncured epoxy components is crucial to inducing order in the thermoset, the miscibility of ordered BIx*n* copolymers with epoxy components as a function of *n* was examined. A series of blends of BIx*n* (20 wt %) with BPA348/MDA was prepared for $n = 46$, 59, 73, 87, and 95. The optical transparency of samples with $n > 73$ was indicative of the homogeneity of these uncured blends and therefore the miscibility of highly epoxidized BIx*n* blocks with the epoxy precursors. The **BIx59** blend was uniformly opaque due to phase separation on length scales greater than ~100 nm, while the **BIx46** blend appeared to have macrophase-separated into millimeter-scale epoxy-rich transparent regions and copolymer-rich regions. As the epoxy content of the PIOx block decreases, its immiscibility in the epoxy resin approaches that of the immiscible parent diene block.

(ii) Phase Behavior. BIx*n* blends were subjected to a two-stage cure: a low-temperature cure (55 °C, 48 h) well below cross-linking temperatures and T_{ODT}, but above the melting point of BPA348 (mp ≈ 41–44 °C), was followed by a high-temperature treatment (200 °C, 1 h) to ensure complete curing of the composites. Phase behavior as a function of both epoxy content (*n*) and copolymer weight fraction was examined by SAXS prior to cure and after each stage of cure. TEM images of cured specimens were utilized for verification of the determined morphologies.

Blends of copolymers with highly epoxidized ($n > 85$) PIOx*n* blocks remain homogeneous and ordered after cure and exhibit phase behavior which qualitatively resembles that of the symmetric OP copolymers previously examined.[8] Neat **BIx87** self-assembles into a lamellar (L) morphology with a principal spacing $d^* =$ 23.1 nm at room temperature (Figure 2a).[21] As BPA348 and MDA selectively swell the PIOx block, interfacial curvature increases as cylindrical (H), spherical (S), and micellar (M) morphologies are expressed. The presence of local SAXS maxima at values of $\sqrt{4}q^*$ and $\sqrt{9}q^*$ point to the presence of lamellar morphologies at high copolymer concentrations (Figure 2b). At concentrations between 40 and 70 wt %, scattering maxima at ratios of $q^*{:}\sqrt{4}q^*{:}\sqrt{7}q^*$ indicate self-assembly of the blends into hexagonal cylindrical morphologies (Figure 2c,d). At lower concentrations, the breadth of the scattering maxima preclude differentiation between ordered spherical and spherical micellar arrangements, but it is clear from the length scales involved that the spheres are well-dispersed in the epoxy matrix (Figure 2e,f).

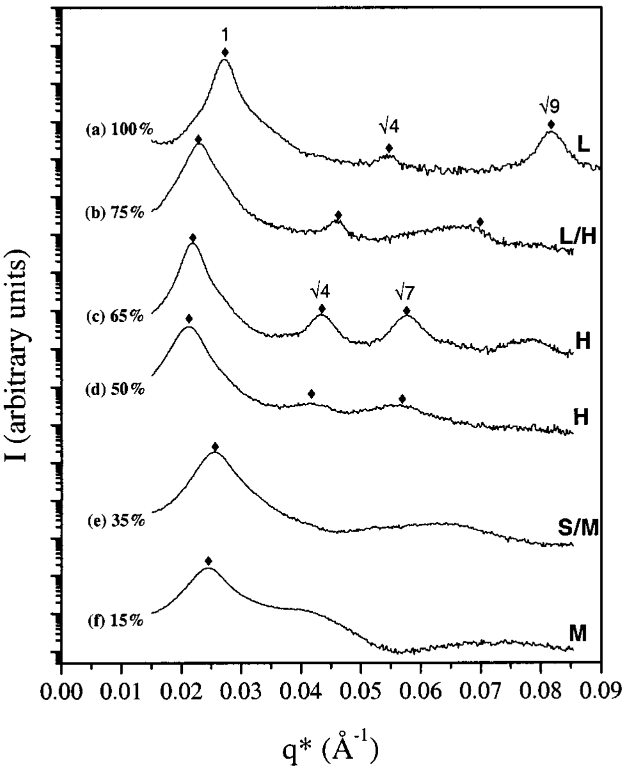


Figure 2. SAXS patterns for uncured **BIx87**/BPA348/MDA blends: (a) **BIx87**, (b) 75 wt %, (c) 65 wt %, (d) 50 wt %, (e) 35 wt %, and (f) 15 wt % **BIx87**. Marked values indicate multiples of q^*. Unlabeled markers correspond to multiples annotated on patterns above given pattern. Assigned microstructures: **L**, lamellae; **H**, hexagonal cylinders; **S**, ordered spheres; **M**, spherical micelles. Patterns are progressively shifted 2 decades vertically for clarity.

After complete cure, the same range of morphologies is retained yet, as was observed with symmetric OP copolymers, there is a shift toward morphologies with decreased interfacial curvature (Figure 3). For example, at 65 wt % **BIx87**, the uncured blend self-assembles into a cylindrical morphology (Figure 2c). After completion of the curing process, SAXS patterns for this blend exhibit maxima in the ratio $q^*{:}\sqrt{4}q^*{:}\sqrt{9}q^*$, consistent with the less-curved lamellar morphology (Figure 3b).

TEM images clearly show the transition from lamellar to spherical morphologies in cured composites as copolymer concentration decreases (Figure 4). In the cured composites, it is again difficult to determine where (and if) the transition from disordered spherical micelles to ordered spheres on a bcc lattice occurs. Despite the broad scattering maxima for a composite at 20 wt % **BIx87**, it is apparent from the TEM image that the copolymer spheres are well-dispersed in the epoxy resin and that there is most likely some degree of short-range order to the arrangement (Figure 4c).

Blends of **BIx75**, while initially homogeneous over a broad range of copolymer compositions, become heterogeneous after short curing times, indicating the occurrence of cure-induced phase separation on scales larger than the polymeric length scale. For example, TEM confirms the formation of large phase-separated inclu-

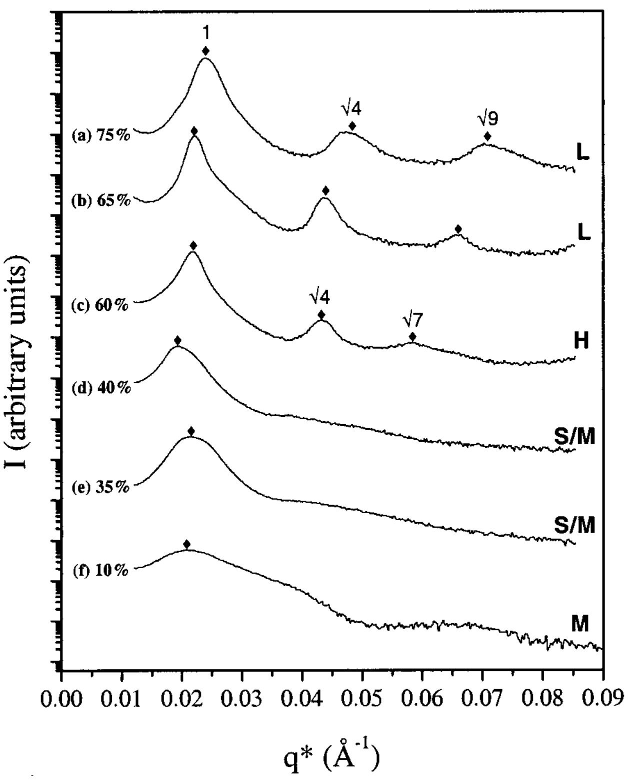


Figure 3. SAXS patterns for cured **BIx87**/BPA348/MDA blends: (a) 75 wt %, (b) 65 wt %, (c) 60 wt %, (d) 40 wt %, (e) 35 wt %, and (f) 10 wt % **BIx87**. Microstructures are assigned as in Figure 2. Patterns are progressively shifted 2 decades vertically for clarity.

sions in a cured 5 wt % **BIx75** blend in which the lamellar architecture of the microphase-separated copolymer is clearly visible (Figure 5). Blends of BIx*n* with $n < 75$ remain phase-separated throughout the curing process on length scales too large for analysis by SAXS.

(iii) Reactivity. The reactivity of PIOx*n* epoxy groups with the curing epoxy resin was probed through thermal analysis and solubility studies. Initial attempts at following the reaction by monitoring changes in blend FT-IR spectra during cure were thwarted by the extensive overlap of resin absorbance bands with copolymer bands.

Blends of **BIx87** (0−40 wt %) with BPA348 and MDA were analyzed by DSC to examine the reactivity of copolymer epoxy groups during cure. **BIx87** blends exhibit two distinct irreversible exotherms in initial heating scans (Figure 6). Subsequent scans show no residual reactivity and allow measurement of the T_g of the copolymer−epoxy composite. The lower temperature exotherm (Figure 6, T_1, $T_{peak} = 131-145$ °C, $\Delta H \leq 105$ kJ/mol of BPA348 epoxy groups) corresponds to the cure exotherm for unmodified BPA348/MDA epoxy resin ($T_{peak} = 163$ °C, $\Delta H \approx 110$ kJ/mol of BPA348 epoxy groups). The relative area of the higher temperature exotherm (Figure 6, T_2, $T_{peak} = 263-287$ °C; $\Delta H \leq 35$ kJ/mol of BIx*n* epoxy group) increases as larger amounts of copolymer **BIx*n*** are included in the blend, suggesting that this thermal transition arises from reaction of the MDA curing agent with the less reactive **BIx87** epoxy groups.[34] The chemical stability of the triply substituted oxirane ring is corroborated by a recent synthetic report.[35] A similar trend in peak areas and temperatures is observed for **BIx75** blends. The epoxy resin cure exotherm presumably masks the much smaller exotherm ascribed to PB cross-linking ($T_{peak} \approx 105$ °C); it seems likely that the occurrence of thermal cross-linking within PB domains is not hindered by epoxy blending.

T_g's for DSC-cured samples remain close to that of the unmodified resin ($T_g \approx 165$ °C) up to about 10 wt % **BIx87** but decrease with increasing copolymer content to 98.5 °C at 40 wt % **BIx87**. Notably, the addition of up to 10 wt % copolymer to the epoxy resin leads to little change in the T_g of the resulting composite.

To verify the origins of the two cure exotherms, blends containing a stoichiometric equivalence of MDA amine protons and BPA348 epoxy groups ($[NH]_{MDA} = [epoxy]_{BPA348}$) were prepared. These blends lack the high-*T* exotherm (Figure 7b) present in blends containing sufficient curing agent to react with both BPA and **BIx87** epoxy groups (Figure 7a, T_2). To provide additional evidence of PIOx/MDA reaction, copolymer **BIx87** was prereacted with an excess of aniline, and the resulting copolymer **BIan** was isolated before blending with BPA348 and MDA (Scheme 2). DSC traces for the resulting blends show a loss of the T_2 exotherm accompanied by the appearance of a small exotherm at $T = 260$ °C (T_2) and a broadening of the lower temperature exotherm when compared with the standard stoichiometric blends (Figure 7c).

Because the solubility behavior of a cross-linking polymerization system (i.e., an epoxy-based thermoset) is intimately related to the extent of polymerization, the conclusions drawn from the presence of a bimodal cure exotherm were tested through dissolution studies on partially and fully cured blends. Blends of **BIx87** (5−78.1 wt %) with BPA348/MDA were subjected to a low-temperature cure at 55 °C for 48 h and tested for solubility in methylene chloride. Blends at less than 50 wt % copolymer were insoluble after this treatment. The 60 wt % blend produced a uniform cloudy suspension, but blends with block copolymer compositions above 60 wt % copolymer appeared entirely soluble. After the completion of cure at 200 °C for 1 h, none of the blends were soluble.

Asymmetric Reactive Block Copolymers. Uncured blends of asymmetric OP block copolymers with epoxy exhibit phase behavior in line with that predicted from mean-field theory for blends of a block copolymer with a block-selective solvent.[36] Neat **OP4** self-assembles such that a hexagonal array of PEO cylinders is formed within a PEP matrix. Added epoxy swells the minority PEO domains and results in interfacial flattening as gyroid and lamellar morphologies are progressively formed with increasing epoxy concentration. As the lamellar spacing increases with further dilution by epoxy, the loss of interlamellar interactions eventually leads to the formation of vesicular inclusions of **OP4** in the epoxy matrix. The vesicle walls consist of a bilayer of PEP domains from which PEO chains extend inward and outward toward epoxy domains.[24]

As noted above in the comparison of symmetric **BIx87** blends to symmetric PEP−PEO blends, the phase behavior of asymmetric copolymer **B$_{0.8}$Ix87** in epoxy blends is very similar to that seen with asymmetric OP copolymers. The neat copolymer **B$_{0.8}$Ix87** self-assembles into minority domains of PIOx within a continuous PB matrix—the breadth of the SAXS maxima and shape of the pattern suggest that the PIOx domains take the form of poorly ordered spheres, but this is by no means a conclusive determination. As BPA348 and MDA are added, the PIOx domains are selectively swollen, and

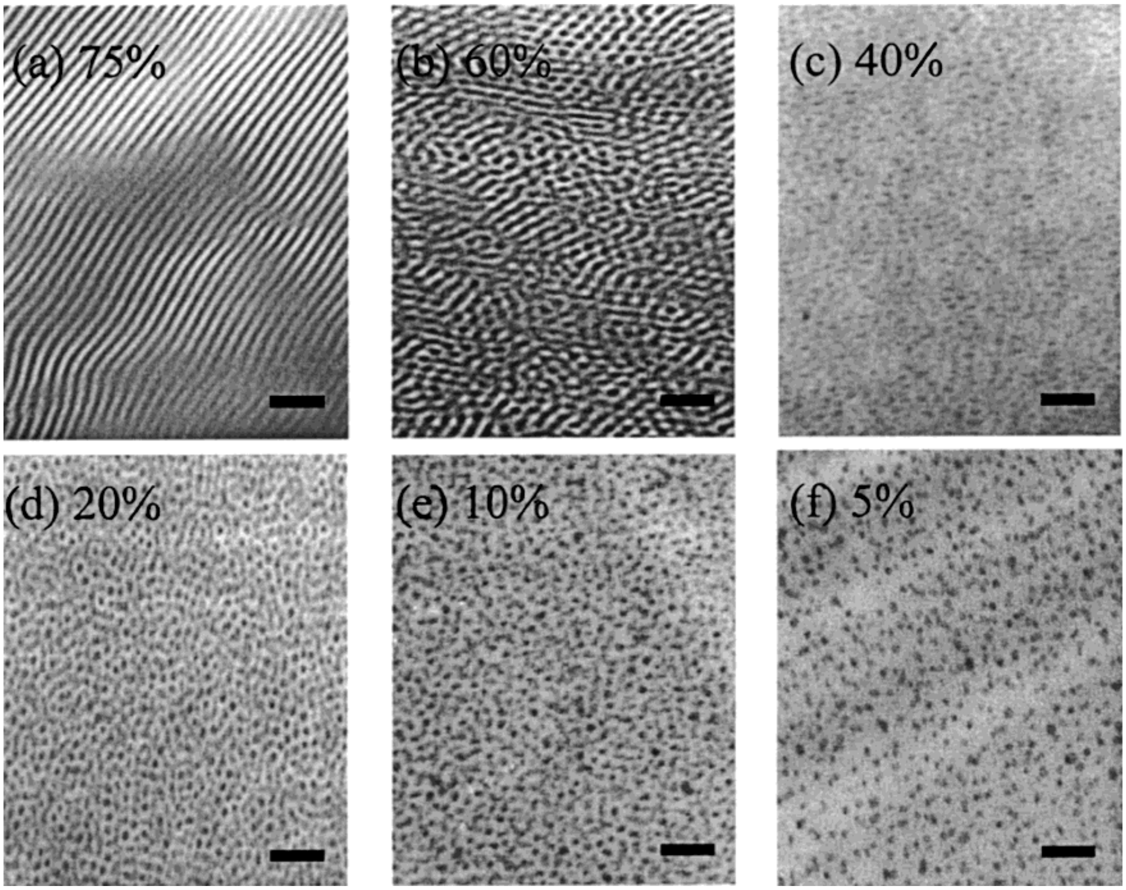


Figure 4. TEM images of cured **BIx87**/epoxy blends: (a) 75 wt %, (b) 60 wt %, (c) 40 wt %, (d) 20 wt %, (e) 10 wt %, and (f) 5 wt % **BIx87**. Scale bars = 100 nm.

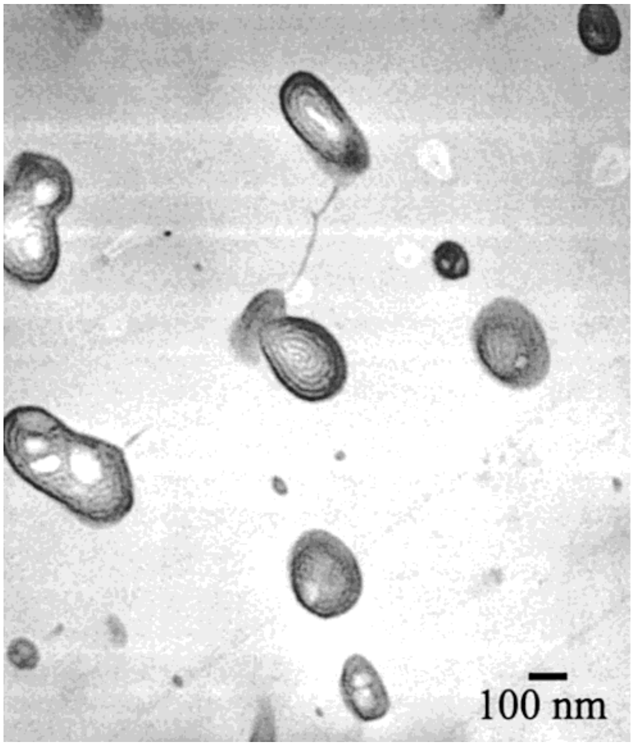


Figure 5. TEM image of cured 5 wt % **BIx75**/epoxy blend.

the equilibrium morphology shifts as epoxy content increases (Figure 8). There is a small concentration window at high copolymer concentration where the SAXS maxima (q^*:$\sqrt{4}q^*$:$\sqrt{7}q^*$) indicate adoption of the H morphology (Figure 8b). Between 50 and 80 wt %, the presence of scattering maxima at integral values of q^* attests to formation of lamellar microstructures (Figure 8c–f). At 40 wt % **B$_{0.8}$Ix87**, there is lamellar character to the scattering pattern, but the pattern is most likely complicated by the formation of vesicular structures as the long-range order of the lamellae becomes diluted (Figure 8g). At lower copolymer concentrations, the SAXS maxima shift to progressively lower q^* values as lamellae are swollen into vesicular structures (Figure 8h–j). DSC cure traces for epoxy/

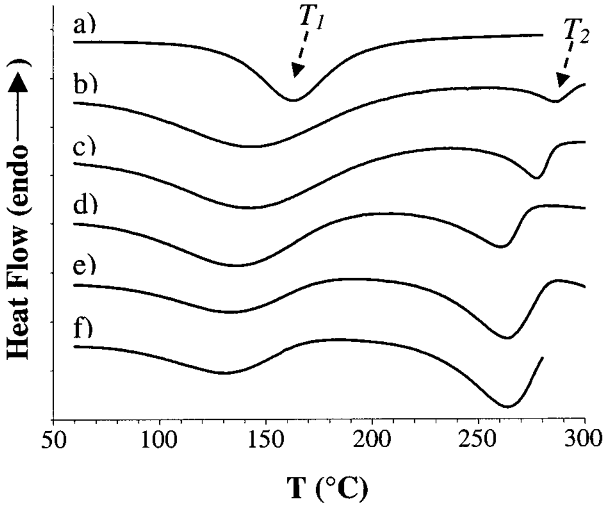


Figure 6. DSC heating scans for **BIx87**/BPA348/MDA blends: (a) 0 wt %, (b) 5 wt %, (c) 10 wt %, (d) 20 wt %, (e) 30 wt %, and (f) 40 wt % **BIx87**. T_1 and T_2 represent low- and high-temperature exotherms, respectively. Traces shifted vertically for clarity.

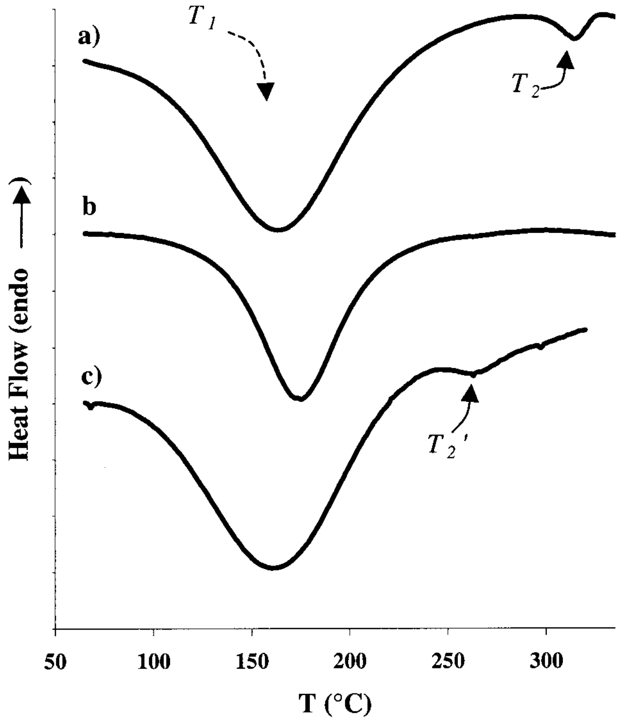


Figure 7. DSC heating traces for (a) 5 wt % **BIx87**/BPA348/MDA blend with enough curing agent to react with both BPA348 and **BIx87** epoxy groups ($[\mathrm{NH}]_{\mathrm{MDA}} = [\mathrm{epoxy}]_{\mathrm{BIx87}} + [\mathrm{epoxy}]_{\mathrm{BPA348}}$), (b) 5 wt % **BIx87**/BPA348/MDA blend with only enough curing agent to react with BPA348 epoxy groups ($[\mathrm{NH}]_{\mathrm{MDA}} = [\mathrm{epoxy}]_{\mathrm{BPA348}}$), and (c) 5 wt % **BIan**/BPA348/MDA blend (see text).

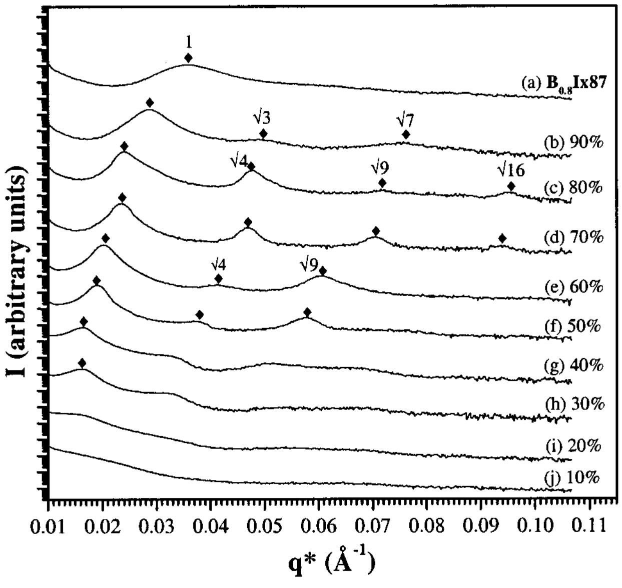


Figure 8. SAXS patterns for uncured **B$_{0.8}$Ix87**/BPA348/MDA blends: (a) **B$_{0.8}$Ix87**, (b) 90 wt %, (c) 80 wt %, (d) 70 wt %, (e) 60 wt %, (f) 50 wt %, (g) 40 wt %, (h) 30 wt %, (i) 20 wt %, and (j) 10 wt % **B$_{0.8}$Ix87**. Markers indicate multiples of q^*. Patterns are progressively shifted 2−3 decades vertically for clarity.

B$_{0.8}$Ix87 blends show two separate exotherms as observed for symmetric **BIx87** blends.

TEM images of cured dilute blends of **B$_{0.8}$Ix87** with epoxy show the formation of spherical vesicles with radii of several hundred nanometers and wall widths on the order of 10 nm (Figure 9). The spatial density of vesicles decreases as copolymer concentration is lowered, and as the concentration of included copolymer is decreased below 5 wt %, the average vesicle diameter decreases, and at 0.5 wt % copolymer, what appear to be spherical micelles are the dominant feature.

MG-I Copolymers. To increase the reactivity of the epoxy reactive block as well as the 1,4-content of the epoxy-immiscible block (thereby improving elastomeric properties of the included phase and potentially allowing reactive etching of the resulting composite), an alternate class of reactive copolymer was prepared. Glycidyl methacrylate was chosen as the reactive monomer: the singly substituted glycidyl epoxy group is many times more reactive than the triply substituted PIOx epoxides, the methacrylate functionality is readily polymerized by a variety of methods, and the monomer is commercially available. Though block copolymers of methacrylates, including glycidyl methacrylate, and dienes with low polydispersity indices have been successfully prepared through living anionic polymerization, these syntheses require stringent monomer purification and careful exclusion of oxygen and moisture.[37,38] The recent extension of nitroxide-mediated living free radical polymerization methods to allow polymerization of monomers other than styrene suggests these techniques can provide an alternate route to block copolymers containing GMA and 1,4-polydiene blocks.[27,28]

MG-I copolymers were prepared by the sequential nitroxide-mediated free-radical polymerization of a methyl acrylate/glycidyl methacrylate mixture and isoprene (Scheme 1). Up to 30 mol % glycidyl methacrylate has been incorporated into the first block without serious increase in polydispersity ($M_w/M_n < 1.3$).

SAXS patterns from **MG-I** copolymers indicate that segregation between the two blocks occurs. For example, a series of block copolymers prepared by the growth of various lengths of PI blocks from a single MG block (**MG**: 30 mol % GMA; $M_n = 6700$ g/mol) show SAXS q^* values which increase smoothly as the lengths of the PI blocks and the overall MWs of the polymers increase (Figure 10). Because the SAXS maxima exhibited are relatively broad and higher order reflections are not readily identifiable, conclusive determination of the equilibrium morphologies of these polymers has not been possible.

TEM images of cured dilute **MG-I**/epoxy blends show the liquidlike dispersion of micelles typical for the related anionically prepared systems. For example, blends of polymer **MG-I70** ($M_n = 20\,150$ g/mol; 67 wt % PI; $M_w/M_n = 1.2$) form micelles at low concentrations and more densely packed spherical arrangements at higher copolymer concentration (Figure 11). Remarkably, both TEM and SAXS data confirm that these copolymers form dilute spherical micelles at low concentration despite the high volume fraction of polyisoprene (Figure 11a). This behavior presumably results from specific interactions (e.g., hydrogen bonding) between the polar moieties of the epoxy resin and the carbonyl groups of the MG block. At higher copolymer concentrations, the spherical micelles become more densely packed (Figure 11b), and at a level of 30 wt % **MG-I70** the spheres appear to exhibit long-range order (Figure 11c).

The increased reactivity of the glycidyl methacrylate epoxy group toward the curing agent is evidenced by a single exotherm in the cure DSC trace (Figure 12). While the number of copolymer epoxy groups in the 47 wt % **MG-I50** blend is much lower than in the 50 wt % **BIx87** blend used for comparison in Figure 12, **BIx87** blends with a copolymer epoxy group concentration

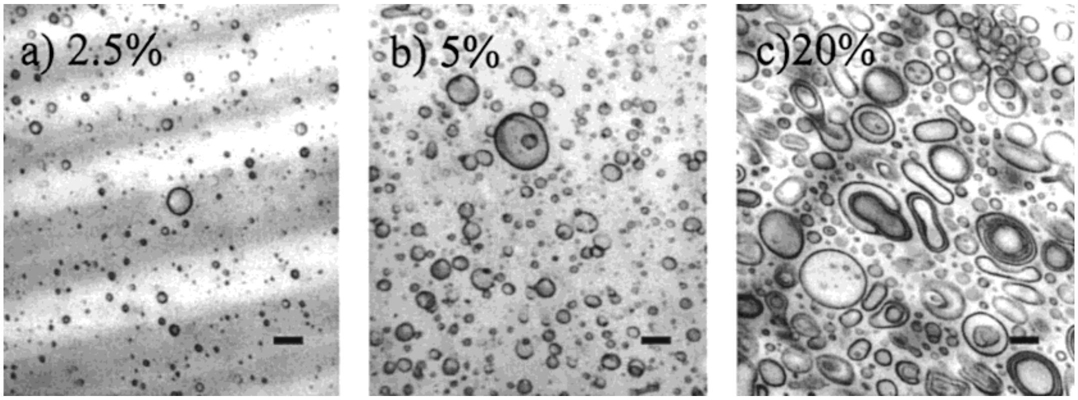


Figure 9. TEM images of cured $B_{0.8}Ix87$/epoxy blends: (a) 2.5 wt %, (b) 5 wt %, and (c) 20 wt % $B_{0.8}Ix87$. Scale bar = 200 nm.

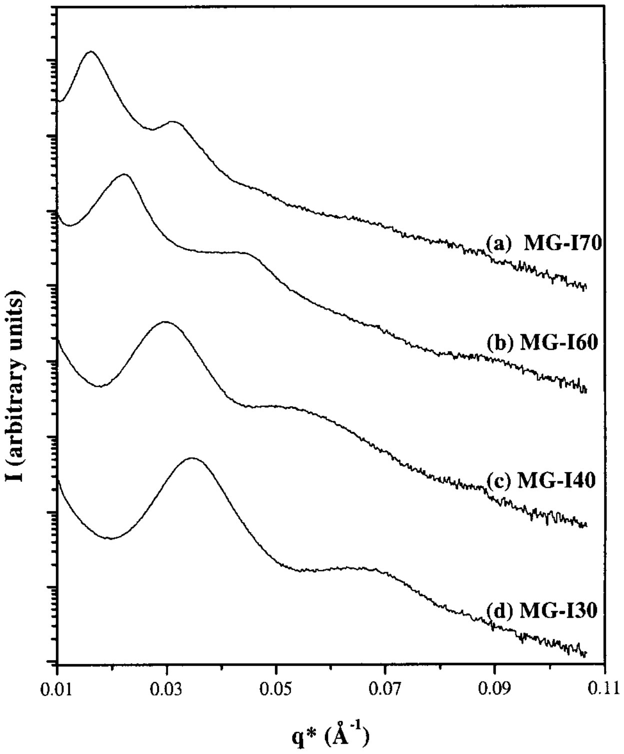


Figure 10. SAXS patterns for MG-I block copolymers prepared from polymer **MG** (M_n = 6600; 70 mol % MA): (a) **MG-I70** (M_n = 20 150; ϕ_I = 0.7), (b) **MG-I60** (M_n = 13 550; ϕ_I = 0.6), (c) **MG-I40** (M_n = 10 200; ϕ_I = 0.4), and (d) **MG-I30** (M_n = 9050; ϕ_I = 0.3).

equivalent to that in the **MG-I50** blend still exhibit a noticeable higher temperature exotherm.

Attempts at providing definitive evidence of GMA co-cure through FTIR monitoring during cure were again futile due to epoxy-band overlap between copolymer and resin and carbonyl-band overlap between GMA and MA.

Discussion

Phase behavior of block copolymer/epoxy blends can be roughly modeled by treating each system as a solution of a copolymer in a block-selective solvent which evolves during cure, through a copolymer/block-selective homopolymer blend, into an infinite epoxy network containing inclusions of copolymer. This analysis is greatly complicated at low copolymer concentration, however, by factors arising from the divergence of epoxy MW to infinity and the corresponding decrease in copolymer mobility as network formation progresses.

While the absence of macrophase separation in these copolymer-modified systems is potentially the result of both kinetic and thermodynamic factors, it is likely that the rigidification of the epoxy phase arising during network growth plays a major factor in the prevention of macrophase separation. At high copolymer concentration, however, the rigid epoxy domains make up the minority phase of a given morphology and mobility within the system is not as severely limited. The heightened mobility in these composites is expected to allow ready phase separation of the curing epoxy domains and disruption of the copolymer-induced order in the uncured blend. While the BIx*n* systems examined do not appear to undergo macrophase separation at high copolymer concentration, possibly due to thermal cross-linking of the immiscible PB phase, loss of order has been observed in cured blends of **OP4** at high copolymer concentrations.

Because of the tendency of noncontinuous epoxy domains to phase-separate and because the main thrust of these studies is to prepare materials with the epoxy resin as the matrix component, we have directed our examination of cured reactive systems toward the dilute copolymer regime.

Phase Behavior. Uncured epoxy/OP phase behavior has been understood to result from the morphological changes induced as PEO domains, anchored by epoxy immiscible PEP chains, are swollen into a “wet-brush”-type structure by epoxy components.[11,39] Phase behavior in the uncured state corresponds well with the behavior predicted and observed for blends of block copolymers with a solvent selective for one block. During cure, PEO blocks are desolvated by the growing epoxy network, and a transition to the “dry brush” state is induced as the nanostructured epoxy network forms (Figure 13A).

In the case of symmetric **BIx87** (and OP) blends, the block copolymer self-assembles into lamellae, and interfacial curvature is induced by addition of epoxy components to epoxy-miscible (PEO/PIOx) domains. Phase transitions (with PEP or 1,2PB as the minority component) in the direction of increasing interfacial curvature, from lamellae (to gyroid with low-MW OP) to cylinders to spheres, result as epoxy concentration is increased. Once the epoxy concentration approaches a large enough value (dependent upon the molecular weight of the copolymer), long-range ordering of the spheres is disrupted, but the spherical micelles of copolymer remain well-dispersed in the epoxy matrix (for example, see Figure 4).

Examination of the phase behavior of BIx*n* indicates that highly epoxidized isoprene blocks ($n > 85$) clearly

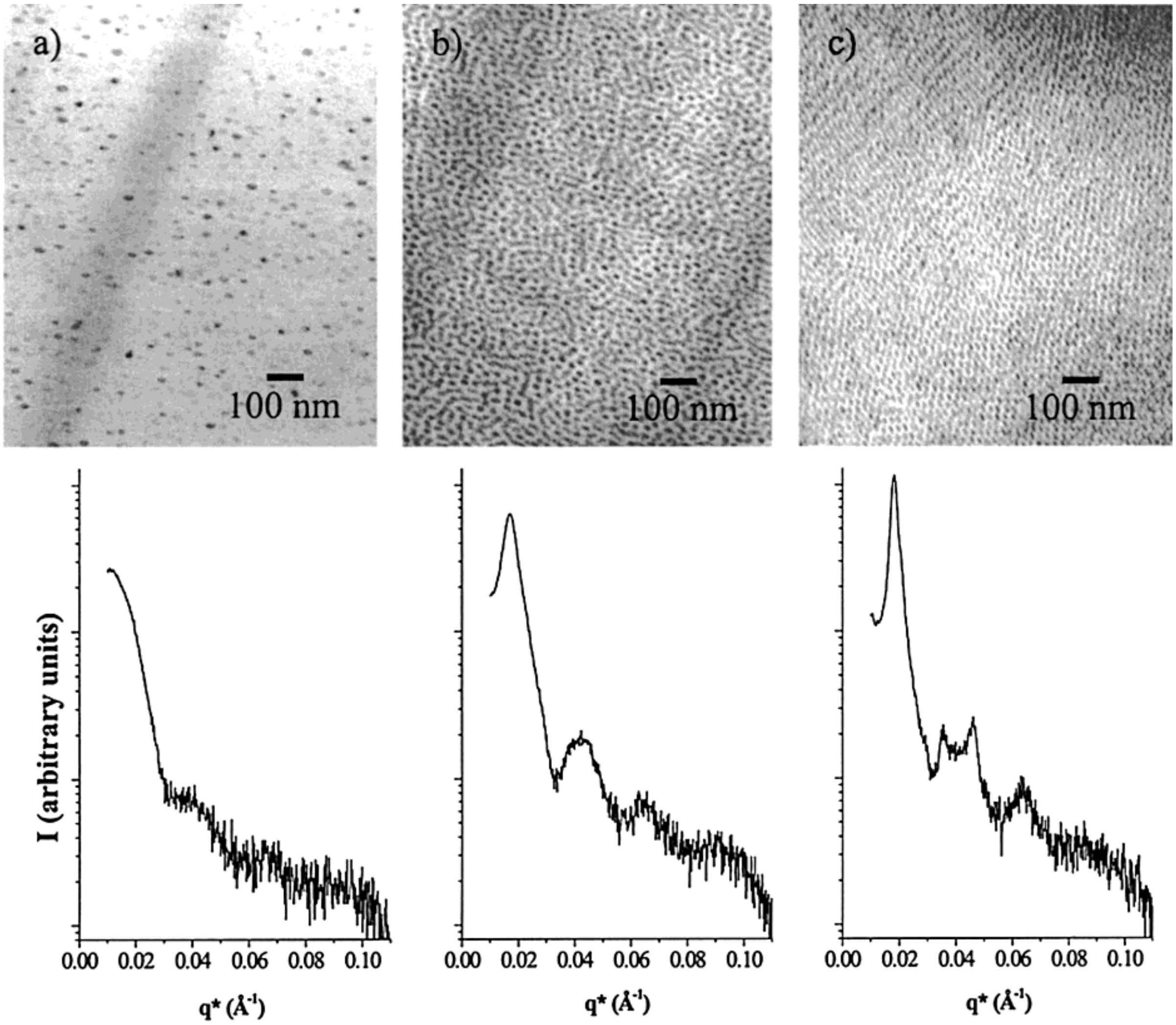


Figure 11. TEM images and SAXS patterns for cured **MG-I70**/epoxy blends: (a) 5 wt %, (b) 20 wt %, and (c) 30 wt % **MG-I70**.

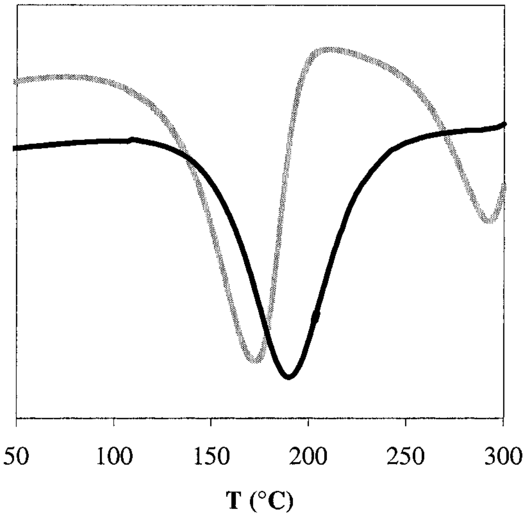


Figure 12. DSC heating traces for cure of 47 wt % **BIx87** (gray) and 50 wt % **MG-I50** (black) blends with BPA348/MDA.

function identically to PEO blocks in their ability to template epoxy resin: the expected range of ordered structures is observed by both SAXS and TEM (Figures 2−4), and no macrophase separation is seen to occur. The gyroid phase is not observed, most likely as a consequence of the high MW of BIx87, the strong repulsion between PB and PIOx blocks, and the relatively small composition window wherein the gyroid morphology is predicted to occur.[7]

In the case of OP blends, the change of f_{PEO} to 0.26 in **OP4** blends results in a range of ordered microstructures consistent with the wet-brush model, but the asymmetry of the copolymers results in access to a different segment of the range of diblock copolymer morphologies. **OP4** self-assembles into hexagonally packed cylinders of PEO in a PEP matrix. Addition of BPA348 to the PEO cylinders forces phase transitions to geometries of reduced interfacial curvature to accommodate the increased size of the PEO/BPA348 domains and results in morphological transitions from hexagonally packed cylinders to gyroid to lamellae. At lower copolymer compositions, the equilibrium lamellar morphology is diluted and ultimately collapses into disordered vesicular inclusions of **OP4** in epoxy. The dilution of lamellae into vesicular structures in this system is analogous to the dilution of ordered spheres into disordered spherical micelles in the symmetric systems.[36,40]

Similar trends are evident in blends of asymmetric **B$_{0.8}$Ix87** with epoxy. Cylindrical PIOx domains of the copolymer are swollen by epoxy components through lamellar and vesicular morphologies as the concentration of epoxy is increased. Again, the gyroid phase is not observed, most likely for the same reasons outlined above for symmetric blends. Vesicular inclusions as a dominant feature have been observed in cured blends

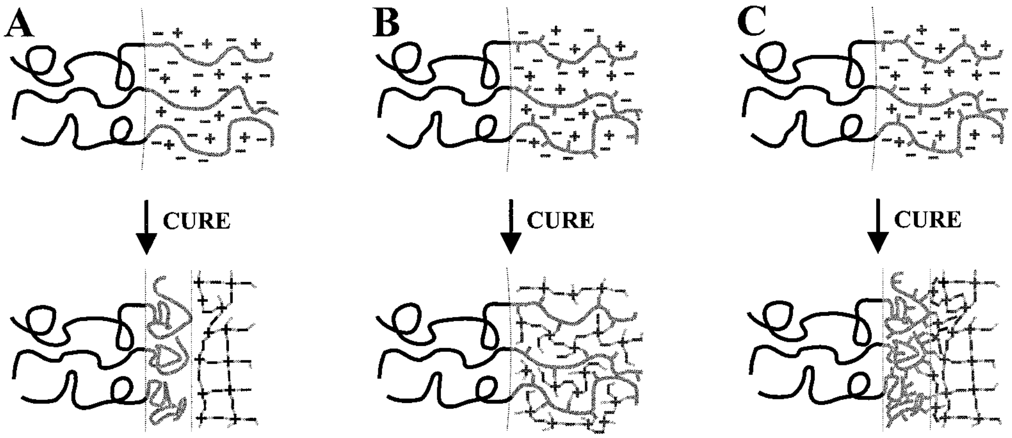


Figure 13. Comparison of microphase-separation processes during cure of nonreactive OP copolymers (A) and reactive copolymers: copolymer cures within epoxy matrix (B) or copolymer cures interfacially after expulsion from epoxy phase (C).

at compositions containing as low as 2.5 wt % **B$_{0.8}$Ix87** (Figure 9). As the concentration of copolymer is decreased below this level, the size of the vesicular inclusions decreases, and spherical micelles appear to become the major form of copolymeric inclusion. This transition between two disordered, but well-dissolved, states is anticipated from results obtained from studies of PS-*b*-PI/PS blends.[41] The absence of an intermediate cylindrical micellar phase ("wormlike" micelles) presumably is a consequence of the large copolymer MW relative to the epoxy MW.

Reactivity. The clear separation between the two cure exotherms in DSC traces for **BIx87** copolymers suggests that a two-stage cure is effected by the curing schedule used (Figure 6), wherein the BPA348/MDA cure reaction goes to completion prior to reaction of the remaining MDA with the less-reactive BIx*n* epoxy groups. To test this model, a ternary blend of **BIx87** (5 wt %) with BPA348/MDA containing a 1:1 molar ratio of amine hydrogens to BPA348 was analyzed by DSC (Figure 7). If a two-stage curing process is operative, the supply of amine groups in these blends should be exhausted by reaction with BPA348 groups, leaving none to react with **BIx87** epoxy groups. The absence of a noticeable higher temperature exotherm supports this two-stage cure mechanism and precludes significant opening of copolymer epoxy groups by epoxy resin alcohol groups. Likewise, when ~60% of **BIx87** epoxy groups are opened with aniline to give copolymer **BIan** (Scheme 2), the area of the lower *T* exotherm in the resulting blends broadens as the resulting secondary amines react with BPA348 at roughly the same rate as MDA does, and the area of the higher *T* exotherm decreases as the number of available reactive copolymer epoxy groups is reduced. These observations suggest that the epoxidized copolymer is capable of curing with the epoxy resin but that the reaction between the MDA curing agent and the copolymer occurs at a much slower rate than that between MDA and BPA348.

While calculation of exact values of ΔH for each cure reaction has proven difficult, it is apparent that ΔH_{cure} for BIx87/MDA is at least 50 kJ/mol less than ΔH_{cure} for BPA348/MDA on an epoxy-group basis. Although no residual reactivity is noted on subsequent DSC heating scans, the difference in calculated ΔH values suggests that complete reaction of BIx87 epoxy groups with MDA most likely does not occur, especially considering the rigidity of the resin at the stage of cure where copolymer cure begins.

Despite the likelihood of incomplete cure, it is apparent that sufficient copolymer/epoxy cross-linking occurs from the gelation behavior of the curing blends. Flory–Stockmayer theory predicts gelation ($M_w \to \infty$) in a stoichiometric A_2/B_4 polycondensation such as the BPA/MDA system ($n_{\text{epoxy}} = 2$, $n_{\text{NH}} = 4$) to occur at a conversion (p_{gel}) of 0.577 ($1/\sqrt{3}$).[42,43] Because the total number of epoxy groups in each blend is held constant ($[\text{epoxy}]_{\text{BPA348}} + [\text{epoxy}]_{\text{BIx}n} = [\text{NH}]_{\text{MDA}}$), the ratio of BPA348 epoxy groups to active amine hydrogens ($r = [\text{epoxy}]_{\text{BPA348}}/[\text{NH}]_{\text{MDA}}$) decreases as the amount of copolymer in the blend is increased. At a certain blend composition, the ratio *r* becomes low enough that the system cannot reach the theoretical gel point solely by reaction between BPA348 and MDA. For example, at 50 wt % **BIx87**, $r = 2.76$, and $p_{\text{gel}} = 0.96$, but at 55 wt % **BIx87**, $r = 3.35$, and p_{gel} theoretically becomes greater than one. Because of the greater reactivity of the BPA348 epoxy groups relative to the copolymer epoxy groups, the two different epoxy species can be cured sequentially by temperature: an initial low-temperature cure allows preferential reaction of BPA348 with MDA, and then a higher curing temperature enables complete reaction of both BPA348 and polymer epoxy groups with MDA.

The fact that blends with compositions of >60 wt % copolymer are soluble while blends with lower copolymer compositions are insoluble agrees well with the theory and provides further support for the two-stage cure mechanism.

While cure of PIOx epoxy groups with MDA evidently does not occur simultaneously with cure of BPA348 epoxy groups (Figure 13B), the above evidence suggests that expulsion of PIOx blocks from the curing resin occurs as is observed with PEO blocks. This expulsion must then be followed by *interfacial* reaction of the majority of the reactive PIOx epoxy groups with the epoxy resin (Figure 13C). However, while microphase-separated PEO domains in OP blends can be detected by TEM, DSC, and SAXS due to the semicrystalline nature of the PEO blocks, no such separate domains have been observed in the amorphous BIx*n* systems, precluding any definitive statements as to the detailed microstructure of these systems.

Phase Behavior and *n*. The ready variation of the solubility of BIx*n* through control of *n* through reaction stoichiometry allows investigation into the fundamental role of copolymer/epoxy miscibility in determining behavior during cure.[21] Solubility parameters (δ) provide an approximate measure for determination of the comiscibility of different chemical species; those species with similar values tend to be miscible with one another.[30] While the calculated δ values for **BIx87** ($\delta_{\mathrm{BIx87}} = 18.4\ \mathrm{J}^{1/2}/\mathrm{cm}^{3/2}$) and **BIx75** ($\delta_{\mathrm{BIx75}} = 18.2\ \mathrm{J}^{1/2}/\mathrm{cm}^{3/2}$)[15] are not as high as that of PEO ($\delta_{\mathrm{PEO}} \approx 20\ \mathrm{J}^{1/2}/\mathrm{cm}^{3/2}$),[46] interactions between the PIOx blocks and uncured epoxy are apparently favorable enough to enable miscibility of these highly epoxidized blocks with the uncured epoxy components. At lower epoxidation levels, interactions with the epoxy components are sufficiently disfavorable and phase separation occurs.

Regardless of the favorable energetics of the interactions between the epoxidized block and the uncured resin (the strength of interblock repulsion scales with the product of the Flory–Huggins interaction parameter, χ, and the copolymer degree of polymerization, N), as the epoxy resin cures and its molecular weight diverges (M_w, $N \rightarrow \infty$), the correspondingly large increase in N should overcome all but the most favorably low values of χ and drive χN to values large enough to promote phase separation. (Negative χ values have been reported for epoxy/PEO systems, but still microphase separation is observed upon cure.) However, in a highly cross-linked network such as the epoxy system under scrutiny, this tendency toward macrophase separation is greatly retarded by the same increases in molecular weight and branching predicted to drive phase separation, as the mobility of copolymer chains, and therefore the possibility for the nucleation and growth of phase-separated domains, becomes substantially more limited as the epoxy network rigidifies.

These competing effects are manifested in the following observed behavior. TEM images of a cured **BIx75** blend (5 wt %) suggest that copolymer domains have phase-separated into regions of lamellar copolymer on the order of several hundred nanometers across (Figure 5). This observation suggests that epoxyisoprene blocks with epoxidation levels in this range are only sparingly miscible with the uncured epoxy resin at room temperature. As the molecular weight of the epoxy resin increases during the curing process, epoxyisoprene/epoxy resin miscibility decreases to the point where phase separation begins at much lower conversions than with the more highly epoxidized PIOx blocks or PEO. When phase separation begins at these lower conversions, the viscosity of the growing epoxy network is apparently low enough to allow nucleation and growth of block-copolymer-rich domains. Growth of phase-separated domain size in **BIx75** is presumably arrested at submicron lengths by subsequent gelation of the curing resin.

The comparatively more epoxy-miscible PEO and PIOx (n > 85) blocks begin microphase separation at a point in the cure process where macrophase separation is most likely prohibited by an inability of larger copolymer domains to nucleate in the rigid epoxy matrix, thus allowing order in the cured composite to reflect order in the initial blend. For blocks with lower n values (<75) and less epoxy-miscible blocks, however, the miscibility of the epoxidized block with epoxy is greatly reduced, and nucleation of phase-separated domains begins at much earlier stages in the cure process (even before cure begins if the block is sufficiently immiscible with epoxy), where barriers to copolymer nucleation are not so great.

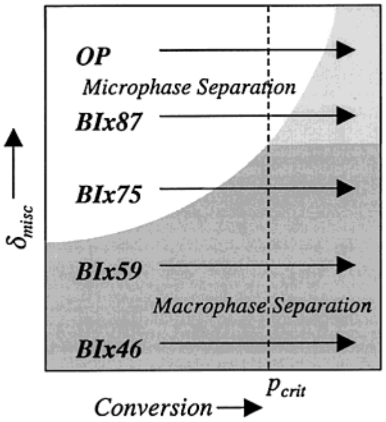


Figure 14. Proposed mapping of phase separation in epoxy-majority BPA348/MDA/copolymer blends as a function of miscibility and epoxy conversion.

This concept is roughly diagrammed in Figure 14 with a hypothetical mapping of miscible-block solubility parameter (δ_{misc}) vs epoxy conversion for blends where epoxy constitutes the matrix component. Cure profiles at constant δ_{misc} are drawn for various block copolymers. A critical conversion (p_{crit}) after which macrophase separation is discouraged by network rigidification is drawn as a dashed line at an arbitrary high conversion, and the shaded region represents the portion of the cure profile where phase separation occurs (Figure 14). In this representation, copolymers with highly epoxy-miscible blocks (i.e., **OP4**, **BIx87**) reach p_{crit} before traversing into the region of phase separation and therefore microphase-separate within the cure-delineated copolymeric regions of the blend. The cure profile of copolymer **BIx75** is drawn such that p_{crit} is reached shortly after entry into the phase-separation region—this is intended to describe the observed trapping of copolymer-rich regions at submicron-sized lengths shortly after phase separation begins. Copolymers with lower values of δ_{misc} travel the entire cure profile within the phase-separated region.

The key factor in imparting order to the cured composite appears to lie in matching the solubility parameters of the miscible block and the resin. For example, while **BIx87** copolymers are successful with BPA348/MDA resins, preliminary results with *o*-cresol novolac resins suggest that the interaction between the **Ix87** block and the high MW and differently structured novolac components (relative to BPA348) is not sufficiently strong to enable effective copolymer dispersion in the resin. Further studies in block/resin matching are underway in attempts to enable ordering of more useful high-temperature epoxy materials.

This increased understanding of the general behavior of block copolymers in epoxy systems has allowed the preparation of epoxy composites containing new types of copolymers. The critical design features of these copolymers reflect our general understanding of these block-copolymer-modified epoxies, as described above and previously.[11]

In this second class of reactive block copolymer, methyl acrylate (MA) and glycidyl methacrylate (GMA) comprise the epoxy-miscible/reactive block. In contrast to the BIx*n* systems, each component of this block is miscible with epoxy, potentially enabling variation in the number of reactive sites per chain without significantly affecting block miscibility with epoxy resin. Additionally, the singly substituted GMA epoxy groups are much more reactive toward nucleophilic opening than the triply substituted epoxy groups of the BI*xn* copolymers.[45] The epoxy-immiscible block remains a polydiene, but, due to the free radical methodology used, the polyisoprene has 90% 1,4-content—a microstructure with superior physical properties[46] that is unattainable for the epoxy-immiscible block in BI*xn* copolymers due to the specific selectivity of the epoxidation chemistry.

SAXS patterns show the scattering resulting from the microphase separation between the MA/GMA block and the isoprene block (Figure 10). This microphase separation in a copolymer with epoxy-miscible and immiscible blocks again translates to ordered epoxy blends when the copolymer is dissolved in epoxy: TEM images and SAXS patterns of the cured composites demonstrate that MG-I block copolymers within a curing epoxy resin cure without macrophase separation of the block copolymer (Figure 11). DSC evidence attests to the ability of the reactive GMA epoxy groups to competitively cure with the epoxy resin (Figure 12). Presumably, this faster reaction of MG-I copolymers with the curing resin enables the copolymers to cure within the epoxy matrix as described in Figure 13B.

Conclusion

Control over the morphology of elastomer-modified epoxy resins is essential for successful modification of epoxy composites. The predictable behavior of several classes of diblock copolymers comprised of epoxy-miscible and immiscible blocks in blends with epoxy resin points toward the universality of this process. Effective ordering of cured thermosets is predicated on (1) a high degree of miscibility of the epoxy-miscible block with the uncured resin components and (2) the kinetic retardation of macrophase separation by gelation of the curing thermoset.

Two new types of copolymers exhibit thermoset-ordering properties similar to those previously observed for PEO-based block copolymers. The incorporation of reactive groups in the epoxy-miscible blocks of these polymers has been shown to allow covalent linkage of block copolymers to the resin without loss of order in the resulting composites.

The effects of these two types of copolymer at low concentration on epoxy toughening will be examined. Both the formation of vesicles and covalent linkages between copolymer and the epoxy matrix are expected to have highly beneficial effects upon epoxy fracture toughness.

Acknowledgment. Funding for this work was provided by AFOSR Grant AF/F49620-99-1-0028. TEM and SAXS facilities are supported in part by the University of Minnesota MRSEC. J.M.D. acknowledges financial support from the National Physical Science Consortium and Ford Motor Company. M.E.B. was supported by the University of Minnesota MRSEC outreach program. Dr. C. J. Hawker (IBM−Almaden) is thanked for the provision of authentic samples of nitroxide and alkoxyamine initiator and for advice concerning the preparation and use of these compounds. Dr. K. Fagerquist (Chemistry Department, University of Minnesota) is thanked for the acquisition of MALDI spectra. The authors acknowledge useful discussions with Dr. M. B. Kossuth, Dr. Y. Y. Won, Dr. N. Washburn, and Dr. M. E. Vigild.

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83 kJ/mol as fewer secondary amines are included in the first stage of the curing process. See: Prime, R. B. In *Thermal Characterization of Polymeric Materials*, 2nd ed.; Turi, E. A., Ed.; Academic Press: San Diego, 1981; Chapter 6, pp 1380−1766.

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MA001414F