Methacrylic Block Copolymers through Metal-Mediated Living Free Radical Polymerization for Modification of Thermosetting Epoxy

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Evidence from this lab and others suggests that the ability of diblock copolymers consisting of an epoxy-miscible block and an epoxy-immiscible block to form well-defined ordered and disordered microstructures in thermosetting epoxy resins is not specific to any one class of copolymer or thermoset.[1−5] This behavior appears to be highly dependent upon the extent of favorable energetic interaction between the epoxy-miscible block and the curing epoxy network and results in the formation of the ordered and disordered morphologies typical for blends of a block copolymer with a block-selective solvent. We have initially focused on the toughening applications of diblock copolymers of this type in model bisphenol A, diglycidyl ether (BPA348)/4,4′-methylenedianiline (MDA) resins at low concentrations in the disordered vesicular morphology.[6] To further promote epoxy toughening, we have recently targeted the introduction of reactive functionality (epoxides) to the epoxy-miscible block of appropriate block copolymers.[3]

Thermal characterization of these copolymer-modified epoxies has revealed fundamental differences in the mechanisms of copolymer cure dependent upon the substitution pattern of the oxirane ring displayed by the copolymer. The triply substituted backbone epoxide groups of epoxidized polyisoprene (PIOx) react much more slowly with MDA amine groups during cure than do the singly substituted glycidyl ethers of BPA348, while the singly substituted epoxide groups contained in glycidyl methacrylate (GMA)-based copolymers appear to react at a comparative rate.[3] This reactivity difference has led us to draw different reactivity-dependent representations of the fate of the epoxy-miscible block during cure: less-reactive blocks (i.e., PIOx) most likely undergo the microphase separation processes observed for nonreactive blocks, such as poly(ethylene oxide) (PEO), prior to reacting interfacially with the curing resin, while more reactive blocks (e.g., GMA-containing blocks) will cure within the epoxy matrix and resist the microphase separation driven by epoxy cure.

Despite the typical use of these block copolymers at low concentrations (0.5−5 wt %) in epoxy toughening studies, significant quantities of polymer are still necessary for the preparation of the statistically relevant number of samples needed for mechanical testing.[6] Our initial investigation of GMA-containing systems involved the use of a nitroxide-mediated living free radical polymerization[7] process for the preparation of poly(methyl acrylate-*co*-GMA)-*b*-poly(isoprene) (MG-I*n*) copolymers, as these systems are much more tolerant of functionality than typical living anionic polymerization systems.[3] While MG-I*n* copolymers are readily prepared with control over molecular weight, composition, and polydispersity index and are well-behaved when cured with epoxy, the quantities of the noncommercially available initiator required to prepare the relatively low molecular weight block copolymers of interest were prohibitive with respect to large-scale polymer preparation. Additionally, even at relatively high levels of compositional asymmetry ($f_{\mathrm{PI}} > 70\%$), these copolymers have tended to form spherical micellar morphologies in cured epoxy in the dilute limit, rather than the desired vesicular morphology.

With this in mind, we have turned to the examination of alternate living free-radical polymerization methodologies for the preparation of related block copolymers. Specifically, metal-mediated or atom transfer radical polymerization methods (1) are known to be relatively tolerant of monomer functionality, (2) have been effective with a range of monomers, and (3) utilize a variety of initiating species, many of which are inexpensive and available in quantity.[8−10] Additionally, numerous compatible nonpolar methacrylic esters are readily available for incorporation in the epoxy-immiscible block. These monomers allow more precise tuning of immiscible block volume and facilitate preparation of block copolymers of specific disordered morphologies in epoxy.

Random copolymers of methyl methacrylate (MMA) and GMA were targeted for the epoxy-miscible block. As GMA is considerably more hazardous and expensive than MMA, block compositions with GMA as the minority component that still exhibited the desired epoxy miscibility and reactivity were sought. The reactivity ratios of the two monomers are such that azeotropic copolymerization occurs at 40 mol % GMA, and the entire range of compositions is potentially accessible.[11] As block copolymers of MMA with longer chain alkyl (meth)acrylates have been demonstrated to exhibit the bulk microphase segregation desired for effective epoxy modification, copolymers containing 2-ethylhexyl methacrylate (EHMA) as a hydrophobic/epoxy-immiscible block were examined.[12] EHMA is relatively inexpensive, and the bulky side chain was expected to help promote formation of the desired vesicular morphologies in epoxy.

Copolymerization of MMA and GMA was effected by heating a degassed solution of the monomers, *p*-toluenesulfonyl chloride, copper(I) bromide, and 2,2′-bipyridine in anisole at 90 °C for 6 h (Scheme 1).[13] Polymerizations using the homogeneous CuBr/*N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA) catalysis system rapidly gelled, presumably through competing catalysis of epoxide polymerization by the tertiary amine groups of the ligand.[14,15] Because molecular weight distributions through heterogeneous catalysis (see below) were acceptably low, other homogeneous systems (e.g., with alkylated bipyridine ligands) were not examined. Samples of poly(MMA-*ran*-GMA) ($\mathrm{MMG}(x)_y$, where x is the mole fraction of GMA in the copolymer and y is M_{n} in kg/mol) with a range of GMA content ($x = 0$, 0.2, 0.4, 0.6, 0.8, 1.0) and a low target M_{n} ($y \approx 3.5$) were prepared (Table 1). Notably, reasonable control over molecular weight was observed, and polydispersities were relatively low despite the use of the heterogeneous bpy/CuBr catalyst system (Table 1). The amount of

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Scheme 1

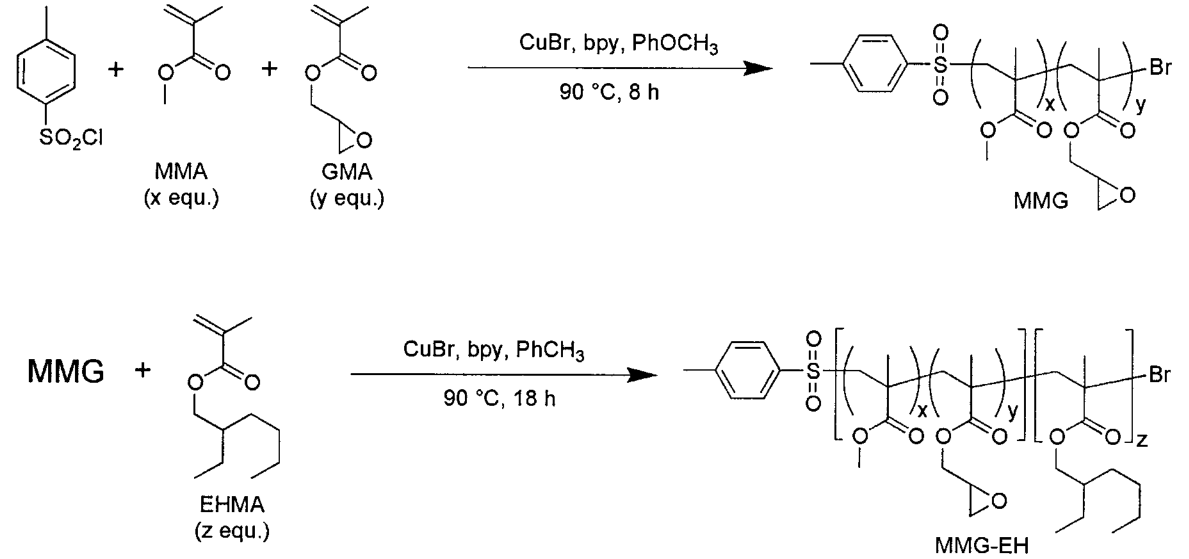

Table 1. Characteristics of Copolymers of GMA and MMA with Varying Composition

	mol % GMA (feed)	mol % GMA (polymer)[a]	M_n (theor)[b]	M_n (SEC)[c]	M_n (NMR)	M_w/M_n[c]
a	0.0	0	3500	3840	3700	1.20
b	20.3	21	3480	3590	3910	1.12
c	39.9	40	3540	3650	3900	1.13
d	61.2	62	3540	4460	3970	1.16
e	81.3	79	3510	4630	4020	1.18
f	100	100	3560	4830	4100	1.19

[a] Determined by ^{1}H NMR. [b] Calculations assume retention of Cl at chain end. [c] Measured vs polystyrene standards.

Table 2. Characteristics of MMG-EH Block Copolymers

MMG block[a]	equiv EHMA (feed)	equiv EHMA (polymer)[b]	M_n (theor) (g/mol)	M_n (SEC)[c]	M_n (NMR)	M_w/M_n[c]
a	79.8	74.7	19 500	19 200	18 500	1.27
b	80.5	88.5	19 900	17 500	21 500	1.22
c	79.8	86.5	19 700	17 100	21 050	1.21

[a] See Table 1. [b] Determined by ^{1}H NMR. [c] Measured vs polystyrene standards.

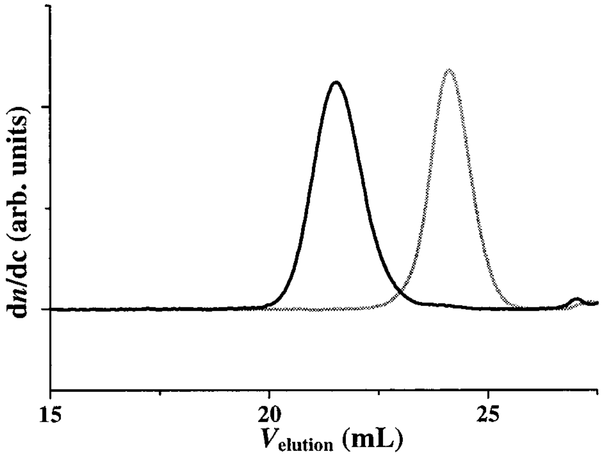

Figure 1. SEC traces (RI detector; THF, 1 mL/min) for random copolymer MMG(40)$_{3.9}$ (right, gray) and block copolymer MMG(40)$_{3.9}$EH$_{21}$ (left, black). For molecular characteristics for these polymers, see Table 1, entry c, and Table 2, entry c, respectively.

GMA incorporated in the copolymer correlates fairly well with that in the monomer feed under these conditions—the relevant reactivity ratios are such that no great compositional drift is expected.[11] SEC measurements vs polystyrene standards systematically overestimate molecular weights for these polymers at high GMA compositions. As GMA composition increases, removal of residual color from the catalyst becomes more difficult—presumably, the more polar GMA residues effectively complex a small amount of the copper catalyst even after several precipitations into methanol and filtrations through alumina.

Purified MMG(x)$_{3.5}$ samples were dissolved in toluene, mixed with EHMA (80 equ.), and polymerized as above at 80 °C for 18 h (Scheme 1).[16] For $x > 40$, miscibility of MMG(x)$_{3.5}$ copolymers with EHMA and toluene is minimal, and the polymerization mixture becomes undesirably heterogeneous. For MMG(x)$_{3.5}$ blocks with $x < 40$, polymerization of EHMA proceeded readily to give block copolymers MMG(x)$_{3.5}$EH$_z$ (where z is M_n for the EHMA block in kg/mol) with polydispersity indices between 1.2 and 1.3 (Table 2). Slight positive deviation from predicted molecular weights is observed in the GMA-containing polymers, but importantly, the polymerizations result in unimodal, relatively narrow molecular weight distributions with insignificant amounts of contamination with the parent block (Figure 1).

Blends of MMG-EH copolymers with the BPA348/MDA epoxy system at higher copolymer concentrations (40−55 wt %) were used to examine the efficacy of various solvents for the solvent casting process. A 55 wt % MMG(0.4)$_{5.6}$EH$_{17.5}$ blend cast from dichloromethane became cloudy prior to complete solvent evaporation, while the same blend cast from less polar solvents (toluene, benzene, or chloroform) remained homogeneous throughout the casting process. It was necessary to examine this behavior with concentrated samples as the desired vesicular morphologies result in opaque samples despite homogeneous dispersion of the block copolymers due to their large length scales relative to the wavelengths of visible light. Indeed, cured blends of copolymer MMG(0.4)$_{5.6}$EH$_{17.5}$ with epoxy at 5 wt % are opaque and were microtomed for TEM analysis.

TEM images of cured/epoxy blends cast from chloroform and stained with RuO$_4$ vapor (which selectively darkens aromatic components in the micrograph) reveal that these copolymers exhibit behavior very similar to

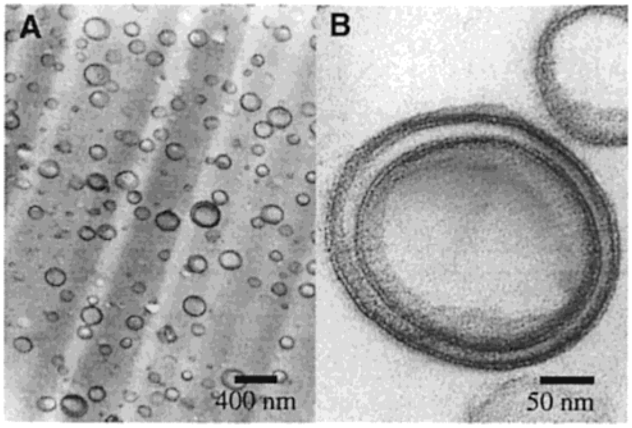

Figure 2. TEM images (RuO_4 stain) of a microtomed sample of cured 5 wt % MMG(0.4)$_{5.6}$EH$_{17.5}$ in BPA348/MDA epoxy. Image A shows a representative region of the sample at 20 000 times magnification. Image B shows a close-up of a large vesicular feature from an image at 80 000 times magnification.

that shown in the previously examined block copolymer-modified epoxy systems. For example, a cured blend of MMG(0.4)$_{5.6}$EH$_{17.5}$ (5 wt %) in epoxy shows the block copolymer to form spherical vesicular structures (with diameters from 100 to 300 nm) typical for dilute blends of asymmetric block copolymers with a solvent selective for the minority block (Figure 2). With this staining agent, the largely aromatic epoxy matrix appears gray, the unstained p(EHMA) interior of the vesicular bilayer appears white, and the region between the two (MMG + epoxy) appears black. Presumably, the MMG block sufficiently flexibilizes the epoxy network surrounding the vesicles to allow greater penetration of the staining agent into the sample in these regions than in the more rigid purer epoxy domains.

The homogeneity of these methacrylic block copolymers in epoxy further supports the notion that this behavior is general to block copolymer/epoxy systems in which the epoxy blocks are designed such that one block is miscible with the resin and the other block is incompatible. Examination of the extent of toughening afforded epoxy resins by these block copolymers is underway. The series of block copolymers, essentially identical except for GMA content, is expected to allow investigation of the effect of how tightly tied in the block copolymer is to the epoxy matrix (and the extent of epoxy network flexibilization by the block copolymer) upon the ultimate properties of the modified resin.

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(13) For a typical MMG(0.4) preparation: 4-Toluenesulfonyl chloride (1.09 g, 5.71 mmol) was dissolved in MMA (9.58 g, 95.7 mmol), GMA (9.07 g, 63.8 g), and anisole (37 mL). The resulting solution was degassed for 20 min with an argon sparge. Copper(I) bromide (0.41 g, 2.86 mmol) was added to the solution under argon flow followed by 2,2′-bipyridine (0.89 g, 5.7 mmol). The heterogeneous mixture was sealed under argon and heated at 90 °C for 6 h. The greenish mixture was allowed to cool and precipitated with hexanes. The solid was redissolved in dichloromethane, filtered through an alumina/Celite pad, concentrated, and reprecipitated into methanol. The residue was dried in vacuo to a glassy solid. Typical yield = 70−80%. ^{1}H NMR ($CDCl_3$) δ: 7.75 (d, Ar*H*, 2H), 7.35 (d, Ar*H*, 2H), 4.4−4.2 (br, GMA −OC*H*H), 3.72−3.65 (br, GMA −OCH*H*), 3.6 (br, MMA −OC*H*$_3$), 3.3−3.18 (br, GMA −C*H*), 2.9−2.8 (br, GMA −C*H*H), 2.7−2.6 (br, GMA −CH*H*), 2.45 (s, ArC*H*$_3$, 3H), 2.2−1.8 (br, −C*H*$_2$−), 1.09, 0.93 (br, C*H*$_3$). PGMA peak assignments from: Yu, J. M.; Dubois, Ph.; Jerome, R. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3507−3515.

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(16) For a typical EHMA polymerization: To copolymer MMG-(0.4) (2.00 g, 0.51 mmol) dissolved in toluene (28 mL) was added EHMA (8.14 g, 41 mmol), and the solution was sparged with argon for 20 min. Copper(I) bromide (36.8 mg, 0.257 mmol) was added to the solution under argon flow followed by 2,2′-bipyridine (80.1 mg, 0.513 mmol). The heterogeneous solution was sealed under argon and heated at 80 °C for 18 h. The polymer was recovered from solution by precipitation with methanol and worked up as described for the MMG block. Typical yield = 70−80%. ^{1}H NMR ($CDCl_3$) spectrum as for MMG block with the following additional peaks δ: 3.84 (br, EHMA −OC*H*$_2$), 1.55 (br, EHMA −C*H*), 1.31 (br, EHMA −C*H*$_2$−), 0.92 (br, EHMA −C*H*$_3$).

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