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Reactive Tetrablock Copolymers Containing Glycidyl Methacrylate. Synthesis and Morphology Control in Epoxy−Amine Networks

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ABSTRACT: Polystyrene-*block*-polybutadiene-*block*-poly(glycidyl methacrylate) (SBG) and polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)-*block*-poly(glycidyl methacrylate) copolymers (SBMG) were synthesized by sequential living anionic polymerization in tetrahydrofuran (THF). SBMG copolymers were used as modifiers for epoxy thermosets based on the diglycidyl ether of bisphenol A (DGEBA). Different techniques including differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), transmission electron microscopy (TEM), and optical cloud point measurements have been used to demonstrate the advantage of having a reactive copolymer to finely tune and control the morphology of nanostructured materials. The FT-IR and DSC studies were used to follow both the kinetics of reaction of the reactive block G with the epoxy−amine system and of cross-linking of the epoxy−amine system. They give an interesting insight into the problem of factors governing the expulsion of the methacrylic block out of the epoxy−amine phase during network formation. Morphological characteristics revealed by TEM appear to be closely related to the optical properties of these composites.

Introduction

Nowadays, the development of new polymer architectures is interesting, especially when permitting a better use of conventional old ones.

It has been found that the self-assembling power of block copolymers is retained in their mixtures with numerous homopolymers.[1−7] Block copolymers in this respect appear as promising candidates in the development of new formulation methods.

Because of their very nature, triblock copolymers self-assemble in hierarchical substructures. This property is exploited in SBM (polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) triblock copolymers) reinforced materials in which the amount of the elastomeric inclusions can be limited to the strictly necessary quantity, due to the spontaneous formation of core−shell inclusions.

Ideal blending conditions are fulfilled when the homopolymer is compatible with one of the copolymer's blocks. This concept has been used by ATOFINA[6] for poly(vinylidene fluoride) (PVDF), poly(vinyl chloride) (PVC), and poly(ethylene oxide) (PEO). It was shown that the obtained materials have improved mechanical properties: they keep high modulus and are supertough.

A case of particular interest is the blend of block copolymers with thermosets.[7−19] In comparison with non-cross-linked binary mixtures, such systems are entropically penalized due to the topological complexity and practically infinite molecular mass after curing. In this context, any control of morphology and interfacial adhesion seems hardly possible unless the two polymers display a negative mixing enthalpy ($\chi_{AB} < 0$).[20,21]

As a matter of fact, SBM copolymers are readily soluble in many noncured epoxy−amine mixtures. Preserving the compatibility throughout the whole curing process was found to be possible, but only for some very specific choice of the hardener.[7,15−17]

Indeed, to our knowledge, the blending of SBM triblock copolymers with epoxy−amine networks is restricted to the DGEBA/MCDEA system (diglycidyl ether of bisphenol A/4,4′-methylene bis(3-chloro-2,6-diethylaniline)), which shows the required affinity. Further progress in this field could be gained if stable morphologies are accessible for a much larger choice of ingredients (hardeners).

Starting from initially miscible compositions, a way of quenching the desired morphology is the formation of covalent links between the matrix and the additive.[18,19] In this paper, we explore the synthesis of modified SBM copolymers containing a certain number of reactive groups. The introduction of versatile monomers by means of anionic polymerization is by definition difficult since reactive groups are a source of undesirable terminations. There are a few reports mentioning the use of glycidyl methacrylate (GMA) in anionic polymerizations.[22−28] In our case, the traditional synthesis of SBM was adapted in order to incorporate GMA units as an end block. The preparation of polystyrene-*block*-polybutadiene-*block*-poly(glycidyl methacrylate) triblock copolymers (SBG) and polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)-*block*-poly(glycidyl methacrylate) tetrablock copolymers (SBMG) is hereby reported.

Blends of epoxy−amine with SBMG were prepared to investigate the effect of chemical grafting with respect to spontaneous mixing. 4,4′-Diaminodiphenyl sulfone (DDS) was chosen as the hardener, as it is usually preferred to other aromatic diamines in the field of high-T_g applications (T_g up to 220 °C).

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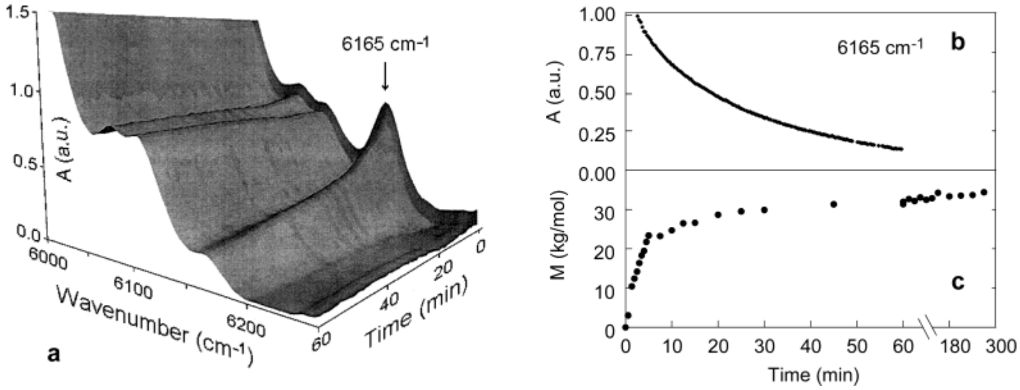

Figure 1. (a) Variation of the FT-NIR spectrum of the anionic polymerization of GMA on the living chains of SB diblock as a function of time. (b) Intensity variation of the 6165 cm^{-1} band of GMA as a function of time during the anionic polymerization of SBG. (c) Evolution of molecular mass of the PGMA formed as a function of time, during the anionic polymerization of GMA.

The effects of GMA content of the block copolymers and curing temperature on the morphology and the optical properties are explored.

Experimental Section

Materials. Purifications and anionic polymerizations were carried out under an ultrapure nitrogen atmosphere. *sec*-Butyllithium (*sec*-BuLi) was purchased from Acros (as 1.3 M solution in cyclohexane/hexane 92/8) and handled with syringes. Tetrahydrofuran (THF, Merck) was refluxed 2 days over calcium hydride and distilled and then 2 other days over potassium and again distilled, prior to being transferred into the polymerization reactor. Styrene (Acros) was stirred overnight over calcium hydride and then distilled under vacuum into a Schlenk flask containing di-*n*-butylmagnesium ($MgBu_2$) obtained by evaporation of a 1 M heptane solution (Aldrich). The mixture was stirred overnight and carefully degassed by a 3-fold freeze−thaw cycle under high vacuum. Last, the monomer was condensed into a separate vessel and stored in a steel ampule at the liquid nitrogen temperature until use. Gaseous 1,3-butadiene was passed through molecular sieves (4 Å) and basic alumina columns and condensed into a cooled pressure-resistant glass reactor, where it was stirred with $MgBu_2$ until use. The initiator *sec*-BuLi was added to 1,1-diphenylethylene (DPE, Aldrich) until the solution turned to a deep red color. The monomer was then purified by distillation and handled with syringes. Methyl methacrylate (MMA, BASF) was stirred for 2 days over calcium hydride, carefully degassed by a 3-fold freeze−thaw cycle under high vacuum, and condensed into a separate Schlenk flask containing triethylaluminum (from a 1 M solution in hexanes, Aldrich, evaporated to dryness). The mixture was stirred in the darkness for 3 h (a light yellow color indicates purity) and stored in a dewar filled with liquid nitrogen. Immediately before use, it was condensed into a glass ampule. Glycidyl methacrylate (GMA, Aldrich) was distilled twice carefully over calcium hydride powder (after 1 day of stirring), under vacuum, with the first and last fractions being eliminated. Immediately before use, the monomer was passed through a column of neutral alumina (previously treated at 240 °C under vacuum for 3 days) in a glovebox. The monomer was transferred to the reactor using a nitrogen-flushed syringe. Ciba-Geigy LY556 resin (Vantico) was used as DGEBA epoxy prepolymer, with an average number of hydroxyl groups per molecule of $n = 0.15$ ($M = 382.6$ g/mol); 4,4′-diaminodiphenyl sulfone (DDS) was purchased from Fluka. Unless otherwise mentioned, the diamine was used at the stoichiometric ratio of epoxy to N−H amino groups.

Polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)-*block*-poly(glycidyl methacrylate), SBMG-6. In a 1 L pressure-resistant glass reactor (Büchi) equipped with a stirrer, a thermostated cooling jacket, temperature and pressure controllers, and steel capillary inlets, 600 mL of THF and 6 mL of the *sec*-BuLi solution were allowed to stand overnight to neutralize the residual protic impurities. Styrene (12.5 mL, 109 mmol) was added to the solution and polymerized at −80 °C with *sec*-butyllithium (0.25 mL, 0.33 mmol) as the initiator. The yellow/orange solution was stirred for 30 min, and 14.3 mL (172 mmol) of 1,3-butadiene was added at −10 °C. The mixture was stirred for another 5 h and reacted (−40 °C/30 min) with an excess amount of DPE (0.5 mL, 2.8 mmol) before 9.0 mL (84 mmol) of MMA and 0.83 mL (6.3 mmol) of GMA were successively added at −70 °C (the reaction mixture becomes nearly colorless; 30 min stirring for MMA and 2 h for GMA). During the process, aliquots of 1 mL were taken out from the preparation after each polymerization step to determine the molecular weights of the S, SB, and SBM precursors. Eventually, 10 mL of degassed methanol was added to terminate the reaction. The block copolymer was then precipitated into 6 L of distilled water, filtered, washed several times with water, dried in a vacuum, redissolved in THF, and reprecipitated in methanol.

SBMG-11, SBG-7, and SBG-13 were synthesized similarly. All the copolymers were stabilized with 0.6 g (2.7 mmol) of 2,4-di-*tert*-butyl-*p*-cresol.

Molecular weights of the block copolymers were determined using ^{1}H NMR spectroscopy in combination with the molecular weights of the polystyrene precursors obtained from gel permeation chromatography (GPC) (calibrated with PS). ^{1}H NMR spectra were recorded on a Bruker AC 250 (250 MHz) in $CDCl_3$ and GPC traces on a Waters GPC equipped with column sets of particle size 5 μm and pore sizes of 10^5, 10^4, 10^3, and 100 Å with THF as eluent.

Fourier Transform Near-Infrared Spectroscopy (FT-NIR). NIR spectra were recorded with a Nicolet Magna 560 FT-IR optical bench equipped with an all-glass low-temperature immersion transmission probe (Hellma) with an optical path length of 10 mm and connected to the FT-IR by 2 m fiber-optical cables.

Fourier Transform Infrared Spectroscopy (FT-IR). Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Perkin-Elmer 1600 series FTIR spectrometer (KBr windows, four scans, resolution 4 cm^{-1}) equipped with a Specac 5750 heating jacket. Because of the low amount of reactive units in the block copolymers, investigations have been carried out using the reactive polymer PGMA as model compound. For all blends, the components were dissolved in THF prior to being cast onto KBr windows. The solvent was removed at room temperature first at normal pressure and then under vacuum for 5 min. Polycondensation was carried out at 135 °C in the thermal jacket. The advancement of the reaction in DGEBA/DDS and PGMA/DDS was measured by recording the IR absorption (optical density) at 906 cm^{-1} (ν_{as} PGMA epoxide) and 1630 cm^{-1} (δ_s DDS NH_2). The DDS absorption at 1145 cm^{-1} (ν_s SO_2) was taken as internal standard; degrees of conversion in Figure 2 were calculated from the band intensity ratio 1630/1145.

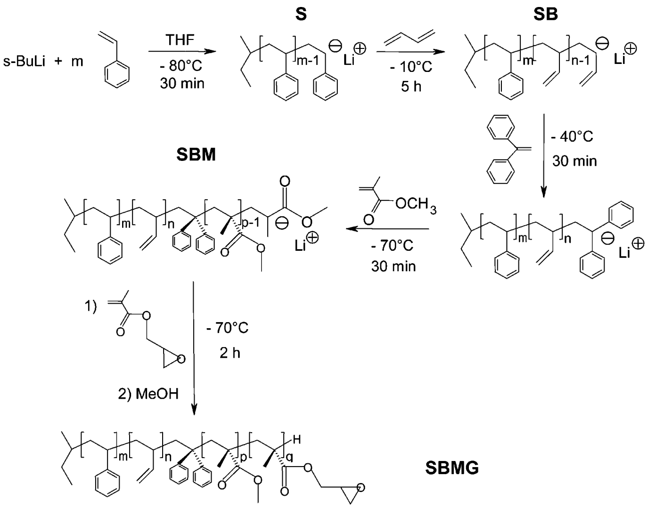

Figure 2. Synthesis of SBMG block copolymers by anionic polymerization.

After all experiments, the samples were overheated at 180 °C for 24 h to determine the reference absorption levels corresponding to 100% conversion.

Differential Scanning Calorimetry (DSC). Thermal analyses were performed at a heating rate of 10 °C/min under nitrogen with a TA Instruments Q1000 apparatus equipped with a quench cooling accessory or RCS thermocryostate and operating in the T4 mode. Samples of 5−10 mg, prepared from solvent-cast films, were embedded in nonhermetic aluminum pans. Transition temperatures and heats of reactions were measured from two different blends: DGEBA/DDS (epoxide/N−H = 1) and DDS/SBMG-6 (N−H/epoxide = 4.6).

Transmission Electron Microscopy (TEM). Transparent 2 mm thick films of unblended block copolymers were slowly cast from CHCl$_3$ (SBM, SBG, and SBMG-6) or THF (SBMG-11) at room temperature over a period of 2 days. The temperature was subsequently raised under vacuum up to 145 °C, by steps of 10 °C every 12 h. Electron micrographs were taken from a Zeiss CEM 902 transmission electron microscope operating at 80 kV in the bright field mode. Ultrathin sections of the samples of about 60 nm thickness were obtained at −100 °C using a Reichert-Jung Ultracut E ultramicrotome equipped with a diamond knife and a liquid nitrogen cryostate. Staining was achieved by treating the ultrathin samples for 1 min with osmium tetroxide vapor. The blends with epoxy−amine were treated similarly: transparent films of 1 mm thickness were prepared by slow evaporation from a three-component solution (DGEBA/DDS/SBMX block copolymer) in THF. Solvent evaporation was achieved over 1 week at room temperature, followed by 24 h under vacuum. Curing was fixed to 5 h at 135 or 220 °C. Staining was performed by treating the ultrathin samples for 30 min with a 4% aqueous solution of osmium tetroxide. Electron micrographs were taken from a LEO 902 transmission electron microscope equipped with a Megaview-2 SIS digital camera.

Cloud Point Measurement. Pieces of the transparent films prepared for TEM were placed on the path of the light beam of a Leitz Orthoplan microscope equipped with a 12 V halogen lamp (color temperature about 3000 K) and a Mettler FP82 hot stage. The light intensity was measured using a Siemens BPW 34 photodiode under −9 V polarization. The reverse current flowing through a 3 kΩ serial resistance was recorded using a Keithley 197A multimeter in the 200 mV range. The data were collected as a function of time at 135 °C. The transmission Tr was determined by the relation $\mathrm{Tr}(t) = (I(t) - I_D)/(I_0 - I_D)$, where I_0 is the current corresponding to the intensity at $t = 0$ and I_D the dark current of the photodiode.

Results and Discussion

Synthesis and Characterization of SBG and SBMG. In presence of strong nucleophiles, glycidyl methacrylate (GMA) is able to react by three different ways: (i) by addition onto the ethylenic double bond, (ii) by addition onto the carbonyl group, or (iii) by ring-opening of the epoxide. By proceeding under specific conditions, i.e., at low temperature (−70 °C), in the presence of lithium as counterion, and using DPE to match the reactivity of the nucleophile, it is possible to perform a selective polymerization through the first of these mechanisms.[24]

The anionic polymerization of glycidyl methacrylate (GMA) is particularly delicate and very dependent on the quality of the monomer. The commercial qualities (purity 95 or 97%) contain protic impurities, among them methacrylic acid, which cannot be eliminated by drying and distillation and are sources of termination reactions. This characteristic is critical in multiblock synthesis, since termination at this stage results in contamination of the final product with its nonglycidylated precursor.[29] Active alumina filtration proved to be efficient to get rid of contaminants.

The kinetics of anionic polymerization of styrene, butadiene, and methyl methacrylate are well-known.[30] To determine the duration of anionic polymerization of glycidyl methacrylate, the advancement of the reaction is followed by the technique of Fourier transform near-infrared spectroscopy (FT-NIR).[31,32] Figure 1a displays a 3-dimensional view of the surface of the intensity as a function of time and wavelength, during the synthesis of an SBG triblock copolymer. Consumption of the GMA monomer was monitored by recording the intensity of the 6165 cm^{-1} band (first overtone of the vinylic C−H asymmetric stretching mode) as a function of time (Figure 1b). The decay is roughly exponential with a time constant of about 20 min, which means a polymerization accomplished to about 95% after 1 h.

In addition, to confirm these results, a model study of anionic polymerization of GMA at −70 °C was carried out. Test samples were taken out of the reaction mixture, precipitated into methanol, dried, and analyzed by GPC. The variation of molecular mass of the homopoly(glycidyl methacrylate) was followed as a function of time (Figure 1c). After 1 h, the molecular mass reaches a plateau; i.e., it nearly does not evolve afterward. In further experiments, the duration of GMA polymerization was fixed to 2 h for complete conversion.

The general scheme of the synthesis of block copolymers based on styrene (S), butadiene (B), methyl methacrylate (M), and glycidyl methacrylate (G) by anionic polymerization is presented in Figure 2. The GPC traces of the SBMG-11 block copolymer and its corresponding precursors are shown in Figure 3. The curves indicate a constant narrow mass distribution throughout the process. The addition of each new monomer involves a reduction of the elution volume, hence confirming the quasi-absence of termination reactions. The ^{1}H NMR spectra of the SBMG-11 block copolymer and its SBM precursor (SBM-11) are shown in Figure 4. The five characteristic peaks of poly(GMA) between 2.5 and 4.5 ppm are present, confirming that vinylic polymerization is the only reaction of the SBM$^-$ living chain end with GMA.

Polybutadiene mainly shows the 1,2 microstructure and PMMA is predominantly syndiotactic, as expected from the experimental conditions.

The composition, morphology, and molecular parameters of the synthesized block copolymers are summarized in Table 1. In our nomenclature, the copolymers

Table 1. Characteristics of the Synthesized Block Copolymers

			PS precursor		block copolymer		microstructure
sample	polymer	morphology	M_n (kg/mol)	M_w/M_n	M_n (kg/mol)	M_w/M_n	1,2-PB (%)[a]
SBM-11	$S_{38}B_{30}M_{32}$	lamellae	40	1.01	106	1.08	89
SBMG-11	$S_{35}B_{27}M_{30}G_8$	lamellae	40	1.01	116	1.04	89
SBMG-6	$S_{38}B_{31}M_{28}G_3$	lamellae	35	1.02	93	1.05	89
SBG-7	$S_{46}B_{41}G_{13}$	core−shell cylinders (distorted)	61.5	1.01	134	1.06	88
SBG-13	$S_{30}B_9G_{61}$	spheres at lamellae	24.5	1.08		1.16[b]	86

[a] Determined by ^{1}H NMR. [b] Due to the presence of SB diblock copolymer.

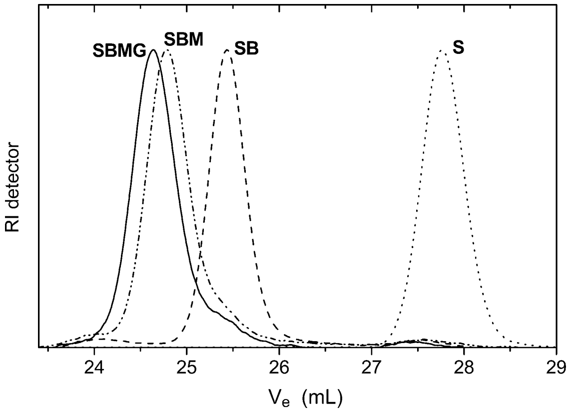

Figure 3. GPC traces of an SBMG block copolymer and its precursors.

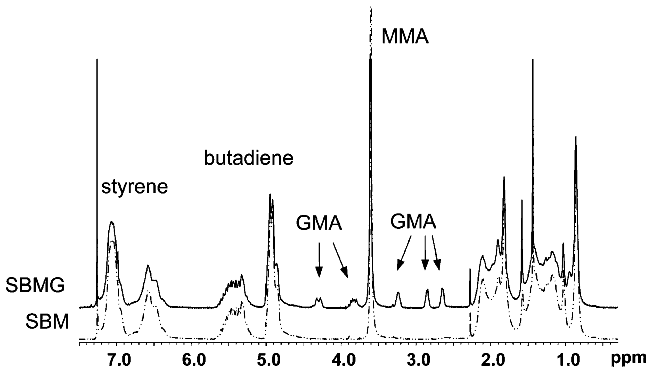

Figure 4. ^{1}H NMR spectra of an SBMG block copolymer and its SBM precursor.

are described as $S_uB_vM_wG_x$, where *u*, *v*, *w*, and *x* correspond to the weight percent of the components.

Hence, formally SBMG-6 and SBMG-11 belong to the almost unexplored family of ABCD tetrablock copolymers.[33,34] In both compounds the G-block is relatively short; the question then arises whether this fourth block is able to induce particular morphologies. In other words, will the M−G subunit, considered as a diblock, form one single or two segregated domains? From the theory of block copolymers,[35] microphase separation is likely to take place whenever the product $N\chi$ (number of monomers times the interaction parameter) is large. Using the molar volumes which are known for PMMA and PGMA and the attraction factors tabulated for the various groups present in the monomers,[36] we found that $N\chi$ is close to 10 in both SBMG-6 and SBMG-11. However, in these copolymers the volume fraction of G in MG is of about 0.20. For such unsymmetrical compositions, the phase diagram[35] suggests that the separation between PMMA and PGMA blocks is unlikely. Still in lamellar organization, there must be some polarization of the blocks. Some insight can be gained in analogy with the simple situation of an AB block copolymer end-grafted to a surface.[36] Because of the fact that one of the ends is fastened in a predetermined position, such a copolymer brush always displays a smooth concentration gradient even for negative values of χ.

TEM micrographs of SBM-11, SBMG-6, and SBMG-11 are shown in parts a, b, and c of Figure 5, respectively. As is usual in symmetrical SBM, SBM-11 shows the ABCBA double-band morphology with dark lamellae of PB between fine lamellae of PMMA and broader lamellae of PS.[38] SBMG-6, which contains approximately the same overall volume fraction of methacrylic units, presents a similar morphology without evidence of segregation of G and M fragments. In SBMG-11, the volume fraction of unstained methacrylic blocks is larger, hence resulting in equilibration of widths of the PS and PMMA/PGMA sublayers. Figure 5d displays a TEM micrograph of SBG-7. Because of the staining conditions, PS as the matrix-forming component appears gray. PB can be recognized as black rings surrounding bright cylindrical PGMA cores corresponding to a coaxial view of core−shell cylinders designated as the cylinder in cylinder (c_ic) morphology[39] without long-range order. A TEM micrograph of SBG-13 is shown in Figure 5e. The PB block forms spheres at the interface of the PS (stained gray) and PGMA (unstained) lamellae. This corresponds to a “ball at the wall” morphology showing a lamellar−spherical (ls) structure.[38,40] Because of the presence of some SB diblock copolymer resulting from some termination in the synthesis, a characteristic structure of a blend of SB diblock and SBG triblock copolymers appears in some regions of the examined sample. BS core−shell cylinders are surrounded by spheres of PB from the triblock copolymer in a PGMA matrix. SBG-7 and SBG-13, which are respectively G-poor and B-poor, exhibit classical morphologies already encountered in unsymmetrical SBM triblock copolymers.

Blends with the Epoxy−Amine System. The kinetics of the DGEBA−DDS condensation is well-documented.[41] In the stoichiometrically balanced system, the gel point is reached at a degree of conversion of about 0.6, which corresponds to a reaction time of 120 min at 135 °C. As known from previous works, SBM is able to form nanostructured dispersions in many epoxy−amine mixtures due to the compatibility of DGEBA with the M-block, but on curing such dispersions become unstable and SBM is squeezed out, well before the gel point. This is indeed the case of the (DGEBA/DDS)/SBM system investigated by Ritzenthaler et al.[7,16,17] Starting from an initially well-dispersed triblock/prepolymer blend, the authors observed a macrophase separation in the form of light diffusing filaments, even though PMMA was the major triblock component. This situation is illustrated in Figure 6, showing the light transmission of such a film as a function of curing time. At 135 °C, the transparency suddenly drops after 80 min

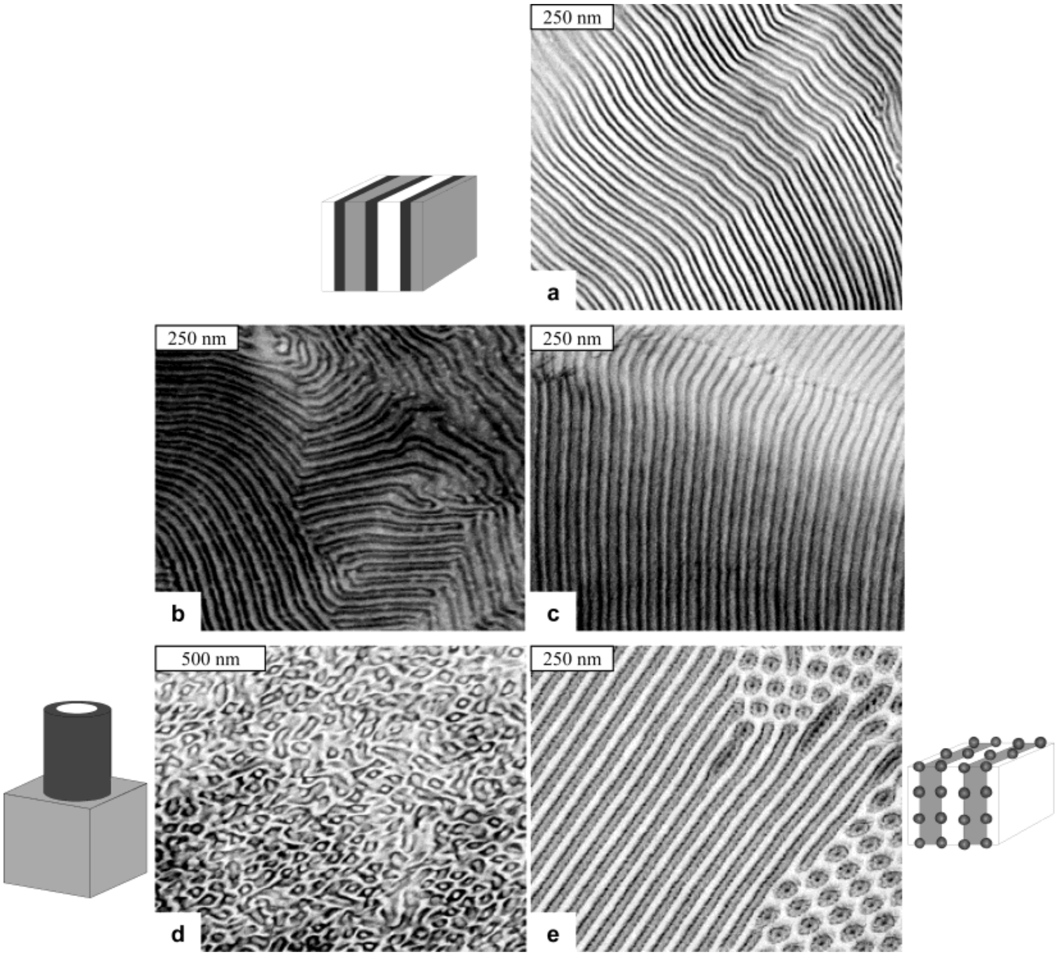

Figure 5. TEM micrographs of the block copolymers (a) SBM-11, (b) SBMG-6, (c) SBMG-11, (d) SBG-7, and (e) SBG-13. Films prepared from a solution in $CHCl_3$, except (d) (solution in THF).

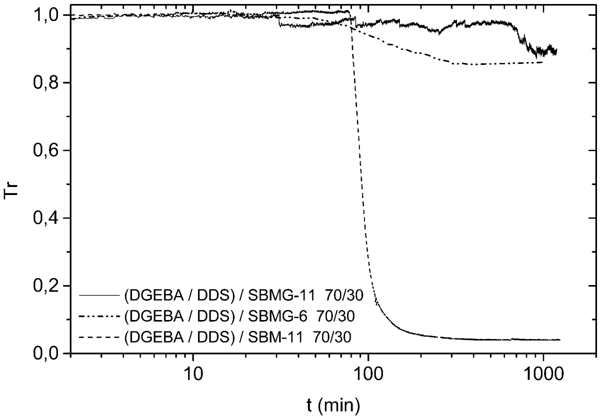

Figure 6. Cloud point curves of (DGEBA/DDS) blends with 30 wt % of SBMG-6, SBMG-11, and SBM-11 at 135 °C.

reaction. Clearly, the behavior is typical of a system with large mixing enthalpy ($\chi > 0$). In this context, playing with the curing conditions (time and temperature) is not of great help; the normal fate of such systems is the macrophase separation as soon as a certain degree of polymerization is reached. As an exception to this law, nanostructured morphologies were retained beyond the gel point in MCDEA cured compositions.[7,16,17] At the cost of a very accurate choice of the hardener, it is therefore possible to decrease the χ parameter to a less positive (or even negative) value.

Another possible way of quenching a nonequilibrium morphology is to form a certain amount of covalent links between the matrix and the dopant in the early stage of the curing cycle. In this approach, SBMG is the predisposed candidate as it presents a compatibilizing M-block, together with a potentially reactive G-block.

Before curing, DGEBA/DDS/SBMG samples give the aspect of tacky transparent films, in all points similar to those obtained with SBM, but on curing, striking differences appear when using the reactive copolymer. As seen in Figure 6, the films based on SBMG-6 and SBMG-11 do not lose more than 15% light transmission after complete curing at 135 °C. Eventually, the films present an opalescent blue coloration (yellow in transmission), which is characteristic of the Rayleigh-type scattering by particles smaller than the visible wavelengths. In this regime, the cross section is inversely proportional to the fourth power of the wavelength; scattering is therefore more effective at the blue end of the visible spectrum.

The TEM micrographs of the SBMG-6 and SBMG-11 based blends are presented in Figure 7a,b. Before curing, the fine dispersion of block copolymer nodules exhibit a raspberry-like morphology[4] with dark spheres of polybutadiene on light spheres of polystyrene in the epoxy–amine matrix, which also appears clear. In agreement with the optical transparency of the film, the block copolymer inclusions are remarkably uniform with an average size of 70 nm, hence confirming the initial miscibility of the PMMA block with the DGEBA/DDS prepolymer mixture. These “panther-skin patterns”resemble the ones recorded with all DGEBA/SBM blends at the same concentration before curing.[7,16,17]

The morphologies after curing at 135 and 220 °C are presented in Figures 7c–f. In SBMG-11, the initial nanostructured morphology is retained, almost unchanged, whatever the curing temperature. In particular, the size of included objects remains smaller than 70 nm, in agreement with the visual aspect of the films, which appear slightly opalescent after curing. The most evident difference (compare parts b and d of Figure 7) is the sharpening of the interfaces in cured samples, which may be responsible for the small change in light transmission. In the case of SBMG-6, a haze was observed in cured films, especially in those cured at 220 °C. Actually, this change of the visual aspect correlates with changes in the morphologies (Figure 7c,e), where a coalescence phenomenon between neighboring raspberry particles leading to objects of up to 300 nm length can be observed. The amount of G, which is smaller in SBMG-6 than in SBMG-11 (3 and 8%, respectively), could explain this behavior. Interestingly, when the cure is achieved at high temperature (220 °C), the PS and PB domains of aggregated raspberry particles merge, giving rise to large homogeneous domains of polystyrene surrounded by a continuous polybutadiene layer. Such behavior suggests the formation of wormlike micelles or vesicles. In nanostructured epoxy thermosets, it is known that this transition is triggered when decreasing the volume fraction of matrix-compatible chains in the block copolymer.[42] In SBMG–epoxy composites, this result is attained when reducing the number of reactive groups.

Thus, SBMG copolymers are efficient in ordering the epoxy–amine system at the nanoscopic level and to maintain the morphology and the optical aspect of the blends throughout the whole curing process. Moreover, the number of reactive groups determines the features of the final morphology. It seems reasonable to ask whether these reactive groups actually participate in the polycondensation.

A first possible effect of introducing glycidyl groups in the methacrylic sequence of SBM is to modulate the thermodynamic stability of the DGEBA/DDS/SBMG blends, in other words, to change the value of χ. Eventually, this will influence the degree of conversion at which macrophase separation occurs. The amplitude of this effect may be estimated by considering the Hansen parameters' variations induced by glycidyl side groups. On the basis of the additivity approximation[36,43] and considering the MG part as a single block, we find that the effect of introducing polar and H-bond functionalities through the glycidyl ring is almost compensated by the increase of the molar volume. As a result, the solubility parameter of the methacrylic block is not expected to be shifted by more than 3% in SBMG-6 and SBMG-11. This modification by itself can hardly explain the compatibilization of SBMG with DGEBA-DDS until complete hardening.

To understand the effects of reactive blending on the final morphology, we investigated the competition between SBMG and DGEBA epoxy functions in their reaction with DDS. In this study, the homopolymer PGMA was taken as a model compound. IR monitored reactions with DDS were achieved at 135 °C for an epoxide/N–H ratio equal to unity. Figure 8 shows that the PGMA + DDS and DGEBA + DDS reactions display similar conversion profiles. In particular, the conversion curves in logarithmic scales have their inflection points for the same reaction time. At low conversions, the reaction rate of DGEBA is approximately 3 times the one of PGMA. Beyond 50% conversion, the tendency is inversed with a higher reaction rate for PGMA. The behavior at higher temperatures may be conveniently inferred from DSC data (Figure 9). The thermogram of the SBMG-6/DDS blend presents an exothermic event with a maximum heat flow at 210 °C. In DGEBA/DDS, the large reaction exotherm beginning at 135 °C shows its maximum at 227 °C. Again, the experimental data suggest a quicker reactivity of DGEBA at low conversion stage.

From cloud point measurements in DGEBA/DDS/SBM, we know that the phase separation is triggered in the first 80 min of curing at 135 °C, which is more than necessary to induce the reaction of PGMA units with DDS. It is worth stressing that reaching an average number of one grafting per SBMG chain does not require more than 1.5% conversion for SBMG-11 or 5% for SBMG-6. Thus, the formation of a sufficient amount of surface active grafted chains in the early reaction stage helps to limit the interfacial tension and to maintain phase stability during the process. Nonetheless, the formation of more than one graft per chain leading to PGMA cross-links seems to be important in the long time relaxation of the morphology. In SBMG-6, which is less likely to form an important number of cross-links, the nonequilibrium morphology is able to relax before the ultimate stage of curing.

Conclusion

As a conclusion, it may be remembered that in many applications of block copolymers, the compatibility with homopolymer is exploited. Taking advantage of this concept in many different systems would require a purpose-made block copolymer in each case. Reactive block copolymers hence are of particular interest in this field, as reactive blending is a way of forcing compatibility when none of the blocks are miscible with the matrix. Furthermore, a single reactive copolymer may form covalent links with several different polymer families. Thus, SBG and SBMG described in this paper are potentially reactive with phenolates, carboxylic acids, amines, anhydrides, ..., with possible applications in thermosets, in photocure methacrylate systems,[44] in cross-linkable waterborne coatings,[45] etc. On the other hand, the reactivity of the G-block might be used to bring additional functionality by introduction of covalently linked side groups such as chromophores[46,47] or liquid crystalline moieties. Glycidyl methacrylate derivatives are also very attractive for the binding of biomolecules like heparin,[48] for heterogenization of homogeneous catalysts, or in the development of chelatants for separation of isotopes.[49] In all such concepts, block copolymer architectures may be helpful for controlling the structure and efficiency of the end products. As exemplified in this paper, block copolymers incorporating a certain amount of reactive groups may be synthesized by living anionic polymerization. In our case, up to five different monomers were combined sequentially, including GMA as the reactive one. A careful purification of the monomers was efficient to avoid contamination with dead chain precursors.

In the absence of any curing agent, SBG and SBMG copolymers are stable and self-assemble, showing typical morphologies of ABC triblock copolymers. When being

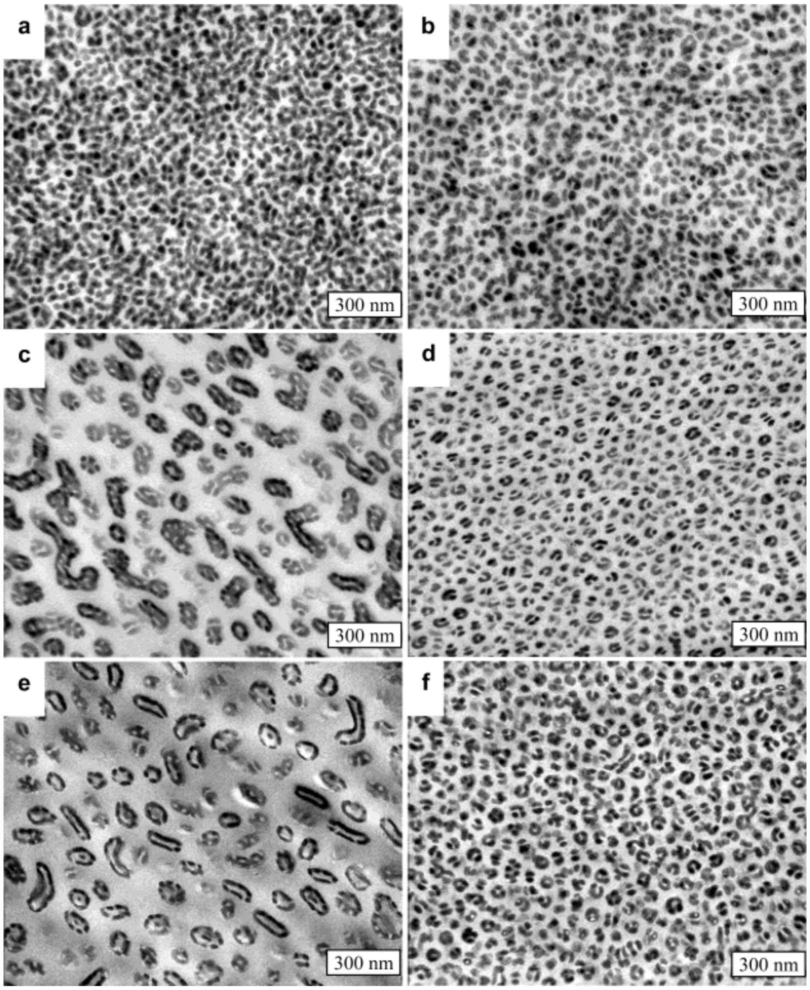

Figure 7. TEM micrographs of (DGEBA/DDS) blends with 30 wt % of (a) SBMG-6 before curing, (b) SBMG-11 before curing, (c) SBMG-6 after curing 5 h at 135 °C, (d) SBMG-11 after curing 5 h at 135 °C, (e) SBMG-6 after curing 5 h at 220 °C, and (f) SBMG-11 after curing 5 h at 220 °C.

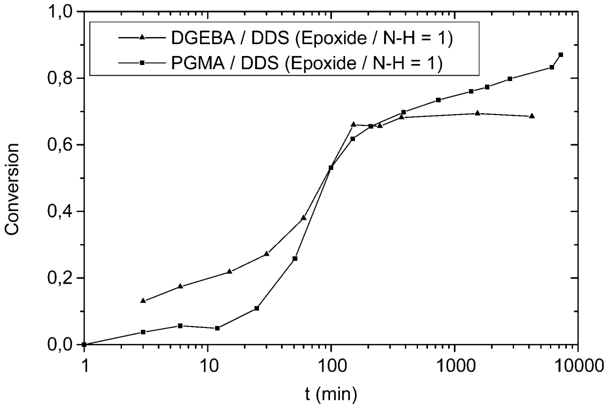

Figure 8. Kinetic studies of the DGEBA + DDS and PGMA + DDS reactions by infrared spectroscopy at 135 °C.

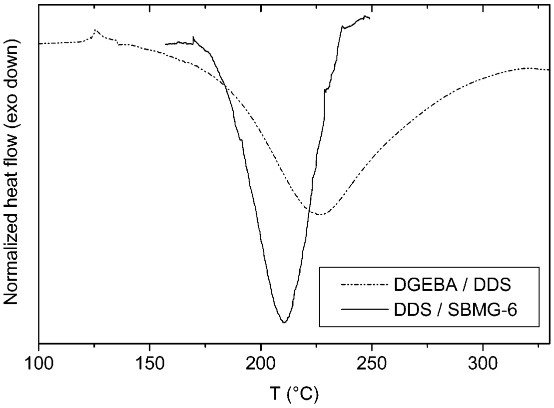

Figure 9. DSC heating traces for cure of DGEBA/DDS and DDS/SBMG-6; Normalized data: the exotherms recorded in the 150−275 °C region have been normalized by taking into account only the fraction of potentially reactive functional groups in a one-to-one ratio.

mixed with the amorphous epoxy−amine system, SBMG behaves as a strong structuring agent. The nanostructured morphologies of the DGEBA/DDS/SBMG blends are retained after cure. This demonstrates the effectiveness of the reaction-induced modification of the epoxy thermoset compared to that with nonreactive SBM triblock copolymers, which are expelled from the epoxy−amine network during its formation. It is shown that the use of reactive block copolymers of well-defined composition permits to finely adjust the final morphology of the composite. Thus, in one case, when the block copolymer was fitted with a large number of reactive groups, the formation of covalent links proved to be efficient for quenching the morphology already present before cure.

The size of triblock inclusions measured by TEM is in agreement with the optical appearance of these composites. Nanostructured epoxy networks synthesized by this means may present enhanced mechanical resistance without loss in transparency.[50] In another case, when the number of reactive monomers was reduced, a morphology transition has been observed on curing, with the appearance of vesicules. In such blends, the transparency is lost but the particular shape of the inclusions may be interesting for toughening epoxy at low loadings.[42] Thus, SBMG copolymers appear as key intermediates in the formulation of block copolymer/thermoset reactive blends.

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