ABC Triblock Copolymers/Epoxy−Diamine Blends. 2. Parameters Controlling the Morphologies and Properties

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ABSTRACT: The effect of composition and concentration of polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) copolymer triblock on final morphologies and properties of modified epoxy networks has been investigated. The DGEBA−MCDEA epoxy system, which ensures the miscibility of most of the PMMA blocks until the end of the reaction and thus the generation of a nanostructurated material, has been chosen. For low copolymer concentration (10 wt %), the network structure is found to be independent of the composition and micelles of PS and PB blocks can be undifferently observed. However, increasing copolymer amounts from 10 to 50 wt % induces a morphology change to either "spheres on spheres" or "core−shell" structure depending on the PB content in the triblock. For copolymer concentration higher than 50 wt %, the morphology strongly depends on the processing technique used, and only films prepared by solvent casting show an organization with long-range order similar to the neat block copolymer. The toughness of nanostructured epoxy networks has been evaluated. For low SBM concentration the toughness was observed to linearly vary with the PB concentration. For higher SBM concentrations (30 and 50 wt %) the "spheres on spheres" morphology is found to be more efficient than the "core−shell" one to improve the toughness of the epoxy network. But in all cases a higher toughness is obtained when the nanostructure is preserved; when a macrophase separation occurs, the toughness increase is lower.

I. Introduction

In a previous paper,[1] an epoxy network modified with 50 wt % of a polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate), SBM, with a low butadiene content was studied. The main conclusion was that the generation of transparent nanostructurated thermosets requires the solubility of the corresponding PMMA homopolymer with the growing thermoset polymer during the whole reaction. This requirement is respected when 4,4′-methylenebis[3-chloro-2,6-diethylaniline], MCDEA, is used as epoxy hardener. The final structure in this case is composed of undiluted PS and PB blocks forming a "spheres on spheres" morphology, and most of the PMMA fraction remain embedded in the epoxy network, even if some PMMA units phase separate at the interface with the PB nodules. On the other hand, the use of 4,4′-diaminophenyl sulfone (DDS) or 4,4′-methylenedianiline (MDA) as epoxy hardener induces the macrophase separation of the PMMA blocks during reaction, leading to flocculated micrometer sizes nanostructures and opaque materials.

The SBM triblock used was synthesized anionically at an industrial scale which means the presence of SB "impurities". When blended with epoxy and MCDEA, the triblock was shown to behave like an efficient compatibilizer by fully incorporating SB diblock. Thus, the generation of nanostructured thermosets from such industrial SBM presents the substantial advantage of not requiring any purification step.

The purpose of the present work is to study the effect of both composition of the copolymer on final morphologies and mechanical properties of modified epoxy−MCDEA networks.

II. Experimental Part

II.1. Materials. The thermoset precursors have already been described in part 1 of this series.[1] Their specifications are listed in Table 1.

Table 2 gathers the characteristics of the polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate) (SBM) triblock copolymers and the nomenclature used in this study. For instance, $S_{22}^{27}B_9M_{69}$−SB21 represents a copolymer as received and composed of $S_{22}^{27}B_9M_{69}$ pure triblock copolymer and 21 wt % of SB diblock. The numbers 22, 9, and 69 represent the weight of the respective PS, PB, and PMMA blocks; 27 is the molar mass of the PS block in kg mol^{-1}. The presence of SB diblock "impurities" is due to the process used for the triblock copolymer synthesis. The purification of the SBM copolymer can be achieved by precipitating initial SBM in cyclohexane at 80 °C three times successively. Cyclohexane is then removed during 20 h under vacuum, and pure SBM and SB impurities are isolated. It is important to point out that the two copolymers in Table 2 have equal molar mass and similar lengths for the PMMA blocks. They only differ by their composition of PS and PB blocks, both containing low "impurities" fraction (<20%).

II.2. Blends Protocol. The blends containing low triblock amounts (≤10 wt %) are prepared by mechanical stirring in a classical glass reactor. At a temperature of 135 °C, a kneading time of 12 h is required to obtain a complete dissolution of the triblock copolymer in DGEBA. The hardener MCDEA is then added and mixed for 5 min at 135 °C. To prevent significant reaction during the blending step from occurring, the mixing time was reduced as much as possible. The blends are then

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Table 1. Characteristics of the Epoxy and Amine Monomers Used

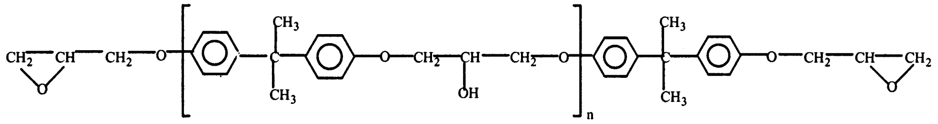
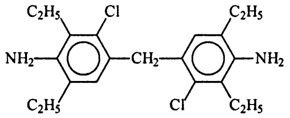
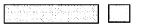
Name	Chemical Structure	Molar Mass (g/mol)	Supplier
Diglycidyl ether of bisphenol A (DGEBA)		382.6 $\bar{n}$=0.15	Ciba Geigy
4,4'-methylenebis-[3-chloro 2,6 diethylaniline] (MCDEA)		380	Lonza

Table 2. Characteristics of Copolymers Used (As-Received)

Purity (wt %)	*Triblock Composition (wt %)*	*Nomenclature*
 79 21	 22 9 69	$S_{22}^{27}B_9M_{69}$ − SB21
 90 10	 12 18 70	$S_{12}^{14}B_{18}M_{70}$ − SB10

casted and cured in a mold. For blends with triblock amounts above 10 wt %, a premix containing 10 wt % of copolymer is prepared with the method described above. This premixed is then blended with the appropriate amount of copolymer to adjust the desired composition, in either a roll mix (IM30 from Lescuyer & Villeneuve) or a twin-screw kneader (Brabender W50) for 1 h at 135 °C. Once the mixture is cooled and freezer-milled, the diamine powder is then added. Finally, mixtures are pressed in a mold at the curing temperature.

For triblock concentrations higher than 50 wt %, because of the high viscosity of the solution and in order to prepare model samples, blending has also been prepared by solvent casting. DGEBA, diamine, and triblocks were then codissolved in toluene or chloroform. The solvent was slowly evaporated for 1 week to avoid macrophase separation between SBM triblocks and SB diblocks impurities and then 12 h under vacuum to ensure complete removal of the solvent.

II.3. Curing Protocol. Blends are precured at 135 °C for 14, 20, 24, or 185 h and postcured for 4 h at 190 °C. The precuring time was increased with the triblock concentration to take into account the increase of the dilution effect of reactive functions.

II.4. Methods. *Dynamic Mechanical Thermal Analysis (DMTA).* DMTA was carried out on cured blends with a Rheometrics solid analyzer (RSA II) to obtain tensile dynamic mechanical spectra (storage modulus E', loss modulus E'', and loss factor tan δ) between 50 and 250 °C at a frequency of 1 Hz. The samples used were parallelepipedic bars ($1 \times 2.5 \times 34$ mm^3).

Small-Angle X-ray Scattering (SAXS). SAXS experiments were performed with a setup including a rotating anode X-ray generator with copper target and nickel filter ($\lambda = 1.54$ Å), a point collimation produced mainly by two orthogonal mirrors, and a line position sensitive proportional counter connected to a computer (cf. Part 1). The scattered intensity I was recorded at ambient temperature as a function of the scattering vector q ($q = 4\pi/\lambda \sin\theta$, θ being the scattering angle) in the range 0.01−0.1 Å^{-1}.

Transmission Electron Microscopy (TEM). Ultrathin sections were prepared with an ultramicrotome equipped with a diamond knife and stained 2 h with osmium tetraoxide (OsO_4) vapors. To increase sample rigidity when it was not high enough to prepare high-quality ultrathin sections at room temperature, pyramid-shaped pieces were cut and treated with a 4% aqueous solution of osmium tetraoxide for 1 week. Ultrathin sections were then microtomed on the flat tops of the pieces. Because of the applied staining conditions, PB appears black, PS is gray, and PMMA is slightly whiter than the epoxy−amine network.[2]

For some samples, ruthenium tetraoxide (RuO_4) staining has also been used. For the same purpose the ultrathin sections were placed on copper grids and stained 30 min with RuO_4 vapors. The ruthenium tetraoxide may also react with the polybutadiene double bonds and the DGEBA aromatic rings. The PS blocks are then preferentially stained due to the oxidation of the aromatic rings.[3,4] No reaction was noticed with PMMA.

Sections were observed with a Philips CM120 transmission electron microscope at an accelerating voltage of 80 kV.

Toughness. The critical stress intensity factor, K_{Ic}, was obtained from three-point bending test performed on single-edge notched specimens (SEN). The procedure proposed by Williams and Cawood[5] was strictly followed with a crosshead speed of 10 mm min^{-1}. K_{Ic} was calculated as the mean value of 10 tests at least.

III. Results and Discussion

III.1. Morphologies of Neat SBM Triblock Copolymers. Before studying the epoxy-modified networks, the effect of the increase of PB content on the nanostructuration of the neat triblock has been determined. The morphologies obtained for neat triblock copolymers films prepared by solvent casting (the block copolymer is dissolved in tetrahydrofuran and placed in flat-bottomed Petri dishes; the solvent evaporates slowly for 1 week and then one night under vacuum) are given in Figure 1a,b. The formation of morphologies in the SBM system is governed by the relatively weak immiscibility of the PS and PMMA end blocks compared to the strong immiscibility of the PB midblock: $\chi_{SM} \ll \chi_{SB} < \chi_{MB}$.[6] Concerning the first block copolymer, $S_{22}^{27}B_9M_{69}$−SB21, the lamellar structure (Figure 1a) of PS and PMMA blocks has been discussed in part 1 and explained by the incorporation of the SB diblock in the SBM structure, leading to an effective increase of the volume fraction of both PS and PB toward PMMA.

The copolymer $S_{12}^{14}B_{18}M_{70}$−SB10 with higher volume fraction of PB (Figure 1b) shows the formation of a hexagonally ordered core−shell structure, designated as “cylinder in cylinder (cic)” morphology.[7] The PS blocks can be recognized as the inner cylinder surrounded by the PB midblocks forming the outer shell. The micrographs present a coaxial view of the core−shell cylinders as well as cylinders which were cut parallel to the main

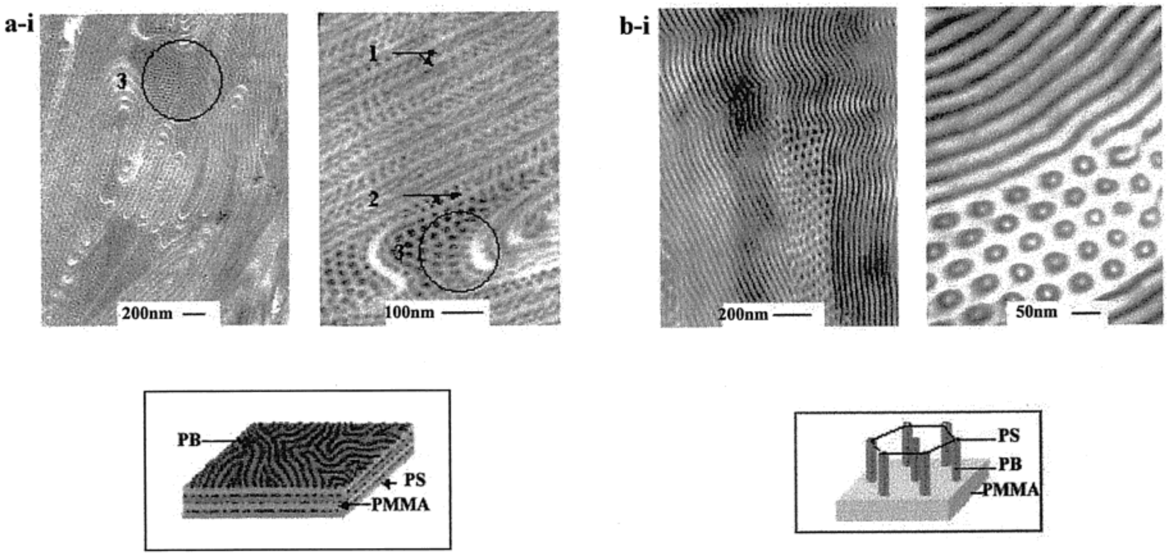


Figure 1. Transmission electron micrographs of triblock copolymer obtained by solvent casting and the schematic representation of the structure (OsO_4 staining). (a) $S_{22}^{27}B_9M_{69}$−SB21 and (b) $S_{12}^{14}B_{18}M_{70}$−SB10.

Table 3. Radius of Particles (nm) Obtained by Small-Angle X-ray Scattering in Cured Epoxy Systems Modified with 3 and 10 wt % $S_{22}^{27}B_9M_{69}$−SB21 and $S_{12}^{14}B_{18}M_{70}$−SB10

copolymer (%)	$S_{22}^{27}B_9M_{69}$−SB21	$S_{12}^{14}B_{18}M_{70}$−SB10
3	15	16
10	16	16

axis. Schematic descriptions of the organization of both copolymers are given below their respective micrographs.

III.2. Influence of the Copolymer Concentration on the Morphology of DGEBA−MCDEA-Based Blends. Different from part 1,[1] the morphological studies were therein restricted to (as-received) nonpurified triblocks.

Figure 2a−d, i and ii, displays typical electron micrographs of fully reacted blends of DGEBA/MCDEA with low copolymer amounts of as-received $S_{22}^{27}B_9M_{69}$−SB21 at two different magnifications. A schematic description of the structure (Figure 2a−d, iii) is proposed below each micrograph. The blend with 50 wt % copolymer has already been described in part 1.[1] For 10 wt % copolymer, dispersed microdomains of approximately 30 nm in diameter are observed, as expected for block copolymer solutions. The staining of these microparticles by osmium tetraoxide and ruthenium tetraoxide reveals that they are composed of both PS and PB blocks, but the lack of contrast inside the nodules does not allow to distinguish PS domains from PB domains.

The particles sizes have been determined from the scattering profiles.[1] The results, presented in Table 3, indicate that the particles radii, close to 15 nm, do not depend on the copolymer concentration. Indeed, increasing the copolymer concentration only leads to an increase in the number of nodules. The size and the structure of the micelles depend on the copolymer composition, the block length, and the solvent quality. In our case, the epoxy system behaves as a selective solvent of PMMA blocks, and the micelles sizes therefore only depend on the lengths of PS and PB segments, which are similar for both triblocks.

The white shell surrounding the particles (Figure 2a−d) which can be particularly observed when the samples are stained before microtoming certainly denotes the presence of a PMMA shell. This also means that PMMA blocks are partially and locally expulsed from the epoxy network during curing, as observed by Lipic et al.[8] for the PEO blocks in the case of PEO-*b*-PEP block copolymer. As explained in part 1, the PMMA blocks are initially miscible with the epoxy precursors whereas the PS and PB blocks are immiscible. The PMMA blocks remain soluble up to the end of the reaction, but the strong immiscibility of PB blocks with the matrix leads to a partial deswelling of the PMMA chains at the PMMA/PB phase boundary.

For block copolymer concentrations higher than 10 wt % (Figure 2b−d), a "spheres on spheres" (raspberry) morphology is observed[9] with gray PS nodules surrounded by dark polybutadiene particles in a PMMA−epoxy matrix. A PMMA shell encircling the particles can also be noted. Increasing block copolymer contents from 15 to 30 and 50 wt % induces a significant modification of both the size and the structure of copolymer domains. The polybutadiene midblock organizes into cylinders at the interface between the PS and the PMMA-modified epoxy domains when the copolymer concentration reaches 50 wt %. Some PB nodules can also be observed inside the PS domains (Figure 2c,d) as a result of the presence of SB diblock in the as-received SBM copolymer. The polybutadiene blocks of the diblock SB, which are immiscible with the epoxy precursors and the PMMA blocks, phase separate far from the interface of the nodules, that is to say, in the PS particles. Besides, because of the high concentration of SB "impurities", all the diblock cannot be incorporated into the SBM structure, leading to some SB macrophase separation in PS large domains including cubic packed PB spheres (Figure 2d−i, the 50 wt % sample is slightly opaque).

Dynamic mechanical thermal analysis, DMTA, carried out on fully reacted samples containing $S_{22}^{27}B_9M_{69}$−SB21 is given in Figure 3. For low copolymer contents (≤10 wt %), the presence of a single relaxation, which is located at a lower temperature than that of the neat epoxy network, confirms that some PMMA units remain solubilized in the epoxy matrix. At such a low triblock concentration, the relaxation corresponding to segregated PS and PB domains is not detected. Alternatively,

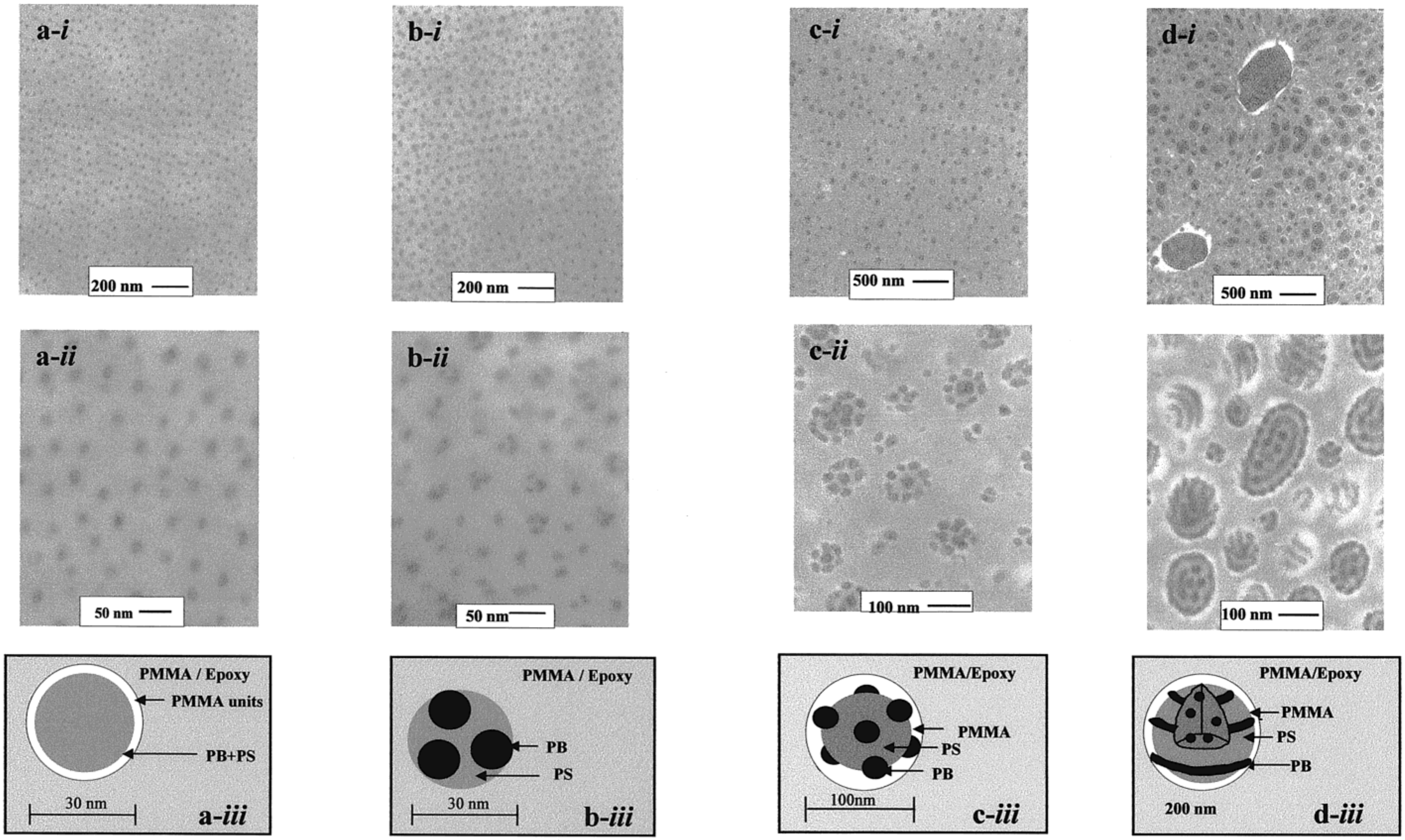


Figure 2. Transmission electron micrographs (i, ii) and schematic representation of the structure (iii) obtained for DGEBA−MCDEA epoxy system containing 10 (a), 15 (b), 30 (c), and 50 wt % (d) $S_{22}^{27}B_{69}M_{69}$−SB21 copolymer (OsO_4 staining).

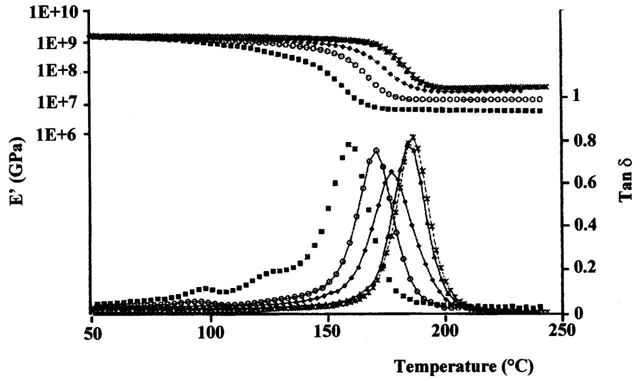


Figure 3. DMTA spectra obtained at 1 Hz of the neat (*) and modified DGEBA−MCDEA epoxy networks with 3 (▲), 10 (◆), 30 (○), and 50 wt % (■) of $S_{22}^{27}B_9M_{69}$−SB21 copolymer.

three other relaxations are observed when the copolymer amount is increased: (i) a very low-temperature relaxation (−90 °C) (not shown here) which corresponds to the relaxation of strongly immiscible PB domains; (ii) a relaxation at 98 °C which corresponds to the relaxation of the segregated PS blocks of the copolymer; and (iii) a relaxation at 132 °C which characterizes the partial segregation of PMMA units from the epoxy-rich matrix.

We observe that the epoxy network does not affect the PS and PB block relaxations, confirming the purity of these two microphases. On the contrary, the main relaxation of the network is shifted toward lower temperature when the copolymer concentration, i.e., dissolved PMMA concentration, increased as the result of a further plastification effect. The same phenomenon has already been observed for homoPMMA/DGEBA−MCDEA blends.[10] In this system, the homoPMMA was fully solubilized in the epoxy network, and at the end of the curing process, a homogeneous material was obtained. A single broad relaxation, located between those of the pure PMMA and the neat epoxy network, was shifted to lower temperature as the PMMA content was increased, strengthening the idea that the structure of homoPMMA/DGEBA−MCDEA blends is homogeneous. These results suggest that, in the case of SBM/DGEBA−MCDEA blends, a large part of the PMMA blocks are solubilized in the epoxy network and that partial segregation of PMMA units is certainly limited at the very vicinity of the PB blocks, which are strongly immiscible with the epoxy network. This partial segregation of PMMA units forms a "dry brush" near the PB interface.

For copolymer concentration higher than 50 wt %, blends have been prepared either by mechanical mixing or by solvent casting. Contrary to blends containing low copolymer amounts (≤50 wt %), the final morphology does depend on the preparation method used. Blends prepared mechanically exhibit a strongly nonequilibrium bicontinuous structure that depends on many parameters such as pressing time and temperature. One example for a blend with 80 wt % copolymer is given in Figure 4a. Similar morphologies (Figure 4b) can be obtained for neat triblock copolymer films also prepared mechanically. The micrographs in Figure 5a−c exhibit the final morphologies of blends prepared by solvent casting and containing 70, 80, and 90 wt % $S_{22}^{27}B_9M_{69}$−SB21, respectively. At such high concentrations, the morphologies remain very close to the one of the neat triblock. With 80 wt % copolymer (Figure 5b), the SBM tends to create lamellar of PS and PMMA-modified epoxy thermoset with PB cylinders at the interface, referred as the "cylinders at the wall" (lc) morphology,[6] and some lamellar are swollen by SB impurities.

With 90 wt % copolymer (Figure 5c), the morphology of the blend is further close to the one of the pure copolymer, that is to say, lamellae of PS and PMMA with PB cylinders at the interface (cf. Figure 1a). It can be noted the macroseparation of SB impurities in large PS-rich domains containing organized PB nodules.

III.3. Influence of the SBM Composition on the Final Morphologies. Considering that strongly nonequilibrium structures are generated by mechanical stirring for high block copolymer concentrations, only concentrations of block copolymers lower than or equal to 50 wt % have been selected to investigate the influence of PB concentration. Micrographs in Figure 6 corresponding to the morphologies of blends with 10,

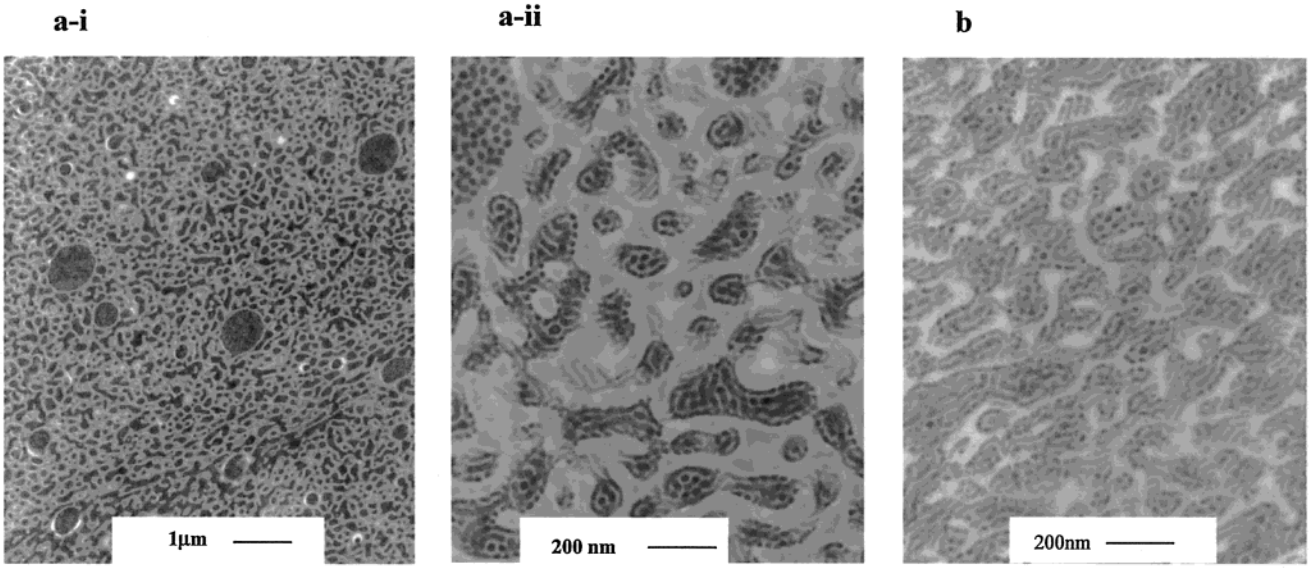


Figure 4. Transmission electron micrograph (OsO_4 staining) of films obtained by mechanical mixing: (a) a blend containing 80 wt % $S_{22}^{27}B_9M_{69}$−SB21 after curing and (b) the neat triblock copolymer for a comparison.

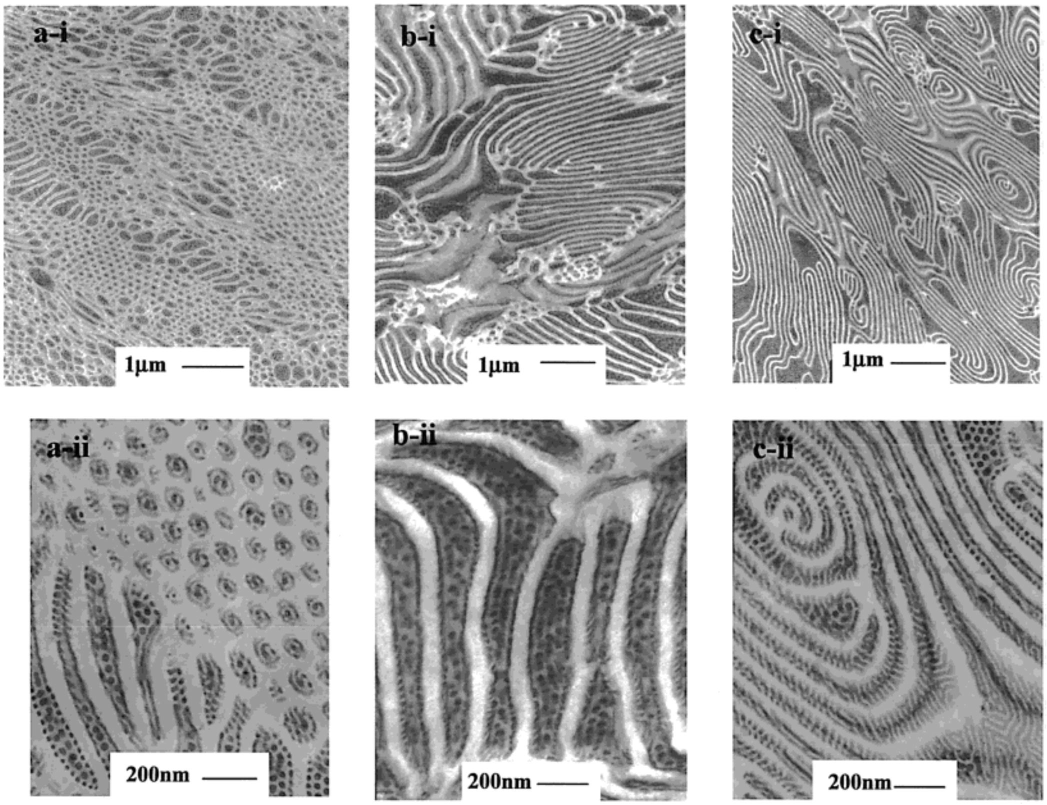


Figure 5. Transmission electron micrographs obtained with DGEBA–MCDEA epoxy networks containing (a) 70, (b) 80, and (c) 90 wt % $S_{22}^{27}B_9M_{69}$–SB21 and prepared by solvent casting (OsO_4 staining).

30, and 50 wt % of triblock $S_{12}^{14}B_{18}M_{70}$–SB10 can be compared to those obtained for 10, 30, and 50 wt % of $S_{22}^{27}B_9M_{69}$–SB21 copolymer (Figure 2).

At 10 wt % copolymer (Figures 2a and 6a), the copolymer composition does not affect the final morphology. Concerning the size of the particles measured by SAXS and given in Table 3, the triblock composition seems to have no influence on the size of the nodules. This result combined with the staining of these micelles by both ruthenium and osmium tetraoxide suggests that the microparticles observed are certainly composed of both PS and PB blocks. Even if the block copolymer composition changes, the global PS plus PB concentration remains identical for the two copolymers, and the microsegregated domains finally exhibit similar sizes.

When increasing the copolymer content to 30 and 50 wt %, micrographs exhibit core–shell (“onion”) structure with a PS core and PB shell. The high polybutadiene concentration of the $S_{12}^{14}B_{18}M_{70}$–SB10 block copolymer allows the longer PB blocks to totally surround the PS spheres. Alternatively, for the first $S_{22}^{27}B_9M_{69}$–SB21 block copolymer, the fraction of butadiene is not high enough for the PB to form a continuous and homogeneous shell around the PS spheres. Riess et al.[11] also obtained identical structure with neat polystyrene-*block*-polyisoprene-*block*-poly(methyl methacrylate) triblock copolymers. For high PMMA concentration, they could observe PS nodules surrounded by small PI spheres in a PMMA matrix. When increasing the PI fraction at the expanse of PS, the morphology changes into a core–shell structure formed by PS core surrounded by a PI shell.

However, our results suggest that the structuration of our two triblock modified epoxy networks is equivalent to that of a neat SBM triblock copolymer which would have a higher PMMA weight fraction as the consequence of the miscibility of most the PMMA block with the epoxy network during the whole epoxy–amine reaction.

Besides, some nodules present multilayer structures as a result of the incorporation of SB impurities in the triblock structure. For the $S_{12}^{14}B_{18}M_{70}$–SB10 triblock copolymer, the volume fraction of PB is high enough for PB blocks to organize in layers surrounding PS domains.

The dynamic mechanical spectra carried out on these samples after reaction for various copolymer concentrations are given in Figure 7. The results obtained are similar to those of the first $S_{22}^{27}B_9M_{69}$–SB21 triblock copolymer (Figure 3). Once again we observe a shift of the network main relaxation to lower temperature with increasing the triblock amount and the presence of two additional relaxations: (i) A low temperature (98 °C) one, corresponding to the relaxation of PS block. Compared to the $S_{22}^{27}B_9M_{69}$–SB21 copolymer, the lower amplitude is consistent with the smaller PS volume fraction. (ii) A higher temperature (132 °C) one, attesting from the partially segregation of PMMA blocks. A schematic representation of the two structures for 30–50 wt % of the triblock copolymers in DGEBA–MCDEA network is given in Figure 8a for $S_{22}^{27}B_9M_{69}$–SB21 and in Figure 8b for $S_{12}^{14}B_{18}M_{70}$–SB10. Finally, the modification of the block copolymer composition only affects the organization of the PS and PB blocks while PMMA blocks which favorably interact with epoxy ensures the structuration of the material at a nanometer scale.

III.4. Use of SBM Triblock Copolymers as Epoxy Toughners. The neat DGEBA–MCDEA epoxy matrix is very brittle, with a toughness K_{Ic} value of 0.65 MPa $m^{1/2}$ for a glass transition temperature $T_g = 187$ °C.[12]

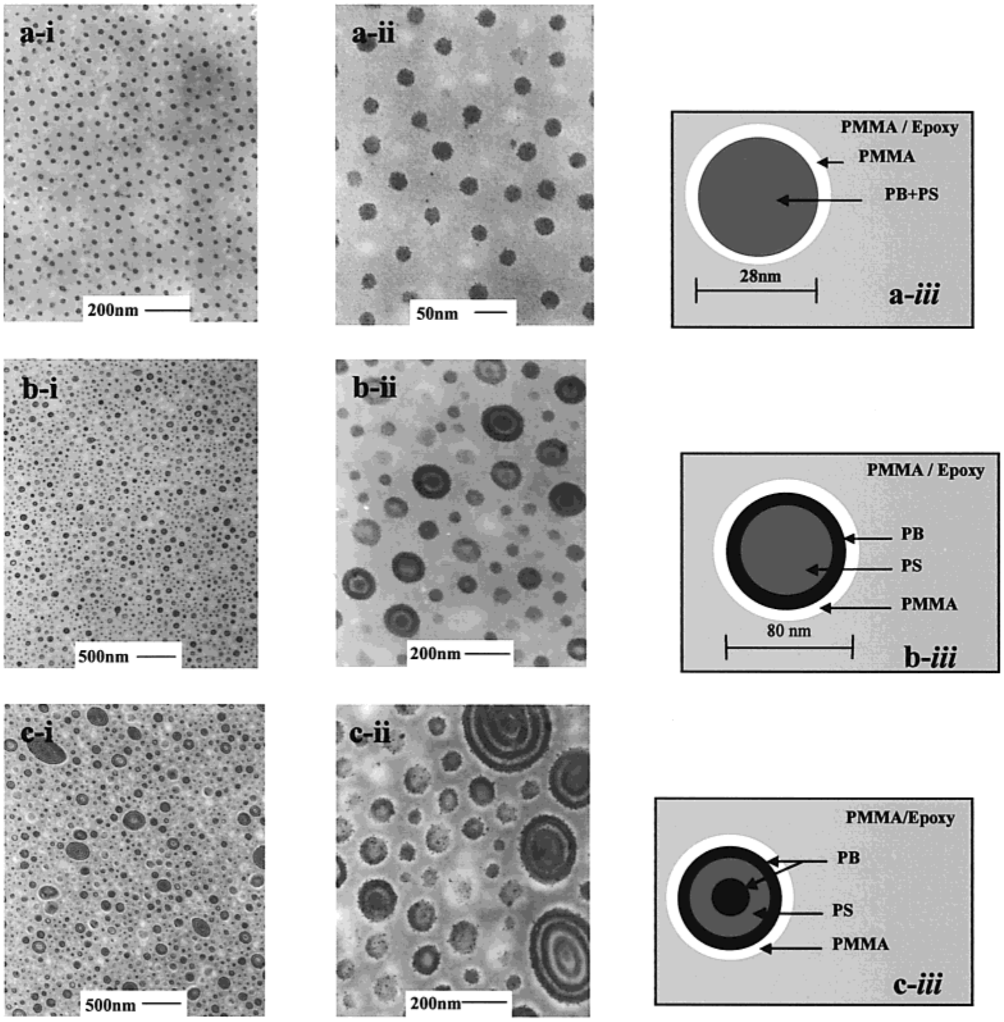


Figure 6. Transmission electron micrographs (i, ii) and schematic description (iii) of the structure obtained for DGEBA−MCDEA epoxy systems containing 10 (a), 30 (b), and 50 (c) wt % $S_{12}^{14}B_{18}M_{70}$−SB10 copolymer (OsO_4 staining).

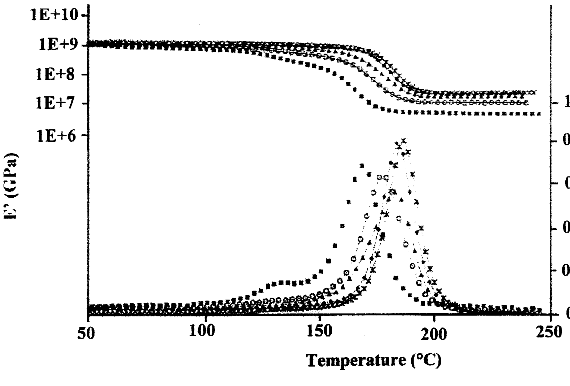


Figure 7. DMTA spectra obtained at 1 Hz of the neat (*) and modified epoxy network with 3 (▲), 10 (◆), 30 (○), and 50 wt % (■) of $S_{12}^{14}B_{18}M_{70}$−SB10 copolymer.

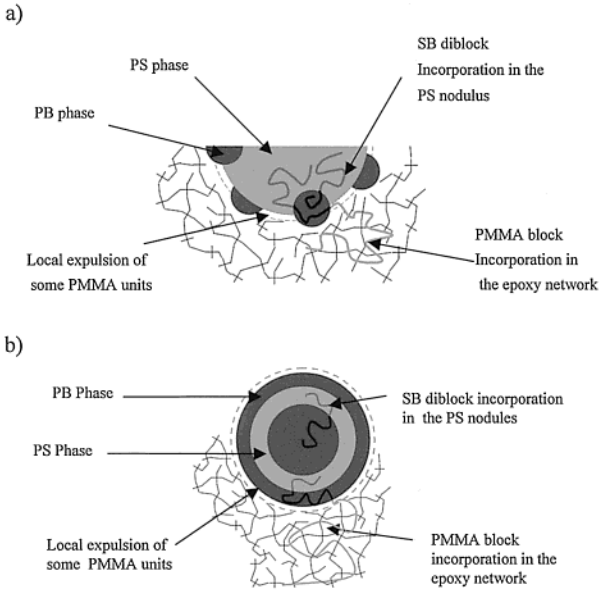


Figure 8. Schematic representations of the blocks organization for a 30 or 50 wt % blend after epoxy reaction (a) $S_{22}^{27}B_9M_{69}$−SB21 and (b) $S_{12}^{14}B_{18}M_{70}$−SB10 copolymers.

The addition of SBM triblocks can then be expected to be a powerful way of improving the poor fracture resistance of epoxy thermosets. In Figure 9 are plotted the K_{Ic} values obtained for different concentrations of SBM up to 50 wt %. All the samples have been prepared by mechanical stirring. It is worth noting that the continuous matrix always remains the epoxy−diamine component whatever the SBM concentration in the investigated range. This constitutes a major difference and advantage compared to the classical use of low molar mass reactive rubbers, for which phase inversion occurs when the concentration is higher than 20 wt %.[13] For both SBM copolymers, the toughness very signifi-

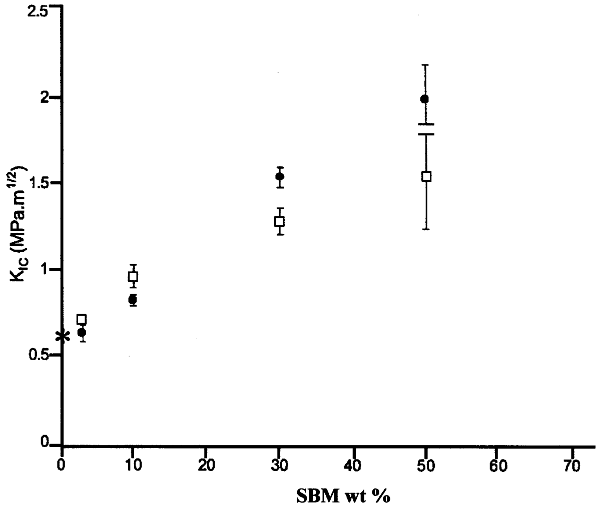


Figure 9. Influence of as-received SBM concentrations and compositions on material toughness; (*) and neat DGEBA−MCDEA, (●) $S_{22}^{27}B_9M_{69}$−SB21, (□) $S_{12}^{14}B_{18}M_{70}$−SB10 as toughner agents at different concentrations.

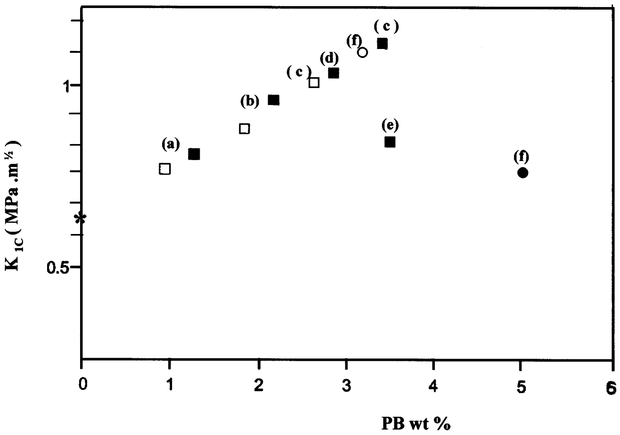


Figure 10. Influence of the SBM characteristics on the impact modification of 10 wt % SBM/DGEBA−MCDEA blend: purified (□) and as received (■) SBM; (a) $S_{22}^{27}B_9M_{69}$−SB21; (b) $S_{12}^{14}B_{18}M_{70}$−SB10; (c) $S_{24}^{21}B_{26}M_{50}$−SB35; (d) $S_{11}^{18}B_{22}M_{67}$−SB26; (e) $S_{21}^{33}B_{24}M_{55}$−SB48; and (f) purified (○) and as-received (●) $B_{30}^{8}M_{70}$−PB25.

cantly increases with the triblocks concentration. Until 10 wt % of SBM, the toughness is slightly higher for the blends based on the SBM containing the longer PB block. Alternatively, for higher concentrations, blends based on $S_{22}^{27}B_9M_{69}$−SB21 exhibit higher toughness, suggesting that the "raspberry" morphology (Figure 2c) is more efficient in improving mechanical properties than the "onion" (Figure 6b) morphology.

For blends containing 10 wt % of SBM, the relationship between toughness and PB concentration has been studied. To get a broad range of PB concentrations, different blends have been prepared with both as-received and purified SBM (due to the presence of SB "impurities", the as-received SBM contains a higher PB wt % compared to the purified one) and with other SBM triblocks with higher PB amounts. Note that all blends were transparent (except two) and exhibited a similar morphology (Figures 2a and 6a): ordered SB nanoparticules with diameters lower than 30 nm.

It appears from Figure 10 that the K_{Ic} of all the samples (except two opaque samples, discussed later) increases with the PB wt %. For example, K_{Ic} is equal to 0.81 MPa m$^{1/2}$ for $S_{22}^{27}B_9M_{70}$−SB21 and increases up to 1.18 MPa m$^{1/2}$ for $S_{24}^{21}B_{26}M_{50}$−SB35. Both blends have the same T_g = 184 °C, with a decrease of only 3 °C compared to the neat matrix.

A very interesting result is the fact that as the SB "impurities" increase the overall PB wt % in the blend, the K_{Ic} value is concurrently increased. Typically, K_{Ic} = 1.05 MPa m$^{1/2}$ for the purified $S_{24}^{21}B_{26}M_{50}$ compared to K_{Ic} = 1.18 MPa m$^{1/2}$ for the as-received $S_{24}^{21}B_{26}M_{50}$−SB35 (Figure 10d). This favorable "booster" effect of SB "impurities" on mechanical properties has of course a limit: when the SB concentration is higher than 45%, for instance with $S_{21}^{33}B_{24}M_{35}$−SB48, or when the PMMA block is too short, part of SB "impurities" can no more be fully incorporated in the SBM structure and thus macroseparates. The sample becomes opaque with a large drop of K_{Ic} compared to that expected from the curve (Figure 10e). This result means that an ordered structure of dispersed nanoparticles in the sample is an important parameter for controlling the toughness.

Also interesting is the comparison between SBM triblock and BM diblocks. The blend prepared with purified $B_{30}^{8}M_{70}$ follows the same trend (Figure 10f) than the blends based on purified or as-received SBM (Figure 10a−d). But contrary to SBM, BM diblocks are not able to stabilize the PB "impurities" always present in the as-received sample, leading to opaque blends with isolated macrophase-separated domains with diameters in the range 100−500 nm.[1] The effect on fracture resistance is dramatic. From a value of 0.95 MPa m$^{1/2}$ with purified $B_{30}^{8}M_{70}$, the toughness of the blend decreases up to 0.77 MPa m$^{1/2}$ for the blend prepared with the as-received $B_{30}^{8}M_{70}$−PB25.

IV. Conclusion

The requirement to obtain nanostructured thermosets with SBM triblocks is the solubility of the corresponding PMMA homopolymer with the growing thermoset during the whole reaction. In this part the various parameters affecting the nanostructure of SBM modified DGEBA−MCDEA epoxy network have been presented.

For low copolymer concentration, a micellar structure formed by both PS and PB blocks is generated as the consequence of the immiscibility of those blocks with the epoxy precursors, while the favorable interaction of PMMA with epoxy ensures the structuration of the blend at a nanometer scale. Depending on the copolymer composition, increasing block copolymer concentration from 10 to 50 wt % induces a change to either more complex "spheres on spheres" (raspberry) structure, with PB nodules localized around PS spheres or a core−shell (onion) morphology composed of PS spheres surrounded by PB shells, when the PB concentration is high enough. For high copolymer concentration (typically higher than 50 wt %), the morphology of the blends dramatically depends on the processing technique used (as for the neat block copolymer). A mechanical mixing leads to strongly nonequilibrium structures whereas films obtained by solvent casting present morphologies with long-range order similar to the block copolymer ones.

The addition of SBM was found to be a powerfull way to solve the problem of poor toughness of epoxy networks with an increase from 0.65 to 2 MPa m$^{1/2}$ for a 50−50 blend without the drawback of phase inversion, which classically occurs in the case of liquid rubber additives.[13] At low copolymer concentration, 10 wt %, toughness was observed to linearly increase with the PB wt % in the triblock. SB diblocks, which are inherently present in the SBM, were shown to behave as toughness "boosters" as long as a transparent nanostructured material is preserved. Indeed, for concentrations higher than 45 wt % in the as-received copolymer, the SBM triblock is no more able to fully stabilize the SB diblocks which partially macrophase separate and induce a significant decrease of the toughness.

However, one major advantage of SBM triblocks compared to BM diblocks remains their ability to stabilize a larger amount of "impurities" (SB in the case of SBM and homoPB in the case of BM) and then to further ensure the formation of a nanostructured thermoset without the need of a purification step.

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References and Notes

(1) Ritzenthaler, S.; Court, F.; David, L.; Girard-Reydet, E.; Leibler, L.; Pascault, J, P. *Macromolecules* **2002**, *35*, 6245−6254.
(2) Sawyer, L.; Grubb, D. T. *Polymer Microscopy*; Chapman and Hall: London, 1997; pp 93−109.
(3) Trent, J. S.; Scheinbeim, J. I.; Couchman, P. R. *J. Polym. Sci., Polym. Lett. Ed*. **1981**, *19*, 315−319.
(4) Trent, J. S.; Scheinbeim, J. I.; Couchman, P. R. *Macromolecules* **1983**, *16*, 589−598.
(5) Williams, J. G.; Cawood, M. J. *Polym. Test*. **1990**, *9*, 15.
(6) Stadler, R.; Auschra, C.; Beckmann, J.; Krappe, U.; Voigt-Martin, I.; Leibler, L. *Macromolecules* **1995**, *28*, 3080−3097.
(7) Goldacker, T.; Abetz, V. *Macromolecules* **1999**, *32*, 5165−5167.
(8) Lipic, P. M.; Bates, F. S.; Hillmyer, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 8963−8970.
(9) Breiner, U.; Krappe, U.; Jakob, T.; Abetz, V.; Stadler, R. *Polym. Bull. (Berlin)* **1998**, *40*, 219−226.
(10) Ritzenthaler, S.; Girard-Reydet, E.; Pascault, J. P. *Polymer* **2000**, *41*, 6375−6386.
(11) Riess, G.; Schlienger, M.; Marti, S. *J. Macromol. Sci., Phys.* **1980**, *17*, 355−374.
(12) Girard-Reydet, E.; Vicard, V.; Pascault, J. P.; Sautereau, H. *J. Appl. Polym. Sci.* **1997**, *65*, 2433−2445.
(13) Williams, R. J. J.; Rozenberg, B. A.; Pascault, J. P. *Adv. Polym. Sci.* **1997**, *128*, 95−156.

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