Nanostructured Polymer Blends: From Core/Shell Nanoobjects to Continuous Three-Phase Morphologies

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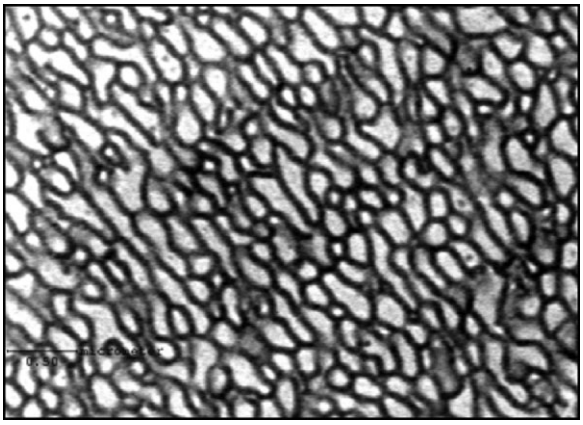
A PS-*b*-PIP-*b*-PMMA copolymer has been melt-blended with homo-PMMA with a similar molecular weight as the PMMA block. For a 50:50 wt.-% mixture, the components form 3D bicontinuous lamellae. Upon annealing at 190 °C, a more regular network is observed, which consists of PMMA and 55 nm-thick bilayered lamellae of triblock copolymer, both being continuous. This co-continuity persists even when $\overline{M}_n$ of the homo-PMMA is twice that of the PMMA block in the copolymer. For 30:70 and 20:80 wt.-% copolymer/homopolymer pair, the copolymer forms cylindrical and spherical phases, respectively. Blends have also been prepared by solvent casting. Large domains of copolymer interconnected by few lamellae are observed in the 50:50 blend that reorganize into a bicontinuous network upon annealing.



Introduction

Polymer blending is a very simple and cost-effective method for producing new materials from existing polymers. Because polymer immiscibility is the rule, most polymer blends are multiphase with a morphology that depends on composition, interaction parameter, and processing conditions. Manipulation of phase morphology is of the utmost importance because of a direct influence on the physico-mechanical properties of the blends. General organization and size of the phases are primarily dictated by the state of interconnection of the phase-separating polymers. Indeed, block copolymers usually form nanophases with a high periodicity, whereas physical blends of the same composition phase-separate irregularly at a micrometer scale. A combination of these two extreme situations paves the way to the nanostructuring of a polymer A by a block copolymer AB or ABC that contains a block identical to the matrix.

Among the possible nanostructures, continuous lamellae of copolymers throughout the (continuous) polymer matrix, thus bicontinuous phase morphology, is of the utmost importance because of direct impact on the physicochemical properties of the blends.[1] Indeed,

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uninterruptedly connected nanophases of an AB diblock (nanophased B) or ABC triblock (two phases B and C) in the A matrix can contribute to the design of the electronic, optical, catalytic, and barrier properties of the material.[2–5] ABC triblock copolymers have the advantage to form more complex nanostructures. In the past decades, some continuous network or gyroid structures were reported for ABC linear triblock copolymers. Mogi et al. suggested an ordered tricontinuous double diamond mesostructure for a polyisoprene-*block*-polystyrene-*block*-poly(2-vinylpyridine) film prepared by solvent casting and subsequent thermal annealing.[6] Suzuki et al. also observed a morphological transition from lamellae to tricontinuous gyroid structure upon annealing of a film of a polyisoprene-*block*-polystyrene-*block*-poly(2-vinylpyridine) copolymer.[7] Bates and coworkers also observed a network of phases in a polyisoprene-*block*-polystyrene-*block*-poly(ethylene oxide) copolymer.[1] Network morphologies were also been reported in several other triblock copolymer systems and the structures and properties of these network morphologies were systematically summarized in several reviews.[8–10]

The addition of a homopolymer (A) to a block copolymer (AB or ABC) can manipulate the phase structure of this polymer blend system and a large variety researches have been reported in this field.[6,9–11] The phase behavior of these binary blends is primarily governed by the composition and degree of polymerization of the homopolymer chain compared to the copolymer in the blend system. Normally, homopolymer molecular weight is roughly equal to or less than the analogous block molecular weight, otherwise, macrophase separation can occur.[11] Continuous network phase structures were also been reported in these A/AB, especially A/ABC blends.[9] Epps et al.[12] reported several tricontinuous ordered morphologies for polyisoprene-*block*-polystyrene-*block*-polyethylene (ISO) triblock blends with isoprene or styrene homopolymers of molecular weights close to the corresponding block molecular weights. In this research, homopolymer concentrations up to 21 vol.-% were explored without evidence of phase separation. Tuning the overall composition by adding homopolymer resulted in transitions from three-domain lamellae to the network phase. Also, Suzuki et al. studied the blends of polyisoprene-*block*-polystyrene-*block*-poly(vinyl pyridine) (ISP) triblocks mixed with styrene or isoprene homopolymers, which also form tricontinuous phases.[13] The results demonstrate an efficient method for exploring triblock copolymer phase structure based on precise and continuous composition control.

That ABC block copolymers are able to self-assemble into well-defined nanostructures within a melted polymer identical to one of the blocks was emphasized by Koulic and Jérôme.[14,15] A liposome-like vesicular morphology was indeed observed by melt-blending poly(methyl methacrylate) ($PMMA_{16k}$) with 20 wt.-% of a symmetrical polystyrene-*block*-polyisoprene-*block*-poly(methyl methacrylate) (PS_{17k} -*b*-PIP_{18k} -*b*-$PMMA_{16k}$) triblock copolymer. Similarly, reactive melt blending of 20 wt.-% of phthalic anhydride end-capped polystyrene-*block*-polyisoprene (PS_{16k} -*b*-PIP_{18k}-anh) with polyamide 12 ($PA12_{20k}$) led to double layered vesicles with a diameter of 100 nm. The morphology of the in situ formed nanostructures however changes with the composition of the triblock copolymer. Core/shell particles with a ''cucumber-like'' internal structure were indeed observed for $PA12_{20k}$ containing 30 wt.-% of PS_{31k} -*b*-PIP_{7k} -*b*-$PA12_{20k}$. In the previous examples, the triblock content was kept essentially constant. It is therefore attractive to investigate how the nanostructuring of PMMA depends on the content of a well-defined PS_{36k} -*b*-PIP_{8k} -*b*-$PMMA_{24k}$ [or PS_{36k} -*b*-PIP_{6k} -*b*-$PMMA_{17k}$ for atomic force microscopy (AFM) analysis] triblock copolymer. The question is also to determine whether this strategy can lead to a bicontinuous network of phases.

Experimental Part

Materials

All the monomers, 1,1-diphenylethylene (DPE), CaH_2, and LiCl were purchased from Aldrich. The 1 M solutions of dibutylmagnesium in heptane ($MgBu_2$), of butyllithium in hexane (BuLi), and of triethylaluminum in hexane ($AlEt_3$) were used as received from Aldrich. Styrene (St) and α-methylstyrene (α-mSt) were distilled under reduced pressure over CaH_2 and then over $AlEt_3$ before polymerization. Isoprene (IP) was pre-dried by distillation under reduced pressure over CaH_2 and then over $MgBu_2$ and finally over BuLi prior to use. Methyl methacrylate (MMA) was twice distilled under reduced pressure over CaH_2 and then over $AlEt_3$ prior to polymerization. DPE was added with sec-BuLi until a deep red color persisted and then distilled before use. Liquids were transferred with flamed stainless steel capillaries under dry argon.

Synthesis

Polystyrene-*block*-polyisoprene-*block*-poly(methyl methacrylate) (PS-*b*-PIP-*b*-PMMA), was synthesized by sequential living anionic polymerization of St, Ip, and MMA, respectively. Polymerization of styrene was initiated by α-mSt/sec-BuLi in the presence of LiCl (10 equiv. with respect to the initiator), and polymerized in a previously flamed glass reactor at –78 °C. After 1 h, isoprene was added, and the reaction medium was kept at –20 °C overnight. Then, the diblock copolymer chains (PS-*b*-PIP) were end-capped by 1.5 equivalents of 1,1-diphenylethylene at –78 °C, followed by the addition of MMA. After 1 h at –78 °C, the polymerization was terminated by addition of degassed methanol. The final copolymer was twice precipitated from tetrahydrofuran (THF) to methanol in order to remove LiCl. Unreacted PS and PS-*b*-PIP diblock were

Table 1. Molecular characteristics of the (co)polymers used in the study.

Polymer $\overline{M}_n$ [a)]	$\overline{M}_w/\overline{M}_n$
PS_{36k}(0.53)-*b*-$PIP_{8.0k}$(0.12)-*b*-$PMMA_{24k}$ (0.35)	1.09
homo-$PMMA_{19k}$ [a)]	1.02
homo-$PMMA_{56k}$ [a)]	1.01

[a)]Values in parentheses indicate volume fraction of the corresponding block; $\overline{M}_n$ values are from SEC for the PS block and the PMMA homopolymers and from ^{1}H NMR data (relative to $\overline{M}_n$ of the PS block) for the PIP and PMMA blocks.

eliminated by Soxhlet extraction with cyclohexane. Homo PMMA was also prepared by anionic polymerization, initiated by LiCl/lithium *tert*-butoxide at −78 °C in dry THF.[16]

Molecular Characterization

Size exclusion chromatography (SEC) was carried out in THF at 40 °C with a HP 1090 liquid chromatograph equipped with a HP 1037 refractive index detector and calibrated by polystyrene standards (Polysciences). ^{1}H NMR spectra were recorded with a Bruker AM 400 MHz spectrometer in $CDCl_3$ at 25 °C. The (co)polymers used in this study are listed in Table 1, with their molecular characteristics.

Melt Blending

Triblock copolymer/homopolymer blends were prepared in a 5 cm^3 DSM microextruder at 190 °C under nitrogen at 200 rpm for 4 min. Three compositions were considered, i.e., 20, 30, and 50 wt.-%.

Solvent Casting

A toluene (or THF) solution of triblock copolymer/homopolymer mixtures (10 wt.-%) of different compositions were cast on a glass plate or mica substrate (for AFM studies) and toluene was let to evaporate for 3–4 weeks, followed by drying in vacuo at 50 °C for 8 h.

Annealing

The blends formed by either melt blending or solvent casting were compression molded into a 1 mm thick disk between aluminum foils, at 190 °C (above the glass transition temperature of PMMA = 132 °C) for 60 min and rapidly quenched to room temperature under pressure. Samples were treated at 190 °C for different periods, such as 30 min, 60 min, 6 h, or 24 h to exam the correlation between equilibrium morphology and the annealing time. However, there is no evident change in phase structure, based on the transmission electron microscopy (TEM) results.

Morphology

The phase morphology was studied with a Philips CM100 TEM. The ultrathin TEM samples were prepared at –78 °C with a Reichtert-Jung ultracryomicrotome equipped with a diamond knife. The PIP phases were selectively contrasted by OsO_4. The error on the characteristic size of the nanoobjects was estimated at 3 nm for all the micrographs. Complementary morphological information was provided by atomic force microscopy in tapping mode (TMAFM). Phase imaging is a powerful technique for the characterization of the phase-morphology and microstructure of block copolymers, since the phase lag can be directly related to the elastic modulus of the material and allows the observation of phase-separated microdomains.[17] The AFM images were recorded with a Nanoscope IIIa microscope (Veeco, Inc) operated at room temperature in air using commercial cantilevers with a spring constant of 30 N · m^{-1}.

Results and Discussion

Blends of a diblock copolymer (AB) with one of the parent homopolymer (A) were extensively studied.[11,18,19] The phase behavior of these binary blends is primarily governed by the length of the homopolymer chains (N_A) compared to that of the parent blocks (N_{AB}). Three distinct regimes were identified. Whenever $N_A < N_{AB}$, the homopolymer A is selectively dissolved in the A domains of the AB block copolymer, which results in the swelling of these domains and in an increased interfacial area. This regime has been designated as the "wet-brush" regime. In the "dry-brush" regime ($N_A = N_{AB}$), although the A chains are miscible with the A blocks of the copolymer, the interfacial area does not change significantly. If $N_A > N_{AB}$, the A chains are insoluble within the A microdomains, and a macrophase separation occurs. Although no systematic study of ABC/C blends was reported, one may expect that the same rules are applicable. Therefore, blends of the PS_{36k}-*b*-PIP_{8k}-*b*-$PMMA_{24k}$ (or PS_{36k}-*b*-PIP_{6k}-*b*-$PMMA_{17k}$ for AFM analysis) triblock have been prepared with homo PMMA of a molecular weight (19 kDa) lower than the PMMA block (24 kDa), not only by melt blending but also by solvent casting. In the two cases, the phase morphology has been observed before and after annealing at 190 °C. By reference to the AB/A binary systems, the blends herein prepared would be in the wet-brush regime.

Melt Blending

Extrusion and injection are very powerful tools to disperse block copolymer aggregates in home polymer and form nanostructured blends, in spite of the fact that nanophase morphologies, formed by 4 min extrusion and then quenching to room temperature, are far from the thermodynamic equilibrium. Figure 1 shows the phase

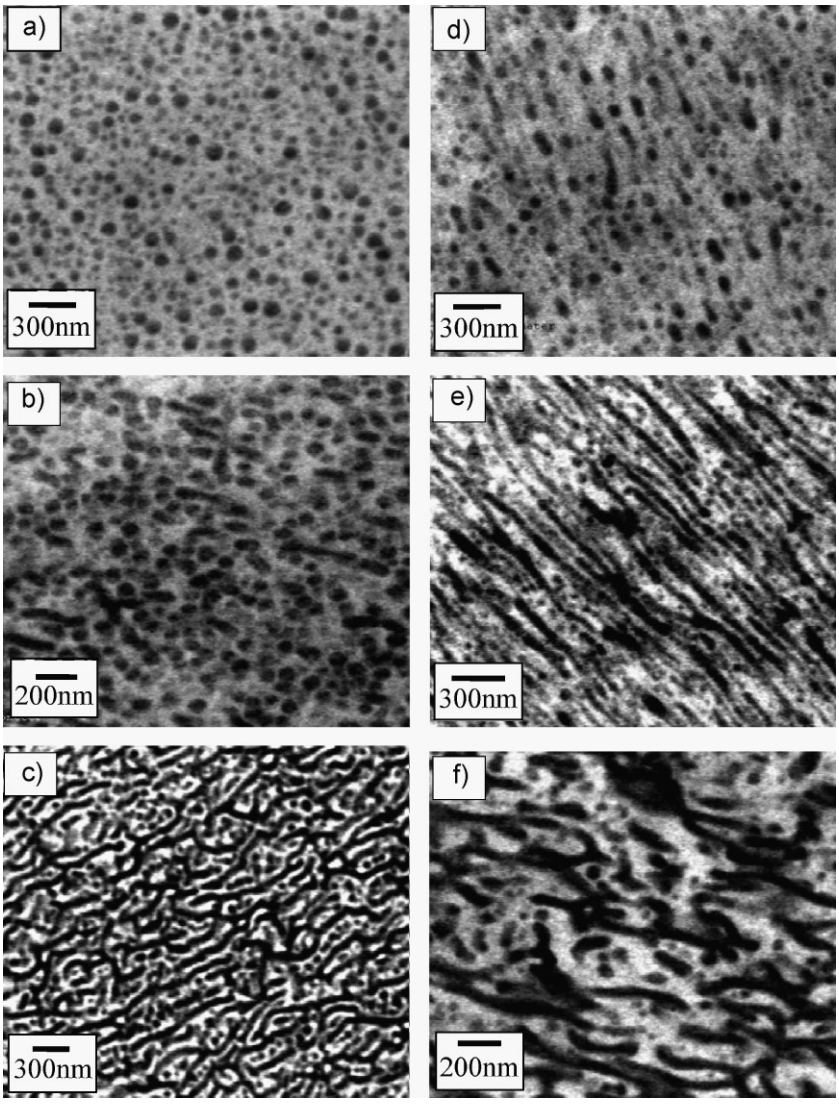

Figure 1. Phase morphology of melt-blended PS_{36k} -*b*-PIP_{8k} -*b*-$PMMA_{24k}$/$PMMA_{19k}$ blends of different copolymer contents (a,d: 20; b,e: 30; c,f: 50 wt.-%). The samples were observed in the direction either parallel (a–c) or perpendicular (d–f) to the extrusion direction.

nanostructures observed by TEM for binary blends of three different compositions, after 4 min of melt blending at 190 °C. Figure 1a–c show ultrathin sections prepared by ultracryotomy perpendicularly to the extrusion direction and contrasted by OsO_4 for staining PIP selectively (dark domain). In spite of a short mixing time in the melt, the copolymer forms nanophases either discontinuous or extensively interconnected depending on the blend composition. It is thus clear that the nanophase structure can be manipulated merely by changing the composition of the binary blends. Indeed, this morphology appears to change from spherical to cylindrical and finally to lamellae when the content of the triblock copolymer is increased from 20 to 30 and to 50 wt.-%. In order to confirm this assignment, the nanophase morphology has been observed in the direction parallel to the extrusion (Figure 1d–f).

The spherical morphology is observed for both the cross-section and the side-section of the binary blend containing 20 wt.-% of triblock copolymer. Expectedly, spheres are slightly elongated in the flow direction. The morphology is thus typically anisotropic. The large diameter observed as result of the equatorial cross-section of the spheres is ≈100 nm, which is much larger than expected for a typical core (PS)/shell (PIP) internal organization of the triblock, with PMMA as the external corona. A higher magnification is needed to clear up the structure of the self-assembled nanodomains (vesicle, onion-like, or else).

Although far from being ideal, the cylindrical morphology of the blend with 30 wt.-% of triblock is confirmed by TEM observation parallel to the extrusion direction. The apparent diameter (PS + PIP) is estimated at 85 nm. Because the rod-like nanoobjects are not perfectly aligned in the flow direction, cross-sections through some of them are observed in Figure 1e.

At 50 wt.-% of triblock copolymer, extensively interconnected nanostructures are observed parallel and perpendicular to the extrusion direction (Figure 1c and f). They are thinner (≈55 nm) than the cylinders observed at 30 wt.-% (85 nm) and they are more likely lamellae of triblock chains. By analogy, lamellae were also observed in a PIP-*b*-PS/PS blend when the volume fraction of the PS matrix was decreased sufficiently.[20]

This composition-dependence of the nanophase morphology is not surprising. What must be noted is that well-defined nanostructures are formed without the assistance of selective solvents, thus under experimental conditions unfavorable to self-organization of the copolymer (short time, melt state, disturbing flow). The sphere-to-cylinder transition when the triblock content is increased from 20 to 30 wt.-% is dictated by a decrease in free energy as result of a decreased interfacial surface area, which otherwise should increase in case of unmodified spherical morphology. In large spheres, the PS and PIP chains should adopt a stretched conformation, whereas this entropy penalty may be canceled in cylindrical self-organization.[21] As a rule, the

interface between PS (53 vol.-%) and PIP + PMMA (47 vol.-% for the two blocks) must spontaneously tend to be flat, thus to be part of lamellae when possible. This lamellar organization seems actually to dominate when 50 wt.-% of triblock is melt blended with PMMA, a transition from cylinders to lamellae occurring in between 30 and 50 wt.-% of triblock. Nevertheless, the aforementioned transitions are not complete and the nanostructures are frozen out of equilibrium because of the experimental conditions used for the blend preparation. In order to detail further these nanostructures, all these binary blends have been annealed at 190 °C for 60 min and investigated again by TEM (Figure 2).

Annealing

It must be noted that the phase structures (Figure 1) of the extruded blends are far from thermodynamic equilibrium, and these samples were accordingly treated with hot annealing under 190 °C for 60 min. Extruded blends were annealed respectively under different annealing times (such as 60 min, 6 h, or 24 h), and TEM observation results show no obvious distinction in phase morphologies between samples from different annealing times. As a rule, the same morphological features were observed perpendicularly and parallel to the extrusion direction, and TEM observations demonstrates, after 60 min treatment under 190 °C, sample turn to an isotropic plastic. This means that it is enough for polymer molecules to assemble and reach equilibrium phase morphology in 60 min under a high temperature (190 °C).

A comparison of Figure 1 and 2 confirms the beneficial effect that annealing usually has on the phase morphology of multiphase materials originally frozen in a nonequilibrium state. Indeed, it is now possible to observe the detailed structure of the spherical nanodomains with TEM at high magnification (Figure 2a). Core/shell particles with an internal cucumber-like substructure are formed, as was previously observed in case of reactive melt blending of 20 wt.-% of PS_{16k} -*b*-PIP_{18k}-anh with polyamide 12 ($PA12_{20k}$) with formation of 20–30 wt.-% of PS_{16k} -*b*-PIP_{18k} -*b*-$PA12_{20k}$ triblock copolymer in the polyamide matrix.[15]

At 30 wt.-% of triblock, the cylinders (oriented perpendicular to the cross-section, thus parallel to the extrusion direction before annealing) are in the process of reorganizing themselves into large size bilayered vesicles and bilayered lamellae of the same thickness as the bilayer in vesicles. No preferential orientation of these nanophases is observed. The transition is complete at 50 wt.-% of triblock. Then a continuous three-dimensional (3D) network of bilayered lamellae is formed with the same layer characteristics as the vesicles formed by 30 wt.-% of triblock. The structure observed in Figure 2c is independent of the direction (parallel and perpendicular to the extrusion flow),

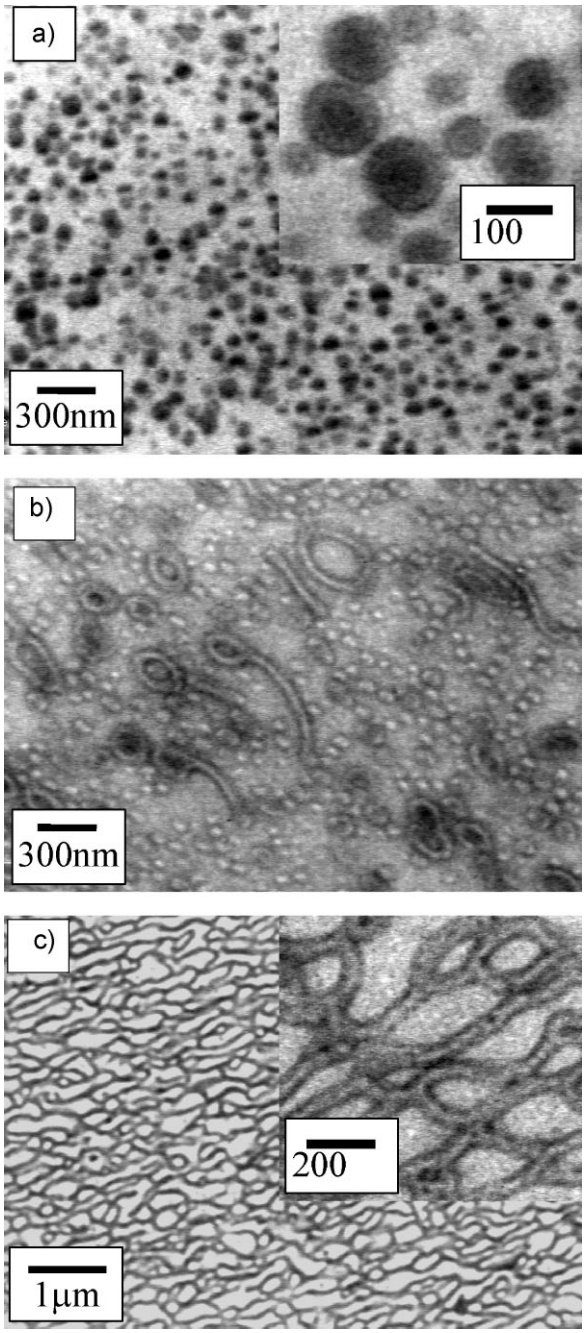

Figure 2. Phase morphology of annealed PS_{36k} -*b*-PIP_{8k} -*b*-$PMMA_{24k}$/$PMMA_{19k}$ blends of different copolymer contents (a: 20; b: 30; c: 50 wt.-%), previously prepared by melt blending.

which confirms that the layers have built up an isotropic network.

A very surprising observation is that the network of bilayered lamellae is maintained even when the molecular weight of the PMMA homopolymer (56 000, calibrated with PMMA standards and $\overline{M}_w/\overline{M}_n = 1.01$) is two times higher than that of the PMMA block (24 000, Figure 3). Although

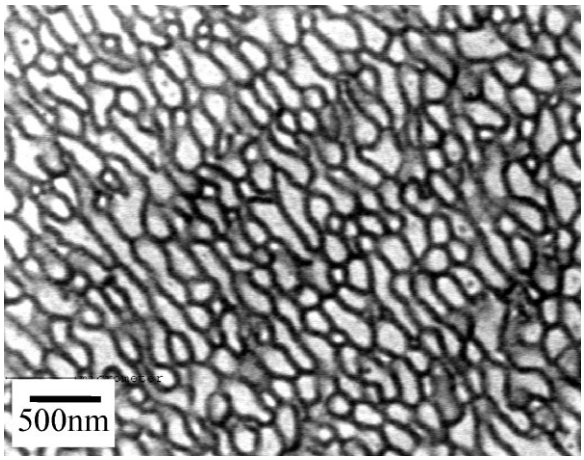

Figure 3. 3D continuous network of bilayered lamellae formed by the annealed PS_{36k} -*b*-PIP_{8k} -*b*-$PMMA_{24k}$/$PMMA_{56k}$ (50:50 wt.-%) blend previously prepared by melt blending.

this binary system is neither in the wet-brush nor in the "dry-brush" regime, no macrophase separation occurs. This interesting result may be mainly attributed to the interaction between polar PMMA chains from both homo PMMA and triblock copolymer. The polydispersity and stereoregularity of polymers in the blend may act upon the blending properties. Therefore, it would be useful to study the molecular parameters for both homopolymers and the triblock copolymer with ^{1}H and ^{13}C NMR spectra. This is what should be focused on in our next study.

It must be noted that the copolymer lamellae in the network are ≈55 nm thick, thus smaller than in the spherical and cylindrical nanostructures, which suggests that the chain stretching is lower in the lamellar morphology. This 3D network of triblock lamellae is a very interesting situation because the three phases are simultaneously continuous, i.e., PS and PIP lamellae in addition to the PMMA matrix. This triple connectivity is a unique strategy to provide the matrix with quite unusual properties (e.g., of transport) depending on the characteristic features of the minor continuous phases.

Solvent Casting

In a previous work, Koulic and Jérôme prepared films of $PMMA_{16k}$ blended with 20 wt.-% of symmetric PS_{17k} -*b*-PIP_{18k} -*b*-$PMMA_{16k}$ triblock, thus in the dry-brush regime by solvent (toluene) casting.[14] A continuous network of triblock lamellar sheets was formed throughout the PMMA matrix. The lamellae consisted of a double layer of triblock copolymer and they were interconnected by microdomains of block copolymer that played the role of physical cross-links. The triblock copolymer/homopolymer blends under consideration in this study have also been prepared by casting a toluene solution of the PS_{36k} -*b*-$PIP_{8.0k}$ -*b*-$PMMA_{24k}$/$PMMA_{19k}$ mixtures (10 wt.-% polymer). The solvent was let to evaporate over 3 weekd at room temperature.

At a content of 30 wt.-% of triblock, randomly bent ribbons of copolymer, more or less parallel one to each other, are formed in the PMMA matrix (Figure 4a). The three-layer phase structure is confirmed by the selective OsO_4 staining of the PIP block, which allows one to distinguish two PIP layers that sandwich PS, whereas the PMMA chains are mixed with the PMMA matrix. An inset in Figure 4a shows a sandwich-like structure with a thickness of 15 nm for the PS core and 40 nm for the PIP/PS/PIP three-layer. Two major differences with respect to melt blending should be emphasized. Instead of cylinders in the melt, ribbons are formed by solvent casting at the same blend composition (30 wt.-% triblock). These ribbons are thinner than the lamellae formed in the melt in case of 50 wt.-% of triblock containing blend (30 and 55 nm for the PS core and the PIP/PS/PIP assembly, respectively), which indicates that the chains are less stretched in these bilayered ribbons formed by solvent casting and containing 30 wt.-% copolymer than

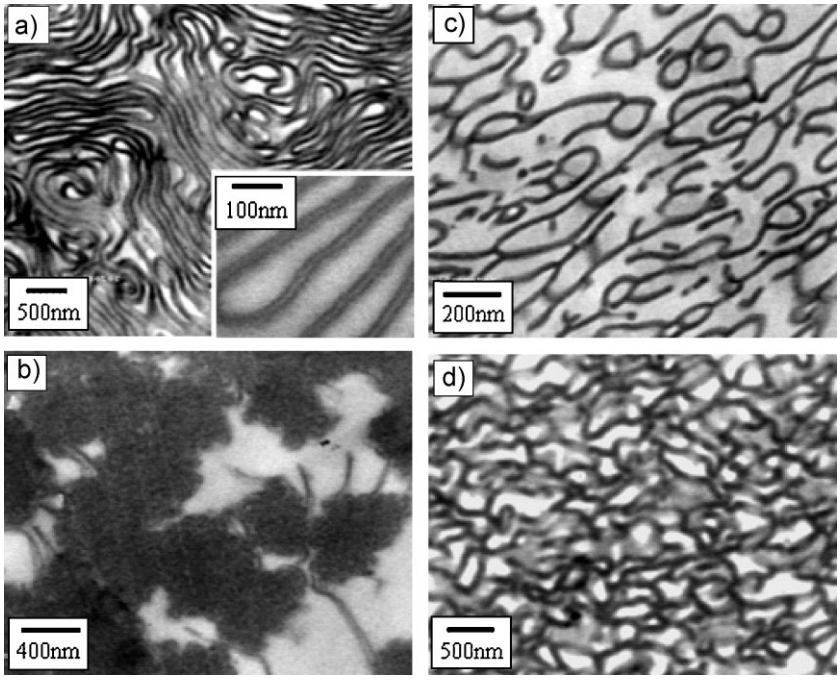

Figure 4. Phase morphology of solvent cast PS_{36k} -*b*-PIP_{8k} -*b*-$PMMA_{24k}$/$PMMA_{19k}$ blends of different copolymer contents (a,c: 30; b,d: 50 wt.-%) before (a,b) and after (c,d) annealing (190 °C, 60 min).

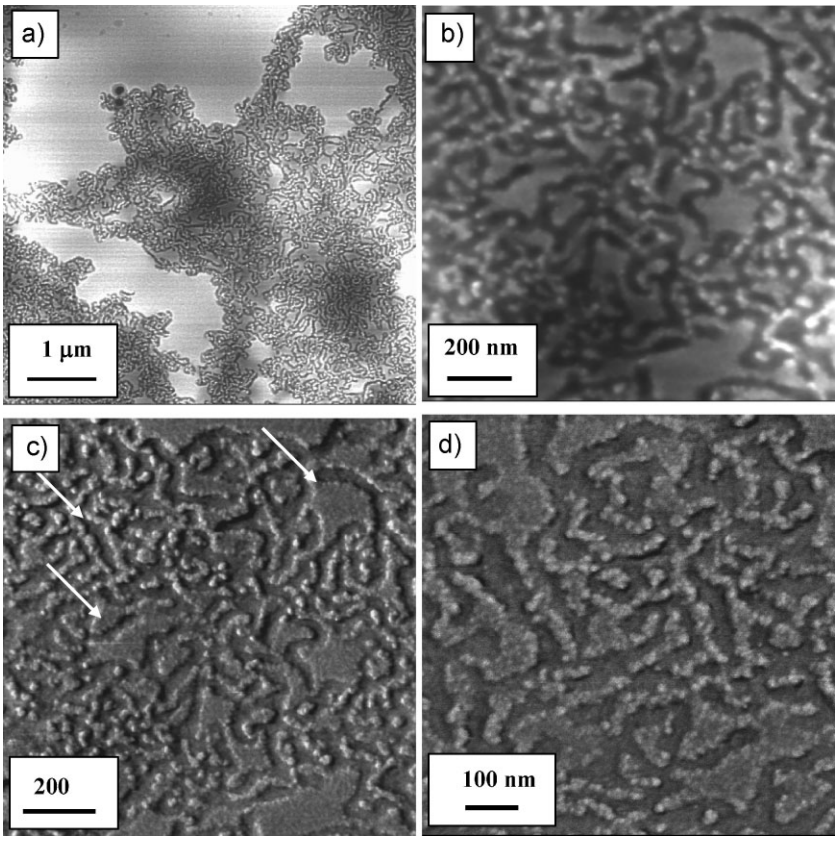

Figure 5. Microscopic morphology of solvent-cast PS_{36k} -*b*-PIP_{6k} -*b*-$PMMA_{17k}$/$PMMA_{19k}$ 50:50 blends, as observed with TMAFM: height (a, b) and phase (c, d) images.

in lamellae prepared by melt blending of blend of 50 wt.-% copolymer.

Upon annealing at 190 °C for 60 min, the density of cross-sectioned lamellae of triblock (same thickness as before annealing) has substantially decreased (comparison of Figure 4a and c, at the same magnification). A reasonable explanation might be that ribbons with a smaller width were formed by solvent casting and that they merged into very large lamellar sheets upon annealing. When the copolymer content is increased up to 50 wt.-%, a macrophase separation occurs, with however individual lamellae emerging from the copolymer macrodomains or interconnecting them; this can be observed in both TEM and AFM images (Figure 4b and 5a). This situation is reminiscent of that observed by Koulic and Jérôme,[14] except that it is dominated in this work by the microdomains (bounded lamellae), whereas many more unbounded lamellae were visible in Koulic's samples. AFM images give more insight on the internal structure of the copolymer macrodomains. Figure 5a confirms the microphase separation of the PS-PIP-PMMA triblock, with formation of a network of 35 ± 5 nm-wide bounded lamellae (Figure 5b). Small domains of homo PMMA (some of them are shown with white arrows in Figure 5c) are however entrapped within the lamellae, the apparent width of which is characteristic of the PIP/PS/PIP assembly which cannot be resolved by AFM. Upon closer inspection (Figure 5d), the boundary between the lamellae and the homo PMMA microdomains has a "grainy" structure and a stronger contrast in the phase signal. This observation suggests that the periphery of the lamellae is harder and denser, which might result from the interpenetration of the PMMA segments of the copolymer and homo PMMA chains.

Upon annealing, the homo PMMA macrodomains disappear and a homogeneous continuous network of lamellae is formed (Figure 4d), as was the case for the same samples prepared by melt blending and annealed further.

Finally, attention was paid to binary copolymer/PMMA blends of various compositions (20, 30, and 50 wt.-% triblock) with however a PMMA homopolymer of $\overline{M}_n$ (56 000) at least two times higher than $\overline{M}_n$ of the PMMA block (24 000, Figure 6). Ill-defined sub-μm aggregates of copolymer were systematically formed by solvent casting, the density of which expectedly increased with the copolymer content.

Once again, the annealing of the samples at 190 °C for 60 min has a decisive effect on the phase morphology. Indeed, the sub-structuring (thus the ordering) of the microdomains formed by 20 wt.-% triblock is clearly observed. The phase morphology was transformed by annealing indicates these macromolecules in this employed system need more energy to self-assemble into ordered microdomains. When the triblock content is higher, the copolymer tends to be continuous throughout PMMA, which is definitely the case at the content of 50 wt.-%. The typical lamellar network observed in the wet-brush regime upon annealing of 50:50 wt/wt blends prepared by either melt blending or solvent casting is completely restored even in PMMA of molecular weight higher than that of the PMMA block.

Conclusion

Modification of $PMMA_{19k}$ by increasing amounts of an asymmetric PS_{36k} -*b*-$PIP_{8.0k}$ -*b*-$PMMA_{24k}$ triblock copolymer (from 20 to 50 wt.-%) is a valuable strategy for nanostructuring PMMA and for manipulating these nanostruc-

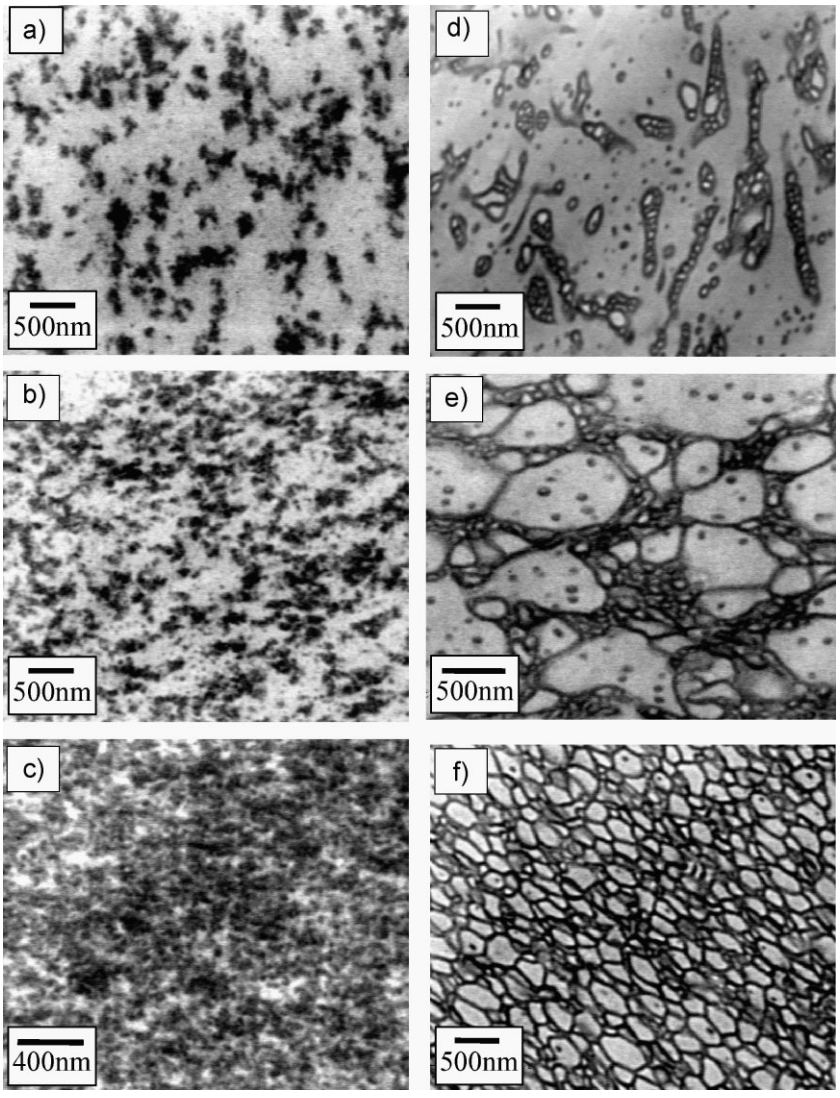

Figure 6. Phase morphology of solvent cast PS_{36k} -*b*-PIP_{8k} -*b*-$PMMA_{24k}$/$PMMA_{56k}$ blends of different copolymer contents (a,d: 20; b,e: 30; c,f: 50 wt.-%) before (a–c) and after (d–f) annealing (190 °C, 60 min).

tures. The melt blended samples (190 °C for 4 min) show transitions from spheres to cylinders and to lamellae upon increasing the content of the triblock copolymer from 20 to 50 wt.-%. Annealing at 190 °C for 60 min has a very beneficial effect on the degree of order of the in situ formed nanostructures. The formation of a regular network of 50 nm thick bilayered lamellae must be noted when the copolymer content is 50 wt.-%. Still more surprising is that this nanostructuring of PMMA is maintained even when the $\overline{M}_n$ of PMMA (56 000) is higher than the $\overline{M}_n$ of the PMMA block (24 000). This 3D networking of the PS, PIP at PMMA phases (thus tri-continuity) is systematically generated upon annealing of 50:50 wt.-% blends prepared by solvent (toluene) casting whatever the relative $\overline{M}_n$ of the PMMA block and the PMMA matrix.

This quite reproducible 3D network of three (continuous) phases whatever the preparation techniques and $\overline{M}_n$ of the common partners paves the way to the engineering of materials with upgraded performances.

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