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Tailored Morphologies of Poly(styrene-*block*-butadiene-*block*-methyl methacrylate) Triblock Copolymers and Their Blends with Polystyrene Homopolymers†

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Summary: Self-assembly is an interesting strategy for the creation of periodic structures at the nanoscale. The microphase separation in a linear ternary block copolymer consisting on three immiscible components (ABC), give rise to the formation of different final morphologies that can be controlled by various parameters. In this work, the morphologies of three poly(styrene-*b*-butadien-*b*-methyl methacrylate) triblock copolymers with similar molecular weight and their blends with PS homopolymers were studied by atomic force microscopy (AFM). Redistribution of the homopolymer in blends generates new structures could be tailored according to the desired applications.

Keywords: blends; block copolymers; nanocomposites; SBM; self-assembly

Introduction

Due to the potential application in different areas much attention has been focused on investigating the self-assembling behavior of amphiphilic block copolymers. Linear ABC triblock copolymers have received significant attention because of the existence of a wide range of novel morphologies. The greater diversity in morphology afforded by ABC triblock copolymers is due to their three binary interaction parameters, two independent volume fractions, and three different block sequences, as opposed to one binary interaction parameter, one volume fraction, and a single block sequence for traditional diblock copolymers.[1] Blending block copolymers with homopolymers has been proved to be an effective and economical way to probe the general behavior of neat block copolymers containing adequate composition and segregation strength. These findings demonstrate that appropriate triblock/homopolymer blending can help identifying and refining the phase windows of different copolymer behavior.[2,3]

Experimental Part

Materials

Three different poly(styrene-*block*-butadiene-*block*-methyl methacrylate) (SBM) triblock copolymers synthesized anionically at pilot scale by Arkema were used in this study. In all cases, the PB block contained more than 85 wt % of 1,4-butadiene units and the PMMA block was highly syndiotactic (>70%).[4,5] Moreover, PS homopolymers supplied by Polymer Source with different molecular weight (Mn = 30,000, Mn = 20,800 and Mn = 10,000) were also used.

Purification of Triblock Copolymers

As well know from the literature, SBM copolymers contain PS and SB diblock copolymers due to the synthesis method employed in their preparation process via

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†In memoriam of Prof. Iñaki Mondragon

anionic polymerization.[4,5] These impurities can be separated by successive washes with selective solvents such as cyclohexane and n-heptane. The procedure for the purification is described below. The synthesized SBM copolymers were placed under reflux in a suitable mixture of cyclohexane/ n-heptane for 2 h with magnetic stirring in order to obtain a good solution without losing any solvent. Here it should be pointed out that the relative proportions of two solvents strongly depend on the employed copolymer, the block ratio and the percentage of impurities. As PMMA is block is not soluble in used solvents mixture, it caused the precipitation of the triblock copolymer. The mixture was then filtered and triblock copolymers were recovered, while PS and PB impurities remained in the cyclohexane/n-heptane solution. This operation was repeated three times and then solvent was removed under vacuum for 24 h.

Characterization

The composition of triblock copolymers was determined by 1H nuclear magnetic resonance (1H-NMR, Bruker 300 MHz). Molecular weights were determined by gel permeation chromatography (GPC, Perkin Elmer series 200) using tetrahydrofuran (THF) as eluent, a refractive index (RI) detector and PS standards. Figure 1 shows a typical chromatogram obtained for brut and purified copolymers. Dotted curve corresponding to the brut copolymer indicates that the elimination of impurities was carried out correctly.

Figure 2 and 3 show the proton distribution corresponding to the peaks obtained by H-RMN and a typical H-RMN curve for these triblock copolymers, respectively. Table 1 shows the characteristics of SBM copolymers obtained from GPC and H-RMN techniques. The code to identify each SBM triblock copolymer denotes the weight fraction of the elasto-

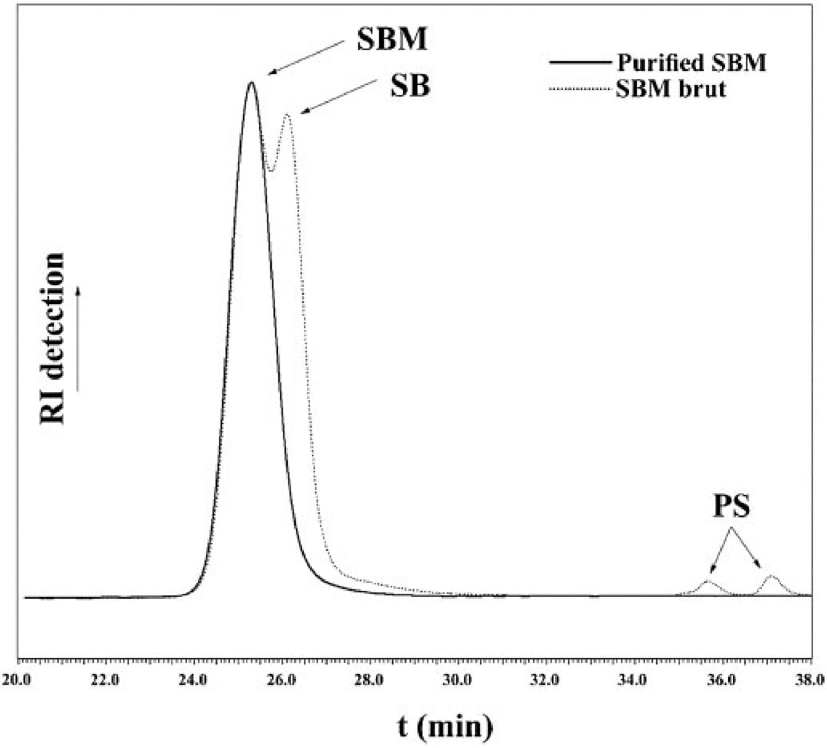

Figure 1.
GPC chromatograms for brut and a purified SBM triblock copolymers.

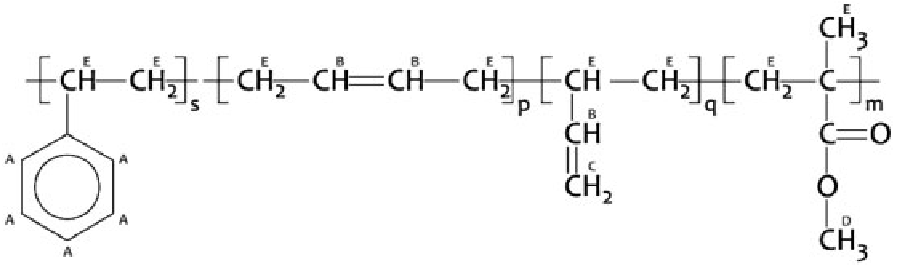

Figure 2.
Formula of a SBM triblock copolymer showing proton distribution.

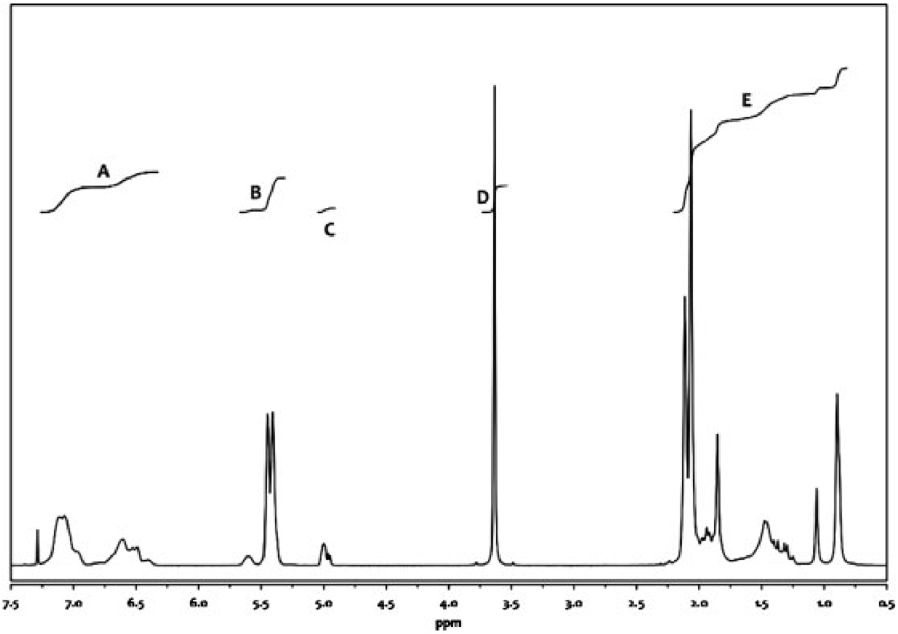

Figure 3.
H-RMN analysis for SBM triblock copolymer.

Table 1.
GPC characteristics of used SBM copolymers.

Copolymer	10^{-3}Mn	M_w/M_n	w_{PS}	ϕ_{PS}	w_{PB}	ϕ_{PB}	w_{PMMA}	ϕ_{PMMA}
SBM52	97	1.24	0.23	0.15	0.52	0.70	0.25	0.15
SBM18	97	1.16	0.16	0.14	0.18	0.33	0.66	0.53
SBM10	96	1.26	0.37	0.34	0.10	0.20	0.53	0.46

meric midblock. W_{PS}, W_{PB} and W_{PMMA} are the weight fractions of the components as determined by H-RMN; ϕ_{PS}, ϕ_{PB} and ϕ_{PMMA} correspond to calculated volume fractions of each block of SBM. Table 2 shows the molecular weights of each blocks of SBM, calculated using the molecular weight of each triblock copolymer and the mass fraction of the blocks.

Table 2.
Molecular weights of each block of SBM copolymers.

Copolymer	10^{-3} M_{nPS}	10^{-3} M_{nPB}	10^{-3} M_{nPMMA}
SBM52	22	50	24
SBM18	16	17	64
SBM10	36	9.6	51

Atomic force microscopy (AFM) measurements were performed using a Digital Instruments Multimode scanning probe microscope equipped with a Nanoscope IIIa controller. All images were recorded in tapping mode using silicon TESP tips having a resonance frequency of approximately 340 kHz and a cantilever spring constant about 40 N/m. Films of copolymers were prepared by spin-coating from 5 wt % solutions in toluene using a P6700 spincoater from Cookson Electronics. The spinner program was 2000 rpm for 60 s. Residual solvent was removed by evaporation at room temperature.

Results and Discussion

Following the work done by Stadler and coworkers[6,7] the general phase diagram of synthetized SBM triblock copolymers is shown in Figure 4. Taking this into account the main aim of this work was the preparation of blends of SBM triblock copolymers with an homopolymer chemically identical to one of the blocks (PS), which allow to obtain a controlled microstructure predicted in this scheme assuming a ternary behavior of the mixture.

As it is well known from the literature, the miscibility between block copolymers and homopolymers occurrs when the homopolymer has lower molecular weight than that of the corresponding block of the block copolymer. On the contrary, an homopolymer with higher molecular weight leads to micro- or macrophase separation. The first favorable case corresponds to the "wet brush" situation, while the second case corresponds to the "dry brush" situation, where a free chain cannot diffuse into domains of shorter chains, since the loss of conformational entropy is larger than the gain in translational or mixing entropies. Additionally, microphase separation also takes also place when the molecular weight of the homopolymer is higher than that of the corresponding block of block copolymers.[6] Taking this into account, in this study PS homopolymers with adequate molecular weight were chosen in order to prepare SBM/PS blends (100/0, 70/30 and 20/80). The ratio between SBM and PS was selected with the aim to reach a s_os (spheres over spheres) or s_oc (spheres over cylinders) morphology through a *ll* (lamellar) morphology in each case. Figure 5 shows the ternary diagram in

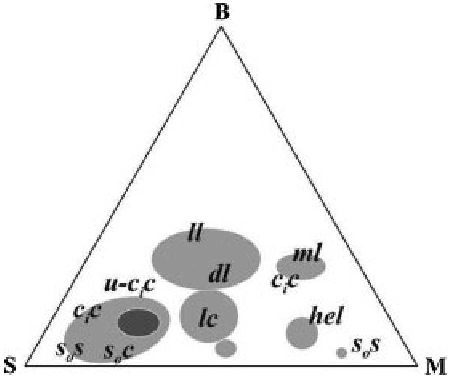

Figure 4.
Scheme of morphologies generated for synthetized SBM triblock copolymers.

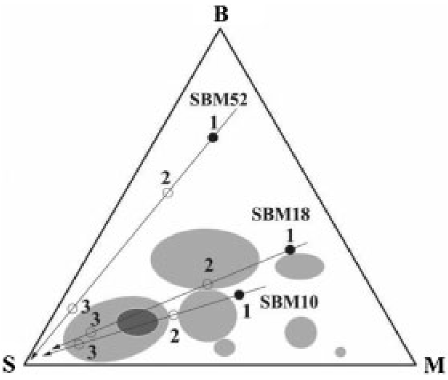

Figure 5.
Location of the different triblock/homopolymer blends.

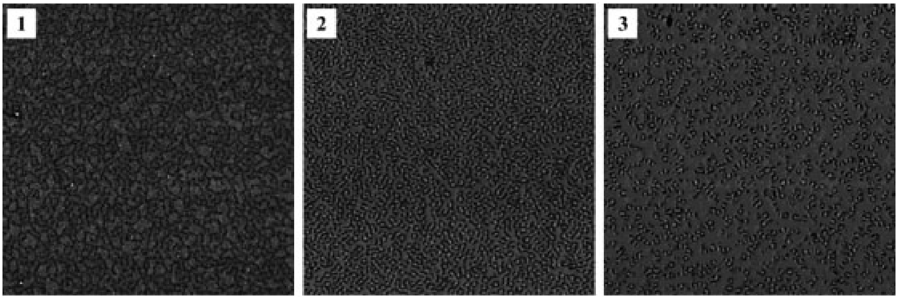

Figure 6.
AFM phase images of the evolution of the morphology for SBM52 blends ($3 \times 3\,\mu m$).

which SBM/PS blends used in this work are indicated.

Figure 6 shows AFM phase images of the evolution of SBM52 blends morphology with increasing of PS homopolymer content. The expected initial lamellar structure of this SBM copolymer related to similar content of end blocks was not reached since, as predicted from the ternary diagram, the starting point of this mixture was situated away from any known morphology. The progressive addition of PS homopolymer effectively changed the morphology, one being able to observe the beginning of the separation of PMMA and PB blocks from the PS matrix in form of cylinders or spheres, although this structure does not seem to be fully achieved.

In the case of SBM18 copolymer, the ternary diagram predicted a morphology close to *ml* morphology, due to the higher amount of M block. Figure 7 shows AFM phase images of the evolution of the morphology for this copolymer. Taking into account that even small changes in volume fractions of blocks can lead to large variations of final morphologies, the obtained morphology was that expected similar to this from the phase diagram. The progressive addition of PS homopolymer changed the morphology reaching first to an undetermined morphology and finally to a morphology close to c_ic (cylinder in cylinder) morphology (Figure 4).

Finally, Figure 8 shows AFM phase images of the evolution of the morphology for SBM10 blends with increasing PS homopolymer content. The expected initial lamellar *lc* (cylinder at lamellar) shape of this copolymer was obtained, as predicted by the ternary diagram. The progressive addition of PS homopolymer led to the microseparation of PB and PMMA,

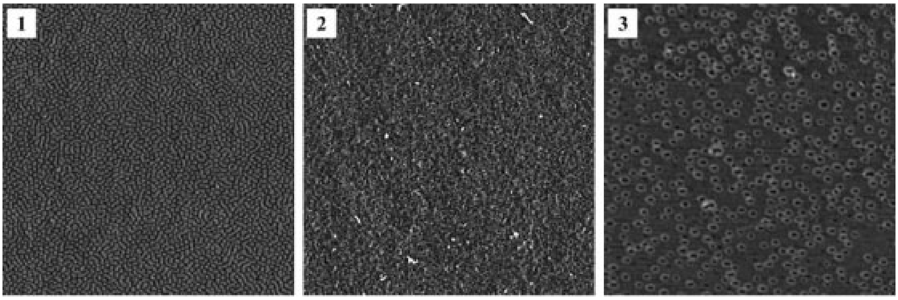

Figure 7.
AFM phase images of the evolution of the morphology for SBM18 blends ($3 \times 3\,\mu m$).

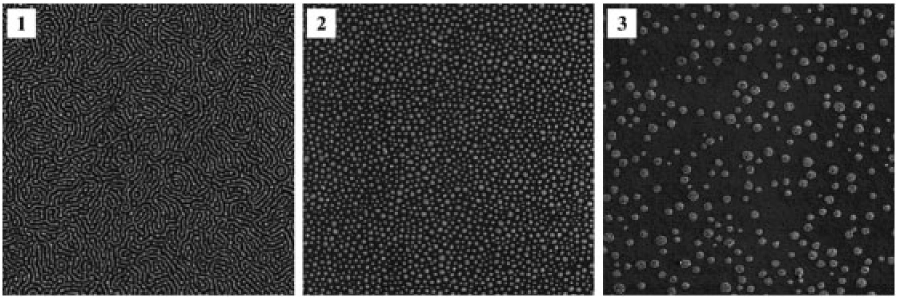

Figure 8.
AFM phase images of the evolution of the morphology for SBM10 blends (3×3 μm).

reaching finally to a morphology close to $s_o s$ (spheres over spheres) morphology (Figure 4).

Conclusion

In this contribution we show a new strategy to tailor nanostructured materials based on triblock copolymers with different nanostructures depending on the desired application. Tapping mode atomic force microscopy reveals detailed structural information of these block copolymers. Significant changes in the final morphologies of SBM-based blends were observed with increasing the amount of homopolymer present in the blends. These morphologies are clearly influenced by different parameters such as the amount of homopolymer and the molecular weights of blocks and homopolymers. The addition of different homopolymers will allow the optimization of final structures in further studies.

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