

Synthesis and Morphological Behavior of Model 6-Miktoarm Star Copolymers, PS(P2MP)₅, of Styrene (S) and 2-Methyl-1,3-Pentadiene (P2MP)

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Received November 10, 2005. Revised Manuscript Received February 3, 2006

Three 6-miktoarm star (6 μ -star) copolymers [PS(P2MP)₅] of styrene (S) and 2-methyl-1,3-pentadiene (2MP) were synthesized by anionic polymerization and controlled chlorosilane chemistry, using high vacuum techniques. In all cases [M_w = 103 kg/mol, [S] = 44% (v/v); M_w = 91.1 kg/mol, [S] = 53% (v/v); M_w = 224 kg/mol, [S] = 92% (v/v)] the P2MP exhibited high 1,4-microstructure (~99%). Molecular characterization (size-exclusion chromatography, membrane osmometry, low-angle laser light scattering, and NMR) revealed high molecular weight/composition homogeneity, and structural analysis (differential scanning calorimetry, transmission electron microscopy, and small-angle X-ray scattering) showed highly ordered patterns. The deviations from predictions based on Milner's morphological model are much more pronounced than that of PS(P2MP)₂ and PS(P2MP)₃ miktoarm stars, which we attribute to greater crowding of the arms for these highly branched molecules.

Introduction

One of the most intriguing (and useful) features of linear and branched block copolymers is that they can exhibit a wide variety of nanometer-scale structures. The appearance of these structures depends very sensitively on the exact topology of the copolymers; that is, on the length of each block, the ways they are attached to each other, and the chemical nature of each block.¹ In particular, the miktoarm star (μ -star) polymers,² which are stars with chemically different arms, display many types of morphology.³ Milner⁴ has developed a model for these structures that is based on balancing the drive to minimize interfacial area (to lower enthalpic terms) with the need to minimize arm stretching (which reduces configurational entropy).

In a previous paper⁵ we studied the self-assembly in bulk of PS(P2MP)₂ [PS = polystyrene; P2MP = poly(2-methyl-1,3-pentadiene)] and PS(P2MP)₃ μ -stars and compared the results with Milner's theory and with those found for the corresponding PS/polyisoprene (PI) μ -stars. While most of

the experimental results of samples³ with low arm number can be predicted by the theory, almost all 4 μ - and 6 μ -stars deviate appreciably. We believe that this is because of the effect of having large domains with very thin interfaces between them, as we explain below. When the disperse domains take up a large volume fraction, the crowding of the arms can have a large effect on the conformational statistics, which is not taken into account in this model. In this paper the synthesis of three samples of 6 μ -stars, PS(P2MP)₅, (Scheme 1), as well as their morphological behavior, is presented, and the agreement between experimental and theoretical results is probed at a higher number of arms.

Experimental Section

All samples were prepared by anionic polymerization using high vacuum techniques (HVT) in evacuated, *n*-BuLi washed and benzene rinsed glass vessels. The HVT as well as the purification procedures for the styrene (S), solvents [benzene, tetrahydrofuran (THF)], and initiator (*sec*-BuLi) to the standards required for anionic polymerization have been described in detail elsewhere.⁶ The purification of 2-methyl-1,3-pentadiene (2MP; Aldrich, *cis/trans* = 30:70) needs to be very thorough because the commercial monomer contains isomers (~90%) that cannot homopolymerize anionically but that might terminate the polymerization. The procedure of purification is described in detail elsewhere,⁵ and the 2MP monomer was always tested, before use, via GC-MS measurements. The linking agent 1,2-bis(trichlorosilyl)ethane (Petrarch) was purified according to the procedure given elsewhere.⁷

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(1) Lohse, D. J.; Hadjichristidis, N. *Curr. Opin. Colloid Interface Sci.* **1997**, *2*, 171.

(2) Hadjichristidis, N. *J. Polym. Sci., Polym. Chem.* **1999**, *37*, 857.

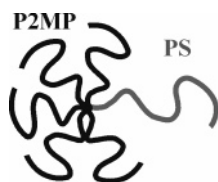
(3) Tselikas, Y.; Hadjichristidis, N.; Iatrou, H.; Liang, K.; Lohse, D. J. *Chem. Phys.* **1996**, *105*, 2456.

(4) Milner, S. T. *Macromolecules* **1994**, *27*, 2333.

(5) Mavroudis, A.; Avgeropoulos, A.; Hadjichristidis, N.; Thomas, E. L.; Lohse, D. J. *Chem. Mater.* **2003**, *15*, 1976.

(6) Hadjichristidis, N.; Iatrou, H.; Pispas, S.; Pitsikalis, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3211.

(7) Roovers, J.; Bywater, S. *Macromolecules* **1974**, *7*, 443.

Scheme 1. 6-Miktoarm Star Copolymer [PS(P2MP)₅]

The molecular characterization was carried out by size-exclusion chromatography (SEC), low-angle laser light scattering (LALLS), and membrane osmometry (MO). The \bar{M}_w values were obtained from the $(Kc/\Delta R_\theta)^{1/2}$ versus c plots (ΔR_θ , excess Raleigh ratio; K , combination of known optical constants; c , concentration), whereas the \bar{M}_n values were determined from the $\sqrt{(\pi/c)}$ versus c plots (π is the osmotic pressure, and c is the concentration). Square root plots were used to minimize the curvature due to the third virial coefficient. More details are given elsewhere.⁸ In all cases the correlation coefficient was better than 0.99.

SEC was calibrated with seven PS standards (M_w : 1.5–700 kg/mol) and five P2MP homopolymers (\bar{M}_n : 10–40 kg/mol), synthesized by anionic polymerization and characterized by MO.

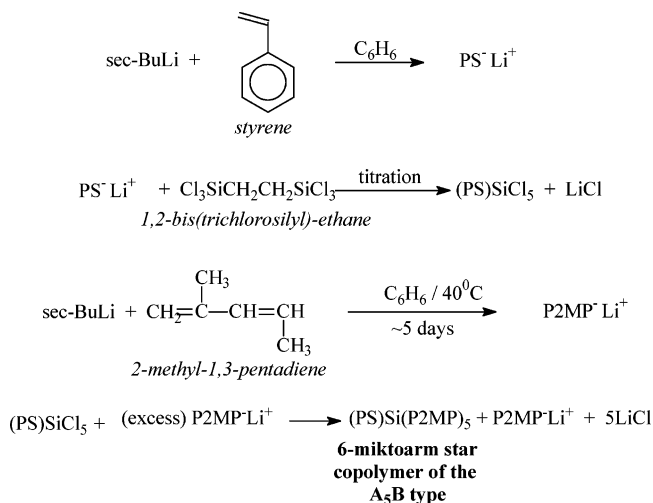
¹H NMR determination of the composition and the microstructure was carried out in CDCl₃ at 30 °C with a Varian Unity Plus 300/54 instrument. The NMR results confirm that the anionic polymerization of the 2MP in benzene leads to high 1,4-microstructure P2MP (99%) in agreement with the literature.⁹

A TA Instruments 2910 modulated differential scanning calorimeter was used to obtain preliminary information about the microphase separation of the two blocks. Two glass transition temperatures were detected: $T_{g1} \sim 0$ °C and $T_{g2} \sim 100$ °C, corresponding to P2MP and PS homopolymers, respectively.¹⁰ The observation of two different glass transition temperatures, corresponding to the two homopolymers, suggests that the system is in the region of strong microphase separation. The T_g of the P2MP is higher than that of 1,4-polybutadiene (1,4-PB; ~ -85 °C) or 1,4-PI (~ -60 °C). This is mostly due to the lower chain flexibility of P2MP resulting from the extra methyl group.

Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were employed for the morphological characterization of the block copolymers. Films (~ 0.7 mm thick) of the materials were cast from a dilute solution (~ 4 wt %) in toluene, which is a nearly nonselective solvent for an S/2MP polymeric system, over a period of 1 week at ambient conditions. To obtain near-equilibrium microstructures, the films were annealed above the T_g of the PS component for 7 days (at 140 °C) under vacuum. For TEM investigation, the P2MP chains were stained selectively with OsO₄. More details are given elsewhere.^{5,11}

Results and Discussion

Synthesis. Although the only chemical difference between 2MP and isoprene (2-methyl-1,3-butadiene) is in having one additional methyl group, their anionic polymerization characteristics are completely different. While the polymerization of isoprene in benzene takes place overnight at room temperature, without stirring, polymerization of 2MP (with stirring) for 5 days produces polymers with a molecular

Scheme 2. Reaction Schemes for the Synthesis of 6 μ -Star Copolymers [PS(P2MP)₅] of S and 2MP

weight of 3 kg/mol at 40 °C and polymers with molecular weights of only 50 kg/mol after 10 days. This different behavior is mainly due to the steric hindrance imposed by the extra methyl group approaching the carbon(4) of the monomer. The lithium prefers carbon(1) for negative charge stabilization reasons.

The general reactions for the synthesis of 6 μ -star copolymers PS(P2MP)₅ are given in Scheme 2. The strategy followed was similar to the case of PS(PI)₅.¹² Stoichiometric amounts of PSLi and 1,2-bis(trichlorosilyl)ethane were used, in this case, for the replacement of only one chlorine by a PS chain. In the previous work on A₂B and A₃B μ -star polymers, we were able to add a high excess of the linking agent (methyltrichlorosilane for A₂B and tetrachlorosilane for A₃B) which are both fairly volatile. 1,2-bis(trichlorosilyl)ethane, which is the linking agent for A₅B, is a solid at room temperature, so we were obliged to add the PSLi dropwise and slowly into the linking agent solution. This was done to avoid a local excess of PSLi, which would lead to the production of (PS)Cl₂SiCH₂CH₂SiCl₂(PS), which is difficult to eliminate before the addition of the P2MP.

Despite the precautions taken, a local excess of PSLi living ends over the linking agent cannot be avoided completely, resulting in the formation of some small amount of two-armed product, (PS)Cl₂SiCH₂CH₂SiCl₂(PS) ($\sim 7\%$, Figure 1B, smaller peak). The presence of these chains with two PS arms will lead to the presence of a small fraction of PS₂(P2MP)₄ mixed with the main PS(P2MP)₅ product. These are expected to have a minimal impact on the final morphology. The addition of PSLi to the 1,2-bis(trichlorosilyl)ethane solution in benzene was completed in approximately 1 day. At different times aliquots of the solution were taken to examine the progress of the reaction. After the incorporation of the PS arm a small excess of the P2MP Li compared to the five remaining chlorines ($\sim 20\%$) was added to produce the 6 μ -star copolymers PS(P2MP)₅. The final product was isolated from the excess of P2MP by fractionation (toluene, solvent; methanol, nonsolvent; polymer concentration $\sim 0.5\%$, w/v). All synthetic steps as well as the fractionation

- (8) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1992**, *25*, 4649.
- (9) Zhongde, X.; Mays, J.; Xuexin, C.; Hadjichristidis, N.; Schilling, F. C.; Bair, H. E.; Pearson, D. S.; Fetters, L. J. *Macromolecules* **1985**, *18*, 2560.
- (10) Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*, 4th ed.; Wiley-Interscience: New York, 1999; Vol. I, p 193.
- (11) Avgeropoulos, A.; Dair, B. J.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **1997**, *30*, 5634.

- (12) Velis, G.; Hadjichristidis, N. *Macromolecules* **1999**, *32*, 534.

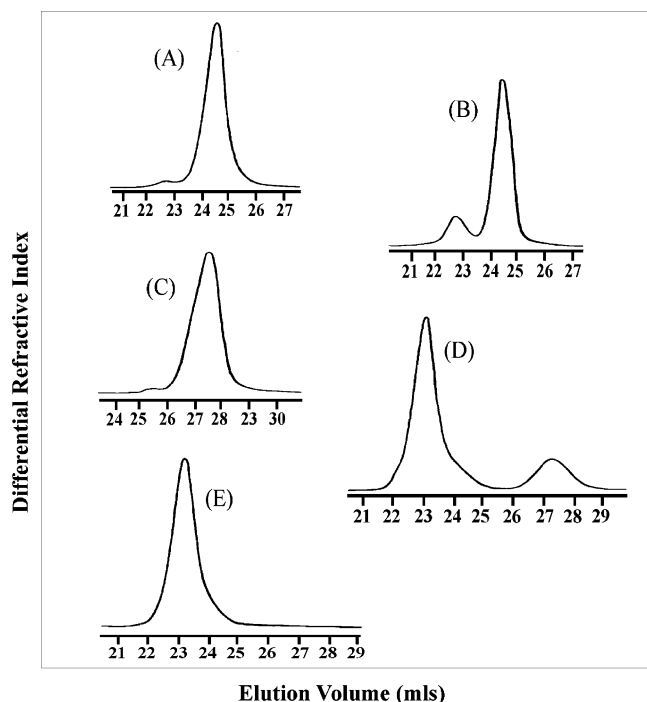


Figure 1. Monitoring the synthesis of 6μ -star copolymers PS(P2MP)₅-2, of S and 2MP, by SEC: (A) PS "living" chain, (B) intermediate linking reagent $\text{PSCl}_2\text{SiCH}_2\text{CH}_2\text{SiCl}_3$, (C) P2MP "living" chain, and (D and E) unfractionated and fractionated 6-miktoarm star copolymers, respectively.

procedure were monitored by SEC. The fractionation procedure was repeated until no precursor appeared in the SEC chromatograph. As an example, the SEC chromatographs of PS(P2MP)₅-2 are given in Figure 1. Similar chromatographs were seen for all other samples.

The molecular characteristics of the synthesized 6μ -stars, PS(P2MP)₅, are shown in Table 1. A high degree of molecular and compositional homogeneity was observed in all cases.

Morphological Characterization. Although we have no direct measure of the interaction energies for the PS–P2MP system, we believe that all of the samples of PS(P2MP)₅ studied in this work were in the strong segregation limit with $\chi N \gg 10.45$. Just as in our previous work,⁵ sharp morphologies were seen for all samples by both microscopy and scattering, so we are confident that all of these samples were far from any microphase separation point. In addition, the T_g 's measured in the μ -star copolymer were close to those of the corresponding homopolymers, which also supports the presence of strong separation.

The OsO₄ staining time for the materials used in this work (at least 3 h) is higher than for the corresponding materials based on PS/PI (~1 h). This is certainly due to the higher steric hindrance of the extra methyl group. Such differentiation was also made for materials consisting of two polydienes (1,4-PB and 3,4-polyisoprene (3,4-PI) with different microstructures),¹³ where by using appropriate staining time one can manage to get two different contrasts (grey for the 3,4-PI and black for the 1,4-PB).

TEM images are exhibited in Figure 2, and $\ln I$ versus q plots from SAXS are shown in Figure 3. It is clear that, for

ϕ_{PS} , the volume fraction of PS, equal to 0.44 and 0.53 (samples PS(P2MP)₅-1 and -2) cylindrical morphologies were exhibited (Figure 2a,b), instead of spherical domains as predicted by Milner. The discrepancies between theoretical predicted structures by Milner and those experimentally observed were reported to be more prominent in the case of the 6-miktoarm PS/PI stars as already cited in the literature.^{14,15} The cylindrical morphology in both samples was also supported from the SAXS data (Figure 3a,3b). The periodicities of the unit cell for each sample are exhibited in Table 1.

It is of major importance to point out that in the PS(P2MP)₅-2 sample, PS cylinders are exhibited even though PS in that case is the majority component. It should be noted here that the volume fraction of PS for this sample is approximately 0.53, very close to a 1:1 ratio, or a symmetric composition. The appearance of such morphology is due to the complex architecture of the polymers and the increased curvature of the interfaces toward the PS domains due to the crowded P2MP domains.

For sample PS(P2MP)₅-3, the μ -star with $\phi_{\text{PS}} = 0.92$, a disordered spherical microdomain morphology was observed, exhibiting TEM images (Figure 2c) identical to those with lower complexity in architecture (3- and 4-miktoarm materials).⁵ The low degree of order is also observed in the SAXS plots (Figure 3c) where only two broad peaks are exhibited. The observed spherical morphology is in disagreement with the theory, which predicts a lamellar structure at such volume fractions.

The morphologies predicted by the Milner theory² depend on the volume fraction of each component and the asymmetry parameter ϵ , which is defined by the following equation:

$$\epsilon = \left(\frac{n_A}{n_B} \right) \left(\frac{p_A}{p_B} \right)^{1/2} \quad (1)$$

where n_i is the number of arms of chains of type i and $p_i = M_i/(\rho_i \langle R_i^2 \rangle_0 N_A)$ is the packing length of the i chain. Here ρ_i is the density of the i polymer, M_i is the molecular weight of the i chain, N_A is Avogadro's number, and $\langle R_i^2 \rangle_0$ is the mean square unperturbed end-to-end distance of the chain i . From the literature¹ an estimated value for the packing length of both P2MP and PS can be achieved leading to values for P2MP at 140 °C equal to 3.3 Å and for PS at this temperature equal to 3.95 Å. Therefore, the asymmetry parameter ϵ for the PS(P2MP)₅ samples is equal to 4.57, corresponding approximately to the analogous value for 6-miktoarm star copolymers of the PS(PI)₅ materials.¹⁴ The morphology data for the three PS(P2MP)₅ samples, plus the PS–P2MP and PS–PI μ -stars previously studied, are plotted versus ϵ and compared to the theory in Figure 4. One striking feature in Figure 4 is that the PS–PI data disagree with the PS–P2MP results at high PS content. At $\epsilon \approx 3$ and near $\phi_s = 0.9$, the two PS–PI miktoarms showed cylindrical domains, while the PS–P2MP appeared to have disordered spheres. It is

(13) Avgeropoulos, A.; Paraskeva, S.; Hadjichristidis, N.; Thomas, E. L. *Macromolecules* **2002**, *35*, 4030.

(14) Beyer, F. L.; Gido, S. P.; Velis, G.; Hadjichristidis, N.; Tan, N. B. *Macromolecules* **1999**, *32*, 6604.

(15) Yang, L.; Hong, S.; Gido, S. P.; Velis, G.; Hadjichristidis, N. *Macromolecules* **2001**, *34*, 9069.

Table 1. Molecular Characteristics of the 6-Miktoarm Star Copolymers and Their Precursors, Mass–Volume Fractions, Morphological Characteristics, and (100) Spacings of the Final Copolymers

sample	\bar{M}_n^a (PS) (kg/mol)	\bar{M}_n^b (P2MP) (kg/mol)	\bar{M}_n^a (total) (kg/mol)	\bar{M}_w^c (total) (kg/mol)	I^d (total)	wt % PS ^e	wt % PS ^f	vol % PS ^g (ϕ_{PS})	morphology	(100) spacing (Å)
PS(P2MP) ₅ -1	54.0 ($I^b = 1.02$)	9.9 ($I = 1.03$)	103.0	109.0	1.04	52.4	49.3	44	PS CYL	395
PS(P2MP) ₅ -2	54.0 ($I^b = 1.02$)	6.4 ($I = 1.09$)	86.7	91.1	1.04	62.3	58.7	53	PS CYL	373
PS(P2MP) ₅ -3	195.0 ($I^b = 1.07$)	3.4 ($I = 1.11$)	213.0	224.0	1.05	91.5	93.5	92	disordered P2MP SPH	570

^a MO in toluene at 35 °C. ^b SEC in THF at 35 °C with P2MP standards. ^c LALLS in THF at 25 °C. ^d SEC in THF at 35 °C with PS standards. ^e Using the equation $\text{wt}\%_{\text{PS, copolymer}} = \bar{M}_{w, \text{PS, arm}} / \bar{M}_{w, \text{copolymer}}$. ^f ¹H NMR in CDCl₃. ^g Volume fraction based on ¹H NMR values using the equation $\text{vol}\%_{\text{PS, copolymer}} = \text{wt}\%_{\text{PS}} \rho_{\text{P2MP}} / [\text{wt}\%_{\text{PS}} \rho_{\text{P2MP}} + (100 - \text{wt}\%_{\text{PS}}) \rho_{\text{PS}}]$ ($\rho_{\text{PS}} = 1.06 \text{ g/mL}$, $\rho_{\text{P2MP}} = 0.850 \text{ g/mL}$).⁹

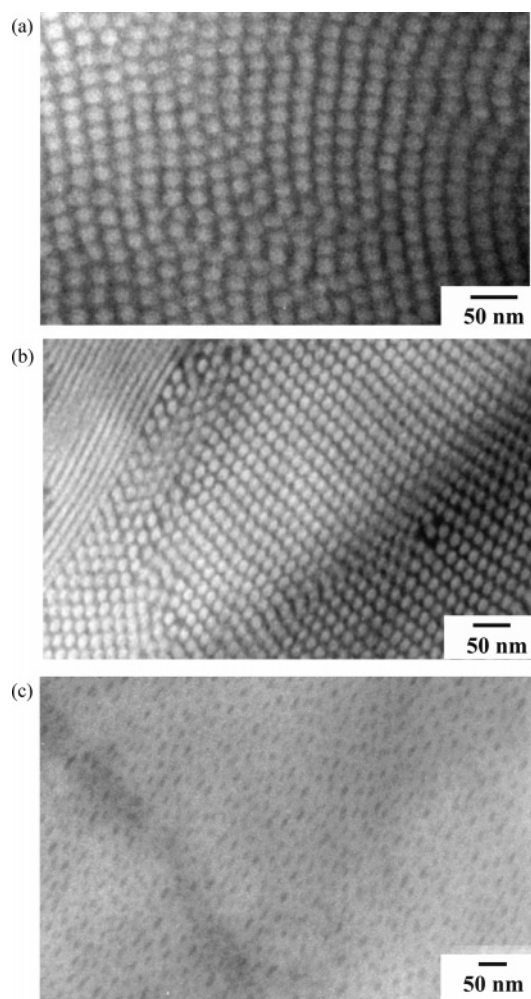


Figure 2. TEM images of the three 6 μ -star copolymer samples. (a) PS(P2MP)₅-1 with $\phi_{\text{PS}} = 0.44$ exhibiting PS cylinders in P2MP matrix, (b) PS(P2MP)₅-2 with $\phi_{\text{PS}} = 0.53$ exhibiting PS cylinders in P2MP matrix, and (c) PS(P2MP)₅-3 with $\phi_{\text{PS}} = 0.92$ exhibiting spherical microdomains.

necessary to understand whether such behavior is due to some chemical effects on the microphase separation, which is not expected.

In agreement with the earlier results, at high ϵ values the Milner model exhibits large discrepancies. In one of the previous papers^{5,14} it is speculated that this discrepancy was probably due to ignoring “multiple-domain” effects in the model. Therefore, it is suspected that the configurational entropy of the arms in the continuous microphase depends on the variation in spacing between the domains, a fact which appears to be most prominent at high arm number. This is the only case where the model predicts disperse domains at high volume fraction, meaning that the spheres or cylinders would be very close to each other because the domains would

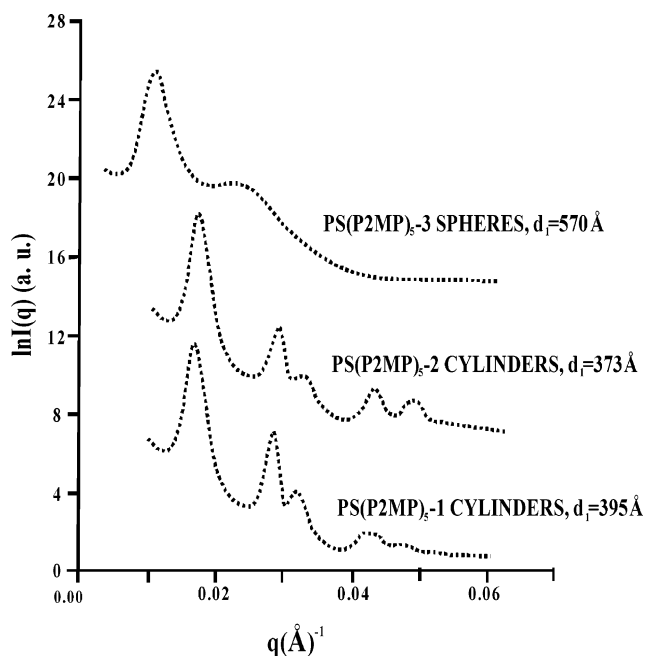


Figure 3. $\ln I(q)$ vs q plots (SAXS) of the 6 μ -star copolymers [PS(P2MP)₅]. The abbreviation of each sample together with the periodicity of the unit cell (d_1) is also indicated.

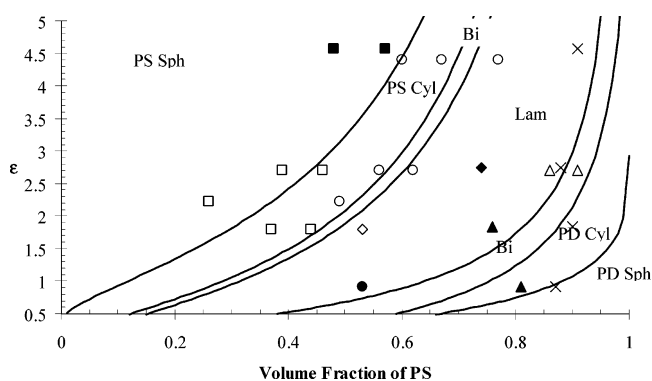


Figure 4. Morphology–volume fraction diagram for PS/P2MP (filled in symbols) and PS/PI (open symbols) miktoarm stars: ■ and □, PS cylinders; ● and ○, lamellar; ◆ and ◇, bicontinuous; ▲ and △, polydiene cylinders; ×, polydiene spheres. Predictions for transitions from the Milner model¹⁴ are shown as solid lines.

consume a large fraction of the volume. So the local environment for the arms depends greatly on exactly where along the surface of the domain they reside, and, therefore, the configurational statistics become quite complex. This is just where the model based on theoretical predictions disagrees with the experimental results. The complete understanding of such behavior requires a more analytical model of such systems, and so the synthesis of additional 3-, 4-, and 6-miktoarm star copolymers of PS/P2MP is required.

Conclusions

The synthesis of 6 μ -star copolymers [PS(P2MP)₅] of S and 2MP exhibiting a high degree of molecular and compositional homogeneity has been reported. From the structural characterization it is obvious that the morphologies are not those anticipated by Milner's predictions. The spherical structure is not well-ordered as in previous cases¹ with lower complexity in architecture. The cylindrical samples are very well-ordered as observed from TEM images and SAXS plots. The two cylindrical samples are in a region where spherical structures are predicted by the model. We suspect that this discrepancy, also seen in PS-PI μ -stars, arises from ignoring multiple domain effects.

Acknowledgment. The authors would like to thank the Center for Materials Science and Engineering at the Massachusetts Institute of Technology for use of the electron microscopy facility and Dr. M. Capel for his technical assistance (SAXS) at the National Synchrotron Light Source at Brookhaven National Laboratory (BNL). A.M. and N.H. acknowledge the Research Committee of the University of Athens and the Greek Ministry of Education (Educational Program on "Polymer Science and Its Applications" Grant 1091 and PYTHAGORAS II postdoctoral program: "Support of the research groups in the Universities") for financial support.

CM052477L