Synthesis and Morphological Behavior of Model Linear and Miktoarm Star Copolymers of 2-Methyl-1,3-Pentadiene and Styrene

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Three linear diblock copolymers (PS-*b*-P2MP), two 3-miktoarm [PS(P2MP)$_2$] copolymers, and two 4-miktoarm star copolymers [PS(P2MP)$_3$] of styrene (S) and 2-methyl-1,3-pentadiene (2MP) were synthesized by anionic polymerization/high vacuum techniques and controlled chlorosilane chemistry. Molecular characterization of the samples was carried out by size exclusion chromatography (SEC), membrane osmometry (MO), low-angle laser light scattering (LALLS), and ^{1}H NMR spectroscopy, and indicated a high degree of molecular and compositional homogeneity. All samples had approximately the same total $\bar{M}_w$ (~100 000), different compositions, and high 1,4-microstructure for the P2MP blocks. The morphological behavior was determined via transmission electron microscopy (TEM), small-angle X-ray scattering (SAXS), and differential scanning calorimetry (DSC). The experimental results were compared with those found for PS/PI block copolymer systems and with Milner's theoretical prediction. Significant discrepancies were found. Also, it is the first time that two morphologies (lamellae/double gyroid) coexist in a neat material, and especially in a 4-miktoarm star copolymer.

Introduction

During the past few decades anionic polymerization has been applied for the synthesis of linear, star-shaped, α,ω-branched, and graft block copolymers consisting of two chemically different blocks (AB,[1,2] ABA,[3] (AB)$_n$,[4,5] A$_n$B,[6,7] A$_2$BA$_2$,[8] A$_3$BA$_3$,[9] A$_5$BA$_5$,[7] grafts,[10−12] etc.). In most of the samples the two different components were polyisoprene (PI) or polybutadiene (PB) together with polystyrene (PS). The design and the synthesis of such complex, well-defined, and nearly monodisperse block copolymers is very interesting since it allows, on one hand, study of the influence of chain architecture on properties, and on the other hand, testing of the theoretical models predicting microphase separation.[1−4,13−25]

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Recently, linear diblock,[26–29] triblock,[30] and 3-miktoarm[31,32] star copolymers (mikto from the Greek word μικτος meaning mixed) of 1,3-cyclohexadiene, a rarely used diene, with butadiene and/or styrene, were synthesized via anionic polymerization and controlled chlorosilane chemistry.[31,32] The interest in such materials arises from the existence of alicyclic moiety in the main chain leading to unique thermal and mechanical properties, especially after hydrogenation. In addition, the self-assembly of these block copolymers in the bulk leads to unexpected microphase separation even in the case of diblock copolymers (e.g., core-cell cylinders).[33,34]

The anionic polymerization of 2-methyl-1,3-pentadiene, another rarely used diene, initiated by *n*-butyllithium in benzene solution, was first studied by Cuzin et al.[35] The microstructure analysis of poly(2-methyl-1,3-pentadiene) [the abbreviation will be P2MP in this manuscript even though the IUPAC name is poly(1,3-dimethyl-2-butenylene) (PDMB)] indicated that the reaction yielded exclusively a 1,4-configuration where the cis:trans ratio was approximately 60:40. Later, more accurate studies by Morton and Falvo[36] showed that monomer incorporation takes place exclusively via 4,1-addition, where the methyl groups are on the β and δ carbons of the terminal unit. Zhongde et al.[37] synthesized well-defined monodisperse homopolymers by polymerization of 2-methyl-1,3-pentadiene in benzene with *sec*-BuLi, under high vacuum conditions, for 1–3 weeks at 40 °C. These extreme polymerization conditions were possibly the reason for limited interest in synthesizing such materials and furthermore for the lack of corresponding morphological studies. The main incentive for the synthesis of this polymer is due to its conversion to 100% atactic polypropylene after hydrogenation. The rheological properties of P2MP and the corresponding hydrogenated polymer (atactic polypropylene) have been reported in the literature.[38] Finally, the relation between molecular weight, density, chain dimensions, and melt viscoelastic properties for hydrogenated P2MP as well as for other polymers has been reviewed by Fetters et al.[39]

The morphological behavior of linear and nonlinear block copolymers of PS and PI (and, to a lesser extent of PS and PB) has been extensively studied and led to the major conclusion that the macromolecular architecture, together with the volume fraction and the degree of segregation, affect the morphology of block copolymers.[13–25] The influence of the macromolecular architecture on the morphology has been predicted by Milner[40] based on a mean-field argument. Some agreements, but also some discrepancies, of the experimental results with this theory were observed, especially for high-arm-number (4-miktoarm[18] and 6-miktoarm[22,41]) star copolymer architectures. It should be pointed out that this theory is applicable only in the strong segregation limit because in this regime the free energy of all the microphases varies the same way with chain length and interfacial tension, leading to phase boundaries independent of χ. Milner's theory[40] explains the difference between linear and miktoarm block copolymers based on the need for the blocks to stretch away from the interface in ordered morphologies. The morphologies predicted by this theory depend on the volume fraction of one component and the asymmetry parameter ϵ,[22] which is defined by the following equation:

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

where n_A and n_B are the number of arms of chains A and B and $p_i = M_i/\rho_i\langle R_i^2\rangle_0 N_A$, where $M_i/\rho_i N_A = V_i$. Here, V_i is the volume occupied by the i chain, 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 p_i is the packing length of the i chain and is used to denote the number of individual chains present in a given small volume of the melt. Finally, $\langle R_i^2\rangle_0$ is the mean square unperturbed end-to-end distance of the chain i.

In this paper, we describe the synthesis of various types of well-defined linear and nonlinear block copolymers consisting of polystyrene (PS) and poly(2-methyl-1,3-pentadiene (P2MP), as well as the morphologies obtained from self-assembly of these systems. Seven samples of approximately the same molecular weight ($\bar{M}_w = 100\,000$) were synthesized and divided into three groups according to their molecular architectures (volume fraction of PS (ϕ_{PS}), as calculated from ^{1}H NMR): (a) PS-*b*-P2MP ($\phi_{PS} = 0.87$), PS-bP2MP ($\phi_{PS} = 0.81$), and *PS*-b-P2MP ($\phi_{PS} = 0.53$); (b) PS(P2MP)$_2$ ($\phi_{PS} = 0.90$) and PS(P2MP)$_2$ ($\phi_{PS} = 0.76$); and (c) PS(P2MP)$_3$ ($\phi_{PS} = 0.88$) and PS(P2MP)$_3$ ($\phi_{PS} = 0.74$).

The structures of 3-miktoarm and 4-miktoarm star copolymers are shown in Scheme 1A.

The major purpose of this study was to further explore Milner's predictions, using a different diene than isoprene. The only difference between the two diene monomers (isoprene and 2-methyl-1,3-pentadiene) is an extra methyl group as exhibited in Scheme 1B.
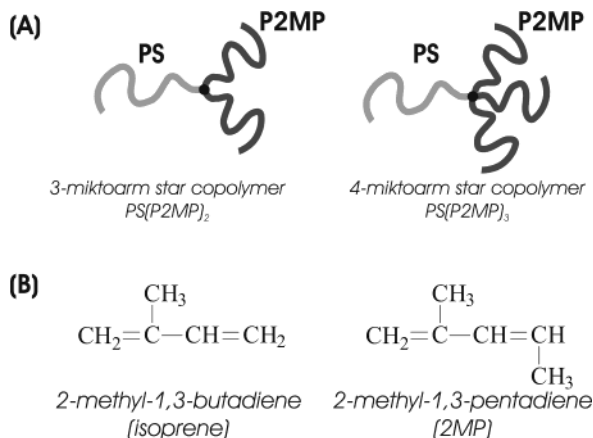
Experimental Section

All samples were prepared by anionic polymerization using high vacuum techniques in glass vessels that had been evacuated, washed with *n*-BuLi, and rinsed with benzene. The purification procedures for the styrene, solvents (benzene and THF), and initiator (*sec*-BuLi) to the standards required for anionic polymerization have been described in detail elsewhere.[42] The purification of 2-methyl-1,3-pentadiene (Aldrich,

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Scheme 1

(A)

PS   P2MP   PS   P2MP

3-miktoarm star copolymer   *4-miktoarm star copolymer*
PS(P2MP)₂   *PS(P2MP)₃*

(B)

$$CH_2=C-CH=CH_2$$
|
CH_3

$$CH_2=C-CH=CH$$
| |
CH_3 CH_3

2-methyl-1,3-butadiene   *2-methyl-1,3-pentadiene*
(isoprene)   *(2MP)*

Scheme 2

sec-BuLi + CH_2=CH $\xrightarrow{C_6H_6 / 25^0C}$ (PS)⁻ Li⁺

(PS)⁻ Li⁺ + CH_2=C—CH=CH $\xrightarrow[\text{5 - 10 days}]{C_6H_6 / 40^0C}$ PS-b-P2MP⁻ Li⁺ $\xrightarrow{MeOH}$ PS-b-P2MP

2-methyl-1,3-pentadiene

Diblock Copolymer

cis:trans 30:70) is a long-term procedure because the purity of the commercial monomer is low (∼90%). The purpose of such a thorough procedure was to eliminate not only the usual impurities but also any isomers of the monomer that might be present. The procedure used consisted of the following six steps: (a) exposure overnight under stirring in calcium hydride at room temperature; (b) exposure overnight under stirring in sodium dispersion at room temperature (repeated until no reaction of the monomer with the sodium dispersion is noticed); (c) exposure overnight under stirring in *n*-butyllithium at room temperature (the slow propagation reaction at room temperature allows this relatively long-term exposure); (d) exposure overnight under stirring in dibutylmagnesium at room temperature; (e) repetition of step (c); and (f) distillation and collection of the purified monomer into glass ampules.

Step (e) is the only step in the procedure that is not mentioned in the literature.[37] This step was very crucial as it increases the monomer's purity more than 1% (from 97.5 to 98.6%) and decreases the percentage of its anionically active isomer, 4-methyl-1,3-pentadiene, approximately 0.5% (from 1.2 to 0.6%), as observed by gas chromatography−mass spectroscopy (GC−MS).

The molecular characterization was carried out via size exclusion chromatography (SEC), low-angle laser light scattering (LALLS), and membrane osmometry (MO). The $\bar{M}_w$ values were obtained from the $(Kc/\Delta R_\theta)^{1/2}$ vs c plots (ΔR_θ, excess Raleigh ratio; K, combination of known optical constants; c, concentration), whereas the $\bar{M}_n$ values from the $\sqrt{\pi/c}$ vs. c plots (π is the osmotic pressure and c is the concentration). Square root plots were used in order to minimize the curvature due to the third virial coefficient. More details are given elsewhere.[43] In all methods the correlation coefficient was greater than 0.99.

SEC was calibrated with five P2MP homopolymers of different molecular weights, synthesized by anionic polymerization, and characterized with membrane osmometry ($\bar{M}_n$, 10−40 kg/mol).

¹H NMR determination of the composition and the microstructure was carried out in CDCl₃ at 30 °C using a Varian Unity Plus 300/54 instrument. The NMR results confirm that the anionic polymerization of the 2-methyl-1,3-pentadiene takes place exclusively via 4,1-addition leading to poly(2-methyl-1,3-pentadiene) with 99% 1,4-microstructure.[37]

A TA Instruments 2910 Modulated DSC was used to obtain preliminary information about the microphase separation of the two blocks. Two different glass transition temperatures were exhibited: $T_{g1} \sim 0$ °C and $T_{g2} \sim 100$ °C, corresponding well to known T_g values of P2MP and PS, respectively.[44] The observation of two different glass transition temperatures suggests a well-microphase separated system.
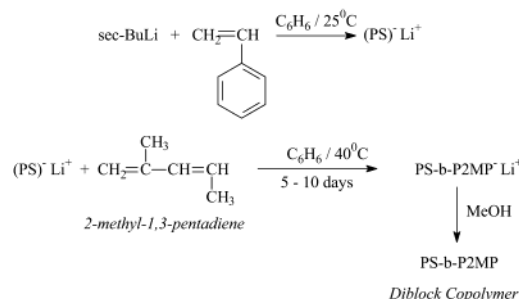
Small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM) were employed for the morphological characterization of the polymers. More details are given elsewhere.[3] Films (∼0.7 mm thick) of the materials were cast from a dilute solution (∼4 wt %) in toluene, which is a nearly nonselective solvent for a styrene/2-methyl-1,3-pentadiene 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 the TEM investigation, 500−1500 Å thick sections were cryomicrotomed and transferred onto 600-mesh copper grids. The grids were then placed in vapors of a 4% OsO₄/water solution for selective staining of the diene phase.

The SAXS diffraction patterns were obtained at room temperature on the Time-Resolved Diffraction Facility (station X12B) of the National Synchrotron Light Source at Brookhaven National Laboratory (BNL; Upton, NY) using a custom-built two-dimensional detector (10 × 10 cm, 512 × 512 pixels) interfaced to a real-time histogramming memory system.[45]

Results and Discussion

Synthesis. The polymerization of 2-methyl-1,3-pentadiene was carried out in benzene, using *sec*-BuLi as the initiator, under stirring at 40 °C. The time length of the polymerization varied from 5 to 10 days, depending on the molecular weights of the P2MP chains. It was impossible to polymerize this monomer to materials having molecular weight higher than 50 kg/mol and low polydispersity. It seems that the propagating chains at the end of the polymerization (low monomer concentration) react with the remaining (after purification) traces of the unsaturated impurities (i.e., monomer's isomer 4-methyl-1,3-pentadiene), and the new formed active centers are unable to continue the polymerization.

The diblock copolymers were synthesized by sequential addition of styrene and 2-methyl-1,3-pentadiene to the initiator. The initiation of 2-methyl-1,3-pentadiene by (PS)⁻Li⁺ took place at 40 °C. The fast initiation at this temperature is obvious from the observed quick color change from the orange (PS)⁻Li⁺ to the light yellow poly(2-methyl-1,3-pentadienyl)lithium. The basic reactions for synthesis of the linear block copolymers are given in Scheme 2.

The nonlinear PS(P2MP)₂ and PS(P2MP)₃ miktoarm star copolymers were synthesized by combining anionic polymerization techniques and controlled chlorosilane chemistry. The synthesis of A₂B miktoarm star copolymers has been presented in detail elsewhere.[43,46] The reactions used for the synthesis of 4-miktoarm star

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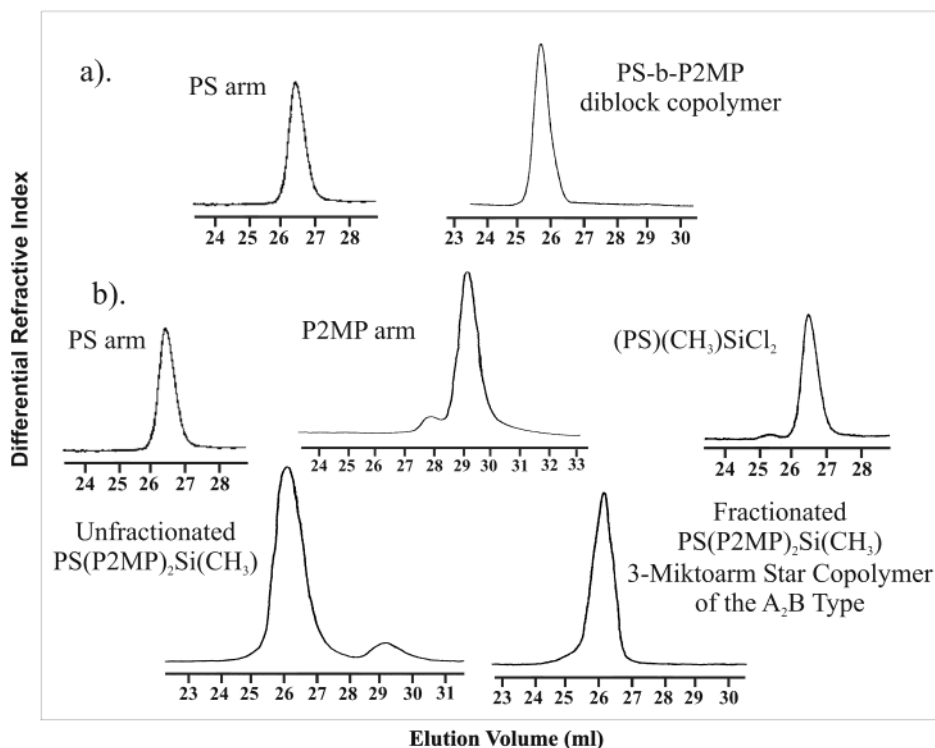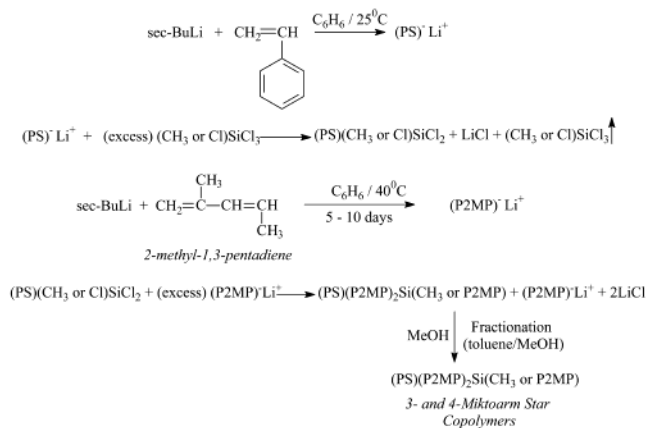(46) Iatrou, H.; Hadjichristidis, N. *Macromolecules* **1993**, *26*, 2479.

Figure 1. (a) SEC chromatographs of the PS arm and the final linear diblock copolymer PS-b-P2MP (ϕ_{PS} = 0.81). (b) SEC chromatographs of the PS precursor, the P2MP precursor, the intermediate products, and the final unfractionated and fractionated 3-miktoarm star copolymer (ϕ_{PS} = 0.76).

Scheme 3

copolymers, PS(P2MP)$_3$, were the same except that a tetrafunctional volatile chlorosilane compound was used (SiCl$_4$ in this case) instead of CH$_3$SiCl$_3$. The basic reactions used for the synthesis of the miktoarm star copoloymers are represented in Scheme 3.

The general procedure involves the reaction of (PS)$^-$Li$^+$ with a big excess of a volatile chlorosilane (CH$_3$SiCl$_3$/ SiCl$_4$) leading to the replacement of only one chlorine atom by the PS chain. After the removal, in the vacuum line, of the excess of the chlorosilane, the silicon-chloride end-capped PS reacts with excess of living P2MP. Before the linking reaction, 2−3 units of butadiene were added to the living P2MP in order to increase the reactivity of the active centers.

All synthetic steps were monitored by SEC. As examples, the SEC chromatographs taken during the different stages of the synthesis of PS-b-P2MP (ϕ_{PS} = 0.81) linear and PS(P2MP)$_2$ (ϕ_{PS} = 0.76) miktoarm star

copolymers are given in Figure 1. Similar chromatographs were taken for all other samples. Fractionation was carried out by addition of methanol (nonsolvent) to the polymer solution (ca. 0.5% w/v) in toluene (solvent) at room temperature with stirring until turbidity was established. The mixture was then heated under stirring until clear, transferred to a warm separatory funnel, and allowed to equilibrate at room temperature overnight. The bottom phase was separated the following day. The procedure was repeated until no precursors or undesirable products were shown to be present by SEC. The molecular characteristics of the synthesized materials are shown in Table 1. A high degree of molecular and compositional homogeneity is observed in all cases.

Morphological Characterization. The morphologies of the samples were determined by TEM and SAXS. The samples studied were three linear diblocks, two 3-miktoarm stars [PS(P2MP)$_2$], and two 4-miktoarm star copolymers [PS(P2MP)$_3$]. The morphological results of all materials are exhibited in Table 2. The volume fractions were carefully selected in order to observe possible similarities with the corresponding PS/PI[13,18] block copolymer systems. The total molecular weight of the samples was approximately 100 000 for comparison reasons. For volume fractions of PS equal to 0.88−0.90, in the case of the 4-miktoarm stars,[18] a transition to the disordered state occurs instead of the sphere morphology. This observation leads to an initial disagreement for this PS/P2MP system between experimental results and Milner's theory.[40] There were also some minor differences between this theory and experiment in the case of the 3-miktoarm stars[13] especially for volume fractions near the boundaries between the various morphologies. The discrepancies were reported

Table 1. Molecular Characteristics of the Linear and Non-Linear Materials and Their Precursors

sample	$\bar{M}_n{}^a$ (PS) (g/mol)	$\bar{M}_n{}^a$ (P2MP) (g/mol)	$\bar{M}_n{}^a$ (final) (g/mol)	$\bar{M}_w{}^b$ (star) (g/mol)	$I^c = \bar{M}_w/\bar{M}_n$	dn/dc^d
(PS-b-P2MP) $\varphi_{PS} = 0.87$	93300	16700^e	110000	114000	1.04	0.176
(PS-b-P2MP) $\varphi_{PS} = 0.81$	79000	22000^e	101000	106000	1.03	0.164
(PS-b-P2MP) $\varphi_{PS} = 0.53$	45800	38100^e	83900	88600	1.08	0.156
(P2MP)$_2$PS $\varphi_{PS} = 0.90$	93300	5200^f	104000	110000	1.03	0.182
(P2MP)$_2$PS $\varphi_{PS} = 0.76$	79000	14500	102000	112000	1.04	0.168
(P2MP)$_3$PS $\varphi_{PS} = 0.88$	93300	3000^f	102000	108000	1.05	0.182
(P2MP)$_3$PS $\varphi_{PS} = 0.74$	79000	9500^f	103000	110000	1.03	0.169

^{a} Membrane osmometry (MO) in toluene at 35 °C. ^{b} Low-angle laser light scattering (LALLS) in THF at 25 °C. ^{c} Size exclusive chromatography (SEC) in THF at 40 °C. ^{d} Laser differential refractometer in THF at 25 °C. ^{e} Calculated $\bar{M}_n$(P2MP) = $\bar{M}_n{}^a$(final) − $\bar{M}_n{}^a$(PS). ^{f} By SEC calibrated with P2MP standards.

Table 2. Mass−Volume Fractions, Morphological Characteristics, and (100) Spacings of the Materials

sample	$f_{PS}{}^a$ (w/w) (calculated)	f_{PS} (w/w) (^{1}H NMR)	ϕ_{PS} (v/v) (based on ^{1}H NMR values)	morphology	(100) spacing (Å)
(PS-b-P2MP) $\varphi_{PS} = 0.87$	0.85	0.89	0.87	disordered SPH	291
(PS-b-P2MP) $\varphi_{PS} = 0.81$	0.78	0.83	0.81	CYL	465
(PS-b-P2MP) $\varphi_{PS} = 0.53$	0.55	0.54	0.53	LAM	500
(P2MP)$_2$PS $\varphi_{PS} = 0.90$	0.90	0.92	0.90	disordered SPH	336
(P2MP)$_2$PS $\varphi_{PS} = 0.76$	0.77	0.78	0.76	CYL	354
(P2MP)$_3$PS $\varphi_{PS} = 0.88$	0.91	0.90	0.88	disordered SPH	363
(P2MP)$_3$PS $\varphi_{PS} = 0.74$	0.76	0.76	0.74	LAM + DG	507

^{a} $f_{PS} = \bar{M}_{n(PS)}/\bar{M}_{n(star)}$ (Table 1).

to be more prominent in the case of the 6-miktoarm stars as cited already in the literature.[22,41]

Unlike the extended studies on PS and PI chain dimensions, there is little information on the chain dimensions of P2MP. In particular, a direct measure of the chain dimensions of P2MP at temperatures (annealing process at 140 °C for 1 week) above the glass transition temperature of PS, where the morphology of these linear and miktoarm block polymers was studied, is not available. Zhongde et al.[37] measured the intrinsic viscosity of P2MP in 2-octanol, a theta solvent, at 30 °C. A value for $\langle R^2 \rangle_0/M$ equal to 0.585 Å^2·mol/g was derived, which corresponds to $C_\infty = 5.5$. At this temperature the density of P2MP is 0.88 g/cm^3, leading to a value for the packing length p equal to 3.22 Å. Pearson et al.[38] measured the plateau modulus of P2MP equal to 0.42 MPa at 75 °C, which corresponds to a packing length of 3.25 Å.[39] For comparison, the packing length of PI is 3.10 Å at 25 °C and 3.20 Å at 140 °C.[39] Thus, a reasonable estimate of the packing length of P2MP at 140 °C is 3.3 Å. Considering the corresponding value of PS at this temperature is 3.95 Å, the relevant values for the asymmetry parameter ϵ (eq 1) at the temperatures where the morphologies were observed is 0.91 for the PS-b-P2MP diblocks, 1.83 for the PS(P2MP)$_2$ miktoarm, and 2.74 for the PS(P2MP)$_3$ miktoarm star copolymer samples.

The TEM and SAXS results of the samples are presented in Figures 2−5. A comparison with the Milner theory is depicted in Figure 6, where the boundaries are elongated to include the case of $\epsilon = 0.91$, involving therefore the case of the linear diblocks. The three linear diblock samples exhibited, from TEM, disordered spherical, cylindrical, and lamellar morphologies (Figure 2a) for PS volume fractions equal to 0.87, 0.81, and 0.53, respectively. The resultant morphologies agree with those for PS/PI systems. The TEM results are confirmed by the SAXS plots exhibited in Figure 2b.

Disordered spheres and cylinders (Figure 3a) were observed, from TEM, for PS(P2MP)$_2$ ($\varphi_{PS} = 0.90$) and PS(P2MP)$_2$ ($\varphi_{PS} = 0.76$), respectively. The SAXS plots are shown in Figure 3b and are in good agreement with the TEM images. Milner's theory (Figure 6) predicts that these samples should be cylindrical and lamellar, respectively. The disagreement is disturbing because the elasticity parameter (p_A/p_B) is only slightly different between the PS/P2MP and PS/PI systems. Moreover, the question of whether the strong segregation limit is relevant for these materials arises.

Finally, disordered spherical microdomain morphology was observed for the PS(P2MP)$_3$ miktoarm star ($\varphi_{PS} = 0.88$) and a unique biphasic structure with coexisting lamellar and double gyroid microdomains (Figure 4a) was observed for the (P2MP)$_3$PS sample ($\varphi_{PS} = 0.74$). SAXS plots verifying these results are shown in Figure 4b. The observed spherical morphology is in disagreement with the theory, as it predicts a cylindrical or lamellar morphology at such volume fractions. It is of
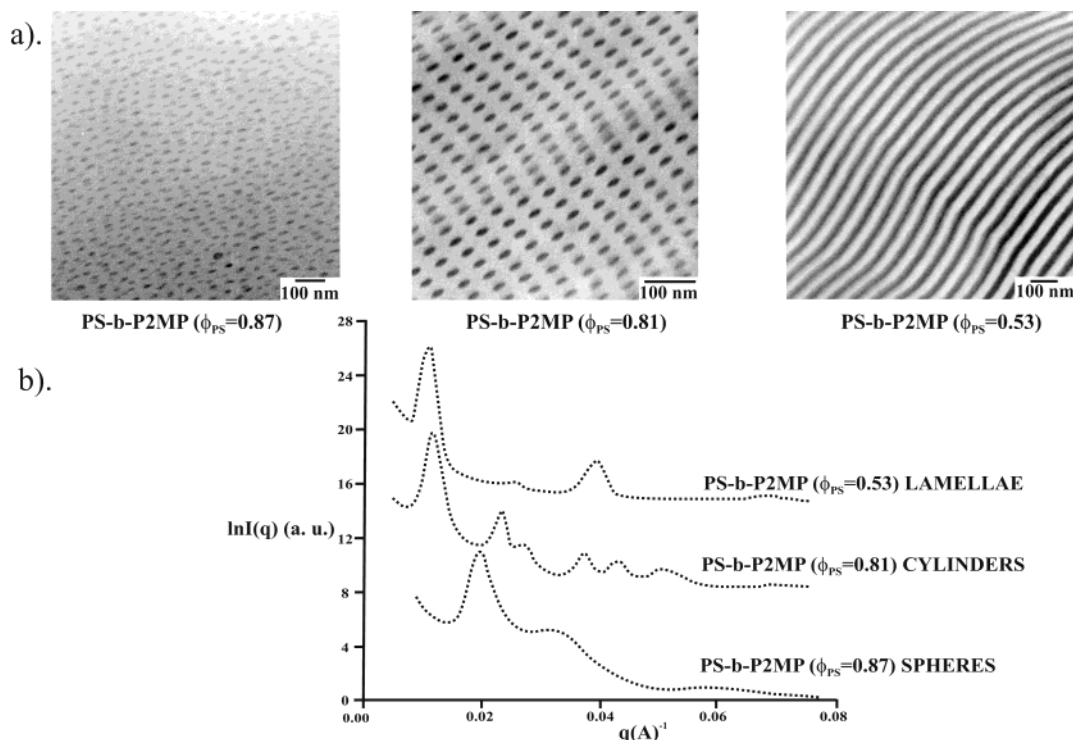
Figure 2. (a) TEM images of the three linear PS-b-P2MP. (b) Corresponding ln$I(q)$ vs q plots (SAXS).
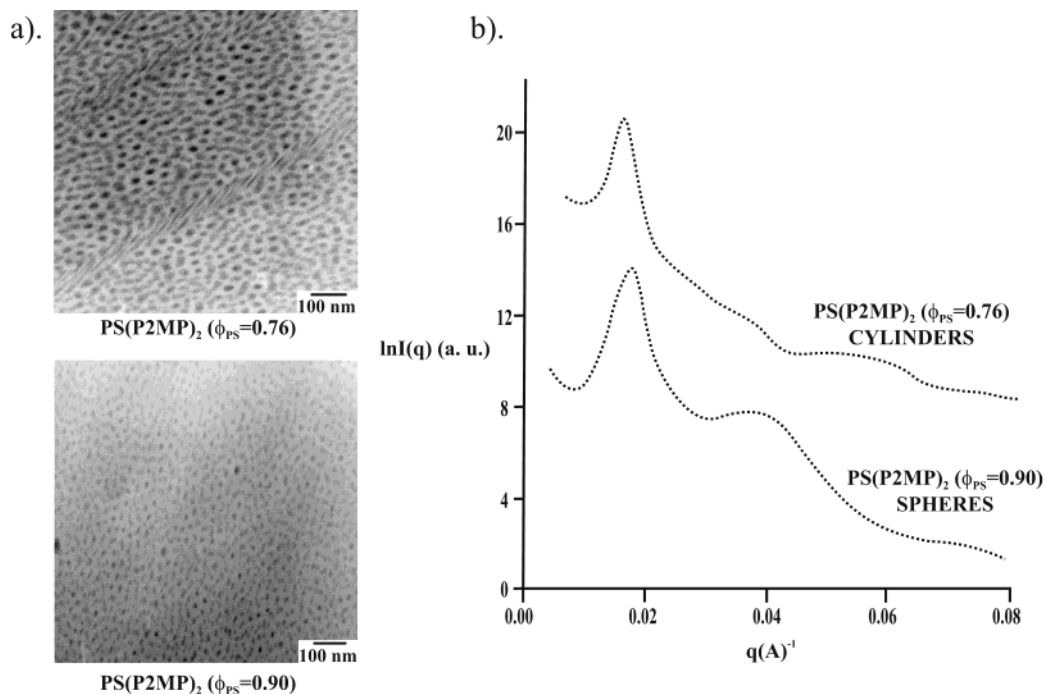

Figure 3. (a) TEM images of the two 3-miktoarm star copolymers of the PS(P2MP)$_2$ type. (b) Corresponding ln$I(q)$ vs q plots (SAXS).

great importance to acknowledge the case of the 4-miktoarm star PS/PI copolymers where the spherical microdomains have completely transformed to a disordered state at this composition.[18] It is therefore understood from the above that at high PS volume fraction (0.88 to 0.90) there is no apparent effect of the chain architecture (linear to miktoarm) on the observed morphology, leading to a conclusion that in Milner's diagram the phase boundary between sphA and cylA must not be as curved as that in the PS/PI systems. It seems that the boundary

approaches a more parallel orientation with respect to the ϵ-axis.

The structure of the PS(P2MP)$_3$ miktoarm copolymers with a PS volume fraction of 0.74 was also unexpected. A lamellar morphology should have been exhibited for a PS(P2MP)$_3$ miktoarm star at this composition, as predicted from the theory. Instead, a biphasic, very well ordered structure of 1D-lamellar and 3D-double gyroid structure was observed. A similar structure has already been reported in the literature[1] in binary blends of a
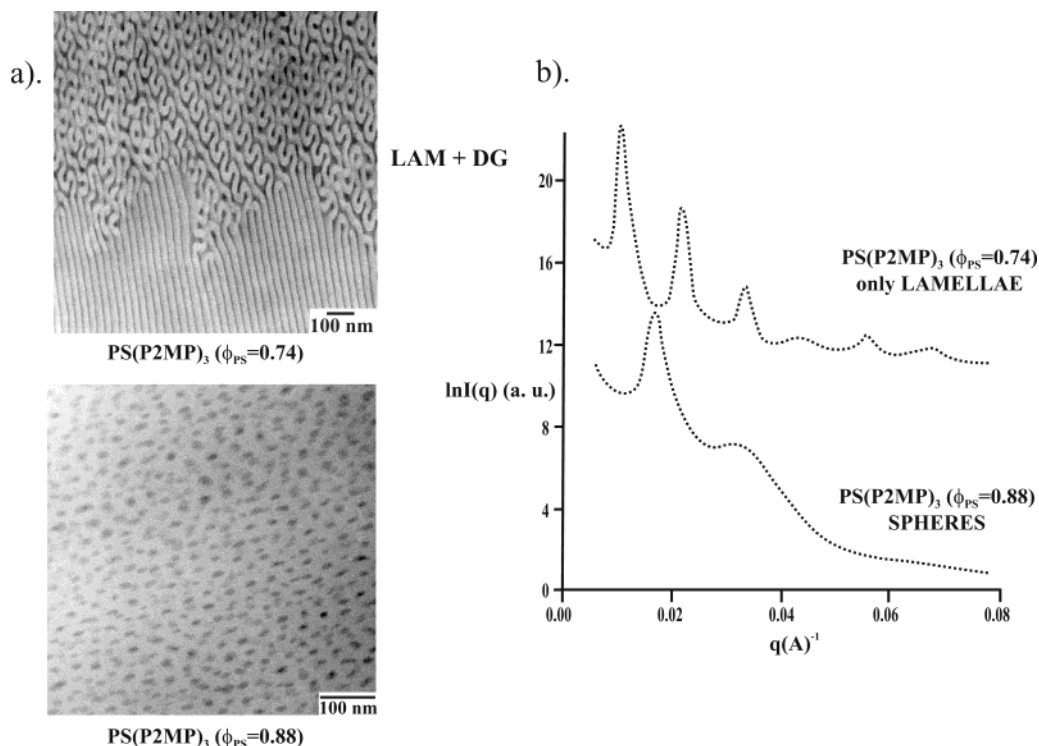
Figure 4. (a) TEM images of the two 4-miktoarm star copolymers of the PS(P2MP)$_3$ type. (b). Corresponding ln$I(q)$ vs q plots (SAXS).
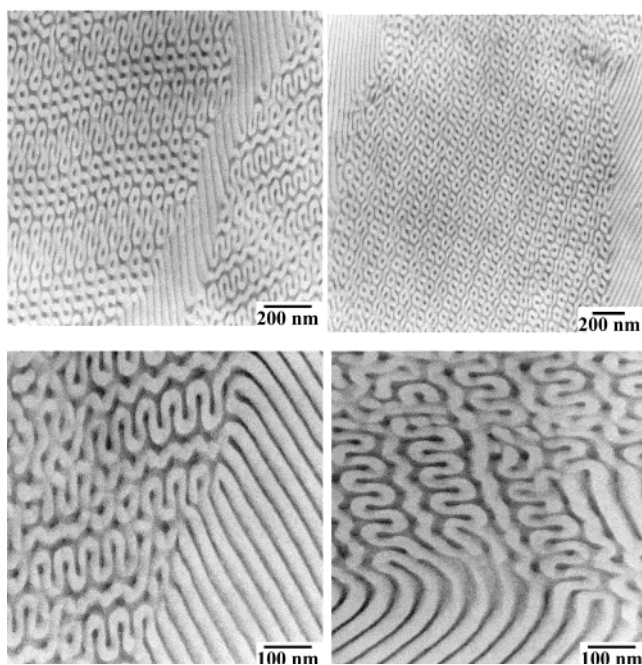

Figure 5. Additional TEM images of the PS(P2MP)$_3$ star copolymer (ϕ_{PS} = 0.74) for accessional proof of the obtained biphasic structure.

Figure 6. Milner's diagram for the morphologies of A/B copolymers as reported in the literature. The observed morphologies of the linear and miktoarm star copolymers of PS/P2MP are represented. ● Lamellar structure, ■ cylinders of P2MP in PS matrix, ▲ sphere of P2MP in PS matrix, ◆ biphasic structure of lamellar/DG microdomains.

linear diblock PS-*b*-PI with hPS at an apparently equivalent volume fraction (ϕ_{PS} = 0.68). It is understood therefore that again there is only minor effect of the macromolecular architecture on the observed morphology as stated above for the materials exhibiting spherical microdomains, and it seems that the boundaries between the phases should be more vertically parallel than curved.

   Such a biphasic structure can be explained in two ways. Either the volume fraction corresponds exactly
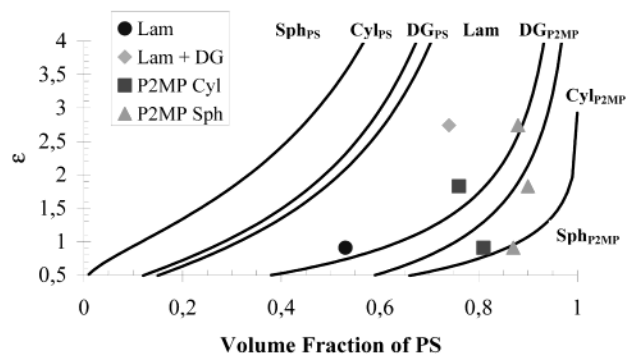
to the boundary between the lamellae and the DG morphologies, or the annealing temperature was appropriate for such structures to coexist (changing the temperature to higher or lower values would lead to one or the other morphology). The SAXS plot (ln$I$ vs q) of the sample exhibits a remarkable long-range order as indicated from the large number (6) of the Bragg reflections. The ratio of these peaks corresponds exactly to the lamellae morphology; constant with the fact that the sample used for the SAXS data mostly exhibited the lamellar structure. Our data for the biphasic structure are from the TEM images where the boundaries of lamellae to DG are very well assembled (Figure 5).

   The microphase separation of most of the miktoarm star copolymers described in this work is not predicted from Milner's theory (Figure 6). There are discrepancies near the boundaries between different morphologies when compared with corresponding PS/PI systems.[18] It

seems that the differences in C_∞ and T_g between P2MP and PI are likely causing these disagreements between experimental results and theoretical predictions. Additionally their chain dimensions are very similar, leading to the fact that their stiffness is of approximately equal value. Calculation of the Flory−Huggins interaction parameter, χ, is necessary in order to determine whether the strong segregation limit is approached, as Milner's theory is sufficient only at this regime. If the resulting χ does not correspond to the SSL then the phase boundaries are dependent on the degree of segregation and Milner's theory is not sufficient to describe the resulting morphologies. Extensive studies of additional star shaped copolymers of the A_2B, A_3B, and A_5B type will be carried out to complete the morphological behavior of the PS/P2MP copolymers.

Conclusions

The synthesis of linear and nonlinear block copolymers of PS and P2MP leads to materials exhibiting a high degree of molecular and compositional homogeneity. The main interest in P2MP arises because it can be converted into atactic PP (polypropylene) with various architectures, leading to unique mechanical and thermal properties. The self-assembly of these materials exhibited morphological results not in agreement with Milner's theory for corresponding PS/PI systems. The morphological results for the various PS/P2MP copolymers led to boundaries between the phases more parallel than curved when compared with the PS/PI polymeric materials and Milner's theory. A biphasic structure (lamellae + DG) is observed in a neat material and especially a 4-miktoarm star copolymer with large grain order, as it is evident from the increased number of Bragg peaks in the SAXS patterns.