Bicontinuous Gyroidic Morphologies in Ferrocenyldimethylsilane-*b*-Methyl Methacrylate Diblock Copolymer Blends

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ABSTRACT: Poly(1,1′-ferrocenyldimethylsilane)-*b*-poly(methyl methacrylate) (PFS-*b*-PMMA) diblock copolymers were blended with the corresponding homopolymers, PFS and PMMA. The obtained blends were investigated with respect to their microphase morphologies in the bulk. Special attention was paid to those compositions which are close to the transition from the cylindrical to the lamellar regime, i.e., where the overall PFS volume fractions in the blends were around $\phi_{\mathrm{PFS}} \approx 0.40$. This is because there the bicontinuous gyroidic morphology should arise. However, in samples prepared from high-molecular-weight diblock copolymers ($M_n \geq 40\,000$ g/mol) and PFS homopolymers a direct transition of the cylindrical into the lamellar phase was found with increasing PFS content. Such a direct transition of two classic morphologies was also observed in blends of low-molecular-weight diblock copolymers ($M_n \approx 27\,000$ g/mol) and PMMA homopolymers where the PFS volume fraction was around $\phi_{\mathrm{PFS}} \approx 0.40$—provided the annealing temperature was rather low (165 °C). The same samples, on the other hand, show the formation of a gyroidic phase when the annealing temperature was raised to 190 or 220 °C. This result can be explained by the lower segregation tendency of the two constituents at higher temperatures, expressed by a lower Flory−Huggins interaction parameter χ.

Introduction

Recently, we reported on a powerful synthetic access to narrowly distributed diblock copolymers composed of poly(1,1′-ferrocenyldimethylsilane) (PFS) and poly(methyl methacrylate) (PMMA) segments of various length.[1] The synthesis was done via ring-opening anionic polymerization of [1]dimethylsilaferrocenophane (FS) followed by anionic polymerization of methyl methacrylate (MMA). The key for this synthetic success was the very efficient modification of the living PFS chain ends prior to MMA addition: 1,1-diphenylethylene (DPE) provides an appropriate anionic chain terminus for subsequent MMA polymerization. However, DPE reacts very slowly and incompletely with the PFS chain termini at ambient temperatures. In combination with 1,1-dimethylsilacyclobutane (DMSB), on the other hand, DPE modifies the PFS chain termini very rapidly and completely according to Scheme 1. Under optimum conditions, PFS-*b*-PMMA diblock copolymers were obtained in >90% yield, having molar masses ranging from approximately 25 000 to 160 000, PFS volume fractions of $\phi_{\mathrm{PFS}} = 0.25−0.50$, and polydispersity indices PDI < 1.1.

Such phase-separated block copolymers might be of broad interest due to the special electronic, optic, and magnetic properties[2−4] of the organometallic segments which are combined here with the excellent mechanical and chemical properties of the thermoplastic PMMA. On the other hand, potential applications depend strongly on how these materials phase separate, i.e., what kind of microphase morphologies can be realized. Therefore, we analyzed the thermal properties as well as the morphologies that are accessible by pure PFS-*b*-PMMA diblock copolymers in the bulk.[5] We could show that, depending on the PFS volume fraction, the three classic morphologies—spheres, cylinders, and lamellae—are the only accessible phases for high-molecular-weight samples. No evidence was found for the occurrence of complex morphologies such as the bicontinuous gyroidic one. Instead, the coexistence of lamellar and cylindric phases was observed in some specific cases. We concluded that PFS and PMMA are highly incompatible and thus strongly segregating. On the other hand, some potential applications of these novel materials would require cocontinuous PMMA and PFS phases: for a durable antistatic coating of parts made from PMMA, for example, the PFS phase—possibly after doping—should

Scheme 1. Synthesis of PFS-*b*-PMMA Diblock Copolymers Using the Strategy of Carbanion Pump Mediated Block Formation

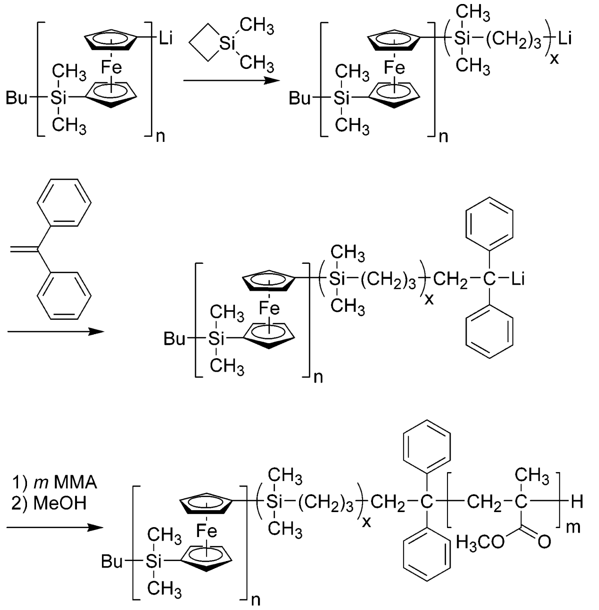

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Table 1. Molecular Characterization of the Blends from PFS-*b*-PMMA Diblock Copolymers with PFS Homopolymers

sample name[a]	M_n[b] (diblock)	M_w/M_n[b] (diblock)	w_{PFS}[c] (diblock)	ϕ_{PFS}[c] (diblock)	M_n[b] homo PFS	vol % homo PFS	overall w_{PFS}	overall ϕ_{PFS}
$F_{36}M_{64}^{48}$ + 4% hF	48 200	1.06	0.38	0.36	18 000	4	0.42	0.40
$F_{37}M_{63}^{38}$ + 2% hF	38 200	1.09	0.40	0.37	15 000	2	0.41	0.39
$F_{40}M_{60}^{41}$ + 4% hF	40 900	1.10	0.42	0.40	17 200	4	0.47	0.44

[a] The block copolymers are named $F_kM_l^x$ where F and M are the abbreviations of the respective blocks, PFS and PMMA. The subscripts k and l represent the volume fractions (in %) while the superscript x represents the overall number-average molecular weight (in kg mol^{-1}). The amount of homopolymer in the blend samples is given afterward (in terms of vol %). [b] Determined by SEC using THF as the eluent and calibration vs PMMA standards. [c] w_{PFS} and ϕ_{PFS} are the weight fraction and the volume fraction, respectively, of the PFS segments in the diblock copolymers. ϕ_{PFS} was calculated utilizing the densities of PFS = 1.26 g mL^{-1} and of PMMA = 1.15 g mL^{-1}, taken from refs 12 and 14.

the charge carriers allow moving over larger distances. Therefore, it was our aim to study in more detail whether the gyroidic morphology can be realized in PFS-*b*-PMMA diblock copolymers.

Original theories on the microphase separation behavior of amorphous diblock copolymers have identified two regimes of incompatibility, depending on the value of χN.[6-9] This is the product of the Flory−Huggins interaction parameter, χ, of the segments in the block copolymer and the total degree of polymerization, N, associated with the sample under investigation. The situation where $\chi N \sim 10$ represents the so-called weak segregation, allowing the formation of rather diffuse phase boundaries. For $\chi N \gg 10$ the strong segregation limit is reached, where the two segments have a very high tendency to form sharp interfaces. While the classical morphologies (lamellar, cylindrical, spherical) can be found over the entire biphasic range, both theory and experiments reveal that bicontinuous phases such as the gyroidic one are only stable at low or moderate values of χN.[10,11] Also, the window of stability of such phases is very narrow with respect to the composition of the block copolymer (in terms of volume fractions). This makes it very difficult to hit these morphologies due to the potentially very high synthetic effort related to the exact adjustment of both the overall molecular weight and the composition. An easier and by far less time-consuming approach is based on the preparation of block copolymer blends with either of the corresponding homopolymers. Several studies have proven that bicontinuous phases exist at nearly the same composition as they were found in the pure diblock copolymers. This is the case for example in blends of polystyrene-*b*-polyisoprene (or polystyrene-*b*-polybutadiene).[7] Even more related with the present work, Vancso et al. could demonstrate that the gyroidic structure can be found in blends of polystyrene-*b*-poly(1,1′-ferrocenyldimethylsilane) diblock copolymers and PFS homopolymers.[12]

It is the aim of the present contribution to show to what extent (i) the decrease of the molecular weight, (ii) the increase of the annealing temperature, and (iii) the fine-tuning of the PFS volume fraction are successful in forcing the PFS-*b*-PMMA block copolymer/PFS homopolymer blends to create the gyroidic structure in the bulk phase.

Experimental Section

Syntheses of the PFS-*b*-PMMA block copolymers and of the PFS homopolymers were done by adaption of the original anionic ring-opening polymerization (ROP) method described by Ni et al. to access well-defined PFS polymers.[13] Details of the carbanion-pump-mediated block copolymerization and the characterization are given in our previous publication.[1] PMMA was synthesized anionically in THF/LiCl at −78 °C, using DPHLi as the initiator. The blend samples were prepared by dissolving the block copolymer together with the corresponding homopolymer in methylene chloride (5% w/v) and stirring this solution for 1 day in order to guarantee complete dissolution and homogeneous mixing. Films were prepared by casting the solutions onto small Petri dishes (4 cm in diameter) and allowing the solvent to evaporate to dryness over a period of 1 week.[5] The subsequent annealing procedure involved a stepwise heating, over a period of 2 h, from room temperature to above the PMMA's glass transition temperature (130 °C). At 130 °C, the temperature was held for 1 h followed by adjusting the final annealing temperature (165, 190, or 220 °C) in one single temperature-rising step. After 24 h annealing the films were quenched in ice water to prevent crystallization of the PFS blocks. From each film prepared in this study ultrathin slices (50 nm diameter) were cut with a diamond knife at room temperature using a Reichert Ultracut E or a Leica Ultracut UCT and collected on copper grids (400 mesh). No staining was required due to the larger electron density of the organometallic phase. TEM experiments were carried out using a Zeiss CEM 902 electron microscope operating at 80 kV. All images were recorded with a Slow-Scan CCD camera obtained from ProScan Inc. in the bright-field mode. Camera control was achieved computer-aided by using the Vario Vision software 3.2 from LEO.

Results and Discussion

In our previous paper[5] we reported that some samples of the PFS-*b*-PMMA diblock copolymers show an unusual morphological behavior: depending on the annealing temperature, different morphologies were found to be coexistent in the films cast from methylene chloride when the PFS content was adjusted to ϕ_{PFS} = 0.40. When the samples were annealed at 165 °C, areas of hexagonally oriented cylinders coexist with lamellar regions. When annealed at 220 °C, on the other hand, the formation of a pure and homogeneous lamellar phase was evident. We interpret this observation as the result of some minor amounts of PFS homopolymer being present in the PFS-*b*-PMMA diblock copolymer. This "impurity" accumulates in some areas of the sample during the film-drying process due to preferential solvation. Thus, local modulations of the overall PFS volume fraction finally force the coexistence of two different morphologies. When rather moderate annealing conditions were applied, this inhomogeneity cannot equilibrate due to the chain's low mobility in the melt. In contrast to this at higher annealing temperatures the molecular mobility is sufficiently high for mixing homopolymers and block copolymers homogeneously over the entire sample. The major conclusion from this observation was that, at least for PFS-*b*-PMMA diblock copolymers of high molecular weight, the lamellar phase directly follows the cylindrical morphology when the PFS content increases.

To investigate this coexistence of cylindrical and lamellar morphologies in PFS-*b*-PMMA diblock copolymers at $\phi_{PFS} \approx 0.40$ further, a series of pure block copolymers were blended with PFS homopolymers hav-

Table 2. Molecular Characterization of the Blends from PFS-*b*-PMMA Diblock Copolymers with PMMA Homopolymers

sample name[a]	M_n[b] (diblock)	M_w/M_n[b] (diblock)	w_{PFS}[c] (diblock)	ϕ_{PFS}[c] (diblock)	M_n[b] homo PFS	vol % homo PFS	overall w_{PFS}	overall ϕ_{PFS}
$F_{45}M_{55}^{27}$ + 5% hPMMA	27 100	1.08	0.47	0.45	9600	5	42	40
F_{45} M_{55}^{27} + 6% hPMMA	27 100	1.08	0.47	0.45	9600	6	41	39

[a] The block copolymers are named $F_kM_l^x$ where F and M are the abbreviations of the respective blocks, PFS and PMMA. The subscripts k and l represent the volume fractions (in %) while the superscript x represents the overall number-average molecular weight (in kg mol^{-1}). The amount of homopolymer in the blend samples is given afterward (in terms of vol %). [b] Determined by SEC using THF as the eluent and calibration vs PMMA standards. [c] w_{PFS} and ϕ_{PFS} are the weight fraction and the volume fraction, respectively, of the PFS segments in the diblock copolymers. ϕ_{PFS} was calculated utilizing the densities of PFS = 1.26 g mL^{-1} and of PMMA = 1.15 g mL^{-1}, taken from refs 12 and 14.

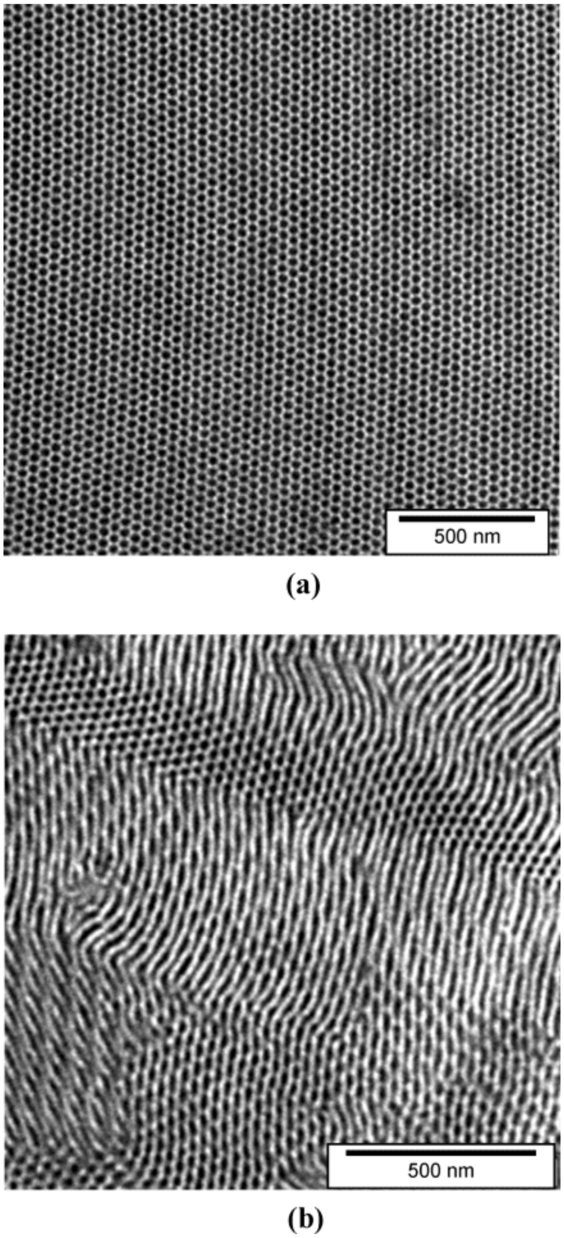


Figure 1. TEM pictures of (a) $F_{36}M_{64}^{48}$ + 4% PFS and (b) $F_{37}M_{63}^{38}$ + 2% PFS. Film casting was done from methylene chloride, and the annealing temperature was 190 °C.

ing the same molecular weight as the corresponding PFS block in the diblock copolymer. Most of these studies were carried out by means of rather low molecular weight samples which were expected to guarantee a more moderate tendency of segregation between the PFS and the PMMA phases. A detailed summary of all relevant data of three representative blends is given in Table 1.

Figure 1 displays the TEM pictures of the blend films of $F_{36}M_{64}^{48}$ + 4% PFS (overall PFS content $\phi_{PFS} = 0.40$) and of $F_{37}M_{63}^{38}$ + 2% PFS (overall PFS content $\phi_{PFS} = 0.39$) after annealing at 190 °C.

In both cases a pure hexagonal phase developed. Additional regions with a stable lamellar phase were not observed. Quite similar results were obtained when the annealing was carried out at 165 °C. For $F_{40}M_{60}^{41}$ + 4% PFS, on the other hand, the expected coexistence of cylindric and lamellar domains was found for lower annealing temperatures while for high annealing temperatures only the lamellar morphology is observed (Figure 2).

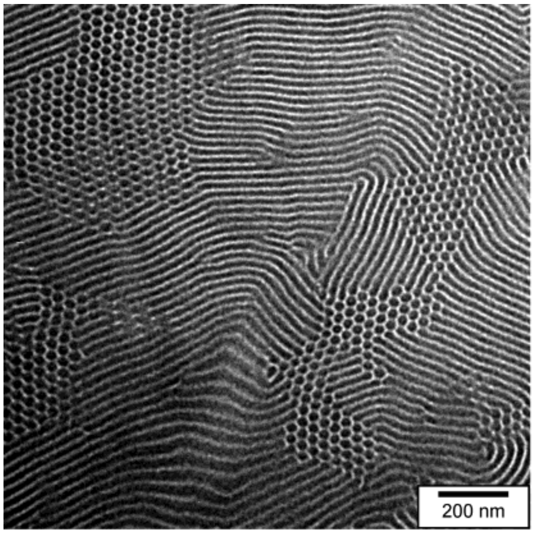
This phase behavior corresponds to that of the block copolymer $F_{40}M_{60}^{41}$ discussed in our previous paper.[5] The only difference is the higher content of PFS homopolymer in the material discussed here. These investigations reconfirm that the transition between cylindrical and lamellar morphology in PFS-*b*-PMMA diblock copolymers is localized at $\phi_{PFS} = 0.40$ in the bulk. A hint toward the existence of a gyroidic phase could not be found in these samples.

The conclusions concerning the microphase separation behavior of PFS-*b*-PMMA diblock copolymers drawn so far base mainly upon the morphological characterization of rather high-molecular-weight samples. In the following, additional blends were prepared from sample $F_{45}M_{55}$.[27] This copolymer has a rather moderate molecular weight and a nearly symmetric composition. Thus, it gives a lamellar morphology when studied as pure material. To reach the already mentioned region of composition next to the transition from the lamellar to the cylindrical phase, the volume fraction of PFS must be lowered. Therefore, low-molecular-weight PMMA homopolymer (M_n = 9600 g mol^{-1}; PDI = 1.06) was synthesized and used as blend partner. Two mixtures will be discussed preferentially in the following (see Table 2).

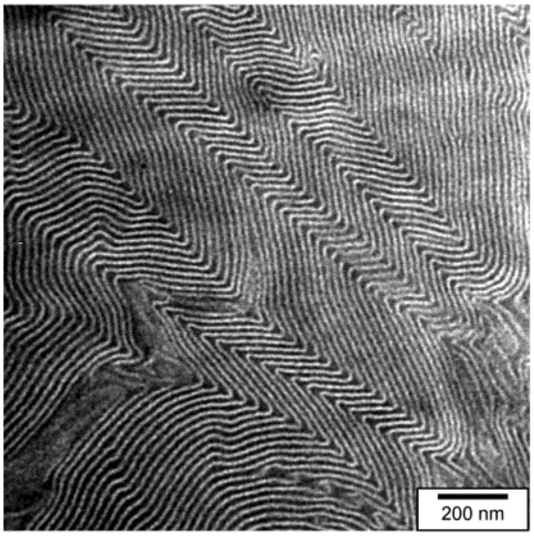
Figure 3 shows—as a function of the PFS content in the blend system—the observed morphologies together with the morphology of the corresponding pure diblock copolymer $F_{47}M_{53}$.[27] In all cases annealing was done at 165 °C. Starting from the lamellar structure (a) of the pure diblock copolymer first 5 vol % of PMMA homopolymer (b) was added. A region is reached where cylinders and lamellae coexist.

This coexistence, however, is found here in particular at the boundaries between lamellar grains of different orientation. Upon further increase of the PMMA content (c), a sharp transition occurs into the cylindrical regime. This result is in full agreement with the results obtained for the high-molecular-weight samples. A completely different situation was found when the annealing temperature was raised to 190 °C (Figure 4).

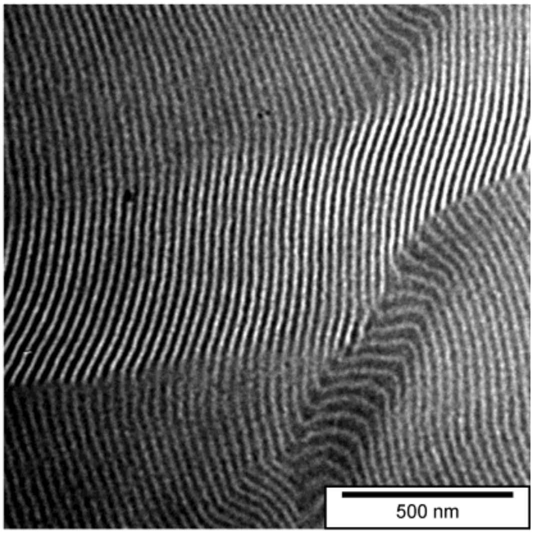
This annealing at higher temperatures is equivalent—due to the temperature dependence of χ—to a decrease



(a) 165 °C

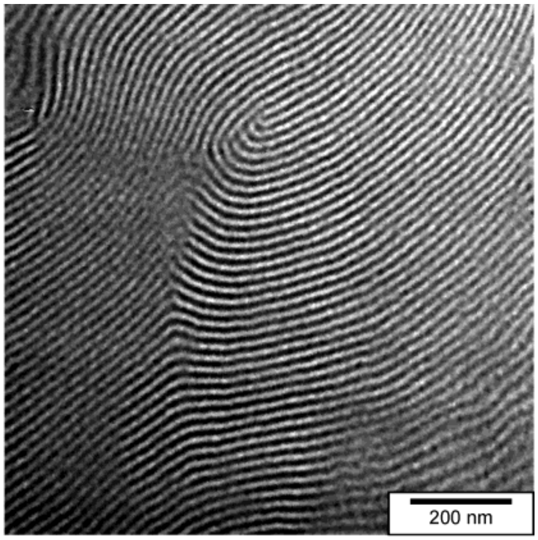


(b) 190 °C

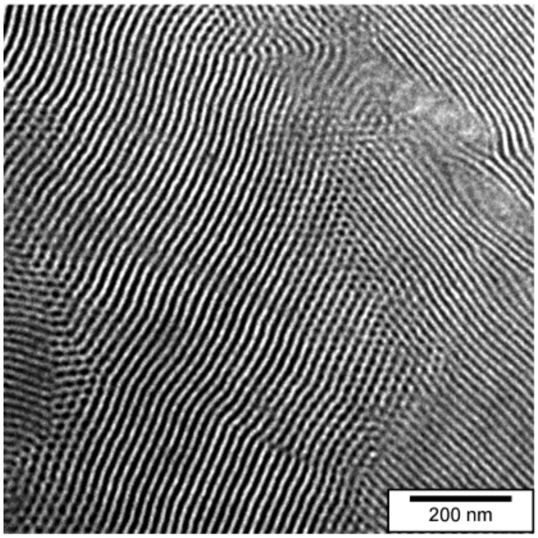


(c) 220 °C

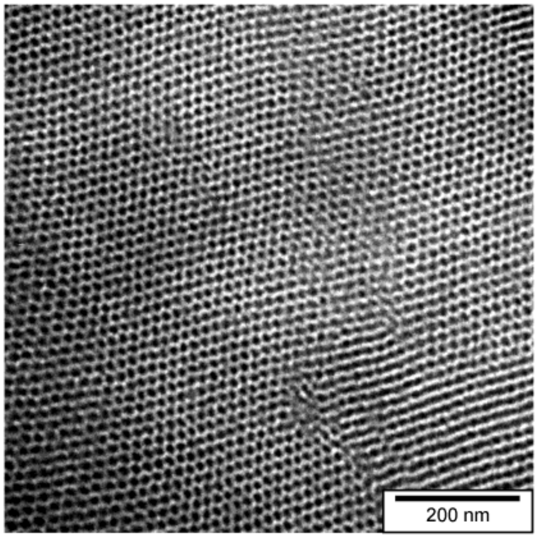
Figure 2. TEM pictures of $F_{40}M_{60}{}^{41}$ + 5% PFS (films cast from methylene chloride solution) as a function of the annealing temperature.



(a) $F_{45}M_{55}{}^{27}$



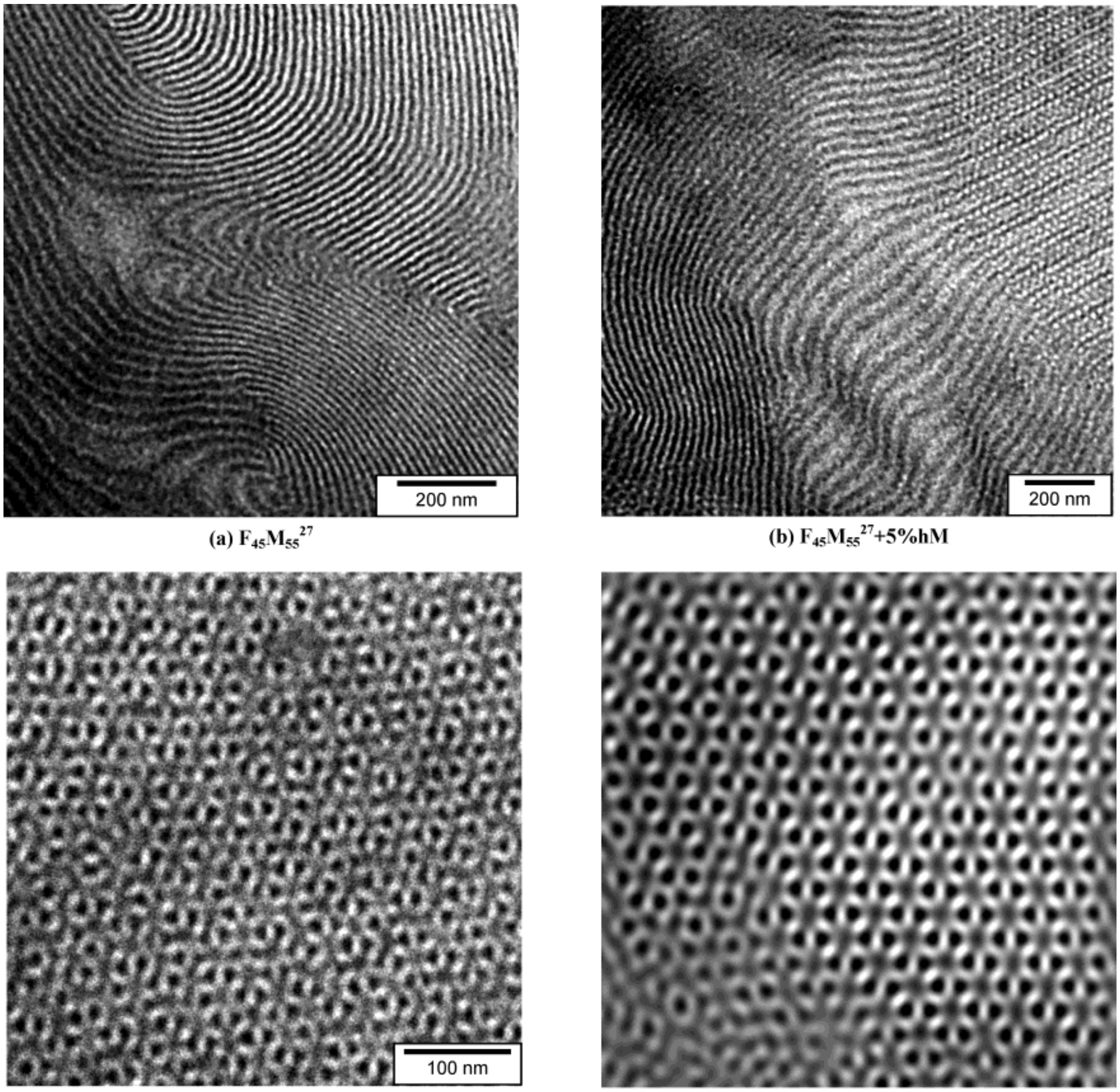
(b) $F_{45}M_{55}{}^{27}$+5%hM



(c) $F_{45}M_{55}{}^{27}$+6%hM

Figure 3. TEM pictures of (a) $F_{45}M_{55}{}^{27}$ diblock copolymer and for blends of $F_{45}M_{55}{}^{27}$ with (b) 5 vol % and (c) 6 vol % PMMA homopolymer (annealed at 165 °C).

of χN and thus to an attenuation of the incompatibility between PFS and PMMA. Upon addition of 5 vol % PMMA homopolymer the original lamellar phase (a) of the pure diblock copolymer switches to a more complex superstructure (b) in which, in addition to the clearly



(a) $F_{45}M_{55}{}^{27}$ **(b) $F_{45}M_{55}{}^{27}$+5%hM**

(c) $F_{45}M_{55}{}^{27}$+6%hM **(d)**

Figure 4. TEM pictures of (a) $F_{45}M_{55}{}^{27}$ and of blends of $F_{45}M_{55}{}^{27}$ with (b) 5 vol % and (c) 6 vol % PMMA homopolymer. Annealing was done at 190 °C. For (c) the fast Fourier transformation (FFT) filtered image of the considered section is additionally shown in (d).

visible lamellar regions, a further phase arises. However, an exact interpretation of this new phase is difficult based only on the TEM picture shown here. The structural assignment of the morphology found for the second blend with 6 vol % PMMA homopolymer shown in Figure 4c is much easier. This projection can be assigned unambiguously to the well-known wagon-wheel projection of the bicontinuous gyroidic phase.[7] The expression "wagon-wheel" was chosen because of the characteristic pattern which is observed in TEM pictures when the cubic gyroid structure is viewed in the 111 direction.[15−17] For better illustration of the structure found for $F_{45}M_{55}{}^{27}$ + 6 vol % PMMA, Figure 4d shows additionally a Fourier transform filtered section of the picture given in Figure 4c. In this case the characteristics of the wagon-wheel projection can be identified fairly easily.

Conclusions and Outlook

The results of this work illustrate that even in the system PFS/PMMA there is, in addition to the classic three phases we previously discovered in pure PFS-*b*-PMMA diblock copolymers, a region of stability for the bicontinuous gyroidic phase—at least for materials of lower molecular weights and when annealing is done at higher temperatures, i.e., for low values of χN. This is an important result when one considers potential applications of these materials in which the accessibility of a bicontinuous phase may be of great significance for the macroscopic behavior. Such potential applications may be found in the area of antistatic coatings, for example, where the bicontinuous PFS phase might serve as a electric charge carrier. However, this morphological behavior is observed only in blends of PFS-*b*-PMMA diblock copolymer and PMMA homopolymer so far. Therefore, it remains a challenge to prove the existence of a gyroidic phase in the pure diblock copolymer as well. A further point of interest is the analysis of the long-range order in the gyroidic phase using techniques such as small-angle X-ray scattering. For a more substantial understanding of the PFS/PMMA phase behavior, moreover, determination of the Flory−Huggins interaction parameters is necessary. These studies are subject of current investigations and will be published in subsequent papers.

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