Nanostructured PMMA: From Lamellar Sheets to Double-Layered Vesicles

Christian Koulic and Robert Jérôme*

Center for Education and Research on Macromolecules (CERM), B6a, University of Liège (ULg), SartTilman, B-4000 Liège, Belgium

Received October 16, 2003; Revised Manuscript Received November 24, 2003

ABSTRACT: PMMA was nanostructured by ∼100 nm liposome-like vesicular objects by melt blending with 20 wt % of a symmetric poly(styrene)-*b*-poly(isoprene)-*b*-poly(methyl methacrylate) (PS-*b*-PIP-*b*-PMMA) triblock copolymer in the dry-brush regime. Whenever the blend was prepared by casting toluene solution, thus under zero-shear conditions, a continuous network of lamellar copolymer sheets was formed in PMMA, which however underwent a transition to the aforementioned vesicles upon application of large amplitude oscillatory shear.

Introduction

The need for nanostructured soft materials is growing dramatically as an answer to the demand for novel combinations of properties by the emerging technologies. In this respect, block copolymers have proven to be very suitable and versatile active materials in nanoscience and nanotechnology.[1] They are known for self-assembling at the nanomolecular length scale (tens of nanometers) with formation of a variety of highly ordered phases, not only in the bulk but also upon dilution by a solvent or a polymer that interacts selectively with one constitutive block. The equilibrium morphologies typically exhibited by neat block copolymers result from the balance between enthalpic penalty arising from contacts between dissimilar blocks and the entropic constraint imposed by the covalent linkage of the blocks. These morphologies are thus governed by the length of the blocks, the copolymer symmetry, and the interblock repulsion strength. In blends and solutions, composition and interaction of the blocks with the polymer matrix and the solvent, respectively, further dictate the phase morphology.[1] Thomas et al.[2] and Hashimoto et al.[3] reported comprehensive studies on the nanostructuration of block copolymer/homopolymer blends (AB/A type). The effect of relevant parameters, such as volume fraction of the constitutive A and B blocks and blend composition, was carefully studied. The phase behavior of the blends was primarily governed by the length of the homopolymer chain (N_{Ah}) compared to the parent block of the copolymer (N_{Ac}). Three regimes were accordingly identified: (i) uniform solubilization ("wet-brush") when $N_{Ah} < N_{Ac}$. This case is similar to micellization in a solvent selective for one block; (ii) localized solubilization ("dry-brush") when $N_{Ah} \sim N_{Ac}$. In this case, the homopolymer chains are solubilized in the domains of the copolymer (or vice versa) without affecting the conformation of the interfacial area; and (iii) macrophase separation when $N_{Ah} > N_{Ac}$. The copolymer phase separates from the homopolymer matrix and forms microphase-separated domains. It is thus possible to exercise a full control over the phase morphology of AB/A copolymer−homopolymer blends.

* To whom correspondence should be addressed: e-mail rjerome@ulg.ac.be.

However, ABC triblock copolymers are known to form a much larger panel of morphologies as compared to AB block copolymers as result of a larger number of independent variables, such as interplay of three distinct (A/B, B/C, A/C) interaction parameters and two independent weight or volume fractions.[4] Thoroughly studied by Stadler et al., triblock copolymers composed of three distinct blocks (ABC) can self-assemble into complex structures, such as spheres on spheres[5] or helical strands surrounding cylinders,[6] both embedded in a continuous matrix of the third block. The preferential location of ABC block copolymers at the interface of A/C blends was also reported.[7] The triblock is then basically a compatibilizer, and the dispersed phases are encapsulated by the B block. A further step toward the development of novel self-assemblies was made by blending an ABC triblock with an AC diblock leading to the formation of noncentrosymmetric superlattices.[7] Except for the study of blends of copolymers by Abetz et al., no work was devoted to the self-assembly of an ABC triblock copolymer diluted in a C homopolymer. Indeed, previous works dealing with ABC/C blends focused on a composition range in which the homopolymer C was the minor phase.[9] This work aims at filling this gap, the purpose being to highlight key parameters that allow for the nanostructuration of the polymer matrix. Emphasis will be placed on the nanostructuration of poly(methyl methacrylate) (PMMA) by 20 wt % of a symmetric poly(styrene)-*b*-poly(isoprene)-*b*-poly(methyl methacrylate) triblock copolymer. Consideration will be given to stable and metastable nanomorphologies that can be formed in relation to the processing technique.

Experimental Section

Materials. All monomers, 1,1-diphenylethylene, CaH_2, and LiCl were purchased from Aldrich. The following solutions were used as received: di-*n*-butylmagnesium ($MgBu_2$, from Aldrich) was used as a 1 M solution in heptane, *n*-butyllithium (*n*-BuLi, from Aldrich) as a 1 M solution in hexane, and both fluorenyllithium (FluoLi, prepared by reacting *sec*-BuLi with fluorene) and triethylaluminum ($AlEt_3$, from Aldrich) as a 1 M solution in hexane. Styrene and α-methylstyrene were predried by distillation over CaH_2 and distilled over FluoLi prior to polymerization. Isoprene was predried by distillation over CaH_2 and distilled over $MgBu_2$ and then over *n*-BuLi prior to use. Methyl methacrylate was predried over CaH_2 and

10.1021/ma035557o CCC: $27.50
Published on Web 01/16/2004

Scheme 1. Synthetic Pathway toward the ABC Triblock Copolymer

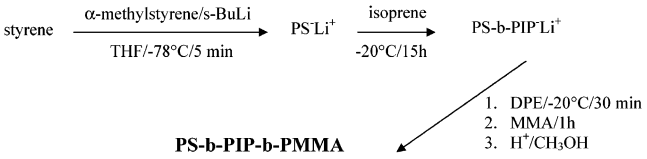


Table 1. Molecular Characteristics of the (Co)polymers Used in This Study

	M_n ($\times 10^{-3}$) (g/mol)	M_w/M_n
PMMA	16[a]	1.07[a]
PS-*b*-PIP-*b*-PMMA	17[b]−18[c]−16[c]	1.06[b]

[a] SEC analysis with universal calibration. [b] SEC analysis with PS calibration. [c] 400 MHz ^{1}H NMR analysis.

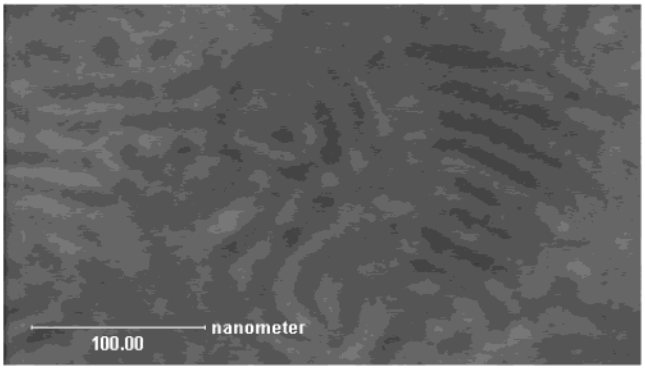


Figure 1. Transmission electron micrograph for neat ABC triblock copolymer.

distilled over $AlEt_3$ prior to polymerization. DPE was added with *sec*-BuLi until a deep red color persisted and distilled before use. Liquids were transferred through preflamed stainless steel capillaries under dry argon.

Polymer Synthesis.[10] In a typical procedure (Scheme 1), poly(styrene)-*b*-poly(isoprene)-*b*-poly(methyl methacrylate) (PS-*b*-PIP-*b*-PMMA) was synthesized by sequential living anionic polymerization of styrene, isoprene, and methyl methacrylate, respectively, in a previously flamed-dried glass reactor. Styrene was first polymerized in THF at −78 °C with an α-methylstyrene/*sec*-butyllithium initiator under argon, in the presence of LiCl (10 equiv with respect to the initiator). After a few minutes, an aliquot of the living polystryryl chains was picked out for characterization. Isoprene was then added to the reactor and let to react at −20 °C overnight. An aliquot of the polymerization medium was picked out for analytical purposes before the living diblock copolymer chains were end-capped by a slight excess (1.5 equiv) of 1,1-diphenylethylene (DPE). The end-capping reaction was conducted at −20 °C for 30 min, followed by the addition of MMA at −78 °C. The polymerization was complete after 30 min, and the triblock copolymer chains were deactivated and collected by precipitation into methanol. Precipitation from THF to methanol was repeated at least three times for removing LiCl and any unreacted compound. Any residual PS and/or PS-*b*-PIP fraction was selectively extracted with cyclohexane.

Poly(methyl methacrylate) (PMMA) was prepared by anionic polymerization as reported elsewhere.[10]

Molecular Characterization. Size exclusion chromatography (SEC) was carried out in THF (at a flow rate of 1 mL/min) at 40 °C with a HP1090 liquid chromatograph equipped with a HP 1037 refractive index and a UV detector (columns HP PL gel 5 μ: 10^5, 10^4, 10^3, 100 Å) and calibrated with polystyrene standards (Polysciences). ^{1}H NMR spectra were recorded with a Bruker AM 400 MHz spectrometer in $CDCl_3$ at 25 °C. The molecular characteristics of the (co)polymers used in this study are listed in Table 1.

Blending. PMMA and the PMMA-containing triblock were blended by two techniques. Melt-blending was carried out in a 5 cm^3 DSM microextruder at 190 °C under nitrogen at 200 rpm for 3 min. The blend was also prepared by casting a 10 wt % solution of (PMMA + 20 wt % triblock) in toluene (or THF) under zero-shear conditions. Slow evaporation for several days followed by drying overnight in a vacuum oven at 80 °C (thus under the T_g of PMMA) left a ∼1 mm thick film.

Morphology. The phase morphology was observed with a Philips CM100 transmission electron micrograph (TEM). A Reichtert-Jung ultracryomicrotome equipped with a diamond knife was used to prepare ultrathin samples at −78 °C. The PIP phase was selectively stained with OsO_4. Figure 1 illustrates the lamellar mesophases formed by the symmetric triblock copolymer listed in Table 1.

Large-Amplitude Oscillatory Shear (LAOS). The film prepared by solvent casting was loaded between the parallel plates (25 mm) of an ARES (Rheometric Scientific) rheometer. It was sheared at 190 °C for 30 min with a frequency of 0.5 rad/s and an amplitude of 99%. It was then cooled at constant strain.

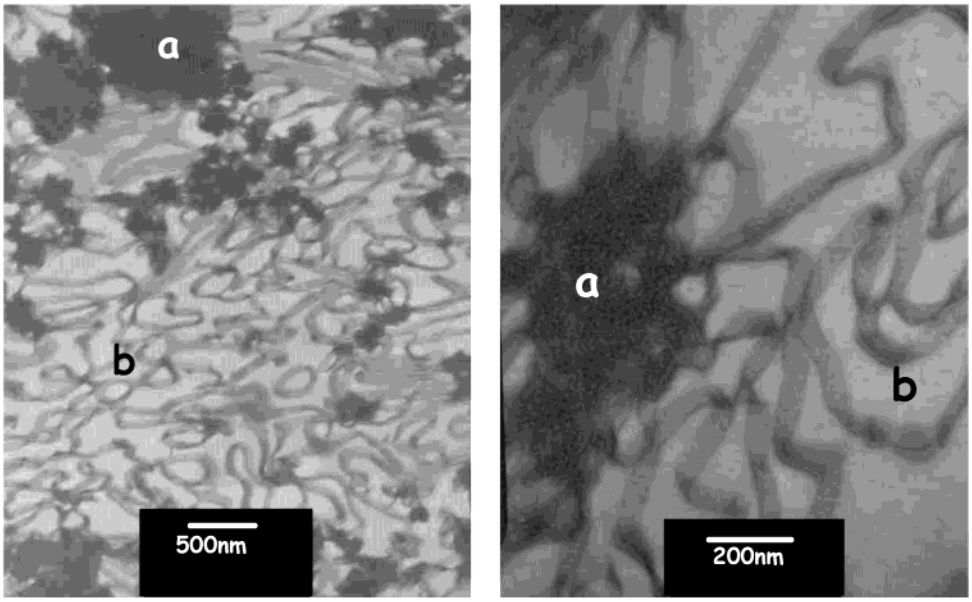
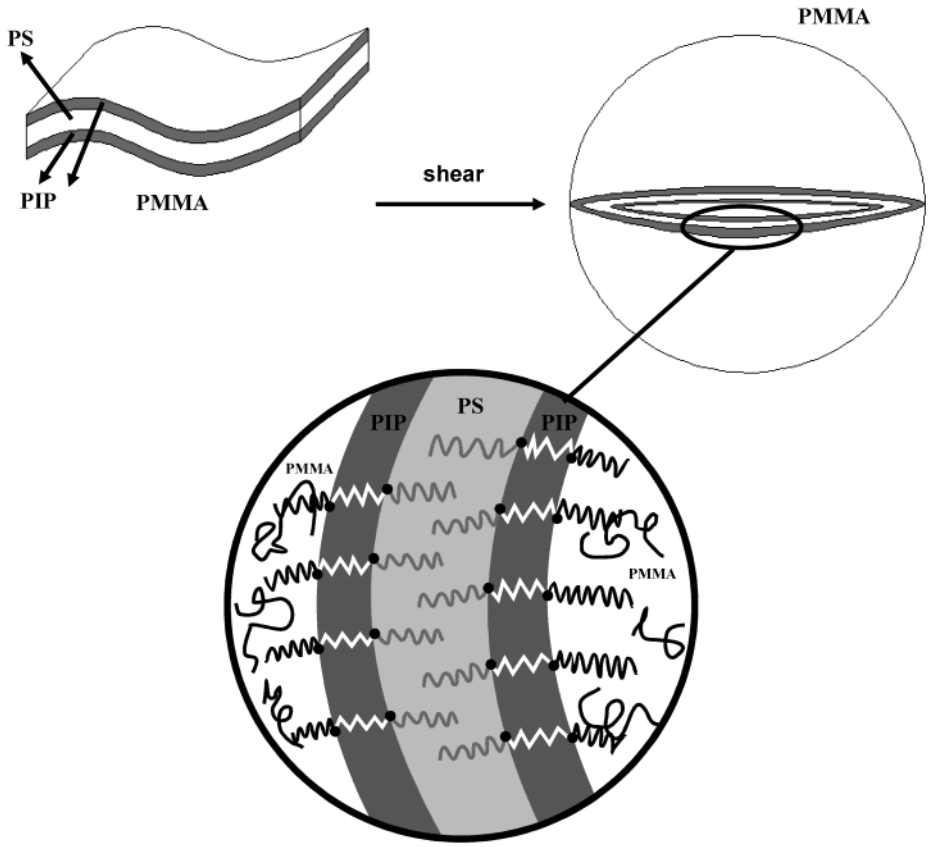


Figure 2. Transmission electron micrographs (at low and high magnifications) for the PMMA/PS-*b*-PIP-*b*-PMMA (80/20 wt/wt) solvent-cast blend.

Scheme 2. Effect of Shear Applied to the Lamellar System and Tentative Sketch of the Organization of the Copolymer Chains within the Vesicular Envelope



Results and Discussion

The first key parameter for the successful nanostructuration of PMMA by self-assembly of the PS-*b*-PIP-*b*-PMMA triblock copolymer is the careful choice for the molecular weight of the PMMA homopolymer relative to that of the PMMA block. Actually, the condition for the dry-brush regime has to be fulfilled; otherwise, either a macrophase separation will occur (matrix of a higher M_n than the parent block), or the interfacial brush will be swollen by the matrix (reverse situation) so increasing the apparent volume fraction of the PMMA block and possibly triggering a transition in the morphology of the triblock.[2,3] In this work, the triblock has been designed for promoting a lamellar phase morphology (Figure 1), which has been used for nanostructuring PMMA. Therefore, homo-PMMA and the PMMA block of the triblock have been synthesized with the same molecular weight, as reported in Table 1.

Solvent-Casting. Nanostructuration of PMMA has been first carried out by solvent-casting a PMMA/PS-*b*-PIP-*b*-PMMA (80/20 wt/wt) mixture to approach the morphology at the thermodynamic equilibrium as closely as possible. A toluene solution containing 10 wt % of the (co)polymer mixture has thus been let to evaporate over several days. Figure 2 illustrates the continuous network of triblock lamellae which is formed throughout the PMMA matrix. This morphology is reproducible even when another common solvent for the three constitutive blocks (e.g., THF) is substituted for toluene. Two morphological characteristic features have to be emphasized. Microdomains of block copolymer (a in Figure 2) act as physical "cross-links" for long lamellar micelles of a uniform thickness (lamellae, b, in Figure 2). These individual lamellae are randomly bent and

Figure 3. Magnification of the edge-on view of a lamellar sheet.

organized in the PMMA matrix. The higher magnification of the TEM micrograph (Figure 2) illustrates better the twisting and folding of the lamellar sheets formed by the triblock. Magnification of the edge-on view of the folding of one lamellar sheet clearly shows that the lamellae consist of a double layer of triblock copolymer chains (Figure 3). Indeed, the selective staining of the PIP block by OsO_4 allows one to distinguish two PIP layers that sandwich PS, whereas the PMMA chains are mixed with the PMMA matrix as sketched in Scheme 2. In a previous work, Hashimoto et al.[3a] blended a PS-*b*-PIP diblock with PS in the dry-brush regime ($N_{Ah} \sim N_{Ac}$), and they observed a morphological transition from lamellae to spherical vesicles upon increasing the

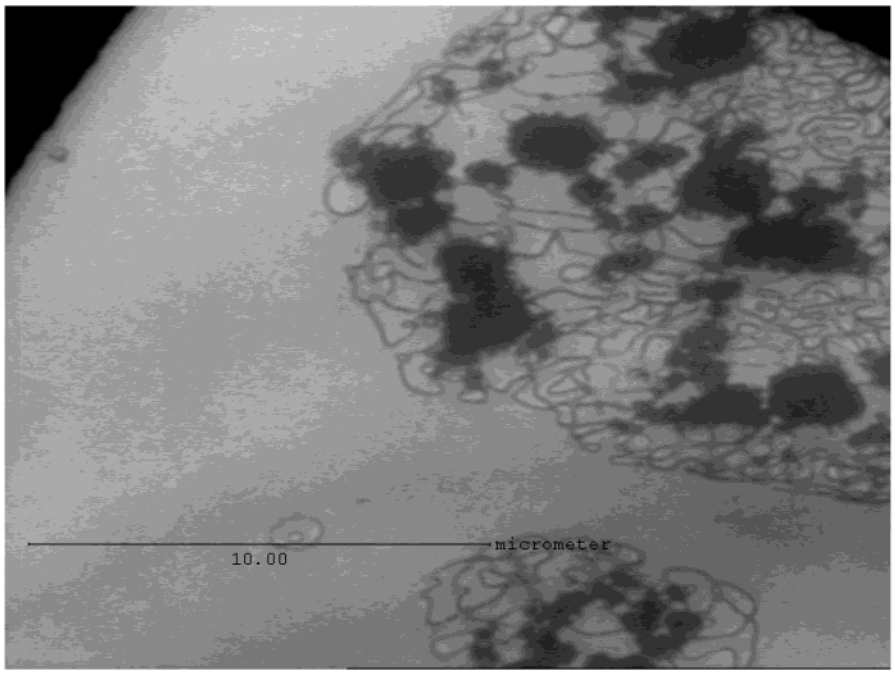


Figure 4. Transmission electron micrograph of the PMMA/PS-*b*-PIP-*b*-PMMA (95/5 wt/wt) solvent-cast blend at a lower copolymer content (5 wt %).

volume fraction of the matrix. In this study, when the volume fraction of the copolymer is decreased, the lamellar sheets formed by the triblock copolymer persist; the only effect is that they do not form an infinite network anymore, but rather finite areas of interconnected sheets are observed (Figure 4). The origin for this discrepancy is still unclear and deserves further investigations.

The stability of the morphology shown in Figure 2 and formed by solvent casting at 25 °C followed by drying at 80 °C has been assessed by annealing at high temperature (190 °C for 30 min), i.e., above the glass transition temperature of the PMMA matrix ($T_g = 132$ °C). No substantial change in the morphology is observed, except for a longer range lamellar organization within the macrophase-separated domains (Figure 5).

Effect of Shear on the Solvent-Cast Blend. As a rule, the self-assembly of block copolymers is sensitive to mechanical energy input. For example, large-amplitude oscillatory shear (LAOS) was extensively used in order to extend the periodic self-assembly, mainly lamellar, to a macroscopic scale.[11,12] The longer-range alignment of lamellae was found to depend on shear frequency, amplitude, and temperature. Similar work has however not been reported for block copolymer/homopolymer blends. Therefore, LAOS has been applied to the solvent-cast film of a 20 wt % triblock-containing blend prepared in this work. Two effects might be anticipated, either the alignment of the lamellar sheets or a morphological transition rather than a longer-range order. Figure 6 clearly shows that LAOS (190 °C, 30 min) does not result in shear-induced long-range alignment but rather triggers a transition to a vesicular morphology. This transition, which is also observed when a constant shear is applied, is reminiscent of a transition exhibited by lyotropic lamellar phases in highly concentrated surfactant solutions to onion-like structures.[10] This transition is also consistent with the formation of vesicular nanoobjects by 20 wt % of a symmetric ABC triblock prepared in a polyamide matrix by reactive blending.[11] The nanoobjects shown in Figure

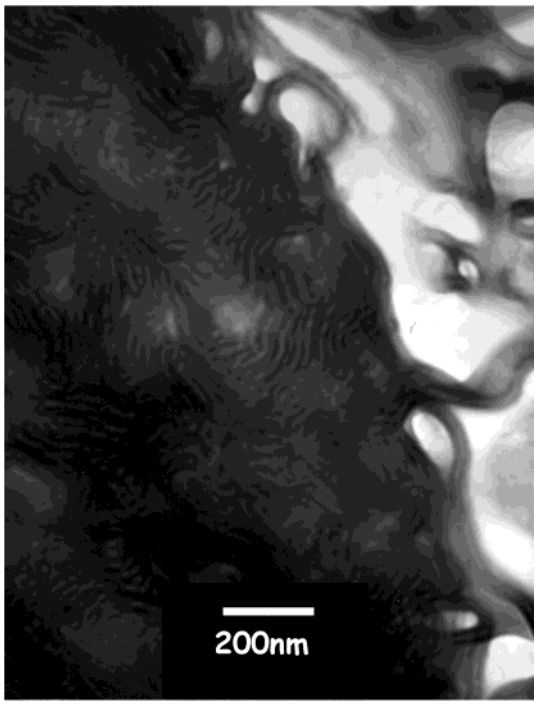


Figure 5. Transmission electron micrograph of the PMMA/PS-*b*-PIP-*b*-PMMA (80/20 wt/wt) solvent-cast blend after annealing at 190 °C, under N_2, for 30 min.

6 are vesicles consisting of a trilayer envelope. The two external black layers are PIP as confirmed by the selective OsO_4 staining. PS has no choice but to form the inner layer, the core of the vesicles being PMMA. Formation of these vesicles is the consequence of the same volume fraction for the constitutive blocks of the copolymer blended with PMMA. Indeed, although they collapse upon mechanical shearing, the free-standing lamellae preserve their thermodynamically favored structure by forming vesicular objects with a low curvature, thus a low envelope thickness/diameter ratio (Figure 6). Therefore, the double-layered vesicles are

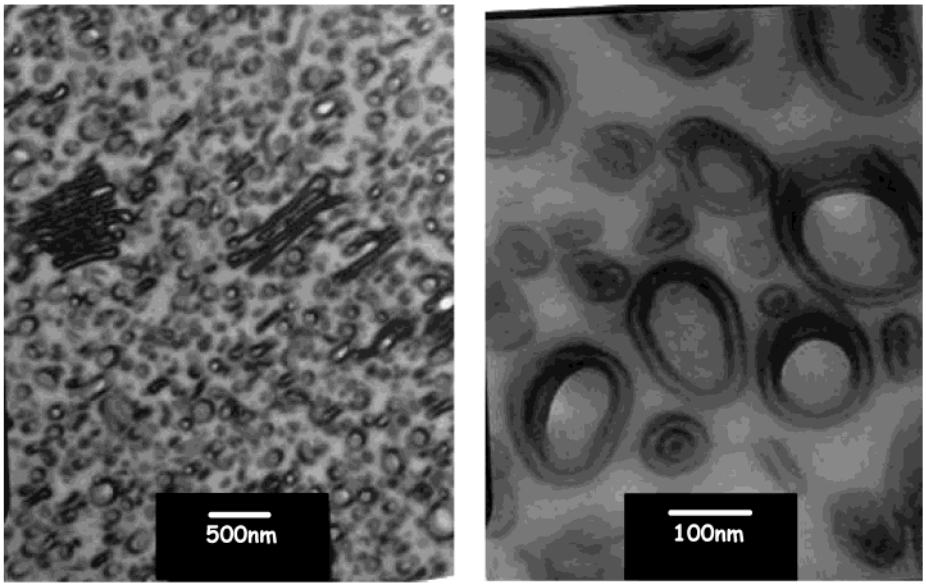


Figure 6. Transmission electron micrographs at two different magnifications for the PMMA/PS-*b*-PIP-*b*-PMMA (80/20 wt/wt) solvent-cast blend modified by LAOS.

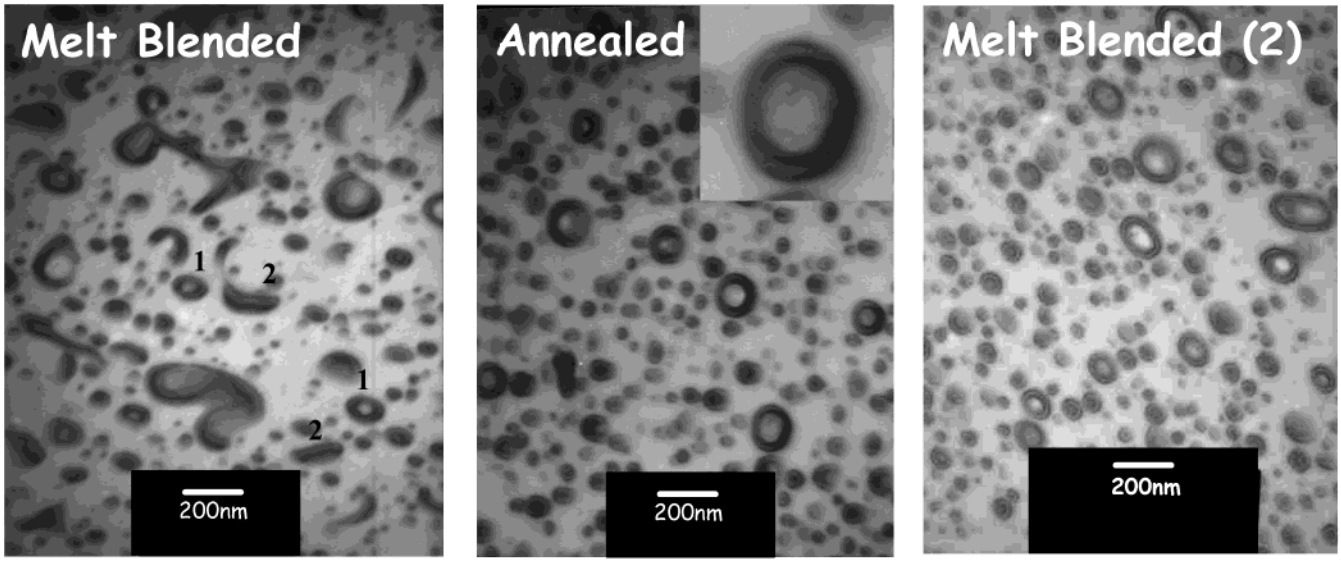


Figure 7. Transmission electron micrographs for the PMMA/PS-*b*-PIP-*b*-PMMA (80/20 wt/wt) blend (a) melt-blended in the microextruder (190 °C; 3 min) with formation of double-layered vesicles (1) and lamellar sheets (2); (b) after annealing at 190 °C under N_2 for 30 min; (c) after a second blending step in the microextruder at 190 °C for 3 min.

metastable nanoobjects formed as result of mechanical input to the interconnected double-layered sheets formed by slow evaporation and supposedly close to thermodynamic equilibrium. These liposome-like objects mimic to some extent the organization of bilayer membranes.

Melt-Blending. To give credit to the aforementioned conclusions, the PMMA/PS-*b*-PIP-*b*-PMMA binary blend has been directly prepared in the melt under shear, i.e., in a microextruder at 190 °C for 3 min. Figure 7a shows the TEM observation for the blend containing 20 wt % of the triblock. Nanoobjects are again formed with a diameter lower than 100 nm and dispersed in the PMMA matrix with no long-range order. The most striking observation is the nanostructuration of these objects, i.e., a liposome-like structure quite similar to that one observed after shearing the solvent-cast blend. In addition to vesicles, small lamellar sheets are observed throughout the sample (domains 2, in Figure 7a). They might however be unstable as result of edges with an energetically unfavorable curvature. This assumption is confirmed by annealing for only 30 min at 190 °C under N_2 (Figure 7b). The lamellar sheets disappear indeed in favor of the double-layered vesicles, which are quite stable upon annealing. The stability is observed not only against temperature but also against a mechanical energy input as assessed by the vesicular morphology of the annealed sample that persists after an additional step of melt blending in the microextruder at 190 °C for 3 min (Figure 7c). It can be safely concluded that the symmetric PS-*b*-PIP-*b*-PMMA triblock copolymer forms quite stable double-layered vesicles when diluted in the melt within a PMMA matrix under shear.

Conclusions

A novel method for the structuration of a polymer matrix on the nanometer scale has been reported. It relies upon blending of a lamellae-forming ABC triblock copolymer, PS-*b*-PIP-*b*-PMMA, within a PMMA matrix, in the dry-brush regime. The homo-PMMA chains are

thus unable to swell the PMMA brush of the copolymer, which tends spontaneously to form objects with a low curvature, when diluted within 80 wt % PMMA. Double-layered vesicles are formed when the triblock dilution is conducted under shear in the melt, i.e., by melt blending in a microextruder at 190 °C, whereas a continuous network of triblock lamellar sheets is formed by solvent-casting the binary blend, thus under zero-shear conditions. A transition from these interconnected copolymer lamellar sheets to a vesicular morphology is observed upon application of large-amplitude oscillatory shear (LAOS) at 190 °C. This practical route to well-defined nanostructures within a polymer matrix paves the way to new materials with well-defined properties and applications. This concept is versatile, being extendable to a variety of polymer matrices and nanostructures actually imposed by the self-assembly of the block copolymer used.

Acknowledgment. The authors are grateful to the "Services Fédéraux des Affaires Scientifiques Techniques et Culturelles" for general support in the frame of the "PAI V/03: Supramolecular Chemistry and Supramolecular Catalysis". They are grateful to Sunyl K. Varshney (Polymer Source Inc., Canada) for training and advice in anionic polymerization, to Mrs. Martine Dejeneffe for ultramicrotomy at low temperature, and to Dr. C. Pagnoulle and Dr. Z. Yin for encouragement and fruitful discussions. C.K. is a Research Fellow by the "Fonds National de la Recherche Scientifique" (FNRS, Belgium).

References and Notes

(1) Hamley, I. W. *The Physics of Block Copolymers*; Oxford University Press: Oxford, 1998.
(2) (a) Kinning, D. J.; Winey, K.; Thomas, E. L. *Macromolecules* **1988**, *21*, 3502. (b) Kinning, D. J.; Thomas, E. L.; Fetters, L. J. *J. Chem. Phys.* **1989**, *90*, 5806. (c) Kinning, D. J.; Winey, K.; Thomas, E. L. *Macromolecules* **1991**, *24*, 3893.
(3) (a) Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromol. Chem., Macromol. Symp.* **1992**, *62*, 75. (b) Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1994**, *27*, 6532. (c) Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1994**, *27*, 7893. (d) Koizumi, S.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1994**, *27*, 4371.
(4) For a review see: Abetz, V. Assemblies in Complex Block Copolymer Systems. In *Supramolecular Polymers*; Cifferi, A., Ed.; Marcel Dekker: New York, 2000; Chapter 6, p 215 and references therein.
(5) Breiner, U.; Krappe, U.; Jacob, T.; Abetz, V.; Stadler, R. *Polym. Bull. (Berlin)* **1998**, *40*, 219.
(6) (a) Breiner, U.; Krappe, U.; Abetz, V.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 1051. (b) Krappe, U.; Stadler, R.; Voigt-Martin, I. *Macromolecules* **1995**, *28*, 4558.
(7) Riess, G.; Schlienger, M.; Marti, S. *J. Macromol. Sci., Phys.* **1980**, *B17*, 355.
(8) Goldacker, T.; Abetz, V.; Stadler, R.; Erukhimovich, I.; Leibler, L. *Nature (London)* **1999**, *398*, 137.
(9) Lesannec, R.; Fetters, L.; Thomas, E. *Macromolecules* **1998**, *31*, 1680.
(10) (a) Wang, J. S.; Jérôme, R.; Teyssié, Ph. *J. Phys. Org. Chem.* **1995**, *8*, 208. (b) Jérôme, R.; Tong, J. *Curr. Opin. Solid State Mater. Sci.* **1998**, *3*, 573. (c) Zune, C.; Jérôme, R. *Prog. Polym. Sci.* **1999**, *24*, 631.
(11) (a) Koppi, K.; Tirrell, M.; Bates, F. *Phys. Rev. Lett.* **1993**, *70*, 1449. (b) Okamoto, S.; Saijo, K.; Hashimoto, T. *Macromolecules* **1994**, *27*, 5547. (c) Pinheiro, B.; Winey, K. *Polym. Prepr.* **1995**, *36*, 174. (d) Gupta, V.; Krishnamoorti, R.; Kornfield, J.; Smith, S. *Macromolecules* **1995**, *28*, 4464. (e) Chen, Z.-R.; Kornfield, J.; Smith, S.; Grothaus, J.; Stakowski, M. *Science* **1997**, *277*, 1248. (f) Chen, Z.-R.; Issaian, A.; Kornfield, J.; Smith, S.; Grothaus, J.; Stakowski, M. *Macromolecules* **1997**, *30*, 7096. (g) Zipfel, J.; Lindner, P.; Tsianou, M.; Alexandridis, P.; Richtering, W. *Langmuir* **1999**, *15*, 2599. (h) Stangler, S.; Abetz, V. *e-Polym.* **2002**, No. 18.
(12) (a) Diat, O.; Roux, D.; Nallet, F. *J. Phys. II* **1993**, *3*, 1427. (b) Sierro, P.; Roux, D. *Phys. Rev. Lett.* **1997**, *78*, 1496. (c) Pianizza, P.; Collin, A.; Coulon, C.; Roux, D. *Eur. Phys. J. B* **1998**, *4*, 65.
(13) Koulic, C.; Yin, Z.; Pagnoulle, C.; Jérôme R. *Angew. Chem., Int. Ed.* **2002**, *41*, 2154.

MA035557O