Macromolecules **1997,** *30,* 1765−1767

Morphology of Polystyrene-*block*-poly(methylphenylsilylene)

E. Fossum and K. Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213

S. S. Sheiko and M. Möller*

Department of Organic Chemistry III, University of Ulm, D-89069 Ulm, Germany

Received December 19, 1995; Revised Manuscript Received August 13, 1996⊗

ABSTRACT: A diblock copolymer consisting of a polystyrene segment with $M_n = 18700$ and a poly(methylphenylsilylene) segment with $M_n = 9000$ was found to microphase separate when a film was cast from THF. The microphase segregation was studied using both transmission electron microscopy and scanning force microscopy. The bulk morphology consisted of cylinders of poly(methylphenylsilylene) in a polystyrene matrix. The deposition of block copolymer micelles assembled in 1,4-dioxane solution was observed by scanning force microscopy when a dilute solution in this selective solvent was cast on mica and quickly evaporated. Besides the micelles, a thin polymer film was formed by adsorption of molecularly dissolved chains.

Introduction

The polysilylene structure is characterized by σ electron delocalization, which gives rise to intense UV absorption in the range 300−400 nm and a number of peculiar electronic properties.[1,2] As a drawback, however, polysilylenes do not possess good mechanical properties. In general, mechanical properties can be improved by formation of a microphase-separated morphology, i.e. by blending and in block copolymers.[3,4] Block copolymers may lead to regular morphologies or can be employed to improve the dispersion of blends. Ultrafine dispersions of polysilylenes may not only be of interest to improve the mechanical properties, but also because of the potential modulation of the electronic properties.[5]

So far only very few reports have described block copolymers in which one of the blocks is a polysilylene.[4,6,7] Synthesis by Wurtz coupling of dichlorosilanes is limited to condensation reactions of halide end-terminated polysilylenes with anionic living polymers. Polymerization of masked disilenes and cyclotetrasilanes provides an alternative synthetic pathway to block copolymers.[6,8] This paper will describe first morphological studies of polystyrene-*block*-poly(methylphenylsilylene) by the addition of cyclotetrasilane monomers to solutions of polystyryllithium.[8]

Polystyrene-*block*-polysilylene samples were prepared using living polystyrene to initiate the ring-opening polymerization (ROP) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenylcyclotetrasilane (Scheme 1). In order to enhance the reactivity of polystyryllithium to initiate ROP of the cyclotetrasilane, 12-crown-4 was added.

Table 1 lists the molecular weight data for a series of block copolymers prepared by this route. As can be seen in Table 1, molecular weights for the polysilylene blocks which were determined by integration of the ^{1}H NMR spectra of the purified block copolymers indicated that the values of the total molecular weight determined by SEC were higher than the actual values. This may result from association of the block copolymers in the solvent, THF, which was used for SEC.

For the studies on the phase morphology, we chose sample 5 from Table 1. Because of their shorter block length, the other samples appeared not to be suitable for morphology studies. Sample 5 was expected to develop a phase texture in the bulk with polysilylene cylinders embedded in a polystyrene matrix[11] and form micelles with a polysilylene core in dilute solution of a solvent which is selective for polystyrene.[12] We have recently shown that such block copolymer micelles can be cast or deposited on a solid substrate and imaged by scanning force microscopy.[13,14]

Scheme 1. Synthesis of Polystyrene-*block*-poly(methylphenylsilylene)

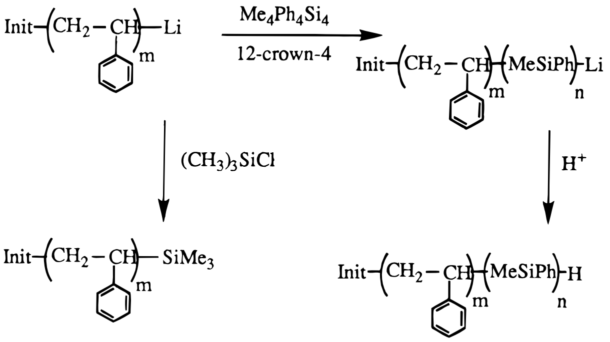

Figure 1 shows a TEM picture of a thin section of a film which was prepared by slow evaporation from THF, which is slightly selective for the polystyrene block. The film was not stained and the dark areas can be assigned to the polysilylene domains according to the stronger electron scattering at silicon compared to carbon. The domains are poorly defined; however, images of the same area yielded essentially the same domain pattern irrespective of the focus conditions, demonstrating that the structure is real. The wormlike dark domains are consistent with a cylindrical morphology of the polysilylene block in a matrix of polystyrene. The worms had approximately the same size throughout the entire sample with a diameter of 7 ± 2 nm. This is roughly half of the extended chain length of 14.8 nm of PMPS with $M_n = 9000$. The latter was calculated by taking 0.4 nm as a repeat unit of the Si backbone in the all-trans planar conformation.[15] The numbers suggest a rather extended conformation of the PDPS block in the core of the cylinders.

Figure 2 gives the surface image of the same specimen recorded by SFM. The method did not allow us to detect the phase texture and to distinguish between the two

---

* To whom correspondence should be sent.

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1997.

S0024-9297(95)01880-8 CCC: $14.00

Table 1. Molecular Weight Data for Polystyrene and Polystyrene-*block*-PMPS Copolymers

	first block					second block				total	
sample	$[St]_0$ (mol/L)	$[I]_0$ (mol/L)	$M_n(th)^a$	$M_n(exp)^b$	$M_w/M_n{}^b$	$[Si_4]_0$ (mol/L)	$[I]_0{}^c$ (mol/L)	$M_n(th)^a$	$M_n(exp)^d$	$M_n{}^b$	$M_w/M_n{}^b$
1	0.91	0.04	2400	2400	1.06	0.23	0.015	7400	8700	13900	1.34
2	1.80	0.04	4800	4700	1.05	0.23	0.015	7400	9700	16300	1.31
3	2.10	0.04	5600	5500	1.05	0.30	0.015	9700		26400	1.24
4	3.60	0.04	9600	9200	1.08	0.23	0.015	7400	10800	26500	1.40
5	7.20	0.04	19300	18900	1.08	0.23	0.015	7400	9000	38900	1.22

[a] Refers to theoretical $[M]_0/[I]_0$. [b] SEC analysis at 254 nm based on linear polystyrene standards. [c] Adjusted initiator concentration after dilution with cyclotetrasilane solution. [d] From ^{1}H NMR intensities of polystyrene and polysilane signals, respectively.

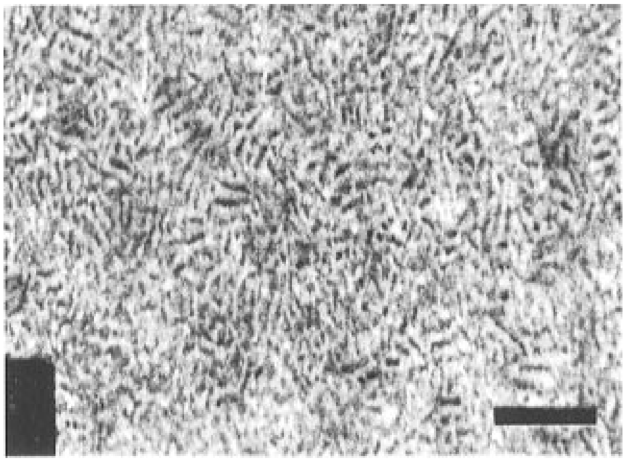

Figure 1. TEM micrographs of a polystyrene-*block*-PMPS with $M_n = 18700$ and 9000 and overall polydispersity $M_w/M_n = 1.22$. Scale bar = 150 nm.

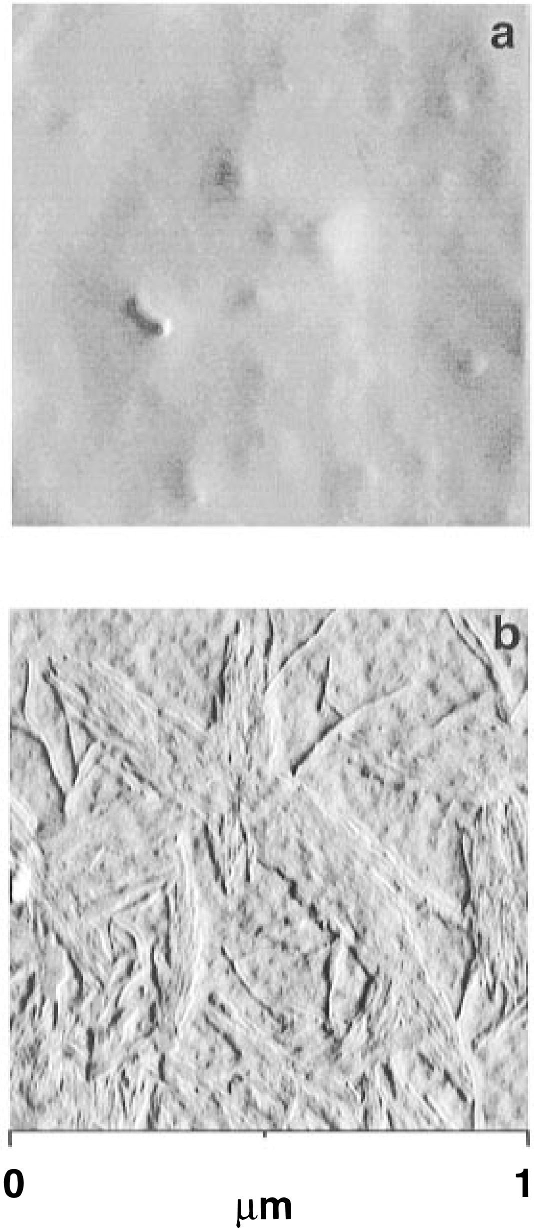

Figure 2. SFM micrographs of a thick film of polystyrene-*block*-PMPS with $M_n = 18700$ and 9000 and overall polydispersity $M_w/M_n = 1.22$ (a) before and (b) after degradation with 360 nm light.

different blocks. However, after the sample was exposed to 360 nm light under an argon atmosphere, a texture was developed consistent with the TEM results (Figure 2b). Apparently, the polysilylene segments were degraded, yielding the bundles of "hills and valleys" on the surface. The width of a typical bundle (five hills and four valleys) is approximately 45 nm, which corresponds to the domain sizes observed in TEM.

Figure 3 shows SFM micrographs obtained from ultrathin films which were cast from dilute solution in 1,4-dioxane. 1,4-Dioxane is a selective solvent for polystyrene, favoring formation of a poly(methylphenylsilylene) core. Figure 3a depicts small particles of a uniform size measuring 7 nm in height and 50 nm in diameter. Apparently, the block copolymers had formed micelles which could not rearrange to the equilibrium structure of the bulk as the solvent was evaporated.

Besides the micelles, the image shows also formation of a flat polymer film. This is explained by the adsorption of polymer chains at the surface of the substrate which did not associate to micelles.[13,14,16] Films which were cast from very dilute solutions possessed areas displaying the bare substrate. The uncovered mica allowed us to determine the film thickness to be about 0.6 nm by drawing the cross-sectional profile shown in Figure 3c.

Upon increasing the polymer concentration, the micelles covered the substrate completely and formed a rather smooth homogeneous film. Figure 3b demonstrates a typical structure of the film assembled of spherical particles, i.e. micelles, showing a rather narrow size distribution. The diameter was estimated directly from the image in Figure 3b to be between 25 and 30 nm. For thin films, the size of the micelles was also measured as the height difference between the surface of the film and the mica substrate. The height difference was determined to vary between 8 and 18 nm. The discrepancy between the height and diameter observed by SFM only partly results from the convolution of the probe geometry and the contour of the particles and can be regarded as an indication for a strongly prolate shape of the micelles.[13,14] The latter might be due to deformation of the micelles caused by adsorption to the substrate but also be induced by the tapping tip

TEM and SFM studies demonstrated for the first time the formation of a phase segregated morphology for a polystyrene-*block*-poly(methylphenylsilylene). The rela-

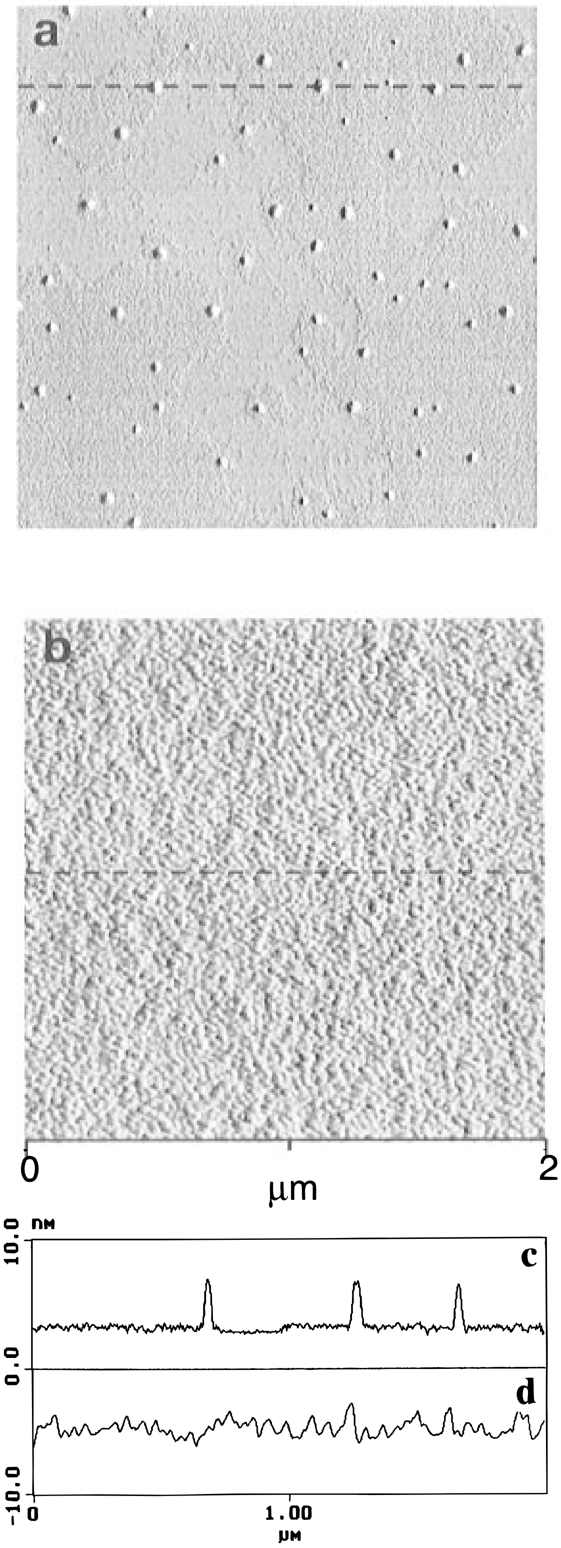

Figure 3. SFM micrographs for an 18700/9000 polystyrene-*block*-PMPS copolymer cast on a mica surface from 1,4-dioxane. The surface coverage was varied by changing the concentration of the solution from which the polymer was cast: 0.01 (a) and 0.1 wt % (b). The cross-sectional profiles (c,d) show variation of height along the dashed lines indicated in (a) and (b), respectively.

tively large domain sizes of both the cylinders and the globular micelles can be explained by stretching the polymer blocks in the core and in the shell.[17,18] While the observed structures correspond to what has to be expected for block copolymers of the corresponding length, the material itself is rather peculiar because of the photoconducting and photodegradable properties of the polysilylene block. Depending on the casting conditions, it has been possible to create this film with wormlike or globular polysilylene domains. Further improvement of the phase texture can be expected to be possible with higher molecular weight samples and is the subject of ongoing studies. As demonstrated by the photodegradation experiments, the self-assembled structures can be used to create striped and possibly also patched surface patterns in the range below 100 nm.

Experimental Section

Polystyrene/Polysilylene Block Copolymers. Styrene was polymerized in benzene using *sec*-BuLi as the initiator. After complete consumption of the monomer, a solution of cyclotetrasilane, benzene, and 12-crown-4 was added and initiation of the second monomer was evidenced by occurrence of the dark gold color of silyllithium.

Transmission Electron Microscopy. TEM micrographs were recorded using a Philips 301 electron microscope operating at 80 kV in the bright field mode. Thin films were formed by evaporating a dilute THF solution over several days (72 h). Ultrathin sections were prepared by means of a Reichert Jung ultramicrotome with a diamond blade. No staining was necessary to observe a sufficient contrast.

Scanning Force Microscopy. Images were recorded with a Nanoscope III scanning force microscope (Digital Instruments, Santa Barbara, CA) using the tapping mode at a frequency of 340 kHz. Si tips were selected with a radius of the probe apex of less than 10 nm using a specially developed calibration standard.[9] Samples were prepared by casting thin films from 0.01 and 0.1 wt % solutions in 1,4-dioxane on a flat piece of mica. Also, the same specimens were imaged as used for TEM. Deformation of soft polymers by the tapping tip was estimated to be less than 2 nm.[10]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft (Ulm, F3, SFB 239) and the National Science Foundation (CMU).

References and Notes

(1) West, R. *J. Organomet. Chem.* **1986**, *300*, 327.
(2) Michl, J.; Miller, R. D. *Chem. Rev.* **1989**, *89*, 1359.
(3) Asuke, T.; Chien-Hua, Y.; West, R. *Macromolecules* **1994**, *27*, 3023.
(4) Demoustier-Champagne, S.; de Mahieu, A.-F.; Devaux, J.; Fayt, R.; Teyssie, P. J. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 2009.
(5) Godovsky, D. Y. *Adv. Polym. Sci.* **1995**, *119*, 79.
(6) Sakamoto, K.; Obata, K.; Hirata, H.; Nakajima, M.; Sakurai, H. *J. Am. Chem. Soc.* **1989**, *111*, 7641.
(7) West, R.; Wolff, A.; Peterson, D. J. *J. Radiat. Curing* **1986**, 35.
(8) Fossum, E.; Love, J. A.; Matyjaszewski, K. *J. Organomet. Chem.* **1995**, *499*, 253.
(9) Sheiko, S. S.; Möller, M.; Reuvekamp, E. M. C. M.; Zandbergen, H. W. *Phys. Rev. B* **1993**, *48*, 5675.
(10) Spatz, J. P.; Sheiko, S. S.; Möller, M.; Winkler, R.; Marti, O. *Nanotechnology* **1995**, *6*, 40.
(11) Semenov, A. N. *Macromolecules* **1992**, *25*, 4967.
(12) Nguyen, D.; Williams, C. E.; Eisenberg, A. *Macromolecules* **1994**, *27*, 5086.
(13) Spatz, J. P.; Sheiko, S.; Möller, M. *Macromolecules* **1996**, *29*, 3220.
(14) Krupers, M. J.; Sheiko, S.; Möller, M. *Macromolecules*, submitted.
(15) Lovinger, A. J.; Schilling, F. C.; Bovey, F. A.; Zeigler, J. M. *Macromolecules* **1986**, *19*, 2660.
(16) Spatz, J. P.; Sheiko, S.; Möller, M. *Adv. Mater.* **1996**, *8*, 513.
(17) Cogan, K. A.; Gast, A. P.; Capel, M. *Macromolecules* **1991**, *24*, 6512.
(18) Halperin, A. *Macromolecules* **1987**, *20*, 2943.

MA951880I