

Microstructure of crystalline–amorphous type block copolymer prepared from ultra-dilute solution

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The microstructures of crystalline–amorphous type block copolymers, poly(tetrahydrofuran-*b*-isoprene), prepared from ultra-dilute solution (0.001 wt%) were studied by transmission electron microscopy. The obtained shape was different from the shape observed in the case of amorphous–amorphous type block copolymers; the shape was deformed by poly(tetrahydrofuran) crystallization.

(Keywords: block copolymer; microstructure; TEM)

Introduction

It is well known that diblock copolymers with two amorphous sequences generally form micelles in solutions above the critical micelle concentration. As the solvent is evaporated, the micelles are deformed and finally various types of microdomains are retained in the film. These have been classified into five types of morphologies¹. The domain formation has been treated theoretically by thermodynamics^{2,3}. However, crystalline–amorphous type block copolymers show more complicated morphologies^{4–7} than amorphous–

amorphous types because the crystallization and micelle formation occur simultaneously.

Recently, poly[tetrahydrofuran (THF)-*b*-styrene (ST)]⁸ and poly(2-methyl-2-oxazoline-*b*-ST)⁹, were synthesized. In these copolymers crystallization occurred after micelle formation during evaporation of the solvent. The resulting domain surface was disturbed by the crystallization. Cohen and co-workers^{10–12} studied crystalline–amorphous type block copolymers. The experimental microstructures were in good agreement with theoretical prediction. However, the structures were changed by the

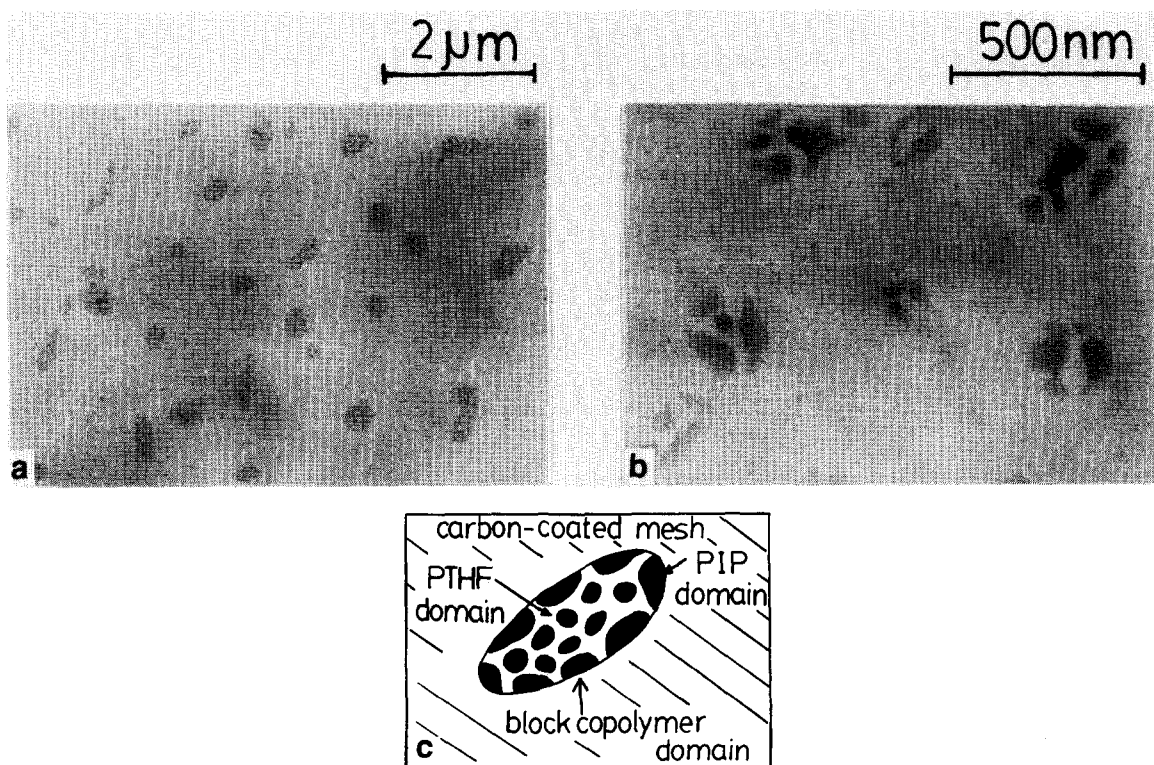


Figure 1 TEM photographs of the specimen prepared from TI-1 solution: (a) low magnification; (b) high magnification; (c) illustration of the block copolymer domain

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conditions of film preparation — casting solvent and annealing.

In the preceding papers^{13–15}, the microstructure of poly[THF-*b*-isoprene (IP)] was studied and a microstructure model was proposed. The bulk structure is a microphase-separated structure with poly(tetrahydrofuran) (PTHF) crystallites. In this case, the crystallization affects only the domain surface causing its deformation. It is expected in the case of an ultra-thin film or micelle prepared from dilute solution that the microstructure is different from that of the bulk. In this case (i.e. prepared from ultra-dilute solution), the structure will be not only microphase-separated but also micellar. The shape of the PTHF crystallite will be reflected in the micelle shape because the polyisoprene (PIP) domain is in the liquid

state (glass transition temperature, $T_g = -73^\circ\text{C}$)¹⁶. In the case of poly(THF-*b*-IP) with a small volume fraction of PIP, the effect will be remarkable.

In this work, the microstructure of poly(THF-*b*-IP) (with a small volume fraction of PIP) prepared from ultra-dilute solution was studied by transmission electron microscopy (TEM).

Experimental

Poly(THF-*b*-IP)s were synthesized by a coupling reaction between living PTHF cation and living PIP anion¹⁷. The characteristics of poly(THF-*b*-IP)s are shown in Table 1.

The ultra-thin block copolymer films were prepared from benzene (good for both sequences) solution (concentration 0.001 wt%). The solution was cast onto a carbon-coated copper mesh. Benzene was evaporated at room temperature and atmospheric pressure. The specimen was kept for 5 days. PIP domains were stained by osmium tetroxide. TEM observations were carried out using a Hitachi model H-500 with an accelerating voltage of 100 kV.

Results and discussion

Figure 1 shows the TEM photographs of the specimen prepared from TI-1 solution. The dark areas are stained

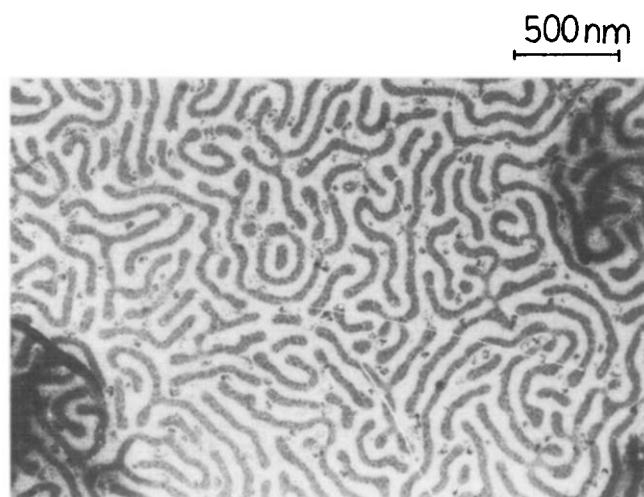


Figure 2 TEM photograph of TI-1 film prepared from 0.05 wt% benzene solution (dark areas are PIP domains)

Table 1 Characteristics of poly(THF-*b*-IP)s

Sample no.	$M_w \times 10^{-4}$ ^a		Composition (wt%)	
	PTHF	PIP	PTHF	PIP
TI-1	11.8	11.0	52	48
TI-3	11.8	4.2	74	26

^a Determined by gel permeation chromatography

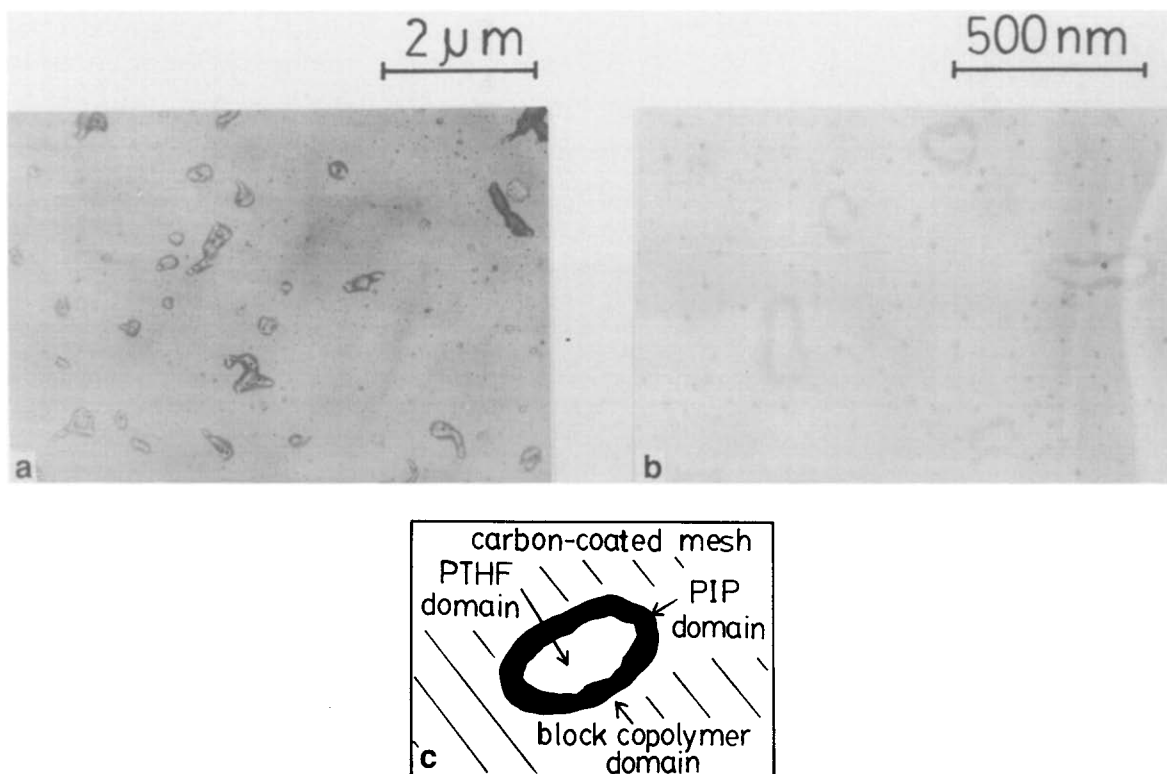


Figure 3 TEM photographs of the specimen prepared from TI-3 solution: (a) low magnification; (b) high magnification; (c) illustration of the block copolymer domain

PIP domains. In this casting condition (0.001 wt%), since the volume of block copolymer was small, the ultra-thin film did not cover the whole area of the mesh. Many small objects with a unique structure, similar to paramecia, were observed. This structure is microphase separation. However, the morphology of microphase separation would be expected to be lamellar or onion-skin type considering the PTHF composition (52 wt%). But in *Figure 1*, the PTHF domain is surrounded by the PIP domain with PIP spheres inside. Interestingly, the PTHF domain crosses the outer PIP domain and forms part of the outline of the object (see *Figure 1c*). The PTHF domain is a continuous phase. This unique structure is not observed in amorphous–amorphous type block copolymer. It is suggested that this structure is caused by PTHF crystallization. During evaporation of the solvent, core–corona type micelles (core = PTHF, corona = PIP) were formed. The crystallization occurred after micelle formation and the PIP domain was deformed because of the low T_g of PIP. In the preceding paper¹⁴, the block copolymer film prepared from 0.05 wt% solution had a lamellar structure (see *Figure 2*) and was different from the structure observed in *Figure 1*. In this experiment the degree of freedom of the PIP domain was large because the domain formed with the block copolymer was small. Then deformation by PTHF crystallization was apt to occur and the unique structure was formed.

Figure 3 shows TEM photographs of the specimen prepared from TI-3 solution. In *Figure 3a*, the onion-skin structure is observed, with the outer domain being PIP. This onion-skin structure has some inner PIP domains. The overall structure is not spherical but a short worm-like structure (see *Figure 3c*). The small spheres of PIP in the PTHF domain observed in *Figure 1* are not observed in *Figure 3*. Considering the energy of interfacial tension, the outer domain should be the PTHF domain (larger volume fraction, 74 wt%) in this system. However, in this case the PIP domain (smaller volume fraction) is the outer part. It is suggested that the PIP domains were extruded to the outer part by PTHF crystallization. Therefore no PIP spheres were observed in the PTHF

domain. The outlines of the PTHF domain (inside line of the PIP domain, see *Figure 3c*) consisted of straight rather than curved lines. The shape of the PTHF crystallites affected the outlines.

The PTHF areas (inner non-stained part) in *Figures 1* and *3* were about 40% and 50%, respectively. These percentages were lower than the respective PTHF weight fractions (TI-1 = 52 wt% and TI-3 = 74 wt%); this was caused by the volume decrease of the PTHF domain caused by PTHF crystallization.

In crystalline–amorphous type block copolymers, the unique domain shape is obtained in the case of small block copolymer domains such as ultra-thin film, and not in the bulk, because of the crystallization.

References

- 1 Molau, G. E. in 'Block Polymers' (Ed. S. L. Aggarwal), Plenum Press, New York, 1970
- 2 Helfand, E. and Wassermann, Z. R. *Macromolecules* 1976, **9**, 879
- 3 Meier, D. J. in 'Block and Graft Copolymers' (Eds D. J. Burke and V. Weiss), Syracuse University Press, New York, 1975
- 4 Skoulios, A. and Finaz, J. *J. Chim. Phys.* 1962, **59**, 473
- 5 Lotz, B. and Kovacs, A. J. *Kolloid-Z. Z.-Polym.* 1966, **209**, 97
- 6 Kawai, T., Shiozaki, S., Sonoda, S., Nakagawa, H., Matsumoto, T. and Maeda, H. *Makromol. Chem.* 1969, **128**, 252
- 7 Hirata, E., Ijitsu, T., Soen, T., Hashimoto, T. and Kawai, H. *Polymer* 1975, **16**, 249
- 8 Takahashi, A. and Yamashita, Y. in 'Copolymers, Polyblends, and Composites' (Ed. A. J. Platzer), American Chemical Society, Washington, DC, 1975, p. 267
- 9 Ishizu, K., Ishikawa, S. and Fukutomi, T. *J. Polym. Sci., Polym. Chem. Edn* 1985, **23**, 445
- 10 Cohen, R. E., Cheng, P. L., Douzinas, K., Kofinas, P. and Berney, C. V. *Macromolecules* 1990, **23**, 324
- 11 Douzinas, K. and Cohen, R. E. *Macromolecules* 1991, **24**, 4457
- 12 Veith, C. A., Cohen, R. E. and Argon, A. S. *Polymer* 1991, **32**, 1545
- 13 Ishikawa, S., Sasaki, S. and Fukutomi, T. *J. Appl. Polym. Sci.* 1993, **48**, 509
- 14 Ishikawa, S., Ishizu, K. and Fukutomi, T. *Eur. Polym. J.* 1992, **28**, 1219
- 15 Ishikawa, S., Ishizu, K. and Fukutomi, T. *Polym. Commun.* 1991, **32**, 374
- 16 Brandrup, J. and Immergut, E. H. (Eds) 'Polymer Handbook', Wiley Interscience, New York, 1975
- 17 Ishikawa, S. and Fukutomi, T. *Polym. Commun.* 1989, **30**, 243