

Microphase Separation and Crystallization of Crystalline-Amorphous Type Block Copolymer.

I. Effect of Solvent

SATOSHI ISHIKAWA,* SINTARO SASAKI, and TAKASHI FUKUTOMI

Department of Polymer Chemistry, Tokyo Institute of Technology, 2-12, Ookayama, Meguro-ku, Tokyo 152, Japan

SYNOPSIS

The formation process of the microphase separation and crystallization of a crystalline-amorphous type diblock copolymer [poly(tetrahydrofuran-*b*-isoprene)] in solution were studied by transmission electron microscope and wide-angle X-ray diffraction measurements. The morphologies formed from three kinds of solvent systems are discussed in relation to the crystallization of poly(tetrahydrofuran) sequence. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that diblock copolymers consisting of both amorphous sequences generally form micelles in solutions exceeding the critical micelle concentration (CMC). As the solvent is evaporated, the micelles are deformed, and finally various types of microdomain structures are retained in the film. These have been classified into five types of morphologies.¹ The thermodynamics of formation have been treated theoretically.^{2,3}

Studies on crystalline-amorphous type diblock copolymers are rather limited. For poly[ethylene oxide (EO) -*b*-styrene (ST)]⁴ and poly(EO-*b*- α -methylstyrene),⁵ crystal domains of poly(ethylene oxide) (PEO) appeared at the initial observation during the solvent evaporation, and the phase separation occurred macroscopically. The models and theories for this structure were proposed.^{6,7}

The microstructure of poly[EO-*b*-isoprene (IP)]⁸ depended on the kinds of solvents; when benzene (good for PEO) was used, a microphase separation appeared, while a macrophase separation with crystal domains appeared with ethylbenzene (poor for PEO). This has been explained in terms of critical concentration for crystallization (CC); a microphase

separation may occur for the case of $CC > CMC$ while a macrophase separation for $CC < CMC$. The PEO is crystalline and hydrophilic, whereas polystyrene, poly(α -methylstyrene), and polyisoprene (PIP) are amorphous and hydrophobic. The PEO is not compatible with the latter polymers, and any kind of solvent is somehow selective for such a pair of polymers. Therefore, the crystallization may proceed before the micelle formation (i.e., $CC < CMC$), and this leads to the macrophase separation.

Recently, poly[tetrahydrofuran (THF) -*b*-ST]⁹ and poly(2-methyl-2-oxazoline-*b*-ST)¹⁰ were synthesized, both of which are crystalline, hydrophobic-amorphous, hydrophobic type. With a good solvent for both sequences, the CC can be higher than CMC. In fact, crystallization after the micelle formation and the microphase separation were observed. The domain surface was disordered and it was suggested that the phenomenon was due to the crystallization. However, the formation process, microphase separation and crystallization, have not been clarified for this complicating structure. The micro-multi-phase structure with crystalline domains may have an application for high functional materials. In order to control the structure, it is important to clarify the formation process of microphase separation and crystallization during evaporation of solvent.

In this work, the structure and behavior of a diblock copolymer of crystalline-amorphous type (both hydrophobic), poly(THF-*b*-IP), were investigated by using three solvent systems. One was good

* To whom correspondence should be addressed.

Table I Characters of poly(THF-*b*-IP)s

Sample No.	M_w		Composition (wt %)	
	PTHF	PIP	PTHF	PIP
TI-1	118000	110000	52	48
TI-2	118000	42000	74	26

for both sequences, and the other two were good for either of them.

EXPERIMENTAL

Poly(THF-*b*-IP)s were synthesized by a coupling reaction between living poly(tetrahydrofuran) (PTHF) and living PIP.¹¹ The characteristics of the block copolymers are listed in Table I.

The 3 wt % solution was prepared for each solvent system. The composition and the selectivity for PTHF and PIP sequences are listed in Table II. In TI-2, only benzene was used for the solvent. The solution was continuously stirred very slowly, and the solvent was allowed to evaporate at room temperature. The compositions of the solvent systems were about constant during the evaporation. At the prescribed concentrations, small amounts of the solutions were sampled for transmission electron microscopy (TEM) and X-ray diffraction.

The observation technique of polymer micelle was established in our preceding paper.¹² The method is the following. The sampled solution was quickly diluted with the same solvent and the solution was cast onto a carbon-coated copper mesh. Then, the sample was quickly dried in vacuum at room temperature and stained with osmium tetroxide. The polymer micelle in solution can be observed as it is by this method. The TEM observations were carried out by Hitachi H-500 model with an acceleration voltage of 100 kV.

Table II Composition and Selectivity of Solvents

Solvent System	Composition	Solubility	
		PIP	PTHF
I	Benzene only	good	good
II	Benzene/ <i>n</i> -hexane/ <i>n</i> -heptane (50/25/25)	good	poor
III	Benzene/ethanol (80/20)	poor	good

X-ray diffraction patterns of the solutions sealed in glass-capillary tubes were taken with Ni-filtered Cu K α radiation by using a flat-plate camera.

RESULTS

Morphology and Crystallization From Benzene Solution

Figure 1 shows the TEM photographs of TI-1 specimens prepared by rapid dilution and dryings at various concentrations. The white parts are the PTHF domains. In 15 and 25 wt % solutions, spherical and cylindrical domains of PTHF were formed, respectively. The shape changed from defective spheres to imperfect cylinders with the increase of the concentration. The disordered structure formed in 30 wt % solution was intermediate between cylinder and lamellar. In the 35 wt % solution, lamellar structure was observed. The domain sizes of PTHF and PIP were about 50 and 70 nm, respectively. Above 40 wt %, the domains were deformed irregularly: the domain size of PTHF was not uniform for one PTHF lamellar. This is considered to be associated with the structural change in the domains of PTHF. Figure 2 shows the X-ray diffraction patterns at various concentrations. No sharp diffraction pattern is observed for the solutions with the concentration less than 40 wt %. For the 40 wt % solution, however, two sharp rings appeared and these were identical to those from homo-PTHF. In this system, the CC of PTHF was 40 wt %. The deformation of the

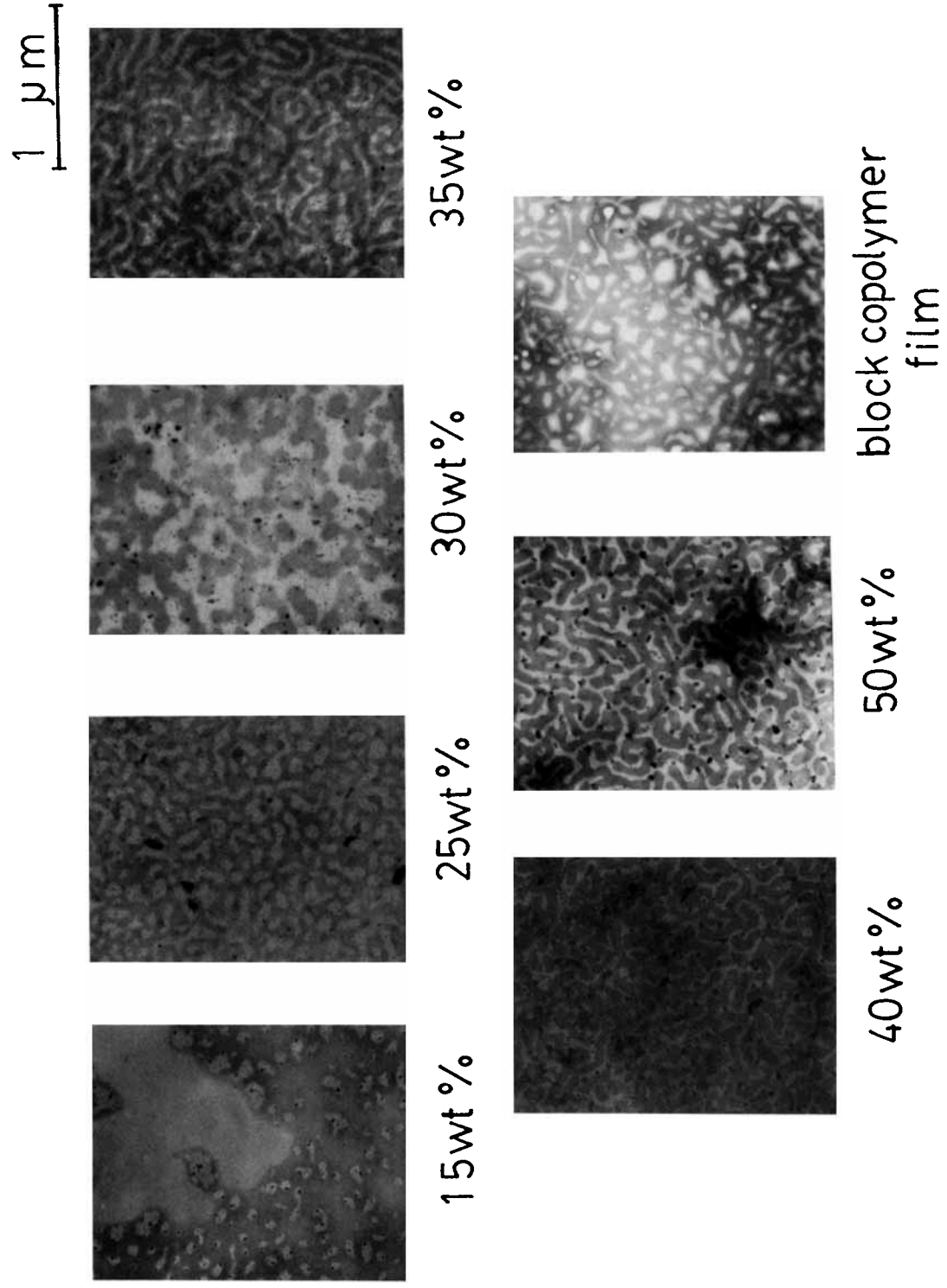


Figure 1 TEM photographs of the domain structures of TI-1 formed in solutions (Solvent System I) in various concentrations. Dark areas are PIP domains.

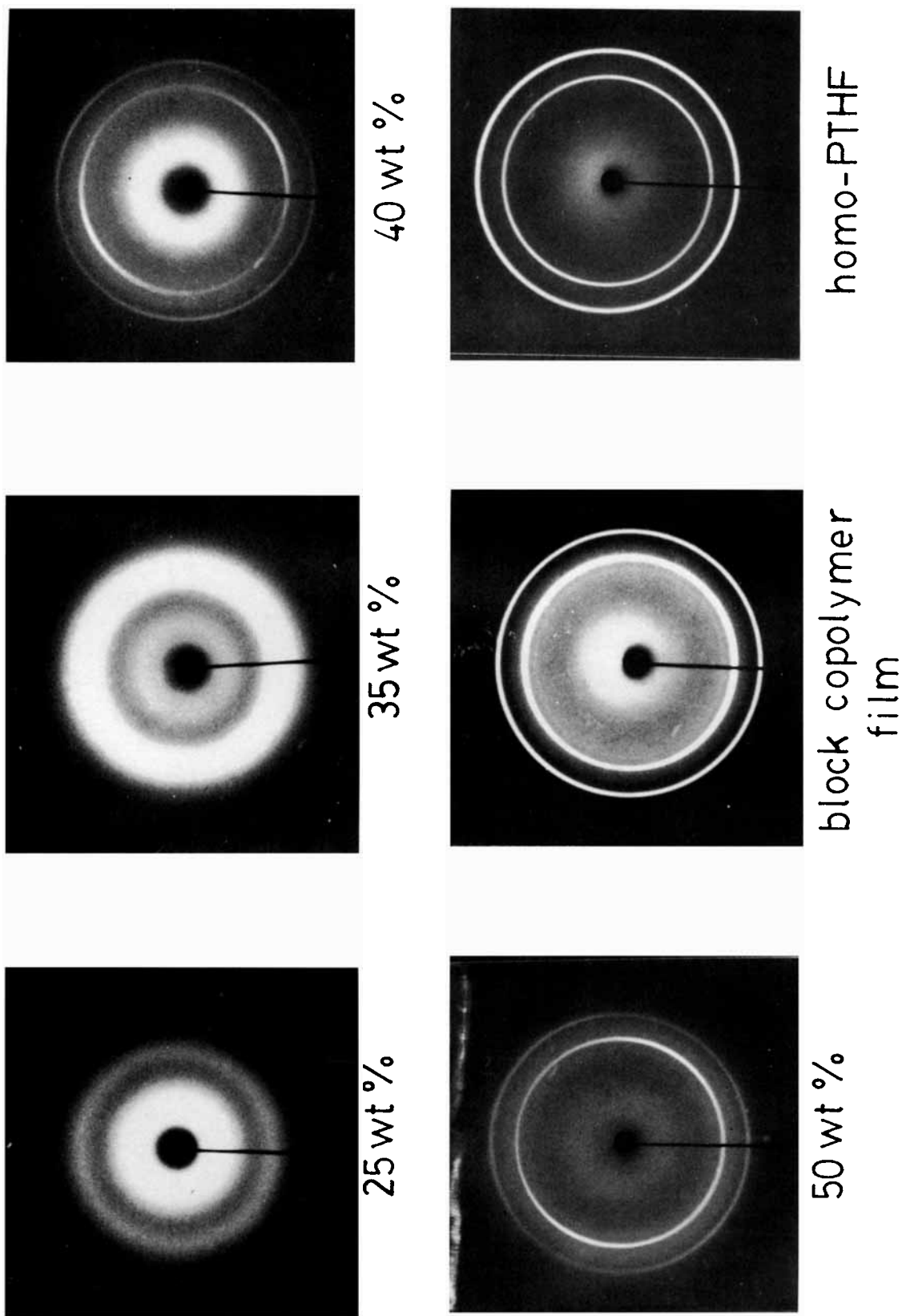


Figure 2 Wide angle X-ray patterns of the solutions (Solvent System I) of TI-1 in various concentrations.

PTHF domains may arise from the crystallization of PTHF. For Takahashi and Yamashita⁹ and Ishizu, et al.¹⁰ the similar deformation of the domains (the heterogeneity of domain sizes) were also observed in the thin block copolymer films.

Figure 3 shows the TEM photographs of TI-2 specimens. Spherical domains with PIP cores were observed in all concentrations. The domain deformation observed in Figure 1 was not observed. Considering the block copolymer composition and solvent, this result is reasonable. Figure 4 shows the X-ray diffraction patterns at the various concentrations. For the 50 wt % solution, diffraction rings

were observed. In this system, the CC of PTHF was 50 wt % and higher than the case of TI-1.

The CC of homo-PTHF could not be determined by this method (more than 50 wt %).

The Case of Solvent System II

Since this system is poor for PTHF, it was expected that the crystallization of PTHF may occur at the lower concentration and the shape of the PTHF domain changes with the decrease of volume fraction of the PTHF domain. In the TEM photographs (Fig. 5), spherical domains with PTHF cores were ob-

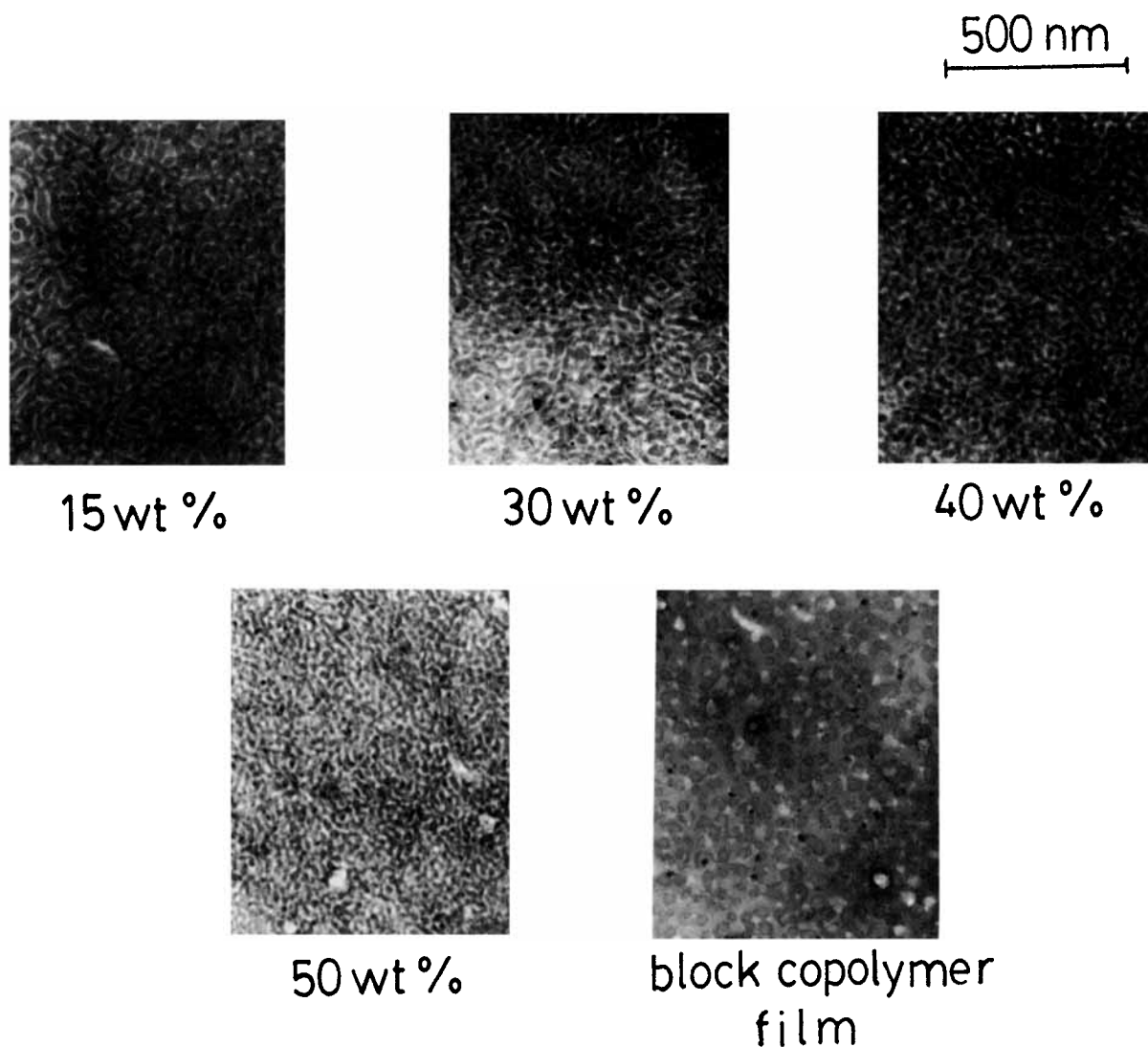


Figure 3 TEM photographs of the domain structures of TI-3 formed in solutions (Solvent System I) in various concentrations. Dark areas are PIP domains.

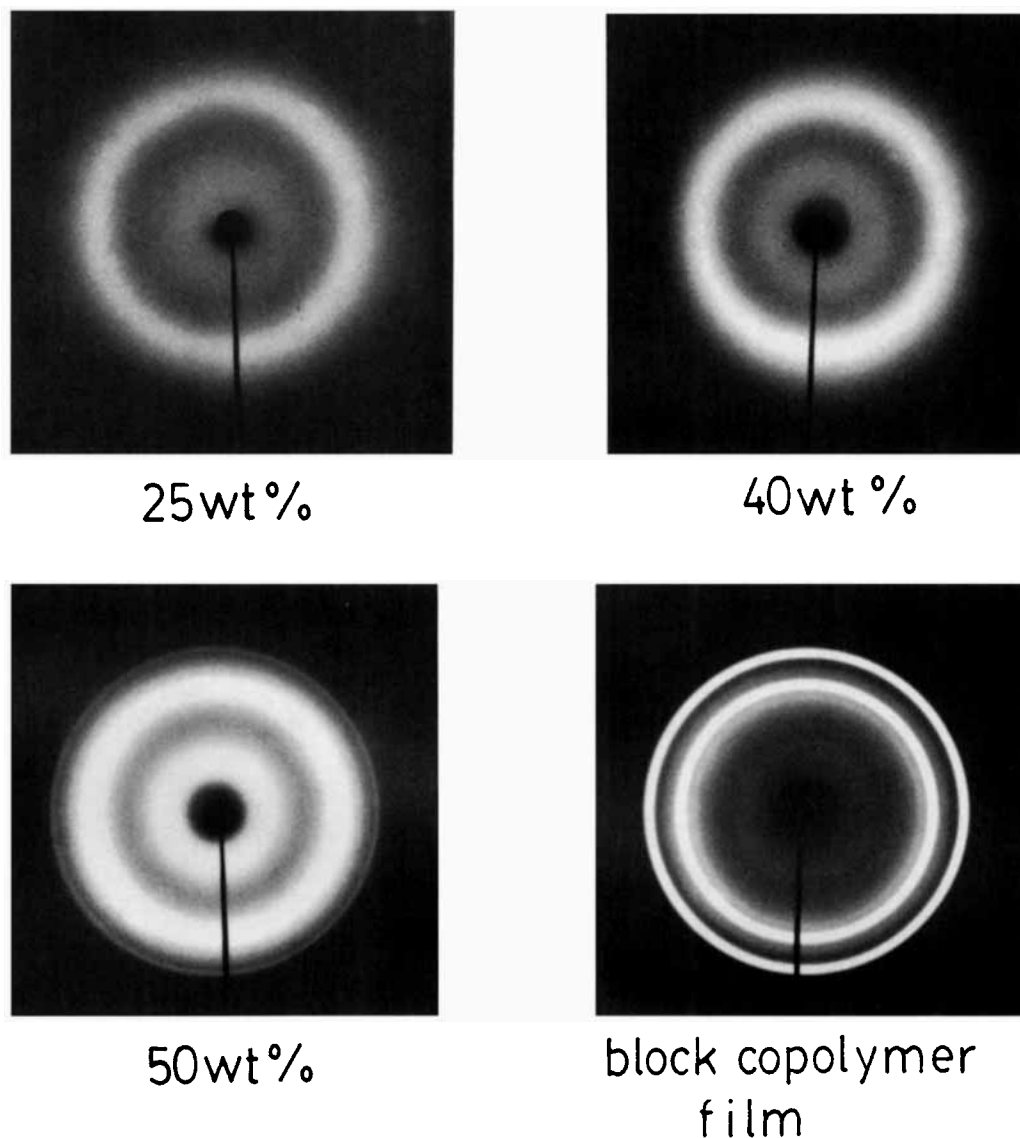


Figure 4 Wide angle X-ray patterns of the solutions (Solvent System I) of TI-3 in various concentrations.

served at all concentrations. The radii of PTHF domains enlarged and the fraction of the PTHF parts recognized in the photograph approached 50 wt % with the increase of polymer concentration. The deformation of the domain surfaces by the crystallization was not observed.

Figure 6 shows the X-ray diffraction patterns at the various concentrations. No sharp patterns were observed for the solutions up to 50 wt %. The CC of PTHF was 50 wt % and higher than the case of TI-1-benzene system. This was different from our expect.

The Case of Solvent System III

Since this system is good for PTHF and poor for PIP, it is expected that the domain shape is only changed by the decrease of the volume fraction of PIP domain. In the TEM photographs (Fig. 7), spherical domains with PIP cores were observed at all concentrations. The deformation of the domain surface was not observed. Figure 8 shows the X-ray diffraction patterns at the various concentrations. As in the case of Solvent System III, two vague diffractions appeared for the 50 wt % solution. The CC

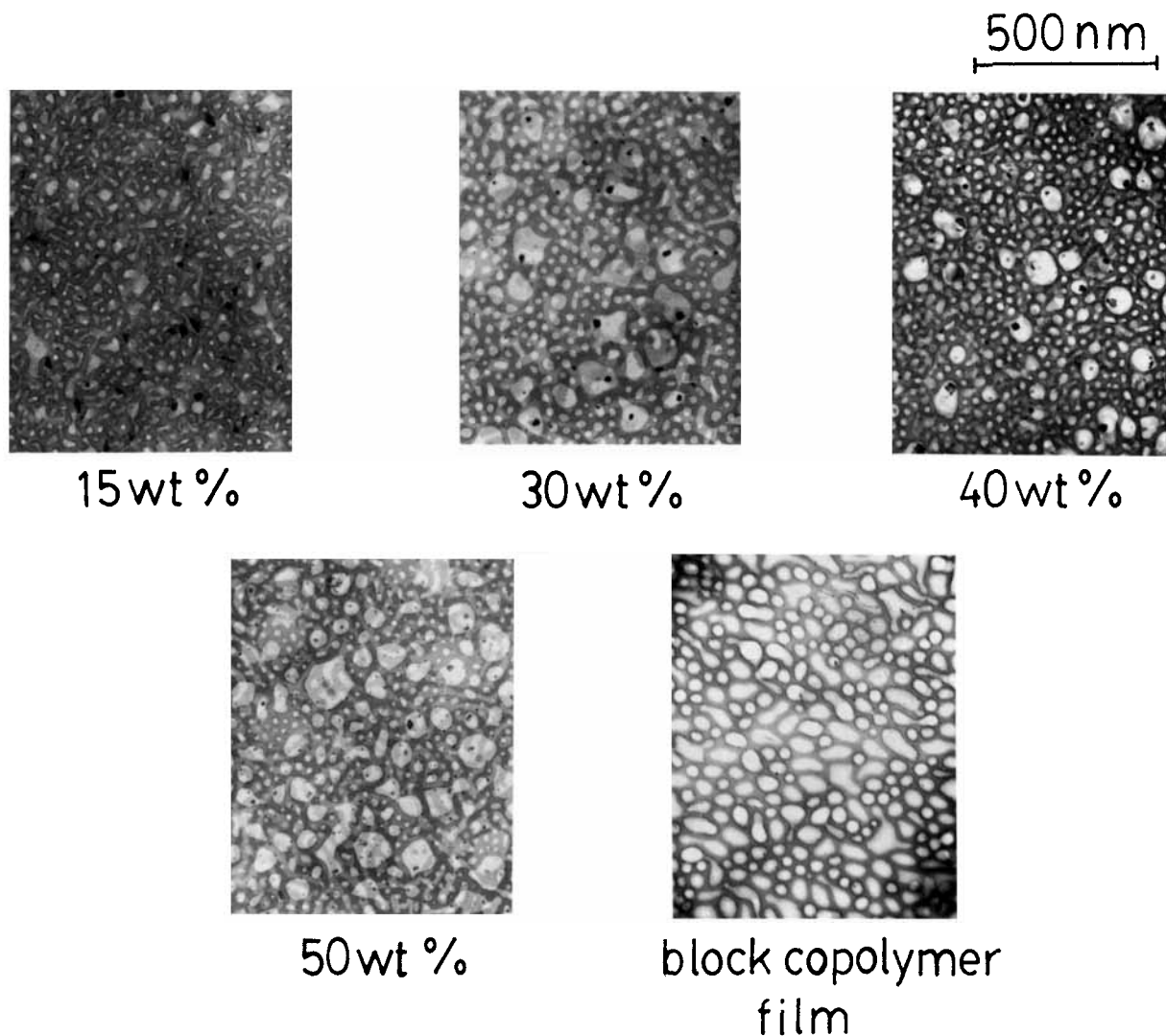


Figure 5 TEM photographs of the domain structures of TI-1 formed in solutions (Solvent System II) in various concentrations. Dark areas are PIP domains.

of PTHF was 50 wt % and higher than the case of TI-1-benzene system.

DISCUSSION

The weight fraction of PTHF in TI-1 is 0.52, that is to say, the volume fraction is about 1 : 1, the microstructure (solid-state) predicted by Molau's rule¹ should be lamellar structure in the case of benzene. It was found that the spherical domain was formed at first and the domain structure changed to cylindrical and finally to lamellar with the increase of the concentration. This is explained by the follow-

ing. Benzene is a better solvent for PIP than PTHF. At the low concentration, the volume fraction of PIP domain (containing solvent) was higher than that of PTHF, so the spherical domain with a core of PTHF was formed. The polymer-polymer interaction began to play a more important role than the solvent-polymer interaction with the increase of polymer concentration. Then the domain structure changed from sphere to lamellar. The difference between theoretical and experimental microstructure was also reported by some workers.^{13,14}

According to the deformation of the domain, it is suggested that the crystallization of PTHF sequence occurs near the surface of the PTHF domains first.

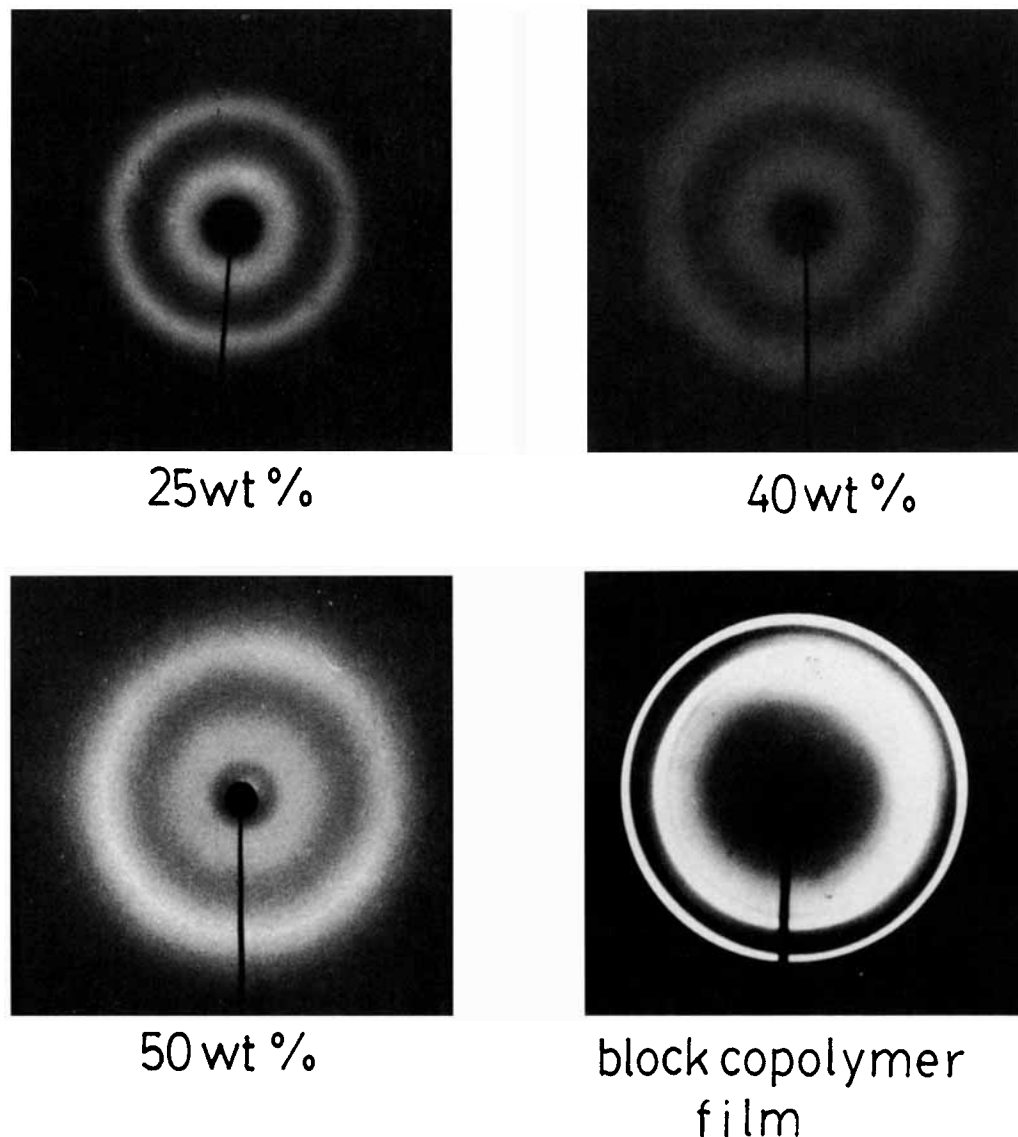


Figure 6 Wide angle X-ray patterns of the solutions (Solvent System II) of TI-1 in various concentrations.

If the crystallization occurs at the inner part of the PTHF domain first, the deformation is not appreciable because the stress caused by the rearrangement of the PTHF chain during the crystallization should be relaxed by the outside liquid PTHF (T_g of PTHF = -78°C)¹⁵ and the interface between the PTHF and PIP is not deformed. But the deformation and crystallization occurred simultaneously. This means that the stress by the crystallization was relaxed by liquid PIP domain (T_g of PIP = -73°C)¹⁵ straightly and the interface was deformed. When a micelle is formed, a junction of both sequences of a block copolymer is placed on the in-

terface of the domains. The PTHF chains are apt to be arranged easily at this part because chain ends of PTHF are fixed and the chains are directed to the opposite direction of the PIP domain by the repulsion force for PIP.

DiMarzio et al.⁶ and Whitmore and Noolandi⁷ proposed the models of the crystalline-amorphous type block copolymer (in the case of lamellar structure) and studied the thermodynamics of formation theoretically. In those models, the crystalline domain consisted of one or two crystallite layers and the crystallite core size was about constant. However, in this experiment, the domain size of PTHF

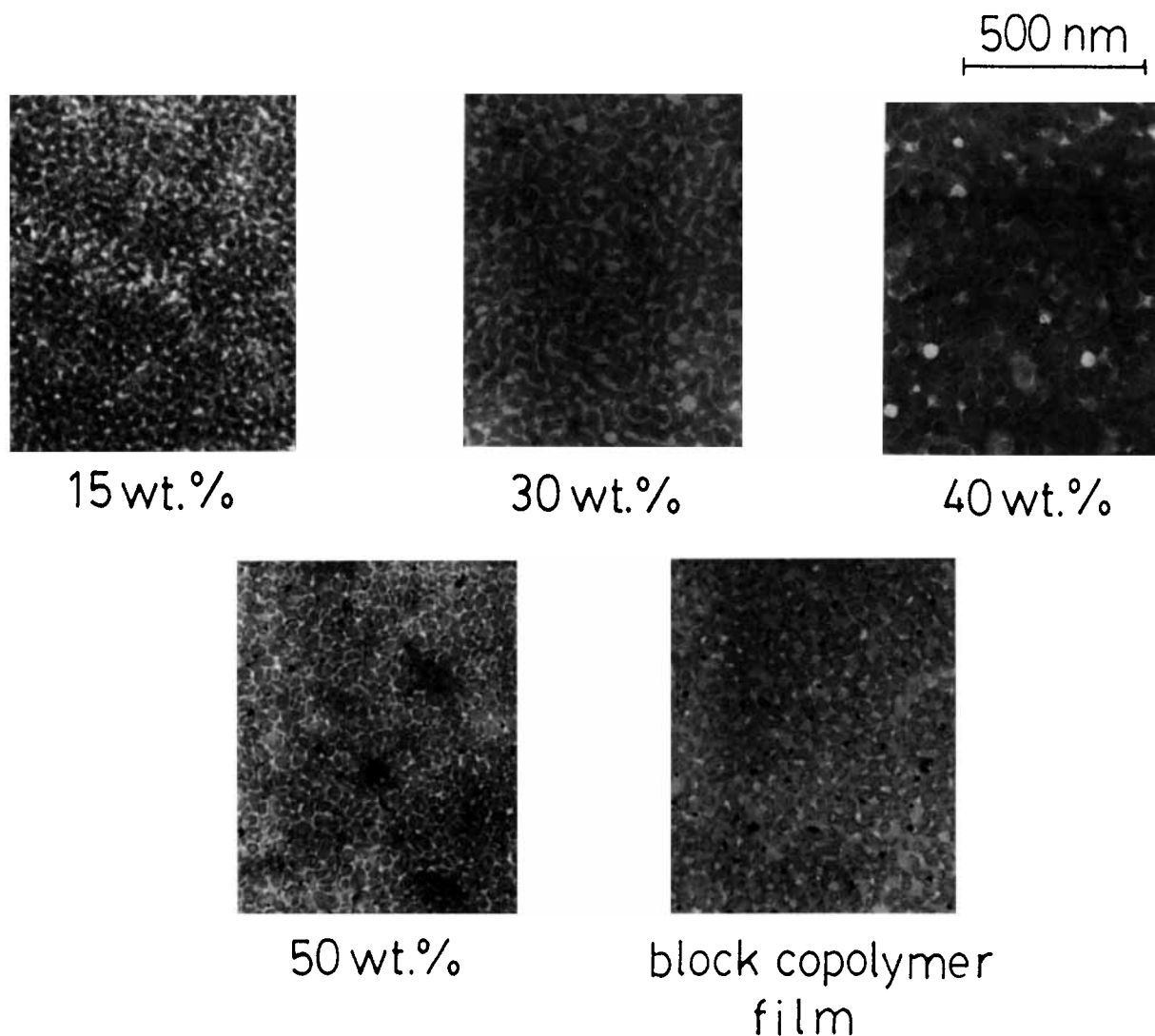


Figure 7 TEM photographs of the domain structures of TI-1 formed in solutions (Solvent System III) in various concentrations. Dark areas are PIP domains.

was not uniform. In other reports,^{9,10} the deformation of crystalline domain were observed. Therefore, those models cannot be adapted to these systems: crystallization occurs after micelle formation ($CMC < CC$). Those models are adapted to the case: crystallization occurs first ($CMC > CC$). The detail structures and the discussion of solid-state for poly(THF-*b*-IP) were reported in preceding papers.^{16,17}

In the case of Solvent System II, the CC was higher than the benzene though the poor solvent for crystalline sequence was used. Considering the theory by Kawai et al.,⁶ the CC should be lower than the benzene. Then, it is found that the theory is

insufficient and the CC is affected by some other factor except for solvent-polymer interaction. In the case of Solvent System III, the CC was higher than the benzene. From these results, it is suggested that the domain shape affects the CC. In the case of the lamellar domain, the crystallization is apt to occur easily because the crystalline chains are arranged easily by the straight interface. On the other hand, in the case of the interface with the radius, the TI-2-benzene system and TI-1-Solvent Systems II and III, the crystalline chains are not arranged easily in comparison with the case of the TI-1-benzene system. The CC of the TI-1-benzene system was lower than that of the TI-2-benzene system. This result

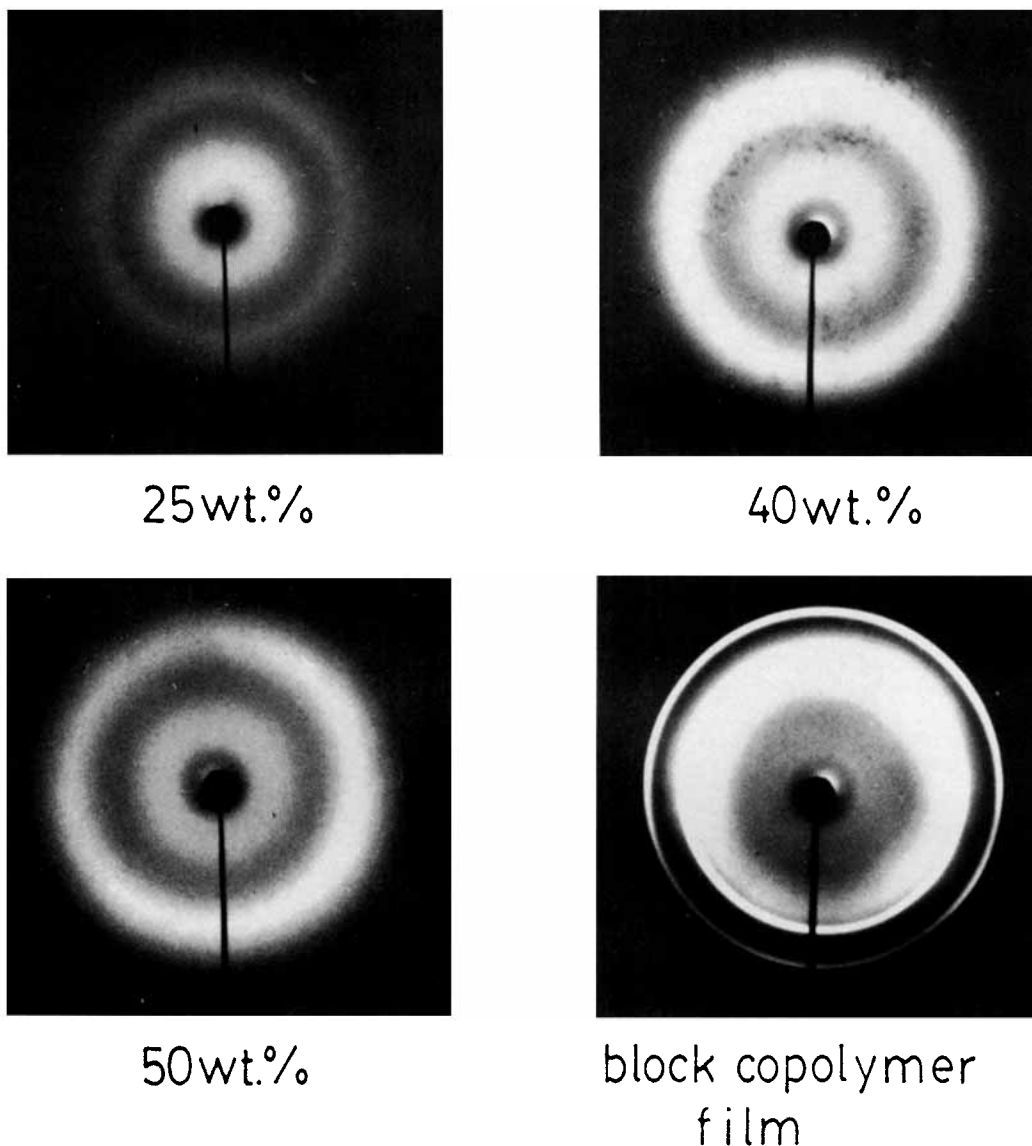


Figure 8 Wide angle X-ray patterns of the solutions (Solvent System III) of TI-1 in various concentrations.

proved that the CC was not affected by the solvent but by the domain shape. In our preceding paper,¹⁶ it was found that the PTHF domain with complicating domain shape is apt to be amorphous. That report agrees with these result. The CC of homo-PTHF was very high (more than 50 wt %, could not be determined by this method). The CC of PTHF in the block copolymer is lower than that of homo-PTHF. Then, especially, when the domain shape is lamellar, the CC is lower.

Thus, the CC is affected on not only polymer-solvent interaction but also the domain shape in the case of $CMC < CC$.

REFERENCES

1. G. E. Molau, *Block Copolymers*, S. L. Aggarwal, Ed., Plenum, New York, 1970, p. 79.
2. E. Helfand and S. R. Wasserman, *Macromolecules*, **9**, 879 (1976).
3. D. J. Meier, *Block and Graft Copolymers*, J. J. Burke and V. Weiss, Eds., Syracuse Univ. Press, New York, 1975.
4. A. Skoulios and G. J. Finaz, *J. Chim. Phys.*, **59**, 473 (1962).
5. T. Kawai, S. Shiozaki, S. Sonoda, H. Nakagawa, T. Matsumoto, and H. Maeda, *Makromol. Chem.*, **128**, 252 (1969).

6. E. A. DiMarzio, C. M. Guttman, and J. D. Hoffman, *Macromolecules*, **13**, 1194 (1980).
7. M. D. Whitmore and J. Noolandi, *Macromolecules*, **21**, 1482 (1988).
8. E. Hirata, T. Ijitsu, T. Soen, T. Hashimoto, and H. Kawai, *Polymer*, **16**, 249 (1975).
9. A. Takahashi and Y. Yamashita, *Copolymers, Polyblends, and Composites*, A. J. Platzer, Ed., Am. Chem. Soc., Washington D.C., 1975, p. 267.
10. K. Ishizu, S. Ishikawa, and T. Fukutomi, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 445 (1985).
11. S. Ishikawa and T. Fukutomi, *Polym. Commun.*, **30**, 243 (1989).
12. S. Ishikawa and T. Fukutomi, *J. Appl. Polym. Sci.*, **40**, 1547 (1990).
13. T. Hashimoto, M. Fijimura, and H. Kawai, *Macromolecules*, **13**, 1660 (1980).
14. R. J. Spontak, M. C. Williams, and D. A. Agard, *Polymer*, **29**, 387 (1988).
15. J. Brandrup and E. H. Immergut, Eds., *Polymer Handbook*, Wiley-Interscience, New York, 1975.
16. S. Ishikawa, K. Ishizu, and T. Fukutomi, *Eur. Polym. J.*, **28**, 1219 (1992).
17. S. Ishikawa, K. Ishizu, and T. Fukutomi, *Polym. Commun.*, **32**, 374 (1991).

Received December 18, 1990

Accepted July 6, 1992