- 3) Kagaku Kōgaku Kyōkai: "Ryūdōsō Hannō Sōchi," Kagaku Kōgyō-sya, p. 194 (1987).
- 4) Kobayashi, H., F. Arai and T. Sunakawa: *Kagaku Kōgaku*, **31**, 239 (1967).
- 5) Kunii, D. and O. Levenspiel: "Fluidization Engineering," Wiley, pp. 181-183, 235 (1969).
- 6) Lewis, W. K., E. R. Gilliland and W. Glass: *AIChE J.*, **5**, 419 (1959).
- 7) Lisa, R. E. and R. G. Barile: *J. Chem. Eng. Japan*, **6**, 283 (1973).
- 8) Miyauchi, T., S. Furusaki, S. Morooka and Y. Ikeda: "Advances in Chemical Engineering," Academic Press, Inc., pp. 363, 371, 399-401 (1981).
- 9) Yamazaki, M. and T. Miyauchi: *J. Chem. Eng. Japan*, **4**, 324 (1971).
- 10) Yamazaki, M. and T. Miyauchi: *J. Chem. Eng. Japan*, **6**, 285 (1973).
- 11) Yamazaki, M. and T. Miyauchi: *Kagaku Kogaku Ronbunshu*, **3**, 261 (1977).

AVERAGE LAMELLAR DOMAIN DISTANCE IN MICROPHASE-SEPARATION STRUCTURE FOR THE SYSTEM OF POLYSTYRENE, POLYISOPRENE AND STYRENE-ISOPRENE DIBLOCK COPOLYMER

SHIGEKI TAKISHIMA, HIDEAKI KURATA, MIKIO KONNO
AND SHOZABURO SAITO

Department of Chemical Engineering, Tohoku University, Sendai 980

Key Words: Thermodynamics, Phase Equilibrium, Microphase Separation, Polymer Alloy, Lamellar Structure, Polystyrene, Polyisoprene, X Ray Scattering

Introduction

Previously, the authors reported an experimental and theoretical study of the microphase-separation structure of a polymer blend of homopolystyrene, homopolyisoprene and styrene-isoprene diblock copolymer cast from benzene solution.³⁾ In a relatively wide range of copolymer concentrations, a highly regular lamellar structure was observed in the phase separation. For that structure, a predictive model derived from the statistical thermodynamic theory of Whitmore and Noolandi⁴⁾ was proposed. The validity of the model was examined by a comparison of experimental and predicted results. However, only limited experimental data were collected for the comparison in the previous work.

In the present work, additional data were obtained for the microphase-separation structure of the polymer system and the solvent effects were studied. The experimental values of the lamellar domain distances were compared with predictions by the previous model.

1. Experimental

1.1 Materials

The homopolyisoprene and the styrene-isoprene diblock copolymer were synthesized by living anionic polymerization as in the previous work.³⁾ The homopolystyrene was supplied by Toyo Soda Ltd. The physical properties of the polymers are summarized in **Table 1**. The molecular weight of the homopolystyrene was almost the same as that of the polystyrene block of the copolymer, while the molecular weight of the homopolyisoprene was about twice that of the polyisoprene block. The molecular weight of each polymer used was larger than in the previous work.³⁾

1.2 Procedure

For the formation of the microphase-separation

Table 1. Characterization of polymer samples used

Polymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
S-I Copolymer*	1.75×10^5	1.16
Homopolyisoprene	1.40×10^5	1.06
Homopolystyrene	1.02×10^5	1.01

* Styrene-isoprene diblock copolymer with 55 wt% polystyrene content.

Received March 1, 1988. Correspondence concerning this article should be addressed to S. Saito. S. Takishima is now at Dept. of Chem. Eng., Hiroshima University, Higashihiroshima, 724. H. Kurata is now with Idemitsu Kosan Co., Ltd.

structure, benzene was adopted as a casting solvent, as in the previous work.³⁾ In addition, cyclohexane was also used to examine the effect of solvents on the phase separation. Cyclohexane is a good solvent for the polyisoprene component and a poor solvent for the polystyrene component, while benzene is a good solvent for both the components. In all the experiments, the weight ratio of homopolystyrene and homopolyisoprene was maintained constant at 1:1, and the content of the diblock copolymer was varied. The specimens of the polymer mixtures prepared by solvent casting were analyzed for the phase-separation structure by transmission electron microscopy (TEM) and by a small-angle X-ray scattering (SAXS) method. Details of the experimental procedure can be found in our previous work.³⁾

2. Experimental Results

Figures 1(a) to (d) show some examples of TEM photographs of the polymer films cast from benzene solutions. In the photographs, the polyisoprene phase, which was stained with OsO_4 , is seen as darker than the polystyrene phase. An alternate lamellar structure of high regularity was observed in the microphase separation in the region of higher copolymer contents. The regularity of the structure gradually lessened with decreasing copolymer content. Below 60 wt% copolymer content, the structure of most specimens became disordered and the lamellar structure appeared only in a limited area. The critical concentration of 60 wt%, at which the regularity of the lamellar structure disappeared, is much higher than the concentration of 30 wt% found in the previous work.³⁾ This may be due to the difference in molecular weight of each component in the present work. The homopolyisoprene, as seen in Table 1, has a particularly high molecular weight, almost twice that of the polyisoprene block of the copolymer. In the previous work, both homopolymers and each block of the copolymer had similar molecular weights. When the molecular weight of a homopolymer is larger than that of the corresponding block of the copolymer, the homopolymer is less solubilized in the region composed of the block chains. Consequently, the region of the homopolymer chains is formed at a lower homopolymer content, and its formation reduces the effect of the long-range forces, which act so as to maintain the regularity of the phase-separation structure. On the contrary, the symmetry of the molecular weights in the previous work allowed the structure to maintain regularity. The effect of the molecular weight of added homopolymer on the order-disorder transition has been studied by Nojima and Roe for the system of polystyrene and styrene-butadiene diblock copolymer.²⁾ They indicated that the concentration region of stable microphase separation

Fig. 1. Transmission electron micrographs of ultrathin sections of polymer specimens cast from benzene solutions

Fig. 2. Transmission electron micrographs of ultrathin sections of polymer specimens cast from cyclohexane solutions

becomes narrower with increasing molecular weight of the added homopolymer.

TEM photographs for the specimens cast from cyclohexane solution are shown in Figs. 2(a) to (d). The lamellar structure was observed only in the range above 90 wt% copolymer content. At 80 wt% copolymer content, the polystyrene component, which has less affinity for cyclohexane, formed a dispersed phase of cylindrical shape. As the copolymer content decreased, the shape of the dispersed phase, which was cylindrical, became spherical. In the specimens where the polystyrene component was cylindrically or spherically dispersed in the matrix phase of the polyisoprene component, the homopolystyrene phase also formed the matrix phase in some areas. Possibly the difference of the phase-separation structures in Figs. 1 and 2 may be explained by the selectivity of the casting solvents. When the copolymer is dissolved in cyclohexane, the micellar structure of the inner sphere of the polystyrene blocks and the outer shell of the polyisoprene blocks is considered stable from the viewpoint of free energy. In other words, the chains of the polystyrene block tend to shrink, excluding cyclohexane molecules, while those of the polyisoprene

block tend to expand to the bulk solvent phase. When homopolymers are added to the copolymer solution, the homopolyisoprene chains are easily solubilized in the domain of the expanding polyisoprene block chains, while homopolystyrene chains are scarcely solubilized in that of the shrinking polystyrene block chains and form an additional macroscopic region. As a result, the spherical micellar structure is more stabilized in the solution state at higher homopolymer contents. During vaporization of the solvent, the shape of the stable micelle may become cylindrical, and finally lamellar, if equilibrium is maintained throughout the vaporization process. However, the structure in the solution state may remain after vaporization at lower copolymer concentrations where the long-range forces are reduced. Reduction of the long-range forces is probably responsible for the difference between the structures in Figs. 1 and 2 for the different solvents.

3. Prediction of Average Domain Distance of Lamellar Structure

In the range of copolymer contents where the lamellar structure was observed, the average domain distances of the structure in the equilibrium solid state were predicted by the previously proposed model.³⁾

In Fig. 3 the calculated results are compared with the experimental ones obtained from SAXS measurements. Since the effect of casting solvent is not considered in the model, the model gives the same result for specimens cast from both the benzene and the cyclohexane solutions. As explained above, the solvent effect is not significant at high copolymer concentrations owing to the strong long-range forces. In addition it is known that when the lamellar structure is formed the equilibrium state can be easily attained.¹⁾ Thus the model can closely predict the

Fig. 3. Comparison between theoretically predicted and experimentally obtained results of average domain distances of lamellar structure, D

experimental values without considering solvent effects.

Nomenclature

D	= average domain distance	[nm]
$\bar{M}_n$	= number-averaged molecular weight	[g/mol]
$\bar{M}_w$	= weight-averaged molecular weight	[g/mol]
W_c	= weight percent of copolymer	[—]
w_H	= weight fraction of total homopolymer	[—]

Literature Cited

- 1) Hashimoto, T., M. Shibayama and H. Kawai: *Macromolecules*, **13**, 1237 (1980).
- 2) Nojima, S. and R. J. Roe: *Macromolecules*, **20**, 1866 (1987).
- 3) Takishima, S., M. Konno, K. Arai and S. Saito: *J. Chem. Eng. Japan*, **19**, 554 (1986).
- 4) Whitmore, M. D. and J. Noolandi: *Macromolecules*, **18**, 657 (1985).