

A Scheme to Predict the Morphology of Diblock Copolymers and Their Blends

GING-HO HSIUE and SOLOMON WENG FENG SHIH, *Polymer Research Institute, National Tsing Hua University, Hsinchu, Taiwan, Republic of China*

Synopsis

Diblock copolymers of α -methylstyrene and isoprene were synthesized anionically. The morphology of the copolymers and of their blends with the homopolymers was studied by transmission electron microscopy. Based on this, a scheme is proposed to predict the morphological behavior associated with the blending of block copolymers with homopolymers. Two blending systems are discussed. They are (i) copolymer AB with homopolymers A and B and (ii) copolymers AB of two different molecular weights with homopolymer A. Two factors are considered to be the most crucial. One is the morphology of the predominant polymer (50 wt %), and the other is the weight ratio of the blends. The solubilizing effect of the block copolymer AB in the blend must also be taken into account. When the two copolymers are blended, the one with lower molecular weight was emulsified by higher one and restricted around the longer chain. It is shown that the present scheme is successful in predicting the morphology of diblock copolymers and their blends.

INTRODUCTION

Rubber morphology has been one of the main subjects of research since the synthesis of diblock copolymers had been achieved. Inoue, Hashimoto, and Kawai¹⁻⁴ pointed out that there are a few rules governing their morphologies, e.g., weight/composition ratio, solvent used in film casting, thermal history, etc.

When a block copolymer AB is blended with two homopolymers A and B, the solubilizing effect is found to be quite general.^{5,6} The physical affinities of the A portion of the copolymer AB toward the A phase and the B portion of AB toward the B phase serve to localize AB at the interface of A and B phases as well as to connect physically the two phases through covalent bonds in the backbone of AB. Solubilizing effect is true only if the homopolymer chain is shorter, when homopolymer chain is longer, incomplete solubilizing or phase separation may result. The scheme proposed by Skoulios⁶ is quite practical.

Aggarwal⁷ proposed a model explaining the arrangement of the block copolymer chains from thermodynamic point of view. Both the entropy reduction due to the restricted volume of the domain of the block copolymer and the placement of a block junction point in the vicinity of the interfacial boundary are important factors which prevent the block copolymer from separating into discrete domains. The possible macroscopic phase separation is therefore replaced by just microscopic phase separation.

Riess⁸ indicated that the solubilizing effect of the block copolymers is responsible for the formation of new morphologies when one blended two

block copolymers with different molecular weights and weight composition ratios with one of the corresponding homopolymer.

In this paper, we shall develop a scheme that qualitatively predicts various possible morphology changes in a triangular phase diagram that describes the blending of a copolymer AB with homopolymers A and B as well as the system used by Riess.

Living anionic polymerization is used to synthesize either a diblock copolymer or a homopolymer. Film cast on the water surface is used to prepare specimens for TEM observations.

EXPERIMENTAL

Materials

α -Methylstyrene (Santo Chemicals Co.). The monomers were first washed twice with 5% sodium hydroxide. After removal of inhibitor, they were washed several times with distilled water to remove residual sodium hydroxide. Calcium hydride was used for the preliminary drying (overnight). The monomers were then distilled at 54°C/12 mm Hg into an ampoule containing calcium hydride. They were then stored at $ms20^{\circ}C$.

Isoprene (Merck Chemicals Co.). Synthetic grade isoprene was used directly after passing through a sodium mirror. It was then transferred into the reaction ampoule.

Toluene (Alps Chemicals Co.). Toluene was first refluxed in the presence of potassium hydroxide pellets for 2 days. The reflux was continued until there were no bubbles left and until it turned blue on addition of benzophenone. It was then distilled into a flask containing a sodium dispersion.

Lithium was from Wako Chemicals Co.

HMPT (Hexamethylene Phosphoric Triamide) and Osmium Tetraoxide were of Merck Chemicals Co.

Instruments

IR: Perkin-Elmer Model 567 Grating Infrared Spectrophotometer; NMR: FX-100 JEOL; GPC: Toyo Soda HLC-802UR with refractive index detector; TEM: Hitachi HU-12A; low temperature bath: Neslab Crycool CC-100.

Polymerization

Block copolymer was synthesized by living anionic polymerization, with *n*-butyl lithium as initiator, and α -methylstyrene and isoprene as monomers. *n*-Butyl lithium was synthesized and standardized according to Gilmann.^{9,10}

The polymerization was carried out as follows: Sodium mirror was first formed in an ampoule. Isoprene was then injected into the ampoule, and the ampoule was degassed to remove any hydrogen gas formed by the reaction of moisture with sodium. Isoprene was then vacuum-transferred to a second ampoule. A very small amount of initiator was injected before

polymerization to diminish trace amounts of impurities. When the solution turned foggy, an exact amount of initiator was again injected. The temperature was raised to about 70°C in about 5 min to facilitate the initiation of the homogeneous anionic polymerization. As soon as the polymerization reaction started, solution appeared slightly yellow, the temperature rose to 90°C, and the solution became viscous. The reaction ampoule was then transferred into a cold bath (−12°C) for further reaction. After reaction was completed, the temperature of the solution was restored to room temperature. A few drops of HMPT and exact amounts of purified α -methylstyrene and toluene were injected by syringes and degassed three times. The solution was frozen before the ampoule was sealed off from the constriction and was left standing until it liquified again. HMPT is to speed up the crossover reaction between isoprene and α -methylstyrene. Bloody red color signified the formation of the anion of α -methylstyrene. The ampoule was again quickly immersed in a cold bath (−70°C). A color change from bloody red to black purple indicated the end of reaction and the viscosity of the solution increased sharply. If isoprene had not been completely reacted, the color would change gradually from yellow to blood red until isoprene was totally consumed.

The highly viscous solution was air-pumped through a predrawn capillary tubing into a large amount of precipitating solution (isopropyl alcohol) with a trace amount of hydrochloric acid. The precipitate was washed several times with distilled water and was dried in vacuum.

Solvent Blending

Blending was obtained by dissolving the polymer in a toluene solution at a total polymer concentration of approximately 5%. After vigorous stirring, the blends were film cast on a water surface, dried, and stained with 1% osmium tetroxide for 0.5 h. The sample was then observed under a transmission electron microscope.

Identification

IR¹¹ and NMR^{12,13} were used to determine the microstructure and the composition distribution. GPC was used to evaluate the molecular weight and the dispersity.

Results and Discussion

The molecular weights and the PA/PI ratios of the polymer synthesized are shown in Table I. The sample points observed and their terminologies as well as the blending compositions are shown in Table II and Figure 1.

We devised a scheme to predict the morphology changes in system A. Each polymer was put in one corner of a triangular phase diagram. The isopleths of constant weight composition ratios (20/80, 40/60, 60/40, 80/20) of poly(α -methylstyrene) and polyisoprene were drawn. The area between two isopleths was appointed as regions having different morphologies: sphere, short rod (cylinder), alternating lamellar, inverse short rod, and inverse sphere. Three lines connecting the midpoints of the three sides were used to judge whether the polymer was predominant (> 50 Wt %).

TABLE I
Weight Composition Ratio and Molecular Weight of Each Sample Used

Sample	M_w	Composition (PA/PI) ^a
412	1.54×10^6	60/40
310	8.32×10^4	40/60
PA	4.22×10^4	100/0
PI ^b	2.41×10^5	0/100

^a PA = poly(α -methyl styrene); PI = polyisoprene.

^b The microstructure of polyisoprene: *cis*-1,4 addition 86.6%, *trans*-1,4 addition 7.0%, 3,4 addition 6.3%.

The rules governing the morphology changes are: (A) The morphology of the three outer triangle is controlled by the predominant polymers. The other two polymers merely fill into their corresponding phases; the weight composition ratio is a secondary effect which influences the alignment of the disperse phase and the morphology inside it. However, if block copolymer is present, the solubilizing effect must be considered. (B) In the central triangle, morphology is primarily determined by the weight composition ratio since there is no predominant polymer. Partial solubilization will be evident in this region.

The detailed scheme of system A is shown in Figure 2. The 40/60 weight composition ratio of 310 suggested a short-rod morphology. When poly-

TABLE II
Blending Composition for Each Observation Point in Ternary Diagram (Fig. 1)^a

System A		
Sample	310/PA/PI	Weight composition ratio (PA/PI)
310	100/0/0	40/60
A-1-2	60/40/0	64/36
B-2-4	50/50/0	70/30
A-1-3	40/60/0	84/16
A-2-2	60/20/20	44/56
A-2-3	20/40/40	48/52
A-2-4	0/50/50	50/50
System B		
Sample	412/310/PA	Weight composition ratio (PA/PI)
412	100/0/0	60/40
B-1-2	70/0/30	72/28
B-1-3	30/0/70	88/12
B-2-2	60/20/20	64/36
B-2-3	20/40/40	68/32
B-2-4	0/50/50	70/30
B-3-2	70/30/0	54/46
B-3-3	30/70/0	46/54
310	0/100/0	40/60

^a PA = poly(α -methyl styrene); PI = polyisoprene.

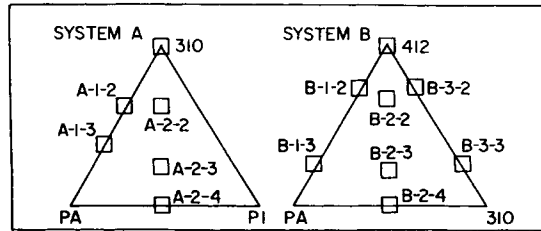


Fig. 1. Three-component system and sample point terminologies: PA = poly(α -methylstyrene), PI = polyisoprene.

(α -methylstyrene) content was increased, incomplete solubilizing of poly(α -methylstyrene) became apparent in A-1-2. The domain of poly(α -methylstyrene) was enlarged but was not evenly distributed. In B-2-4, the high content of poly(α -methylstyrene) overcame the solubilizing capability of diblock 310 and aggregated to form the domain with domain structure. On further addition of poly(α -methylstyrene), severe phase separation occurred. The incompatibility arose from the fact that both phases (PA and PI) had no affinity for each other. The solubilizing effect was not expected to work well when the block copolymer doesn't constitute the continuous phase. The poly(α -methylstyrene) chain aggregated inside the polyisoprene chain accounted for the white domain distribution.

In A-2-2 the stronger restricting force of copolymer 310 determined the

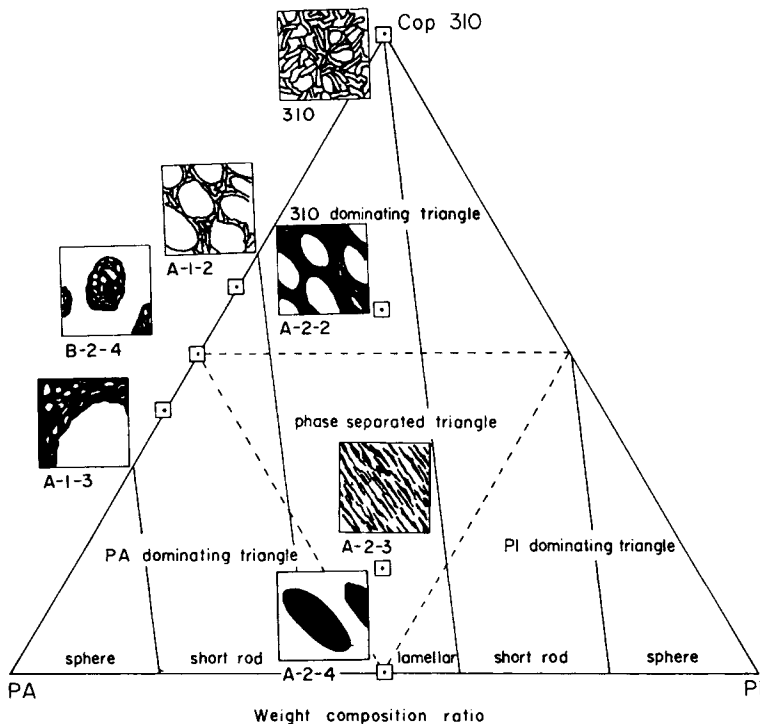
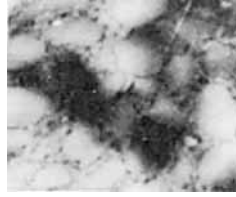
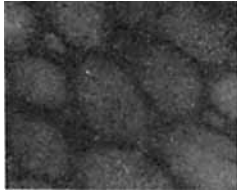


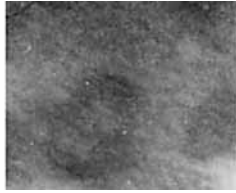
Fig. 2(a). Scheme of A system.



310



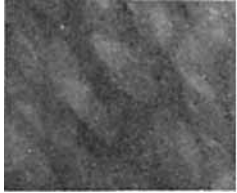
A-1-2



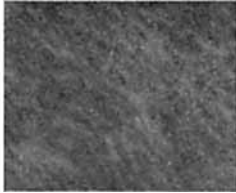
B-2-4



A-1-3



A-2-2



A-2-3

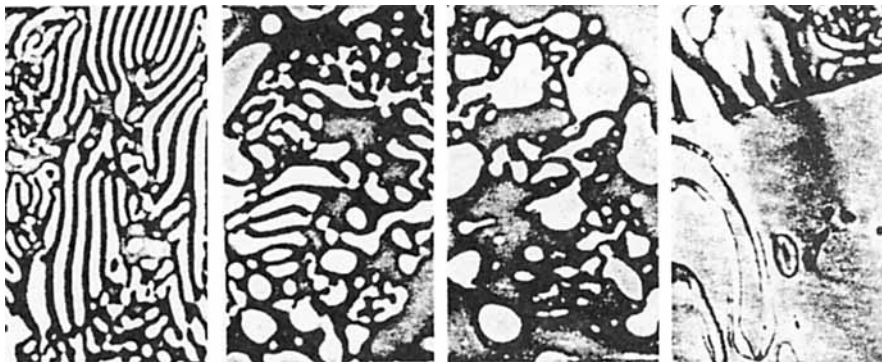
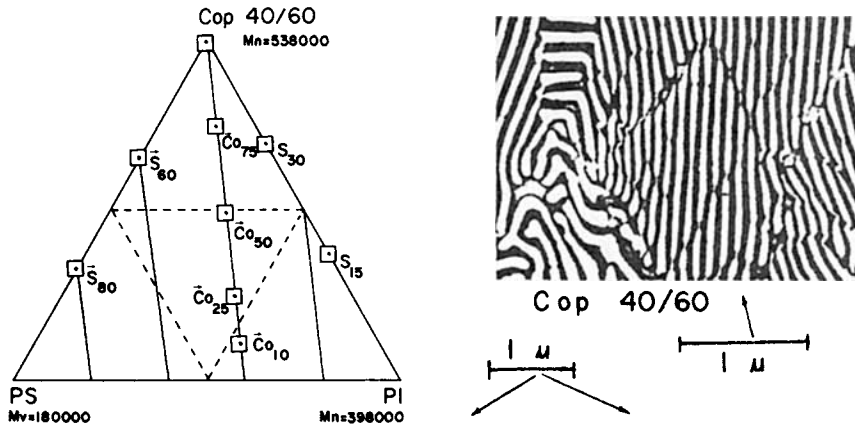


A-2-4

Fig. 2(b). Morphology of A system.

morphology. The weight composition ratio suggested lamellar structure that explained why the enlarged domain aligned itself in lamellar style. Incomplete solubilization and weight composition control accounted for the A-2-3 morphology. The net influence of weight composition ratio was obvious from A-2-4. In it, the phase separated domains remained in directional alignment.

This new approach was used to explain the results of Kawai and Inoue in 1970. In Figure 3, PS and PI are polystyrene and polyisoprene. The sample was film cast on water before TEM observation. The morphology in the top triangle was determined by a copolymer with 40/60 weight composition ratio and with short-rod structure (primary influence). Co75, Co50, Co25, and Co10 all shifted into the short rod region (secondary influence), because isoprene was predominant in the copolymer. S60, S80 shifted likewise. In Co75 and S60 the morphologies of the dispersed phase (polystyrene) were characteristically rodlike. Co50 and Co25 positions in the central triangle showed incomplete solubilizing by the copolymer. Both homopolymers filled into their corresponding phases in the short-rod morphology region. S15 had its position in the sphere region with polyisoprene predominant, and the morphology showed sphere distribution, as expected. The prediction that S80 should show polystyrene predominating short-rod distribution was



Co 75

Co 50

Co 25

Co 10



S 60

S 80

S 30

S 15

Fig. 3. Three-component system by Inoue and Kawai. Co_{75} : Weight composition ratio of Cop 40/60 is 75% and overall PS/PI weight composition ratio (i.e. Co 40/60 is included) remains 40/60. S_{30} : Overall weight composition ratio of polystyrene is 30%.

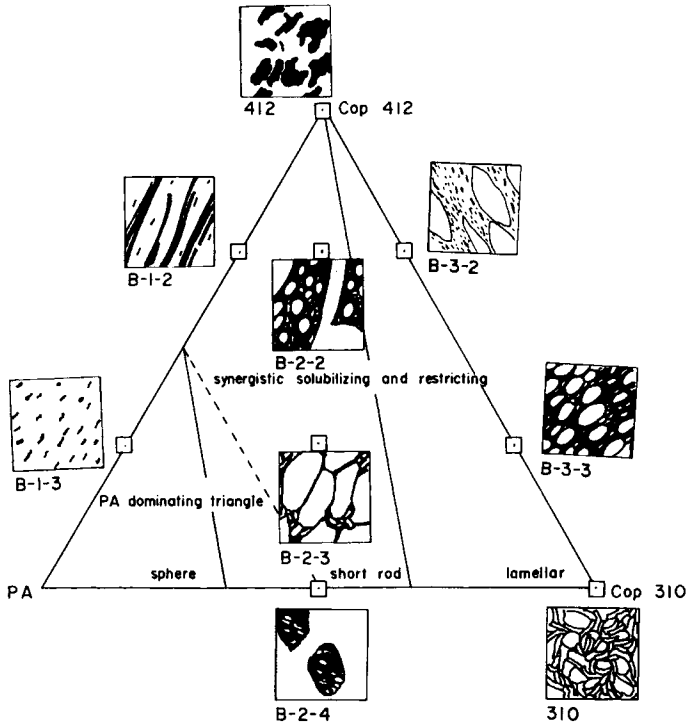


Fig. 4(a). Scheme of B system.

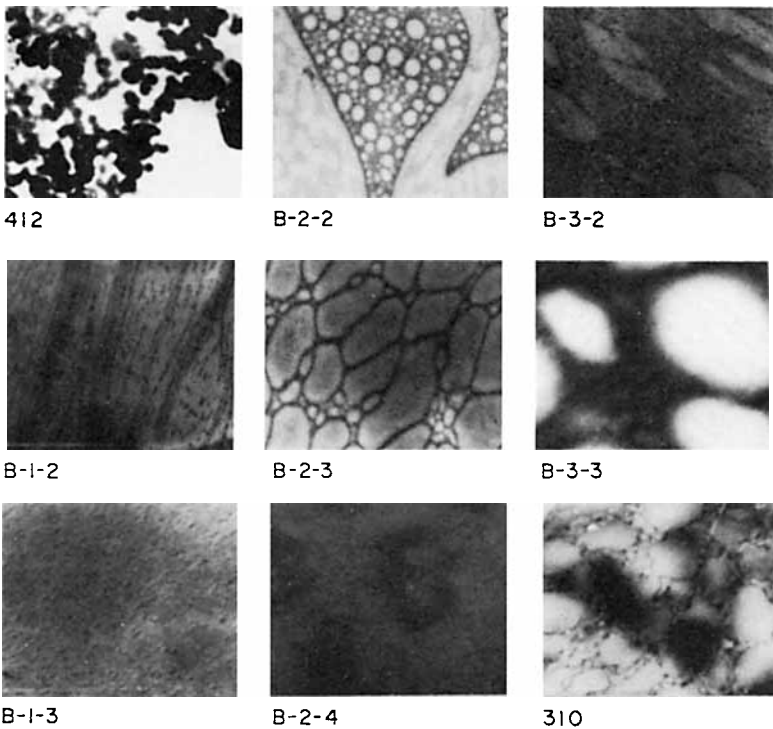


Fig. 4(b). Morphology of B system.

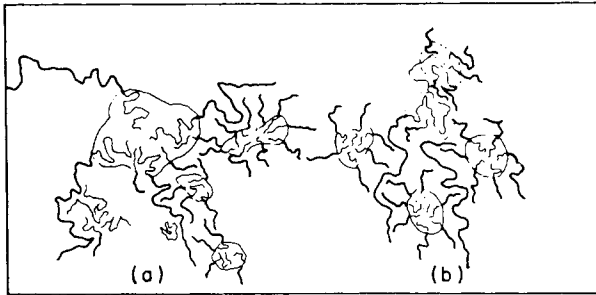


Fig. 5. Possible spacial arrangement of B-3-2 (a) and B-3-3 (b).

also verified. The severe phase separation in Co10 resulted from the insufficiency of copolymer influences and the incompatibility between polystyrene and polyisoprene. Therefore, the scheme has proved to be a powerful tool in the morphology change predictions in like systems.

The same rules held for system B [Figs. 4(a) and 4(b)] illustrated by 412 B-1-2 and B-1-3. However, the block copolymer with low molecular weight was "restricted" by the higher molecular weight copolymer chain ("emulsified," as described by Riess). This effect could also be seen in B-3-2 and B-3-3. The morphology of B-3-2 was predicted to be dominated by copolymer 412; copolymer 310 was restricted around it. This explained the fact that a very small white domain resided around a larger domain. The possible spacial arrangement of the molecular chain is shown in Figure 5(a). In B-3-3 copolymer 310 dominated with a short-rod morphology and which was expected to be partially emulsified by copolymer 412. The possible spacial arrangement of the molecular chain is shown in Figure 5(b). The incomplete solubilizing effect was offset by the synergistic solubilizing effect of two copolymers in the central triangle. The macrophase separation region was limited to the poly(α -methylstyrene)-rich triangle, as shown in Figure 6.

CONCLUSION

The morphology prediction for the three components blend in a triangular phase diagram was made possible. Two factors are considered to be the most crucial: the morphology of the predominant polymer and the weight composition ratio. The first factor (major one) decides the basic morphology and the second factor (minor one) influences the morphology of the dispersed

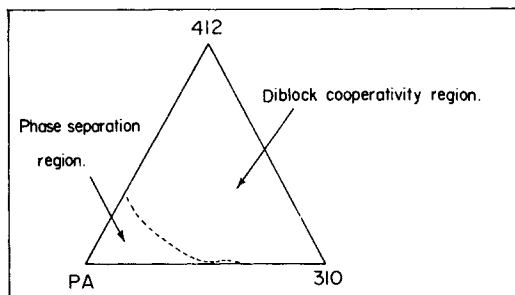


Fig. 6. Cooperative influence of diblocks on morphology.

phase. The morphology of the central triangle is largely influenced by the molecular weight and the composition of the copolymer. When two copolymers are present, the synergistic solubilizing effect must be taken into account.

References

1. T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, *J. Polym. Sci. (A-2)*, **7**, 1283 (1969).
2. T. Inoue, T. Soen, T. Hashimoto, and H. Kawai, in *Block Copolymers*, S. L. Aggarwal, Ed., Plenum, New York, 1970, pp. 53-79.
3. T. Uchida, T. Soen, T. Inoue, and H. Kawai, *J. Polym. Sci. (A-2)*, **10**, 101 (1972).
4. T. Inoue, T. Soen, H. Kawai, M. Fukatsu, and M. Kurata, *J. Polym. Sci., B*, **6**, 75 (1968).
5. D. R. Paul and J. W. Barlow, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C18**, 109 (1980).
6. A. E. Skoulios, in *Sagamore Conference on Block and Graft Copolymer*, J. J. Burke and V. Weiss, Eds., Syracuse Clause Press, New York, 1973, p. 125.
7. S. L. Aggarwal, *Polymer*, **17**, 938 (1976).
8. G. Riess, *J. Macromol. Sci. Phys. B*, **17**(2), 355 (1980).
9. H. Gilman, *J. Am. Chem. Soc.*, **62**, 2333 (1940).
10. H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **71**, 1499 (1948).
11. A. V. Tobolsky and C. E. Rogers, *Rubber Chem. Technol.*, **33**, 655 (1960).
12. H. Y. Chen, *Anal. Chem.*, **34**, 1134 (1962).
13. H. Y. Chen, *Rubber Chem. Technol.*, **41**, 47 (1968).

Received February 24, 1984

Accepted June 1, 1984