Phase separation in polymer blends comprising copolymers: 6. Effect of molecular architecture of block copolymers

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(Received 8 August 1985)

To study the effect of the molecular architecture of a copolymer on its miscibility with corresponding homopolymers a series of block copolymers of styrene and isoprene with diblock, triblock and four-arm star architectures have been prepared and the morphologies of the blends of the copolymers and polyisoprene with different molecular weights have been examined by electron microscopy. The results show that miscibility varies in the sequence diblock > triblock > four-arm star copolymers. This sequence is in the opposite direction to the variation of the architectural complexity of the block copolymers, i.e. the more complex is molecular architecture, the greater is conformation restriction in microdomain formation and the less is solubility of homopolymer in corresponding domains.

(Keywords: phase separation; miscibility; polymer blends; electron microscopy; block copolymer)

INTRODUCTION

Microphase separation of block copolymers comprising two immiscible block chains has been thoroughly studied. Much theoretical work, including papers by Meier[1,2] and Helfand[3,4], has established the equilibrium morphologies and the relations between the shape, size and arrangement of the microdomain structure and the molecular parameters of block copolymers. The predictions of theory have been found in good agreement with many of experimental results[5,6]. However, this is not the case for studied blends of copolymer and homopolymer. As to the solubilization limit of a homopolymer in the corresponding domains of copolymers, there is apparent discrepancy in the literature. The only theory[7] dealing with this subject predicts solubility that is about one order of magnitude less than some experimental results[8]. Based on a systematical examination of blends of diblock copolymers of styrene and isoprene and homo PI and/or homo PS by electron microscopy, Inoue *et al.*[9] concluded that a homopolymer is solubilized in corresponding domains of the blocks if the molecular weight of the former is less than that of the latter; otherwise the homopolymer and the copolymer are immiscible and macrophase separation occurs. Eastmond[11] and Eastmond and Philips[10] studied AB-crosslinked copolymers (ABCP) of relatively complicated structure (for ABCP, a representative structure is two polymer A chains crosslinked by a B chain) and found that the miscibility of ABCP and homopolymer A is rather limited and that macrophase separation occurs.

Previously in this series[12] morphologies of blends of styrene–butadiene graft copolymer of quite simple structure and of homopolystyrene have been studied. Miscibility varies with molecular weight ratio of the homo PS to the PS branches and the blends show considerable solubilization when the ratio is ~ 1. This conclusion is generally in accordance with that found by Inoue *et al.*[9]. However, for blends of the ABCP comprising PS and polycarbonate chains and homopolymer B(PS)[13,14] the miscibility between the copolymer and homopolymer is very limited even when the molecular weight of homo B is far less than that of the B blocks. It should be noted that, instead of homopolymer A, homopolymer B is used for blends with the copolymer so that the ambiguity in the estimation of the effective molecular length of A in the copolymer is avoided and the results obtained are more convincing. The authors, on the basis of their results and published data have argued that miscibility is dependent on the architecture of the copolymer[13,14], and consider that the more complicated is the molecular architecture of a copolymer, the higher is the conformation restriction of the chains in the domains and the more difficult is the solubilization of homopolymer in the domains. Nevertheless, both the graft copolymer and ABCP studied were of molecular polydispersity and, although the molecular architectures of the graft copolymer and ABCP were clearly different, their full characterization is difficult. Besides, as this conclusion has been reached by comparing the results of a variety of copolymers, i.e. styrene–isoprene block copolymer, styrene–butadiene graft copolymer and ABCPs of PS and polycarbonate, the effect caused by the difference in chemical nature of component polymer chains could not be excluded. To study the architectural effect more systematically and minimize the effects of other factors, in this paper a series of copolymers with molecular monodispersity and well-defined structure—diblock, triblock and four-arm star block copolymers—were prepared and blended with homopolymer. The morphological study of the blends clearly demonstrates the effect of the molecular architecture of the copolymers.

EXPERIMENTAL

Synthesis and characterization of polymers

Polystyrene (PS), polyisoprene (PI) and diblock (SI), triblock (SIS) and four-arm star block (F-SI) styrene–isoprene copolymers were prepared by anionic polymerization. Cyclohexane and sec-butyllithium were used as solvent and initiator respectively. The polymerization temperature was kept at 50°C. Styrene and isoprene were polymerized successively to produce SI; SIS was produced by coupling of the active SI ions with 1,2-dibromoethane and F-SI samples were prepared by coupling SI ions with tetrachlorosilane. To remove uncoupled SI species, SIS and F-SI products were twice fractionated in toluene–ethanol. The purified triblock and four-arm star block products were proved to be monodisperse by g.p.c. measurements.

The molecular weights of the PI and copolymers were measured by membrane or vapour-pressure osmometry with toluene as solvent. The molecular weight distributions and compositions of the copolymers were determined by g.p.c. and ultra-violet spectrophotometry at 262 nm. The number-average molecular weights are listed in *Tables 1* and *2*, where $\bar{M}_n(S)$ and $\bar{M}_n(I)$, the molecular weights of PS and PI blocks respectively in the copolymers, are calculated from the total molecular weights $\bar{M}_n$ and compositions. In *Table 2* $\bar{M}_n(S)$ and $\bar{M}_n(I)$ of F-SI denote the molecular weights of PS and PI blocks in a single arm. The triblock structure of SIS can be confirmed by comparing the molecular weight of SIS and that of SI-2 from which SIS was prepared by coupling. Similarly, the four-arm structure of F-SI copolymers can be proved by comparing the molecular weights of F-SI-1, and SI-1 and of F-SI-2 and SI-2 respectively. For F-SI-3, the four-arm structure was defined by measuring the total molecular weight, composition and the molecular weight of a single PS arm, which was determined after selective degradation of polyisoprene blocks[15].

Blend preparation and electron microscope observations

All copolymers and blends were prepared as solvent-cast films for electron microscope observations. High-molecular-weight polystyrene (HPS, $\bar{M}_n = 457 \text{ kg mol}^{-1}$) was intentionally added in preparing the films to avoid ultramicrotoming at low temperature. All films had the same proportion of HPS (77%), which always constituted the matrix and facilitated ultramicrotoming at room temperature. As the molecular weight of HPS is much larger than any molecular weight of PS grafts in the copolymers studied here, the presence of HPS leaves virtually unaffected the morphologies of the copolymers and their blends with homo PI existing in the dispersed phase. In all blends the weight ratio of homo PI to the copolymer was 26/74. The blends were prepared by allowing a 4% solution of the polymer in benzene to evaporate slowly in Teflon cells with covers. The films formed in 6–7 days and were successively dried at room temperature and 80°C in a vacuum oven for 24 h and 3–4 days respectively. The films were stained with OsO_4 solution for 3–4 days and ultramicrotomed into ultrathin

sections. Sections of the films were examined in a Hitachi H500H electron microscope (75 kV). *Table 3* shows the weight percentages of the blends.

RESULTS

Blends of diblock copolymer SI and polyisoprene

The morphology of diblock copolymer SI-1 (14.3–11.7)* is shown in *Figure 1*. The domain sizes of PS and PI are of the order of 10 nm and 8 nm respectively. *Figure 2* presents typical morphology of the blend of SI-1 (14.3–11.7) and of PI-3 (9.1); the molecular weight of the latter is slightly less than that of PI segments in SI. In *Figure 2* the blend comprises the large-size dispersed phase while HPS forms the matrix. The size of the PI domains is increased to about 20–60 nm but without the appearance of macroscopic phase of homo PI. This indicates considerable dissolution of homo PI chains in the PI domains of the block copolymer. However, phase separation on the macroscopic scale takes place in the case of the blend of SI-1 and PI-4 (17.5) as shown in *Figure 3*. The upper region of the micrograph shows a typical morphology of microphase separation of the block copolymer distinct from the PI phase without any internal structure, which clearly indicates the immiscibility of homopolymer and copolymer. In addition, the blends of SI-1 with PI-5, PI-7 and PI-12 with higher molecular weights unexceptionally show macrophase separation between homopolymer and copolymer. Therefore, the variation of miscibility in blends of homopolymer and copolymer with the molecular ratio $\bar{M}_H/\bar{M}_B$, where $\bar{M}_H$ and $\bar{M}_B$ are the molecular weights of homopolymer and corresponding blocks in the copolymer respectively, observed here is in agreement with that suggested by Inoue et al.[9].

Table 2 Number-average molecular weights (kg mol^{-1}) of copolymers

Code	Type	PS (%)	$\bar{M}_n$	$\bar{M}_n(S)$	$\bar{M}_n(I)$
SI-1	diblock	55.0	26.0	14.3	11.7
SI-2	diblock	58.0	50.0	29.0	21.0
SIS	triblock	58.0	101	29.3	42.4
F-SI-1	four-arm	55.5	116	15.8	13.2
F-SI-2	four-arm	53.7	218	29.3	25.2
F-SI-3	four-arm	42.0	622	65.3	90.2

Table 3 Weight composition of the blends

Blend	HPS	Copolymer	Homo PI
For morphological study of copolymers	77	23	—
For morphological study of copolymer–homopolymer blends	77	17	6

*Here and elsewhere the numerical values indicate the molecular weights (kg mol^{-1}) of PS and PI blocks respectively.

Table 1 Number-average molecular weights (kg mol^{-1}) of PI

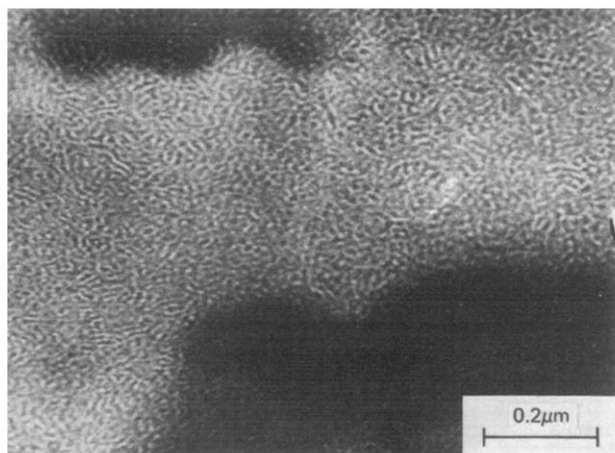| Code	PI-1	PI-2	PI-3	PI-4	PI-5	PI-7	PI-10	PI-11	PI-12
$\bar{M}_n$	6.5	7.9	9.1	17.5	20.9	35.5	61.5	89.8	119

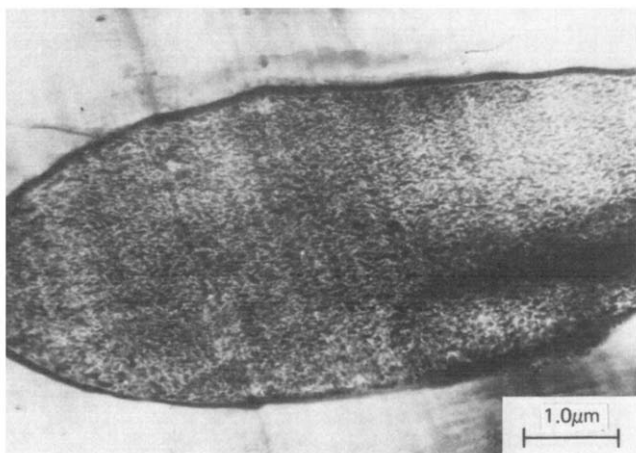**Figure 1** Morphology of diblock copolymer SI-1

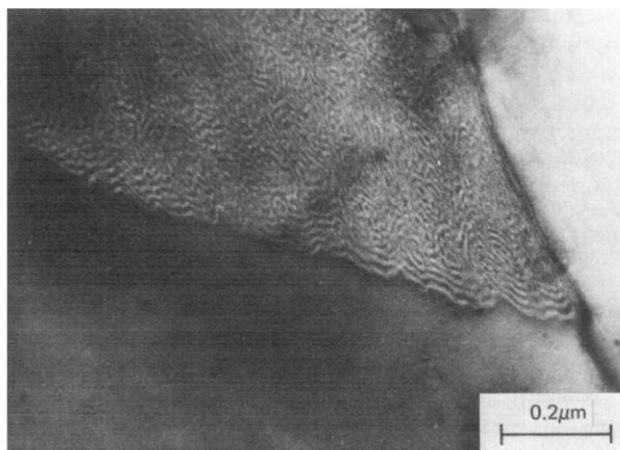**Figure 2** Electron micrograph of SI-1/PI-3 in HPS

Figure 3 Electron micrograph of SI-1/PI-4 in HPS

Blends of triblock copolymer SIS and PI

Although triblock copolymers usually have many more applications than the corresponding diblocks, few published data concerning miscibility with corresponding homopolymers can be found. This section presents some results of morphological observations of blends of SIS and various polyisoprenes.

SIS(29.3–42.4–29.3) exhibits typical lamellar structure, as shown in *Figure 4*, in which the size of PS and PI domains are of the order of 11 nm and 10 nm, respectively. *Figure 5*, for the blend of SIS and PI-3(9.1),

shows a clear increase of the PI domains to about 15–40 nm without the presence of PI macrodomains, which indicates considerable miscibility of copolymer and homopolymer.

The morphology of the blend of SIS and PI-5(20.9) is more interesting as the molecular weight of PI-5 is almost one-half of that of the central blocks in the copolymer and a homogeneous morphology on the macroscopic scale would be expected from arguments of Inoue *et al.*[9]. However, the micrographs of the blend (*Figure 6*) clearly show macroscopic phase separation between PI and copolymer. In comparison with the morphology of SIS
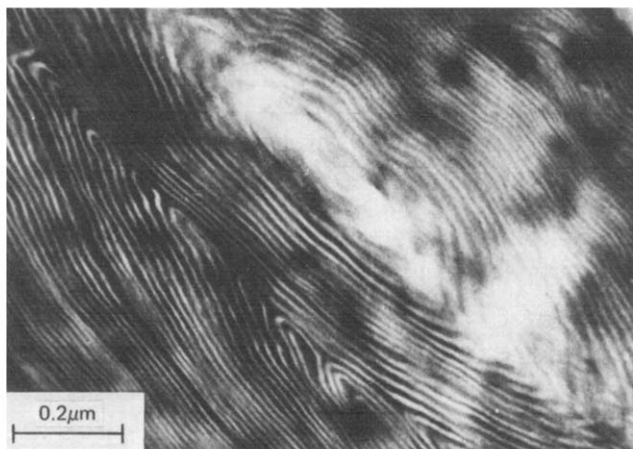

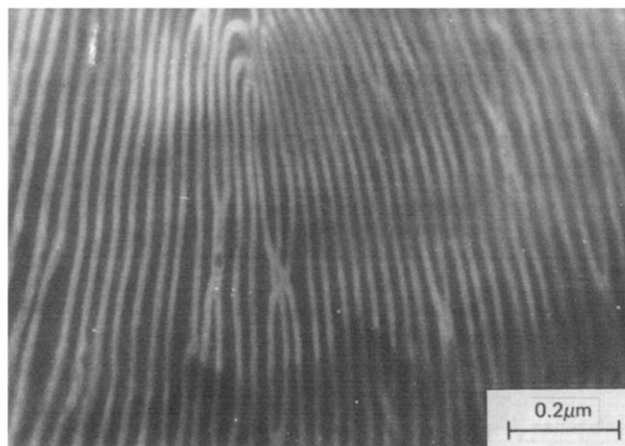**Figure 4** Electron micrograph of SIS
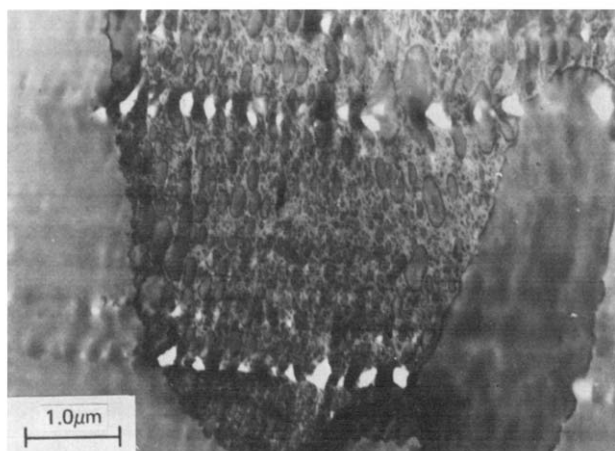

Figure 5 Electron micrograph of SIS/PI-3

Figure 6 Electron micrograph of SIS/PI-5 in HPS

itself, the details of the microphase structure have clearly changed, which may indicate some solubilization of homo PI chains in corresponding domains. It is interesting to note that, by contrast with diblock copolymer, the blend of triblock SIS and homo PI shows macroscopic phase separation when the value of $\bar{M}_H/\bar{M}_B$ is only ~ 0.5. Furthermore, a series of blends of SIS and PI of higher molecular weights were examined and all showed macrophase separation.

Blends of four-arm star block copolymer F-SI and PI

Blends of three four-arm star block copolymers of different molecular weights with various polyisoprenes were studied morphologically. Polyisoprene formed the central blocks in the copolymers and there is a common junction point for each four PI blocks. The molecular weights indicated below apply to single PI arms.

For F-SI-1(15.8–13.2), three blends with PI-1(6.5), PI-2(7.9) and PI-4(17.4) were studied. A common characteristic of the blends is the presence of macroscopic phase separation of homopolymer from copolymer. It is noticeable that among the homopolymers used here the molecular weight of PI-1 is only about one-half of that of corresponding blocks in the copolymer.

This limited miscibility of the four-arm copolymer and homopolymer is confirmed in blends comprising copolymer F-SI-2(29.3 – 25.2). *Figure 7* shows the morphology of the blend of F-SI-2 and PI-3(9.1). Although the molecular weight of PI-3 is only about one-third of that of the PI block, homo PI phase with dimensions as
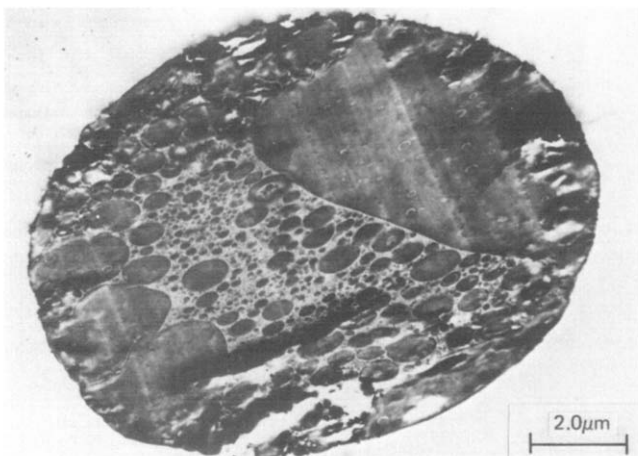

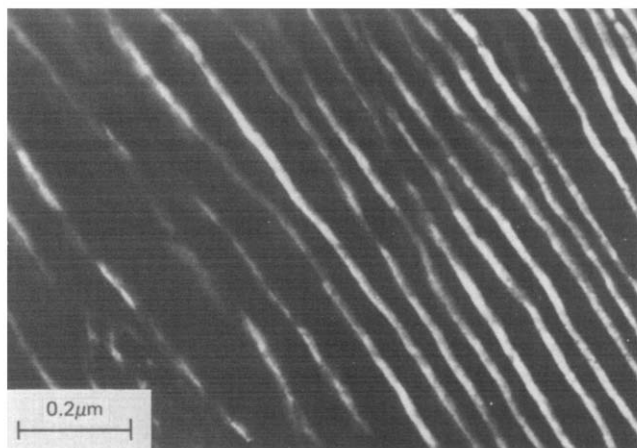**Figure 7** Electron micrograph of F-SI-2/PI-3 in HPS

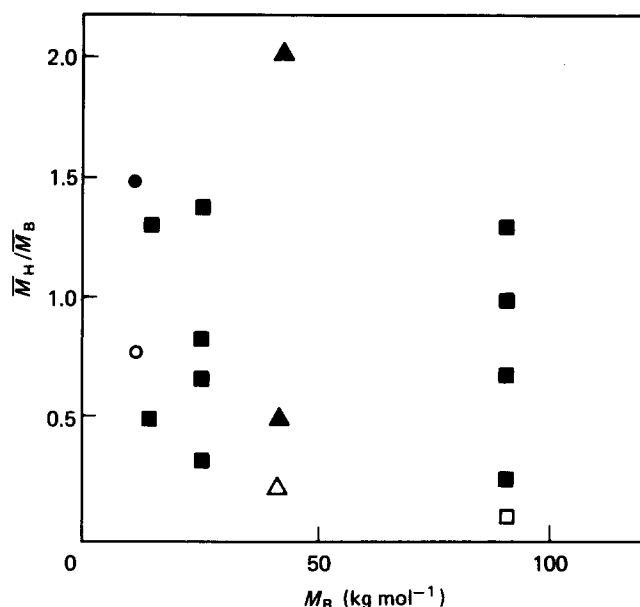**Figure 8** Electron micrograph of F-SI-3/PI-1

Figure 9 Miscibility of blends comprising copolymers with different architectures. (○, ●), diblock copolymers; (△, ▲), triblock copolymers; (□, ■), four-arm star block copolymers. Open symbols (○, △, □) indicate miscible blends and solid symbols (●, ▲, ■) indicate immiscible blends

large as 5–10 μm still exists in the dispersed blend particles. In blends of F-SI-2 with homo PI of higher molecular weight, as expected, macrophase separation remains the main morphological feature.

The only example showing apparent miscibility is the blend of F-SI-3(65–90) and PI-1(6.5). In *Figure 8*, it can be seen that the copolymer keeps its lamellar structure with enlarged PI domains of the size about 100 nm by incorporation of low molecular weight PI. However, macrophase separation can be clearly seen in the blend of copolymer and PI-5(20.9), in which, however, $\bar{M}_H/\bar{M}_B$ is only 0.23. As expected, all the blends of F-SI-3 and PI of higher molecular weight exhibit the morphology characteristic of macrophase separation of copolymer from homopolymer.

DISCUSSION

A summary of the variation of miscibility with molecular parameters and copolymer structure is shown in *Figure 9*. Critical values of $\bar{M}_H/\bar{M}_B$ appear to exist for certain various types of copolymer. If the $\bar{M}_H/\bar{M}_B$ value of a blend is less than this critical value, the blend components are miscible, otherwise they are immiscible. Most interestingly this critical value apparently depends on the molecular architecture of the copolymer. The experiments showed that the critical values are ~ 1, ~ 0.5 and ~ 0.25 for the blends of diblock, triblock and four-arm block copolymers respectively. We have no intention of emphasizing the values themselves, since they might be influenced by some other factors, such as the total molecular weight and composition of the copolymer, and conditions of blend preparation. However, the data clearly show a regular sequence of miscibility variation, i.e. diblock > triblock > four-arm block. Since all the copolymers studied are monodisperse with respect to molecular weight and have similar composition, it is reasonable to attribute this regular variation of miscibility to the difference in molecular architecture.
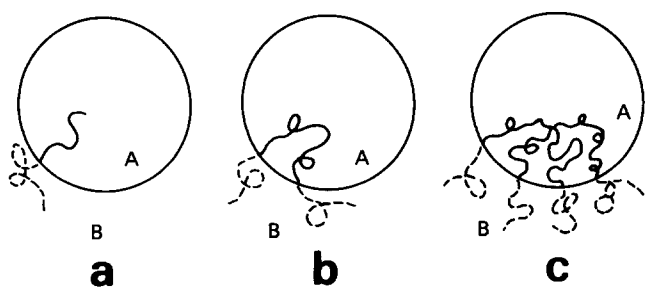
Figure 10 Schematic representations of microphase separation in (a) diblock copolymer, (b) triblock copolymer and (c) four-arm star block copolymer

Meier[7] has treated miscibility of homopolymer and relevant copolymer theoretically. The solubility of a homopolymer in domains of corresponding chains of the copolymer predicted by his theory is very limited and less than the experimental results by one order of magnitude. In a statistical mechanical study of miscibility Xie *et al.*[16] argued that this discrepancy might come from Meier's assumption that the segment densities of homopolymer chains and the corresponding blocks of the copolymer are uniform in the whole solubilized region. This assumption may overestimate the conformation entropy loss of the free and bound chains and therefore makes the entropy loss exceed the driving force of solubilization, i.e. entropy of mixing (combinatorial entropy). For the simplest case, i.e. blend of homopolymer and diblock copolymer with lamellar structure, assuming a gradient density model of homopolymer and copolymer chains, it was demonstrated that for $M_H/M_B < 1$ in the whole composition range the combinatorial entropy will overcome the entropy loss of the chains of homopolymer and corresponding blocks of block copolymer and will make the free energy of mixing negative. Obviously, this argument cannot be extended to copolymers with more complicated structures without taking the architectural difference fully into account.

As shown in *Figure 10* for diblock copolymer any block chains in the domains have a junction point in the interface region while the other end is free. The thermodynamic requirement of uniform density in the domains can be satisfied if the chains assume some unfavourable conformations that entail entropy loss. In the case of triblock copolymer, each central block has two junction points in the interface region, which results in more conformation restriction and more entropy loss because of the requirement for uniform segment density.

As for the central blocks of four-arm block copolymer, besides the restriction of keeping the A–B junction points in the interface region, the common junction for the four central blocks results in a complicated structure that entails even more entropy loss for keeping uniform density in the domains. The essence of the conditional solubilization of homopolymer and corresponding chains of copolymer in spite of their apparent chemical identity is associated with the unfavourable environment in the domains of corresponding blocks, i.e. the solubilized homopolymer chains have to assume unfavourable conformations that entail more entropy loss. Qualitatively, it appears that this extra entropy loss is significant if the blocks in the domains have more conformation restrictions. A fair inference from this idea is that the miscibility should vary in the sequence: diblock > triblock > four-arm block copolymers. This simple argument explains initially the experimental results in this paper. More fundamental and accurate explanation will be dependent on a further study of the statistical theory.

ACKNOWLEDGEMENTS

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