Phase separation in polymer blends comprising copolymers: 4. Polycarbonate/polystyrene ABCP system

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An AB-crosslinked copolymer (ABCP) with polycarbonate as A-chain and polystyrene as B-chain was prepared and characterized. A series of blends of the ABCP and homopolystyrene fractions with different molecular weights were prepared and examined by electron microscopy. The results show that the miscibility between the homopolymer and the like chains in the copolymer is limited even if the molecular weight of the former is much less than that of the latter. Considering the relatively large miscibility in diblock copolymer/homopolymer blends and the limited miscibility in ABCP/homopolymer-A blends reported in literature, this study leads to an argument that the molecular architecture of a copolymer is an important factor governing its miscibility with homopolymer. The relatively complicated architecture of ABCPs causing more restriction to the chain conformation might be one of the main reasons for its low miscibility with homopolymers.

(Keywords: phase separation; miscibility; polymer blends; electron microscopy; polycarbonate; polystyrene)

INTRODUCTION

The outstanding success on achieving a desirable combination of toughness of rubbery polymers and high modulus of glassy polymers in HIPS and ABS has stimulated many studies on the relationship between the morphologies and the properties of such *in-situ* polymerized multicomponent polymers[1]. It is established that the valuable mechanical properties of the blends are closely associated with the particular morphology—the cellular structure of the dispersed rubber-phase, which has considerably enlarged its volume fraction by incorporating a large amount of the glassy homopolymer. This morphology gives rise to a very efficient use of the high modulus of the matrix. In recent years, several approaches have been attempted to make blends of copolymer and homopolymer with new morphologies[2-5]. Obviously, deeper and better understanding of the miscibility rule between copolymer and the corresponding homopolymer is necessary for achieving designed morphologies and improved properties.

As far as the miscibility between a homopolymer and the like segments in the copolymer, most published works concentrate on systems containing polystyrene, polydiene and their block copolymers. Based on systematic electron microscope observations, Inoue and Kawai[6] presented a rule describing the miscibility—homopolymer can be considerably solubilized in the region of the corresponding blocks of the copolymer when the molecular weight of the former is about the same or less than that of the latter. Otherwise, the homopolymer separates from the copolymer on the macroscopic scale. This conclusion is in agreement with the results obtained earlier from turbidity measurements of blend films[7]. Many micrographs of homopolymer/copolymer blends which are consistent with Inoue and Kawai's conclusion can be found in the literature dealing with the properties of blends[8,9]. In a previous work of this series[10], we studied a series of blends of graft copolymer of styrene and butadiene and homopolystyrene with different molecular weight combinations; a regular variation of morphology with the relative molecular weight of the free PS chains to that of the PS grafts was found. This variation, in general, can be understood in terms of Inoue and Kawai's conclusion but with some peculiarities associated with polydispersity of the molecular weight of the component polymers. It is worthwhile to point out that, though the conclusion of Inoue and Kawai is drawn and finds support mainly from the blends of diblock copolymers and homopolymers based on styrene and diene, it has been regarded as a general rule governing the miscibility between homopolymer and copolymer[11]. However, Eastmond *et al.*[12] presented results of electron microscope observations on so-called ABCPs (AB crosslinked polymers) which cannot be understood in the light of Inoue and Kawai's conclusion. The ABCPs were produced by initiating polymerization of monomer B at some active sites in chains of prepolymer A. Combination termination between the propagating B macroradicals produces crosslinks between the A-chains. At low conversion of B, solubilized mixture of AB copolymer and the unreacted prepolymer were obtained. As a variety of monomers, not being confined to diene and styrene, can be introduced as A and B chains, the morphological studies of ABCPs and their blends have greatly extended the research scope of the miscibility in blends of copolymers and homopolymer[13]. According to Eastmond, blends of AB copolymer and a large proportion of prepolymer A, which should have the same molecular weight as the A-chains in the copolymer, exhibit macroscopic phase separation indicating their limited miscibility. Apparently, this result is different from that obtained from blends of diblock of styrene and diene with polystyrene. In searching for the reason for this discrepancy, a question has arisen about the estimation of

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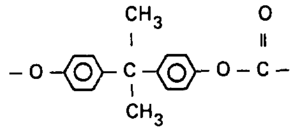
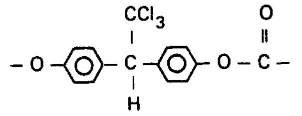
the effective length of A-chain in ABCP. AB-junctions must be located at the interface between the domains and matrix. Thus, the effective chain length of the segments A, which determines its miscibility with the homopolymer chains, should be the length from an A-B junction to the end. Apparently, this length of A-chains in the copolymer is somewhat shorter than that in prepolymer A[10,12]. In order to explore the miscibility in ABCP blends without any ambiguity connected with change of the effective A-chain length, in this study, instead of prepolymer A, several homopolymer B samples with different average molecular weights were used to make blends which were systematically examined by electronic microscopy.

EXPERIMENTAL

Preparation of ABCP

Polycarbonate prepolymer containing $-CCl_3$ side groups was prepared by condensing an equimolar mixture of bisphenol-A and 1,1,1-trichloro-bis-2-(*p*-hydroxyphenyl)ethane with phosgene in dichloromethane in the presence of pyridine. The prepolymer has two types of repeating units (I and II) randomly arranged


$-O-C_6H_4-C(CH_3)_2-C_6H_4-O-C(=O)-$
(I)


$-O-C_6H_4-CH(CCl_3)-C_6H_4-O-C(=O)-$
(II)

After being dissolved and precipitated with dichloromethane/petroleum ether and subsequently with tetrahydrofuran/water systems, the product was used for preparing the ABCP. The number average molecular weight of the prepolymer measured osmometrically was 44000.

An ABCP having polycarbonate (Pcarb) as the A-chain and polystyrene (PS) as the B-chain was prepared in a solution of the prepolymer in styrene/dichloromethane in the presence of dimanganese decacabonyl as photo-initiator. Polymerization was initiated by a parallel beam of radiation (436 nm). The ABCP product was precipitated from the reaction mixture into a large quantity of petroleum ether and was dried under vacuum. As the polymerization was stopped far before gelation (at relative crosslinking index about 0.5) no gel was present in the product. Details of the preparation of ABCPs can be found elsewhere[14].

Characterization of ABCP

The overall composition (by weight) of the ABCP was Pcarb/PS 80/20 measured by n.m.r. It is certain that some unreacted polycarbonate exists in the product. However, as we will discuss later, no phase separation between the unreacted Pcarb chains and the like chains in the copolymer was found (*Figure 1*). Therefore, we believe that the presence of the prepolymer will not affect the validity of the subsequent discussion on the miscibility of the free and graft PS chains. In regard to this problem, the most important parameter of the copolymer is the molecular weight of polystyrene crosslinks (B-chains). In order to determine the parameter a selective degradation procedure for ABCPs with polycarbonate as the A-chain was used in which polycarbonate was degraded by a concentrated sodium hydroxide solution and the residual PS was extracted with an organic solvent[15]. In this study, we used a modified system and found that methanol/chlorobenzene system was suitable to degrade Pcarb in homogeneous solution. In the procedure used ABCP was dissolved in methanol/chlorobenzene (2/8 v/v) and the mixture was kept in a sealed tube, after being degassed to avoid possible contamination of the PS chains by the degradation and oxidation products of Pcarb. The tube was kept at 100°C for 13 days, the mixture was then poured into methanol to recover polystyrene. The molecular weight of the PS and its polydispersity were measured by g.p.c. (Shimadzu LC-3A). The results are shown in *Figure 2* and *Table 1*. A control test of prepolymer treated with methanol/chlorobenzene demonstrated that polycarbonate chains were completely destroyed as no precipitate was found when the reaction mixture was poured into a large quantity of methanol. Meanwhile, another test for a commercial polystyrene sample proved that both the average molecular weights of the PS and its distribution were almost unchanged under the conditions used for the selective degradation (original PS: $\bar{M}_w = 229000$, $\bar{M}_n = 109000$; PS recovered: $\bar{M}_w = 224000$, $\bar{M}_n = 105000$).

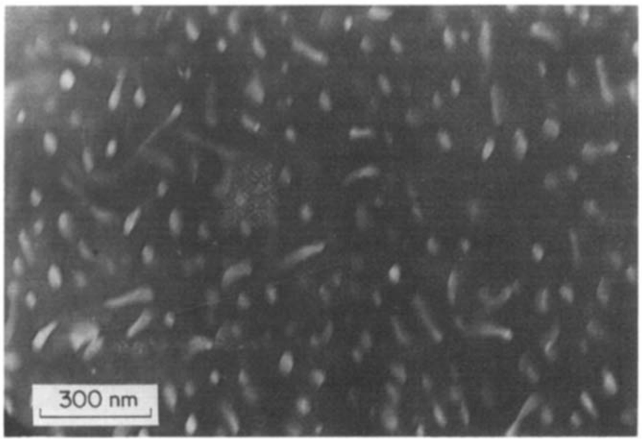


Figure 1 Morphology of ABCP. Pcarb appears dark

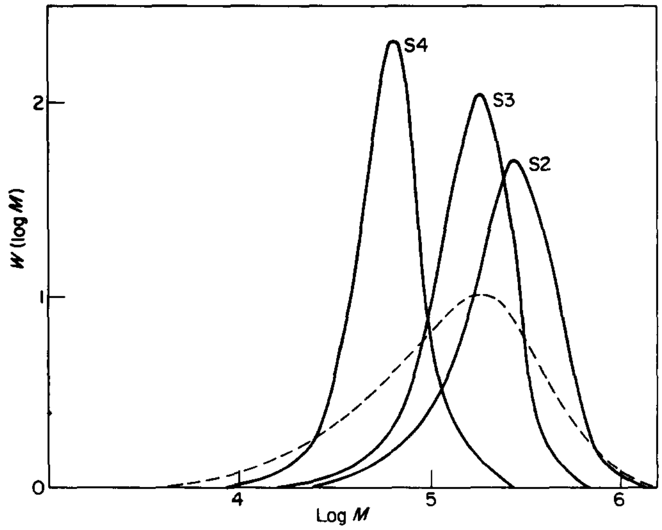


Figure 2 Molecular weight distributions of homopolystyrene S2, S3 and S4 (solid curves) and PS crosslinks (broken curve) in ABCP

Table 1 Molecular weights of homopolystyrene and PS crosslinks in ABCP in blends

	Molecular weight of homopolystyrene		
Blends	Code	$\bar{M}_w$	$\bar{M}_n$
B1	S1	$\bar{M}_\eta = 1500$	
B2	S2	281	186
B3	S3	178	137
B4	S4	68.8	56.9
B5	S5	14.4	13.7

In all the blends, molecular weight of PS chains in ABCP:

$$\bar{M}_w = 192,\ \bar{M}_n = 67.5$$

Polystyrene

High molecular weight polystyrene having viscosity-average molecular weight 1 500 000 (S1) was prepared by emulsion polymerization. A commercial polystyrene sample was purified and fractionated into nine fractions. The second (S2), fifth (S3) and ninth (S4) fractions were used for making the blends. A polystyrene sample (S5) having the smallest molecular weight was prepared by anionic polymerization.

Blend preparation

The ABCP was blended with polystyrene S1, S2, S3, S4 and S5 respectively in dichloroethane. The solutions were allowed to evaporate slowly in Teflon cells with covers and the films formed in 4–5 days. Residual solvent was removed by storing the films in a vacuum oven at ambient temperature for 3 days and subsequently at 70°C for two days.

Electron microscopy

Ultrathin sections of the blend films were obtained by using an ultramicrotome. As the ABCP and its blends provide sufficient natural contrast between the polycarbonate and polystyrene phases, the ultrathin sections were examined with a Hitatch H500H electronic microscope without staining.

RESULTS AND DISCUSSION

As the main aim of this study is to explore the effect of the molecular weights of the homopolystyrene and of the PS chains in the ABCP on the homopolymer–copolymer miscibility, the blends examined in this study were made with the same composition (ABCP/PS 20/80) but different molecular weight combinations of the homopolymer and the PS crosslinks, which is shown in *Table 1*.

Figure 1 shows the morphology of the ABCP itself. This is a typical morphology of microphase separation of copolymer—the minor component PS forms rod-like microdomains (30–50 nm diameter) dispersed in polycarbonate matrix. This morphology is similar to that presented by Eastmond for an ABCP in which the A-chain consists of only the repeating units (II)[12].

A typical micrograph of blend B1 at low magnification is shown in *Figure 3a*. In B1, the molecular weight of homopolymer S1 is about eight times as great as that of PS chains in the ABCP. *Figure 3a* clearly shows that some discrete ellipsoidal domains pervade the matrix. This morphology indicates macroscopic phase separation between copolymer and homopolymer. It is interesting to note that there are mainly two kinds of interior structures of the macrodomains shown in *Figures 3b* and *3c* respectively. Most of the domains present a typical morphology of microscopic phase separation similar to that of the ABCP itself, as shown in *Figure 1* but with a relatively high proportion of PS (*Figure 3b*). It is noticeable that in the middle of the domain in *Figure 3b* there is a large polystyrene region which might be attributed to homopolymer trapped in the process of the macrodomain formation. Some sections of B1 present macrodomains with apparent PS incorporation (*Figure 3c*). Considering the facts that the average molecular weight of the homopolymer in B1 is about eight times as great as that of the like segments in the ABCP and the size distribution of the occluded PS regions is broad, and some occlusions are as large as few microns, we may suppose that this incorporated PS homopolymer is virtually trapped rather than

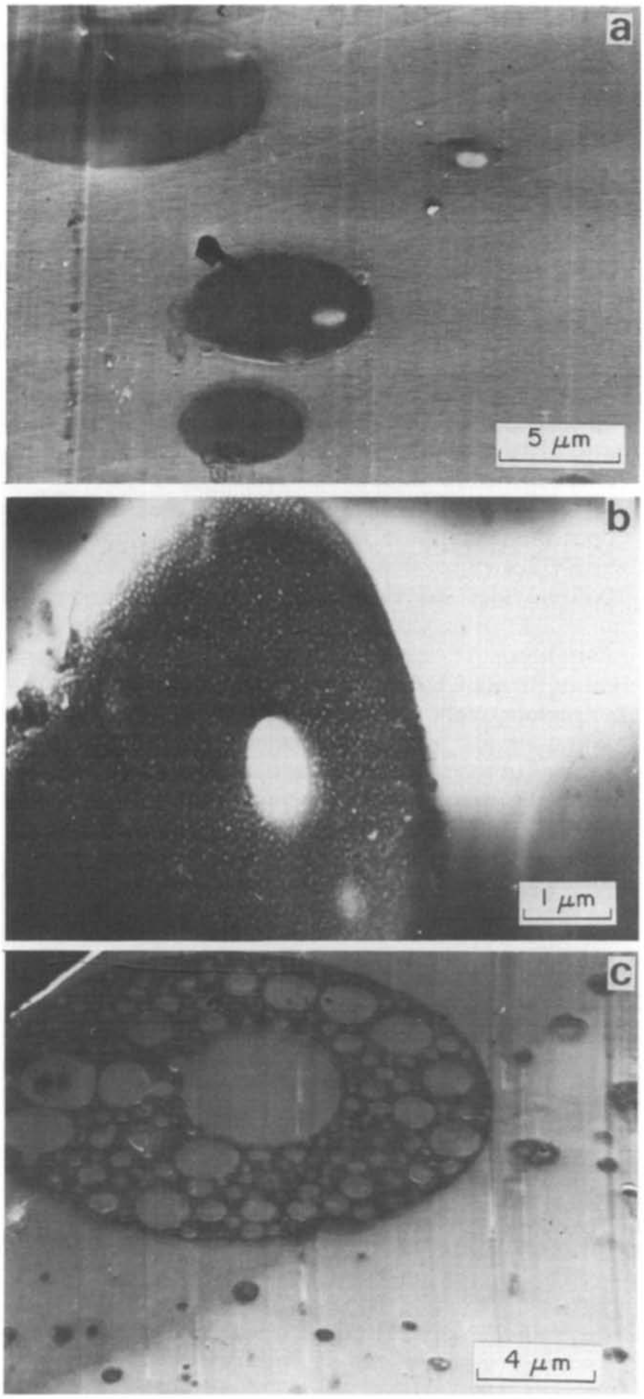


Figure 3 Electron micrographs of blend B1

solubilized. It is understood that the coexistence of different interior morphologies of the dispersed phase may reflect the non-equilibrium nature of the blend films. Nevertheless, as to the problem we are concerned with in this study, phase separation of the homopolymer and copolymer on a macroscopic scale is of more importance. Therefore, the non-equilibrium situation affecting the morphological details of the dispersed phase will not seriously interfere with our discussion.

The relationship between the molecular weights of homopolystyrene S2 and PS segments in the ABCP is clearly revealed in *Figure 2*. In this case, the average molecular weight of the homopolystyrene remains considerably larger than that of PS chains in the ABCP although their molecular weight distribution curves apparently overlap each other. However, the morphological character of blend B2 is still similar to that of B1, i.e. copolymer macrodomains of micron size exhibiting distinct microphase separation randomly pervade in the homopolystyrene matrix. One of the micrographs of B2 at larger magnification is shown in *Figure 4* and reveals a distinct boundary between the copolymer and homopolymer phases.

In the case of B3 there is an interesting combination of the molecular weight, i.e. weight-average molecular weight of homopolymer S3 is very close to that of PS chains in the ABCP and most of their molecular weight distribution curves overlap (*Figure 2*). Recalling the conclusion given by Inoue and Kawai[6] and our previous experimental results on homopolymer and graft copolymer[10] with this kind of molecular weight combination, we may expect considerable miscibility in the blend. However, the micrographs of B3 (*Figures 5a* and *5b*) are characterized by the existence of a dispersed copolymer-rich phase separated from the homopolymer matrix illustrating that, in general, miscibility between the homopolymer and the like chains in the copolymer is limited. It is noticeable that the size of polystyrene microdomains is apparently enlarged in comparison with that of the ABCP itself, which may imply that some low molecular weight polystyrene is solubilized in the block microdomains. Meanwhile, some polycarbonate microdomains in the shapes of spheres and loops can be found in the PS matrix. These morphological features, which have been reported in our previous work[10], can be regarded as a result of a trend to intermixing homopolystyrene and copolymer.

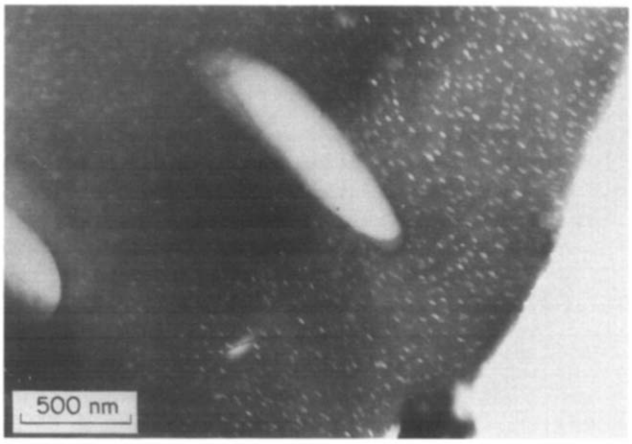


Figure 4 Electron micrographs of blend B2

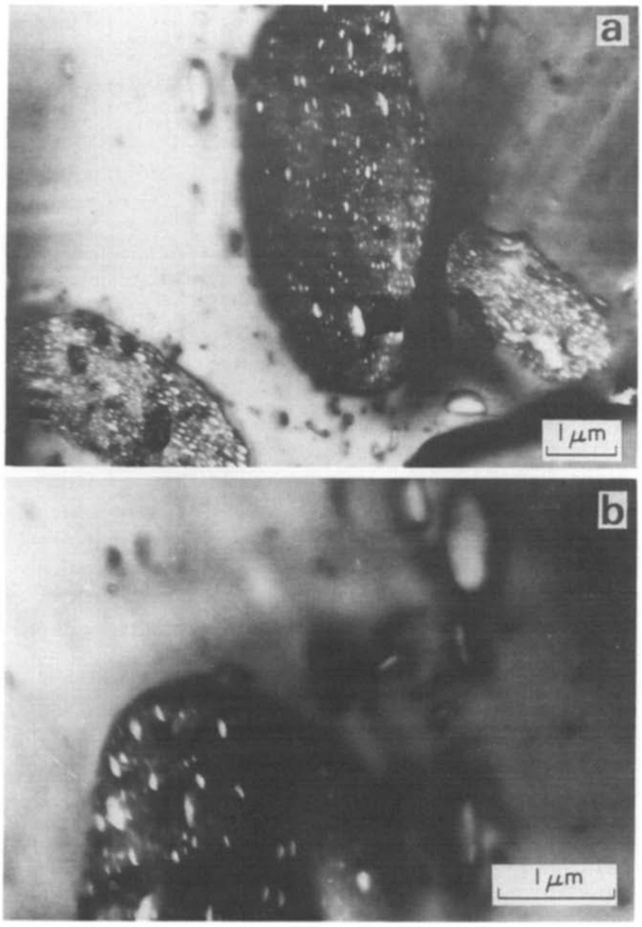


Figure 5 Electron micrographs of blend B3

A comparison between molecular weight distributions of S4 and the PS segments in the ABCP can be found in *Figure 2*. The average molecular weight of the former is apparently less than that of the latter and the molecular weight distribution of S4 overlaps with only the low molecular weight part of that in ABCP. However, in blend B4, microphase separation between the copolymer and homopolymer remains the main morphological feature (*Figure 6*). In the disc-like macrodomains, polystyrene microdomains are enlarged to about 100 nm.

The last blend under investigation is B5 with an extreme molecular weight combination, i.e. the molecular weight of anionic polymerized polystyrene S5 is 14000, only about one quarter of that of PS chains in the ABCP. For this blend, following the argument of Inoue and Kawai, we might expect a simple morphology, namely, a homogeneous system on a macroscopic scale with microphase separation between the phase of Pcarb chains and the phase comprising homopolystyrene and the same type chains in the ABCP. However, this blend presents complicated morphologies. Representative selections of the micrographs of B5 are shown in *Figure 7*. First, the morphology which can be found in most sections and hence can be regarded as predominating (*Figure 7a*), is similar to those of the previous blends. However, as to the interior structure of the domains, there is a relatively large proportion of polystyrene. As much homopolymer is incorporated, the original microphase structure of the copolymer is partially destroyed and the regular microphase separation is not fully developed.

Another type of morphology in B5, showing macrophase separation between the component polymers but

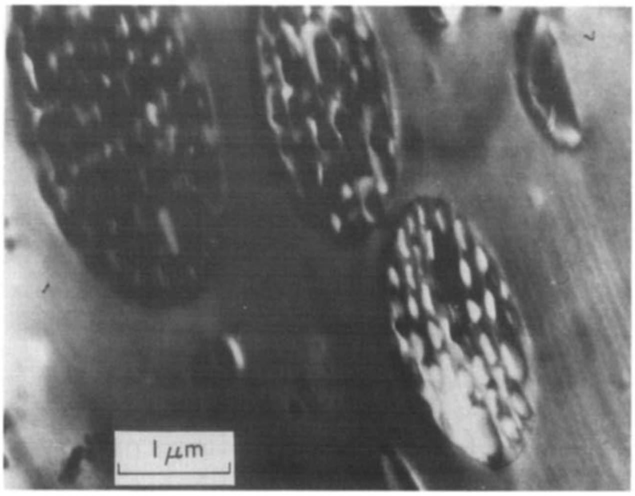


Figure 6 Electron micrographs of blend B4

with a reverse phase relationship, exists in some sections, where the minor component of the blend—the copolymer—constitutes the continuous phase with clear microphase separation and the major component, homopolystyrene, in turn becomes the dispersed phase. *Figure 7b* shows this morphology at higher magnification with emphasis on the boundary between the phases. Eastmond and one of the present authors reported a similar phenomenon for simple blends of poly(methyl methacrylate) and polycarbonate, i.e. both the normal and reverse phase separation exist in the same films. *Figure 7a* and *7b*, though they have different phase relationships, actually show common limited solubility between the component polymers.

That different morphologies could be found in the same blend, even sometimes in the same section, is a common phenomenon for the blend films being studied. This is obviously a reflection of the non-equilibrium of the films. It is widely accepted that true equilibrium is never achieved for the solvent cast blend films because the transfer of macromolecules between phases through diffusion is too slow to maintain equilibrium conditions during the process of solvent removal[12,16]. In this study, as the copolymer is the minor component, it should form droplets within the major homopolymer matrix during the process of solvent evaporation. Transfer of trapped homopolymer from the droplets to the matrix is controlled by many kinetic factors, for example, rate of solvent evaporation, local viscosity, size of the droplets and amount of residual solvent, and so on. Obviously, these factors cannot be kept consistent for the whole film. Therefore, the appearance of a variety of morphologies in macrodomains is almost inevitable. However, in this study, the main interests are not in the detailed morphology and composition within the macrodomains. The matter of interest is whether the copolymer and homopolymer in the blend undergo macroscopic phase separation. Therefore, this inevitable deviation of the films from their equilibrium state should not affect the validity of our discussion. In fact, as for the solvent casting procedure the initial system is homogeneous, appearance of any heterogeneity on a macroscopic scale, which does exist in all the blends studied in this paper, must be something required by a state closer to equilibrium. This argument, of course has a premise that the system of homopolymer/copolymer/solvent making the blends has a normal phase diagram in which, as the total proportion of the polymers increases, both sides of the binodal become closer to the solvent–copolymer and solvent–homopolymer lines.

In summary, the sequence of the morphologies leads to the conclusion that the solubility between homopolymer and the like chains in the ABCP is limited. This conclusion is based on systematic examination of a series of blends covering a wider range of molecular weight combinations, including an extreme case in which the molecular weight of the homopolymer is much less than that of the like segments in the copolymer. Moreover, in this study, the possible uncertainty about the effective length of A-chain in ABCP is averted by using homopolymer B. Thus, this study provides strong support for the argument about the immiscibility of molecules of multicomponent polymers and homopolymers of the individual component[12]. However, this low miscibility, in our opinion, is closely associated with the structural complexity of the copolymer under investigation.

In fact, even with regard to the behaviour of microphase separation, ABCPs exhibit some apparent differences in comparison with linear block copolymers because of their relatively complicated structure[17]. Experiments found that in the case of B-chains forming domains, the average size of the domains is considerably less than either that which might be expected by Meier's theory[18] or that found experimentally for linear block copolymers. Eastmond presented an explanation for this in terms of the structural characteristics of the copolymers[17]. It is known that, in an ABCP, there is always a distribution of molecular

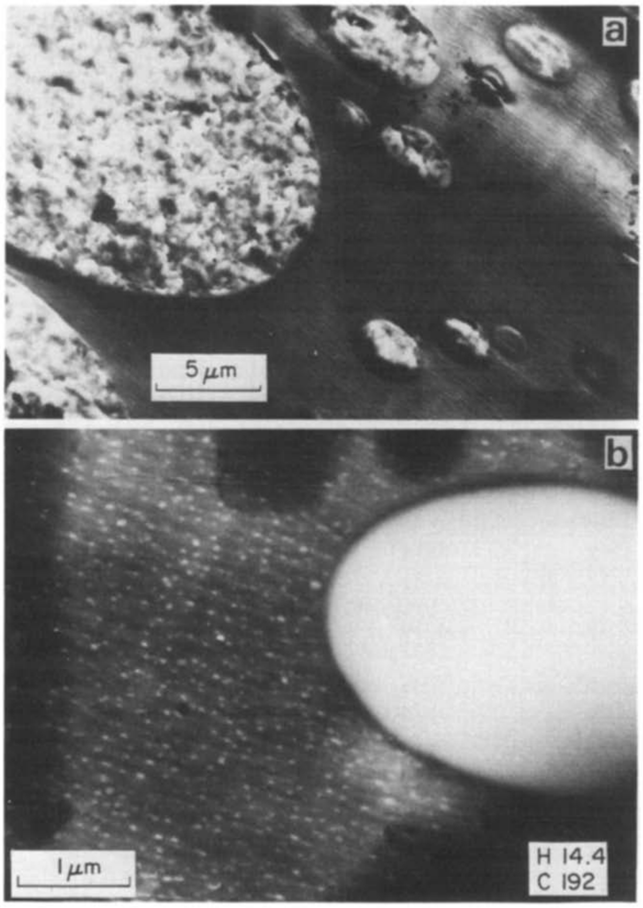


Figure 7 Electron micrographs of blends B5 showing normal and reverse macrophase separation

structures of different complexity[13]. As the simplest one of them, A_2BA_2, is invariably the major species, for simplicity, it is regarded as representative of ABCP in the subsequent discussion. For B-chains of ABCP in the domains, both ends of the chain are restricted to the interface region and, in consequence, B-chains in the domain cannot extend as far as the B-chains of the same length in AB diblocks, which have only one restricted end for each chain. Therefore, for B-chains in ABCP, more conformation restriction and smaller domain size are expected. In comparison with triblock copolymer ABA, though they are common in that each B-chain has two ends, for ABCP, two A-chains are attached to each end of B-chain but only one for ABA; this difference leads B-chains in ABCP to assume more restricted conformation and in turn to form smaller domains than those of ABA. This argument, as we shall see later, seems helpful for understanding the behaviour of ABCP in mixing with homopolymers.

The only theory available for evaluating the miscibility in homopolymer/copolymer blends is that given by Meier[19]. Though his conclusion was drawn from blends of diblock copolymer and homopolymer and was found to disagree with some experimental results[6], the main factors, those unfavourable for the solubilization, are more interesting because they are more sensitive to molecular architecture. They are (a) placement entropy, which is associated with restriction of A-B junctions to the interfacial region, and (b) constraints on and distortions to the conformation of block copolymer and homopolymer chains. One of the direct consequences of solubilization of homopolymer in domains of like type blocks is swelling of the domains. However, it has been reported that the size of the interface region does hardly change with the swelling of the domains[20]. Therefore, the loss of the placement entropy caused by restricting A-B junction to the interface region would increase with the solubilization. Obviously, for ABCP, because of the presence of two junction points for each B-chain, this entropy loss must be greater than that in the case of AB block copolymer with the same length of B-chain. As to the factor (b), it might be difficult to anticipate the effect of swelling on the conformation entropy of B-chains because they are restricted in its domains even without homopolymer chains added. However, the B-chains having two ends at the interface region and connected to two A-chains for each end, have to assume more unfavourable conformation than that in AB or ABA. Therefore, it is reasonable to think that, in the regions near the interface to accommodate homopolymer chains is difficult unless extreme unfavourable conformations associated with a great entropy loss are adopted. This simple argument makes the low miscibility in ABCP/homopolymer blends understandable. Therefore, we would like to argue that, besides the relative molecular weights of the component polymers to which great attention has been paid in the literature, the effect of molecular architecture of copolymer on its solubilization with the homopolymers, to some extent, might be more important. In the light of this point of view, a systematic study on copolymer/homopolymer miscibility with a variety of copolymers including linear, star, and comb-like copolymers is in progress in this laboratory.

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