Phase separation in blends of homopolymer and graft copolymer based on styrene and butadiene

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A series of blends of homopolystyrene and styrene-*g*-butadiene copolymer with different combinations of molecular weights of the copolymer and graft polystyrene segments have been prepared. Phase separation behaviour of the blends has been examined by electron microscopy. The results reveal a regular change of morphology of the blends with the relative molecular weights of the free and graft polystyrene chains. The observed relationships between compatibility of the homopolymer and copolymer and the relative molecular weight are generally in agreement with that observed previously in homopolymer–block copolymer blends. Taking the inherent polydispersity of the molecular weight of the component polymers into account, some peculiarities of the morphologies of the blends have been explained.

Keywords Graft copolymer; compatibility; electron microscopy; morphology; phase separation; polyblends; poly(styrene-*g*-butadiene)

INTRODUCTION

As phase separation behaviour is one of the decisive factors governing the properties of multicomponent polymers, it has received much attention over the years. Recently, great interest has arisen in the field of compatibility of polyblends comprising a graft or block copolymer and one or two corresponding homopolymers[1,2]. This might be connected with the following well known facts. First, one of the most important multicomponent polymers, HIPS, is virtually, though not in the ordinary sense, a blend of homopolystyrene and the graft copolymer of styrene and diene. Some attempts have been made to produce blends consisting of rubber and plastic components with new morphologies rather than the ordinary cellular structure in HIPS or ABS[3,4]. Obviously, whether this kind of effort will successfully result in more outstanding properties will depend on a thorough understanding of the compatibility between the block or graft copolymer and their corresponding homopolymers. Secondly, it is well known that lack of adhesion between the component homopolymers often makes it difficult to produce blends with the desired properties by simple blending. The addition of the corresponding block or graft copolymers to the blends has been proved effective in changing the interface situation and then realizing the desirable combination of properties in the blends[1,2]. This has stimulated some fundamental research on compatibility between the component polymers. Finally, while the rules governing phase separation in the cases of homopolymer blends and block copolymers are rather clear and defined, ambiguity and discrepancy still exist in the cases of homopolymer–copolymer blends.

Research on the compatibility of homopolymer–copolymer blends started with extensive studies on ternary blends of homopolymers and block copolymers, mainly based on styrene and isoprene, presented by Riess *et al.*[5,6] One of the main conclusions from their studies is that the transparency of the films, which is regarded as a criterion for the disappearance of macrophase separation, critically depends on the relative molecular weight of the homopolymers and the corresponding block copolymer segments. When the molecular weights of the homopolymers are less than those of blocks of the same type, films remain transparent in most compositions, indicating no heterogeneity on a macroscopic scale.

Systematic morphological observations on blends of block copolymers of styrene and isoprene and the corresponding homopolymers were made by Inoue and Kawai[7]. They found that homopolymer chains can be solubilized into block domains of the same type provided that the molecular weight of the former is the same as or less than that of the latter. When the molecular weight of the homopolymer is much larger than that of the corresponding block, it cannot be incorporated into the domains and will form its own phase of macroscopic size. However, in their studies, not enough attention was paid to the case of blends in which block copolymer was the minor component and the molecular weight of the block was less than that of the homopolymers. Later, Shen[8], Riess[4], Kotaka[9] and Kawai[10,11] presented more results on phase separation in homopolymer–block copolymer blends, which all confirmed Kawai's previous conclusion about the dependence of compatibility on the relative molecular weight.

However, there were some reports[12,13] concerning the presence of some 'unusual features', i.e. large supramolecular structures with different interior morphologies from

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that in the bulk in certain copolymer–homopolymer blends. Later, in a series of studies on copolymer–homopolymer blends, Eastmond *et al.* explored the nature of these special morphologies and gave a reasonable explanation for their formation[14,15].

The multicomponent polymers studied by Eastmond *et al.* were so-called AB crosslinked copolymers (ABCPs) or non-linear block copolymers, which were formed by polymerization of monomer B initiated at some active sites in the backbones of prepolymer A. Crosslinks between A chains were formed as a result of combination termination of propagating B radicals. In an ABCP product, there is no homopolymer B but unreacted homopolymer A is always present, in amounts which depend on the extent of polymerization. For ABCPs either with very low crosslinking indices or in the presence of a large proportion of added A homopolymer, i.e. the copolymer is present as a minor component, the 'unusual features' characterized by the presence of some discrete macroscopic domains with interior structures different from the matrix are always present in slowly cast films. This was regarded as evidence for the incompatibility of the homopolymers and like blocks.The formation of this unusual feature was explained as the result of a combination of macrophase separation between the copolymer and homopolymer and microphase separation between the blocks in the copolymer-rich phase. As to the dependence of solubilization on the relative molecular weight, Eastmond's conclusion on ABCPs is different from that of the others, his argument being that the solubility of the homopolymer and corresponding block is very limited and the homopolymer cannot be solubilized in domains of the corresponding blocks even when they have the same molecular weight. This conclusion found support from Meier's theoretical results[16]. Though it seems to be universally agreed that, in spite of their chemical identity, solubilization of homopolymer and the corresponding segments of copolymer is not unconditional and the solution limitation depends critically on their molecular weights, a discrepancy on the extent of this limitation does exist. Particularly, when the molecular weight of the homopolymer is about the same as that of the corresponding segments in the block copolymer, whether a significant proportion of homopolymer can be solubilized in the domains of the corresponding blocks is still unknown.

It is noted that among the great number of published scientific studies on the compatibility of homopolymer–copolymer blends, most deal with blends consisting of block copolymers, the graft copolymer of styrene and butadiene being almost neglected, although this kind of copolymer constitutes the basic component of one of the most important multicomponent polymers, HIPS. Apparently, the ill-defined nature of its structure limits its application in scientific research. In this paper we present a compatibility study on a series of blends of homopolymer and graft copolymer based on styrene and butadiene. With the aid of a technique suggested by Riess *et al.*[17], we have been able to characterize the grafts and thus make it possible to correlate the observed morphology of the blends with the molecular parameters of their component polymers. It is interesting to note that the inherent polydispersity of the molecular weights of the graft and free polystyrene used in this study has provided some useful information with respect to the relationship between the solubility and molecular parameters.

EXPERIMENTAL

Polystyrene

A commercial polystyrene sample was fractionated in toluene/methanol at room temperature into seven fractions. The first (H2), fourth (H3) and sixth (H4) fractions were used in making blends with graft copolymers. The weight average and number average molecular weights and molecular weight distributions of the fractions were measured with g.p.c. and the results are shown in *Table 1*.

A high molecular weight polystyrene sample (H1) was prepared by emulsion polymerization with $K_2S_2O_8/Na_2SO_3$ as the initiator system. The limiting viscosity number of the product was determined in toluene at 25°C and the molecular weight was 1.5×10^6, calculated based on[18] $[\eta] = 1.30 \times 10^{-2} M^{0.71}$. No molecular weight distribution data were obtained as its high molecular weight is beyond the working range of g.p.c. in this laboratory.

A low molecular weight polystyrene sample (H5) was prepared by suspension polymerization at 75°C using benzoyl peroxide as the initiator. The molecular weights measured with g.p.c. are listed in *Table 1*.

Preparation of graft copolymers

Two graft copolymers of styrene and butadiene (G1 and G2) were prepared by bulk polymerization of styrene in the presence of 8% polybutadiene at 75°C. The microstructure composition of the polybutadiene used was 96.5% 1,4 and 3.5% 1,2 addition and the viscosity average molecular weight was found to be 5.0×10^5. Two graft copolymers with different molecular weights of polystyrene segments were obtained at different concentrations of benzoyl peroxide in the presence of β-bromostyrene as the chain-transfer agent. The polymerization was allowed to proceed until about 30% conversion. The reaction products were then extracted with 50/50 (v/v) acetone/-methyl ethyl ketone to remove homopolystyrene from the product. These separated graft copolymers were blended with polystyrene samples with various molecular weights for further morphological study.

Characterization of graft copolymers

The most important molecular parameters of the graft copolymers in this study are the molecular weights of the polystyrene grafts. Measurement of the parameters was performed by complete isolation of the graft copolymers from the reaction products and subsequently selective degradation of the polybutadiene backbones using the technique suggested by Riess and Locatelli[17]. This procedure can be briefly described as follows. First, the polymerization product was extracted with 50/50 acetone/methyl ethyl ketone to remove a large part of the homopolystyrene. Then the raw graft copolymer was treated with azobisisobutyronitrile and thioglycolic acid in benzene solution, and subsequently with sodium methylate to attach COONa groups to the polybutadiene backbones. This carboxylated grafted polybutadiene formed a gel in benzene and could be readily separated from the soluble homopolystyrene. When a certain amount of benzene/methanol (9/1 v/v) was added, the gel became soluble and the retained ungrafted polystyrene was released. This cycle of gelation and solution was repeated until complete separation of the copolymer and homopolymer. Then, the purified graft copolymer was treated with OsO_4 and tert-butyl hydrogen peroxide in the presence of

Table 1 Molecular parameters of homopolystyrene and graft copolymers in blends

Designation of blends	Mol. wt of PS grafts in copolymers			Mol. wt of homopolystyrene		
	Copolymer	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$	PS	$\bar{M}_w \times 10^{-5}$	$\bar{M}_n \times 10^{-5}$
G2H1	G2	0.78	0.37	H1	15.0 ($\bar{M}_\eta$)	
G1H2	G1	1.46	0.95	H2	4.6	2.50
G1H3	G1	1.46	0.95	H3	2.20	1.76
G1H4	G1	1.46	0.95	H4	1.51	1.21
G1H5	G1	1.46	0.95	H5	0.81	0.47

benzaldehyde in chlorobenzene to degrade the polybutadiene backbones selectively. Thus, polystyrene grafts were able to be isolated by precipitation. By weighing, the degrees of grafting (the ratio of the amount of polystyrene grafts to that of polybutadiene) of copolymers G1 and G2 were found to be 19% and 15% respectively. The molecular weight distributions and the average molecular weights of the polystyrene grafts were measured with g.p.c. and the results are shown in *Table 1*.

Blend preparation

All the blend films have the same proportion of component polymers, that is 85% homopolystyrene and 15% graft copolymer. The blends were prepared by making a 5% (w/v) solution of the graft copolymer and homopolystyrene in benzene. The solutions were placed in flat glass cells and covered to ensure slow evaporation of the solvent. Films were formed in 4–5 days and then kept under vacuum for several days, the residual solvent being removed by storing the films in a vacuum oven at 60°C for 2 days. Graft copolymer G2 with low molecular weight branches was blended with the high molecular weight homopolystyrene H1, the resultant blend being designated as G2H1. Graft copolymer G1 blended with polystyrene fractions H2, H3, H4 and low molecular weight polystyrene H5 were designated as G1H2, G1H3, G1H4 and G1H5 respectively. These blends have different combinations of molecular weights of homopolystyrene and polystyrene grafts, as shown on a logarithmic scale in *Figure 1*.

Electron microscopy

The blend films were stained in 1% OsO_4 aqueous solution for a few days. Ultrathin sections were obtained by using an ultratome made by the Shanghai University of Science and Technology. These ultrathin sections were examined with a Hitachi H-500H electron microscope at an acceleration voltage of 75 kV.

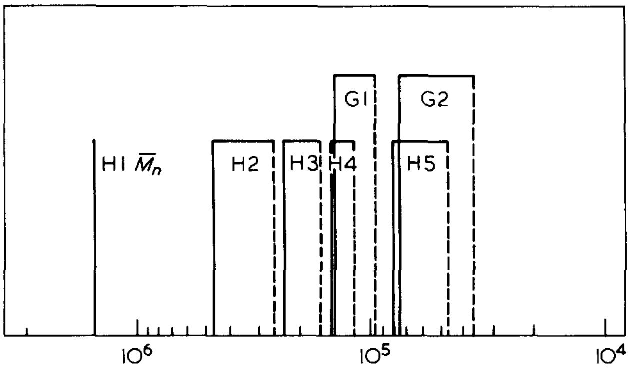

Figure 1 Number average (– – –) and weight average (——) molecular weights of homopolystyrene and polystyrene segments of styrene-*g*-butadiene copolymers on a logarithmic scale

RESULTS AND DISCUSSION

Five solvent-cast blends consisting of a graft copolymer of styrene and butadiene as a minor component (15%) and polystyrene (85%) with different combinations of molecular weights of the graft and free polystyrene chains were systematically examined by electron microscopy. The results clearly reveal a regular change of morphology with relative molecular weight of the graft and homopolystyrene.

Figures 2a and *b* are micrographs of blend G2H1 in which homopolystyrene has the highest molecular weight $\bar{M}_\eta = 1.5 \times 10^6$, i.e. about 20 times as much as the weight average molecular weight (7.8×10^4) of the graft polys-

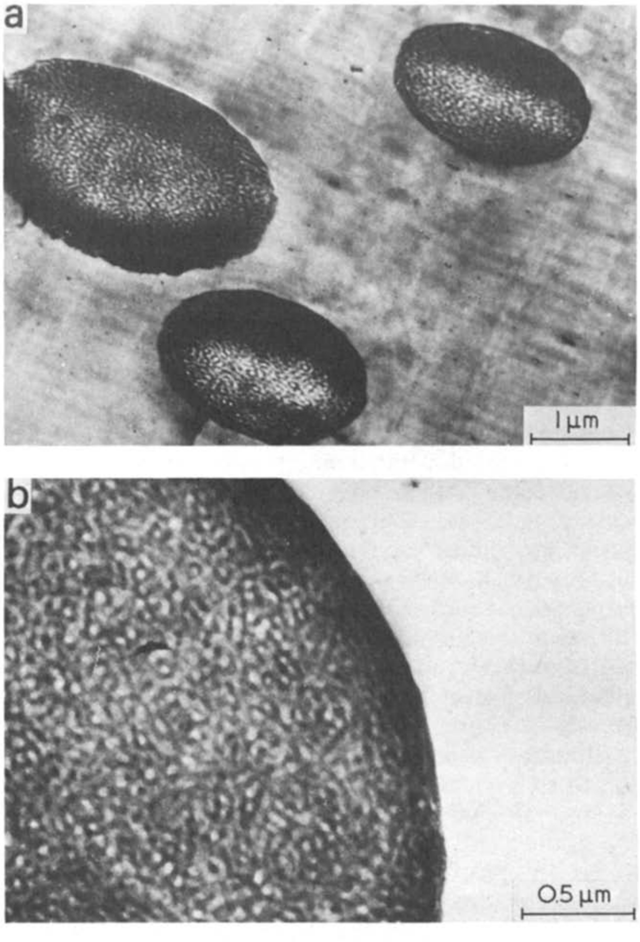

Figure 2 Electron micrographs of blend G2H1 showing a combination of microphase and macrophase separation and the distinct interface

tyrene branches. Thus it provides an extreme combination of molecular weights of the components in the blend. The micrographs clearly show that some discrete ellipsoidal domains with dimensions in the range of 0.2–5 μm pervade the polystyrene matrix. The interior structure of these macrodomains clearly indicates the feature of microphase separation of the copolymer, i.e. the worm-like polybutadiene domains with width 25–30 nm and the polystyrene domains interpenetrate each other. Thus, this complicated morphology is caused by a combination of macrophase separation between the copolymer and homopolymer and microphase separation between the polybutadiene and polystyrene segments of the graft copolymer. Because boundaries between the domains and matrix are quite distinct and no polybutadiene microdomains are observed in the matrix, we may conclude that homopolystyrene and polystyrene grafts are entirely incompatible when the average molecular weight of the former is much larger than that of the latter. This is in good agreement with the conclusion drawn from blends of block copolymer and corresponding homopolymer having monodispersity of molecular weights[7]. It can be clearly seen in *Figure 2a* that all the long axes of the ellipsoids are parallel with each other and are in the same direction as the cutting traces. Therefore, these ellipsoids are likely to be the result of deformation of spherical domains under stress when the sample was ultramicrotomed.

In blend G1H2, the disparity between the average molecular weights of the graft and free polystyrene segments is not so serious as that in G2H1. However, the average molecular weight of the homopolystyrene ($\bar{M}_w = 4.6 \times 10^5$, $\bar{M}_n = 2.5 \times 10^5$) is still considerably larger than that of the graft segment ($\bar{M}_w = 1.46 \times 10^5$, $\bar{M}_n = 9.5 \times 10^4$). In *Figure 3*, while some discrete domains of copolymer-rich phase with the same interior structure as in G2H1 are dispersed in the matrix, a new type of dispersed phase, which is sometimes called 'onion structure'[15], is found as well. In these domains, polystyrene and polybutadiene layers are arranged alternately. In some sections most of the macroscopic domains are in the shape of an onion (*Figure 3b*). A rough estimation using micrographs with larger magnification gives widths of both the polystyrene and polybutadiene layers of around 30–40 nm. In other words, the relative amounts of polystyrene and polybutadiene in the 'onions' are about the same. Compared with domains with worm-like inner structure, the 'onions' have higher polystyrene proportion, indicating some incorporation of homopolystyrene into the polystyrene microdomains of the graft copolymers. Another remarkable feature of the micrographs is that some ribbon-like, rod and sphere polybutadiene microdomains are present in the polystyrene matrix. In G1H2, although the average molecular weight of the graft is much less than that of the homopolystyrene, there is an overlap between the two molecular weight distributions, as seen in *Figure 4*. It is not difficult to see that there is a small proportion of copolymer molecules having graft chains with greater molecular weight than that of the average molecular weight of the homopolystyrene. This proportion of molecules is likely to be able to solubilize the free polystyrene chains in the matrix and subsequently to give rise to polybutadiene microdomains. Similarly, homopolystyrene molecules of smaller molecular weight, which is about the same as or less than the

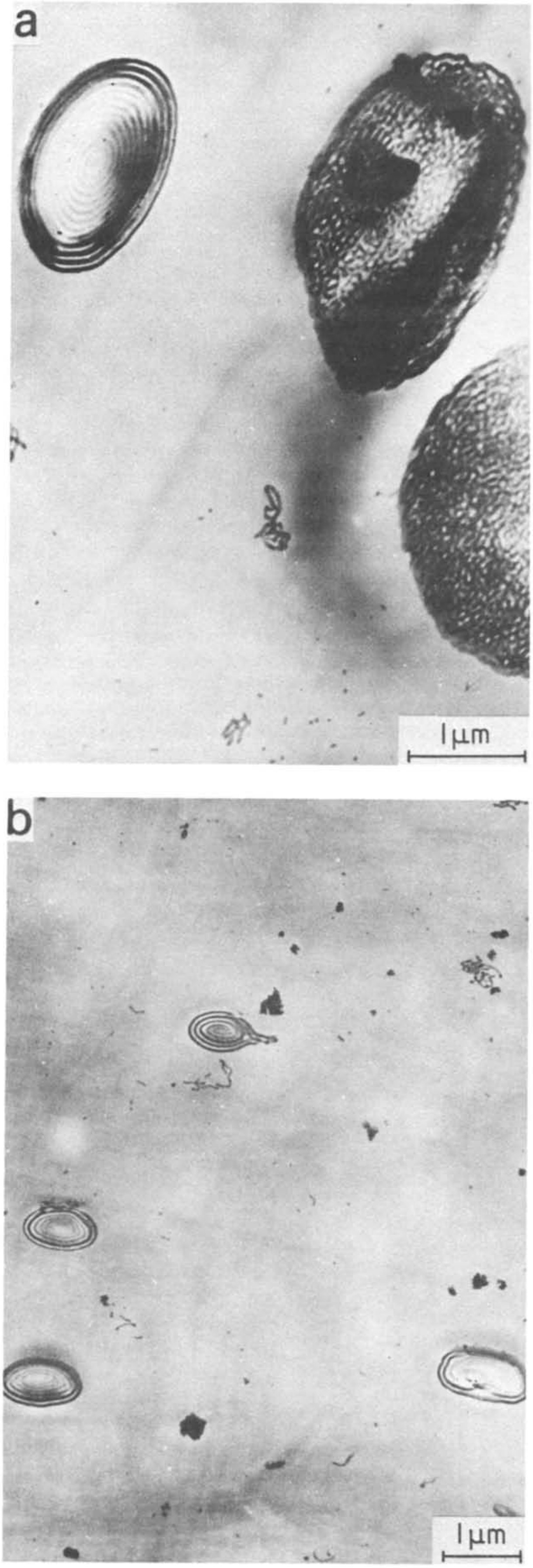

Figure 3 Electron micrographs of blend G1H2 showing macrodomains with different interior structures (a) and dispersed 'onion structure' domains (b)

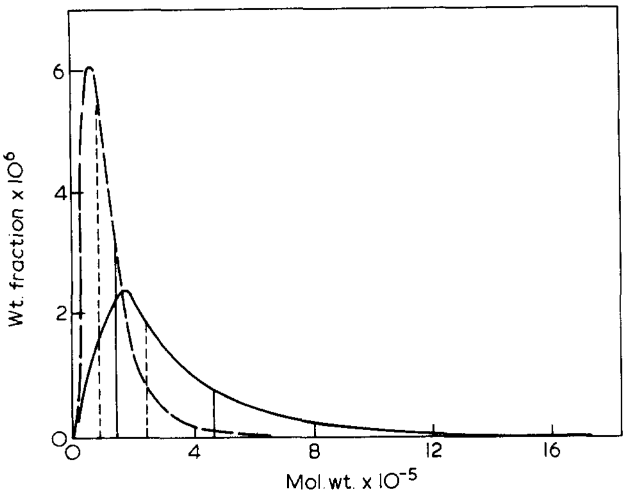

Figure 4 Molecular weight distributions of homopolystyrene H2 (solid curve) and polystyrene grafts G1 (broken) and their number average (– – –) and weight average (——) molecular weights

average molecular weight of the grafts, might be incorporated into the copolymer-rich phase, i.e. the onions, to make them have a higher polystyrene proportion.

The tendency of the graft and free polystyrene chains to intermix can be seen more clearly in the micrographs of G1H3 (*Figure 5*), in which the average molecular weight of homopolymer H3 ($\bar{M}_w = 2.20 \times 10^5$, $\bar{M}_n = 1.76 \times 10^5$) is only about one and a half times that of the graft polymers. *Figure 6* shows that a broader region exists where the molecular weight distributions of the graft and free polystyrene overlap each other. In general, in blend G1H3, the copolymer is still separated as a macroscopic phase, which is clearly shown in *Figure 5*, as a result of incompatibility between the graft and free polymer chains. However, the separated copolymer-rich phase incorporates a significant amount of homopolystyrene, which can be easily judged by the relatively large light regions in the domains. Moreover, the size of the polybutadiene domains in the copolymer-rich phase is apparently decreased, from 30–40 nm in *Figure 3* to about 12 nm in the present case. Shen *et al.*[8] reported a similar result for blends of a block copolymer with the corresponding homopolymers. That is, the domain size of polystyrene blocks decreases when the amount of low molecular weight polybutadiene solubilized in the corresponding microdomains increases. Meanwhile, for some macrodomains, such as those in the right bottom part of *Figure 5b*, no distinct boundary can even be seen, indicating the great separation of polybutadiene domains by homopolystyrene chains. *Figure 5a* displays more polybutadiene microdomains in the shapes of ribbons, rods and spheres than those in G1H2. This can be attributed to the existence of more copolymer molecules with higher molecular weight than the average molecular weight of the free homopolystyrene H3. In addition, in *Figure 5* the matrix appears darker than usual, which might be due to physical absorption of OsO_4 caused by overstaining.

The blend morphology is changed further from G1H3 to G1H4 (*Figure 7*). The average molecular weight of homopolystyrene H4 ($\bar{M}_w = 1.51 \times 10^5$, $\bar{M}_n = 1.21 \times 10^5$) is only a little larger than that of the polystyrene grafts. *Figure 8* indicates that a great proportion of the copol-

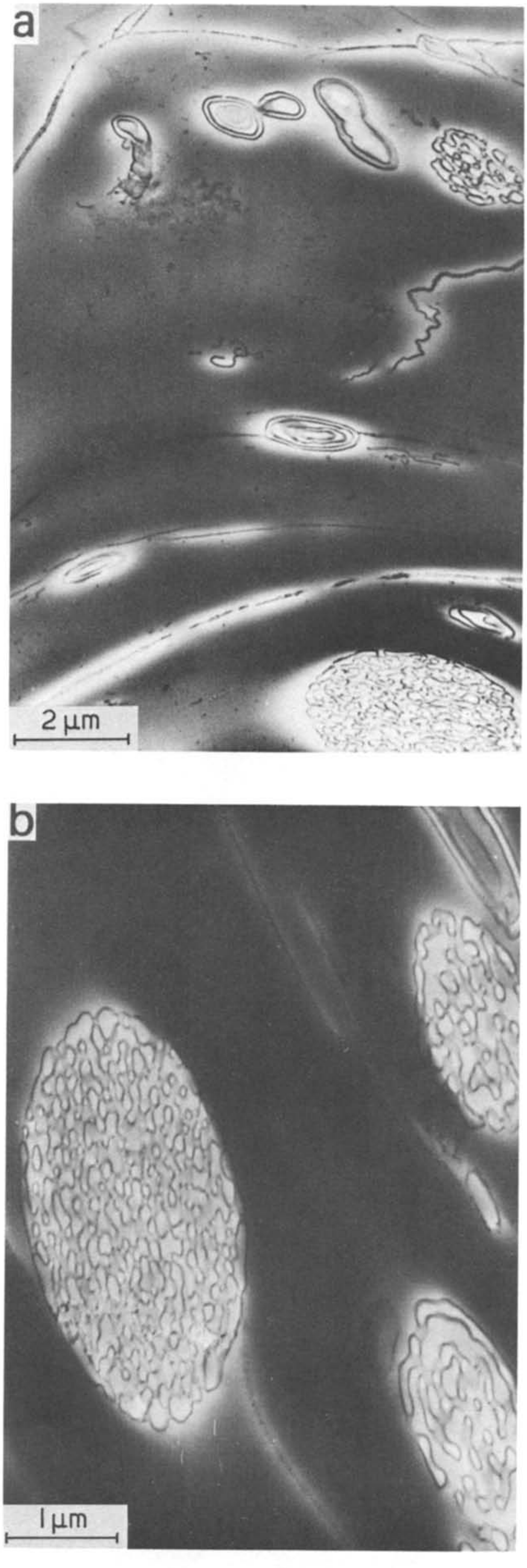

Figure 5 Electron micrographs of blend G1H3 showing a variety of domain structures

ymer molecules have longer graft polystyrene segments than that of homopolystyrene. A great many polybutadiene microdomains in the shapes of spheres or rods seen in the matrix are believed to be from this proportion of copolymers. Meanwhile, some ribbon-like domains can be observed as well. Occasionally, in some sections, relatively concentrated regions of copolymer can be found, as shown in *Figure 7b*.

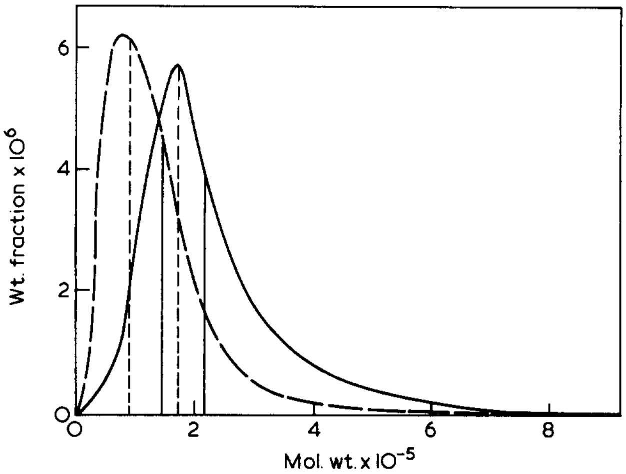

Figure 6 Molecular weight distributions of homopolystyrene H3 (solid curve) and polystyrene grafts G1 (broken curve) and their number average (– – –) and weight average (——) molecular weights

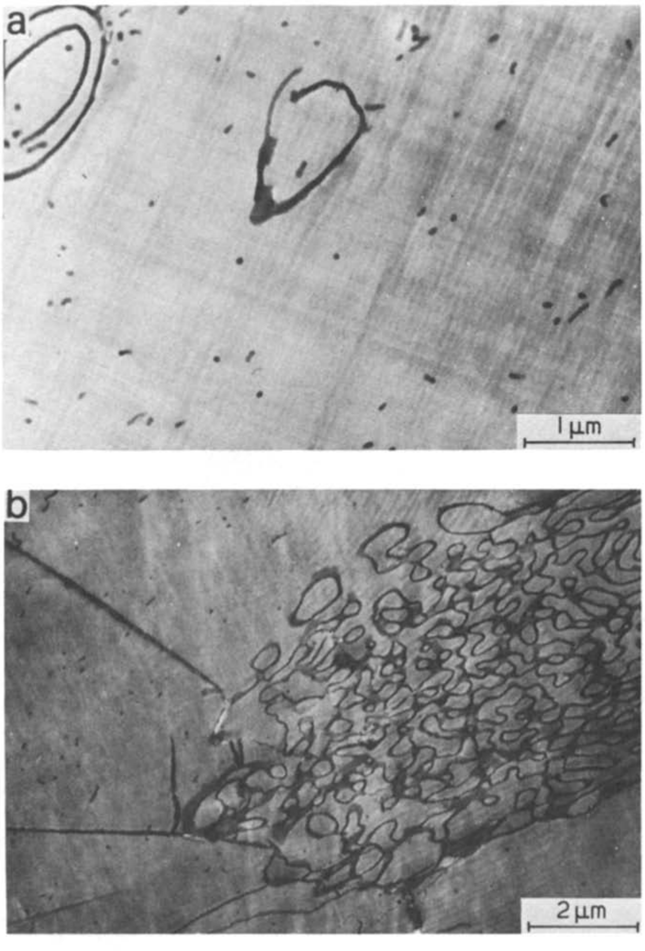

Figure 7 Electron micrographs of blend G1H4 showing a variety of domain structures (a) and copolymer-rich regions (b)

Finally, *Figure 9* shows the morphology of blend G1H5, the only one in which the average molecular weight of the homopolystyrene ($\bar{M}_w = 8.1 \times 10^4$, $\bar{M}_n = 4.7 \times 10^4$) is less than that of the polystyrene branches. The micrograph of G1H5 has a remarkable character, namely uniformity on a macroscopic scale. A large number of spherical or rod-like polybutadiene microdomains are randomly dispersed in the matrix. Occasionally, some ribbon-like domains, as shown in the centre part of *Figure 9*, can be found. Therefore, in general, blend G1H5 forms a macroscopic homogeneous system, indicating considerable solubilization of the graft and free polystyrene segments. Obviously, this can be attributed to the fact that, in blend G1H5, most of the graft polystyrene molecules have higher molecular weights than the average molecular weight of homopolystyrene, as shown in *Figure 10*.

In summary, the sequence of micrographs discussed above depicts the regular variation in morphology of blends with relative molecular weight of the graft and homopolymer. When the average molecular weight of homopolystyrene is much larger than that of the polystyrene grafts, the blends are completely incompatible. As

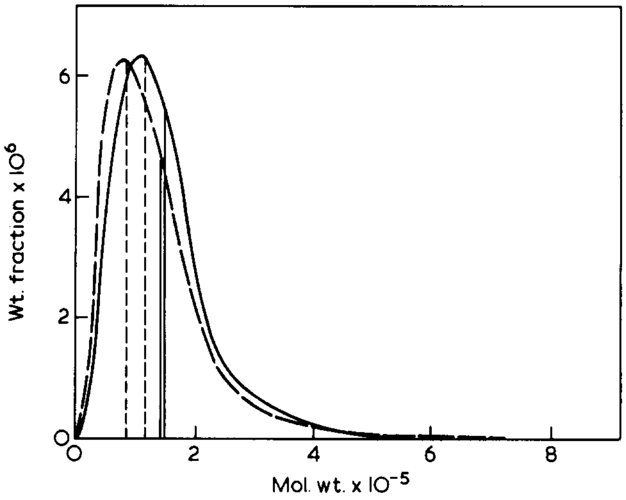

Figure 8 Molecular weight distributions of homopolystyrene H4 (solid curve) and polystyrene grafts G1 (broken curve) and their number average (– – –) and weight average (——) molecular weights

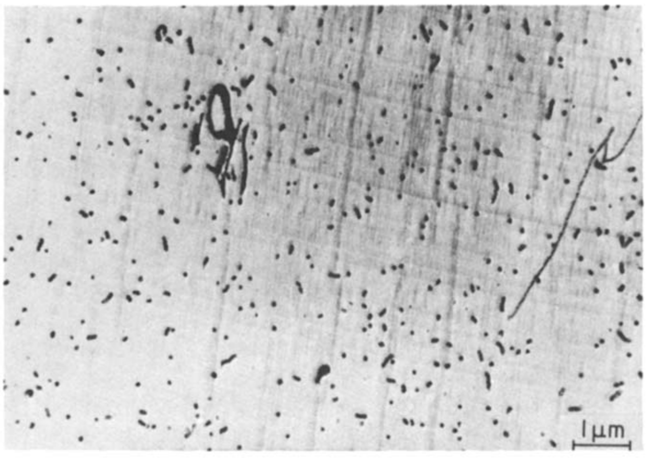

Figure 9 Electron micrograph of blend G1H5 showing solubilization of homopolystyrene H5 and graft copolymer G1

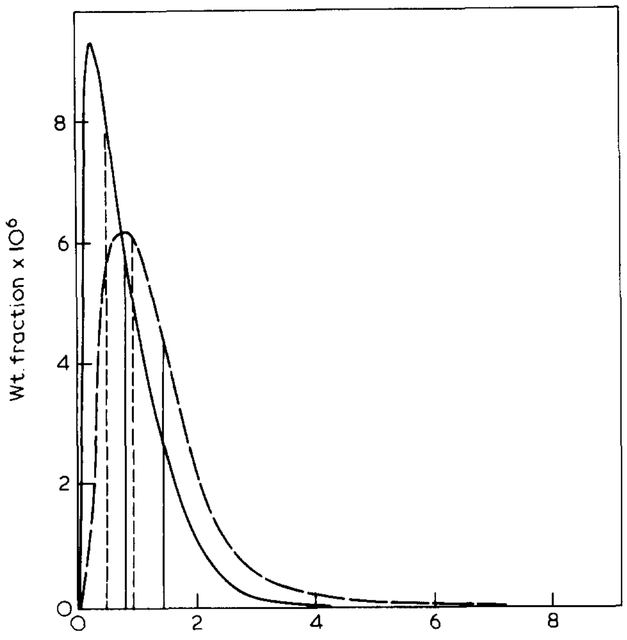

Figure 10 Molecular weight distributions of homopolystyrene H5 (solid curve) and polystyrene grafts G1 (broken curve) and their number average (– – –) and weight average (——) molecular weights

the molecular weight of the homopolymer gradually decreases, intermixing between the graft and free polystryene increases, which is manifested in the swelling of the microdomains of polystyrene in the copolymer-rich phase and the appearance of microdomains of polybutadiene in the matrix. Finally, when the average molecular weight of homopolystyrene is about the same as or less than that of the grafts, the blend changes to an almost homogeneous system on a macroscopic scale. Obviously, these experimental conclusions are generally in accord with those found by Kawai, Shen and Riess *et al.* in homopolymer–block copolymer blends, but contradict Eastmond's studies on ABCPs and Meier's theoretical calculation.

According to Meier's results[16], at equilibrium the amount of homopolymer that can be solubilized into the block domains is very limited and is only about 5% for the case of equal molecular weights of blocks and homopolymer. Meier attributed the great discrepancy between his theory and the experimental results given by Kawai *et al.* to the non-equilibrium nature of the solvent-cast films. He suggested that the morphology observed experimentally depends on whether macrophase separation between copolymer and homopolymer or phase separation of the two components of the block copolymer with solubilized homopolymer occurs first during the process of solvent evaporation. Based on his calculation, for some typical situations of blends of homopolymer and block copolymer of styrene and butadiene, phase separation between the copolymer and homopolymer takes place first provided the ratio of the molecular weights of homopolymer to corresponding segments of block copolymer is greater than 0.4. Of course, this includes the most interesting situation in which homopolymer and like blocks have equal molecular weights. Therefore, the experimental results showing that homopolymer can be considerably solubilized into the domains of the corresponding blocks when their molecular weights are close to each other cannot find a satisfactory explanation in Meier's theory, even if the non-equilibrium nature of the films is taken into account.

As to the effect of non-equilibrium nature on the morphology of solvent-cast films of multicomponent polymers, Eastmond has given a detailed discussion on ABCP blends[15]. In a recent paper[19], Eastmond and one of the present authors explored the effect of solvent evaporation rate on the properties of blends of polycarbonate and poly(methyl methacrylate) with the aid of a phase diagram measured experimentally. It was found that, under ordinary conditions of film preparation, for the immiscible system, the rate of evaporation only affects the compositions of the coexisting phases in the dry films but does not alter the heterogeneous nature of the films. For blends of homopolymer and copolymer, we lack sufficient experimental data on phase diagrams. However, the phase separation behaviour of the polymerization system for preparing HIPS has been studied[20,21]. For the system consisting of 6–8% polybutadiene in styrene, phase separation is reported to occur at a styrene conversion of only 1–2%. Thus, by considering the great similarity in composition between this polymerization system and the blends used in this study, there seems to be no reason to think that, in solvent-cast films of homopolymer–copolymer blends based on styrene and butadiene, the mobility of the macromolecules is so restricted that phase separation, which should occur in relatively dilute solution, can be completely prevented. Thus, the considerable solubilization between the graft and free polystryene chains of similar molecular weight observed in this study cannot simply be regarded as the false appearance of the non-equilibrium films.

In ABCP blends, the average A-chain length from an A–B junction to the end of the copolymer is somewhat less than that of the homopolymer A chain, which might be responsible for the low solubility between the copolymer and homopolymer in ABCPs. However, ABCPs showing macrophase separation are reported to have very low crosslinking index[15], so the bound A-chain length would not be seriously less than that of the free A chains. Therefore, this question seems worth exploring further.

It is interesting to note that the micrographs of blends G1H2, G1H3 and those of some ABCPs (for example, figures 4b and 5 of ref. 15) show a great similarity. All these micrographs present coexistence of macrophase separation and intermixing between the graft and free chains. This characteristic is believed to be associated with the polydispersity of molecular weight which exists in both ABCPs and the present samples.

Without exception, all the results of phase separation studies on copolymer–homopolymer blends demonstrate that the mutual compatibility of the homopolymer and blocks of the same type is conditioned in spite of their great similarity in chemistry. This limitation on the compatibility is caused by an unfavourable entropy of mixing[15]. Quite recently, we found[22] that block copolymers with the same composition and sequence structure but different molecular weights are incompatible. In this case, the unfavourable entropy of mixing seems more understandable, that is, accommodating blocks with discretely different lengths into the same domain will lead to greater heterogeneity in density. Therefore, more restraint and hence more entropy loss is necessary to keep a constant density in the domain. Though we have a sketch of the unfavourable entropy, we obviously need much more work with a larger variety of materials to reach any convincing conclusion about the compatibility–structure relationship in blends comprising copolymers.

CONCLUSIONS

The electron microscope study shows that, in blends of homopolystyrene and styrene-*g*-butadiene copolymer, there is a gradual variation in morphology with relative molecular weight of the free and graft polystyrene chains. When the average molecular weight of homopolymer is much larger than that of grafts, they are completely incompatible. Solubilization increases as the average molecular weight of homopolystryene becomes closer to that of the grafts. Homopolystyrene can be almost solubilized with polystyrene grafts when the average molecular weight of the former becomes less than that of the latter.

If the average molecular weight of homopolymer is larger than that of the grafts but an apparent overlap exists between their molecular weight distributions, the swelling of polystyrene microdomains in the copolymer-rich regions and the presence of microdomains of polybutadiene blocks in the matrix have been observed. This is believed to be associated with the inherent polydispersity of the molecular weights of both graft and free polystyrene chains. It implies that fractionation of the polymers accompanies the process of phase separation.

As far as the mutual solubility of homopolymer and copolymer is concerned, some conclusions based on morphological studies on ABCP blends and theoretical calculations are different from that for the block copolymer–homopolymer blends and from that obtained in this study. This discrepancy cannot solely be explained in terms of the non-equilibrium nature of the blend films.

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