Phase separation in polymer blends comprising copolymers:
5. Polyisoprene/poly(isoprene-*g*-styrene) copolymer system

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As part of a programme of research into miscibility in polymer blends comprising copolymers, this paper presents the morphology of blends of polyisoprene and poly(isoprene-*g*-styrene) with complicated but well defined structure. The graft copolymers were prepared by polymerization of styrene initiated by metallated polyisoprene backbone and were fully characterized. All the studied blends of copolymers and polyisoprene of different molecular weights exhibit macrophase separation even when the molecular weight of the homo PI is apparently less than that of the PI segments between neighbouring junction points in the copolymers. The results provide support for the argument that the molecular architecture of a copolymer is an important factor governing its miscibility with corresponding homopolymers. Besides, it is observed that the copolymer with higher proportion of polystyrene shows apparent solubilization in polystyrene matrix of high molecular weight and solubilization varies predictably with the addition of low molecular weight polyisoprene.

INTRODUCTION

Jiang et al.[1] have found that a remarkable feature of the blends of so-called AB crosslinked copolymer (ABCP) and homopolymer B is the limited solubilization of homopolymer B chains in the B-domains of the copolymer. They suggested that the relatively complicated structure of the ABCP was responsible for the low miscibility, i.e. for each B-chain in the B-domains, two junction points must be located at the interface region, each junction being connected with two A-segments. This model entails more conformation restriction of the B-chains and decreases their ability to accommodate B-chains of homopolymer in B-domains. With regard to the main factors affecting miscibility of homopolymer and copolymer, besides the molecular weight ratio of homopolymer to like chains in the copolymer, to which much attention has been paid[2], the molecular architecture effect is worth exploring further. For this purpose, some results of a morphological study of blends comprising homopolymer and a special type of graft copolymer with complicated but well defined molecular structure are reported here.

It was reported earlier[3,4] that polydiene chains can be metallated by butyllithium and tetramethylethylene-diamine (BuLi + TMEDA), forming polydiene with lithium atoms scattered along the chain, in which lithium–carbon bonds are able to act as active sites that initiate polymerization of vinyl monomers to form graft copolymers. This procedure has advantages for the present research. First, the number of the branches per backbone and the average molecular weight of the branches can be controlled by changing the reaction conditions, such as relative concentrations of BuLi, polydiene and monomer; secondly, as anionically prepared polydiene can be used as the prepolymer and the initiation and propagating mechanism of the monomer is anionic, in the final copolymer both the backbone and branches are of monodisperse molecular weight and can be fully characterized. In addition, the junction points scattered along the backbones present more conformation restriction when microphase separation between the backbone and grafts occurs. Therefore, this special kind of graft copolymer, which sometimes is called comb-like copolymer, provides an ideal material for exploring the architectural effect of copolymer mixed with corresponding homopolymer.

EXPERIMENTAL

Preparation and characterization of isoprene-g-styrene (SGI) copolymers

In the preparation procedure proposed by Tate et al.[4] for graft copolymer with PI backbone and PS grafts, n-BuLi and heptane were used as metallation agent and solvent respectively, although PI chains underwent degradation to some extent during metallation. In preliminary work we found that the reaction system became heterogeneous as the polymerization of styrene proceeded. To avoid these disadvantages, reaction conditions similar to those suggested by Falk et al.[5] were adopted so that sec-BuLi was used for metallation of PI in cyclohexane. Tate and Falk reported only low molecular weight PS grafts (2–6 kg mol^{-1}); therefore, in the present experiments, higher ratios of (styrene)/(PI) and (styrene)/(sec-BuLi) were used for preparing copolymer with higher molecular weight PS grafts, to ensure complete microphase separation between backbones and grafts.

Typically, 3.4 g polyisoprene prepared anionically ($\bar{M}_n = 53.9$ kg mol^{-1}) was dissolved in 70 ml cyclohexane in a flask connected to a vacuum line and then the solution was degassed and purged with dry nitrogen repeatedly. 0.5 mmol sec-BuLi and 0.5 mmol N,N,N',N'-tetramethylethylenediamine (TMEDA) were added with stirring and the mixture was stirred for 2 h at room temperature. Under these mild metallation conditions, no chain scission of PI occurred[5]. Then 9.1 g styrene was added with vigorous stirring, the mixture was stirred for 15 h at 50°C and finally methanol was added to terminate the reaction. The mixture showed slight opacity, which indicated the presence of microgel. After centrifuging the raw product in toluene at 9000 r min^{-1}, the solution became transparent. The g.p.c. traces of the purified products (*Figure 1*) exhibited two peaks, which seemed to indicate the coexistence of homopolystyrene and comb-like copolymer. After being partially precipitated in toluene–ethanol twice, homopolymer was entirely removed from copolymer, which was demonstrated by the single peak of the g.p.c. traces (*Figure 1*).

Three isoprene-*g*-styrene (SGI) with different total compositions and molecular weights of PS branches were prepared by changing the relative amount of polyisoprene and sec-BuLi and used in the morphology studies (*Table 1*). The total molecular weights of the copolymers ($\bar{M}_n$) were measured by membrane osmometry. Ultra-violet spectrometry measurements were used for determining the fractional compositions of PI and PS segments. In order to determine the average molecular weights of the PS branches ($\bar{M}_n(S)$), the PI backbone was selectively degraded with osmium tetroxide in chlorobenzene[6] and the polystyrene branches were recovered and examined by g.p.c. From the experimental data, the average number of PS grafts for each backbone and the average molecular weight of PI segments between two neighbouring junction points (for simplicity, it is referred to as the PI segment below) was calculated (*Table 2*).

Preparation of polyisoprene

All polyisoprenes were prepared anionically[7]. The molecular weights are listed in *Table 3*.

Blend preparation and electron microscopy. The blend preparation started with 4% solutions of the component polymers in benzene; the solutions were allowed to evaporate slowly in Teflon cells with covers. The films formed in 6–7 days and then were dried in a vacuum oven at room temperature and at 80°C for 24 h and for 3–4 days respectively. Ultramicrotomy was used to make sections of the films stained with OsO_4 for morphological examination, which was carried out in a Hitachi H500H electron microscope (75 kV).

In making solvent-cast films, high-molecular-weight polystyrene (HPS) was added in the proportion of 77% to harden the blends so that ultramicrotoming could be carried out at room temperature. Since the added HPS has much higher molecular weight than any PS branches of the copolymers studied here, it leaves virtually unaltered the morphologies of the copolymers and their blends with PI, which always exist in the form of macroscopic dispersed particles in the HPS matrix. In all the blends the weight ratio of homo PI to copolymer is 26/74, so that the weight ratios of homo PI to PI blocks in SGI-1, SGI-2 and SGI-3 are 52/48, 58/42 and 64/36 respectively.

Table 1 Graft polymerization conditions

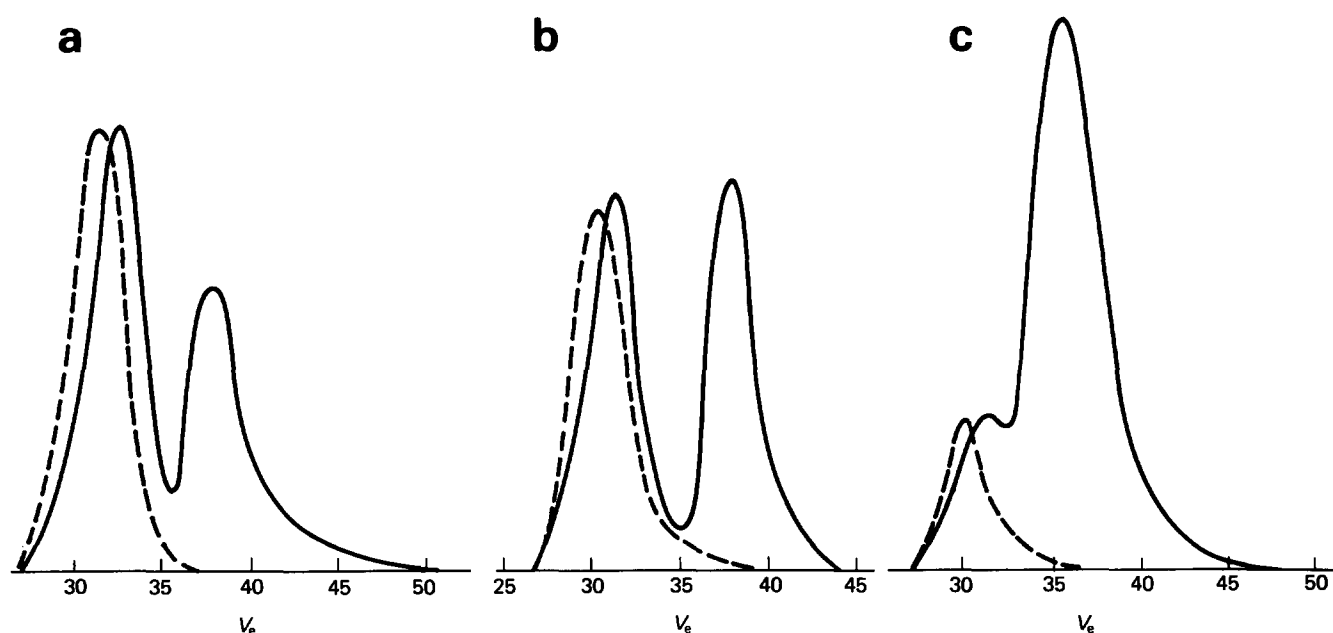| Sample	Cyclohexane (ml)	PI (g)	sec-BuLi (mmol)	TMEDA (mmol)	Styrene (g)
SGI-1	70	3.4	0.5	0.5	9.1
SGI-2	50	1.7	0.5	0.5	9.1
SGI-3	50	0.68	0.25	0.25	9.1

Figure 1 G.p.c. traces of the products of graft polymerization before (solid curves) and after (broken curves) fractionation. (a), SGI-1; (b), SGI-2; and (c), SGI-3

Table 2 Characterization of copolymers

| Sample	$\bar{M}_n$ (kg mol^{-1})	PS (%)	$\bar{M}_n(S)$ (kg mol^{-1})	$\bar{M}_w(S)/\bar{M}_n(S)$	Number of branches per PI backbone	$\bar{M}_n$ of PI segments
SGI-1	214	67.5	29.9	1.2	4.8	9.3
SGI-2	256	75.0	30.1	1.2	6.4	8.4
SGI-3	353	81.5	52.4	1.6	5.5	8.2

Table 3 Number-average molecular weights (kg mol^{-1}) of polyisoprene

Designation of PI	PI-1	PI-2	PI-3	PI-4	PI-5	PI-7	PI-8[a]
$\bar{M}_n$ (kg mol^{-1})	6.5	7.9	9.1	17.5	20.9	35.5	53.9

[a] Used as prepolymer for making copolymers

RESULTS AND DISCUSSION

This section includes observations made during a morphological study of the three styrene-*g*-isoprene copolymers with different molecular parameters and blends of copolymers with polyisoprene with a wide range of average molecular weights. The morphology of co-polymers alone is considered first. *Figure 2* shows SGI-1 in HPS at low magnification. Clearly, some discrete macrodomains with distinct internal structure and with dimensions as large as 5–10 μm pervade the HPS matrix. Although the shape of the dispersed phase is not perfectly ellipsoidal, the long axes of the domains are almost parallel to each other. As suggested before[8] the ellipsoids might result from deformation of the spherical domains during ultramicrotoming. In *Figure 3*, which shows SGI-1 phase at higher magnification, very distinct microphase separation between PI backbones and PS grafts can be seen. It is noticeable that the size distribution of the dispersed phase, which is in the range of 15–18 nm, is relatively narrow and especially that, in some regions, about a few micrometres square in area, the PI microdomains assume regular hexagonal order in the matrix. Considering that usually worm-like or other types of irregular morphology of microphase separation are reported for graft copolymers[8,9], this regular structure to some extent similar to the morphology characteristic of some well defined block copolymers is unexpected. The relatively narrow molecular weight distributions of the grafts and backbone in SGI are assumed to be responsible for the regular morphology. For diblock copolymer of isoprene and styrene with PI molecular weight similar to that of the PI backbone in SGI samples (53.9 kg mol^{-1}), according to the results of the SAXD measurements of Hashimoto *et al.*[10], domain size will be $\sim$ 32 nm, which is about twice as much as that observed for SGI. This inconsistency is understandable if it is taken into account that all the junction points along the PI backbone must locate at the interface region between the domains and matrix so that the PI chains cannot extend as far as PI blocks of the same length of the diblock copolymers do. Therefore, the backbones in comb-like copolymers form much smaller dispersed domains with serious conformation restriction. In addition, the regular arrangement of the microdomains is not the only morphological feature observed for SGI as many
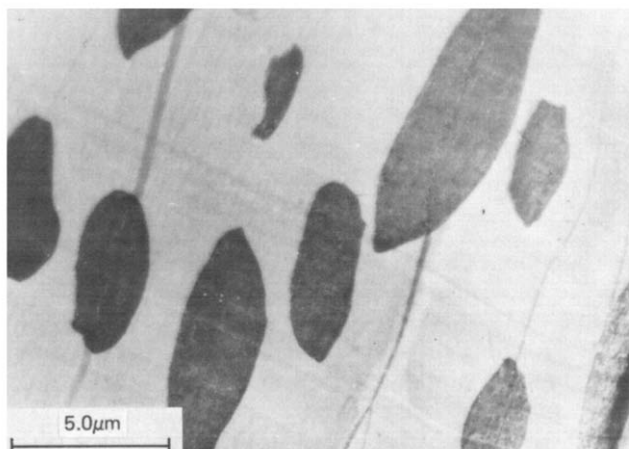
Figure 2 Electron micrograph of SGI-1 in HPS
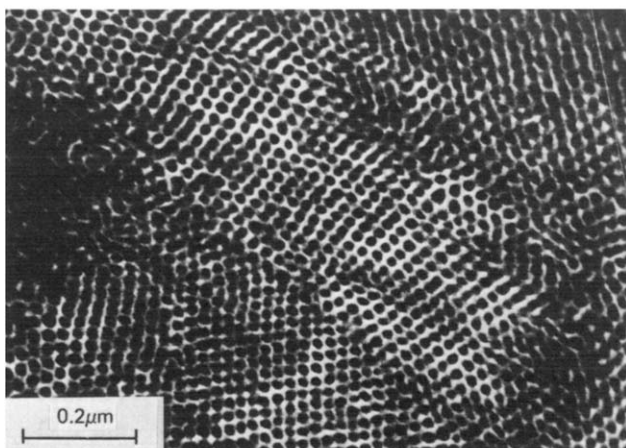
Figure 3 Electron micrograph of SGI-1 at larger magnification showing partially regular arrangement of PI domains

ultrathin sections present morphology of randomly arranged spherical microdomains of PI with relatively broad size distribution. This difference in the morphological regularity can be explained in terms of the difference from section to section in the extent to which equilibrium is approached.

SGI-2, which has a slightly higher average number of PS grafts per backbone than SGI-1, shows very similar morphology to SGI-1. However, SGI-3, which has longer PS branches and higher PS proportion than both SGI-1 and SGI-2, presents some peculiarities, as shown in *Figure 4*. Besides the obvious dispersed macrodomains in the size range of 0.5–5 μm composed of dense PI spherical domains, many discrete PI microdomains of diameter 16–25 nm randomly pervade the PS matrix while a part of the microdomains aggregate to form regions consisting of about only a few tens of microdomains. No definite explanation of the nature of the discrete dispersed
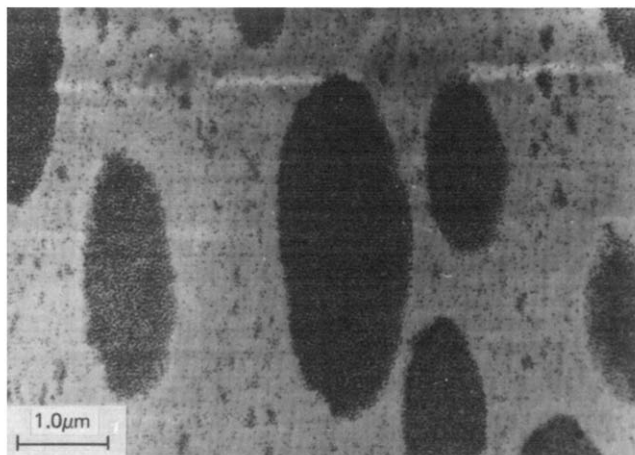
Figure 4 Electron micrograph of SGI-3 in HPS

microdomains can be proposed yet. However, since the average molecular weight of the grafts of SGI-3 is relatively narrowly distributed and only one-tenth of that of HPS forming the matrix, these individually dispersed microdomains cannot be thought to be from 'solubilized' copolymer with molecular weight as large as that of HPS.

Since the main interest of this study concentrates on the miscibility between copolymers with relatively complicated but well-defined structure and homopolymer PI, a series of blends covering a broad combination of the molecular weights of the homo and graft PI chains and with the same composition have been systematically examined by electron microscopy. First, the case where homopolyisoprene (PI-8) in the blend has the same molecular weight as that of the main chains of the SGI copolymers is considered. If the architectural effect is not considered, a homogeneous morphology on the macroscopic scale with randomly dispersed polyisoprene microdomains is expected according to Inoue and Kawai[2]. However, all the blends of SGI-1, SGI-2 and SGI-3 with PI-8 clearly show the morphology of the coexistence of homo PI and SGI phases as shown in *Figures 5* and *6*. In this type of micrograph, since the copolymer exhibits distinct morphology of characteristic microphase separation between the PI and PS segments while the homo PI phase has no internal structure, they are easily recognized. It is of interest to note that in all the micrographs of the blends the separated PI regions, usually with dimensions of the order of 1 μm, are exclusively associated with the copolymer phase. In other words, the homo PI exists as separated internal domains within the macroscopic dispersed phase rather than as discrete regions independently scattered in the matrix. The authors suggest that this characteristic is a result of minimizing the interface energy of the system and that the high interface energy between homo PI and homo PS phases is the driving force for separated homo PI phase to be incorporated into macrodomains of copolymer. In this arrangement, the surface of PI phase is surrounded by copolymer with polyisoprene blocks preferentially extending into the homo PI regions. Therefore, the chemical bonds between PS and PI segments in copolymer that exist in the interface region dramatically alter the surface conditions and decrease the surface energy of the system. Close inspection of the micrographs of SGI/PI-8 blends and all those of the immiscible blends of SGI and PI of different molecular

weights which will be discussed below reveal that a narrow bright band always partly or completely surrounds the separated PI domains. This indicates that the close vicinity of the PI macrodomains is actually composed of polystyrene blocks only of the copolymers while the polyisoprene segments of the copolymer molecules are incorporated into the border of the homo PI phase. Although in studies of the compatibility of copolymer AB in a polymer blend of homo A and homo B it was always assumed that the copolymer preferentially locates at the interface region with blocks solubilized in the corresponding homopolymer phases[11], no direct evidence could be obtained from transmission electron microscopy studies since the blocks of the copolymer are not distinguishable from the corresponding homopolymer chains. In the present study the special morphology in the interface region clearly provides evidence of preferential localization of blocks in the corresponding homopolymer phases. A similar morphological feature in the interface region can be found in micrographs obtained by Argon et al.[12].

As it has been shown that copolymers show very little miscibility with PI homopolymer with the same molecular weight as the backbone in SGI, morphology of blends comprising homo PI with lower molecular weight is examined. In an extreme case, the molecular weight of the added homo PI is even less than that of PI segments between the neighbouring branches. *Figure 7* is a micrograph of the blend SGI-1/PI-1. Although the molecular weight of PI-1 is only about two-thirds of that
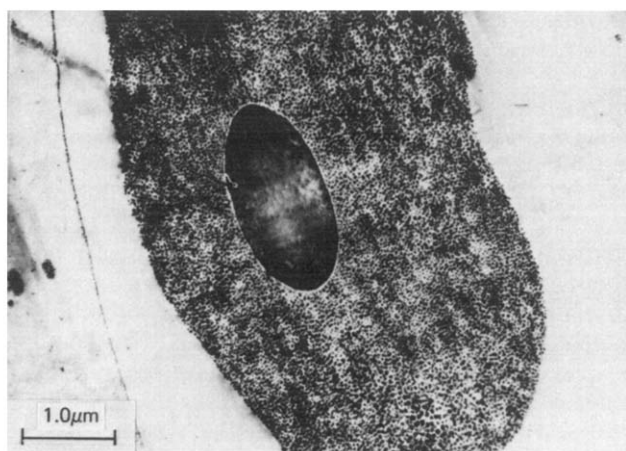

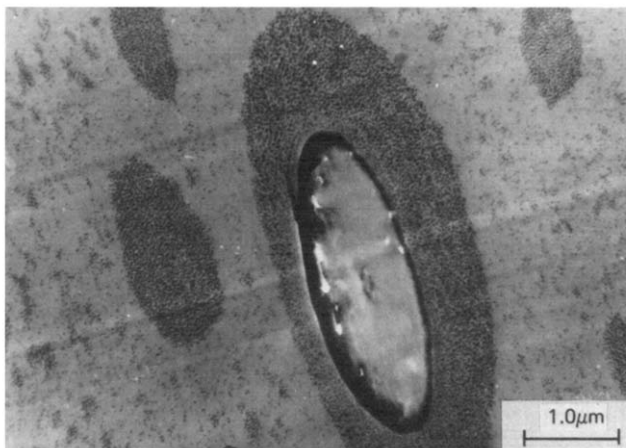**Figure 5** Electron micrograph of SGI-1/PI-8 in HPS

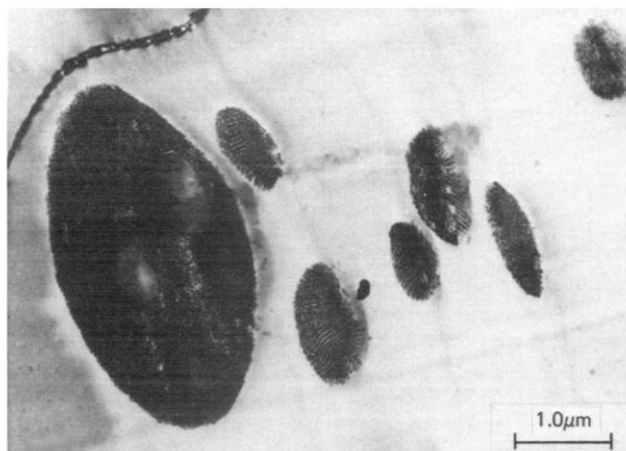**Figure 6** Electron micrograph of SGI-3/PI-8 in HPS

Figure 7 Electron micrograph of SGI-1/PI-1 in HPS

Figure 8 Electron micrograph of SGI-2/PI-1 in HPS

of PI segments of SGI-1, in the dispersed particles large spherical droplets of homo PI are visible, which indicates that the weight ratio of homo PI to the PI segments in SGI-3 is beyond the solubility limit of the homopolymer in PI microdomains. The partial solubilization of PI-1 can be verified by the obvious enlargement of the PI domains apparent in some micrographs of the blend at higher magnification. Blends of SGI-1 with PI-2 and PI-3 respectively were also examined and found to have the same morphological characteristics as SGI-1/PI-1. Furthermore, for copolymer SGI-2, morphological study of blends with both PI-1 and PI-3 provides further evidence of the limitation of the solubilization (*Figure 8*). This relatively limited solubilization of the low molecular weight homo PI in the corresponding microdomains of SGI is considered to be closely associated with the special architecture and then the serious conformation restriction of PI segments in the domains. As expected, all blends of SGI-1 and of SGI-2 with homo PI of higher molecular weight than that of PI segments show macrophase separation and, in particular, the size of PI microdomains hardly changes in comparison with that in the copolymer itself, which indicates complete immiscibility between the homopolymer and the corresponding block chains.

For the blend series of SGI-3, which has higher proportion of PS, with PI homopolymers of different molecular weights the same conclusion as for SGI-1 and SGI-2 blends can be drawn from examination of blend morphologies. However, more interesting for these

blends is the partial solubilization of copolymer in HPS matrix and its variation with the addition of homo PI. As seen in *Figure 4* for SGI-3/HPS, many discrete PI microdomains pervade the HPS matrix while most of the microdomains aggregate to form copolymer macrodomains. However, the morphology of the blend of SGI-3 with low molecular weight PI-1 shows that addition of homo PI-1 results in the appearance of homo PI phase in dispersed particles, an increase in the size of PI microdomains in the particles and, more interestingly, an apparent decrease of the number density of the PI microdomains scattered in the matrix (*Figure 9*). The size of discrete microdomains remains the same as in pure SGI-3 (*Figure 4*) while that of microdomains in the dispersed particles is increased owing to solubilization of low molecular weight PI-1. The same morphology is found for blend SGI-3/PI-2 with almost the same molecular weight combination of homo PI and PI segments. However, when the molecular weights of the added homopolymers (PI-4, PI-5) are larger than that of the PI segments in the copolymer, the number density of the discrete PI microdomains increases in comparison with that in SGI-3/PI-1 and no difference in PI microdomain size between the discrete and aggregated microdomains is apparent (*Figure 10*). With a further increment of the molecular weight of the homo PI, SGI-3/PI-8 (*Figure 6*) returns to almost the same morphology and the same number density of the discrete PI microdomains as that in *Figure 4* for the copolymer itself, except for the appearance of homo PI droplets in the
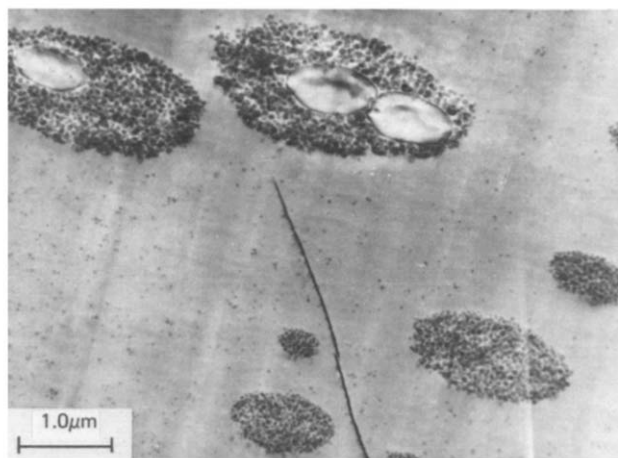

Figure 9 Electron micrograph of SGI-3/PI-1 in HPS

Figure 10 Electron micrograph of SGI-3/PI-4 in HPS

dispersed phase. Since among the three SGI copolymers only SGI-3 shows the discrete PI microdomains randomly dispersed in the HPS matrix, this particular feature that indicates the unexpected apparent miscibility in high molecular weight homopolymer matrix is probably associated with the particular composition of SGI-3, i.e. the higher proportion of polystyrene. In support of this explanation it has been found already that diblock copolymer of styrene and isoprene with $>80\%$ PS can be solubilized in polystyrene matrix with molecular weight twenty times larger than that of the PS blocks, i.e. the blends exhibit the morphology of randomly dispersed PI microdomains without macrophase separation. The gradient density model[13] suggested for calculating miscibility between homopolymer and diblock copolymer of lamellar structure may be useful for understanding the nature of the unexpected apparent miscibility of diblock copolymer of spherical structure in homopolymer that represents the major component of the copolymer.

ACKNOWLEDGEMENTS

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