thalate with bromo-chloromethane failed to give polymer with a molecular weight above 2000, and it is suspected that here cyclization is still an important reaction; nevertheless it may be possible to obtain high polymer under other conditions. Indeed we have evidence which suggests that cyclization is less prevalent when the potassium salts are used, though so far we have been unable to produce more than low molecular weight polymer with such salts. The work reported here has very striking similarities with the study of the cyclization of ω-halo-carboxylate salts reported by Kruizinga and Kellogg[4] who noted remarkable efficiencies in cyclization when using the caesium salts. These workers drew attention, amongst other factors, to the tendency to intramolecular triple ion formation observed with the caesium salts of dicarbanionic species[5,6]; if such behaviour occurred in the case of the caesium dicarboxylates, it might well be a contributory factor to the efficient cyclization indicated in the present study.

The characterization of the poly(methylene esters) is in hand and will be reported elsewhere.

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Studies on phase separation in polyblends of block copolymers

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The morphologies of polyblends of block copolymers of styrene and butadiene with similar composition but different molecular weights have been examined with an electron microscope. The micrographs show that some supramolecular features, with different morphologies to those in the matrix, are randomly dispersed. These results, we believe, provide evidence of the incompatibility of the block copolymers in spite of their chemical identity.

Keywords Block copolymers; compatibility; electron microscopy; morphology; phase separation; polyblends

Introduction

In the field of multicomponent polymers, phase separation is one of the major subjects which has been extensively studied. It is well known that most homopolymer blends are incompatible because of the positive mixing enthalpy and the small mixing entropy. As to block copolymers with well-defined structures, a large number of investigations have demonstrated that the mutual incompatibility of different blocks linked by chemical bonds results in microphase separation forming characteristic domain structures. This experimental result is further substantiated by statistical and thermodynamic calculations. However, in the case of blends of block polymers and homopolymers, a complicated situation arises. Many studies[1,2] published mainly in the early seventies, suggest that homopolymer chains can be considerably solubilized in the domains of the like blocks of the copolymer provided the molecular weight of the former is not larger than that of the latter. Nevertheless, there were some reports[3,4] concerning the presence of some large supramolecular features with different interior structures from the bulk sample in certain copolymer–homopolymer blends. These features were just regarded as 'unusual structures' and no reasonable explanation of their formation was given.

In recent years, Eastmond *et al.* have presented a series of morphology studies on blends of so-called non-linear block copolymers or AB crosslinked copolymers (ABCPs) with their corresponding homopolymers[5]. In order to explain the formation of the 'unusual structures', which were inevitably found to appear in these blends under suitable combinations of molecular species and processing conditions, they suggested that the homopolymer chains are incompatible with the like blocks of copolymers at equilibrium, and the discrete regions found in the blends are virtually the copolymer-rich phase. The unusual morphologies are formed by a combination of macrophase separation between the homopolymer and the block copolymer and microphase separation in the block copolymer itself. This opinion found support from Meier's theoretical calculation[6] on the possibility of the solubilization of homopolymers in their corresponding block domains, which in fact is an extension of his theory concerning microscopic phase separation in block copolymers. According to Meier, only about 5% (w/w) of the homopolymer can be solubilized by the copolymer at equilibrium if they have the same molecular weight. The apparent solubilization of the homopolymer in the copolymer reported earlier is attributed to the non-equilibrium nature of the blend systems. Therefore, from studies presented mainly by Eastmond[5], Meier[6] and Riess[7], it seems reasonable to believe that the solubilization of the homopolymer in the like block of the copolymer is very limited at equilibrium because of the unfavourable entropy for accommodating both unrestrained and restrained polymer chains in the same domain, in spite of their chemical identity. This communication reports the results of an electron microscopy study of the polyblends of two block copolymers which are chemically identical but with different molecular weights.

Experimental

Star block copolymers of styrene and butadiene were prepared anionically in cyclohexane using s-BuLi and epoxidized soyabean oil as the initiator and coupling agent respectively. As polystyrene and polybutadiene blocks were produced successively and the coupling reaction took place between the living polybutadiene chains, the polybutadlene blocks formed the centre of the star copolymers. In order to make sure of the reproducibility of the electron microscopy observations, two sets of the block copolymers, one with high molecular weight (L1, L2 and L3) and the other with low molecular weight (S1, S2 and S3) were made under two different reaction conditions. The products were purified by partial precipitation in toluene/methanol. The samples were characterized by means of g.p.c., osmometry and u.v. spectrophotometry. For example, g.p.c. measurements of S1 and L1 show that they have relatively narrow molecular weight distributions. Their number-average molecular weights determined by osmometry in tetrahydrofuran and the compositions measured by spectrophotometry at 262 μm in trichloromethane are listed as follows:

Sample	$\bar{M}_n$	Composition PS/PB (w/w)
L1	2.21×10^5	70/30
S1	2.97×10^4	67/33

From the results of chemical analysis of the coupling agent and the molecular weights of the polymers obtained before and after the coupling reaction, both the average functionality and coupling degree of the epoxidized soyabean oil were found to be four. Therefore, the block copolymers L and S have four arms and the molecular weights of arms of L and S are 5.5×10^4 and 7.4×10^3 respectively.

Films of pure copolymers were cast from benzene solutions by slow evaporation at room temperature. Blend films were prepared by casting solutions of 75% L and 25% S in benzene or cyclohexane, thus three blends (B1, B2 and B3) were obtained from S1/L1, S2/L2 and S3/L3 respectively. The films were stained in an aqueous solution of osmium tetroxide (1%) and were cut parallel to the film surface with a ultramicrotome. The morphological observations were made using a Hitachi H-500H electron microscope.

Results and Discussion

In the electron microscopic examination of the polyblends, the most remarkable result is a lack of uniformity on a macroscopic scale. For the films of the blends (L/S:75/25), some supramolecular features, which have different morphologies to those in the matrix, are randomly dispersed throughout the sample. Usually, these discrete regions without any regular shape are of 0.3–5 μm in size, mostly 0.5–2 μm. A typical micrograph of blend B1 is shown in *Figure 1*.

Figure 2, a micrograph for blend B1 with a larger magnification, reveals a clear interface between the disper-

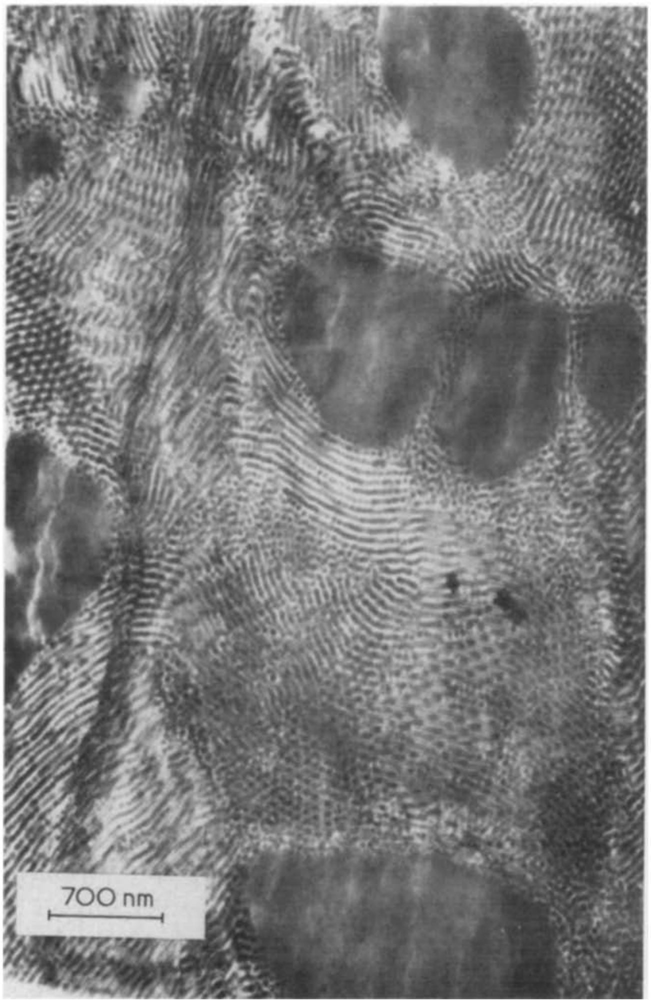

Figure 1 Electron micrograph of polyblend B1 (L1/S1 75/25) cast from benzene

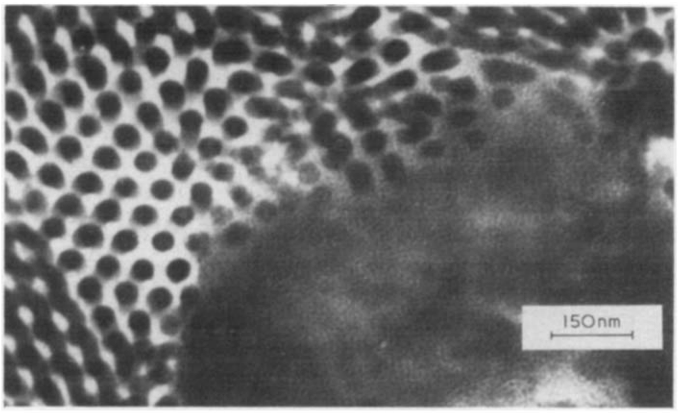

Figure 2 Electron micrograph of polyblend B1 (L1/S1 75/25) cast from benzene

sed phase and the continuous phase. In the dispersed regions, regular microphase separation leading to a worm-like polybutadiene–polystyrene domain structure can be readily seen. The size of these domains is less than 10 nm. Obviously, this small-scale domain structure can only be formed by the low-molecular-weight block copolymer.

As to the morphology in the continuous phase, apparently, rod-like or cylindral domains of the polybutadiene pervade the polystyrene matrix. Although there is no profound long-range order, hexagonally assembled circular polybutadiene domains are present, which might come out from either spherical domains or cross-sectional view of the rods with an orientation perpendicular to the sections (*Figure 3*). As in most of the areas of the sections, only rod-like domains appear, we believe that the hexagonally assembled circular domains are virtually the cross-sections of cylindrical domains rather than spherical ones. A rough estimation gives a value of the polybutadiene domain size in the continuous phase of about 35–40 nm. Compared with the morphology obtained in the pure high-molecular-weight block copolymer (L1) (*Figure 4*) where the rod-like or cylindral polybutadiene domains of 35–40 nm are dispersed in polystyrene matrix, it can be concluded that the major component of the blend, i.e. the high-molecular-weight block copolymer (L1), forms the continuous phase of the blend.

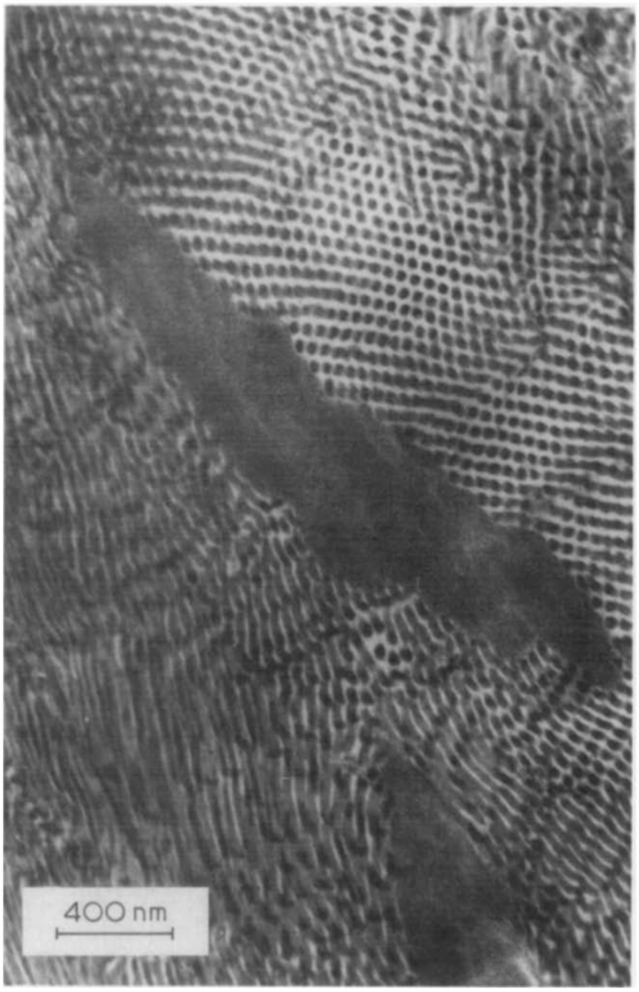

Figure 3 Electron micrograph of polyblend B2 (L2/S2 75/25) cast from benzene

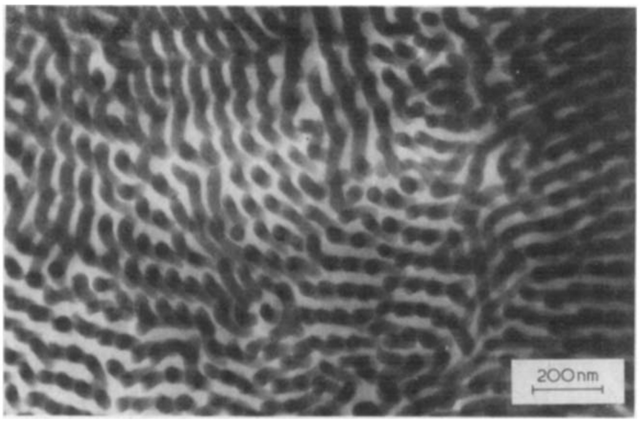

Figure 4 Electron micrograph of block copolymer L1 cast from benzene

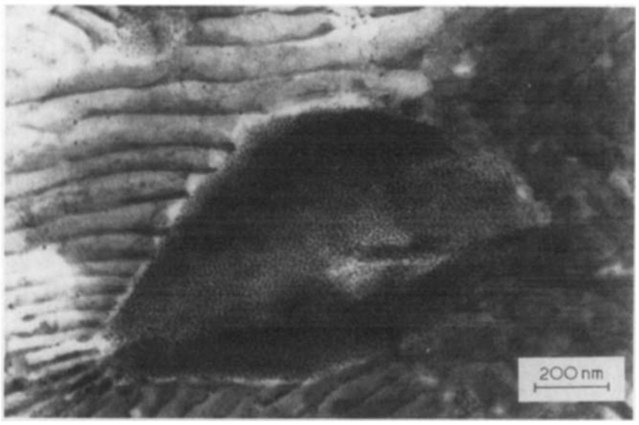

Figure 5 Electron micrograph of polyblend B3 (L3/S3 75/25) cast from cyclohexane

Based on all these observations we suggest that in the blends of the block copolymers with similar chemical compositions but different molecular weights, macrophase separation between the copolymers and microphase separation in each of the macrophases are present. Thus, this kind of blend is virtually a combination of microcomposite and macrocomposite. This conclusion can also be reached from the micrographs of blends B3 which was cast from cyclohexane instead of benzene (*Figure 5*) although the details of the phase separation are somewhat different.

In an extensive study on microphase separation of block copolymers presented by Hoffman *et al.*[8], some information dealing with the blends of diblock copolymers of styrene-butadiene was mentioned also. They reported that in this kind of blend there are two maxima in the domain size distribution associated with the two component block copolymers without evidence of macroscopic phase separation and this fact was regarded as an indication of demixing between the component copolymers. In our opinion, the difference of molecular weights of the component copolymers is not large enough, therefore macrophase separation in the blends they studied could not be clearly observed. Obviously, their observations of diblock copolymers and the present work on the star block copolymers are in agreement as regards proving the incompatibility in the block copolymer–block copolymer blends.

This incompatibility in copolymer blends is understandable if we draw an analogy with the case of blends of block copolymers with the corresponding homopolymers, where unfavourable entropy of mixing is a dominant factor. In the blends of like block copolymers, mixing of the like blocks with different molecular weights in the same domain will, perhaps, lead to a more unfavourable entropy. Thus, supposing a comparable amount of low-molecular-weight blocks exist in a domain of the like high-molecular weight blocks, since the junctures of the block copolymers must be located in the domain interface, the free ends of the low-molecular-weight blocks will not be able to reach the region near the centre of the domain. This fact will cause a greater density heterogeneity. Therefore, more restraint and hence more entropy loss is required to obtain constant density in the domains.

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