

Macroscopic phase separation in multicomponent polymer homopolymer blends: general considerations based on studies of AB—crosslinked polymers

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This paper explores the significance of, and presents additional evidence in support of, our earlier conclusion that molecules of multicomponent polymers (i.e. copolymers consisting of long sequences of different components), such as AB-crosslinked polymers, are normally incompatible with homopolymers of the individual components. The arguments are generalized to include block copolymer systems. After a brief review of relevant previous studies, schematic phase diagrams appropriate to multicomponent polymer/homopolymer blends and common solvent are constructed. The consequences of solvent-casting mixtures of multicomponent species with one homopolymer from homogeneous dilute solution are considered for cases where equilibrium is always achieved, and more practical situations where equilibrium is not attained in bulk polymer. Electron micrographs of ultra-thin sections of solvent-cast blends of AB-crosslinked polymers with homopolymer are presented to substantiate and illustrate points made in the preceding discussion. Conclusions are drawn regarding possible morphologies which can exist in multicomponent polymer/homopolymer blends and it is proposed that unusual morphologies in block copolymer blends reported by various workers are the direct consequences of combinations of macroscopic phase separation and subsequent microphase separation within phases of different composition. We suggest that the incompatibility of chemically identical blocks and homopolymers arises from an unfavourable entropy of mixing as a result of the blocks in the vicinity of microphase interfaces adopting different sets of conformations than randomly-coiled chains in bulk polymer.

INTRODUCTION

Chemically-different high-molecular-weight polymers are normally incompatible and their blends, when cooled from the melt or cast from solution, undergo macroscopic phase separation with complete segregation of the components at equilibrium. If the molecular weights of different blocks in pure multicomponent polymers (e.g. block copolymers) are sufficiently great the mutual incompatibility of those blocks leads to microphase separation with a characteristic morphology existing throughout the sample.

Simple blends of multicomponent polymers and homopolymer present a more complex situation. Some samples exhibit a simple morphology which persists throughout while others exhibit a variety of large isolated supramolecular features. More complex mixtures, such as exist in rubber-modified (high-impact) plastics, present a variety of apparently complex morphologies.

We have studied a number of AB-crosslinked polymers (ABCPs) and their blends and have observed a variety of morphologies, both simple and complex. Recently, we presented a brief description of a mechanism to explain the formation of some of the apparently complex morphologies¹.

The mechanism, based on our conclusion that multicomponent polymers are incompatible with either of the component homopolymers, involves a combination of macroscopic phase separation and microphase separation. We believe that this mechanism has a greater general validity than indicated in our previous paper and is capable of predicting the wide variety of morphologies observed in multicomponent polymer blends. In this paper we provide proof of macroscopic phase separation in copolymer/homopolymer blends; discuss, in more general terms, the mechanism and consequences of macroscopic phase separation in such materials; and provide additional experimental evidence, derived from our studies of ABCPs, to illustrate the conclusions of the preceding discussion. First, we summarize some pertinent observations from earlier studies of multicomponent polymers and their blends.

Block copolymers and their blends

At equilibrium pure linear AB and ABA block copolymers exhibit only certain well-defined morphologies, namely, either spherical or rod-like domains (microphases) of the minor component dispersed in a matrix of the major component or alternating lamellae of the two components²; in carefully prepared samples the microphases show considerable long-range order³. For simple block copolymers the composition

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ranges over which specific morphologies exist have been predicted theoretically⁴ and predictions are in general accord with observations.

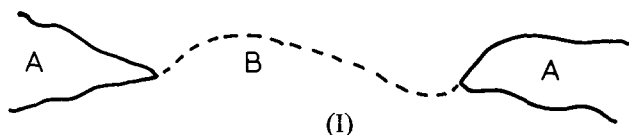
Addition of one homopolymer to block copolymers generally disrupts the long-range order although the intrinsic morphology of the block copolymer may persist^{3,5}. (We define intrinsic morphology as the equilibrium morphology of the multicomponent species in the absence of any homopolymer). Addition of a little homopolymer to block copolymers having extended microphases of the other component, e.g. lamellae, may disrupt the regular packing of the lamellae while excessive amounts may disrupt the lamellae themselves to form short rods and, ultimately, spheres of the (now) minor component⁶.

In addition, some workers have reported the existence of large supramolecular features in blends of block copolymer with one homopolymer^{7,8}. These features (typically 0.3–10 μm across), randomly distributed throughout the sample, are seen as regions of a different morphology to the bulk of the sample and contain a relatively high proportion of the overall minor component.

The observation of fairly uniform morphologies in many homopolymer/block copolymer blends has led various workers to conclude that block copolymers are capable of solubilizing homopolymer which is incorporated into and swells the appropriate microphase. Inoue *et al.*⁹ recognized that if the molecular weight of the homopolymer is greater than that of the corresponding block in the copolymer it is not solubilized but forms a separate phase. However, it is often considered that, if the molecular weight of the homopolymer is equal to or less than that of the corresponding block in the copolymer, significant proportions of homopolymer can be solubilized in the copolymer, as indicated in a number of studies referred to above^{5–8}.

AB-crosslinked polymers and their blends

ABCs consist of chains of a polymer A crosslinked by chains of a different polymer B. We prepare them by a free-radical process in such a way that no B-homopolymer is formed and the crosslinking index is, in most cases, sufficiently low that no gel is formed; the general synthetic procedure has been described previously^{10–12}. ABCs are assemblies of multicomponent species and A-homopolymer and we have described, in general terms, the distribution of structures of multicomponent species present^{1,13}. Although ABCs contain a variety of multicomponent species the structure of all such species involved in materials used in the present study are derived from that of an A₂BA₂ block copolymer (structure (I)); we use structure (I) as a model for discussing ABCP morphologies.



We have not obtained uncontaminated multicomponent species from ABCs and have not, therefore, observed the morphologies of pure species such as (I), but we have observed and reported^{1,13,14} the existence of all the fundamental morphologies which exist for linear block copolymers. In the absence of added, or large excesses of, A-homopolymer solvent-cast ABCs usually exhibit a uniform simple morphology. As the relative molecular weights of the A- and B-blocks are varied systematically the same sequence of morphologies

are observed for non-linear multicomponent species as for linear block copolymers. The only anticipated distinction between linear and non-linear polymers is the composition ranges over which each morphology exists¹³. Further, our observations on ABCs are consistent with studies on block copolymer/homopolymer blends (cf ref 6) and indicate that the presence of A-homopolymer displaces the composition limits of each morphology towards a higher B-content.

During our studies of ABCP morphologies we observed that in the presence of high proportions of A-homopolymer, either at very low cross-linking indices or in the presence of large proportions of added A-homopolymer, unusual morphological features were formed and morphologies were not uniform throughout the samples^{1,14}. Samples exhibited regions (~2 μm across) of one morphology dispersed in a matrix of different morphology. In some cases the internal structure of the dispersed regions was irregular (similar to the features observed by Molau and Wittbrodt⁷ in block copolymer blends) while in other samples the internal structures showed a considerable degree of long-range order. To explain the presence of and to provide a mechanism for the formation of these dispersed regions we were forced to conclude that, at equilibrium, multicomponent species are incompatible with homopolymer¹. We proposed that, during solvent casting of homopolymer-rich samples, macroscopic phase separation occurred to form droplets of a copolymer-rich phase. Subsequent microphase separation in both the matrix and droplets gave rise to different morphologies determined by the local compositions.

EXPERIMENTAL

The procedure adopted for the synthesis of ABCs of known structure involves the controlled graft polymerization of a monomer (to form B-chains) from specific sites (containing reactive halogen) on preformed A-chains, initiation is accomplished with the aid of a suitable metal derivative. More detailed accounts of the synthetic procedure have been presented elsewhere^{10–12}. In this work we employed photoinitiation with dimanganese decacarbonyl ($\lambda = 436$ nm). Propagating radicals of the monomers used (styrene and chloroprene) undergo combination termination¹¹, so that both ends of all B-chains are attached to A-chains; i.e. no B-branches are formed. A-components used in this study were poly(vinyl trichloroacetate) (PVTCA) and a polycarbonate (PCarb).

The polycarbonate was prepared by condensation of carefully purified 1,1,1-trichloro-bis-2-(*p*-hydroxyphenyl)ethane with phosgene in dichloromethane/pyridine solution. After washing with a 10% aqueous solution of hydrogen chloride the polymer was precipitated from solution (diluted to ~5% (w/w) solution in dichloromethane) into petroleum spirit, reprecipitated twice from tetrahydrofuran solution into distilled water and finally from dichloromethane into petroleum spirit. Other starting materials were prepared and purified as described in earlier papers.

ABCs having PVTCA as A-component were prepared using bulk monomer as solvent during formation of B-chains, while those containing PCarb were prepared in the presence of dichloromethane as common solvent to aid dissolution of the polycarbonate (in comparison with the polycarbonate CH₂Cl₂ is ineffective in initiation). Polymers were isolated by precipitation and samples were cast from solvent to produce films ~0.2 mm thick. Casting solvents used were chlorobenzene for polycarbonate/polychloroprene ABCs and dichloromethane for other ABCs. ABCs containing poly-

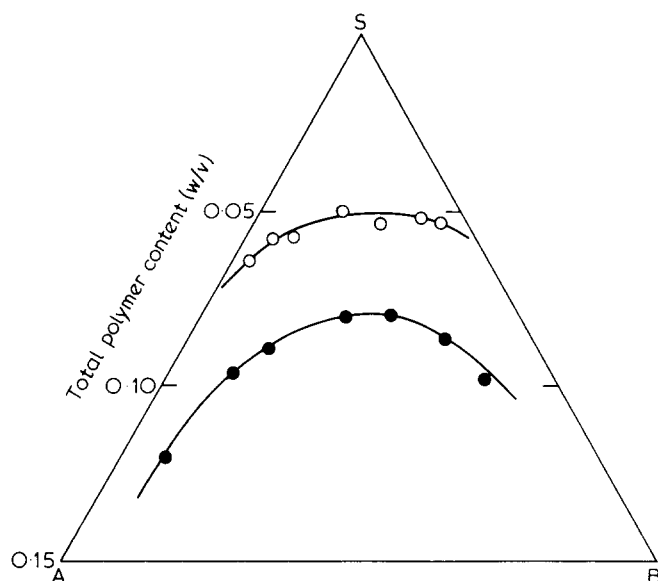


Figure 1 Phase diagrams for two polymer (A)/polymer (B)/common solvent (S) systems. In both cases A is polycarbonate ($M_n = 16 \text{ kg mol}^{-1}$). O: B = polychloroprene ($M_n = 72 \text{ kg mol}^{-1}$), S = chlorobenzene; ●: B = polystyrene ($M_n = 125 \text{ kg mol}^{-1}$), S = dichloromethane

chloroprene were stained and hardened using an aqueous solution of osmic acid ($\sim 1\%$ (w/v)), other polymers were unstained. Identification of components in unstained samples was established in subsidiary experiments. Ultrathin sections (usually $\sim 100 \text{ nm}$ thick) were obtained using an LKB Ultratome III. Samples containing either no polychloroprene or a dispersed phase of hardened polychloroprene were sectioned at room temperature, those having a hardened polychloroprene matrix could be sectioned satisfactorily at low temperatures (knife and sample temperatures were typically -95°C , -105°C , respectively). Typical instrument settings were: knife angle 45° , clearance 5° , cutting speed 2 mm s^{-1} . Sections were examined using an AEI EM6 electron microscope.

PHASE SEPARATION IN POLYMER BLENDS

Homopolymer Blends

Figure 1 shows sections of two typical and relevant phase diagrams for ternary systems consisting of two incompatible homopolymers (A, B) and a common solvent (S). In each case the binodals lie close to the polymer-solvent axes and, except in solutions dilute in total polymer, each polymer has very limited solubility in solutions of the other. Thus, when casting blends from homogeneous solution, assuming equilibration is not restricted by the viscosity of the system and the rate of drying, almost complete separation of the polymers is achieved at moderate polymer concentrations.

We detected phase separation by observing droplet formation of the minor phase with the aid of a microscope. Usually systems were sufficiently dilute that the droplets aggregated readily to form distinct phases, the volumes and compositions of which allowed construction of tie lines on the phase diagrams; in the diagrams in Figure 1 the tie lines were near horizontal.

Multicomponent polymer blends

Early in our investigations the occurrence of macroscopic phase separation in ABCPs and their blends was inferred since we found it necessary to assume incompatibility of

homopolymer and multicomponent species to explain the appearance of onion-like structures in solvent-cast blends of ABCPs with one homopolymer (component A)¹. That the onion type structures occupied spherical volumes ($0.5\text{--}5 \mu\text{m}$ diameter), and had internal structures of concentric shells of A- and B-components was established by examination of successive sections; they were dispersed randomly throughout the sample. We interpreted these structures to be remnants of droplets of a minor B-component-rich phase which had separated from the bulk solution and which developed an internal lamellar structure on microphase separation. Examples of these structures may also be seen in Figures 4b, 5, 11.

These ideas are supported by Meier's recent theoretical calculations on blends of AB block copolymer and A-homopolymer¹⁵. He estimated that the amount of homopolymer which can be solubilized by copolymer at equilibrium decreases as the homopolymer molecular weight increases and is only 5% (w/w) for equal molecular weights of blocks and homopolymer. Thus, he concluded, apparent solubilization of additional homopolymer by copolymer (in bulk) represents a non-equilibrium situation. Meier also calculated that during solvent casting of such blends either a homopolymer phase or a copolymer phase (containing up to 50% (w/w) homopolymer) should be excluded during drying according to whether the homopolymer molecular weight is greater than or less than 0.4 times that of the A-block.

Figure 2 provides direct proof of macroscopic phase separation in a blend of a PVTCA/PSt ABCP blended with PVTCA homopolymer. The sample (ABCP5, Table 1) was cast from dilute homogeneous solution in dichloromethane and solvent was evaporated until phase separation, evident by the

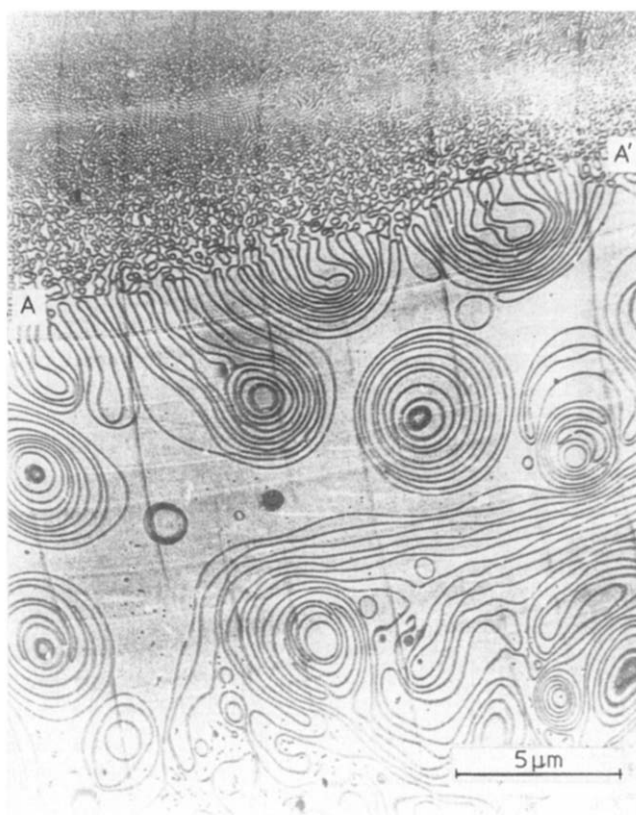


Figure 2 Electron micrograph of unstained section of ABCP5 (PVTCA/PSt). The interface between layers produced by macroscopic phase separation is indicated by AA'. (PSt appears dark)

Table 1 Structural parameters of ABCPs

ABCP	A	B	M_A^b	M_B^b	γ_r	ABCP Composition (% w/w)			Added A % (w/w)
						B Overall	B in C	C in ABCPs	
1	PCarb	PSt	16	96	0.35	34	75	45	0
2 ^a	PCarb	PSt	16	96		10	75	13	240
3	PCarb	PCp	97	581	0.022	5	75	6.6	0
4	PVTCA	PSt	44	354	0.21	30	80	37	0
5 ^a	PVTCA	PSt	44	354		5	80	6.2	500
6	PCarb	PCp	16	227	0.12	34	87	39	0
7 ^a	PCarb	PCp	16	227		21	87	24	62
8	PCarb	PSt	97	123	0.48	17	38	45	0
9	PVTCA	PSt	44	162	0.41	32	64	50	0
10	PCarb	PCp	16	97.4	0.028	5	75	6.6	0

^a Formed by adding the indicated amount of polymer A to the preceding ABCP

^b Values of M_A , M_B are number-average molecular weights in kg mol^{-1}

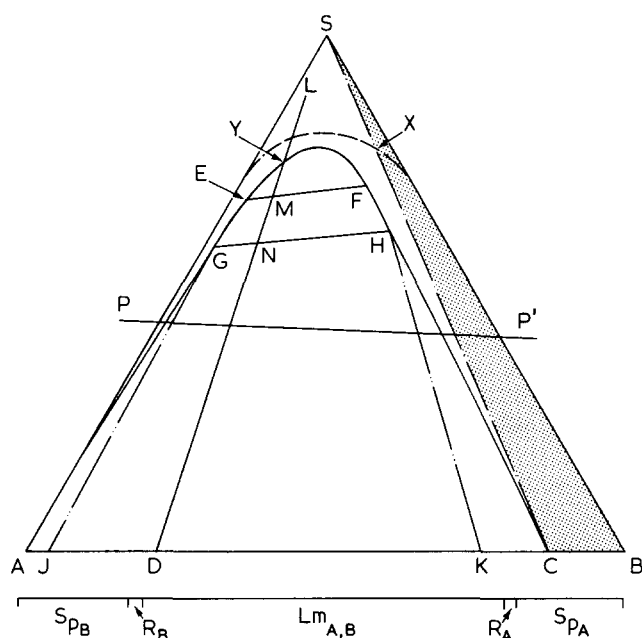


Figure 3 Schematic phase diagram illustrating macroscopic phase separation in mixtures of homopolymer A, copolymer C (block or graft) and common solvent S. The scale, under the phase diagram, indicates the approximate composition ranges (calculated by Meier⁴) over which particular morphologies are stable in pure AB block copolymers. The nature and component of the microphases present are indicated by the symbols Sp (spheres), R (rods), Lm (lamellae) and their subscripts, respectively

appearance of droplets, occurred. The sample container was then sealed. The droplets were very stable but after several days started to coalesce, eventually forming a thin layer of a minor phase on top of the bulk solution. Once the layer was established the remainder of the solvent was removed by slow evaporation. *Figure 2* is an electron micrograph of an ultra-thin section (unstained) of the sample cut perpendicular to the surface layer. Line AA' marks the interface between the upper, minor PSt-rich phase and the lower PVTCA-rich phase; PSt appears dark and PVTCA light. Sections of a few onion-type structures can be seen below and relatively close to the interface. They are the remains of droplets of the polystyrene-rich phase which did not coalesce but were trapped in the PVTCA layer when the sample was finally dried; some droplets were caught in the act of coalescing. Well below the interface the lower layer comprises only small PSt spheres in a PVTCA matrix. Some features of *Figure 2* will be discussed subsequently.

PHASE DIAGRAMS FOR COPOLYMER-HOMOPOLYMER BLENDS

Although the arguments of this section derive largely from our experimental observations of ABCPs and their blends, since AB, ABA and A_2BA_2 block copolymers must be subject to similar thermodynamic relations, the underlying principles and conclusions are equally applicable to blends of one homopolymer with linear block copolymers or other multicomponent species. We propose that a typical phase diagram for a ternary system of homopolymer A, multicomponent polymer (derived from polymers A and B) and common solvent S can be represented schematically as in *Figure 3*. The detailed construction of the phase diagram is based on three assumptions: (a) our basic premise (supported by Meier's calculations¹⁵) that multicomponent species and homopolymer are incompatible; (b) the molecular weights of A- and B-chains or blocks are sufficiently great that B-chains are incompatible with all A-chains; (c) the triangular composition diagram defines the total proportions of polymers A, B present, irrespective of molecular architecture.

Condition (b) produces microphase separation in bulk polymer with essentially complete separation of A- and B-components. Although microphase separation is the process which determines the detailed internal physical structure of the polymer and often largely determines the properties of the polymer, we note that the microphases are not true phases as defined by Gibbs¹⁶; they are not mechanically separable, their dimensions (in the absence of included homopolymer) are restricted by molecular dimensions, their boundaries are diffuse and often non-planar.

It is premise (a) which leads to true, macroscopic phase separation. An implication of this premise is that both B-chains and their attached A-chains are incompatible with A-homopolymer (unless homopolymer A is of very low molecular weight compared with A-chains in the copolymer).

In the absence of homopolymer B all B-chains are attached to A-chains. Although microphase separation leads to local regions of essentially pure B and others of pure A, no true phase can be generated with a greater proportion of B than that contained in the multicomponent species; we represent the composition of such species as C. Therefore, compositions of true phases in the area SBC of *Figure 3* are forbidden.

Dilute solutions of the blend in S are homogeneous and it is therefore possible to draw a binodal curve defining the limits of homogeneity. In general we cannot predict the shape of the binodal theoretically and we have insufficient experimental data to draw the binodal for any specific system. On

the grounds that in dilute solutions of homopolymer A and multicomponent species of composition C (we designate the latter as copolymer C) there will be similar interactions per unit volume as in a blend of homopolymers A and B at the same composition (assuming molecular weights of the components are similar) we could, to a first approximation, use the binodal for mixtures of A, B and S, i.e. AXB (*Figure 3*). The implication of this in a real system is that on casting a blend of A and C from homogeneous solution in S phase separation in dilute solution should readily yield pure multicomponent species; this is not so readily achieved in practice.

We prefer, for the general case, to draw the binodal AYC (*Figure 3*). This curve permits more A-chains (as homopolymer) to be contained in the B-rich phase than were necessarily included (as attached chains) in the former case. Nevertheless, we believe that this curve is in greater accord with observations and with Meier's calculations. As drawn, the binodal predicts complete separation of A and C at equilibrium. The curve may be modified to allow for solubility of A in C and vice versa if this is required in any specific situation. Thus, the phase diagram is the classic diagram for two immiscible (or partially-miscible) substances in a common solvent. It could be redrawn as an equilateral triangle with vertices, A, S and C; we retain the diagram as in *Figure 3* at this stage.

Equilibrium morphologies in copolymer-homopolymer blends

Assuming equilibration occurs at all stages, we consider the consequences of solvent-casting mixtures of multicomponent species and homopolymer. These may be mixtures as produced in the synthesis of ABCPs or predetermined blends. *Figure 3* presents the situation for a copolymer C (rich in B) with large proportions of homopolymer A and corresponds to many of our experimental conditions. Starting with a homogeneous solution of composition L and gradually removing solvent we reach the binodal at Y when macroscopic phase separation first occurs. At composition M a minor copolymer-rich phase (composition F) co-exists with a major homopolymer phase (composition E); initially the minor phase will appear as droplets which coalesce to give two layers. As further solvent is removed the compositions of the conjugate phases will adjust through G and H to A and C, i.e. pure homopolymer and pure copolymer.

Microphase separation must occur in each phase at some total polymer concentration, usually unknown. This process could accompany macroscopic phase separation but we shall assume that it occurs at such polymer concentration (on some line PP') that in most practical situations the system will have already undergone macroscopic phase separation. For idealised systems proceeding to equilibrium the position of PP' is irrelevant but has relevance in practical situations discussed later.

At final equilibrium the bulk polymer will comprise a pure A-homopolymer phase (no B-component, no microphases) and a pure copolymer phase exhibiting microphase separation corresponding to that of the pure copolymer species (its intrinsic morphology). The morphology of the C-phase will be determined by the structure and composition of the copolymer species. The approximate composition limits of possible morphologies for AB block copolymers, as calculated by Meier⁴, are indicated at the foot of *Figure 3*. We have suggested that in species A₂BA₂ (as in ABCPs) the composition limits for pure copolymer would be displaced slightly towards a higher B content and that inclusion of A-

homopolymer in that phase would further displace the limits to a higher B-content; the magnitude of these displacements is unknown. For the situation in *Figure 3* (assuming the morphology-composition limits indicated are applicable) the copolymer phase would have a B-matrix.

Non-equilibrium morphologies in blends

It is almost inevitable that only non-equilibrium morphologies are observed in practical systems. We return to the situation considered in the preceding section, that relating to *Figure 3*. Starting with homogeneous solution composition L and slowly removing solvent macroscopic phase separation occurs at Y. In the relatively dilute and non-viscous solution equilibration will proceed readily, the compositions of the phases following the binodal to, say, point M when we have phases of compositions E, F. As further solvent is removed the solutions will become more viscous and the transfer of polymer molecules between them progressively more difficult. Eventually the solutions will be too viscous for equilibrium to occur in a finite time. The detailed consequences depend on the exact shape of the binodal and the viscosity of the system. For illustration we take the case in which, on the experimental time scale, equilibrium occurs until point N is reached at which stage no further transport of polymer between phases is possible. We then have phases of compositions G, H. Further solvent removal causes the compositions of these phases to follow lines GJ, HK, respectively. Microphase separation occurs at solvent concentrations given by the intersections of GJ, HK with PP'. Assuming the solvent is equally good for both components and has no influence on the type of morphology produced, the final bulk polymer sample will comprise phases of compositions J, K with morphologies characteristic of those compositions. Comparing compositions J, K with the scale under *Figure 3*, the small quantity of B-component trapped in the homopolymer-rich phase will form discrete spheres. The homopolymer A trapped in the copolymer-rich phase will force that phase to adopt a lamellar morphology. Neither phase will exhibit its equilibrium morphology and, in general, the detailed consequences will depend the rate of solvent removal.

A family of phase diagrams can be drawn for different compositions of copolymer C and the consequences of starting with different combinations of copolymer and homopolymer may be examined. The detailed results vary with the shape of the binodal which is controlled by the polymer-polymer and polymer-solvent interaction parameters.

Trapping polymers in the wrong phase as a consequence of high viscosity developed during solvent casting is not the only factor which may affect the final morphology. We consider two other factors.

First, macroscopic phase separation will initially produce droplets of the minor phase in a matrix of the major phase. Equilibration requires coalescence of those droplets, but this may not happen. Assume the minor phase is copolymer rich. Copolymer molecules in the vicinity of the droplet surface will preferentially have their A-blocks in the major A-rich phase and B-blocks in the copolymer-rich (B-rich) phase. Exclusion of further A-homopolymer will increase the concentration of copolymer molecules at the interface, forming a layer rich in B-chains on the inside surface of the droplet. This layer may act as a stabilizing barrier for the droplets which may persist during the remainder of the casting process, resulting in the dispersion of copolymer-rich regions throughout a homopolymer-rich matrix. This is a situation

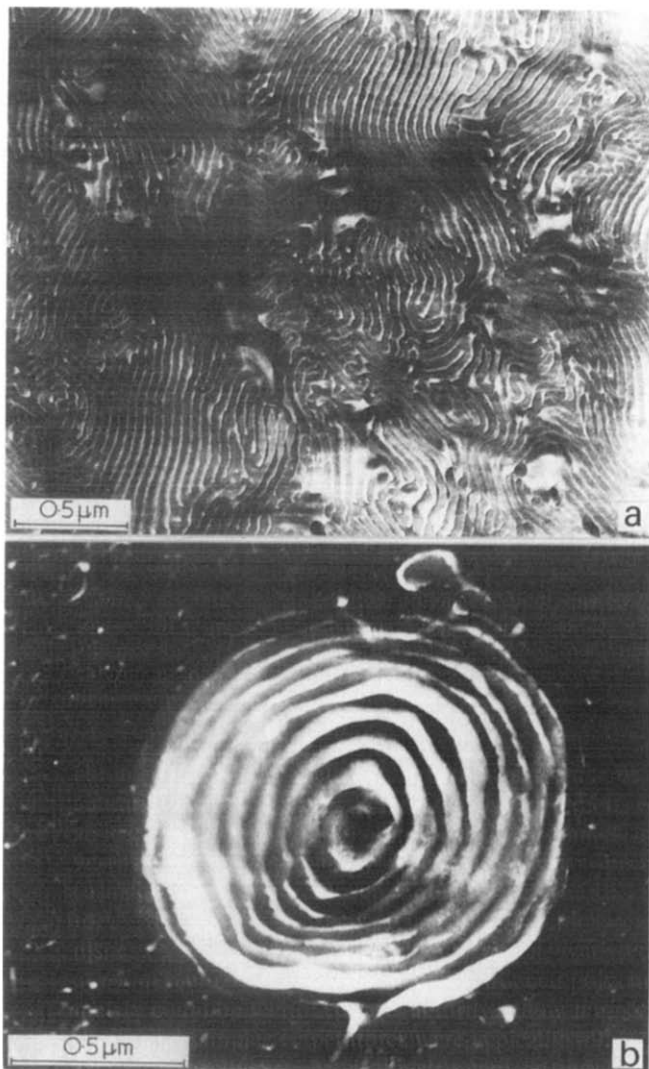


Figure 4 Electron micrographs of unstained sections of (a) ABCP1 (PCarb/PSt) and (b) ABCP2 (ABCP1 + 240% (w/w) added PCarb (PCarb appears dark))

we have observed many times and is responsible for the onion-type morphology we have reported previously¹.

Second, as Meier pointed out, microphase separation in a copolymer-rich phase to give a B-matrix will trap excess A-homopolymer in that phase¹⁵. He suggested that "Once homopolymer has been dissolved in a domain system, there is no realistic way for it to 'escape' or adjust composition to a new equilibrium condition, short of complete disruption (e.g. solution) of the domain system". Certainly the difficulty of transferring a polymer chain from one region to another through a microphase of the other component must be a great deterrent to equilibration. Nevertheless, we have observed approaches to equilibrium in progress (e.g. Figure 2) but have no proof as to whether or not it occurs prior to or after microphase separation. It is conceivable that under suitable circumstances (e.g. of molecular weight and interaction parameters) the phase diagram for A and B homopolymers may allow a finite concentration of, say, homopolymer A in B in the presence of solvent. The presence of a stationary concentration of A in the 'wrong' microphase could provide a mechanism, in a dynamic situation, for an approach to equilibrium, albeit very slow, in the later stages of casting and subsequent to microphase separation.

The above discussion demonstrates that it is virtually impossible to achieve true equilibrium morphologies of solvent-

cast blends of homopolymer with multicomponent polymers. Departure from equilibrium may be seen only as a swelling of one microphase by excess trapped homopolymer. Usually the consequences will be more obvious, such as the formation of dispersed regions of one morphology throughout a matrix of different morphology. In principle, by suitable selection of phase diagram and compositions of copolymer species and of the blend, it is possible to have regions of any basic morphology dispersed in a matrix of any other basic morphology.

ADDITIONAL OBSERVATIONS ON ABCPs

We now describe some observations made during a study of ABCPs and their blends with A-homopolymer chosen to illustrate points raised in the preceding discussion and implications of some views contained therein.

As prepared, ABCPs are themselves blends of multicomponent species and A-homopolymer. Such materials, when cast from solution by drying over a few days, often exhibit a uniform morphology throughout the sample. This is especially true if the B-chains are short and form B-spheres¹³. It is also true if the copolymer species contain long B-chains (to give an intrinsic morphology of lamellae or B-matrix) and, simultaneously, the copolymer species account for at least 30% of the total polymer; usually a uniform lamellar morphology is then observed. An example of this latter situation is seen in Figure 4a, a micrograph of ABCP1 consisting of polycarbonate (PCarb) crosslinked with PSt to a relative crosslinking index γ_r of 0.35; structural parameters of ABCP1 are given in Table 1. (γ_r is the number of crosslinking points per weight-average A-chain; $\gamma_r = 1$ at the gel point). In ABCP1 the A-homopolymer, which should form a separate phase, is contained in and swells the A-lamellae.

In our experience, macroscopic phase separation is most readily achieved if the copolymer species contain high-molecular-weight B-chains (relative to A) and, simultaneously, the copolymer constitutes only a small proportion of the total polymer. This situation can be achieved by (i) casting a blend of ABCP with added A-homopolymer, or (ii) preparing ABCPs with very low crosslinking indices.

Case (i) is illustrated in Figure 4b, obtained from ABCP2, a blend of ABCP1 (responsible for Figure 4a) with 240% (w/w) added PCarb (see Table 1), and shows a section of an 'onion' of alternating PSt (white) and PCarb (dark) lamellae. (The PSt lamellae appear broadened since thick sections were used to obtain adequate contrast in unstained samples). The onion, remains of a droplet of copolymer-rich phase, is surrounded by a matrix of PCarb containing a low concentration of copolymer, the B-component of which forms microphases of short rods and spheres. This example corresponds closely to the situation in Figure 3, except that the intrinsic morphology of pure copolymer species is probably lamellar; the onion is formed from the phase of composition K and the matrix has composition J.

Figure 5 is an example of case (ii) and shows structures formed from droplets of copolymer-rich phase produced by solvent casting ABCP3 prepared by crosslinking PCarb with polychloroprene (PCp) to a very low crosslinking index (Table 1); the PCp, stained with OsO₄, appears dark. In addition to regular structures, Figure 5 also shows some large irregular features produced, we believe, either from droplets formed at a different stage of casting or from droplets equilibrated to a different extent than those giving regular structures.

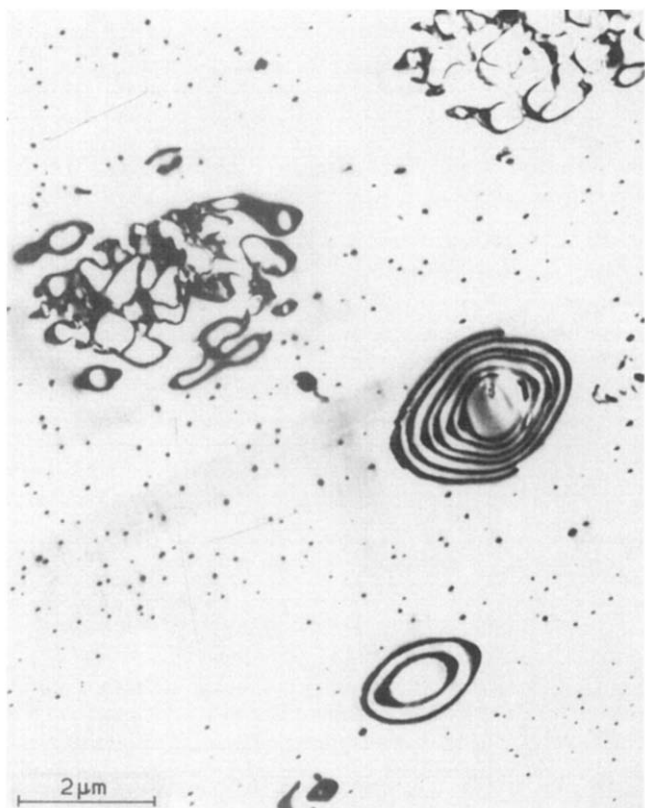


Figure 5 Electron micrograph of ABCP3 (PCarb/PCp). PCp stained with OsO_4 appears dark

Our original observations of supramolecular features in ABCPs^{1,14} provide another example of case (ii) with irregular features in a PCarb/PCp ABCP at low crosslinking indices ($\gamma_r < 0.2$); these were similar to Figure 5 and to features observed by Molau and Wittbrodt⁷ in AB block copolymer blends. This ABCP with higher crosslinking index ($\gamma_r > 0.2$) and higher PCp content gave a more uniform morphology of rods and lamellae, but on blending with PCarb to revert to the original overall composition gave regular onions, i.e. an example of case (i) above; in our original micrographs the spherical structures were distorted into ellipsoids through cutting too rapidly while preparing sections¹⁴.

Onion-like structures are often almost perfectly regular with from one to more than twenty concentric shells of each component. We have also observed these features with structural defects. For example, in Figure 4b the centre of the onion does not consist of concentric shells; the first two and a half layers of each component form a continuous surface as in a conchospiral (equable rather than equiangular). Structural defects are usually incomplete shells of the minor component. Figure 2 shows examples of single incomplete shells of B-component in the interior of some onions. A more common defect is two adjacent incomplete layers of B-component, usually on the surface of an onion, with their edges connected to give a double shell partially enveloping the spherical structure.

Figure 6 shows two morphologies observed in unstained sections of ABCP4 (Table 1) formed by crosslinking PVTCA (light) with PSt (dark). This is an example of macroscopic phase separation in an ABCP containing significant proportions of multicomponent species. One phase gives a tangled mass of PSt rods (Figure 6a) and the other gives alternating lamellae of both components (Figure 6b).

The intrinsic morphology of the multicomponent species is almost certainly a PSt matrix but this is not observed under our experimental conditions.

It is ABCP4, responsible for Figures 6a, b which, with 500% (w/w) added PVTCA, is designated ABCP5 and is responsible for Figure 2. As explained in a preceding section, macroscopic phase separation occurred during solvent casting and droplets of the minor PSt-rich phase coalesced to give a PSt-rich upper layer, leaving a PVTCA-rich lower layer containing residual droplets. The morphology of the bulk of the lower phase (well away from the interface, below the area in Figure 2) shows dispersed spherical microphases of PSt, consistent with a low copolymer content in a homopolymer-rich phase. The upper layer (apart from the vicinity of the interface) has the expected intrinsic morphology of the crosslinked species, i.e. very small spheres of PVTCA in a PSt matrix. The expected phase diagram for this system is similar to Figure 3 but with line LD closer to SA.

In the vicinity of the interface a variety of features are observed arising from local variations in homopolymer content. Apart from the large irregular region in the bottom right-hand portion of Figure 2, the major features are fairly regular and may be understood in terms of phase diagram

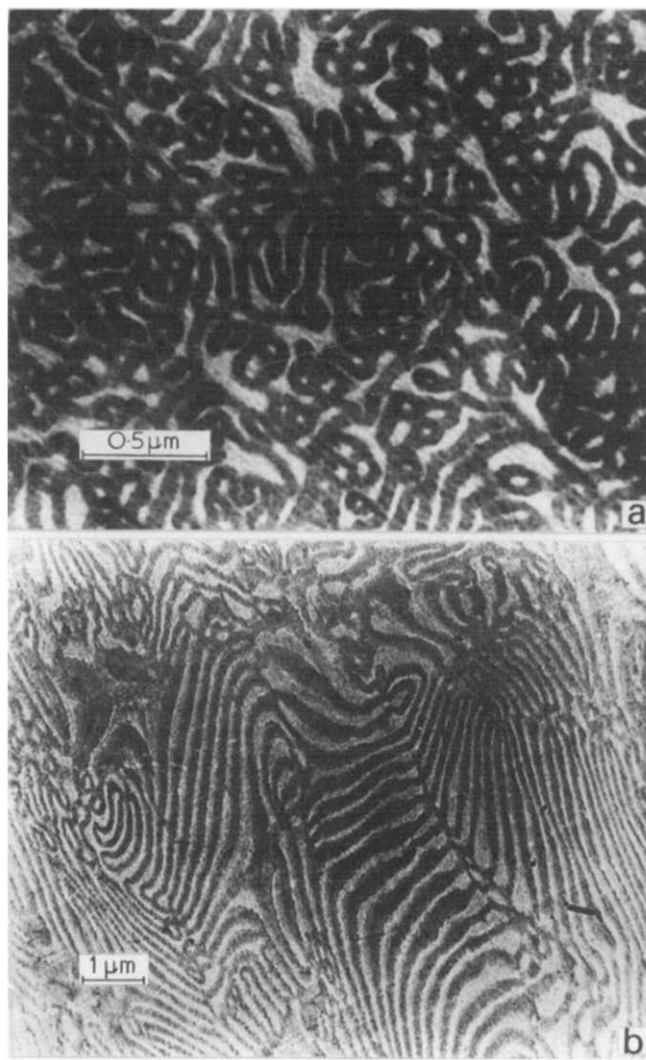


Figure 6 Electron micrographs of unstained sections of ABCP4 (PVTCA/PSt) showing two different morphologies obtained from the same sample (PSt appears dark)



Figure 7 Electron micrograph of ABCP7 (PCarb/PCp) in the interfacial region between a PCp-rich phase (upper) and a PCarb-rich phase (lower); PCp stained with OsO_4 appears dark

Figure 3. The onions below the interface are droplets with a high homopolymer A (PVTCA) content (composition, say, F) trapped in the A-rich phase (composition E) and which have not equilibrated prior to microphase separation, giving a lamellar morphology. Droplets in the immediate vicinity of the interface are in the process of coalescing to form a phase richer in B (PSt) above the interface, losing homopolymer A in the process. Just above the interface the composition corresponds to, say, H (Figure 3). Since the B-content is higher than in the droplets the black lines are probably crumpled B-lamellae viewed almost edge-on. Moving upwards from the interface the morphology changes steadily through regions of different composition and packing to a morphology of small dispersed A-spheres in a B-matrix. This is the intrinsic morphology of the copolymer and corresponds to a composition richer in B than H (Figure 3).

Thus, Figure 2 shows the process of equilibration in progress. Excess polymer A is being excluded from the upper layer and its content far above the interface is very low. It

may be noted that droplets coalescing at the interface retain their integrity. These observations indicate that, given sufficient time to equilibrate, good fractionation of homopolymer and copolymer could be achieved. We do not know at what stage in the casting process microphase separation occurs but the observations described could indicate that equilibration continues after the A- and B-components have separated to at least some extent.

In our experience true macroscopic phase separation and formation of two layers is readily achieved if the ratio of the degree of polymerization of B-chains to that of A-chains is greater than fourteen. Figure 7 shows an interface in PCarb/PCp ABCP7 derived from ABCP6 with 62% (w/w) added PCarb homopolymer (Table 1). The upper PCp-rich layer was distinctly rubbery in texture compared to the rigidity of the lower PCarb-rich phase—reflecting the nature of the matrix polymer in the two phases. In ABCP7 the molecular weight of the B-crosslinks is approximately fourteen times that of the prepolymer and added homopolymer.

ABCPs containing relatively short B-chains and significant amounts of polymer A usually exhibit a uniform, random dispersion of B-spheres, e.g. Figure 8a (samples cast normally formed films dry to the touch in about 3 days). However, slow casting (drying over ten days) can lead to phase separation, as seen in Figure 8b. Figures 8a, b are both derived from ABCP8 (Table 1, PCarb/PSt). There was no visual evidence of phase separation while casting the sample responsible for Figure 8b, but sections cut perpendicular to the surface of the cast film exhibited an upper layer rich in dispersed PSt spheres and a lower, almost pure PCarb layer. The sample shows a gradation in composition through an interfacial region coupled with a continuous variation in diameter of the PSt spheres. This result suggests that, at least in practical situations, domain sizes may be influenced by overall composition and not by molecular structure alone.

Most examples described so far refer to situations in which the copolymer phase is the minor phase. Figure 9 is an electron micrograph of a section from ABCP9, PVTCA crosslinked with PSt. The crosslinked species contain 64% (w/w) PSt (probable intrinsic morphology is lamellar) and the ABCP contains 50% (w/w) homopolymer A. Phase separation has led to a major phase of A and B-lamellae and a minor phase of PVTCA (dark occlusions). This is an example of homopolymer forming the minor phase. (It should be noted that in Figure 9 PVTCA appears dark and PSt appears light. The reverse contrast is observed in Figure 2, due to a reversal of contrast which occurs in the electron microscope as a consequence of beam damage).

Many samples appear to exhibit uniform lamellar morphologies with no obvious evidence of macroscopic phase separation. This situation could arise even if phase separation had taken place during casting. Under such circumstances phases formed initially could have similar composition and, if subsequent drying was rapid compared to the rate of equilibration, the final phases could contain, say, 40% and 60% of B. Both phases would then exhibit a lamellar morphology, distinguished only by different thicknesses of the A-lamellae; the thickness of the B-lamellae should be the same. It is probable that no distinct interface between such phases would be observed.

Similarly, phase separation may also be difficult to detect if the ABCP contains short B-chains which must form spherical domains on microphase separation. Both phases would contain dispersed B-spheres in an A-matrix and no definite interface might be observed; phase separation could be deduced only from variations in domain density. Small

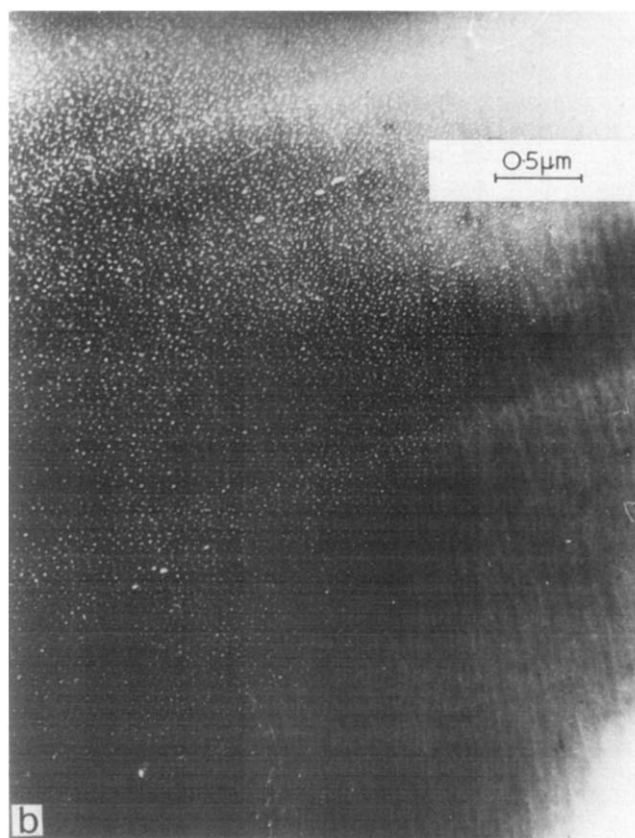
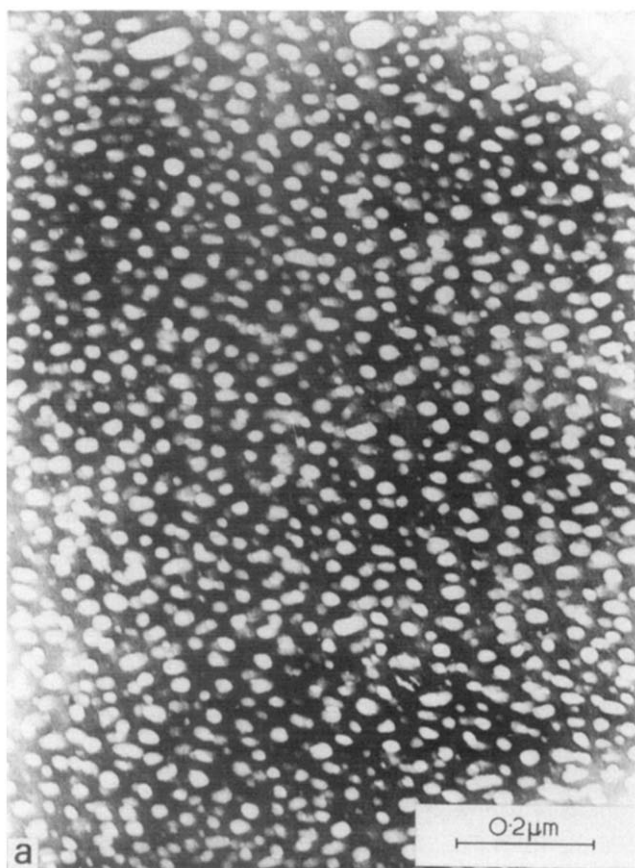


Figure 8 Electron micrographs of unstained sections of ABCP8 (PCarb/PSt PCarb appears dark) showing (a) apparently uniform distribution of spherical PSt domains; (b) non-uniform distribution of PSt domains resulting from phase separation

regions of low domain density from a minor homopolymer-rich phase, may be overlooked when examining polymer sections. Examples of local high concentrations of B-spheres arising from a minor B-rich phase have recently been observed¹⁷.

Compositions of phases

Electron microscopy is a powerful technique for obtaining information on the structures of materials, but a deficiency is its inability to provide detailed information on the compositions of phases or microphases. In the preceding discussions we have referred to copolymer-rich and homopolymer-rich phases without quantitative confirmation. Often the designations appear obvious in view of anticipated trends in morphology with variations in local composition. However, cursory examination of compositions, by comparison of light and dark areas in the micrographs, does not always support large differences in composition where these are anticipated and assumed. More detailed examination of micrographs provides evidence that the assumed differences in composition are real and discussions in terms of copolymer and homopolymer-rich phases are justified.

For example, PCarb/PCp ABCP10 (*Table 1*) consists of 'copolymer-rich' regions of irregular lamellae (*Figure 3a*, *ref. 1a*; *Figure 4a*, *ref. 1b*) and 'homopolymer-rich' regions of PCp domains (*Figure 10*). Estimates of local compositions from a cursory assessment of areas of black (stained PCp) and white (PCarb) gave approximately 5% (w/w) PCp, similar to the overall composition, for both regions. In drawing this comparison we took the thickness of the lamellae to be 6 nm (the smallest thickness observable) and the diameter of the PCp spheres as 40 nm (the full diameter of the spheres). Close inspection of the micrographs revealed that the spherical domains (*Figure 10*) contain a very dark core (~15 nm diameter) and a lighter surrounding region (~12 nm thick), the boundaries of each region are sharp with no evidence of a gradual change in composition. Assuming the core to be pure PCp and the lighter region to be a 'thick interface' of intermediate composition the PCp (and copolymer) content of the homopolymer-rich region is decreased and, if the lamellae are associated with a similarly thick interface, the PCp content of the copolymer-rich region is increased, providing an appropriate disparity in composition. Recent

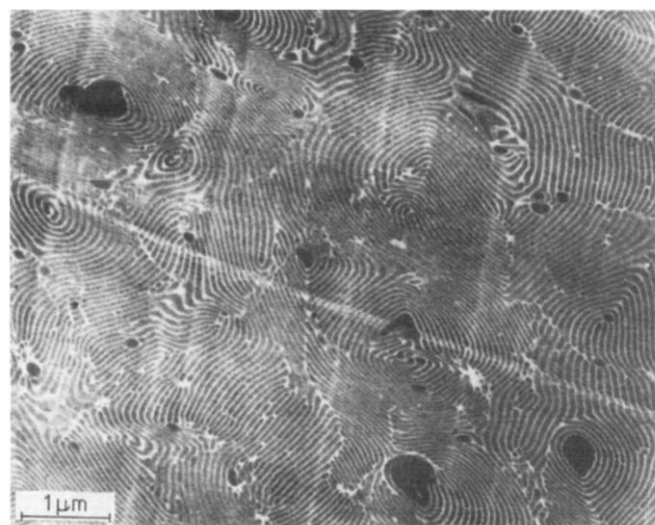


Figure 9 Electron micrograph of ABCP9 (unstained) showing dark occlusions of PVTCA homopolymer arising from a minor homopolymer phase

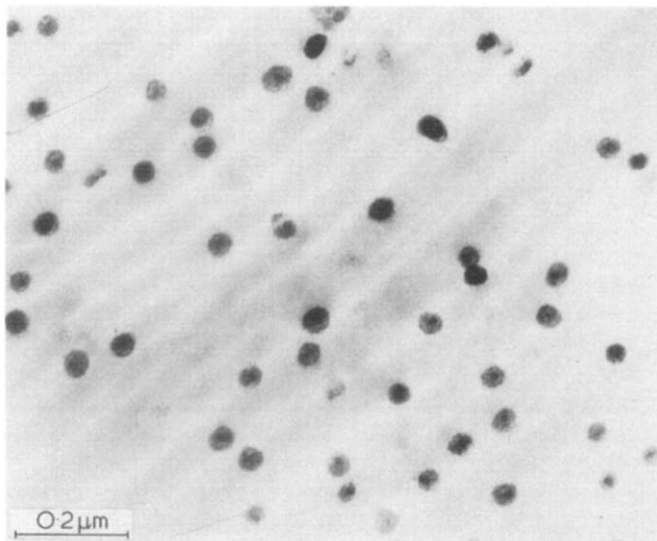


Figure 10 Electron micrograph of ABCP10 'homopolymer-rich' regions showing central PCp core and 'thick interface' in spherical PCp domains

studies of mechanical properties, to be described in subsequent papers, also provide evidence for incomplete separation of the components.

Figure 11 (a higher magnification of an onion in ABCP3, similar to that seen in Figure 5) shows black PCp lamellae and light PCarb lamellae. At A' (and indicated by the arrows) there is a diffuse grey band on both sides of the PCp lamellae. We believe that this is an example of interfacial material of the type referred to above and helps to justify the designation of phases according to composition on qualitative evidence.

CONCLUSIONS AND DISCUSSION

The observations reported in this paper provide clear proof of our earlier conclusion that homopolymers are essentially incompatible with chemically identical blocks in multicomponent polymers, even if the molecular weights of the blocks and homopolymer are similar, i.e. A-blocks in AB and A₂BA₂ block copolymers are incompatible with A-homopolymer of similar molecular weight. This empirical conclusion is supported by Meier's recent calculations¹⁵ which predict that only if the molecular weight of the A-homopolymer is an order of magnitude less than that of the A-block can comparable amounts of homopolymer be solubilized in the blocks.

Possibly the above conclusions can be extended to state that: in general, and at equilibrium, polymer chains which have one end located at an impenetrable interface are not miscible with chemically identical chains of comparable or greater molecular weight which are not so restricted. Certainly this statement must be subject to qualifications with respect to the relative molecular weights of the chains and, probably, to the number of chains attached to unit area of the interface. Indeed there may always be a limited low solubility of homopolymer in attached blocks. Nevertheless, if this statement is generally true it has important implications in the whole field of multicomponent polymeric materials including block copolymer blends, impact-resistant plastics and filled polymers. It does not imply, however, that interesting and useful materials cannot be made by compounding

such mixtures, if only because equilibrium conditions may never be achieved in practice. Indeed, technologically important materials are made from mixtures of homopolymer and copolymer.

The mutual incompatibility of restricted and unrestricted like chains must arise from an unfavourable entropy of mixing. In turn this must be associated with packing of chains and filling of space in the vicinity of the interface, causing chains to adopt a different distribution of conformations than are adopted by the random-coil chain. We have previously suggested, from n.m.r. studies of methyl group rotations in ABCPs, that chains in ABCPs adopt unusual sets of conformations in the vicinity of domain-matrix interfaces¹⁸.

Having interpreted the morphologies observed in ABCPs and their blends (i.e. blends of A₂BA₂ block copolymers with A-homopolymer) we can see how to interpret many unusual morphologies reported by various workers for blends of block copolymer with homopolymer, and for related systems. The reported morphologies usually involve the appearance of discrete regions (1–10 μm across) of regular or irregular internal structure distributed irregularly within the bulk material. We now realise that there is nothing abnormal about these irregular features: they simply arise from a combination of phase separation and microphase separation to produce normal morphologies within restricted volumes and without achieving final equilibrium. The regularity of the internal structure appears to be related to the size of the volumes and the conditions of sample preparation. For example, the irregular regions in Figure 5 are equivalent to similar features in Figure 4b of ref. 7; we have often observed features virtually identical to those shown in Figures 7c and d of ref. 8. One can predict that given suitable combinations of molecular species isolated regions of any standard morphology may be obtained dispersed in a matrix of any other standard morphology. Indeed such results have recently been achieved in both block copolymer^{19,20} and ABCP¹⁷ blends.

Finally, in this paper we have discussed only situations involving multicomponent species blended with one homopolymer. The ideas expressed should be capable of extension to more complex situations (see for example Figure 7 ref. 21), providing a more detailed understanding of complex morphologies observed in such materials as impact-resistant plastics.

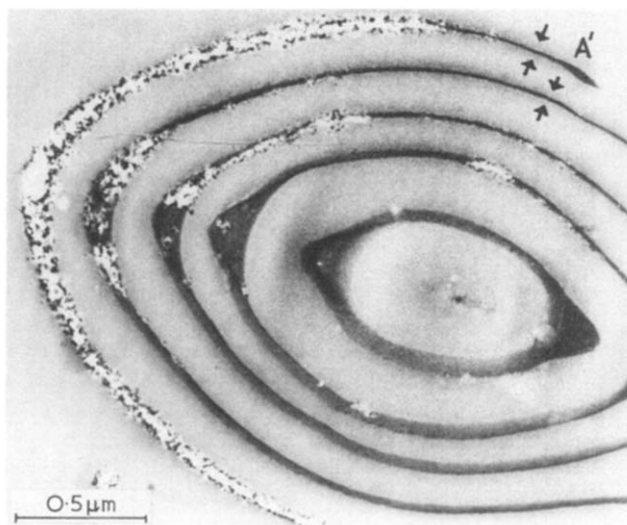


Figure 11 Electron micrograph of an onion-type structure in ABCP3, similar to that in Figure 6 but at higher magnification, showing possible interfacial regions

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