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Transparent microheterogeneous blends containing a multiblock copolymer and a foreign homopolymer

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Several examples of transparent blends of a multiblock copolymer and a foreign homopolymer which is immiscible with each of the copolymer constituent blocks taken separately are described (homopolymers: polystyrene, polymethylmethacrylate and polyvinylchloride; multiblock copolymers: polysulphone/polybutadiene, polycarbonate/polydimethylsiloxane, polysulphone/polydimethylsiloxane and polytetramethylenoxide/ polybutadiene). The blends were prepared by casting films from solutions of the components in a common solvent (tetrahydrofurane or chloroform). The critical content of multiblock copolymer in the homopolymer matrix for transparency was found to be about 5 wt% but may be as much as 20 wt%. It was found that the physical basis of the blend transparency is not thermodynamic compatibility of the components but separation of the multiblock copolymer phase in the homopolymer matrix in the form of small-sized particles (up to 100 nm in diameter). These transparent blends are microheterogeneous systems and they are also similar in the sense that the constituent blocks were found to segregate in the block copolymer microphases. © 1997 Elsevier Science Ltd.

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INTRODUCTION

A great many experimental and theoretical articles, several reviews and monographs, e.g. refs [1,2] have been devoted to polymer–polymer blends over the last 25 years. Interest in such polymer systems is motivated by the fact that mixing of polymers proved to be a very positive approach to developing new polymer materials for various technical applications. In general, the properties of a polymer blend depend on the physical characteristics of its individual components, the adhesion between them and the degree of their dispersion. This last parameter varies widely from micron-sized dispersed particles, such as those obtained by mechanical mixing of immiscible polymer components, to the segmental dimension scale corresponding to their genuine thermodynamic compatibility. The entropy of mixing for macromolecules is very low, so that the enthalpic contribution to the Gibbs free energy of mixing controls miscibility in polymer systems. As a rule, miscible systems of blends have been observed when a favourable specific interaction exists between two constituent macromolecules. The driving force for miscibility of a random copolymer with a homopolymer or another copolymer can also be a so-called 'repulsive interaction' between two dissimilar monomer units comprising the copolymer. Such blends are usually miscible only within a certain range of copolymer compositions—this phenomenon is referred to as the 'miscibility window'[3–6].

In recent years, considerable attention has been paid to the miscibility of a homopolymer with a di- or triblock copolymer containing blocks similar to a homopolymer. It was shown that the homopolymer can either incorporate into domains formed by similar blocks of the copolymer or separate into an individual phase, depending on the homopolymer molecular weight, blend composition, and the relationship between the lengths of the homopolymer chain and the corresponding blocks of the copolymer[7,8].

Blends containing a multiblock copolymer and a homopolymer similar to one of the constituent blocks have been investigated far less frequently. Compared to di- and triblock copolymers, the complete demixing of different blocks of a multiblock copolymer is more complicated[9], as mutual solubility of homopolymer macromolecules and similar blocks of a copolymer can affect the phase behaviour of such systems to a greater extent and promote the formation of compositionally intermediate phases containing blocks of both types.

Experimental data on miscibility of a multiblock copolymer with a homopolymer of dissimilar chemistry (further denoted as the foreign homopolymer) are very scarce[10]. Considering the nature of the driving force for miscibility in the above-mentioned random copolymer–homopolymer system, one may expect that competitive interactions between incompatible blocks in the multiblock copolymer molecule and between these blocks and homopolymer macromolecules can give rise to a specific phase behaviour of such blends and affect their phase separation, morphology and properties.

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In this respect, it is worth mentioning a recent paper[11] which is concerned with blends containing polyvinylchloride (PVC) and [bisphenol A polycarbonate (PC)]/[polydimethylsiloxane (PDMS)] multiblock copolymer. The authors studied the surface composition of these blends and observed the formation of transparent solvent cast films from some of them. This finding is interesting because the refractive indices of PVC, PC and PDMS are different and, consequently, transparency of the blend films may suggest miscibility of their constituents, despite the fact that PVC is incompatible individually with both PC and PDMS[12]. Another possible explanation of this event is that these blends are pseudomiscible and their transparency is caused by the very small size of the dispersed block copolymer phase. As is already known[13], such an optical effect can occur if the size of the dispersed phase particles does not exceed about 100 nm. If this is the case, at certain blend compositions, specific conditions could arise that lead to a very high level of dispersion of the PC/PDMC copolymers in the PVC matrix.

Our preliminary investigation[14] of the nature of this unusual PVC film transparency has shown that PVC is also capable of forming transparent blends with other multiblock copolymers. For this reason, we have decided to study this phenomenon in more detail, taking into account various homopolymers and multiblock copolymers consisting of dissimilar blocks which are incompatible with homopolymers. In the present paper we describe several examples of the formation of transparent blends by such systems in which the block copolymer content can be as high as $\approx$ 20 wt%. The constituents of these blends are homopolymers of various chemical compositions and flexibility, namely polystyrene (PS), polymethylmethacrylate (PMMA) and PVC, and the following multiblock copolymers: PC/PDMS, [polysulphone (PSF)]/PDMS, PSF/[polybutadiene (PB)] and [polytetramethyleneoxide (PTMO)]/PB.

EXPERIMENTAL

Commercial samples of PVC ($M_w = 82\,000$) and PS ($M_w = 60\,000$), and a sample of PMMA prepared by radical polymerization with $M_w = 450\,000$ were used. Samples of the multiblock copolymers were kindly provided by Dr I. M. Rajgorodskii and Dr I. P. Storozhik who synthesised them according to the methods previously described (PC/PDMS[15]; PSF/PDMS and PTMO/PB[16]; PSF/PB [17]). PC/PDMS and PSF/PDMS samples were regular alternating multiblock copolymers with various block lengths. The number average molecular weight (M_n) of the blocks ranged from 74 up to 10\,000 for PDMS, from 1390 up to 12\,000 for PC and from 1500 up to 9000 for PSF.

The synthesis of PTMO/PB and PSF/PB multiblock copolymer samples suggests coupling of two or more similar blocks[15]. Consequently, the length of the constituent blocks in these copolymers was not well defined and varied from that of a single block up to its various multiples depending on the copolymer composition. M_n of the original PTMO, PSF and PB oligomers used for the synthesis of PTMO/PB and PSF/PB samples were respectively equal: [2000], [1600, 4700, 9200] and [2200]. In what follows, the designation of each multiblock copolymer consists of the relevant block abbreviations and their molecular weights given in parentheses. For PTMO/PB and PSF/PB block copolymers the weight ratio of their constituents is also indicated.

The molecular weight characteristics of the multiblock copolymer samples were as follows. The reduced viscosity of a 1 wt% solution of PC/PDMS samples in methylenechloride at 20°C varied between 0.5 and 0.7 dl/g. Gel permeation chromatography molecular weights of PSF/PDMS block copolymer samples ranged from 62\,000 up to 75\,000. M_w of PTMO/PB and PSF/PB samples were about 350\,000 and 53\,000 respectively. According to our measurements, all the neat block copolymers investigated displayed two glass transition temperatures (with the exception of those containing PDMS blocks with $M_n = 74$), corresponding to the glass transition temperatures of their constituent blocks (−125°C for PDMS; 80–140°C for PC and 80–150°C for PSF, depending on the block lengths and preparative conditions of the samples, and −75°C for PB). PTMO blocks in the PTMP/PB samples formed a crystalline phase which melted over a temperature range from 15°C up to 30°C.

Cast films of the blends were prepared by dissolving the components in a common solvent [tetrahydrofurane (THF) or chloroform] with an upper overall concentration of about 1.5 wt% and by subsequent slow solvent evaporation at 15–30°C over 3–4 days, in order to ensure complete phase demixing. The films were then additionally dried in a vacuum at 80–100°C.

Phase diagrams (cloud-point curves) for the ternary systems THF–PMMA–[PC/PDMS block copolymer] and THF–PVC–PC/[PDMS block copolymer] were plotted using the visually identified cloud/clearance points at which solutions became cloudy/clear as the temperature or common polymer concentration was changed.

Differential scanning calorimetry (DSC), thermomechanical analysis (TMA) and dynamic mechanical analysis (DMA) were used for the determination of the glass transition temperatures of the blends and multiblock copolymers. DSC experiments were performed on a DSM-3 scanning calorimeter (Pushino Biopribor, Russia) using samples of about 20 mg weight and a heating rate of 8°C/min. TMA measurements (penetration method) were carried out on a UIP-70 device (Russia) with a dead load of 0.2 MPa and a heating rate of 5°C/min. A Du Pont dynamic mechanical analyser Model 983 DMA operated at 1 Hz frequency and 1°C/min heating rate was used for DMA measurements. For reasons of space, original DSC and TMA traces will not be presented in this article.

Radiothermoluminescence (RTL) spectra for PMMA/[PC/PDMC] blends were taken with a thermoluminograph TLG-69M (Russia) at a heating rate of 20°C/min. The γ-radiation dose of samples sealed in evacuated glass tubes and fast cooled to liquid nitrogen temperature was 1 Mrad.

The morphology of solvent cast blend films was studied by means of transition electron microscopy (TEM). TEM micrographs of films about 500 nm thick were obtained with an EM-125 electron microscope. The films were cast onto a glass substrate and then floated from the substrate onto the surface of a water bath. The PS/[PSF/PB] blend films were previously exposed to sO_4 vapour for a week in order to stain phases containing PB blocks.

RESULTS

Optical characteristics of blends

Three qualitative levels of white light transmittance through the blend films (transparency characteristics), namely transparent, opalescent or opaque, were used for

Table 1 List of homopolymer/[block copolymers] blends characterised in *Figures 1–6*

Copolymer	Homopolymer		
	PMMA	PVC	PS
PC/PDMS	$(+)^a$*Figure 1*	$(+)$*Figure 3*	$(-)$*Figure 5*
PSF/PDMS	$(+)$*Figure 1*	$(-)$*Figure 3*	$(+)$*Figure 5*
PSF/PB	$(-)^b$*Figure 2*	$(-)$	$(+)$*Figure 6*
PTMO/PB	$(+)$*Figure 2*	$(+)$*Figure 4*	$(-)$*Figure 6*

$^a(+)$, some blends are transparent; $^b(-)$ no transparent blend is found
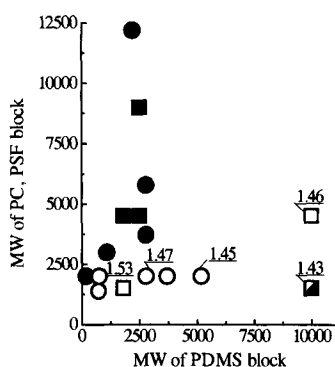
Figure 1 Transparency characteristics [transparent (O□), opalescent (◑◪), opaque (●■)] of films cast at ambient temperature from THF solutions of 95/5 mixtures of PMMA with PC/PDMS (O) and PSF/PDMS (□) block copolymer as a function of molecular weight of the constituent blocks. Figures near the experimental points indicate average refractive indices estimated for the whole block copolymer molecule (see text)
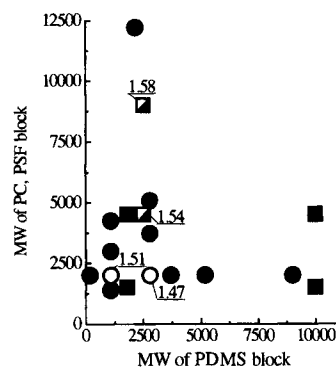

Figure 3 Transparency characteristics [transparent (O□), opalescent (◑◪), opaque (●■)] of films cast at ambient temperature from THF solutions of 95/5 mixtures of PVC with PC/PDMS (O) and PSF/PDMS (□) block copolymers as a function of molecular weight of the constituent blocks. Figures are refractive indices (see the caption to *Figure 1*)
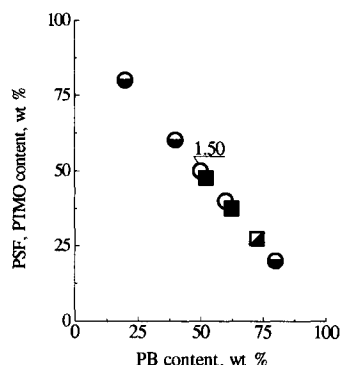

Figure 2 Transparency characteristics [transparent (O□), opalescent (◑◪), opaque (●■)] of films cast at ambient temperature from chloroform solutions of 95/5 mixtures of PMMA with PTMO(2000)/PB(2200) (O) and PSF(4700)/PB(2000) (□) block copolymers of various composition. Figures are refractive indices (see the caption to *Figure 1*)
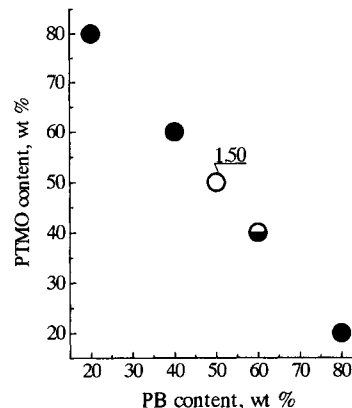

Figure 4 Transparency characteristics [transparent (O), opalescent (◑), opaque (●)] of films cast at ambient temperature from THF solutions of 95/5 mixtures of PVC with PTMO(2000)/PB(2200) block copolymers of various composition. Figures are refractive indices (see the caption to *Figure 1*)

the description of their optical properties and as a preliminary criterion of their possible one-phase state. Many examples of transparent blend films or slightly opalescent ones (particularly if viewed when inclined to incident light) were found. All these blends are considered here to be transparent. The critical content of the multiblock copolymer in the homopolymer matrix for transparency was typically about 5 wt% but could reach as high as 20 wt%.

The transparency characteristics of films cast from solutions of 95/5 mixtures of homopolymers with multiblock copolymers are presented in *Figures 1–6* as a function of the block copolymer composition i.e. the molecular weights of both the constituent blocks or their contents in the block copolymer which are plotted as ordinates and abscissas (see also *Table 1* as a guide).

Although no well-defined general relationship can be deduced from these data, it can be seen that transparent films are obtained in a rather narrow range of the block copolymer composition and mainly when both, or at least one, of the constituent blocks are relatively short. In the case of the PSF/PB and PTMO/PB block copolymers, in which the length of the constituent blocks varies depending on the copolymer's composition (see Section Section 2), this condition occurs at block weight ratios close to 1:1. PMMA proved to be a more universal homopolymer in the sense that it is capable of forming transparent blends with the biggest number of block copolymers of different types, regardless of the solvent used. PVC formed transparent blends with PC/PDMS and PTMO/PB copolymers consisting of rather short blocks of each type. On the contrary, PS
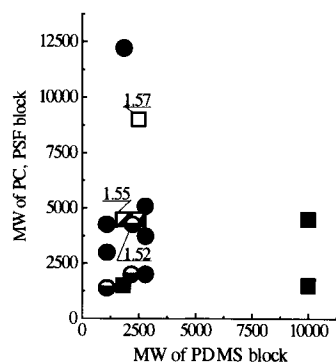
Figure 5 Transparency characteristics [transparent (O□), opalescent (◕◪), opaque (●■)] of films cast at ambient temperature from chloroform solutions of 95/5 mixtures of PS with PC/PDMS (O) and PSF/PDMS (□) block copolymers as a function of molecular weight of the constituent blocks. Figures are refractive indices (see the caption to *Figure 1*)
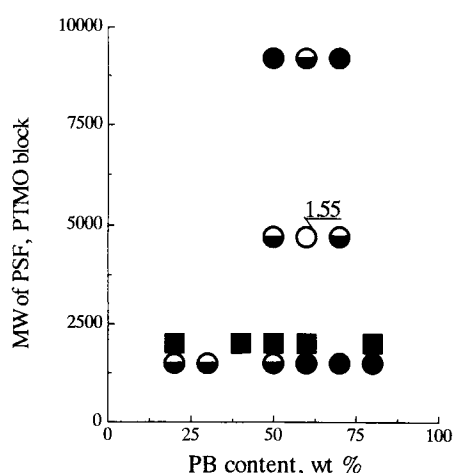

Figure 6 Transparency characteristics [transparent (O□), opalescent (◕◪), opaque (●■)] of films cast at ambient temperature from chloroform solutions of 95/5 mixtures of PS with PSF/BP(2200) (O) and PTMO(2000) (□) block copolymers as a function of their composition and molecular weight of the constituent blocks. Figures are refractive indices (see the caption to *Figure 1*)
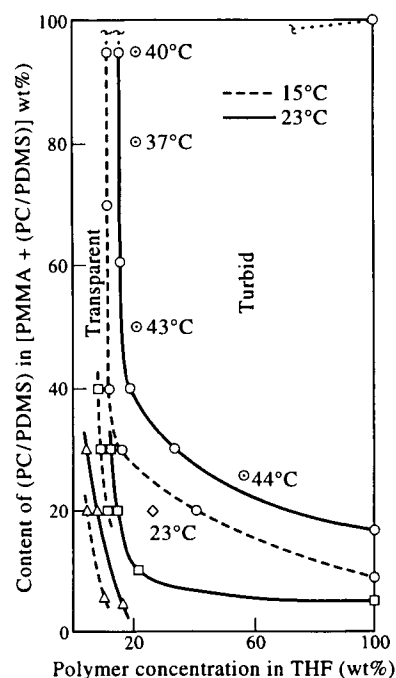

Figure 7 Cloud-point diagram for the ternary system THF-PMMA-PC/PDMS block copolymer [PC(2200)/PDMS(2780) (O,○); PC/(2200)/PDMS(3700) (□); PC(2200)/PDMS(74) (△)] at various temperatures. Cloud point for PC oligomer with molecular weight 3900 (◇) at 20°C is also shown. Ordinate: block copolymer content in [homopolymer + block copolymer] component. Abscissa: overall polymer concentration in THF solution

Table 2 Refractive index (n^D), density (ρ) and solubility parameter (δ) of polymers and solvents*

Polymer	n^D	ρ (g/cm³)	$\delta \times 10^{-3}$ (J/m³)^{0.5}
PSF	1.633	1.24	20.1
PC	1.589	1.20	20.1
PB	1.516	0.892	17.2
PS	1.591	1.05	18.2
PVC	1.544	1.40	19.1
PMMA	1.487	1.18	18.6
PDMS	1.406	0.98	14.6
PTMO	1.480	1.18	17.4
Chloroform	1.446	1.48	18.6
THF	1.405	0.889	19.8

* Data are taken from ref. [26]

produced transparent blends only with block copolymers containing PSF blocks and these blocks are longer than flexible PDMS and PB ones.

It should be emphasized that the transparency of the above-mentioned blends is not due to the fact that refractive indices of the homopolymer matrices and the multiblock copolymer additives are equal. This immediately follows from the fact that at higher concentrations of the block copolymers all the blends were opaque. The differences between refractive indices of the homopolymers and blocks comprising the copolymers can be seen from *Table 2*. Refractive indices of the homopolymers also differ from the average values for the copolymers used. Expected values of the average refractive index n_b of the block copolymers which yield transparent blends with the homopolymers are given in *Figures 1–6* near the corresponding experimental points. They were estimated from the equation:

$$n_b = \varphi_1 n_1 + \varphi_2 n_2$$

where n_1 and n_2 are the refractive indices of block 1 and block 2, respectively, and ϕ_1 and ϕ_2 denote the volume fraction of these blocks in the multiblock copolymer.

Phase diagrams

As was mentioned above, transparency of blend films can be due both to the thermodynamic compatibility of a homopolymer and a block copolymer and to the small size of dispersed block copolymer domains, which result from a specific demixing path. It is therefore of interest to consider the phase state of ternary solutions of the block copolymers and homopolymer in a common solvent, from which the transparent blend films were cast.

It was found that the one-phase state of solutions of all the studied multiblock copolymer/homopolymer mixtures in common solvents, and retention of this state up to high polymer concentrations, is a necessary prerequisite for formation of transparent films. This can be illustrated by the consideration of the phase state of the ternary systems THF–PMMA–PC/PDMS and THF–PVC–PC(2000)/PDMS(2780), which were studied in more detail. *Figures 7 and 8* show the phase diagrams of these systems. These are cloud-point curves plotted on the
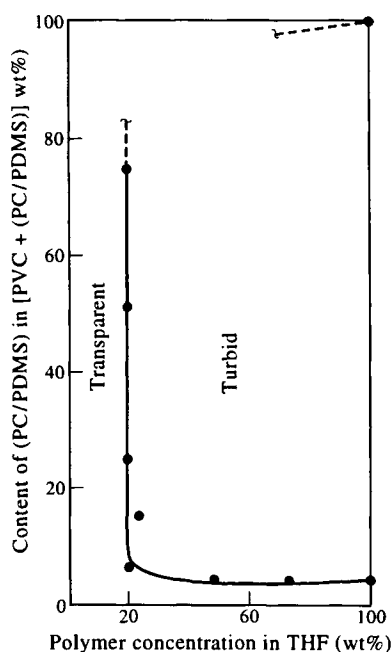
Figure 8 Cloud-point diagram for the ternary system THF-PVC-PC(2200)/PDMS(2780) block copolymer at 20°C. Ordinate: block copolymer content in [homopolymer + block copolymer] component. Abscissa: overall polymer concentration in THF solution

coordinates: block copolymer content in [homopolymer + block copolymer] component versus overall polymer concentration in THF solutions.

The phase behaviour of the systems containing PMMA is exemplified in *Figure 7* by the cloud-point curves obtained for two block copolymers PC(2200)/PDMS(2780) and PC(2200)/PDMS(3700) capable of forming transparent blends and for one block copolymer PC(2200)/PDMS(74) producing only opaque films. The curves depicted are the boundaries between the region of transparent one-phase solutions (to the left of the curves) and that of at least two-phase turbid solutions (to the right of the curves), but they do not characterise the genuine equilibrium phase state of the systems over the whole range of their compositions. This is firstly due to the fact that the systems considered above are, strictly speaking, not ternary but quaternary, in that the constituent copolymer blocks can segregate and consequently should be regarded as individual components. Further, it is not quite clear whether these curves correspond to the equilibrium phase boundaries or merely reflect the fact that the phase separation, being kinetically delayed, is entirely suppressed or yields such a high dispersion level of a separated phase that the system remains transparent. However, in the range of low and moderate polymer concentrations the demixing kinetics should not be the decisive factor and the corresponding sections of these cloud-point diagrams can objectively reflect the mutual influence of the polymer components on their solubility in common solvents and, therefore, be useful for understanding the reasons for formation of transparent blends consisting of a multiblock copolymer and a foreign homopolymer which is immiscible with each of the copolymer blocks taken separately.

Inspection of the phase diagrams presented in *Figure 7* reveals the following particular features of the miscibility behaviour of PMMA and PC/PDMS multiblock copolymers in THF solutions. When added into a PC/PDMS block copolymer solution even a small amount

of PMMA causes phase separation of the resulting ternary system. For example, if the weight ratio of PMMA to the PC(2200)/PDMS(2780) copolymer is 5/95 the cloud-point overall polymer concentration in the solution ranges from 10-20 wt% depending on the temperature. With further increase in the PMMA/[block copolymer] ratio, up to ≈ 60/40, the phase boundary position remains practically unchanged with respect to the overall polymer concentration, but then the cloud-point overall polymer concentration increases steeply and can achieve values close to 100 wt%. As mentioned above, however, at such high concentrations the transparency of the system cannot be taken as unambiguous evidence of thermodynamic compatibility of the components.

The expansion of the transparent one-phase region due to the increase in the cloud-point overall polymer concentration, which occurs starting with a certain PMMA/[block copolymer] ratio, is a common trend for different PC/PDMS block copolymers, but it manifests itself to various degrees depending on their composition. In particular, *Figure 7* shows that the longer the PDMS block (at a given length of PC blocks), the greater is the expansion. One can also see a considerable widening of the one-phase region with increasing temperature that leads to an increase of the PC/PDMS content in resulting cast transparent blend films. Thus, with the increase in temperature from 15°C to 22°C the content of PC(2200)/PDMS(2780) block copolymer in the PMMA matrix, which is crucial for transparency, rises by approximately 10 wt %. Such a strong temperature effect necessitates rigid control over solvent evaporation conditions during film casting at ambient temperature in order to obtain reproducible results for the transparency characteristics of blends which contain more than 10 wt% of the block copolymers.

A similar expansion of the one-phase region is also observed for ternary systems containing PVC. In this case, however, it occurs more drastically and at a higher homopolymer/[multiblock copolymer] ratio, resulting in the appearance of a narrow horizontal miscibility region (see *Figure 8*). It is likely that such a phase behaviour is due, at least in part, to gelation of the solution. PVC was found to form gels if its concentration in THF solution exceeded 10 wt%; the trend to gelation is retained in the ternary system at an overall polymer concentration above 16 wt%.

Thus, the increase in miscibility of a multiblock copolymer and a foreign homopolymer in common solutions with increasing homopolymer/[block copolymer] ratio seems to be an inherent feature of the above ternary systems, which, being responsible for a very high terminal level of the block copolymer dispersion in the homopolymer matrix, underlies the formation of transparent cast blend films.

Morphology of blends

A TEM study of the morphology of transparent blend films has shown that the level of dispersion varies over a wide range from indiscernible small-sized aggregates, which probably consist of several multiblock copolymer molecules, to domains greater than 100 nm in size, depending on the copolymer content and casting temperature.

This fact can be illustrated by TEM micrographs of PMMA/[PC(2000)/PDMS(2780)] and PS/[PSF(4700)/PB(2200)] blend films presented in *Figures 9 and 10*. The much higher electron density of PDMS blocks, compared to
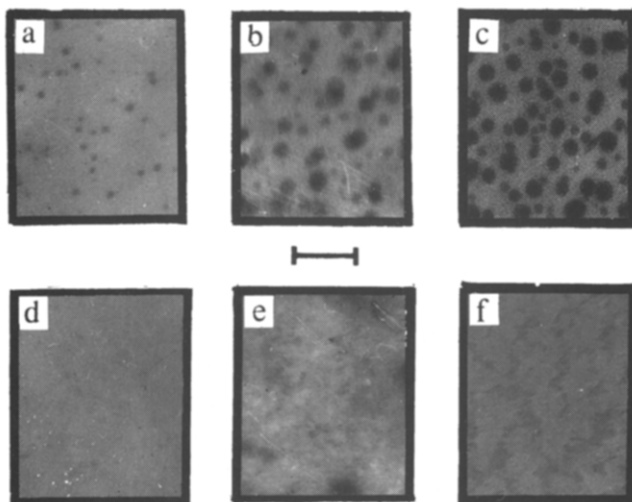
Figure 9 Transmission electron micrographs of films cast at different temperatures [(a), (b) and (c) ambient temperature; (d) 30°C; (e) 30°C and then heated up to 150°C] from THF solutions of PMMA/block copolymer PC(2200)/PDMS(2780) mixtures of various compositions: (a) 97/3; (b), (d) 90/10; and (c), (e) 80/20. Micrograph (f) shows the morphology of a neat block copolymer film. The scale bar is 0.5 mμ
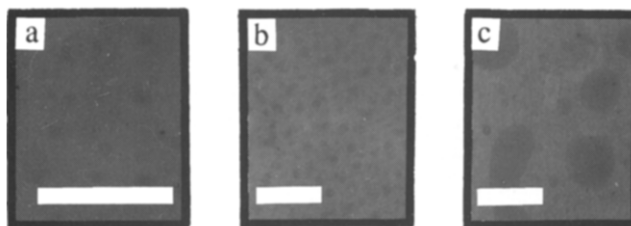

Figure 10 Transmission electron micrographs of films cast at ambient temperature from chloroform solutions of PS/[block copolymer PSF(4700)/PB(2200) containing 40 wt% of PSF blocks] of various compositions: (a) 95/5; (b) 90/10; (c) 80/20. The PB phase was stained by OsO$_4$. The scale bar is 0.5 mμ

that of the PMMA matrix, allowed us to observe the block copolymer microphases in as-cast films without staining. *Figure 9f* shows the micrograph of a neat PC/[PDMS block copolymer] film which reveals its two-phase morphology and additionally demonstrates the possibility of discriminating PDMS domains against the hydrocarbon matrix.

An inspection of the micrographs shown in *Figures 9 and 10* leads to the conclusion that all the transparent blend films investigated are microheterogeneous and their transparency stems from the very small size of the dispersed block copolymer phase. The size of the spherical block copolymer particles depends on the PC/PDMS copolymer content and casting temperature. Even at 3/97 block copolymer/PMMA ratio the block copolymer separates into a dispersed microspherical phase with a maximum sphere diameter of $\approx$ 40 nm. For a molecular weight of the order of 100 000 this corresponds to aggregates of approximately 200 multiblock copolymer molecules. With increasing copolymer content in the blend, the number and size of such spherical particles increases. At 10 wt % copolymer the particles range in diameter from 60–140 nm with the majority at about 100 nm. When the block copolymer content reaches 20 wt% the diameter of the majority of the particles increases up to 140 nm, although there exist many particles of larger sizes. Such dimensions of the dispersed phase are already large enough to cause

considerable light scattering. This fact is consistent with the phase diagram shown in *Figure 7*, according to which blend films containing 20 wt% of PC(2200)/PDMS(2870) and cast at ambient temperature are opaque. However, the morphology of the very thin films used for TEM investigation may be expected to differ from that of the films 100–200 μm thick, whose optical characteristics are given in *Figures 1–6*, due to surface effects and more complicated control over solvent evaporation rate.

An increase in the casting temperature results in a decrease in the size of PC/PDMS copolymer particles in the PMMA matrix. For instance, most TEM micrographs of films cast at 30°C and containing up to 10 wt% of the block copolymer look homogeneous (*Figure 9d*) although some regions of the film containing 10 wt% of the block copolymer can exhibit a morphology similar to that shown in *Figure 9a*. If a film was cast such that after evaporation of most of the THF for some minutes at 30°C its drying was completed at 150°C, even at 20 wt% block copolymer content, TEM micrographs of such a film showed a very obliterated morphology of phase separation (as shown in *Figure 9e*) or did not reveal the copolymer phase at all. Nevertheless, these 'structureless' films were actually microheterogeneous, as was shown by data on their glass transition temperatures (see below).

Similar patterns of phase demixing were also observed for PS/[PSF/PB multiblock copolymer] blends. The morphology of these blends can be seen from the TEM micrographs in *Figure 10*. It is interesting to note that at block copolymer contents up to 10 wt% the sizes of PSF/PB block copolymer microphases in the PS matrix are practically identical to those of PC/PDMS particles in the PMMA matrix. The blend film containing 20 wt % of PSF/PB copolymer was already very turbid and micron-sized domains can be observed in its TEM micrographs (see *Figure 10c*).

Glass transition temperature of blends

Immiscibility of the components at the segmental level in these blends is also evidenced by measurements of their glass transition temperature. It was found that the T_g of the matrices measured by means of DSC, TMA and DMA techniques do not change with increasing block copolymer content and remain practically equal to those of the corresponding homopolymers (respectively 110°C, 106°C and 78°C for PMMA, PS and PVC). Even the T_g of the PMMA matrix in the above-mentioned blend film, which contained 20 wt% of PC/PDMS copolymer and revealed no two-phase morphology in TEM micrographs, proved to be equal to that of the neat PMMA.

The separation of the block copolymers in the transparent blend films into individual phases of very small size raises in turn the question of what is the structure of these microphases, i.e. whether they are uniform or whether demixing of the constituent blocks occurs in them much as it takes place in the corresponding neat block copolymers. We can elucidate this problem to some degree using PMMA/[PC(2200)/PDMS(2780) block copolymer] blends as an example.

Our DMA measurements have clearly demonstrated that at a PC/PDMS copolymer content in the blends of $\geq$15 wt%, PDMS blocks manifest themselves as a separate phase. As shown in *Figure 11*, for the blend containing 15 wt% of PC/PDMS copolymer, a very small but appreciable drop in the storage modulus G' and a small loss tangent peak in the vicinity of the T_g of PDMS
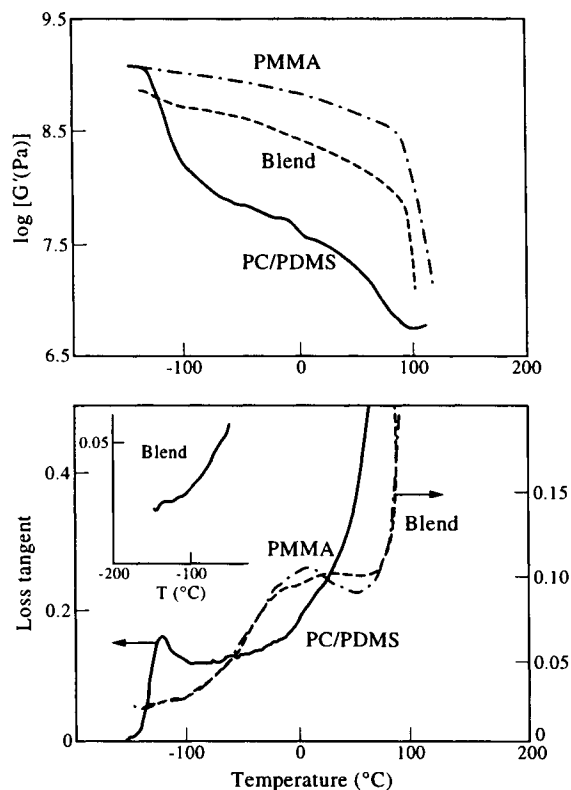
Figure 11 Storage modulus G' and loss tangent for samples of neat PMMA, PC(2200)/PDMS(2780) block copolymer and 85/15 blend of PMMA with the block copolymer as a function of temperature. The insert more clearly reveals the loss tangent maximum associated with the T_g of the PDMS phase in the blend

$(-125°C)$ are observed. However, at lower block copolymer concentrations we have failed to distinguish the PDMS phase in the blends using DMA, TMA and DSC techniques. RTL measurements were found to be more informative for this purpose.

As already known[18-20], thermoluminescence of polymer samples, previously γ-irradiated at liquid nitrogen temperature, occurs upon heating, due to recombination of electrons and ions released from electron traps which are destroyed with the introduction of molecular mobility at relaxation transitions, in particular glass transition. The intensity of thermoluminescence is, as a rule, sufficiently high and RTL measurements were found to be a useful tool to monitor T_g and, thus, to recognise small amounts of separated phases in multicomponent polymer mixtures[18].

It was earlier reported[21] that the glass transition of PDMS is accompanied by intense luminescence, and we made use of this fact in analysing the phase state of blend samples containing various amounts of the PC/PDMS block copolymer. In *Figure 12* thermoluminescence curves for samples of neat PDMS, PC(2200)/PDMS(2780) block copolymer and its blends with PMMA are presented. The thermoluminescence curve for PDMS, which is taken from ref. [21], is not normalised to the others presented in *Figure 12* and is given only to show the position of the luminescence peak corresponding to the glass transition on the temperature axis. This peak is located at $-118°C$, which is higher by 7°C than the accepted T_g of PDMS. There is also a second peak on the PDMS thermoluminescence curve in the vicinity of $-148°C$, which is attributed to a secondary relaxation transition or considered to be an artefact[21]. On the thermoluminescence curve for the block copolymer this peak is superimposed on that from the PC phase. The latter
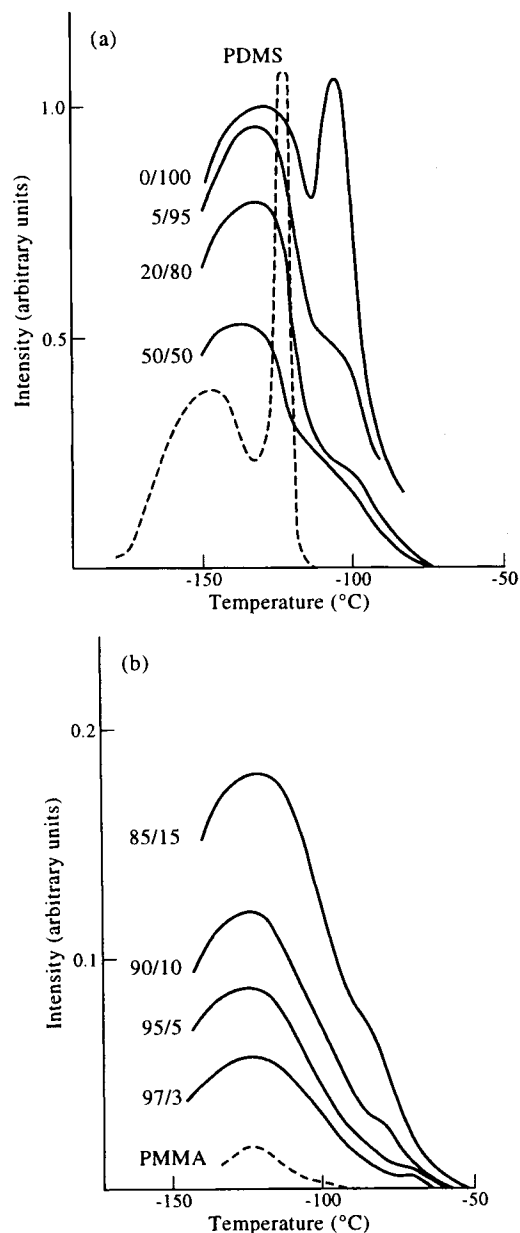

Figure 12 Thermoluminescence intensity as a function of temperature for films cast from THF solutions of PMMA/[block copolymer PC(2200)/PDMS(2780)] mixtures with (a) high and (b) low content of the copolymer. Thermoluminescence curves for samples of neat PDMS (not normalized with respect to the other curves) and PMMA are also shown

is a very broad peak centered at about $-130°C$. Its relative intensity varies linearly with the block copolymer content in the blend samples. Similar peaks are observed both for high molecular weight PC samples and PC(2200) oligomer (not shown in *Figure 12*) and they are supposedly associated with the onset of small-scale molecular mobilities. For neat PMMA a thermoluminescence peak is also monitored in the same temperature range but its intensity is less than that of the block copolymer sample by a factor of about 50 (see *Figure 12a* and *b*).

As shown in *Figure 12a*, the glass transition of the separated PDMS phase in the block copolymer sample is manifested as a thermoluminescence peak located at $-103°C$, which is higher by 15°C compared with the corresponding peak observed for neat PDMS, and also appears to be wider than the latter, although it is very difficult to assess quantitatively the difference between them as in the case of the block copolymer this peak

overlaps with the right wing of the thermoluminescence peak pertaining to the PC phase. When PMMA is mixed with the PC/PDMS block copolymer, the relative intensity of the PDMS phase peak falls dramatically, especially upon adding the first 5 wt % of PMMA, and it degenerates into a right shoulder of the PC thermoluminescence peak. At PMMA contents up to ≈ 50 wt% the temperature corresponding to the inflexion point on this shoulder remains unchanged and approximately identical with the thermoluminescence peak temperature observed for the block copolymer sample (see *Figure 12a*). With further increasing PMMA content the thermoluminescence peak associated with the glass transition in the PDMS phase becomes so broad that it is very difficult to establish its position unambiguously. However, on the thermoluminescence curves for the transparent blend samples containing above 80 wt% of PMMA this peak is shifted to higher temperatures and is again displayed as a relatively clear-cut shoulder (see *Figure 12b*). For 97/3 PMMA/block copolymer blends the shoulder (inflexion point) is located at $-78°C$. The relative intensity of luminescence at the inflexion point for the blend samples containing from 3–15 wt% of the block copolymer increases directly with its concentration. This relationship holds for all the blend films cast at ambient temperature. For the blend films of the same compositions but cast at 30°C, which displayed no clear-cut microphase separation in TEM micrographs, we observed smaller and more diffuse shoulders shifted to somewhat higher temperatures.

Leaving aside possible reasons for the sharp decrease in the relative thermoluminescence intensity of the PDMS phase in the mixture upon adding the first 20 wt% of PMMA one can arrive at the following conclusions based on the above RTL data. Firstly, these data additionally evidence the two-phase state of PC(2200)/PDMS(2780) multiblock copolymer and point out that at high contents of this block copolymer in the blend samples, which are turbid due to the large size of the dispersed phase particles, the PMMA phase does not influence demixing of the PC and PDMS blocks in the block copolymer phase. The second, more important, issue is that in the transparent microheterogeneous blends in which, according to our TEM data, the microphase sizes range from 40–140 nm, the block copolymer microphases are not homogeneous but are heterogeneous due to demixing of PDMS and PC blocks. In this case, however, the T_g of the PDMS blocks is higher than their T_g in the neat multiblock copolymer and increases with decreasing size of dispersed block copolymer particles in the PMMA matrix. This fact can be attributed to an incomplete demixing of the constituent blocks or to the influence of the hard PMMA matrix on molecular mobilities in PDMS phases of very small size.

DISCUSSION

Many examples have been presented here of transparent blend systems formed by a multiblock copolymer and a foreign homopolymer which is immiscible with each of the copolymer constituent blocks. These examples include homopolymers and multiblock copolymers which are different in their chemical structure and thus in their cohesion energy and flexibility. They suggest that the formation of transparent blends may be a universal phenomenon for various types of their constituent pairs. At the same time, as can be seen from *Figures 1–6*, the structure of each kind of block copolymer, i.e. the lengths of

constituent blocks and their ratio, can be a critical factor controlling transparency of a given blend system. It should also be noted that the same multiblock copolymer can produce transparent blends with several different homopolymers. The upper block copolymer content in the transparent blends cast at ambient temperature is relatively low and does not usually exceed 5–10 wt%. However, the PMMA/[PC/PDMS block copolymer] blends show that this value can markedly increase with temperature.

According to the above data on the glass transition temperature and morphology of the transparent blends, their transparency does not arise from thermodynamic miscibility of the homopolymer and block copolymer at the segmental level, but is a result of microphase separation, i.e. segregation of the block copolymer macromolecules in the form of dispersed spherical particles whose sizes range from being so small that they cannot be discerned in electron micrographs up to nearly 100 nm which corresponds to aggregates composed of some thousands of the macromolecules.

A prerequisite for casting a transparent film from a homopolymer/ [multiblock copolymer] mixture is the formation of one-phase solutions by the components in common solvents and the retention of the one-phase state up to very high overall polymer concentrations. This occurs in proper solvents and only at certain compositions of multiblock copolymers of a given type. As seen from the cloud-point diagrams presented in *Figures 7 and 8*, a characteristic feature of the ternary systems studied is the expansion of the one-phase region after the homopolymer fraction in the polymer (homopolymer + block copolymer) component reaches a sufficiently high value (above 50 wt% for all the pairs studied).

Let us consider possible reasons for such a pattern of the phase behaviour using the THF–PMMA–PC/PDMS system as an example. According to the previously developed theories for the ternary system solvent (1)–polymer (2)–polymer (3)[22,23], the equality of the solvent–polymer interaction parameters ($\chi_{12} = \chi_{13}$), if $\chi_{23} > 0$, or the existence of specific intermolecular interactions ($\chi_{23} < 0$), if $\chi_{12} \neq \chi_{13}$, can lead to limitedly compatible solutions. However, there exist no specific interactions between any pair of the monomer units which constitute PC, PDMS, PMMA and PVC macromolecules and, as is known, these polymers are immiscible with each other[12]. High molecular weight PDMS and PC are also incompatible or partially compatible only on a very limited scale with PMMA in solution[12,24]. For instance, the cloud point in the THF–PMMA–PDMS system for a 1/1 ratio of polymer components was reported to correspond to an overall polymer concentration of 1.6 g/cm³ [24]. The widening of the one-phase region on the phase diagram for the THF–PMMA–PC/PDMS system with increasing temperature (see *Figure 7*) indicates that the entropic factor should mainly control miscibility of the components in THF solution. Thus, one can suggest a particular behaviour of macromolecules of PC/PDMS multiblock copolymer in concentrated solutions where they are surrounded by PMMA macromolecules and, correspondingly, a specific structure of such solutions, which is retained at extremely high overall polymer concentrations and eventually results in the observed microphase segregation of the copolymer at the very high dispersion level in the PMMA matrix.

One of the possible speculative descriptions of this structure may be as follows. Taking into account the values of the solubility parameters (δ) for THF, PDMS and PC (see
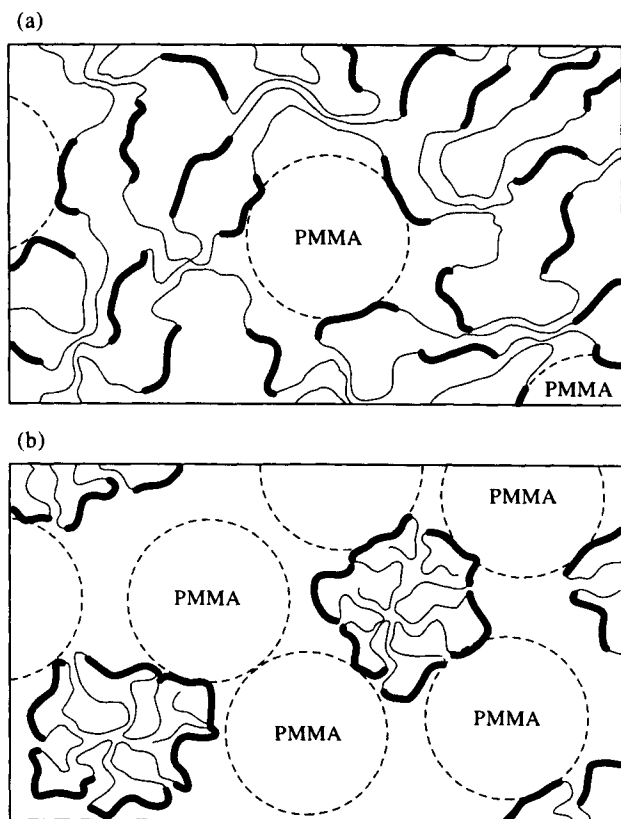
(a)

(b)

Figure 13 Schematic representation of two proposed regimes of the behaviour of PC/PDMS multiblock copolymer molecules in ternary solutions with PMMA in THF at high overall polymer concentrations for (a) low and (b) high PMMA content in the [PMMA + PC/PDMS] component. The thick line corresponds to the PC block and the PDMS block is represented by a thin line. PMMA macromolecules are drawn in the form of circles

Table 2), the interaction parameter between THF and PDMS should be higher than that between THF and PC and, therefore, it is reasonable to assume that in concentrated THF solutions, PDMS blocks, in contrast to PC ones, display a strong tendency to intermolecular association (see *Figure 13*). As a consequence, even a small amount of PMMA, a high molecular weight component with δ considerably different from that for PDMS, added to such a solution can act as a precipitant, leading to phase segregation. This expectation is in line with the very low cloud-point polymer concentration in the THF–PMMA–PDMS system cited above (see [24]).

When the PMMA fraction in the polymer component [PMMA + PC/PDMS] dissolved in THF exceeds 50 wt% the situation apparently changes. In this case, the solution of PMMA macromolecules becomes the matrix in which the multiblock copolymer molecules are dispersed and for the PMMA macromolecules the contacts with PC blocks should be more favourable than with PDMS ones, judging by the differences between δ for these polymers (see *Table 2*). The 'tolerance' of PMMA macromolecules to PC blocks in the THF solution is evidenced by the fact that they are compatible with original PC oligomers at relatively high concentrations of the latter (see, as an example, the cloud point for the oligomer with $M_w = 3300$ in *Figure 7*). Correspondingly, it is expected that at high PMMA fraction, PDMS blocks of each multiblock copolymer molecule will tend to form mainly intramolecular contacts with each other. This should result in macromolecular conformations in which PDMS blocks form the inner core and PC blocks are

predominantly located in the outer layer of the macro-molecular coil, the PDMS core density and the concentration of PC blocks at the coil surface being controlled by the composition of the multiblock copolymer molecules (see *Figure 13*). PMMA macromolecules appear to be compatible with copolymer molecules having such a conformation up to relatively high overall polymer concentrations in THF solutions.

It is obvious that the model of compatibility of a foreign homopolymer and a multiblock copolymer in common solvents proposed above imposes certain restrictions upon the copolymer structure. Two of these at least are relatively obvious: (i) the length of one of the constituent blocks should not be too large and the value of its solubility parameter must be close enough to that of the homopolymer in order to ensure their sufficiently high compatibility in the solution; (ii) these blocks should easily move into the outer layer of the copolymer molecule coil and, consequently, the second block has to be sufficiently flexible and its length has to relate to the length of the former block so that the free energy and geometry requirements for the occurrence of the suggested copolymer molecule conformation can be met.

At very high polymer concentrations the block copolymer molecules, due to their inherent immiscibility with PMMA molecules, must tend to aggregate, forming associates of various sizes and stability (supposedly including stable micelles having a two-layer structure such as that proposed above for the single block copolymer molecule) and eventually separate into an individual phase. Owing to the very high viscosity of highly concentrated solutions, the evolution of the block copolymer phase can be kinetically delayed and may proceed only at a microphase separation level, in particular at a nanometer-sized one. The aggregation of the block copolymer molecules has in turn to be accompanied by segregation of immiscible PDMS and PC blocks. As in multiblock copolymers there exist considerable steric hindrances to full segregation and if the size of dispersed block copolymer phases is very small, the retention of some contacts between PC blocks and PMMA macromolecules may be thermodynamically favourable. This factor can additionally impede the above segregation process and increase even more the high end degree of PC/PDMS copolymer dispersion leading to an incompletely segregated morphology inside the dispersed particles.

In the context of the above model a relatively narrow composition range for each type of the block copolymers studied, within which the formation of the transparent cast blend films was observed, can be attributed to the second restriction upon the copolymer structure. The temperature effect on the blend's transparency may be explained by the fact that an increase in temperature decreases the aggregation of the copolymer molecules in concentrated solutions and promotes the formation of stable micelles of small sizes.

CONCLUSION

The formation of transparent films cast from solutions of a multiblock copolymer and a foreign homopolymer which is not compatible with the constituent blocks of the copolymer is probably a rather widespread phenomenon. It is observed for copolymers and homopolymers of various chemical structures but the composition range for each type of block copolymer, within which the formation transparent blend films takes place, is relatively narrow. This phenomenon is similar to an extent to another, consisting of the appearance

of the so-called 'miscibility window' in some blends of a random copolymer of certain composition and an inert homopolymer which is miscible with none of the monomer units which compose the copolymer[3]. However, in contrast to the latter, transparent miscible blends of the former do not exhibit thermodynamic compatibility. Microphase separation and the evolution of the multiblock copolymer phase in the form of small-sized particles (up to 100 nm in diameter) is the physical basis of their transparency. Such transparent blends are microheterogeneous systems and they are also the same in the sense that the constituent blocks were found to segregate in the block copolymer microphases.

Detailed theoretical treatment and more sophisticated experimental investigation of the structure of highly concentrated solutions of homopolymer–multiblock copolymer mixtures in a common solvent and cast blend films are needed for the full understanding of the nature of the phenomenon. However, the comprehensive theoretical consideration of these systems is a complicated task as many factors resulting from the multiblock structure of the copolymer must be taken into account. The problem can apparently be solved step-by-step starting with the treatment of a simpler diblock (triblock) copolymer–homopolymer system. In this context it is worth mentioning a recent paper pertaining to miscibility in a blend of A–B block copolymer–homopolymer C [25].

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