# Compatibilizing effect of block copolymers in heterogeneous polystyrene/poly(methyl methacrylate) blends

**Sabu Thomas* and Robert E. Prud'homme†**
*Centre de recherche en sciences et ingénierie des macromolécules, Chemistry Department, Université Laval, Québec (Que), Canada G1K 7P4*
*(Received 15 May 1991; revised 6 December 1991; accepted 10 December 1991)*

The morphology of heterogeneous polystyrene/poly(methyl methacrylate) (PS/PMMA) blends has been modified by the addition of diblock copolymers of PS and PMMA and investigated as a function of block copolymer composition, molecular weight and concentration by optical and electron microscopies. A sharp decrease in dispersed phase dimension is observed with the addition of a few per cent of block copolymers having equal segmental mass (50/50 PS/PMMA), followed by a levelling off as the copolymer content is increased above the critical micelle concentration. For concentrations below the critical value, the particle size reduction is linear with copolymer volume fraction and agrees well with the predictions of Noolandi and Hong. The compatibilizing efficiency of the copolymer is strongly dependent on its composition and molecular weight. The effects of processing conditions, such as casting solvents and compression moulding, on the phase morphology have also been studied. Finally, the conformation of the copolymer at the interface is discussed with the help of models: calculations based on the experimental results indicate that the compatibilizer is neither located entirely at the interface, nor penetrates completely into the corresponding homopolymer phases.

**(Keywords: compatibilization; blends; interface; copolymers; critical micelle concentration; morphology)**

## INTRODUCTION

Most pairs of high molecular weight polymers are incompatible[1–5]. These samples are characterized by a two-phase morphology, a narrow interface, and poor physical and chemical interactions across the phase boundaries. As a consequence of this, incompatible blends often exhibit poor mechanical properties. This problem can be alleviated by the addition or the *in situ* formation of a compatibilizer, also called an emulsifying agent or an interfacial agent[6–8]. It is considered that a properly chosen compatibilizer will preferentially locate at the interface between the two immiscible polymers. As pointed out by Paul[6], 'this type of surface activity should (1) reduce the interfacial energy between the phases, (2) permit finer dispersion during mixing, (3) provide a measure of stability against gross segregation and (4) result in improved interfacial adhesion'. In the ideal case, this component is a block or graft copolymer with segments that are chemically identical to those in the respective phases. However, this condition is not always required. The same effect can be obtained if one of the arms of the block or graft is miscible with or adheres to one of the phases.

Several studies have been reported on the compatibilizing action of copolymers in heterogeneous polymer systems. Molau *et al.*[9–11] clearly demonstrated the ability of block copolymers to emulsify polymer dispersions in solution and thus inhibit phase separation. Riess *et al.*[12–15] found that block copolymers are more effective than graft copolymers in increasing the compatibility of polystyrene/poly(methyl methacrylate) (PS/PMMA) and PS/polyisoprene blends. In these studies, the compatibility was monitored by the degree of optical transparency of thin films cast from various solutions of the three components. These authors also reported that the best compatibilizing action is obtained with a block copolymer whose composition is ~50:50 and whose molecular weight is higher than those of the homopolymers.

Gailard and co-workers[16,17] have further examined the surface activity of copolymers by studying the interfacial tension reduction in demixed polymer solutions. Addition of poly(styrene-*b*-butadiene) to PS/polybutadiene/styrene ternary systems showed first a characteristic decrease in interfacial tension, followed by a levelling off. The effect of addition of poly(dimethylsiloxane-*b*-oxymethylene) on the interfacial tension between methyl terminated poly(dimethylsiloxane) and poly(oxyethylene-*b*-oxypropylene) has been studied by Patterson *et al.*[18]. They found that <2% of the block copolymer was sufficient to saturate the interface and reach the limiting interfacial tension value. Recently, Anastasiadis *et al.*[19] also reported on the interfacial tension reduction of PS/1,2-polybutadiene blends by the addition of the corresponding block copolymer. They also arrived at a similar conclusion as that of Gailard and co-workers[16,17] and Patterson *et al.*[18].

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* Present address: School of Chemical Sciences, Mahatma Gandhi University, Kottayam, Kerala 686 635, India

† To whom correspondence should be addressed

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Inoue *et al.*[20] reported on the mechanism of domain formation on a ternary system consisting of PS/poly(styrene-*b*-isoprene)/polyisoprene. The domain structure was investigated by light and electron microscopies using an osmium tetroxide fixation technique. They concluded that, when the molecular weight of the homopolymer is much higher than that of the corresponding arm of the copolymer, the block copolymer can no longer act as an emulsifier, thus justifying the initial speculations of Riess *et al.*[12–15] for the emulsifying effect of block copolymers. Several additional studies in the area of compatibilization of binary blends by the addition of copolymers have also been reported[21–24]. For example, the studies of Coumans *et al.*[21] and Paul and co-workers[23,24] deal with the emulsification of heterogeneous polyethylene (PE)/PS blends by the addition of block copolymers.

In other studies, the addition of graft copolymer was reported as a means of improving the properties of high impact PS, poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) and PS/PE blends[25–28]. The decrease of particle size of the dispersed phase upon the addition of graft copolymer was substantiated by optical and electron microscopies. Ide and Hasegawa[29] studied the use of maleic anhydride modified isotactic polypropylene (iPP) in iPP/nylon 6 blends. During the melt mixing process, the anhydride groups react with the amino end groups of nylon to yield a graft copolymer. This sort of reactive compatibilization technique has also been followed by Cimmino *et al.*[30], and Saleem and Baker[31].

Recently, Teyssié *et al.*[32–40] reported a large number of systems, in which the beneficial effects of polymeric emulsifiers in polymer blends have been illustrated. For example, they observed a significant reduction in the dispersed phase size and an increase in interfacial adhesion as a result of melt blending PE and PS with as little as 2 wt% of poly(butadiene-*b*-styrene)[34]. The copolymer also stabilized the system against coalescence. Moreover, Teyssié *et al.*[40] clearly demonstrated that the copolymer is uniformly adsorbed at the interface between the two polymers. The more recent papers of van Ballegooie and Rudin[41], Xanthos[42], Willis and Favis[43] and Chen *et al.*[44] also report on the compatibilization of heterogeneous polymer blends.

Finally, Leibler[45] and Noolandi *et al.*[46–49] have proposed statistical thermodynamic theories concerning the emulsifying effect of copolymers. The theory of Leibler[45] holds for nearly compatible systems, whereas the theories of Noolandi *et al.*[46–49] apply to the case of highly incompatible systems for concentrations below the critical micelle concentration (*CMC*). Leibler[45] developed a mean field formalism to study the interfacial properties of mixtures of two polymers, A and B, with an A–B copolymer. Noolandi *et al.*[46–49] reported that both copolymer concentration and molecular weight are equally important in reducing the interfacial tension. The localization of the copolymer at the interface and the separation of the blocks into corresponding homopolymer phases led to various phenomena such as the lowering of the interaction energy between the two immiscible homopolymers, the broadening of the interface between the homopolymers, the reduction in entropy of the system, a decrease in the energy of interaction of the two blocks with each other, and a large decrease in the interaction energy of the oriented blocks with homopolymers. The sum of all these contributions should be considered to determine the effect of copolymers on the surface tension between the two phases[48].

Blends of high molecular weight PS and PMMA exhibit two-phase morphology and have been shown to be incompatible by different techniques[12,41,50–54]. Some studies have already been reported[12,41,53,54] on the compatibilization of PS/PMMA binary blends by the addition of copolymers. However, more detailed investigations relating the compatibilizing efficiency to the physical nature and concentration of the copolymer are lacking. The main goal of this work is to investigate quantitatively the effect of molecular weight, composition and concentration of diblock copolymer of PS and PMMA on the morphology of PS/PMMA binary blends. The experimental results are compared to the predictions of current theories of Noolandi and Hong. Attempts have been made to deduce the conformation of the compatibilizer at the interface from the experimental results.

## EXPERIMENTAL

PS and PMMA were supplied by Polysar Corporation and Pressure Chemicals, respectively. The four copolymers used, of different molecular weights and compositions, were synthesized at the University of Liège, Belgium. The copolymers are designated as COP-170E, COP-200E, COP-750E and COP-200U where the number indicates the molecular weight (kg mol$^{-1}$) and the letters E and U refer to the copolymers having equal and unequal segmental mass, respectively. The characterization data of the polymers are given in *Table 1*. An interesting feature of the block copolymers is that, depending on the ratio of the length of the two blocks, the microdomain structure may show different shapes. The 89/11 PS/PMMA block copolymer (COP-200U) has spherical morphology while copolymers having equal lengths of the two blocks have a lamellar morphology[48].

Blends are designated as P30, P50, P70, P30C, P50C and P70C, where the number indicates the weight per cent of PS in the blend and the letter C indicates systems containing compatibilizer. Blends were prepared by solvent casting from 1,2-dichloroethane (DCE). A few compositions were cast from chloroform. The solvent was

**Table 1** Characterization data of the polymers

| Polymer | $M_w$ | $M_w/M_n$ | PMMA (wt%) | PS (wt%) | $\alpha$ | $\beta$ |
|---|---|---|---|---|---|---|
| PS | 50 000 | 1.02 | — | — | — | — |
| PMMA | 49 000 | 1.06 | — | — | — | — |
| COP-170E | 170 000 | 1.09 | 50 | 50 | 0.58 | 0.57 |
| COP-200E | 200 000 | 1.08 | 50 | 50 | 0.45 | 0.44 |
| COP-750E | 750 000 | 1.04 | 50 | 50 | 0.13 | 0.13 |
| COP-200U | 200 000 | 1.03 | 11 | 89 | 0.28 | 2.22 |

allowed to evaporate slowly for 2 days at room temperature. The films were further dried under vacuum at 80°C for 2 weeks, followed by heating at 120°C for 48 h to remove the last traces of solvent. Morphology of the blends was studied using a phase contrast microscope (Polyvar, Reichert-Jung). Cast films (10 $\mu$m thick) were used for optical microscopy studies. For scanning electron microscopy (Jeol model JSM-25S3) studies, the dispersed phase (PS or PMMA depending on the composition) was preferentially extracted. Cyclohexane was used for the preferential extraction of PS and acetic acid was used for the PMMA phase. Dispersed phase diameter was measured from the photomicrographs of $\sim$100 particles.

D.s.c. measurements were carried out with a Perkin Elmer DSC-4 apparatus equipped with a TADS microcomputer. The calibration of the apparatus was carried out using indium. The glass transition temperatures ($T_g$s) were recorded at the half-height of the corresponding heat capacity jump. The first scan was made at a heating rate of 20°C min$^{-1}$ up to 200°C. The sample was kept at that temperature for 1 min and then quenched at 25°C. Subsequent scans were made at a heating rate of 10°C min$^{-1}$. D.s.c. traces were always recorded during the third scan. Dynamic mechanical properties were measured on a Polymer Laboratories DMTA-MK11 apparatus equipped with an IBM microcomputer and a liquid nitrogen cooling system. The dynamic mechanical testing was performed at a heating rate of 1°C min$^{-1}$ and at a strain of 64 $\mu$m. The frequency of testing was 10 Hz.

## RESULTS

### *Effect of copolymer on dispersed phase size*

The influence of the compatibilizer on the phase morphology of heterogeneous polymer blends is due to the ability of the compatibilizer to reduce the interfacial tension between the dispersed phase and the matrix. The efficiency of this process depends on various factors such as mixing conditions, interaction of the compatibilizer with the dispersed phase, molecular weight and composition of the compatibilizer, and rate of absorption and orientation of the compatibilizer at the interface.

As a representative sample, *Figure 1* shows the tan $\delta$ values of COP-170E copolymer as a function of temperature. It shows two well defined transitions at 112 and 140°C which correspond to the glass transitions of PS and PMMA blocks, respectively. D.s.c. also showed two transitions at 109 and 132°C corresponding to PS and PMMA blocks, respectively. This type of phase segregation is essential for the location of the block copolymer at the interface[6].

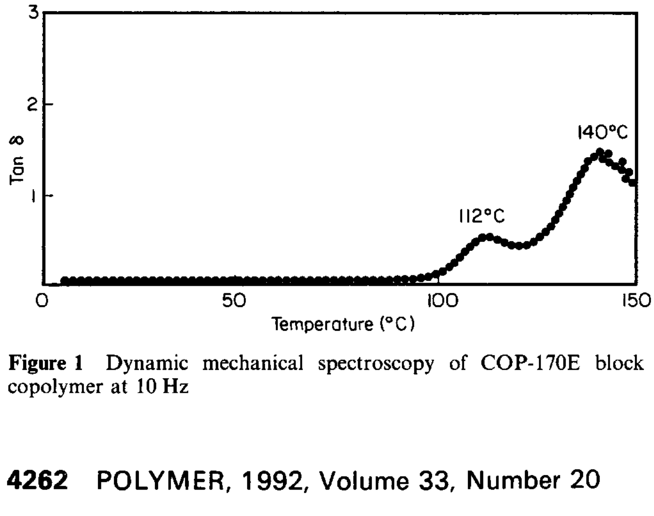

**Figure 1** Dynamic mechanical spectroscopy of COP-170E block copolymer at 10 Hz

*Figure 2a* shows the morphology of P30 blend containing no compatibilizer. The morphology of P30C containing 2.5 wt% COP-170E, COP-200E, COP-750E and COP-200U copolymers is given in *Figures 2b, c, d* and *e*, respectively. The effect of molecular weight, composition and concentration of the copolymer on the dispersed phase domain diameter of 30/70 PS/PMMA blend is given in *Figure 3*. It is seen that all the curves, except that with COP-200U, show a similar trend: there is a sharp decrease in dispersed phase dimension with the addition of small amounts of copolymer (2.5–5 vol%), followed by a levelling off as the copolymer content is increased above this equilibrium concentration which can be considered as the so-called apparent *CMC*, i.e. the concentration at which micelles are formed. In this context, it is important to mention that generally *CMC* is estimated from the plot of interfacial tension *versus* copolymer concentration[19]. Since the interfacial tension is directly proportional to the domain size[55], the estimation of *CMC* from the plot of domain size *versus* concentration is warranted. It is interesting to note that, at concentrations below the *CMC*, the particle size reduction is linear with increasing copolymer content. Noolandi and Hong[47] pointed out that the reduction in interfacial tension with increasing copolymer concentration and molecular weight could be accounted for by the reduction in interaction energy of the block copolymers at the interface, taking into account the associated entropy loss of the localized chains. The levelling off of particle dimension at high block copolymer concentration in these blends is an indication of interfacial saturation. The addition of more copolymers may be wasteful since it does not modify the interfacial zone but rather produces copolymer micelles in homopolymer phases. The 50/50 and 70/30 PS/PMMA blends also showed a similar behaviour upon the addition of copolymer.

In the case of COP-200U copolymer, no compatibilizing action is observed (*Figure 3*). This is associated with the preferential solubilization of the copolymer in the PS phase of the binary blend[6,12]. As pointed out by Riess and Jolivet[15], the emulsifying efficiency of different copolymers can be compared by defining the ratio of the molecular weight of the homopolymer and of the block copolymer as follows: If

$$\alpha = \frac{\text{mol. wt of PS homopolymer}}{\text{mol. wt of PS homopolymer}} \qquad (1)$$

$$\beta = \frac{\text{mol. wt of PMMA homopolymer}}{\text{mol. wt of PMMA component of the copolymer}} \qquad (2)$$

then, the copolymer is less efficient as an emulsifier if $\alpha > 1$ and $\beta > 1$. The emulsifying properties of the copolymer are at an optimum when $\alpha < 1$ and $\beta < 1$. In an ideal case, when $\alpha = \beta < 1$, the copolymer has no preferential solubility. The $\alpha$ and $\beta$ values of the copolymers used are given in *Table 1*. In the case of COP-200U copolymer, there is a large difference in $\alpha$ and $\beta$ values because of the unequal segmental mass, and $\beta$ is much higher than unity. This clearly indicates the preferential solubilization of the copolymer by the PS phase of the blend. As a consequence of this, the copolymer cannot stay at the interface. This accounts for the absence of compatibilizing property in COP-200U

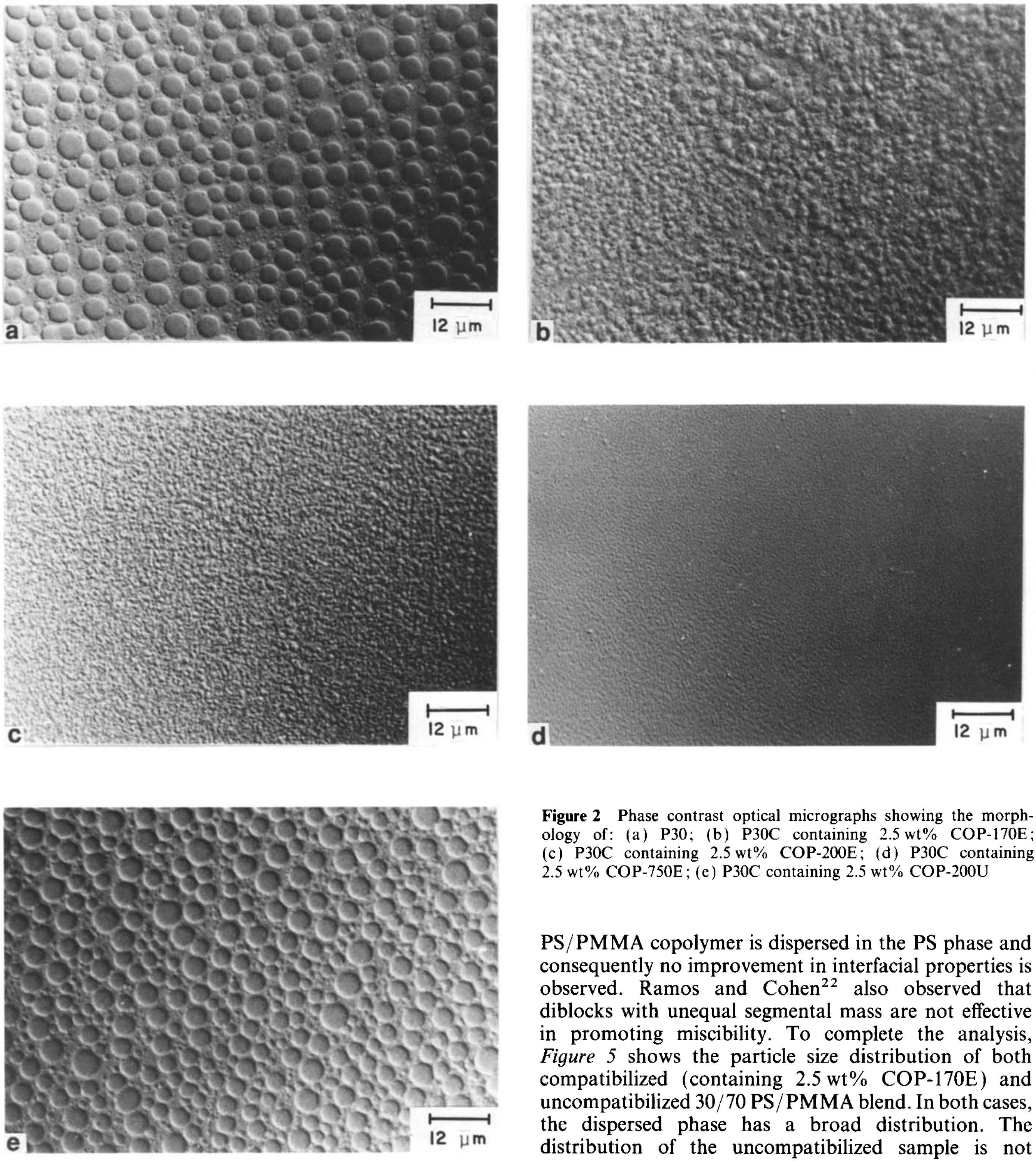

**Figure 2** Phase contrast optical micrographs showing the morphology of: (a) P30; (b) P30C containing 2.5 wt% COP-170E; (c) P30C containing 2.5 wt% COP-200E; (d) P30C containing 2.5 wt% COP-750E; (e) P30C containing 2.5 wt% COP-200U

copolymer. On the other hand, block copolymers COP-170E, COP-200E and COP-750E with equal segmental mass show remarkable compatibilizing action (*Figure 3*). From $\alpha$ and $\beta$ values of these copolymers (*Table 1*), it is expected that they have no preferential solubility in either of the phases, and that these copolymers are more or less located at the interface. This is shown schematically in *Figure 4* where the copolymer having equal segmental mass is represented at the interface between PS and PMMA phases. This behaviour leads to a large reduction in interfacial tension and domain size, and an increase in interfacial thickness. In contrast, due to its unequal segmental mass, the 89/11 PS/PMMA copolymer is dispersed in the PS phase and consequently no improvement in interfacial properties is observed. Ramos and Cohen[22] also observed that diblocks with unequal segmental mass are not effective in promoting miscibility. To complete the analysis, *Figure 5* shows the particle size distribution of both compatibilized (containing 2.5 wt% COP-170E) and uncompatibilized 30/70 PS/PMMA blend. In both cases, the dispersed phase has a broad distribution. The distribution of the uncompatibilized sample is not significantly broader, except for a tail which was never observed after the addition of the copolymer.

### *Effect of processing conditions on phase morphology*

*Table 2* shows the effect of processing conditions on the morphology of PS/PMMA blends. Films cast from chloroform have a coarser morphology than those cast from DCE. It has been observed in various systems that the same polymer blend can give different morphologies depending on the solvent from which the film is cast[56–59]. This is associated with the preferential interaction of the solvent with one of the components in the mixture[60,61]. The particle size of the films cast from DCE is nearly half the size of chloroform cast films. In both cases, the addition of compatibilizer reduces the dispersed phase

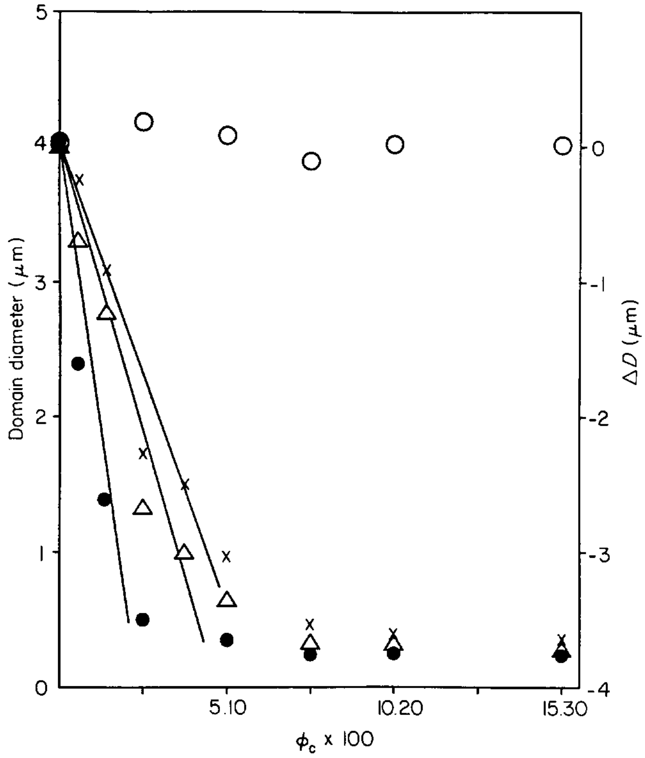

**Figure 3** Effect of per cent volume fraction ($\phi_c$) of different copolymers on the domain diameter and the domain diameter increment ($\Delta D$) of 30/70 PS/PMMA blends: (×) COP-170E; (△) COP-200E; (●) COP-750E; (○) COP-200U

dimension. However, the percentage reduction in phase dimension upon the addition of the compatibilizer in film cast from DCE is 75% while that cast from chloroform is 50%. This indicates that selection of the solvent for the blend preparation is also an important parameter controlling the compatibilizing efficiency. The chloroform cast films were further compression moulded. The particle size of the compression moulded samples is nearly the same as that of chloroform cast films (*Table 2*). This is because the shear forces involved in compression moulding are negligible. Hence, the original morphology is retained.

### *Effect of copolymer on blend miscibility*

D.s.c. and d.m.t.a. studies of the compatibilized (containing 5 wt% COP-170E) and uncompatibilized blends indicated the existence of two transitions corresponding to PS and PMMA phases. The compatibilized blends did not show any appreciable shift in the $T_g$ values. This indicates that addition of the compatibilizer does not alter the level of miscibility. In other words, incorporation of the compatibilizer does not promote molecular level miscibility. This is in agreement with the conclusions made by Paul[6], who suggested that, if two polymers are far from being miscible, then no copolymer is likely to make a one-phase system. In a completely immiscible system, the main role of the copolymer is to act as an interfacial agent.

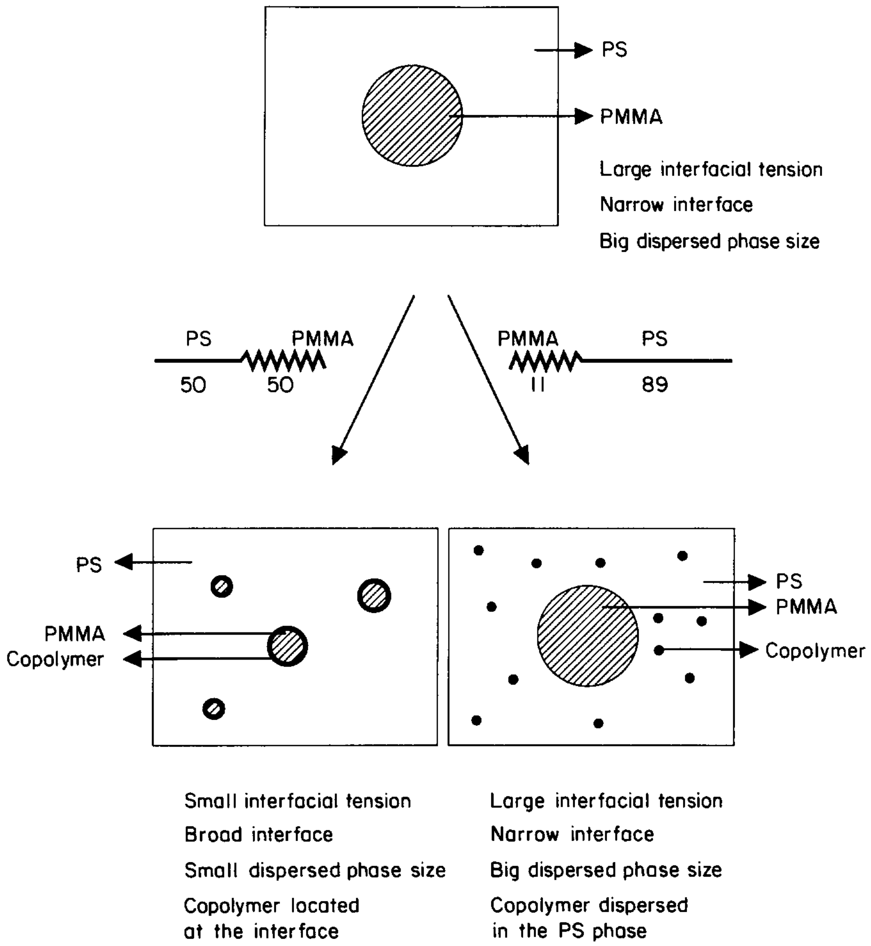

**Figure 4** Speculative model representing the behaviour of copolymers having different compositions

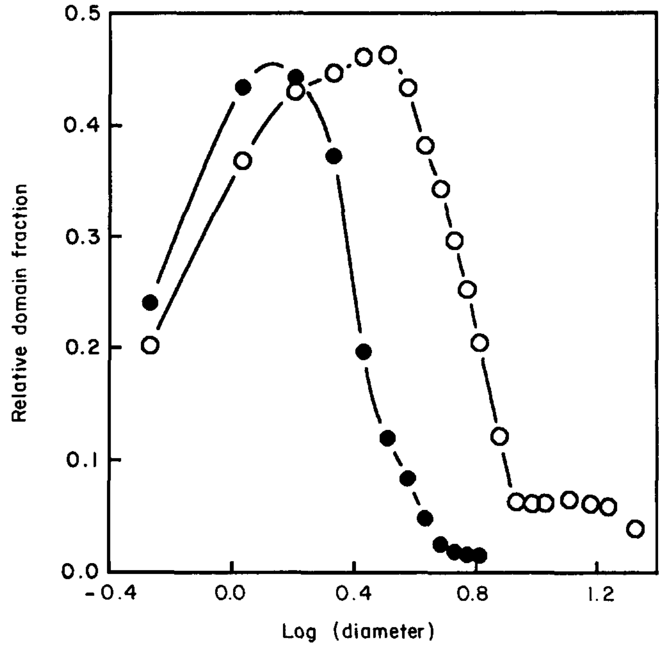

**Figure 5** Effect of copolymer (2.5 wt% COP-170E) on the domain size distribution of 30/70 PS/PMMA blends: (○) P30; (●) P30C

**Table 2** Effect of processing conditions on dispersed phase diameter (μm)[a]

| Mix no. | 1,2-Dichloroethane cast film | Chloroform cast film | Compression moulded |
|---|---|---|---|
| P30 | 4 ± 3.0[b] | 8 ± 4.0 | 6 ± 3.0 |
| P30C[c] | 1.0 ± 0.2 | 4.0 ± 0.4 | 3.8 ± 0.8 |
| P70 | 2.0 ± 0.9 | 6.0 ± 1.2 | 5.0 ± 1.5 |
| P70C[c] | 0.6 ± 0.2 | 3.0 ± 0.5 | 2.7 ± 0.8 |

[a] Arithmetic mean diameter
[b] Standard deviation
[c] Contains 5 wt% COP-170E

## DISCUSSION

Many experimental studies have been reported on the interfacial saturation of binary polymer blends by the addition of copolymers[16–19,34,43]. Anastasiadis *et al.*[19] have observed a sharp decrease in interfacial tension with the addition of small amounts (1.5 wt%) of poly(styrene-*b*-butadiene) in PS/1,2-polybutadiene blends, followed by a levelling off at higher copolymer concentrations. The *CMC* was estimated from the plot of interfacial tension *versus* block copolymer concentration. They concluded that further addition of the compatibilizer beyond the *CMC* would not modify the interface any more. Fayt *et al.*[34] observed an equilibration in the dispersed phase dimension with increasing block copolymer concentration in PE/PS blends. In this case, the major reduction in phase dimension occurred from 0.5 to 1 wt% of the compatibilizer. Willis and Favis[43] also reported that an equilibrium concentration of 5% of ionomer (based on the dispersed phase) was sufficient to compatibilize polyolefin/polyamide blends. All these experimental observations suggest that there is a maximum quantity of compatibilizer which can saturate the interface. Addition of compatibilizer beyond this point will not modify the interface any more.

The theories of Noolandi and Hong[46,47] can be applied to highly incompatible systems, such as PS/PMMA blends, for concentrations less than the *CMC*. According to their theories, for concentrations smaller than the *CMC*, the interfacial tension is expected to decrease linearly with copolymer concentration, whereas above the *CMC* a levelling off is expected. In the absence of a solvent, for a ternary system A/A-*b*-B/B, the interfacial tension reduction or increment ($\Delta\gamma$), upon the addition of the copolymer, is given by the following expression[46,47]:

$$\Delta\gamma \cong d\phi_c[1/2\chi + 1/Z_c - 1/Z_c \exp(Z_c\chi/2)] \qquad (3)$$

where $d$ is the width at half-height of the copolymer profile reduced by the Kuhn statistical segment length, $\phi_c$ is the bulk volume fraction of the copolymer in the system, $\chi$ is the Flory–Huggins interaction parameter between A and B segments of the copolymer, and $Z_c$ is the degree of polymerization of the copolymer. According to this equation, the plot of interfacial tension reduction *versus* $\phi_c$ should yield a straight line. Since interfacial tension reduction is directly proportional to the particle size reduction[55], it can be argued that

$$\Delta D \cong Kd\phi_c[1/2\chi + 1/Z_c - 1/Z_c \exp(Z_c\chi/2)] \qquad (4)$$

where $\Delta D$ is the particle size reduction or increment upon the addition of the compatibilizer, and $K$ is a proportionality constant. The plot of experimental values of $\Delta D$ as a function of copolymer volume fraction appears in *Figure 3*. It can be seen that at low copolymer concentrations (below the *CMC*), $\Delta D$ decreases linearly with increasing copolymer volume fraction whereas, at higher concentrations (above the *CMC*), it levels off, in agreement with the theories of Noolandi and Hong.

*CMC* values were then estimated from the intersection of the straight line drawn in *Figure 3* at low concentrations and the levelling off line at high concentrations. Values of 5.2, 4.3 and 2.2% were found for COP-170E, COP-200E and COP-750E, respectively (*Figure 3*). It can be concluded that, below the *CMC*, the high molecular weight copolymer (COP-750E) is more efficient as a compatibilizer than its low molecular weight counterparts (COP-170E and COP-200E). This suggests that there are two choices to compatibilize a heterogeneous system; either to select a relatively high concentration of a small molecular weight copolymer (but it must be higher than the molecular weight of the homopolymers) or, conversely, a small amount of high molecular weight block copolymer. Obviously, it would be preferable at the industrial scale to add a very high molecular weight block copolymer. However, if the molecular weight becomes extremely high, the large molecules of copolymer will form micelles. Moreover, there can be dispersion problems due to high viscosity. In such a case, the compatibilizing effect cannot be obtained.

It is possible to estimate the area $a$ occupied by a compatibilizer molecule at the interface by deriving an equation which relates it to the volume fraction and the dimension of the dispersed phase, to the molecular weight of the compatibilizer, and to the amount of compatibilizer needed to saturate the interface[6,62]. Let us consider a binary blend that contains a volume fraction $\phi_A$ of polymer A as spherical domains of radius $R$ in a B matrix. The total interfacial area per unit volume of the original blend is equal to $3\phi_A/R$. If each copolymer molecule occupies an area $a$ at the interface, then the mass, $m$, of the block copolymer required to saturate per unit volume

**Table 3** Diameter ($2R$, $\mu$m) of the dispersed phase at the *CMC*

| Composition | P30C | P50C | P70C |
|---|---|---|---|
| COP-170E | 1.0 | 2.0 | 0.6 |
| COP-200E | 0.6 | 1.6 | 1.0 |
| COP-750E | 0.5 | 1.0 | 0.5 |

**Table 4** $a$ values of the copolymer systems at different blend ratios

| Copolymer | Lateral random coil surface area (nm$^2$) | $a$ (nm$^2$) | | |
|---|---|---|---|---|
| | | P30C | P50C | P70C |
| COP-170E | 200 | 10 | 8 | 16 |
| COP-200E | 260 | 23 | 14 | 23 |
| COP-750E | 810 | 204 | 170 | 204 |

of the blend is given by the following equation[6,62]:

$$a = 3\phi_A M/mRN \tag{5}$$

where $M$ is the molecular weight of the copolymer and $N$ is Avogadro's number. In the present study, since the *CMC* is the interfacial saturation point, it would be reasonable to consider the *CMC* as the value for $m$. As indicated above, the values of *CMC* are 5.2, 4.3 and 2.2% for COP-170E, COP-200E and COP-750E, respectively. $R$ is the radius of the dispersed phase at the *CMC* which was measured by microscopy (*Table 3*). *Table 4* shows the $a$ values of the copolymer systems at different blend ratios. In this calculation, the *CMC* values are crudely estimated from *Figure 3*. However, even an error by a factor of two, which is the most pessimistic hypothesis, would not modify the following conclusions.

It is now possible to deduce the conformation of the compatibilizer at the interface based on the $a$ values. Two physical models illustrating the conformation of the compatibilizer at the interface are given in the literature[6,62,63]. One model visualizes the blocks as extending into the corresponding homopolymer phases as shown in *Figure 6a*. In such a case, the occupied area at the interface is the cross-sectional area of the extended copolymer molecule. In the case of poly(styrene-*b*-methyl methacrylate), the theoretical average cross-sectional area of the extended copolymer molecule and, therefore, the area it occupies at the interface is $\sim$0.5 nm$^2$. In the second model (*Figure 6b*), the copolymer lies almost completely flat at the interface, in which case the occupied area is the lateral surface area of the entire copolymer molecule[63]. By considering each block of the copolymer as a spherical random coil, we have calculated the lateral surface areas of the copolymers (*Table 4*) using the experimental values of root mean square radius of gyration of the PMMA block reported in the literature[64,65], which are 8.0, 9.1 and 16 nm, for COP-170E, COP-200E and COP-750E, respectively.

In order to test the applicability of these models, a comparison could be made between the $a$ values obtained from equation (5) (*Table 4*) and those calculated from the two physical models. For example, in the 30/70 PS/PMMA blend, the area occupied by the COP-170E copolymer molecule, as calculated from equation (5), is 10 nm$^2$. This value is intermediate to those values obtained from the two models (0.5 and 200 nm$^2$). This suggests that neither of these models represent the actual situation. The behaviour of the copolymers is intermediate to those of the two models and can be represented by a third model which is a combined form of the two earlier models (*Figure 6c*). In other words, the copolymers cannot penetrate completely into the corresponding homopolymer phases. A substantial part of the copolymer molecule stays at the interface between the PS and PMMA phases. The extent of penetration of the different copolymers is in the order COP-170E > COP-200E > COP-750E, which is dependent on their molecular weight. This can be easily understood from *Table 4*. For example, in the case of P30C blend, COP-170E occupies an area which is 4.5% of its lateral surface area, while COP-750E occupies an area which is 25% of its lateral surface area.

It is important to consider one more point supporting this argument. Gaylord[8] has suggested that, in the case of high molecular weight copolymers where the molecular weight of the copolymer is >150 000, macromolecular interactions such as chain entanglements hinder the complete penetration of each segment into the corresponding homopolymer phases. This further suggests that the copolymers cannot penetrate completely into the homopolymer phases and, therefore, it is expected that part of the copolymer may be staying at the interface. This could lead to an increase in interfacial thickness and this would be maximum in the case of COP-750E which occupies the maximum area at the interface. Recently, Russell *et al.*[66] have reported that the addition of copolymer increases the interfacial thickness of PS/PMMA blends, which is in agreement with our own results[67]. In this study, the interfacial thickness was measured by neutron reflectivity. In the

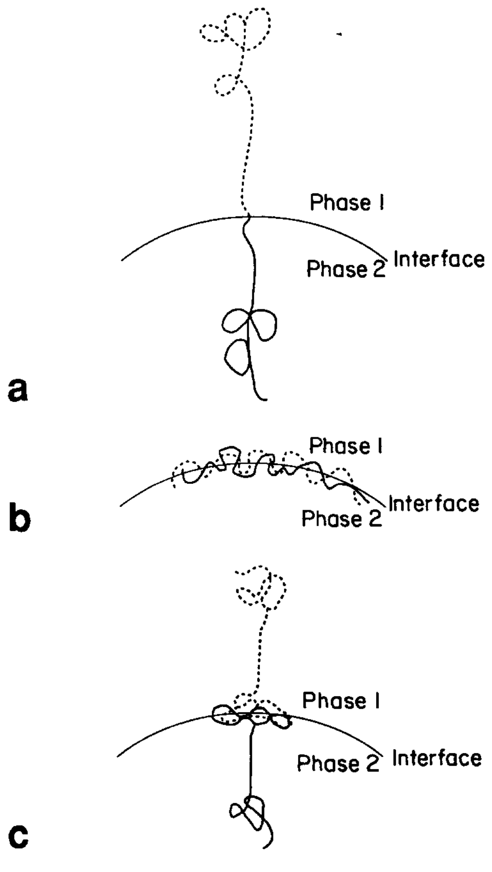

**Figure 6** Physical models illustrating the conformation of the copolymer at the interface

case of compatibilized blends, the effective width of the interface was found to be 7.5 nm which was 50% larger than that of the uncompatibilized PS/PMMA interface. According to Wu[55], interfacial tension ($\gamma_{12}$) and interfacial thickness ($L$) are related by the following equation:

$$\gamma_{12} = 7.6/L^{0.86} \qquad (6)$$

This indicates that the superior compatibilizing action of the COP-750E copolymer compared with other copolymers is associated with the larger increase in interfacial thickness and a consequent reduction in interfacial tension. Recent experimental investigations of Anastasiadis *et al.*[19] on the compatibilizing action of poly(styrene-*b*-1,2-butadiene) in PS/1,2-polybutadiene blends clearly showed that ~24% (63.5 monomer units) of the contour length of the copolymer chain (degree of polymerization of 261 repeat units) is located at the interface and this corresponds to a length of 38 nm. This sort of conformation of the compatibilizer can be explained only based on the model of *Figure 6c*.

## CONCLUSIONS

The results presented show that the addition of properly chosen diblock copolymer has a great influence on the morphology of binary PS/PMMA blends. The extent and the influence of this beneficial effect on the final morphology seem to be strictly related, as shown by experimental data, to the composition, molecular weight and concentration of the copolymer. The domain size of the dispersed phase decreases sharply with the addition of small amounts (2.5–5%) of copolymer, followed by a levelling off as the copolymer content is increased, which is an indication of interfacial saturation by the copolymer. For concentrations less than the *CMC*, the theories of Noolandi and Hong predict a linear decrease of interfacial tension with copolymer volume fraction. Considering that interfacial tension is directly proportional to the domain size, it is demonstrated that the experimental data are in agreement with these theories. Of the various copolymers studied, 50/50 PS/PMMA copolymer having a molecular weight of 750000 was found to be the most efficient one. This behaviour is related to its conformation at the interface. The absence of compatibilizing action in 89/11 PS/PMMA copolymer is due to the preferential solubilization of the copolymer in the PS phase.

Applicability of different models to illustrate the conformation of the compatibilizer at the interface has been discussed. It has been noticed that the actual conformation of the copolymer at the interface is different from those models reported in the literature. The copolymers neither stay completely at the interface between PS and PMMA phases nor penetrate completely into the corresponding homopolymer phases. The actual conformation is better represented by a combined model in which part of the copolymer molecule stays at the interface and the rest penetrates to the corresponding homopolymer phases. Among the various copolymers, the one having the highest molecular weight occupies the maximum area at the interface.

## ACKNOWLEDGEMENTS

The authors would like to thank Polysar Corporation, Sarnia, Ontario, for partial financial assistance. They also thank the Natural Sciences and Engineering Research Council of Canada and the Department of Education of the Province of Québec (FCAR program) for financial support. Thanks are finally due to Dr R. Fayt of Université of Liège, Belgium, for supplying the copolymers.

## REFERENCES

1 Paul, D. R. and Barlow, J. W. *J. Macromol. Sci. Rev. Macromol. Chem.* 1980, **C18**(1), 109
2 Utracki, L. A. 'Polymer Alloys and Blends', Hanser, New York, 1990
3 Shaw, M. T. *Polym. Eng. Sci.* 1982, **22**, 115
4 Avgeropoulos, G. N., Weissert, F. C., Biddison, P. H. and Bohn, G. G. A., *Rubber Chem. Technol.* 1976, **49**, 93
5 Nolley, E., Barlow, J. W. and Paul, D. R. *Polym. Eng. Sci.* 1980, **20**, 364
6 Paul, D. R. in 'Polymer Blends' (Eds D. R. Paul and S. Newman), Academic Press, New York, 1978, Ch. 12
7 Paul, D. R. and Barlow, J. W. *Am. Chem. Soc. Adv. Chem. Ser.* 1979, **176**, 315
8 Gaylord, N. G. *Am. Chem. Soc. Adv. Chem. Ser.* 1975, **142**, 76
9 Molau, G. E. *J. Polym. Sci.* 1965, **A3**, 1267
10 Molau, G. E. *J. Polym. Sci.* 1965, **A3**, 4235
11 Molau, G. E. and Wittbrodt, W. M. *Macromolecules* 1968, **1**, 260
12 Riess, G., Kohler, J., Tournut, C. and Banderet, A. *Makromol. Chem.* 1967, **101**, 58
13 Kohler, J., Riess, G. and Banderet, A. *Eur. Polym. J.* 1968, **4**, 173
14 Periard, J. and Riess, G. *Colloid Polym. Sci.* 1975, **253**, 362
15 Riess, G. and Jolivet, Y. *Am. Chem. Soc. Adv. Chem. Ser.* 1975, **142**, 243
16 Gailard, P., Ossenbach-Sauter, M. and Riess, G. *Makromol. Chem., Rapid Commun.* 1980, **1**, 771
17 Gailard, P., Ossenbach-Sauter, M. and Riess, G. in 'Polymer Compatibility and Incompatibility: Principles and Practice' (Ed. K. Solc), MMI Symposium Series 2, Harwood, New York, 1982
18 Patterson, H. T., Hu, K. H. and Grindstaff, T. H. *J. Polym. Sci. C* 1971, **34**, 31
19 Anastasiadis, S. H., Gancarz, I. and Koberstein, J. T. *Macromolecules* 1989, **22**, 1449
20 Inoue, T., Soen, T., Hashimoto, T. and Kawai, H. *Macromolecules* 1970, **3**, 87
21 Coumans, W. J., Heikens, D. and Sjoerdsma, S. D. *Polymer* 1980, **21**, 103
22 Ramos, A. R. and Cohen, R. E. *Polym. Eng. Sci.* 1977, **17**, 639
23 Lindsey, C. R., Paul, D. R. and Barlow, J. W. *J. Appl. Polym. Sci.* 1981, **26**, 1
24 Schwarz, M. C., Barlow, J. W. and Paul, D. R. *J. Appl. Polym. Sci.* 1989, **37**, 403
25 Turley, S. G. *Appl. Polym. Symp.* 1968, **7**, 237
26 Durst, R. R., *US Pats 3 906 057* and *3 906 058*, 1975
27 Barentsen, W. M., Heikens, D. and Piet, P. *Polymer* 1974, **15**, 119
28 Locke, C. E. and Paul, D. R. *J. Appl. Polym. Sci.* 1973, **13**, 2791
29 Ide, F. and Hasegawa, A. *J. Appl. Polym. Sci.* 1974, **18**, 963
30 Cimmino, S., D'Orazio, L., Greco, R., Maglio, G., Malinconico, M., Mancarella, C., Martuscelli, E., Palumbo, R. and Ragosta, G. *Polym. Eng. Sci.* 1984, **24**, 48
31 Saleem, M. and Baker, W. E. *J. Appl. Polym. Sci.* 1990, **39**, 365
32 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Edn*, 1981, **19**, 79
33 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Edn* 1981, **19**, 1269
34 Fayt, R., Jérôme, R. and Teyssié, Ph. *Makromol. Chem.* 1986, **187**, 837
35 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Phys. Edn*, 1982, **20**, 2209
36 Fayt, R., Hadjiandreou, P. and Teyssié, Ph. *J. Polym. Sci., Polym. Chem. Edn*, 1985, **23**, 337
37 Ouhadi, T., Fayt, R., Jérôme, R. and Teyssié, Ph. *Polym. Commun* 1986, **27**, 212
38 Ouhadi, T., Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Appl. Polym. Sci.* 1986, **32**, 5647
39 Fayt, R., Jérôme, R. and Teyssié, Ph. *Polym. Eng. Sci.* 1987, **27**, 328

40 Fayt, R., Jérôme, R. and Teyssié, Ph. *J. Polym. Sci., Polym. Lett. Edn* 1986, **24**, 25

41 van Ballegooie, P. and Rudin, A. *Makromol. Chem.* 1989, **190**, 3153

42 Xanthos, M. *Polym. Eng. Sci.* 1988, **28**, 1392

43 Willis, J. M. and Favis, D. B. *Polym. Eng. Sci.* 1988, **28**, 1416

44 Chen, C. C., Fontan, E., Min, K. and White, J. L. *Polym. Eng. Sci.* 1988, **28**, 69

45 Leibler, L. *Macromolecules* 1982, **15**, 1283

46 Noolandi, J. and Hong, K. M. *Macromolecules* 1984, **17**, 1531

47 Noolandi, J. and Hong, K. M. *Macromolecules* 1982, **15**, 482

48 Noolandi, J. *Polym. Eng. Sci.* 1984, **24**, 70

49 Vilgis, T. A. and Noolandi, J. *Macromolecules* 1990, **23**, 2491

50 Van Oene, H. *J. Colloid Interface Sci.* 1972, **40**, 448

51 Manabe, S., Murakami, R., Takayanagi, M. and Uemura, S. *Int. J. Polym. Mater.* 1971, **1**, 47

52 Hong, S. D. and Burns, C. M. *J. Appl. Polym. Sci.* 1971, **15**, 1995

53 Brown, H. R. *Macromolecules* 1989, **22**, 2859

54 Lowenhaupt, B. and Hellmann, G. P. *Colloid Polym. Sci.* 1990, **268**, 885

55 Wu, S. *Polym. Eng. Sci.* 1987, **27**, 335

56 Djakovic, L., Dokic, P., Radivojevic, P., Sefer, I. and Sovilij, V. *Colloid Polym. Sci.* 1987, **265**, 993

57 Bank, M., Leffingwell, J. and Thies, C. *Macromolecules* 1971, **4**, 43

58 Barlow, J. W. and Paul, D. R. *J. Polym. Sci., Polym. Phys. Edn* 1987, **25**, 1459

59 Caravatti, P., Neuenschwander, P. and Ernst, R. R. *Macromolecules* 1985, **18**, 119

60 Robard, A. and Patterson, D. A. *Macromolecules* 1977, **10**, 1021

61 Chen, C. T. and Morawetz, H. *Macromolecules* 1989, **22**, 159

62 Heikens, D. *Kem. Ind.* 1982, **31**, 165

63 Plochocki, A. P., Dagli, S. S. and Andrews, R. D. *Polym. Eng. Sci.* 1990, **30**, 741

64 Tamai, Y., Konishi, T., Einaga, Y., Fujii, M. and Yamakawa, H. *Macromolecules* 1990, **23**, 4067

65 Kirste, R. G., Kruse, W. A. and Ibel, K. *Polymer* 1975, **16**, 120

66 Russell, T. P., Menelle, A., Hamilton, W. A., Smith, G. S., Satija, S. K. and Majkrzak, C. F. *Macromolecules* 1991, **24**, 5721

67 Perrin, P. and Prud'homme, R. E. in preparation