Interfacial activity of polycarbonate/polystyrene graft copolymers in polycarbonate/polystyrene blends

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This paper examines the influence of adding polycarbonate/polystyrene graft copolymers to blends of a chlorinated polycarbonate and polystyrene; the backbone of the graft copolymers is the same chlorinated polycarbonate. The interaction parameter between the polycarbonate and polystyrene is calculated. The copolymer acts as an interfacial agent and its influence on the morphologies, dynamic-mechanical properties and interfacial area of the blends is investigated. Morphologies of both polycarbonate-rich and polystyrene-rich blends were determined; in one case dispersed particles of the minor phase are stabilized by polycarbonate chains with one end attached to the interface, in the other case stabilization is by polystyrene chains with two ends attached to the interface (loops). This system is one in which the component polymers are very immiscible. The results are compared with data determined previously on a system based on the same polycarbonate and poly(methyl methacrylate), which is characterized by very limited miscibility.

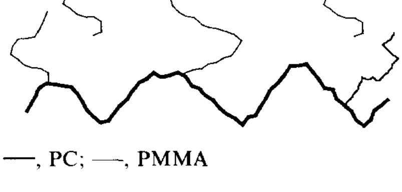
(Keywords: polycarbonate; polystyrene; blends; morphology; dynamic mechanical properties; interfacial area)

INTRODUCTION

For several years interest has been shown in the efficiency of copolymers with different architectures as interfacial agents in blends of immiscible polymers. There has been speculation as to the relative merits of diblock, triblock and graft copolymers as interfacial agents. It is usually considered that chains with only one end located at the interface (simple grafts) provide better stabilization of dispersed phases than do loops[1].

In recent publications[2–5] this group reported on a systematic study of the interfacial activity of graft copolymers in polymer blends; chains with one end restricted to the interface were the main stabilizing units. The system investigated consisted of solvent-cast blends of a chlorine-containing polycarbonate (PC) with poly(methyl methacrylate) (PMMA) with added copolymers of PMMA grafts attached to chains of the same PC. The graft copolymers were shown to act primarily as interfacial agents but also to provide some limited enhanced miscibility. Small amounts of copolymer created interface, increased interfacial areas and decreased the size of dispersed-phase domains. When the copolymer content exceeded about 8 wt% its efficiency to further increase interfacial area diminished; this phenomenon was attributed to unfavourable free energy changes when the size of small dispersed particles (diameter ~ 500 nm) was decreased still further. Maximum interfacial activity required the lengths of blocks in the copolymer to be significantly greater than those of the corresponding homopolymer. The importance of the ratio of molecular weights of the PC block (MAC) to that of the corresponding ungrafted polymer (MAH) was rationalized in terms of the mechanism of emulsification by copolymers[5]. Optimum utilization of copolymer in the blend involved segregation of its constituents during solvent evaporation concurrent with formation of the dispersed phase. Mean field theory successfully predicts the critical conditions for reduced interfacial activity at higher MAH/MAC ratios[5].

The earlier study involved stabilizing PC-rich domains in PMMA-rich blends primarily by PMMA grafts. This was a consequence of the average structure **I** of copolymer species used. Four-fifths of the PMMA chains exist as grafts, one-fifth are crosslinks, because of the mode of the termination reaction in the free-radical polymerization of methyl methacrylate used in graft copolymer synthesis[6].



Structure I —, PC; —, PMMA

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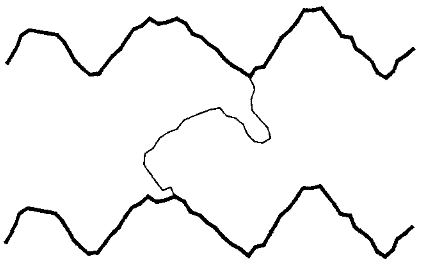
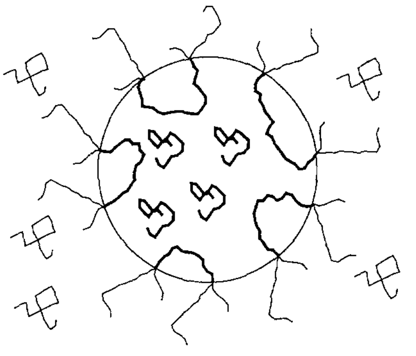
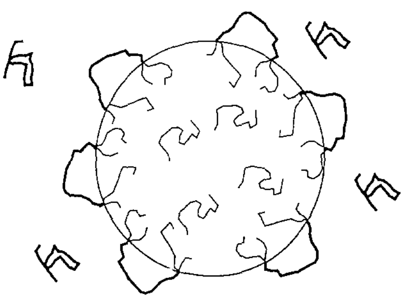


Structure II —, PC; —, PS



Scheme 1 Polycarbonate-rich system. —, PS; —, PC



Scheme 2 Polystyrene-rich system. —, PS; —, PC

We now report data on PC/polystyrene (PS) blends, using the same chlorinated PC. We have previously established the immiscibility of these two polymers[7], and have studied their dynamic mechanical properties in the absence of copolymer[8] and the morphologies of one homopolymer (PC) blended with copolymer[7]. This is a comparable system to the former in which the polymer grafts attached to PC are virtually exclusively in the form of crosslinks. The system is the same PC with PS grafts (crosslinks) formed by combination termination of propagating PS grafts. Typical copolymer species have structure **II**. Use of these copolymer species allows both simple grafts (PS domains in PC-rich blends, *Scheme 1*) and loops (PC domains in PS-rich blends, *Scheme 2*) to be examined as stabilizing species; we presume that it is the copolymer blocks on the outside of the dispersed phases which primarily provide a barrier against coalescence of the dispersed phases. This paper discusses both systems. Information is provided on the efficiencies of PS loops and PC grafts as stabilizers of dispersed phases in terms of phase dimensions produced and extents of molecular mixing.

EXPERIMENTAL

Materials

The PC used in this study was a chlorine-containing random copolymer of bisphenol-A and 1,1-trichloro-*bis*-2-(*p*-hydroxyphenyl) ethane prepared by condensation polymerization of an equimolar mixture of the two monomers with phosgene[9]. Its molecular weight was determined by gel permeation chromatography (g.p.c.) with tetrahydrofuran as carrier solvent and with respect to PS calibration. PS homopolymer was prepared by free radical polymerization ($\bar{M}_n = 65\,000$, $\bar{M}_w/\bar{M}_n = 1.65$).

Copolymers were prepared by initiating free radical polymerization of styrene from the trichloromethyl groups on the PC prepolymer. Photolysis ($\lambda = 436$ nm) of dimanganese decacarbonyl, $Mn_2(CO)_{10}$, produced PC macroradicals by abstraction of a chlorine atom from the pendant trichloromethyl groups[10]. Reactions were carried out in dilute solutions ($\sim 1.5\%$ w/v) of PC in styrene at 25°C under nitrogen in large, shallow photochemical reactors in a room illuminated with inactive sodium light[11]. Radicals were created randomly from only a small fraction of trichloromethyl groups on the PC. The initiation reaction is highly specific and chain transfer to polymer is negligible at the low conversions used. All PS chains are, consequently, attached to the PC. The propagating chains undergo termination almost exclusively by combination, producing a crosslink between two PC chains[12,13]. The mode of termination and the multiple functionality of the polycarbonate will eventually lead to network formation. In this work network formation was avoided by limiting reaction times, and only soluble species were produced. PS homopolymer was prepared by the same process using a low-molecular-weight halide initiator.

The relationship between copolymer structure and polymerization kinetics has been discussed extensively in earlier publications, which are summarized in ref. 11. Before gelation, the reaction mixture contains crosslinked structures and unreacted PC. We have used the relative crosslinking index, γ_r, as a parameter for copolymer design[14]. This parameter is directly proportional to the number of crosslinks in the system relative to those necessary for incipient network formation. The critical condition for network formation is one crosslinked unit per weight-average PC chain[15,16]. From the definition it follows that $\gamma_r = 1$ at this point. The crosslinking index was kept below 1 for all the copolymers used (typically $\gamma_r = 0.65$). The predominant structure of the copolymer species is depicted by **II**. The reaction product consists of a range of multicomponent species, including dimers (i.e. two PC chains crosslinked by one PS chain) and high-order *n*-mers, and unreacted PC homopolymer. Dimers have been predicted by Flory[15,16] and experimentally shown by Eastmond and Richardson[17] to dominate the distribution of the multicomponent species under the reaction kinetics conditions used for copolymer synthesis. Detailed accounts of the conditions for random crosslinking and optimization of copolymer architecture in these systems have been presented elsewhere[10,17,18].

PS crosslinks were characterized by g.p.c. following selective base-degradation of the PC backbone and isolation of the crosslinks[18]. The molecular weights of homopolymer and copolymers are abbreviated as follows: MAH, $\bar{M}_n$ of PC homopolymer; MAC, $\bar{M}_n$ of PC backbone; MBH, $\bar{M}_n$ of PS homopolymer; MBC, $\bar{M}_n$ of PS crosslinks.

Techniques

Films (0.2 mm thick) were cast from dilute (4% w/v) homogeneous solutions in dichloromethane under reproducible conditions in open Petri dishes at room temperature. Residual solvent was removed at 115°C under vacuum over 1 week.

Film morphologies were studied by phase-contrast microscopy and transmission electron microscopy (TEM). Relatively thick sections (10–15 μm) cut parallel to the bulk film surface were used for optical microscopy. TEM studies used ultrathin sections cut parallel to the bulk film surface. Adequate phase contrast was provided by the electron density difference between the two polymers. Dynamic mechanical spectra were obtained at 110 Hz with a heating rate of 1°C min^{-1} using a Rheovibron viscoelastometer (DDV-IIC, Toyo-Balwin Ltd, Tokyo) on samples (2 × 30 mm^2) cut from cast films.

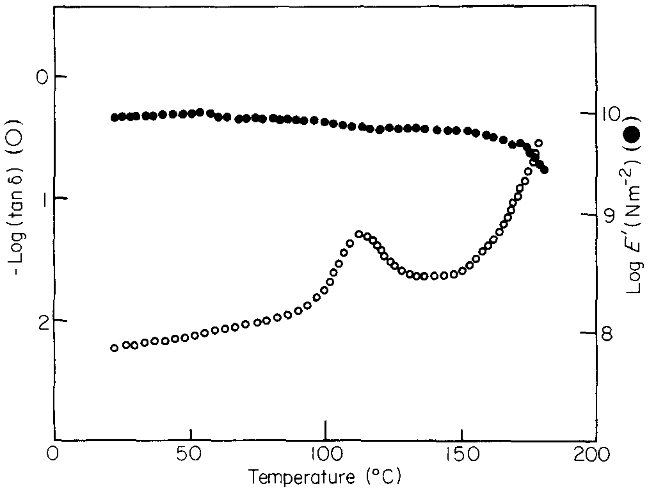


Figure 1 Dynamic mechanical spectra for PC/PS blends with 65 wt% PC at 110 Hz, in the absence of added copolymer

RESULTS

Unmodified blends

Figure 1 presents dynamic mechanical data for solvent-cast PC/PS blends containing 65 wt% PC at 110 Hz in the absence of copolymers. The system exhibited typical two-phase behaviour with two α-relaxations at temperatures close to the glass transition temperatures of the pure components, indicative of complete phase separation, as observed previously in blends containing 75 wt% PS[8]; in this study blends with 65 wt% PS were too brittle for mechanical measurements.

Morphologies of the same blends are shown in *Figure 2a* and *b*. The optical micrographs confirm separation of the components and the formation of two distinct layers in a laminate structure. Transmission electron micrographs, *Figure 2c* and *d*, reveal the presence of a limited

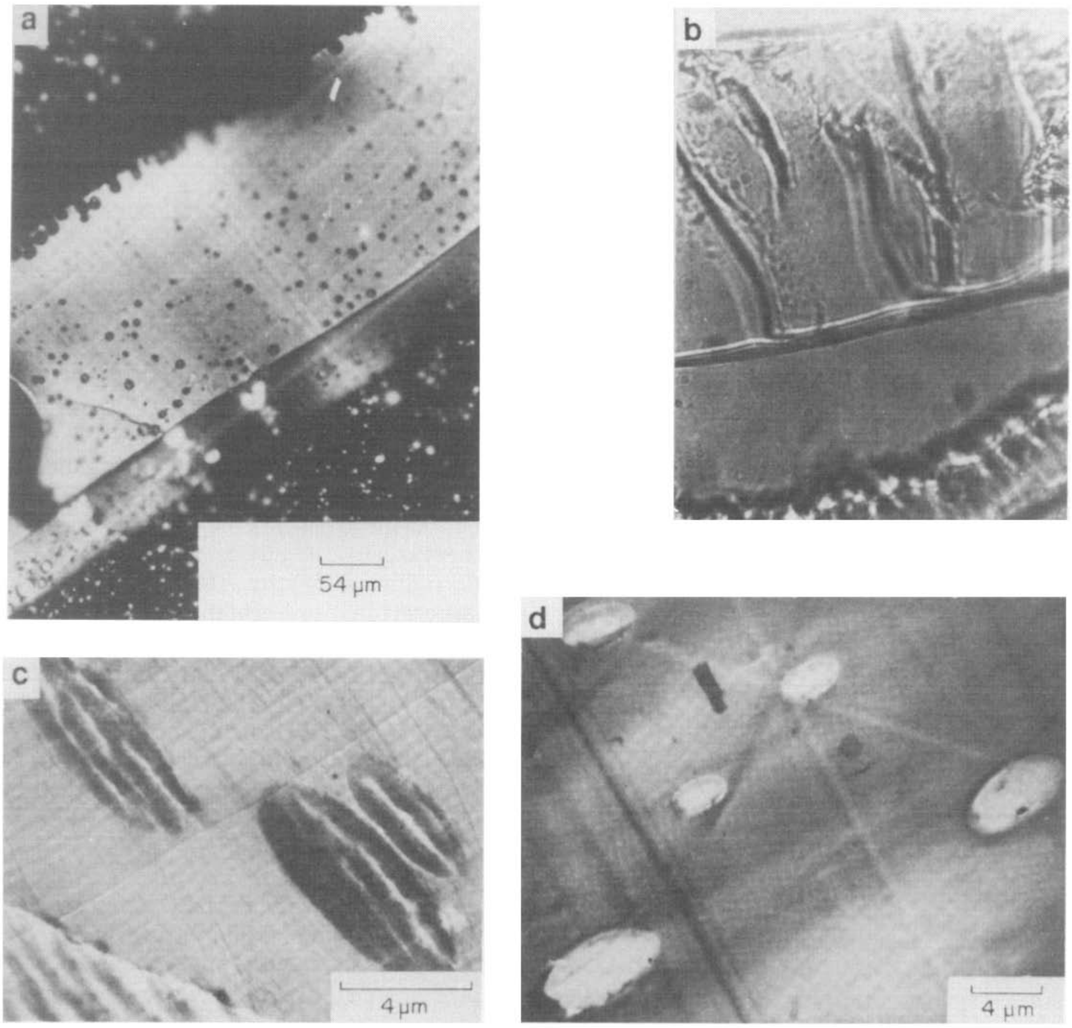


Figure 2 (a) (b) Optical (same scale) and (c) (d) transmission electron micrographs of PC/PS blends having 65 wt% PC

number of small domains (diameter ~3–9 μm) of one component dispersed in the other with sharp interfaces. Both the mechanical property data and morphologies are consistent with the known immiscibility of the PC with PS[7,8].

The ternary phase diagram for this PC and PS in dichloromethane[7] corroborates this immiscibility; the plait point is at a polymer volume fraction of 0.08 and dichloromethane is a good solvent for both components. The critical Flory–Huggins parameter, $\chi_{23,\mathrm{crit}}$, was calculated from equation (1) where x_2, x_3 are the degrees of polymerization of the components; subscripts 2 and 3 refer to PC and PS, respectively. The calculated value of $\chi_{23,\mathrm{crit}}$ was 0.010. The interaction parameter for the blend, $\chi_{23}^{\mathrm{blend}}$, was estimated from the solubility parameters of the two polymers to be 0.027. A literature value of 9.2 (cal cm^{-3})$^{1/2}$ was used for the solubility parameter for PS[19]. The value of 9.9 (cal cm^{-3})$^{1/2}$ calculated previously was used for PC[20].

$$\chi_{23,\mathrm{crit}} = \tfrac{1}{2}(x_2^{-1/2} + x_3^{-1/2})^2 \qquad (1)$$

The fact that $\chi_{23}^{\mathrm{blend}} > \chi_{23,\mathrm{crit}}$ is consistent with immiscibility of the components, a strong tendency to phase-separate in dilute solution and for volumes of the same components to coalesce readily in mobile solution[21].

Copolymer-modified blends

Polystyrene matrix. We now consider the behaviour of PC/PS blends (35 wt% PC) containing 5 to 17 wt% PC/PS copolymer; some fraction of the added 'copolymer' (approximately half of the PC content) is ungrafted PC with a molecular weight of MAC. The total volume fraction of the PS was maintained constant (0.80–0.82). The molecular weight of the ungrafted PC (MAH = 10 200) was lower than that of the corresponding block in the copolymer (MAC = 20 200). Similarly, the molecular weights of the PS copolymer block (MBC) and homopolymer (MBH) were 98 000 and 65 000, respectively. By analogy with the stabilizing influence of PC/PMMA copolymer in PC/PMMA blends[3–5], the molecular weight of the PS block was sufficiently high for us to expect it to provide an efficient steric barrier against coalescence and eventual lamination of the PC-rich dispersed phase. In this case the steric barrier is provided by PS loops (*Scheme 2*), as discussed earlier.

Addition of PC/PS copolymer to the blend had a marked influence on the morphology as seen in both optical (*Figure 3*) and transmission electron micrographs (*Figure 4*); a much more uniform texture of small dispersed phases is observed. The laminar nature of the films was retained in all systems but one, that with 5 wt% copolymer, where a relatively fine textured blend was found; that sample actually shows both dark dispersed phases in a white matrix and regions of the reverse morphology but without laminate formation. The top (major) layer of the laminates (volume fraction 0.80–0.82) had a PS-rich (light) (PS density = 1.1 g cm^{-3}) matrix with dispersed PC (dark) (PC density = 1.3 g cm^{-3}) inclusions.

The dispersed regions in the two layers are stabilized by copolymer. The average size of the dispersed particles in the bottom layer appears smaller than that in the top; this effect may reflect differences in interfacial activity of grafts and loops according to the nature of the matrix. In the lower layer (PC matrix) the dispersed particles may be more efficiently stabilized by PC grafts. In the upper layer the particles are stabilized against coalescence by PS loops which may be less effective. Thus, relatively unstabilized particles could coalesce to give rise to the lower layer, as described previously[21]. This process involves phase inversion and only occurs when the system is sufficiently mobile during the casting process.

Figure 3 illustrates the influence of copolymer content. A small amount of copolymer (5 wt%) gives the most uniform texture with no clear lamination. Addition of more copolymer brings back the lamination, unlike in the previous study on PC/PMMA blends[5]. We are not certain of the explanation of this observation except to note that addition of copolymer actually involves the simultaneous addition of unreacted (ungrafted) PC to the system; on grafting to low crosslink densities large proportions of unreacted PC will remain, which was not separated from copolymer. While addition of increasing amounts of copolymer gives a more uniform texture to the blend there is not the same reduction in dispersed phase dimensions (*Figure 4*) as was observed for the PC/PMMA blends[3–5].

Polycarbonate matrix. For PC-rich (65 wt%) blends the dispersed particles are mainly PS-rich and are stabilized by PC grafts. We have investigated the influences of both PC block molecular weight and copolymer content on the morphology of the blends. *Table 1* summarizes the molecular weights of PC (MAC) and PS (MBC) chains in the copolymers used. The actual molecular weight of individual PC blocks at an interface are smaller than quoted because PS chains are attached at some point along the PC chain. Thus two PC chains emanate from each junction point and, on average, one will have a molecular weight equal to 0.75 MAC and the other 0.25 MAC. The molecular weights of the ungrafted PC (10 200) and PS homopolymer (65 000) were kept constant and lower than those of the corresponding blocks in copolymer. Overall the morphologies were similar to those with a PS matrix, having a laminar structure with dispersed particles in each layer.

Effect of PC block molecular weight on interfacial activity

The effect of varying the molecular weight of the PC chains, and hence of the PC blocks, in the copolymer on the morphology at constant copolymer content (10 wt%) is illustrated in *Figure 5*. Increasing the PC molecular weight from 20 200 to 143 800 produced no dramatic effect on the gross morphology as seen in the size of the dispersed particles by optical microscopy, and there was little influence on the relative volume fractions of the upper and lower layers in the laminate. These observations contrast markedly with those reported for PC/PMMA blends when copolymer with high-molecular-weight

Table 1 Compositions of copolymers added to blends

Copolymer	Molecular weight MAC	Molecular weight MBC	Copolymer content (%)[a]
CS1	20 200	98 000	10
CS2	143 800	126 000	10
CS3	78 000	96 000	10

[a] By virtue of the method of preparation the copolymer added contains only a proportion of true copolymer and a larger proportion of unreacted polycarbonate[11]

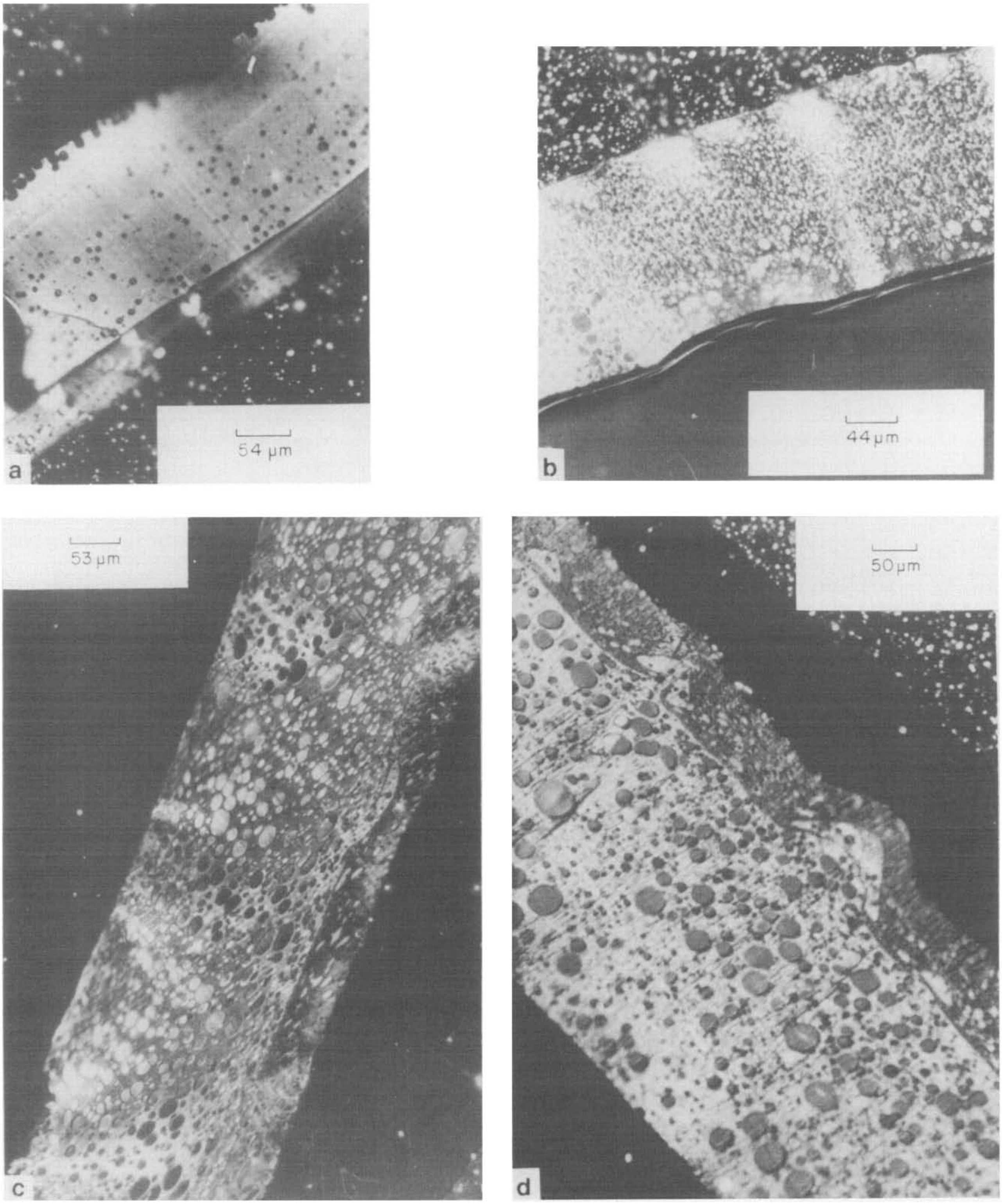


Figure 3 Optical micrographs of PC/PS blends (35 wt% PC overall) containing (a) 0, (b) 5, (c) 9 and (d) 17 wt% PC/PS copolymer; molecular weights are given in text

blocks markedly reduced the size of dispersed regions[4] and with high-molecular-weight copolymer blocks the blend became transparent; heterogeneity could only be seen by transmission electron microscopy. The only evidence for weaker interfacial activity in blends with lower-molecular-weight PC blocks (MAH/MAC = 0.5, average molecular weight of the PC blocks is very similar to that of the ungrafted polymer) was in the formation of large (40 μm diameter) droplets with an internal structure (*Figure 5a*) probably forming as part of the coalescence and phase inversion process. Transmission electron micrographs (*Figure 6*) indicate a decrease in the size and increase in number of small domains per unit volume as the molecular weight of the PC blocks increases.

Dynamic mechanical spectra (110 Hz) for these blends are shown in *Figure 7*. For the unmodified blend and with 10 wt% added copolymer CS2 the samples became

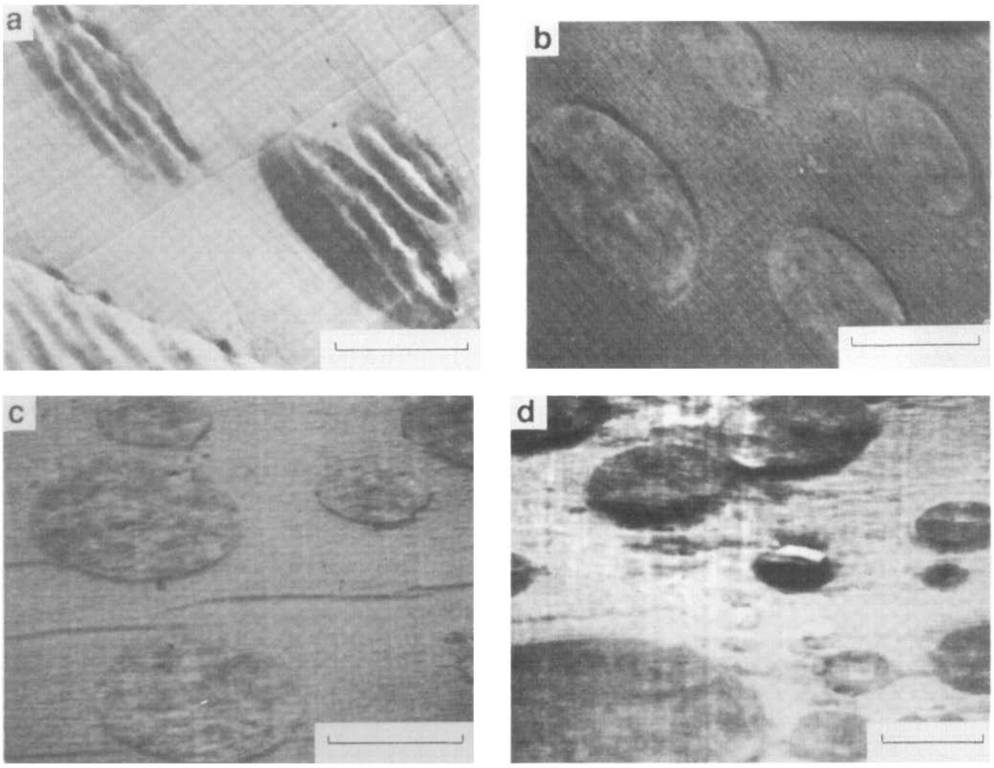


Figure 4 Transmission electron micrographs of PC/PS blends with (a) 0, (b) 5, (c) 9 and (d) 17 wt% added copolymer as described in *Figure 3*. Bar = 4 μm

too weak to obtain data up to the glass transition temperature of the major (PC) component (~210°C); presumably there was insufficient continuity in the PC component. Clearly all samples exhibited two α-relaxations corresponding to those of PS- and PC-rich phases. They all showed a lower glass transition temperature, close to that for pure PS. The unmodified blend and that with added copolymer CS1 showed upper glass transition temperatures close to those for the pure PC but that with added copolymer CS2 showed an upper glass transition temperature at a reduced temperature consistent with incorporation of some PS in the PC phase. In this case it is possible that the longer PC chains take into the PC phase some of the shorter PS chains grafted to them, against the unfavourable thermodynamic barrier, while the shorter PC chains in CS1 are unable to do this.

Effect of copolymer concentration on interfacial activity

The influence of adding up to 40 wt% copolymer CS2 to PC-rich blends is seen in *Figure 8*. The figure shows optical micrographs of cross-sections of cast films; sections cut parallel to the film surface showed the same morphologies. Increasing amounts of copolymer produce finer dispersions but the laminate nature of the films persists until 40 wt% of copolymer is added; even then some large dispersed phases are present. The sample with 20 wt% added copolymer shows gross irregular droplet-like features; each phase, droplet and matrix, has dispersed phases within it. Samples with 40 wt% added copolymer exhibit a more uniform morphology but, even then, regions with PS and with PC matrixes are evident. While the fine textures of blends of PC with PMMA rendered electron micrographs amenable to stereological analysis, because of the scale of irregularity of heterogeneities, this was not so easy in the present case. Transmission electron micrographs from some ultrathin sections, cut parallel to the film surface, are shown in *Figure 9*; the sections were unstained and PC appeared dark. With 20 wt% added copolymer, regions with each polymer forming the matrix were found. Using standard stereological relations, as used in a preceding paper[5], estimates were made of interfacial area per unit volume, $\langle S_v \rangle$, and interfacial area per unit volume of dispersed phase, $\langle S_D \rangle$. Dispersed phases have a broad distribution of diameters (*Figure 10*); the average diameter decreases slightly with increasing copolymer content. However, unlike the results for addition of copolymer to PC/PMMA blends, where low concentrations of copolymer produced a massive decrease in dispersed phase dimensions, in this system the interfacial area appears to increase slowly and linearly with copolymer content (*Figure 11*). As elsewhere in this system, interfaces observed appeared sharp.

Dynamic mechanical data reinforce the fact that addition of copolymer does not enhance miscibility of the components but simply acts as an interfacial agent. Data in *Figure 12* show that addition of 40 wt% copolymer CS3 has hardly any influence on the transition behaviour; just a small reduction in the glass transition temperature of the PC-rich phase is possibly apparent.

DISCUSSION

The results presented above show that PC/PS copolymers act as weak interfacial agents in PC/PS polymer blends. These results, however, contrast strongly with our previous observations that similar PC/PMMA copolymers act as strong interfacial agents in PC/PMMA blends; in this system less than 5 wt% of added copolymer can render the blends optically transparent with heterogeneities only observable by electron microscopy.

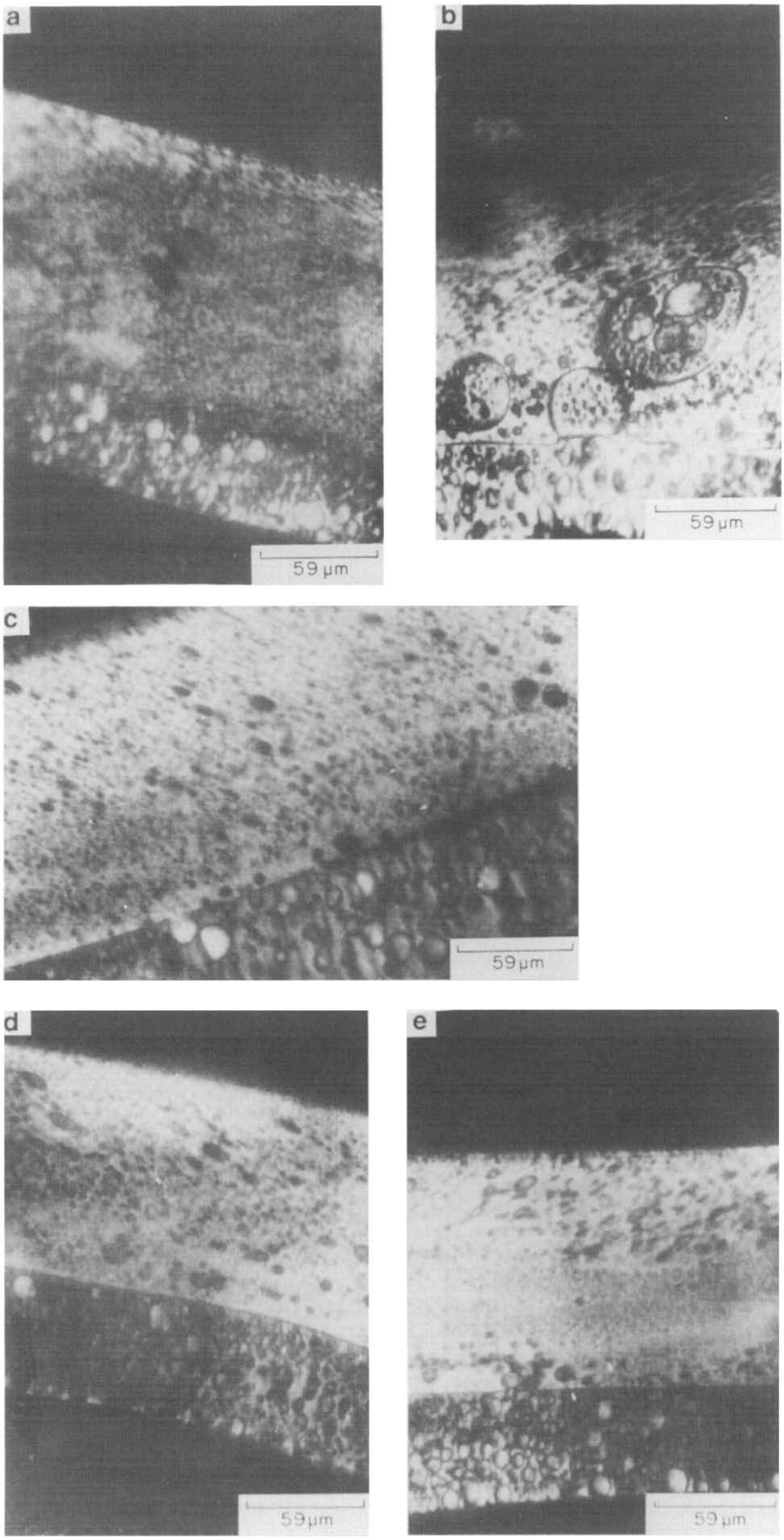


Figure 5 Optical micrographs of PC/PS blends (65 wt% PC) to illustrate the influence of relative molecular weights of ungrafted PC (MAH) and grafted PC (MAC) on blend morphology. Copolymer content in blends, 10 wt%. MAH = 10 200, MBH = 65 000. Added copolymers were: (a) (b) CS1; (c) CS2; (d) (e) CS3, as described in *Table 1*. Bar = 59 μm

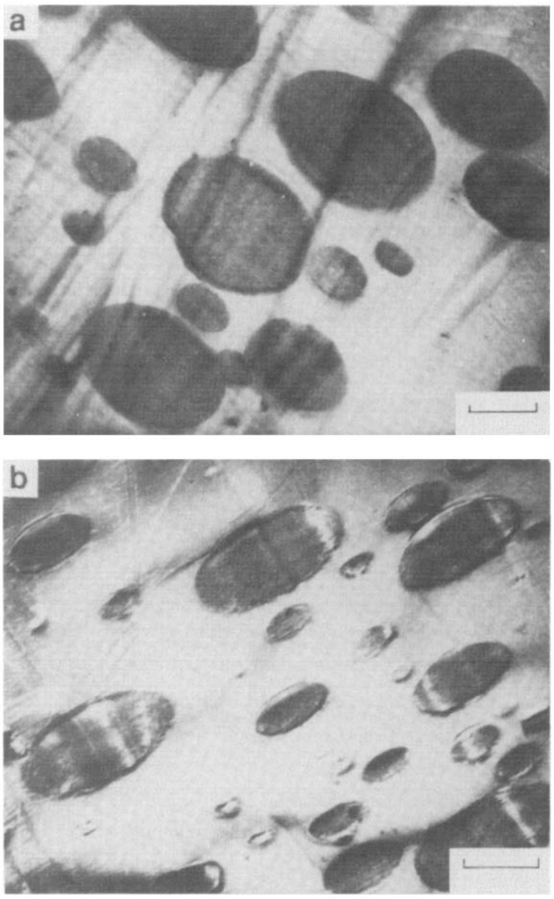


Figure 6 Transmission electron micrographs of PC/PS blends (65 wt% PC) with 10 wt% added PC/PS copolymer. Added copolymers were: (a) CS1, (b) CS3. Bar = 4 μm

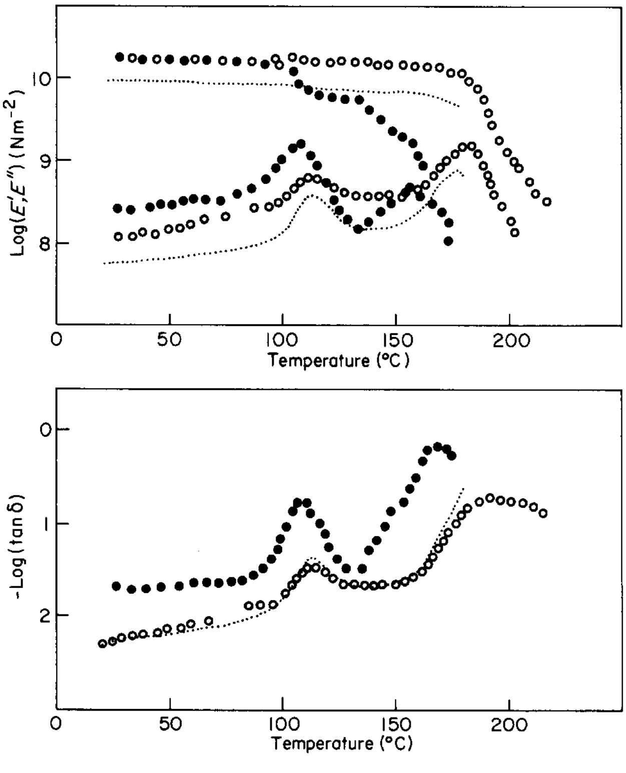


Figure 7 Dynamic mechanical spectra of PC/PS blends (65 wt% PC, MAH = 10 200) without (....) and with 10 wt% added copolymer (○) CS1 and (●) CS2

Previously we have argued[3–5], in agreement with other workers[22,23], that the equilibrium morphology is that which minimizes unfavourable A–B contacts in binary blends of polymers A and B, moderated by the fact that minimizing contacts implies a narrow interface which has an attendant entropic penalty. Thus, entropic factors tend to broaden the interface. The interfacial thickness is dependent on the magnitude of the interaction parameter between the component polymers.

The PC used in our studies is immiscible with both PMMA and PS. However, the estimated interaction parameter between PC and PS is large and the driving force to immiscibility is greater than with PMMA. In the latter case, solvent-casting blends, even in the absence of copolymer, can lead to incomplete segregation of the component polymers (unless the casting process is very slow) because the partial miscibility in relatively high polymer concentrations means that final segregation must take place in systems of high viscosity.

In the previous studies of PC/PMMA blends we estimated that the interfacial area per copolymer molecule at the interface was relatively large, because of the massive increase in interfacial area, and the interface is relatively dilute in copolymer. The blends with added copolymer had a very fine texture. In PC/PS blends the texture is much coarser and it follows that, because there is also no increase in miscibility of the components, the interface must be relatively more concentrated in copolymer. This study group[7,24] and others[22,25–27] have argued that if an interface is relatively concentrated in attached chains (chains 'grafted' to an interface and not necessarily in the form of graft copolymer), the chains so attached are not miscible with chemically identical homopolymer chains. This was argued on the basis of the entropy of mixing of free and attached chains. Thus, it might be expected that the PC/PS interface will not provide such good adhesion between the chains at the interface and the matrix polymers.

We can then argue that in the case where the driving force towards immiscibility is less strong (PC/PMMA) there is likely to be a stronger interface, and a broader one, between the components. This leads us to speculate that, especially in blends where the components are highly immiscible, rather than using a copolymer of the identical components as an interfacial agent, it may be better to use a copolymer which has less unfavourable interactions with the polymer forming the blend. Ideally it is probably best to use a copolymer in which the components have negative interaction parameters with the components of the blend.

The study just undertaken provides some limited information for a comparison of the relative stabilizing propensities of loops and singly attached chains. Whichever polymer is the dispersed phase the same copolymer is located at the interface, controlling interfacial tension and the nature of the interface. Stabilities of dispersed phases (against coalescence) might be expected to vary according to whether loops or simple chains are at the outside of the dispersed phases. There does not seem to be any dramatic difference between the tendencies of dispersed PC or PS phases to coalesce. PS phases seem to be slightly smaller than PC phases under comparable conditions and this observation suggests that PS loops (on the outside of PC phases) may provide a less effective barrier than simple PC chains (on the outside of PS phases).

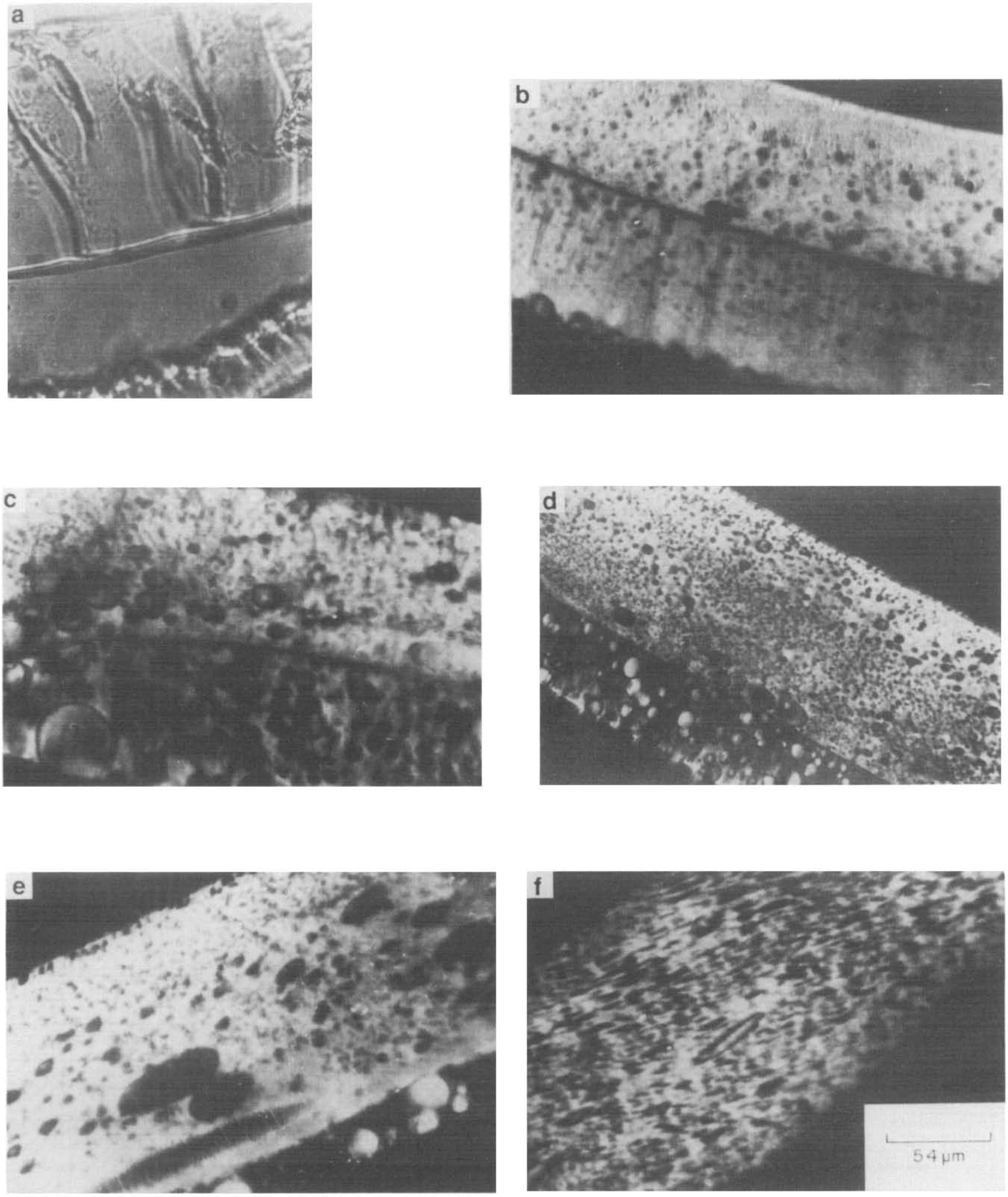


Figure 8 Optical micrographs of PC/PS blends (65 wt% PC) with added copolymer CS2, to illustrate the influence of copolymer content: (a) 0, (b) 1, (c) 5, (d) 10, (e) 20, (f) 40 wt% copolymer. Sections were cut perpendicular to the film surface

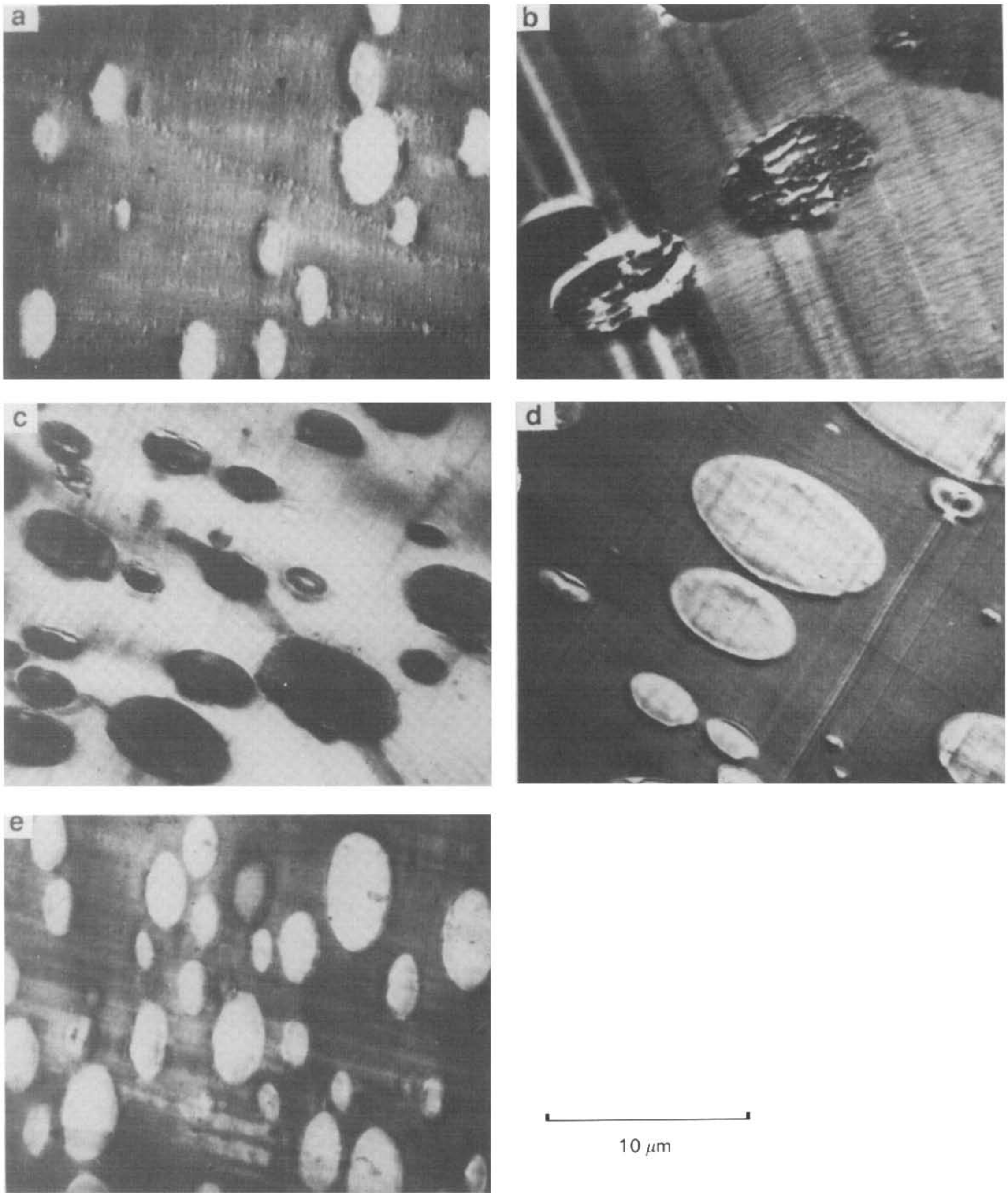


Figure 9 Transmission electron micrographs of PC/PS blends (65 wt% PC) with: (a) 1, (b) 5, (c) (d) 20, (e) 40 wt% added copolymer CS1. Sections, unstained, were cut parallel to the film surface. Samples cut as in *Figure 8*

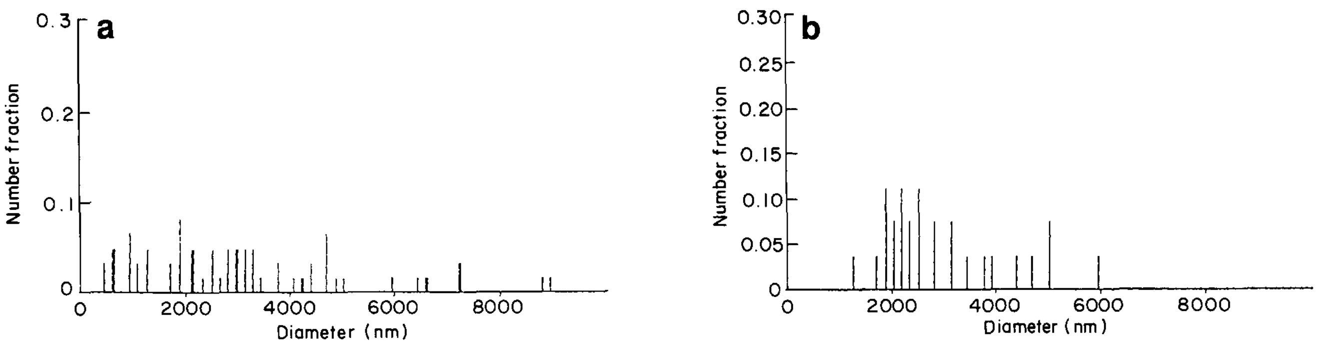


Figure 10 Frequency distributions of diameters of PS dispersed phases in PC/PS blends (65 wt% PC) with (a) 20 wt% and (b) 40 wt% added copolymer CS1

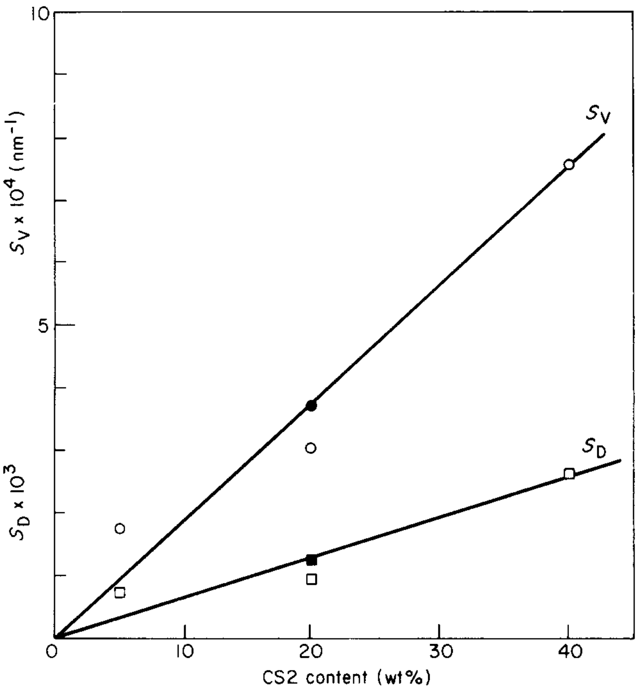


Figure 11 Variation in (○, ●) interfacial area per unit volume (S_v) and (□, ■) interfacial area per unit volume of PS dispersed phase (S_D) in PC/PS blends (65 wt% PS) with added copolymer CS2. (●, ■), Dark domains in bright matrix; (○, □) bright domains in dark matrix

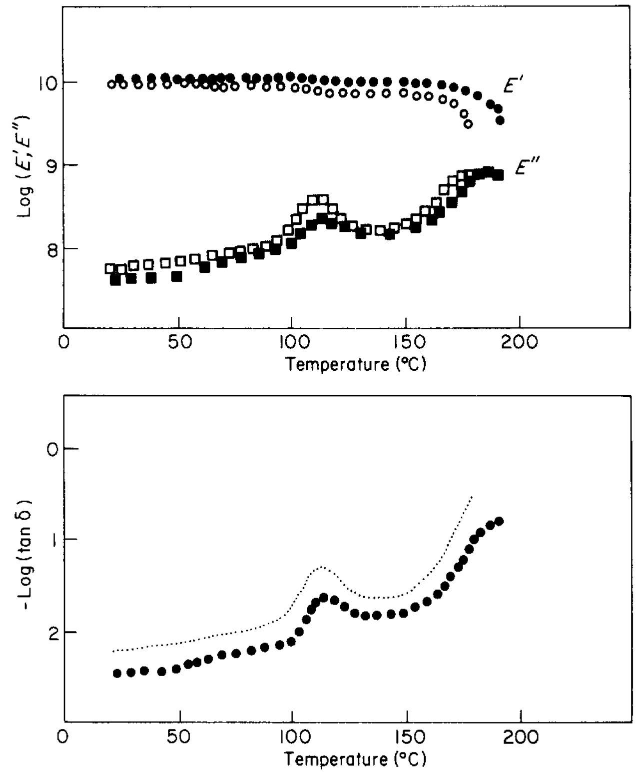


Figure 12 Dynamic mechanical spectra of PC/PS blends (65 wt% PC) (○, □, ...) and with 40 wt% added copolymer CS3 (●, ■)

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