Stereoregular poly(alkyl methacrylate)s: polymer–polymer and copolymer–polymer blends

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Amorphous blends of isotactic and syndiotactic poly(methyl methacrylate) were found to be compatible. To evaluate the interaction between these tactic polymers, random copolymers of isotactic poly(methyl/ethyl methacrylate) were blended with syndiotactic poly(methyl methacrylate). Only the copolymers with an ethyl methacrylate content below 45% were compatible with syndiotactic poly(methyl methacrylate). Using a Flory–Huggins type treatment of copolymer mixtures, the segmental interaction parameters for poly(methyl methacrylate) with poly(ethyl methacrylate) and for isotactic with syndiotactic poly(methyl methacrylate) were calculated. The interaction parameter for the tactic poly(methyl methacrylate) pair was found to be small and negative.

(Keywords: blends; miscibility; copolymers; poly(methyl methacrylate); interaction parameters)

INTRODUCTION

It is known that tacticity affects blend compatibility when two chemically different polymers are blended and one of the blend components is available in different tactic forms. For example, isotactic poly(methyl methacrylate) (iPMMA) and poly(vinyl chloride) (PVC) are incompatible but syndiotactic poly(methyl methacrylate) (sPMMA) and PVC are compatible for blends of up to 60% sPMMA[1]. Isotactic and syndiotactic PMMA form compatible blends with poly(vinylidene fluoride) (PVF_2) but the interaction is stronger between iPMMA and PVF_2 than between sPMMA and PVF_2, as shown by melting point depression[2] and infra-red[3] studies. Since the two forms of PMMA interact differently with a given polymer, a non-zero interaction between the isotactic and syndiotactic PMMA's might be expected.

Therefore the behaviour of amorphous blends of isotactic and syndiotactic PMMA was investigated in this study. An amorphous blend is considered to be compatible if a single glass transition temperature, T_g, intermediate to the T_g's of the pure components, is observed. Partial blend compatibility is indicated by a shifting and broadening of the original transitions. The compatibility of isotactic and syndiotactic PMMA may be determined by T_g measurements since, despite the chemical identity of these polymers, the T_g's of the polymers are widely separated (by ~75°C). Previously, Krause and Roman[4] found isotactic and syndiotactic PMMA to be compatible while Bauer and Bletso[5] found them incompatible. These results are not necessarily contradictory as neither the molecular weights nor the tacticities of the respective polymers in the two studies were identical. In the current study, the compatibility of isotactic poly(methyl/ethyl methacrylate) random copolymer and isotactic poly(ethyl methacrylate) (iPEMA) blends with sPMMA was also investigated. A mean field treatment based on the Flory–Huggins theory of polymer mixing, recently introduced by ten Brinke, Karasz and MacKnight[6] to describe the phase behaviour of copolymer systems, was used to analyse the blend data. Using this treatment, it was possible to estimate the interaction parameter for isotactic and syndiotactic PMMA.

EXPERIMENTAL

Isotactic and syndiotactic poly(methyl methacrylate)s were obtained from Polymer Laboratories, Ltd., Church Stretton, England. The syndiotactic polymer was used as received; the isotactic polymer was fractionated prior to use to obtain samples with near monomodal molecular weight distributions. The isotactic poly(methyl/ethyl methacrylate) copolymers were prepared from iPMMA, rather than synthesized from monomer, to ensure the same degree of tacticity for the copolymers as for the isotactic homopolymer (>99% isotactic triads). A two step reaction was performed: the iPMMA was hydrolysed using concentrated sulphuric acid and the resulting poly(methacrylic acid) was re-esterified by adding appropriate amounts of ethereal diazomethane and diazoethane to the polymer suspended in benzene[7]. This procedure caused a random placement of the ester groups. A small amount of a side-product of the reactions, which caused a yellow–brown discolouration of the samples, remained in the copolymers and could not be extracted. iPEMA was also prepared in this manner.

The samples were characterized using a Varian CFT-20 Fourier Transform ^{13}C-n.m.r. and a Waters Associates Liquid Chromatograph Model 201 with differential refractometer. The g.p.c. was calibrated with narrow molecular-weight-distribution polystyrene standards, which were obtained from Polysciences, Inc. The tacticities, molecular weights, and poly-dispersities of the polymers are listed in *Tables 1* and *2*. The ratio of methyl

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Table 1 $\bar{M}_n$, $\bar{M}_w$, $\bar{M}_w/\bar{M}_n$ and tacticities of isotactic and syndiotactic poly(methyl methacrylate)s

Sample	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Triad tacticity I	H	S
PL-1 iPMMA	43 000	163 000	4	>99%	–	–
PL-2 iPMMA	54 000	264 000	5	>99%	–	–
PL-3 iPMMA	26 000	132 000	5	>99%	–	–
PL-1 sPMMA	94 000	296 000	3	–	~25%	~75%
PL-2 sPMMA	94 000	241 000	3	–	~25%	~75%
PL-4 sPMMA	153 000	302 000	2	–	~25%	~75%

Table 2 Isotactic* poly(methyl/ethyl methacrylate) copolymers and isotactic poly(ethyl methacrylate)

Sample	Molar ratio methyl:ethyl ester	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
iPEMA	0:100	49 000	144 000	3
co-A	77:23	24 000	210 000	9
co-B	29:71	16 000	98 000	6
co-C	52:48	48 000	671 000	14
co-D	39:61	42 000	527 000	12

*Isotactic triads >99%

ester to ethyl ester in the copolymers, as given in *Table 2*, was obtained by ^{1}H-n.m.r. and provided by Polymer Laboratories.

Amorphous blends of isotactic and syndiotactic PMMA were prepared by coprecipitation from 4% chloroform solutions using petroleum ether as the non-solvent[8]. The precipitate was collected and dried overnight under vacuum at room temperature. Films were prepared from the powder by compression moulding. Blends containing iPEMA or iPMMA/PEMA copolymers were prepared by casting thin films from 4% chloroform solutions. The solvent was allowed to evaporate slowly overnight and the films were then vacuum dried at room temperature.

Polymer and blend T_g's were measured using a Perkin–Elmer DSC-2 equipped with a thermal analysis station (TADS). Samples were heated at a rate of $+20°\text{C min}^{-1}$ and quench cooled at a range setting of 5 mcal s^{-1}. The temperatures observed at the midpoint of the heat capacity transition are reported as the glass transition. The error in T_g is approximately $\pm 2°\text{C}$. Each sample was scanned several times to make certain that sample behaviour, especially for the blends, was reproducible; the T_g's from the second run are reported. Annealing experiments, holding the samples at 450 K for periods ranging from 20 min to 2 h and then quenching, were performed to determine whether phase separation occurred in any of the (compatible) blends in the melt. The T_g's of the unblended isotactic and syndiotactic PMMA homopolymers, iPEMA, and iPMMA/PEMA copolymers are listed in *Table 3*. The unblended copolymers exhibit a slight T_g vs. composition minimum; such minima have been observed with other copolymer systems[9–14].

RESULTS AND DISCUSSION

The glass transition temperatures of PL-1 10i/90s, 25i/75s, 50i/50s and 75i/25s PMMA blends, and PL-2 20i/80s, 40i/60s, 50i/50s, 60i/40s and 80i/20s PMMA blends were measured. The ratios indicate the relative amounts, by weight, of isotactic and syndiotactic polymers. The results are shown in *Figure 1*. Each amorphous blend exhibits a single transition whose temperature varies smoothly with composition between the T_g's of the pure syndiotactic and isotactic PMMA, thus meeting the criterion for a compatible polymer–polymer blend. This is in agreement with the work of Krause and Roman[4] who found, by dilatometry, that isotactic and syndiotactic PMMA, ($\bar{M}_{n,\text{iso}} = 29\,700$ and $\bar{M}_{n,\text{syndio}} = 95\,200$) were compatible. The molecular weights of the polymers in their study were comparable to the molecular weights of the polymers used in the current work.

Table 3 T_g's of unblended isotactic and syndiotactic poly(methyl methacrylate)s, isotactic poly(ethyl methacrylate), and isotactic poly(methyl/ethyl methacrylate) copolymers

Sample	T_g (°C)	Transition width (°C)
PL-1 iPMMA	60	16
PL-2 iPMMA	61	13
PL-3 iPMMA	56	10
PL-1 sPMMA	125	21
PL-2 sPMMA	132	29
PL-4 sPMMA	130	11
iPEMA	39	4
co-A	51	10
co-B	36	14
co-C	30	14
co-D	29	13

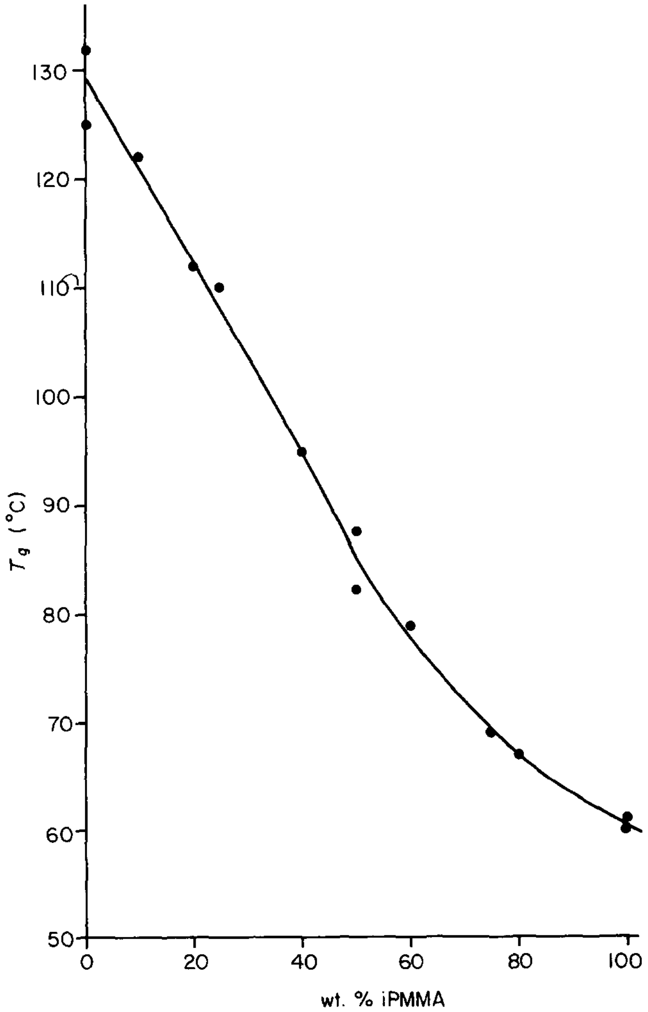

Figure 1 T_g vs. composition for blends of isotactic and syndiotactic poly(methyl methacrylate)s

The glass transitions of the blends are broadened with respect to the transitions of the pure polymers. For example, the transition widths of the PL-1 and PL-2 50i/50s blends are 40°C, suggesting that the blends are only marginally compatible. However, no evidence of phase separation was observed when annealing experiments were performed. The lower critical solution temperature, *LCST*, of these blends, if it exists, is above the degradation temperature of the polymers.

Amorphous blends of iPEMA with PL-3 iPMMA and with PL-4 sPMMA were prepared. The d.s.c. results are shown in *Figures 2* and *3*. In each blend, the observed T_g's correspond with those of the pure homopolymers. Annealing the samples at a temperature above the component T_g's produced no change in the d.s.c. thermograms. These blends are clearly incompatible. Hughes and Britt[15] and Kwei *et al.*[16] found PMMA and PEMA incompatible; their polymers were probably heterotactic. Bosscher *et al.*[17] reported that iPEMA and sPMMA were incompatible. It would seem that the tacticity of the PMMA–PEMA pair does not influence the results; the chemical difference between PMMA and PEMA, though only a CH_2 group, is the overriding factor.

Since the isotactic and syndiotactic PMMA's used in this investigation are compatible with each other, and iPEMA is incompatible with both forms of PMMA, there must be a concentration of ethyl methacrylate (EMA) in an isotactic PMMA/PEMA copolymer above which an i-co(PMMA/PEMA)/sPMMA blend is incompatible. To determine the critical EMA concentration, blends of the four isotactic copolymers, co-A, B, C and D with PL-4 sPMMA were prepared and the blend T_g's measured. The results are presented in *Figures 4–7*. co-A, the copolymer with only 23 mol% EMA, forms a compatible blend with sPMMA as shown in *Figure 4*. The apparent minimum in the T_g vs. composition curve at 80% co-A content is a likely result of a large uncertainty in the measured T_g due to a broadening of the blend transition with respect to the transitions of the component polymers. Annealing the

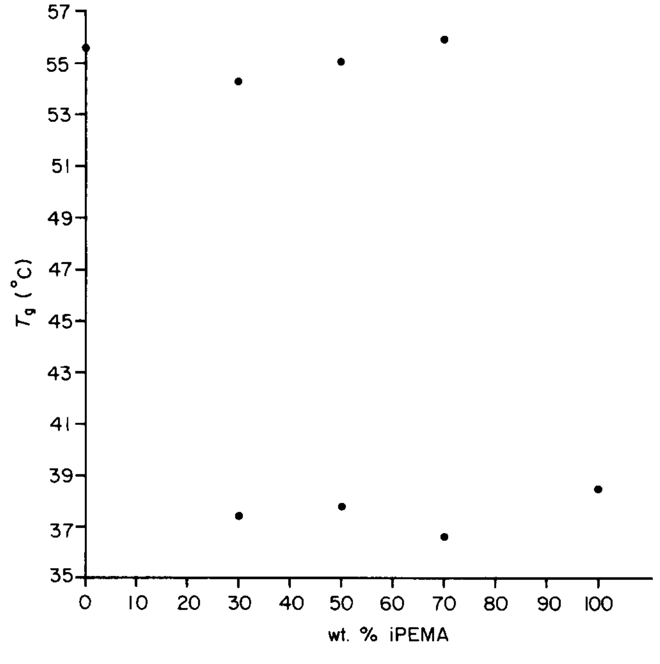

Figure 2 T_g vs. composition for blends of isotactic poly(methyl methacrylate) and isotactic poly(ethyl methacrylate)

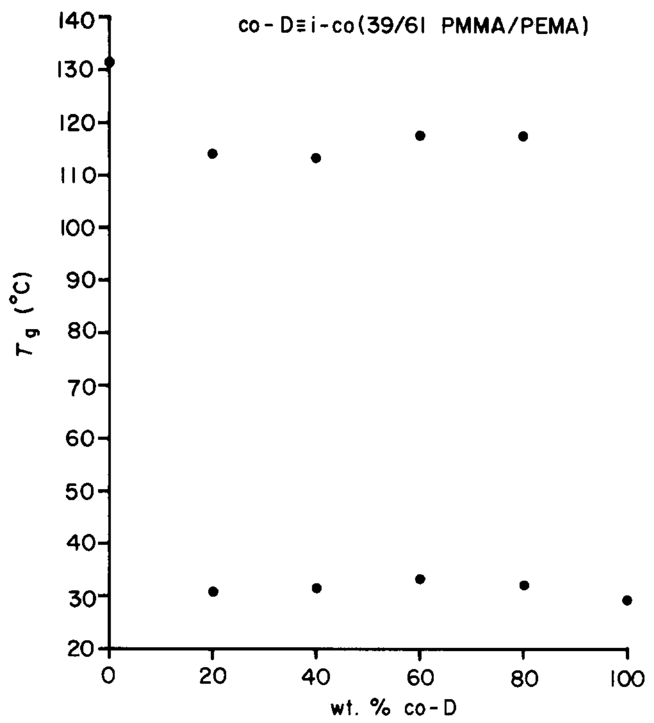

Figure 3 T_g vs. composition for blends of isotactic poly(ethyl methacrylate) and syndiotactic poly(methyl methacrylate)

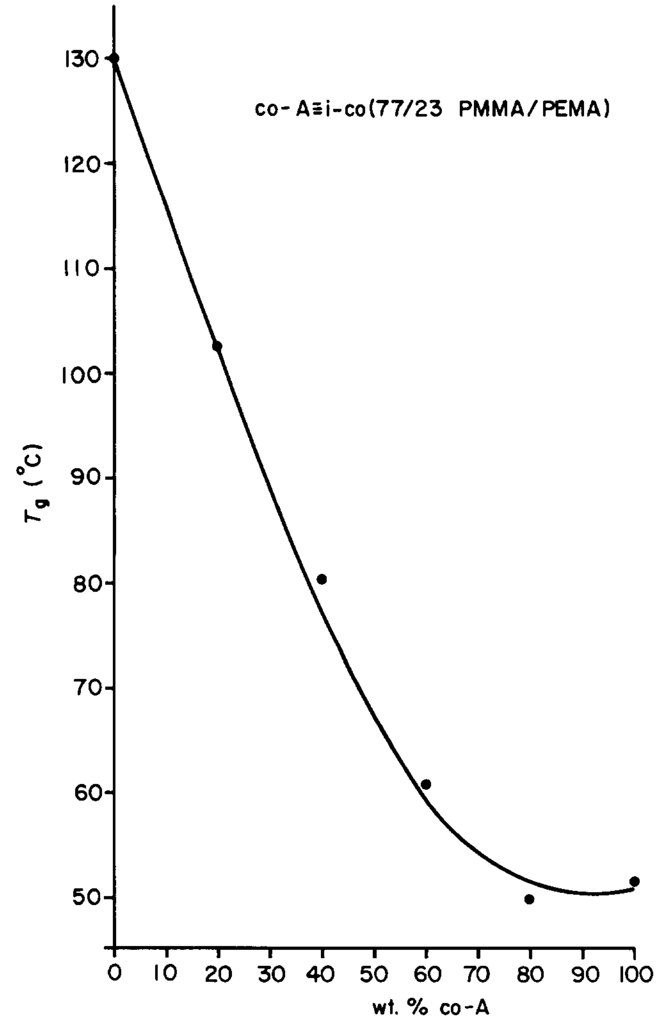

Figure 4 T_g vs. composition for blends of co-A [i-co(77/23 PMMA/PEMA)] and syndiotactic poly(methyl methacrylate)

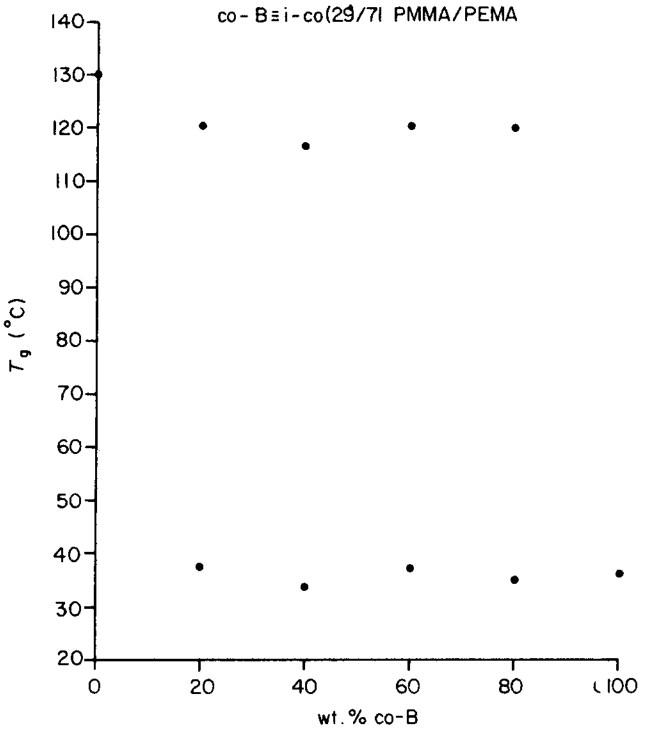

Figure 5 T_g vs. composition for blends of co-B [i-co(29/71 PMMA/PEMA)] and syndiotactic poly(methyl methacrylate)

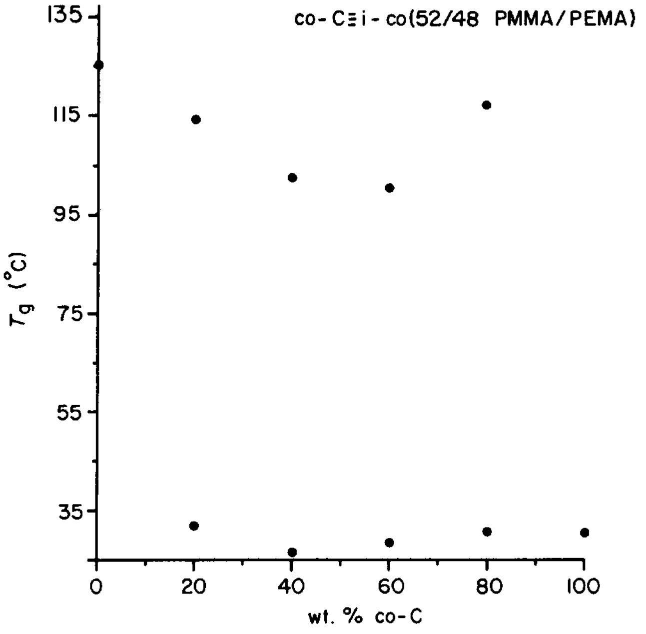

Figure 6 T_g vs. composition for blends of co-C [i-co(52/48 PMMA/PEMA)] and syndiotactic poly(methyl methacrylate)

samples above T_g produced no change in the thermograms. It is unlikely that the compatibility of these particular blends has been caused by the low molecular weight of co-A since, as shown in *Figure 5*, the co-B/s PMMA blends are incompatible Co-B has a lower molecular weight than co-A.

Blends of co-C, 48% EMA, with PL-4 sPMMA all exhibit two transitions as shown in *Figure 6*. However, the sPMMA T_g decreased as the amount of isotactic copolymer was increased from 0–60 wt%. The copolymer T_g remained virtually unchanged. This indicates that a small amount of co-C has mixed with sPMMA to form a sPMMA-rich phase distinct from pure sPMMA and that a pure co-C phase also exists. Annealing the blends above the temperature of the higher T_g narrowed the transitions somewhat, signifying phase separation in the sPMMA-rich domain at high temperature. As shown in *Figure 7*, co-D and sPMMA are incompatible. The above results imply that the critical concentration in an iPMMA/PEMA copolymer for compatibility with sPMMA is slightly under 48% EMA; our estimate is 45%.

Ten Brinke *et al.*[6] as well as two other groups[18] have recently presented mean field treatments to describe phase behaviour in multi-component polymeric systems. This analysis is applicable both to random copolymer–homopolymer blends and to random copolymer–copolymer blends with four distinct repeat units. Using this treatment, an expression for the Flory–Huggins interaction parameter, χ_{blend}, can be obtained in terms of the segmental interaction parameters[6,18]:

$$\chi_{\text{blend}} = x\chi_{AC} + (1-x)\chi_{BC} - x(1-x)\chi_{AB} \qquad (1)$$

where χ_{AC}, χ_{AB} and χ_{BC} are the segmental interaction parameters for a blend of random copolymer $(A_xB_{1-x})_n$ with polymer $(C)_n$. Here x is the volume fraction of monomer A in the copolymer. In the system currently under investigation, A and B represent EMA and MMA units, respectively, in the isotactic PMMA/PEMA copolymers and C represents the monomer units in the sPMMA. Initially, χ_{AB} and χ_{AC} were set equal; this approximation was based on the previous conclusion that 'chemistry' is more important than tacticity in determining PMMA/PEMA miscibility.

Equation (1) then reduces to:

$$\chi_{\text{blend}} = (1-x)\chi_{BC} + x^2\chi_{AB} \qquad (2)$$

where x is the volume fraction of EMA in the copolymer, χ_{BC} is the interaction parameter for isotactic and syndiotactic MMA segments, and χ_{AB} is the interaction

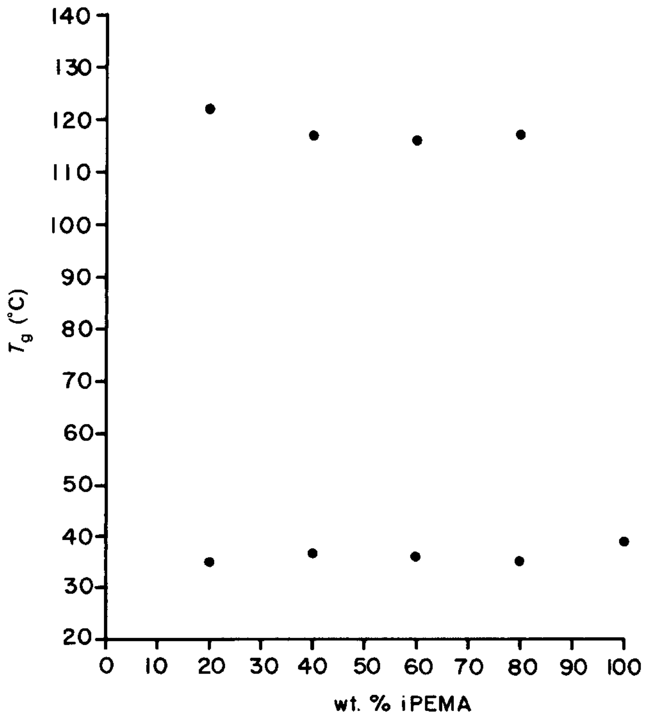

Figure 7 T_g vs. composition for blends of co-D [i-co(39/61 PMMA/PEMA)] and syndiotactic poly(methyl methacrylate)

parameter for MMA and EMA segments of unspecified tacticity. The parameters χ_{blend} and χ_{AB} must be determined in order to calculate the interaction parameter for isotactic and syndiotactic MMA segments from equation (2). In performing these calculations, volume fractions were converted to mole fractions.

At the critical point of phase separation, χ_{blend} is given, at constant temperature and pressure, by[19]:

$$\chi_{\text{blend}}^{\text{crit}} = \tfrac{1}{2}(r_1^{-1/2} + r_2^{-1/2})^2 \tag{3}$$

where r_1 and r_2 are the degrees of polymerization of the copolymer and homopolymer respectively. For PL-4 sPMMA, r_2 is equal to 1530 ($\bar{M}_N = 153\,000$ and $\text{m.w.}_{\text{repeat unit}} = 100$). To obtain r_1, M_N was averaged over the four copolymers and the average repeat-unit molecular weight was used; r_1 equals 304 ($\bar{M}_N = 32\,500$ and $\text{m.r.}_{\text{repeat unit}} = 107$). $\chi_{\text{blend}}^{\text{crit}}$ is then equal to 0.003 and χ_{blend} must be smaller than this value for compatibility to occur.

To determine χ_{AB} we adopted a solubility parameter approach since ancillary data were unavailable.

The interaction parameter for molecules of similar size, χ_{12}, has been expressed as[19,20]:

$$\chi_{12} = (V_r/RT)(\delta_1 - \delta_2)^2 \tag{4}$$

where δ_1 and δ_2 are the Hildebrand solubility parameters for the two substances[21], V_r is the reference volume, R is the gas constant, and T is the absolute temperature. If the reference volume is taken as $100\,\text{cm}^3\,\text{mol}^{-1}$, R as $1.978\,\text{cal}\,\text{deg}^{-1}\,\text{mol}^{-1}$, and T as 298°C, V_r/RT is equal to $0.16\,\text{cm}^3\,\text{cal}^{-1}$ [20] and δ is in units of $(\text{cal}\,\text{cm}^{-3})^{1/2}$. The well known limitations of the solubility parameter approach, when applied to polymeric systems, have been reviewed in the literature[20,24]. The most obvious shortcoming of this expression is that χ_{12} can never be negative, the requirement for compatibility in high polymer systems. However, since PMMA and PEMA are incompatible, $\chi_{\text{MMA,EMA}}$ should be positive and equation (4) was used to estimate the χ_{AB} in equation (2).

Values of 8.9–9.1 have been experimentally obtained for the solubility parameter of PEMA[23]. Cowie[25] found δ for PMMA's of varying tacticity: 9.28 for a sample with 5% syndiotactic diads and 9.55 for a sample with 95% syndiotactic diads. The parameters for the PMMA's were averaged to give $\delta_{\text{PMMA}} = 9.4$; $\delta_{\text{PEMA}} = 9.0$. From equation (4), χ_{AB} is then found to be 0.027.

Equations (2) and (3) can now be used to calculate the interaction parameter for isotactic and syndiotactic PMMA units, χ_{BC}. The EMA content in the PMMA/PEMA copolymer, x, at the critical point must be substituted into the right hand side of equation (2) since $\chi_{\text{blend}}^{\text{crit}}$ from equation (3) is being substituted for the left side of the equation. At room temperature, the critical EMA content in the isotactic copolymers was estimated previously to be 45%. $\chi_{\text{blend}}^{\text{crit}}$ and χ_{AB} have already been calculated and, for $x = 0.45$, χ_{BC} is equal to -0.004. The sign of the interaction parameter is correct since the isotactic and syndiotactic PMMA in this study are compatible. The absolute magnitude of the interaction between the two forms of PMMA is less than that for the chemically distinct species, PMMA and PEMA.

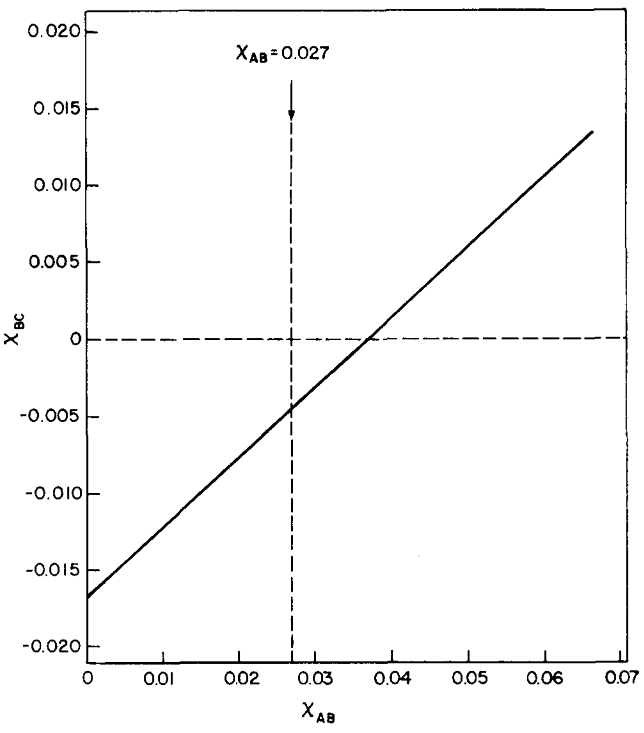

Figure 8 χ_{BC} vs. χ_{AB} for $\chi_{AC} = 0.027$, using equation (1)

Table 4 Calculated χ_{blend} values

Blends	x (EMA content in copolymer)	χ_{blend}
co-A/sPMMA	0.23	−0.002
co-B/sPMMA	0.71	0.012
co-C/sPMMA	0.48	0.004
co-D/sPMMA	0.61	0.008

Figure 8 shows the effect on the calculated value of χ_{BC} of removing the restriction, $\chi_{AB} = \chi_{AC}$. χ_{BC} is shown as a function of χ_{AB}, for $\chi_{AC} = 0.027$. It is immediately apparent that χ_{BC} is negative for $\chi_{AB} < 0.037$. Thus, for most probable χ_{AB} values, χ_{BC} will be negative; this is consistent with the results obtained in the previous paragraphs.

χ_{blend} for the copolymer–polymer i-co(PMMA/PEMA)/sPMMA blends may be calculated from the segmental interaction parameters using equation (2). For example, for co-A/sPMMA, where $x = 0.23$, $\chi_{\text{blend}} = -0.002$. This is less than $\chi_{\text{blend}}^{\text{crit}}$ and shows, as was found experimentally, that this is a compatible blend at all compositions. χ_{blend} for the co-D/sPMMA blend was found to be 0.008, a value greater than $\chi_{\text{blend}}^{\text{crit}}$. As determined experimentally, this blend is not compatible at all compositions. χ_{blend} values, calculated from equation (2), for all the i-co(PMMA/PEMA)/sPMMA blends are listed in *Table 4*.

A phase diagram illustrates the compositions and temperatures for which a blend is compatible. The compositions, at a given temperature, for which the blend will be compatible can be found from the equation of the spinodal if χ_{blend} is known. The spinodal is the boundary between the unstable (incompatible) and metastable compositions; the spinodal is given by[20]:

$$(\chi_{\text{blend}})_{\text{sp}} = \frac{1}{2}\left(\frac{1}{r_1\Phi_1} + \frac{1}{r_2\Phi_2}\right) \tag{5}$$

where r_1 and r_2 are previously defined and Φ_1 and Φ_2 are the volume fractions of the copolymer and homopolymer, respectively. For the co-D/sPMMA blend at room tem-

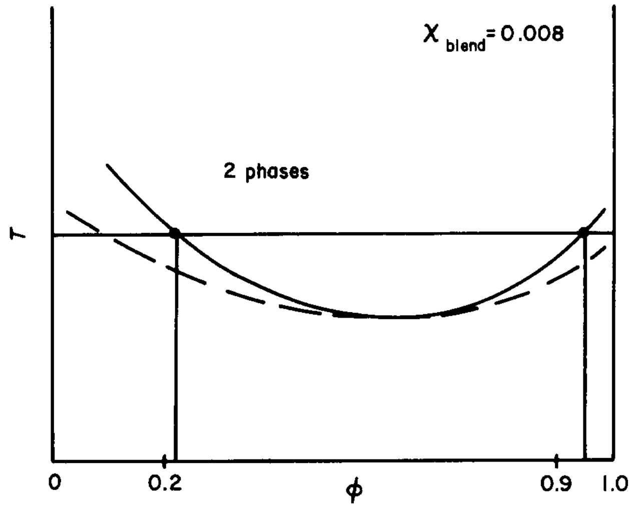

Figure 9 Hypothetical phase diagram for co-D/sPMMA blends. (———): spinodal; (- - -): binodal

perature, where $\chi_{blend} = 0.008$, the spinodal concentrations are 0.95 and 0.22. This system will be compatible only if the copolymer concentration is less than 22% or greater than 95%. Because the binodal, the boundary between the stable (compatible) and metastable compositions, lies outside the spinodal, the range of compatibility is actually smaller than indicated above. This is consistent with the co-D/sPMMA blend being incompatible at the compositions examined. A hypothetical phase diagram, extending from the known values at room temperature (22% and 95%) has been constructed for this blend; see *Figure 9*. It was assumed that χ_{blend} (though not necessarily the individual χ_{ij}'s) are composition independent.

CONCLUSION

Several assumptions were made in the theoretical model from which equation (1) was derived[6]. The segmental interaction parameters were taken to be composition-independent and the effects of free volume and polydispersity were neglected. In going from equation (1) to equation (2), the interaction parameters for isotactic EMA with isotactic and syndiotactic MMA were treated as equal; this averaged out any differences in EMA/MMA interaction due to tacticity. The use of solubility parameters is also inexact. For these reasons, the calculated values of χ_{blend}'s can only be viewed as estimates. However, applying the mean-field analysis to blends of i-co(PMMA/PEMA) with sPMMA does lead to predictions of blend behaviour that all agree with the experimental results, and to the finding of a small, negative segmental interaction parameter for isotactic and syndiotactic PMMA.

ACKNOWLEDGEMENT

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