Interaction parameters for blends containing polycarbonates: 3. Polycarbonate copolymers/styrene-based copolymers

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The phase behaviour of binary blends of copolycarbonates of tetramethyl bisphenol-A and bisphenol-A (TMPC-PC) with copolymers of styrene with acrylonitrile (SAN) or styrene with methyl methacrylate (SMMA) has been examined as a function of composition of each copolymer. The interaction parameters for TMPC-PC blends with each SAN copolymer and each SMMA copolymer were evaluated from the lower critical solution temperature type phase boundary using the lattice fluid theory of Sanchez and Lacombe. From such information for several copolymer compositions, bare interaction parameters for mixing of various monomer unit pairs (ΔP^*_{ij}) were calculated using a binary interaction model. Additionally, from miscibility maps, Flory–Huggins type energy densities (B_{ij}) have been computed for various monomer unit pairs. The interactions of acrylonitrile with other monomer units (styrene, PC and TMPC) are strongly repulsive in each case while the interactions of MMA with these monomer units are weakly repulsive.

(Keywords: blends; copolycarbonates; SAN; SMMA; *LCST*; equation of state; binary interaction model)

INTRODUCTION

Quantitative information about polymer–polymer interactions is an important element in predicting the thermodynamic phase behaviour of polymer blends and some of their physical properties. In the first two papers of this series[1,2], a reverse procedure was described for extracting interaction parameters from the phase diagram for miscible systems which show low critical solution temperature (*LCST*) behaviour. This approach was applied to homopolymer–homopolymer [polystyrene (PS)-tetramethyl bisphenol-A polycarbonate (TMPC)][1] and homopolymer–copolymer [TMPC with styrene/acrylonitrile (SAN) and styrene/methyl methacrylate (SMMA) copolymers][2] blends.

The purpose here is to deduce binary interaction energies for all remaining pair-wise combinations of S/MMA/PC/TMPC and S/AN/PC/TMPC. A number of difficulties have to be duly considered to reach this goal including the following. The approach is based on the Sanchez–Lacombe lattice fluid theory[3–6] and the system must exhibit either *LCST* or upper critical solution temperature (*UCST*) behaviour in order to extract an interaction energy. Blends of bisphenol-A polycarbonate (PC) with TMPC are miscible for all compositions but do not phase separate prior to decomposition[7–9] while PC blends with PS and with SAN are immiscible and do not show *USCT*[10,11]. Recent studies indicate that blends of PC with PMMA are not miscible but are nearly so[12–20]. The physical state of mixing in blends of PC with PMMA and its copolymers depends critically on the method of preparation. For example, some solution casting procedures lead to non-equilibrium, homogeneous mixtures that will proceed to their equilibrium state when heated above the glass transition temperature (T_g), but the rate of the phase separation can be very slow.

Previous papers in this series[1,2] and other studies[21–30] have shown that the system TMPC/PS and TMPC blends with styrene copolymers containing limited amounts of either MMA or AN exhibit single-phase behaviour. Blends of TMPC with styrene copolymers containing modest amounts of either MMA or AN show higher phase separation temperatures (*LCST* type) than the TMPC/PS system[1,2,26,30]. Based on the favourable interactions between TMPC and PC and unfavourable interactions between PC and styrene copolymers, it can be anticipated that TMPC-PC copolycarbonate blends with SAN or SMMA will show more narrow miscibility windows and lower *LCST* than those of blends of pure TMPC with these styrenic copolymers. Quantifying these expectations provides a strategy for evaluating the various pair-wise interaction energies mentioned above. Thus, we have synthesized TMPC-PC copolymers and have examined the phase behaviour of their blends with SAN and SMMA copolymers.

We extend here the previous approach based on a combination of the binary interaction model with the Sanchez-Lacombe theory to copolymer–copolymer systems in order to deduce bare binary interaction energies (ΔP^*_{ij}) for the pairs PC-TMPC, PC-S, PC-MMA and PC-AN. The interaction parameters for the other pairs involved in the TMPC-PC/SAN and TMPC-PC/SMMA systems were obtained in the earlier papers

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of this series[1,2]. In addition, we also extract Flory–Huggins type binary interaction energies (B_{ij}) from the measured miscibility boundaries using the simple binary interaction model[31–34].

EXPERIMENTAL

The materials used in this study are listed in *Tables 1* and *2*. Four TMPC-PC copolycarbonates of varying composition were provided by Mitsubishi Gas Chemical Co. Five other compositions were synthesized in our laboratory using an interfacial polymerization technique[35–38]. The as-received bisphenol monomers were purified by sublimation and then dissolved in the aqueous phase. Bis(trichloromethyl) carbonate, triphosgene[39–41], dissolved in methylene chloride was reacted with these monomers using trimethylamine as a phase transfer catalyst[42,43]. Molecular weights of TMPC, PC and the synthesized copolycarbonates were determined by g.p.c. using polystyrene standards. *Figure 1* shows the T_g *versus* composition for the copolycarbonates. Those containing 60 and 80 wt% TMPC show lower T_g than predicted by the Fox equation, which is most likely due to their low molecular weight as shown in *Table 1*. The SAN and SMMA copolymers are the same as those used previously[2,26,30]. The numerical value included as a part of the code for these copolymers indicates the weight per cent of TMPC, AN or MMA.

Blends of copolycarbonates and styrene copolymers were prepared by solution casting from tetrahydrofuran (THF) in a Petri dish. The cast films were dried at 70°C for 10 min in an air circulating oven until most of the solvent evaporated. The resulting films were further dried for a week in a vacuum oven at a temperature 20°C higher than the T_g.

Glass transition temperatures were measured by a Perkin-Elmer DSC-7 at a scanning rate of 20°C min^{-1}. The onset of the change in the heat capacity was defined

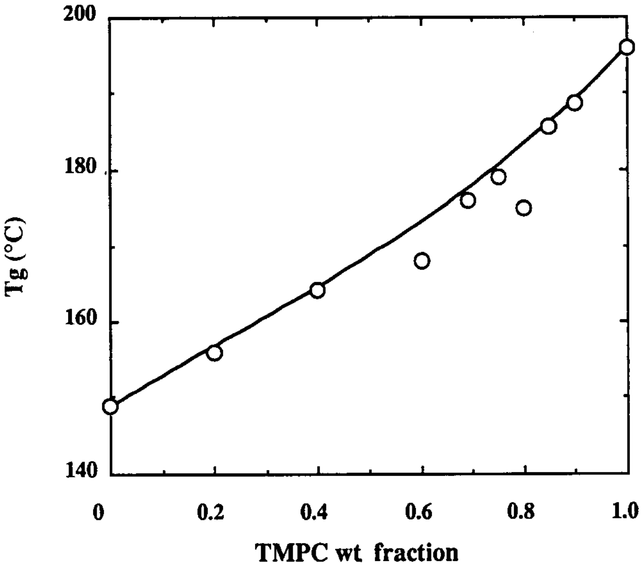

Figure 1 Glass transition temperature behaviour of TMPC-PC copolymers determined by d.s.c. at 20°C min^{-1} using onset method. (Note low values for copolymers containing 60 and 80 wt% TMPC)

Table 1 Polycarbonates used

			Molecular weight information			
Abbreviation	Composition	Density (g cm^{-3})	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	[η]^b (dl g^{-1})	Source
PC	Bisphenol-A polycarbonate	1.1983	37 000	76 500^c	0.46	General Electric Co. (Lexan 131-111)
TMPC	Tetramethyl bisphenol-A polycarbonate	1.0840	27 800	52 000^d	0.39	Bayer AG
TMPC90	Bisphenol-A polycarbonate 10 wt%-*co*-tetramethyl bisphenol-A polycarbonate 90 wt%	1.0955	40 000	72 000	0.41	Synthesized in this laboratory
TMPC85	Bisphenol-A polycarbonate 15 wt%-*co*-tetramethyl bisphenol-A polycarbonate 85 wt%	–	34 000	69 600	–	Synthesized in this laboratory
TMPC80	Bisphenol-A polycarbonate 20 wt%-*co*-tetramethyl bisphenol-A polycarbonate 80 wt%	1.1060	21 000	41 000	0.27	Mitsubishi Gas Chemical Co.
TMPC78	Bisphenol-A polycarbonate 22 wt%-*co*-tetramethyl bisphenol-A polycarbonate 78 wt%	–	30 000	61 000	–	Synthesized in this laboratory
TMPC75	Bisphenol-A polycarbonate 25 wt%-*co*-tetramethyl bisphenol-A polycarbonate 75 wt%	1.1109	–	–	0.39	Synthesized in this laboratory
TMPC70	Bisphenol-A polycarbonate 30 wt%-*co*-tetramethyl bisphenol-A polycarbonate 70 wt%	–	–	–	0.41	Synthesized in this laboratory
TMPC60	Bisphenol-A polycarbonate 40 wt%-*co*-tetramethyl bisphenol-A polycarbonate 60 wt%	1.1249	–	–	0.33	Mitsubishi Gas Chemical Co.
TMPC40	Bisphenol-A polycarbonate 60 wt%-*co*-tetramethyl bisphenol-A polycarbonate 40 wt%	1.1458	–	–	0.42	Mitsubishi Gas Chemical Co.
TMPC20	Bisphenol-A polycarbonate 80 wt%-*co*-tetramethyl bisphenol-A polycarbonate 20 wt%	1.1714	38 000	66 700	0.46	Mitsubishi Gas Chemical Co.

[a] Determined by g.p.c. using polystyrene standards except where noted otherwise
[b] Measured in THF at 23°C
[c] $\bar{M}_w = 38\,000$ determined by light scattering in this laboratory; molecular weight information provided by supplier $\bar{M}_n = 13\,000$, $\bar{M}_w = 34\,200$
[d] $\bar{M}_w = 33\,000$ determined by light scattering in this laboratory

Table 2 Other polymers used

Abbreviation	Polymer	Copolymer[a] composition (wt%)	Molecular weight information[b]		Source
			$\bar{M}_n$	$\bar{M}_w$	
PS	Polystyrene	–	100000	330000	Cosden Oil & Chemical Co. (Cosden 550)
SAN 2	Poly(styrene-*co*-acrylonitrile)	2.7 AN	93500	204000	Asahi Chemical
SAN 3.5	Poly(styrene-*co*-acrylonitrile)	3.5 AN	96400	211000	Asahi Chemical
SAN 5.7	Poly(styrene-*co*-acrylonitrile)	5.7 AN	–	270000	Asahi Chemical
SAN 6.3	Poly(styrene-*co*-acrylonitrile)	–	92100	343000	Asahi Chemical
SAN 9.5	Poly(styrene-*co*-acrylonitrile)	–	–	–	Asahi Chemical
SAN 11.5	Poly(styrene-*co*-acrylonitrile)	–	–	–	Asahi Chemical
SAN 13.5	Poly(styrene-*co*-acrylonitrile)	15.3 AN	56300	149000	Asahi Chemical
SAN 14.7	Poly(styrene-*co*-acrylonitrile)	14.7 AN	83000	182000	Asahi Chemical
SAN 15.5	Poly(styrene-*co*-acrylonitrile)	18.0 AN	–	197000	Asahi Chemical
SAN 19.7	Poly(styrene-*co*-acrylonitrile)	19.7 AN	–	–	Asahi Chemical
SAN 25	Poly(styrene-*co*-acrylonitrile)	25 AN	77000	152000	Dow Chemical (Tyril 1000)
SAN 30	Poly(styrene-*co*-acrylonitrile)	30 AN	81000	160000	Dow Chemical (Tyril 880)
SMMA 5	Poly(styrene-*co*-methyl methacrylate)	4.5 MMA	98000	281000	Synthesized by Min[30]
SMMA 10	Poly(styrene-*co*-methyl methacrylate)	–	59100	106000	Synthesized
SMMA 15	Poly(styrene-*co*-methyl methacrylate)	–	60000	106000	Synthesized
SMMA 20	Poly(styrene-*co*-methyl methacrylate)	20.5 MMA	110000	268000	Richardson Polymer (Noan 81)
SMMA 25	Poly(styrene-*co*-methyl methacrylate)	25.5 MMA	57000	150000	Synthesized by Min[30]
SMMA 30	Poly(styrene-*co*-methyl methacrylate)	–	60000	109000	Synthesized
SMMA 32	Poly(styrene-*co*-methyl methacrylate)	32.5 MMA	78000	167000	Synthesized by Min[30]
SMMA 34	Poly(styrene-*co*-methyl methacrylate)	33.5 MMA	87100	217000	Synthesized by Min[30]
SMMA 39	Poly(styrene-*co*-methyl methacrylate)	38.5 MMA	–	–	Synthesized by Min[30]
SMMA 60	Poly(styrene-*co*-methyl methacrylate)	58.5 MMA	–	–	Richardson Polymer (RPC 100)

[a] Determined by elemental analysis

[b] Molecular weights of SMMA and SAN copolymers were determined by g.p.c. using polystyrene standards

as the T_g. Phase separation temperatures on heating, i.e. *LCST* behaviour, were determined in a manner designed to eliminate rate effects and to minimize artifacts caused by slow phase separation kinetics[18,44]. Blend samples were annealed on a hot stage (Mettler, FP82 HT) equipped with a temperature controller (Mettler, FP80 HT) at various constant temperatures around the phase separation temperature for certain time periods. The phase separation temperatures reported here were determined by such visual observations or by use of a d.s.c. technique described previously[1–2].

PHASE BEHAVIOUR OF BLENDS

Copolycarbonate/PS blends

When the copolycarbonate contains 85 wt% or more TMPC, blends with PS exhibit a single glass transition that changes with blend composition. On the other hand, blends of PS with copolycarbonates containing 80 wt% or less TMPC were cloudy at the casting condition and exhibited two glass transitions that were distinctly separated in some cases and overlapped in others. *Figure 2* shows the observed phase behaviour of TMPC 90/PS blends determined by isothermal annealing in the hot stage for the time periods indicated. Phase separation occurs at considerably lower temperatures than observed for TMPC/PS blends[1,26,29]. These results indicate that the miscibility of these copolycarbonates with PS decreases as the PC content increases as expected. Note

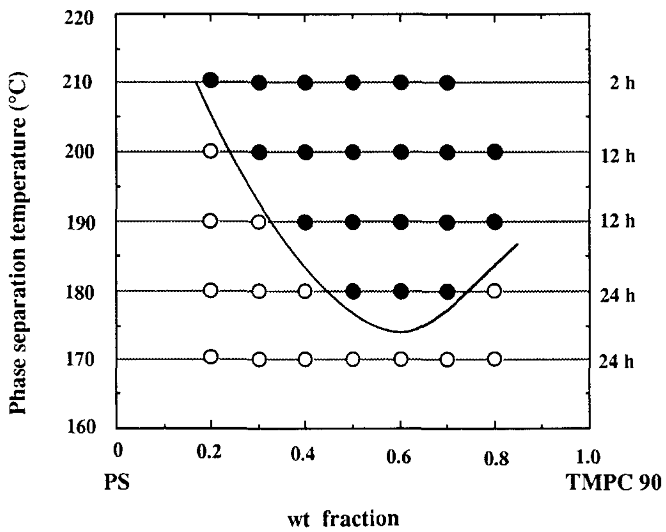

Figure 2 Phase behaviour of TMPC 90/PS blends determined after annealing for the times shown at various temperatures: (○) clear; (●) opaque

that PC is miscible with TMPC but is immiscible with PS. The unfavourable interaction of PC with PS and the favourable interaction of PC with TMPC both act against miscibility of these polycarbonates with PS according to the binary interaction model[31–34].

Copolycarbonate/SAN blends

In a previous paper[2], we showed that TMPC is miscible with SAN copolymers containing 18 wt% or less AN and that addition of AN to the styrenic polymer initially increases the *LCST* before ultimately leading to immiscibility. *Figure 3* shows the experimental copolymer composition regions where these copolycarbonates form miscible blends with SAN copolymers. *Figure 4* shows for four copolycarbonates experimentally determined temperatures at which 50/50 blends phase separate as a function of AN content in the SAN copolymer. TMPC blends with SAN copolymers containing between 3.5 wt% and 11.5 wt% AN did not phase separate on heating[2]. TMPC 90 blends with SAN copolymers containing between 5.7 wt% and 9.5 wt% AN also did not phase separate, while copolycarbonates containing 85 wt% or less TMPC exhibited phase separation over the range where these blends are miscible. These phase boundaries are replotted in *Figure 5 versus* PC content in the copolycarbonate. The blend phase separation temperature decreases as the PC content in copolycarbonate increases when the AN content of the SAN copolymer is held fixed. Phase separation temperatures of SAN 14.7 tend to bend down at low PC content while the others tend to bend up. These trends reflect that addition of AN to the styrene initially increases the phase separation temperatures but ultimately leads to immiscibility[2]. (Note that the optimum AN content for the most favourable interaction with TMPC and TMPC-PC is around 6 wt% AN.) The phase separation temperatures for TMPC 80 blends are higher than expected probably because of the low molecular weight of this copolycarbonate. These results confirm that the presence of PC in the copolycarbonate acts against miscibility with SAN.

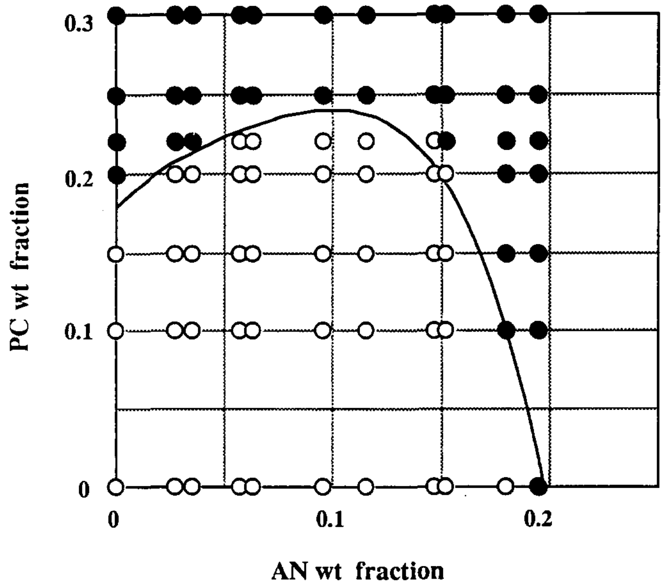

Figure 3 Miscibility map for 50/50 blends of SAN copolymers with TMPC-PC copolymers at 140°C: (○) clear; (●) opaque. The curve was calculated using parameters obtained from the regression method

Copolycarbonte/SMMA blends

Figure 6 combines previous results for TMPC/SMMA copolymer blends with those obtained in this study to form a copolymer–copolymer miscibility map. *Figures 7* and *8* show the effect of copolycarbonate composition on the phase separation temperatures as a function of the MMA content of the SMMA copolymer. Combining the results shown in *Figures 6–8* indicates that the presence of PC in the copolycarbonate also acts against miscibility with styrene-rich SMMA copolymers.

INTERACTION ENERGY CALCULATION

Binary interaction model approach

According to the van Laar-type formulation, the excess enthalpy per unit volume of a multicomponent blend is given by[31–34]:

$$\Delta h_{\mathrm{m}} = \sum_{i>j} \sum_{j} B_{(i,j)} \phi_i \phi_j \qquad (1)$$

where $B_{(i,j)}$ is the net interaction energy density between polymers i and j. By extending this concept of binary interaction to the monomer units that form each polymer, the net interaction parameter between the pair of multicomponent polymers i and j can be expressed as:

$$B_{(i,j)} = \sum_{k>l} \sum B_{kl} (\phi_{ki} - \phi_{kj})(\phi_{lj} - \phi_{li}) \qquad (2)$$

In the above, B_{kl} is the binary interaction energy density between k and l units, while ϕ_{ki} is the volume fraction of k units in polymer i. For a binary blend of copolymer i composed of units 1 and 2 with another copolymer j composed of units 3 and 4, the net interaction energy density polymers i and j is given by:

$$\begin{aligned} B = {} & B_{13}\phi'_1\phi''_3 + B_{14}\phi'_1\phi''_4 + B_{23}\phi'_2\phi''_3 + B_{24}\phi'_2\phi''_4 \\ & - B_{12}\phi'_1\phi'_2 - B_{34}\phi''_3\phi''_4 \qquad (3) \end{aligned}$$

where ϕ'_k and ϕ''_k denote the volume fractions of k units in polymers i and j. We have dropped the subscript (i,j) on B for simplicity since no confusion can arise for a binary blend. The Flory–Huggins theory predicts miscibility when

$$B \leqslant \frac{RT}{2}\left(\frac{1}{\sqrt{\tilde{V}_1}} + \frac{1}{\sqrt{\tilde{V}_2}}\right)^2 \qquad (4)$$

where $\tilde{V}_i$ is the molar volume of component i. Since the combinatorial entropy is negligible in the high molecular weight limit, miscible blends can only be obtained if the net interaction is negative. In this limit, the boundaries for miscibility correspond to $B=0$.

Each point on the copolymer–copolymer phase maps shown in *Figures 3* and *6* either does or does not satisfy the thermodynamic criteria for miscibility at the 50/50 ratio of the two copolymers. These maps may be interpreted as an isothermal plane defined by the drying condition of 140°C which is ~10–20°C higher than the T_g expected for miscible blends of the polymers used here. For copolymer–copolymer systems, equations (3) and (4) dictate that the miscibility boundary will be either an ellipse, a parabola or a hyperbola. A computer program was used to determine the best curve that separates miscible and immiscible points by minimizing an objective function defined as the sum of the squares of the orthogonal distance from the experimental data points to the curve. The best phase boundaries computed by

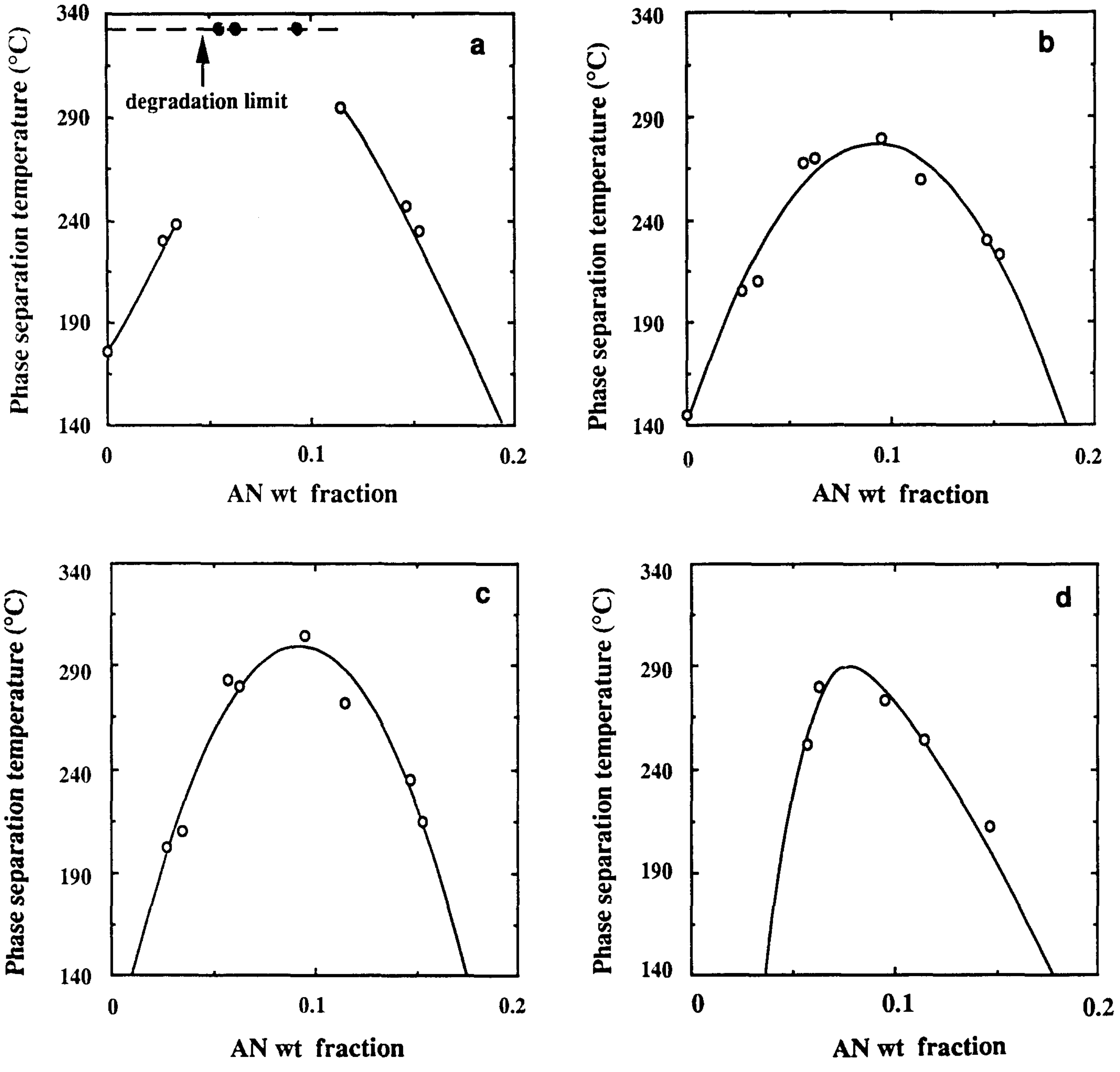

Figure 4 Phase separation temperatures for 50/50 blends of various copolycarbonates with SAN copolymers as a function of AN content. Note that blends of TMPC 90 with SAN copolymers containing between 5.7 wt% and 9.5 wt% AN do not phase separate prior to degradation (~330°C). The solid line is the calculated spinodal from the Sanchez–Lacombe theory using bare interaction energies computed from inserting appropriate parameters from *Table 4* into equation (5): (a) TMPC 90; (b) TMPC 85; (c) TMPC 80; (d) TMPC 78

this method are shown as the solid line in *Figure 3* for TMPC-PC/SAN and in *Figure 6* for TMPC-PC/SMMA. There are six unknown B_{ij} values for a copolymer–copolymer system. A set of B_{ij} values scaled by an arbitrary non-zero real number can be obtained by minimizing the objective function. To obtain the absolute B_{ij} set, at least one B_{ij} has to be determined from other independent information. The interaction energy for the S-MMA pair, 0.18 cal cm^{-3}, determined by Fukuda *et al.*[45–47] from osmotic pressure measurements on concentrated ternary solutions was used to obtain the absolute B_{ij} set for the TMPC-PC/SMMA system. Similarly, to obtain the absolute B_{ij} set for the TMPC-PC/SAN system, we assumed that the S-AN interaction energy is well-represented by the value 6.8 cal cm^{-3} determined by Nishimoto *et al.*[48] from an experimentally determined copolymer–copolymer miscibility boundary. This evaluation of the S-AN interaction energy is also based on the validity of the S-MMA interaction energy reported by Fukuda *et al.*[45–47].

The B_{ij} values obtained here for various binary pairs are listed in *Table 3* and are compared with those from other sources. A key issue here is the relatively small but repulsive interaction of MMA with other monomer units while the interactions of AN with these same monomer units are large and repulsive. For SAN copolymers, the edges of the miscibility window with other polymers are quite steep because of the strong repulsion between S and AN on mixing. Conversely, the edges of the miscibility windows for SMMA copolymers with other polymers are not so steep owing to the weakly repulsive interaction between the S and MMA units. These general comments about SAN and SMMA copolymers apply specifically to their blends with copolycarbonates. It is

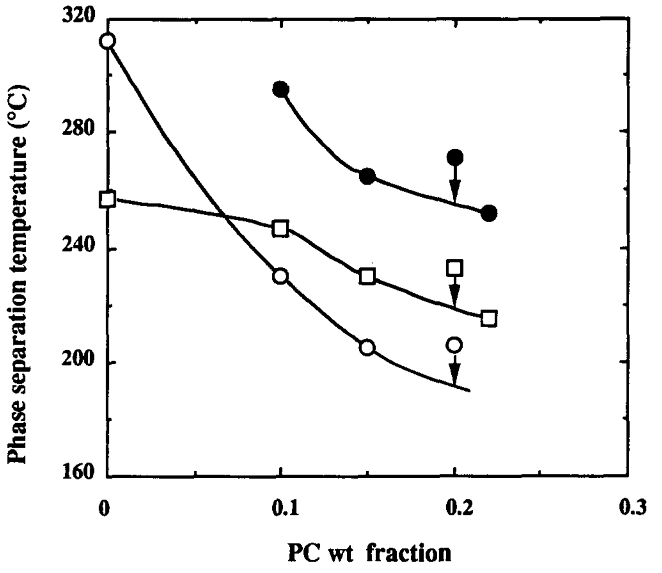

Figure 5 Effect of PC content of the copolycarbonate on the phase separation temperature for 50/50 blends with SAN copolymers: (●) SAN 11.5; (□) SAN 14.7; (○) SAN 2

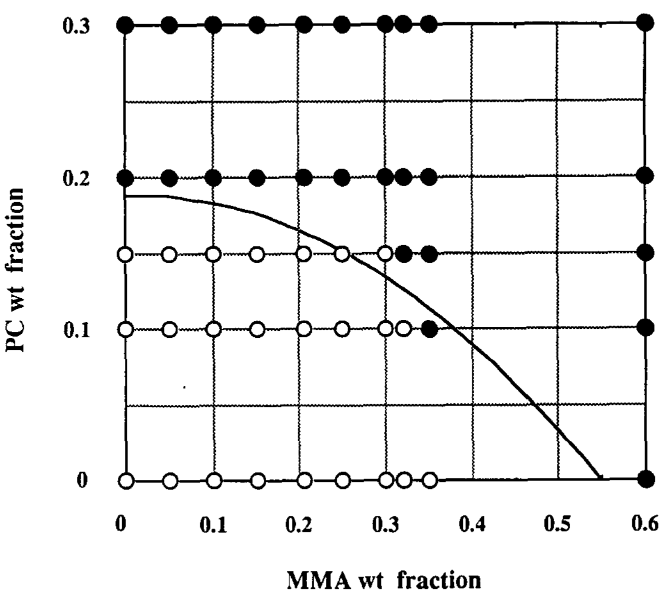

Figure 6 Miscibility map for 50/50 blends of SMMA copolymers with TMPC-PC copolymers at 140°C: (○) clear; (●) opaque. The curve was calculated using parameters obtained from the regression method

interesting to note that blends of PC with SAN copolymers having various AN contents are immiscible but the PC-SAN pair exhibits maximum adhesion when the SAN copolymer contains around 25–27 wt% AN[10]. *Figure 9* shows interaction energy densities for the PC–SAN pair as a function of AN content calculated from the appropriate form of equation (3) using the interaction energies given here. These results confirm that high molecular weight blends of PC and SAN copolymers are immiscible but that the most favourable interaction occurs around 28 wt% AN where $B_{\text{PC-SAN}} = 0.04\ \text{cal cm}^{-3}$ at 140°C.

Equation-of-state approach

The interaction energy densities deduced above stem from a framework like the Flory–Huggins theory which ignores the compressibility of these materials and their mixtures. It is now well-recognized that equation-of-state or compressibility effects may be very important in blends. We use the lattice fluid theory of Sanchez–Lacombe to describe such effects. Detailed descriptions of this theory and its applications to blends have been noted in the previous papers of this series[1,2] and elsewhere[3–6]. To apply this equation-of-state theory to the copolymer–copolymer system of interest, we adapt the following expression for the bare interaction energy parameter between copolymers (ΔP^*) in analogy with equation (3)[2,49]:

$$\Delta P^* = \Delta P^*_{13}\phi'_1\phi''_3 + \Delta P^*_{14}\phi'_1\phi''_4 + \Delta P^*_{23}\phi'_2\phi''_3 + \Delta P^*_{24}\phi'_2\phi''_4 - \Delta P^*_{12}\phi'_1\phi'_2 - \Delta P^*_{34}\phi''_3\phi''_4 \quad (5)$$

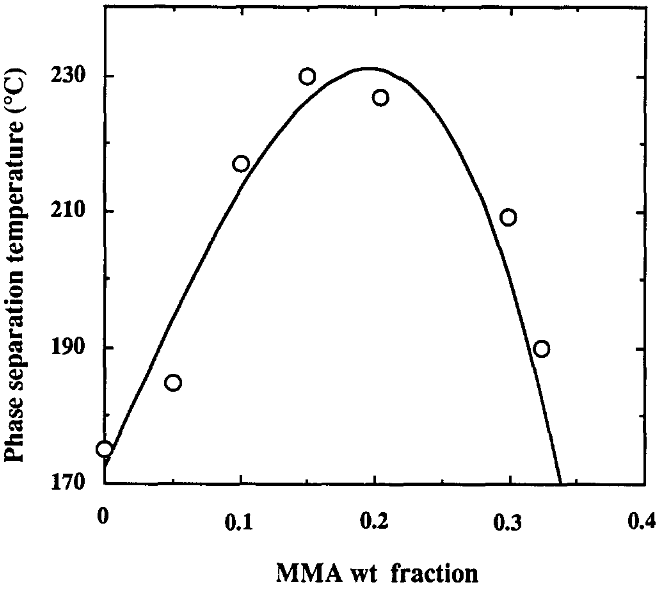

Figure 7 Phase separation temperatures for 50/50 blends of TMPC 90 with SMMA copolymers of varying MMA content. The solid line is the calculated spinodal from the Sanchez–Lacombe theory using bare interaction energies computed from inserting appropriate parameters from *Table 4* into equation (5)

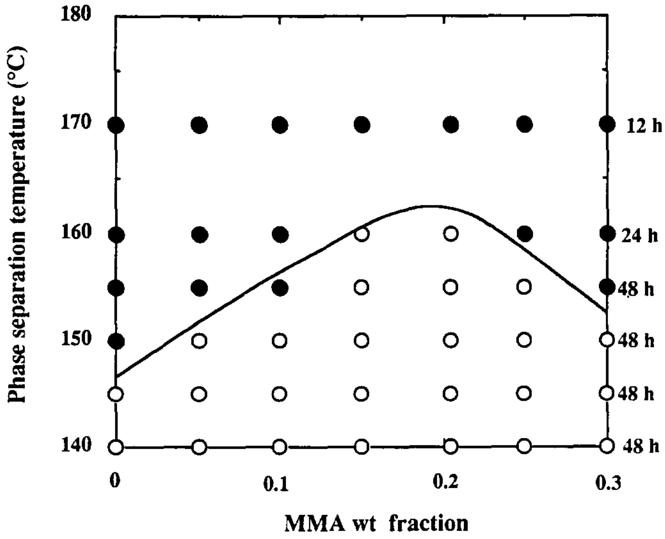

Figure 8 Phase separation temperatures for 50/50 blends of TMPC 85 with various SMMA copolymers determined after annealing for the time period indicated: (○) clear; (●) opaque. The solid line is the calculated spinodal from the Sanchez–Lacombe theory using bare interaction energies computed from inserting appropriate parameters from *Table 4* into equation (5)

Table 3 Flory–Huggins interaction energy densities (cal cm^{-3}) for various monomer pairs

Interacting pair	This paper: B_{ij} (from TMPC-PC/SAN)	This paper: B_{ij} (from TMPC-PC/SMMA)	Other sources: B_{ij}	Other sources: Method
S-MMA	-	0.18[a]	0.13	SANS analysis of PS-PMMA block copolymer at 30°C[51]
S-AN	6.8[b]	-	5.45[a]	SAN/PMMA miscibility boundaries[52]
			8.00	SAN/SAN miscibility boundaries[53]
			6.90	Calorimetry of low molecular weight analogues at 25°C[54]
			8.14[a]	SAN/PMMA miscibility boundaries[55]
			3.17	Calorimetry of low molecular weight analogues at 25°C[49]
TMPC-MMA	-	0.26	-	
TMPC-AN	6.10	-	-	
TMPC-PS	−0.15	−0.21	−	
TMPC-PC	−0.32	−0.33	−0.22 ~ −0.08[c]	SANS analysis at 25°C[8]
PC-AN	3.80	-	-	
PC-S	0.49	0.61	-	
PC-MMA		0.05	-	

[a] Interaction energy of S-MMA is from the work of Fukuda *et al.*[45–47]
[b] Interaction energy of S-AN is from the work of Nishimoto *et al.*[48]
[c] Variation of interaction energy reflects composition dependence

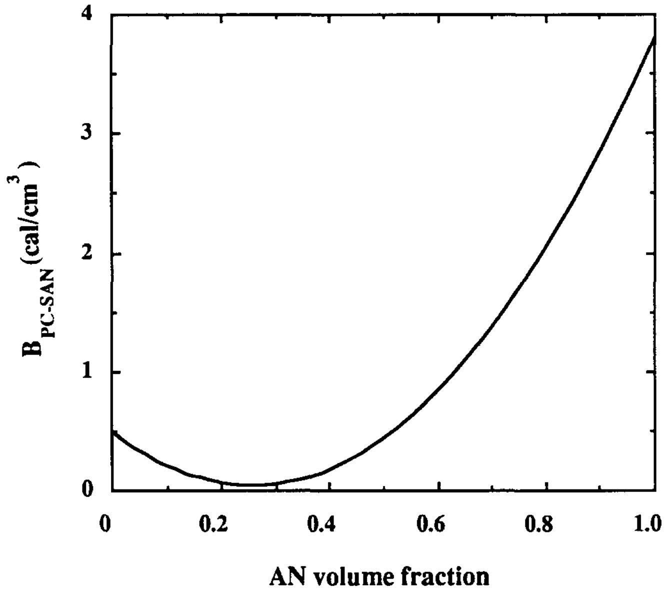

Figure 9 Interaction energy densities for PC/SAN blends calculated from the binary interaction energies given in *Table 3*

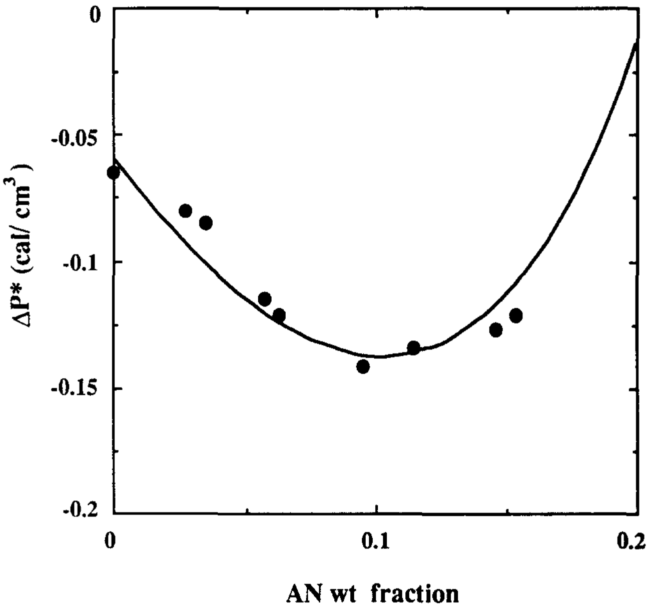

Figure 10 Effect of copolymer composition on the bare interaction parameter for TMPC 85/SAN blends. The solid line was calculated by inserting appropriate parameters from *Table 4* into equation (5)

Hard core volume fractions are used here to describe the copolymer composition.

To extract ΔP^* for any copolymer–copolymer pair from phase behaviour, we assume that the measured phase boundary corresponds to the spinodal curve, and that ΔP^* does not depend on temperature[1,2]. Interaction parameters for TMPC-PC/SAN and TMPC-PC/SMMA blends were computed from their experimental phase separation temperatures using the theoretical spinodal condition. Characteristic properties of the polymer units involved required by the equation-of-state theory have been determined previously from *PVT* data[1,2,50]. *Figure 10* shows a representative ΔP^* curve calculated for TMPC 85/SAN blends from the corresponding phase boundary information shown in *Figure 4*. For each copolycarbonate there exists an optimum content of AN in the SAN where the interaction is most favourable. As discussed before[2], the more favourable interaction of TMPC-PC blends with certain SAN copolymers relative to PS is caused by the strong intramolecular repulsion between S and AN. Of course, PC units in copolycarbonates are unfavourable for miscibility. This is illustrated by replotting the ΔP^* values *versus* PC content for fixed AN levels, as shown in *Figure 11*.

Figure 12 shows a representative ΔP^* curve for TMPC 90/SMMA blends calculated from the phase boundary information in *Figure 7*. As discussed previously[2], TMPC-PC copolymer/SMMA blends exhibit entirely similar phase behaviour as TMPC/SMMA blends. At

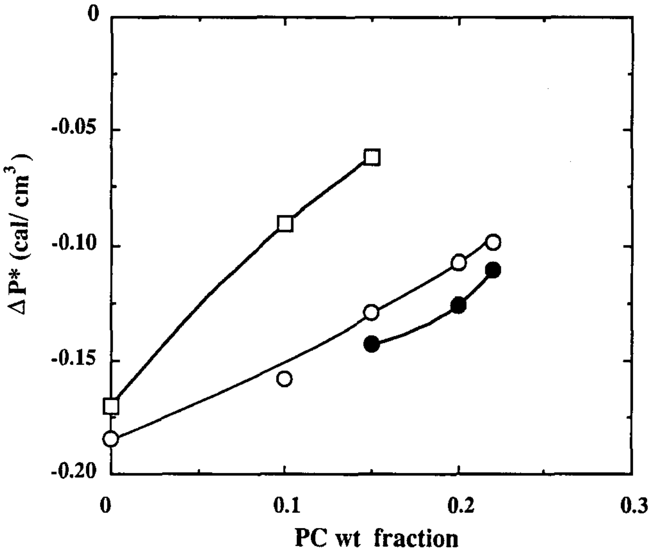

Figure 11 Effect of PC content on the bare interaction parameters for blends of TMPC-PC copolymers with PS and SAN copolymers: (□) PS; (○) SAN 14.7; (●) SAN 9.5

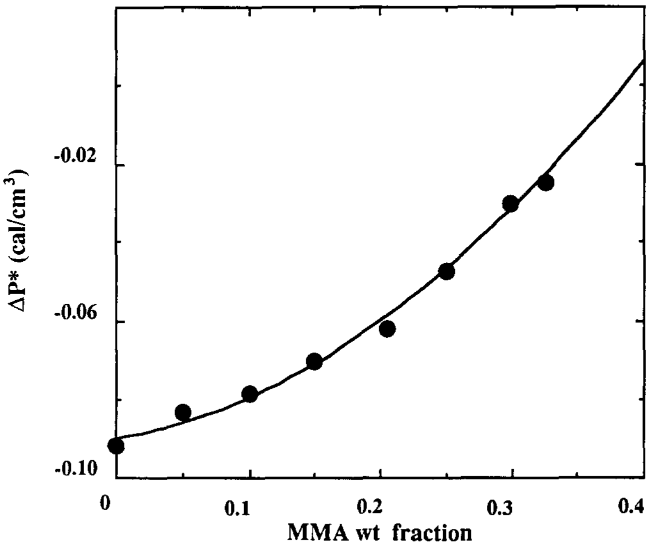

Figure 12 Effect of copolymer composition on the bare interaction parameter for TMPC 90/SMMA blends. The solid line was calculated by inserting appropriate parameters from *Table 4* into equation (5)

fixed PC content in the copolycarbonate, the computed ΔP^* for each SMMA is negative and monotonically increases with MMA content; whereas, the blend phase separation temperature reaches a maximum when the MMA content of SMMA is near 20 wt% (see *Figure 7*). Such behaviour has been discussed in terms of the compressible nature of these materials or equation-of-state effects.

Using $\Delta P^*_{\text{TMPC-PS}} = -0.17\,\text{cal cm}^{-3}$, $\Delta P^*_{\text{S-AN}} = 7.37\,\text{cal cm}^{-3}$, and $\Delta P^*_{\text{TMPC-AN}} = 6.01\,\text{cal cm}^{-3}$ determined in the previous papers[1,2], the bare interaction energies for the remaining monomer unit pairs in the TMPC-PC/SAN system were obtained by fitting the calculated ΔP^* values to equation (5) using linear regression. Three unknown ΔP^*_{ij} values in equation (5) were calculated by minimizing the squares of the errors in the ΔP^* values computed from experimental phase separation temperatures using the theoretical spinodal condition.

Using $\Delta P^*_{\text{TMPC-PS}} = -0.17\,\text{cal cm}^{-3}$, $\Delta P^*_{\text{S-MMA}} = 0.15\,\text{cal cm}^{-3}$ and $\Delta P^*_{\text{TMPC-MMA}} = 0.25\,\text{cal cm}^{-3}$, the bare interaction energies for the remaining monomer unit pairs for the TMPC-PC/SMMA system were obtained in a similar fashion. The results are listed in *Table 4*. The bare interaction energies of the PC–SAN pair as a function of AN content using the bare interaction energies of each pair obtained here are quite similar in form and magnitude as the results shown in *Figure 9*. This confirms that high molecular weight blends of PC and SAN copolymers are immiscible but that the most favourable interaction occurs around 25 wt% AN where $\Delta P^*_{\text{PC-SAN}} = 0.04\,\text{cal cm}^{-3}$.

According to the theory, the cohesive energy density (*CED*) is:

$$CED = \tilde{\rho}^2 P^* \tag{6}$$

For simplicity, we take $\tilde{\rho} \sim 1$ to obtain[50]:

$$\delta \equiv \sqrt{CED} \approx \sqrt{P^*} \tag{7}$$

If the *absolute* interaction energy between unlike *i* and *j* units is simply the geometric mean of the absolute interaction energy for the two like pairs *i–i* and *j–j*, then there results

$$B_{ij} = (\delta_i - \delta_j)^2 \tag{8}$$

Table 4 Sanchez–Lacombe bare interaction parameters (cal cm⁻³) for various monomer pairs

	This paper		Other sources	
Interacting pair	B_{ij} (from TMPC-PC/SAN)	B_{ij} (from TMPC-PC/SMMA)	B_{ij}	Method
S-MMA	–	0.15[c]	0.13	PS/P(MMA-CHMA) miscibility boundaries[56]
S-AN	7.37[a]	–	5.91	Calorimetry of low molecular weight analogues at 25°C[49]
TMPC-MMA	–	0.25[c]		
TMPC-AN	5.92[a]	–		
TMPC-PS	−0.17[b]	–		
TMPC-PC	−0.25	−0.23		
PC-AN	4.40	–		
PC-S	0.43	0.41		
PC-MMA	–	0.05	0.03	Phase separation temperature of blends of PMMA with low molecular weight PC[50]

[a] Determined from the phase behaviour of TMPC/SAN blends
[b] Determined from the phase behaviour of TMPC/PS blends
[c] Determined from the phase behaviour of TMPC/SMMA blends
Note that these results do not rely on the interaction energy for S-MMA determined by Fukuda *et al.*[45–47]

Table 5 Comparison of estimates of solubility parameters and interaction energies

Solubility parameters [$\delta(\mathrm{cal}^{1/2}\,\mathrm{cm}^{-3/2})$					Interaction energies ($\mathrm{cal\,cm}^{-3}$)				
								$(\delta_i-\delta_j)^2$	
Polymer	Abbreviations	Small[57]	Coleman *et al.*[58]	$\sqrt{P^*}$	Interaction pair	ΔP^*_{ij}	$(\sqrt{P^*_i}-\sqrt{P^*_j})^2$	by Small[57]	by Coleman *et al.*[58]
Poly(methyl methacrylate)	PMMA	9.10	9.1	11.03	S-MMA	0.15	2.56	0	0.16
Polystyrene	PS	9.10	9.5	9.43	S-AN	7.37	2.93	15.20	18.50
Bisphenol-A polycarbonate	PC	10.60	10.6	10.9	TMPC-MMA	0.25	0.61	1.85	0.16
Tetramethylbisphenol-A polycarbonate	TMPC	10.46	9.5	10.25	TMPC-AN	5.92	0.79	6.45	18.50
					TMPC-S	−0.17	0.67	1.85	0
Bisphenol chloral polycarbonate	BCPC	11.24	12.2	11.24	TMPC-PC	−0.25	0.41	0.02	1.20
					PC-AN	4.40	0.06	5.70	10.20
Hexafluorobisphenol-A polycarbonate	HFPC	10.00	–	10.22	PC-S	0.43	2.31	2.30	1.20
					PC-MMA	0.05	0.02	2.30	2.30
Polyacrylonitrile	PAN	13.00	13.8	11.14	BCPC-MMA	−0.08	0.04	4.60	9.70
					BCPC-PC	<0	0.12	0.41	2.60
					BCPC-HFPC	>0	1.04	1.04	–
					HFPC-PC	0.67	0.49	0.81	–
					HFPC-MMA	−0.80	0.85	0.65	–

All information for HFPC and BCPC comes from ref. 50

or

$$\Delta P^*_{ij}=(\sqrt{P^*_i}-\sqrt{P^*_j})^2 \tag{9}$$

Table 5 compares the ΔP^*_{ij} values determined from the experimental phase behaviour with estimates based on the geometric mean assumption, i.e. $(\sqrt{P^*_i}-\sqrt{P^*_j})^2$ and $(\delta_i-\delta_j)^2$, for the various pairs of repeat units. The δ values used here were calculated by group contribution methods developed by Small[57] and by Coleman *et al.*[58]. In spite of the difficulties in obtaining accurate enough estimates of δ and P^*, equations (8) and (9) provide useful predictions of interaction energies for certain pairs. In most cases shown in *Table 5*, however, the interaction parameters estimated in this way are rather different from the ΔP^*_{ij} values extracted from experimental blend phase behaviour.

CONCLUSIONS

Binary interaction energy densities for the Flory–Huggins and the Sanchez–Lacombe lattice fluid theory were deduced from phase boundaries of TMPC-PC/SAN and TMPC-PC/SMMA systems. The interaction energies for the pairs TMPC-PS and TMPC-PC, which form miscible blends, are negative while those for all other monomer unit pairs involved in these systems are positive.

Acrylonitrile units have large repulsive interactions with all other monomer units while MMA units have relatively small positive interactions with all other monomer units. Because of the above, TMPC-PC copolymers exhibit somewhat different miscibility maps with SAN copolymers compared to SMMA copolymers. One consequence is that the edges of the miscibility window are quite steep for SAN copolymers while they are not so steep for SMMA copolymers.

Flory–Huggins type B or B_{ij} values known at one temperature can be used for mapping composition boundaries between miscibility and immiscibility in copolymer systems; however, their detailed temperature dependence is needed to calculate a complete phase diagram. On the contrary, bare interaction energies obtained from the Sanchez–Lacombe lattice fluid theory which accounts for effects of compressibility can be more useful for the design of polymer blends since the phase diagram can, in principle, be predicted.

By adding PC to TMPC, the phase separation temperatures for blends with PS and its copolymers were decreased. The addition of either AN or MMA as comonomers with styrene affects the values of ΔP^* and the phase separation temperatures for blends with TMPC-PC copolymers in exactly similar ways as found previously for the TMPC homopolymer[2].

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