# Polycarbonate–SAN copolymer interaction

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Blends of polycarbonate (PC) with ABS (acrylonitrile–butadiene–styrene) materials have commercially useful properties without requiring a compatibilizer, which is necessary for most other commercial multiphase blends. It has been proposed that this is due to a favourable thermodynamic interaction between PC and the styrene–acrylonitrile (SAN) copolymer matrix of ABS. A variety of evidence suggests this interaction is optimum at about 25 wt% acrylonitrile, which is roughly the composition of the azeotrope and of most commercial materials. A critical molecular weight analysis of the phase behaviour of PC–SAN blends is presented here, which leads to a quantitative estimate of the interaction energy that is consistent with available facts. When the molecular weights of the PC and SAN components are reduced to about 3000 each, their blends become miscible and the observed phase behaviour allows calculation of interaction energies in terms of a binary interaction model using both the Flory–Huggins and the Sanchez–Lacombe equation of state theories. End-group effects were accounted for as necessary. The estimated interaction energy is a refinement of a previous estimate based on the phase behaviour of copolycarbonates and SAN copolymer blends. The current estimate allows prediction of interfacial tensions that are consistent with morphology observations for PC–SAN blends presented here and elsewhere. It also predicts that the extent of partial miscibility is very limited and should produce very small shifts in the glass transitions of the components when blended as observed here and by others for purified SAN materials. Prior claims to the contrary result from partitioning between the phases of oligomers in commercial SAN copolymers.

**(Keywords: blends; polycarbonate; SAN copolymers)**

## INTRODUCTION

Blends of polycarbonate (PC) and ABS (acrylonitrile–butadiene–styrene) materials have been commercially available for many years[1–13]. Unlike most multiphase polymer alloys that have emerged more recently[14–19], these commercial PC–ABS products do not, as far as we know, employ any compatibilizer component, such as a suitable block or graft copolymer for interfacial modification. That useful properties can be generated without a compatibilizer has raised considerable interest in the nature of the thermodynamic interaction[10,20–33] between PC and the styrene–acrylonitrile (SAN) copolymer matrix of ABS. It is well recognized that this interaction is not favourable enough to produce complete miscibility, although evidence for varying extents of miscibility has been presented[10,20–33]. On the other hand, the PC–SAN interaction is apparently sufficiently favourable to form an interface strong enough that the blends can develop useful mechanical properties. Based on measurements of adhesion of PC to various SAN copolymers[10], it has been suggested that the thermodynamic interaction is at an optimum level when the acrylonitrile (AN) content of the copolymer is ~25 wt%. This is near the copolymerization azeotrope where most commercial copolymers are produced. Since this proposal was made in 1984 considerable other facts about this system have emerged[20–33]. The purpose here is to review all of the existing information and to present several new observations relating to this issue. It becomes apparent that in practical terms there is indeed an optimum AN content in the range suggested, based on a number of related facts, which can be explained in terms of thermodynamic analyses. The new results include: (a) a novel approach to obtain the PC–SAN thermodynamic interaction energy in terms of a binary interaction model[34–36]; (b) a further examination of the recent suggestion that prior reports of PC–SAN partial miscibility stem from partitioning of SAN oligomers[22]; and (c) observations of the size of SAN particles dispersed in a PC matrix by melt mixing and an interpretation of the effect of AN content in terms of interfacial tension. The approach to obtain the thermodynamic interaction energies involves finding the critical molecular weights at which PC–SAN mixtures become one phase[37–39] and analyses based on the Flory–Huggins and the Sanchez–Lacombe equation of state theories[40–43]. These results agree broadly with estimates made by an entirely independent approach based on analysis of the phase behaviour of blends of SAN and PC copolymers[20], but the two differ in some details. The thermodynamic results allow assessment of interfacial properties using existing theories[44–47].

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## REVIEW OF MECHANICAL BEHAVIOUR OF PC–SAN INTERFACES AND BLENDS

The purpose here is to review several types of mechanical behaviour from a variety of sources that relate to the proposition that the PC–SAN 'interaction' is optimum at a particular AN content. Many of these results are difficult to interpret in an unambiguous way since other factors influence the properties measured. However, the information presented in generally consistent with an optimum AN content in the vicinity of 25 wt%.

Perhaps the most straightforward mechanical indication of the PC–SAN affinity for each other is the interfacial adhesion results of Keitz *et al.*[10] that are reproduced in *Figure 1*. In these experiments, PC/SAN/PC laminates were formed by melt compression of preformed sheets and then appropriately cut and notched to form a lap shear joint that was stressed to failure. The average lap shear stress for interfacial failure strongly depends on the AN content of the SAN copolymer reaching a sharp maximum near 25 wt% (see *Figure 1*).

More indirect indications may be seen in the mechanical properties of injection-moulded blends of PC and SAN. *Figure 2* shows tensile properties reported by Keitz *et al.*[10]. Blends rich in PC showed ductile yielding while those containing less PC did not yield. While only four AN levels were examined, the results in *Figure 2* show that the blend based on SAN containing 24.8 wt% AN has the highest strength for all PC contents. This same SAN copolymer retains ductility (see elongation-at-break curves in *Figure 2*) to the lowest PC content. One simple interpretation of these results is that the interface between PC and SAN domains is strongest for SAN24.8. Obviously, the mechanical properties of the neat SAN copolymers change with AN level but do not show an extreme value in this range[48,49]. In fact, the inherent ductility of SAN copolymers appears to increase continuously from that of polystyrene up to at least 68 wt% AN[48,49]. Quintens *et al.*[27] have shown results for 60/40 PC/SAN blends as a function of AN level, and their trends are quite similar to those shown in *Figure 2*. They used a wider range of AN levels, which show even more convincingly that there is a sharp maximum in ductility at about 25 wt% AN. Quintens *et al.*[27] provide further insight about the role of morphology on the mechanical properties of these mixtures. Their as-moulded blends had a fine texture with significant co-continuous character. Melt annealing at 200°C (without flow) leads to a coarsening of the morphology as judged by the Chalkey-type stereological analysis[27] and apparently some decrease in the co-continuous character[24]. With phase coarsening, these blends exhibited strong decreases in elongation at break and smaller reductions in strength.

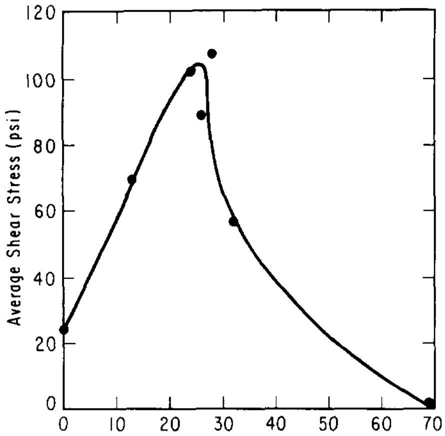


**Figure 1** Average shear stress for interfacial failure of PC/SAN/PC laminates (formed by compression moulding) in a lap shear configuration. Reproduced by permission of John Wiley and Sons, Inc.

In a more recent investigation, Cheng *et al.*[11] explored the mechanical properties of ternary blends containing 60/30/10 PC/SAN/MBS. The latter component is a core–shell impact modifier with a poly(methyl methacrylate) shell and a crosslinked butadiene-based rubber core. Room temperature Izod impact data for the ternary blends (and the binary blends without the MBS) are reproduced in *Figure 3* as a function of the wt% AN in the SAN component. While these are complicated systems whose properties can be influenced by many factors, like the distribution of the MBS modifier, there is clearly a maximum in toughness at about 25 wt% AN that, at least in naive terms, can be attributed to the optimum nature of the PC–SAN interface.

The remainder of this paper is devoted to exploring the evidence for a thermodynamic basis of an optimum PC–SAN 'interaction' near 25 wt% AN.

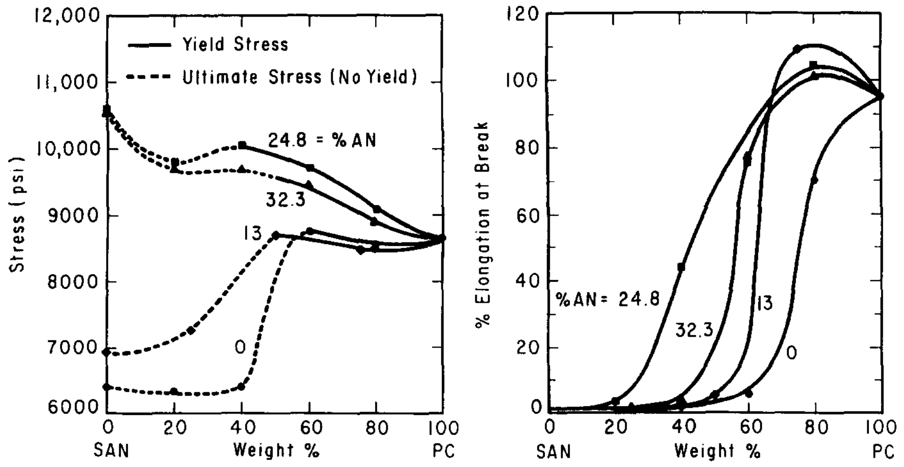


**Figure 2** Mechanical properties of injection-moulded blends of PC with various SAN copolymers. Solid lines on left-hand graph indicate a yield stress while the dashed lines indicate the ultimate stress for materials that did not yield. Reproduced by permission of John Wiley and Sons, Inc.

## EXPERIMENTAL

### *Materials*

A variety of PC and SAN materials were used in the experiments reported here. *Table 1* provides pertinent information about these materials and their sources. Some are commercially available while others are experimental materials. Some of these polymers were specially synthesized or purified for the current work.

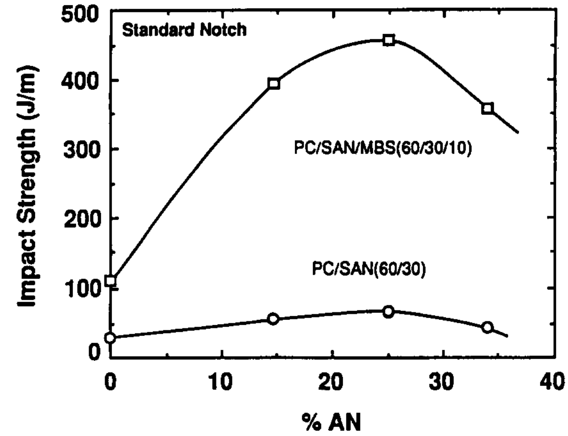


**Figure 3** Notched Izod impact strength at room temperature of injection-moulded PC/SAN copolymer blends. The upper curve gives results for blends containing an MBS core–shell impact modifier while the lower curve is for blends with no modifier. Reproduced by permission of Butterworth–Heinemann Ltd

### *Synthesis of experimental low-molecular-weight SAN*

The very-low-molecular-weight SAN copolymers used for the current thermodynamic analysis were prepared according to the following procedure, which yields very nearly the azeotropic composition. S and AN monomers (commercial polymerization grade) were polymerized with varying amounts of 2-methyl-2-propanethiol (Eastman Kodak, practial grade) as a chain transfer agent. *N*,*N*-dimethylformamide (Fisher, reagent grade) was used as a polymerization solvent. All other solvents were reagent grade. Each polymerization used 50 wt% of 3/1 (w/w) S/AN monomers, the remainder being solvent and chain transfer agent. The solutions were placed in 8 mm diameter glass tubing, cooled with dry ice, purged with nitrogen and flame sealed. The sealed tubes were immersed in an oil bath at 155°C. After the desired polymerization time (1–4 h), the tubes were cooled to room temperature and the conversion determined gravimetrically (typically 13–36%) by placing an aliquot in a 50 ml glass centrifuge tube, filling with methanol, centrifuging the precipitated polymer, decanting and drying to constant weight. The remaining polymer solution was precipitated in methanol in a high-speed

**Table 1** Polymers used in this study

| Polymer | Designation[a] | Copolymer composition (wt% AN) | $\bar{M}_w$[b] | $\bar{M}_w/\bar{M}_n$[b] | $T_g$ (°C) | Brabender torque[c] (m g) | Source |
|---|---|---|---|---|---|---|---|
| Polycarbonate | PC(3.8) | – | 3800[d] | – | 104 | – | Synthesized |
| Polycarbonate | PC(9.9) | – | 9900 | 2.2 | 131 | – | Dow Chemical Co. |
| Polycarbonate | PC(18) | – | 18 000[e] | – | 148 | 390 | Mitsubishi Gas Chemical |
| Polycarbonate | PC(38) | – | 38 000[d] | 2.6 | 146 | – | General Electric<br>(Lexan 131-111) |
| Polystyrene | PS | – | 341 000[d] | 3.3 | 105 | 380 | Fina Oil and Chemical<br>(Cosden 550) |
| Poly(styrene-*co*-acrylonitrile) | SAN25(3.1) | 24.6 | 3137 | 1.30 | 81 | – | Synthesized |
| Poly(styrene-*co*-acrylonitrile) | SAN25(6.0) | 24.6 | 6085 | 1.15 | 98 | – | Synthesized |
| Poly(styrene-*co*-acrylonitrile) | SAN25(7.9) | 24.8 | 7992 | 1.24 | 101 | – | Synthesized |
| Poly(styrene-*co*-acrylonitrile) | SAN25(12.8) | 25.2 | 12 810 | 1.38 | 103 | – | Synthesized |
| Poly(styrene-*co*-acrylonitrile) | SAN4 | 3.5 | 211 000 | 2.19 | 107 | 200 | Asahi Chemical Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN6 | 5.7 | 212 000 | 2.42 | 105 | 240 | Dow Chemical Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN16 | 15.9 | 173 900 | 2.10 | 105 | 250 | Dow Chemical Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN18 | 18 | 172 000 | 2.26 | 106 | – | Monsanto Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN20 | 20 | 178 000 | 2.02 | 106 | 360 | Dow Chemical Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN24 | 23.5 | 160 000 | 2.22 | 108 | – | Monsanto Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN25 | 25 | 152 000 | 1.97 | 110 | 300 | Dow Chemical Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN27 | 26 | 142 000 | 2.49 | 108 | – | Monsanto Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN33 | 32.5 | 146 000 | 2.15 | 110 | 300 | Monsanto Co. |
| Poly(styrene-*co*-acrylonitrile) | SAN40 | 40 | 122 000 | 2.00 | 113 | 420 | Asahi Chemical Co. |

[a] The numbers in parentheses correspond to the weight-average molecular weight in thousands
[b] Molecular weight information from supplier (measured by g.p.c.)
[c] Measured at 60 rev min$^{-1}$ and 270°C after 10 min
[d] Determined from light scattering in this laboratory
[e] Molecular weight determined from intrinsic viscosity measurement

blender. The precipitated polymer was vacuum filtered, air dried overnight, redissolved in 2-butanone to about 5 wt% solids and precipitated in 6 volumes of methanol. The filtered polymer was dried *in vacuo* at 70°C overnight.

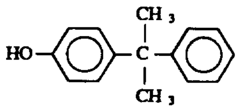
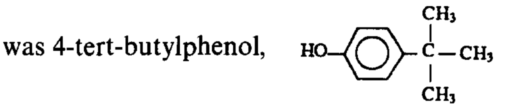
The AN content was estimated by automated Carlo-Erba CHN elemental analysis. The wt% AN was calculated from the summed elemental percentages, normalized to 100%, ignoring the small weight contribution from sulfur. Molecular weights were estimated by g.p.c. in tetrahydrofuran (THF) using four columns containing a mixed pore size bed of 5 $\mu$m beads (Polymer Labs, Amherst, MA). The flow rate was 1 ml min$^{-1}$ at 35°C with a refractive index detector. The column was calibrated with polystyrene (PS) standards by the universal calibration method and corrected to absolute molecular weights by using Mark–Houwink constants for 3/1 (w/w) S/AN copolymer in THF.

Due to the thermal initiation and the chain transfer agent used (2-methyl-2-propanethiol), it is reasonable to assume that each chain contains one hydrogen and one tert-butyl mercaptan (t-Bu-S), $(CH_3)_3C$–S–, end group.

### *Purification of commercial SAN copolymers*

Commercial SAN polymerization processes typically produce a variety of oligomers, and the mechanism of their formation continues to be of interest[50]. Several of the commercial SAN copolymers in *Table 1* were purified to remove these oligomers. Each was dissolved in methyl ethyl ketone and precipitated into methanol. This procedure was repeated. These materials were subsequently used for detailed glass transition analysis, described later.

### *Synthesis of low-molecular-weight PC*

Low-molecular-weight PC was synthesized by an interfacial polymerization technique[6,51–53]. The bisphenol-A monomer and 4-cumylphenol (Aldrich) were purified by sublimation. Bisphenol-A was dissolved in 1 molar sodium hydroxide solution and bis(trichloromethyl) carbonate[54–56], triphosgene, added in equal molar ratio to that of bisphenol-A and subsequently dissolved with methylene chloride under a constant nitrogen purge at room temperature. The chain terminator, 4-cumylphenol, was added to the mixture and the solution vigorously stirred until all reactants had dissolved. Triethylamine was used as a phase transfer catalyst. The molarity of triethylamine was one-tenth that of bisphenol-A. Additional sodium hydroxide was added and the pH checked until the reaction had gone to completion (i.e. the pH remained constant for ~4 h). The aqueous phase was discarded and the organic phase was washed in a high-speed blender with distilled water. The mixture was allowed to separate into two phases with the aqueous phase being discarded. The wash was repeated three times and the polymer recovered by precipitation into 10 volumes of methanol and vacuum filtered. The polymer was dried *in vacuo* at 100°C for 2 days. The chain terminator , used to control the molecular weight in the PC(3.8) oligomer is structurally similar to the PC repeat unit and avoids hydroxyl end groups. This should minimize end-group effects that may contribute to the phase behaviour when blended and, ultimately, the calculated interaction energy. The chain terminator used in PC(9.9), supplied by Dow Chemical Co., was 4-tert-butylphenol, , which is also similar to the repeat unit[57].

## THERMODYNAMIC ANALYSES

### *Theory*

A brief summary of the pertinent equations from both the Flory–Huggins theory and the Sanchez–Lacombe equation of state theory will be given. In the classical Flory–Huggins theory, the change in the Gibbs free energy per unit volume, $\Delta g$, is expressed as a sum of combinatorial entropy[40,41] and non-combinatorial terms as follows:

$$\Delta g_{\text{mix}}=\left(RT\sum_{i=1}^{2}\frac{\phi_i\ln\phi_i}{\tilde{V}_i}\right)+B\phi_1\phi_2 \tag{1}$$

where $R$ is the universal gas constant, $T$ is the absolute temperature and $\phi_i$ and $\tilde{V}_i$ are the volume fraction and molar volume of component $i$, respectively. The non-combinatorial term in this theory employs the van-Laar form where $B$ is the Flory–Huggins interaction energy density. The change in Gibbs free energy must be negative to attain miscibility, but to ensure stability its curvature must be positive. Differentiation of equation (1) gives the spinodal condition:

$$B_{\text{sc}}=\frac{RT}{2}\left(\frac{1}{\phi_1\tilde{V}_1}+\frac{1}{\phi_2\tilde{V}_2}\right) \tag{2}$$

where $B_{\text{sc}}$ is an interaction parameter defined by this relation but is equal to $B$ in equation (1) if $B$ is independent of composition and temperature[58]. At this point the subscript sc on $B$ will be dropped and $B$ will be understood to mean $B_{\text{sc}}$. At the critical temperature, $T_c$, and composition, $\phi_{1c}$, equation (2) reduces to:

$$\phi_{1c}=\frac{1}{1+\sqrt{\tilde{V}_1/\tilde{V}_2}} \tag{3}$$

$$B_c=\frac{RT_c}{2}\left(\frac{1}{\sqrt{\tilde{V}_1}}+\frac{1}{\sqrt{\tilde{V}_2}}\right)^2 \tag{4}$$

The molar volume is equal to the molecular weight divided by density, and accurate values for both are required. For polydisperse polymers Koningsveld and co-workers[59–62] have shown that the thermodynamic equations are similar and that the weight-average molecular weight should be used to determine the molar volume. The spinodal curve will generally be skewed in the direction of the polymer with the lower molecular weight.

Similarly, thermodynamic relations can be derived from the Sanchez–Lacombe lattice fluid theory[42,43,63–66]. The configurational Gibbs free energy per hard core volume of mixture can be written as:

$$g=\frac{G}{rNv^*}=\left(\frac{kT}{v^*}\sum_i\frac{\phi_i}{r_i}\ln\phi_i\right)-\tilde{\rho}P^*+P\tilde{v}+\frac{kT}{v^*}\left[\frac{(1-\tilde{\rho})}{\tilde{\rho}}\ln(1-\tilde{\rho})+\frac{1}{r}\ln\tilde{\rho}\right] \tag{5}$$

Here, $N$ is the number of polymer chains, $v^*$ is the hard core volume of a mer, and $r$ is the chain length defined as:

$$r=\frac{MP^*}{kT^*\rho^*}=\frac{M}{v^*\rho^*} \tag{6}$$

where $M$ is the weight-average molecular weight. Reduced variables are given by:

$$\tilde{P}=P/P^*;\quad \tilde{T}=T/T^*;\quad \tilde{\rho}=\rho/\rho^*=1/\tilde{v} \tag{7}$$

At equilibrium the free energy is at a minimum and the equation of state is:

$$\tilde{\rho}^2+\tilde{P}+\tilde{T}\left[\ln(1-\tilde{\rho})+\left(1-\frac{1}{r}\right)\tilde{\rho}\right]=0 \tag{8}$$

For polymer liquids where $r\rightarrow\infty$, the equation of state reduces to a simple corresponding-states equation. Mixing rules are required in all statistical mechanical theories and are often quite arbitrary; the ones used here are those outlined by Sanchez and Lacombe[42]. The characteristic pressures for the mixture are pairwise additive and given by:

$$P^*=\sum_i \phi_i P_i^*-\sum_{i<j}\sum \phi_i\phi_j\Delta P^* \tag{9}$$

where $\Delta P^*$ is the characteristic energy density of the blend between components $i$ and $j$. This has also been called the 'bare' interaction parameter[58] because of its relation to $B$. The interaction parameter $B$, inherently, includes all the equation-of-state effects, whereas $\Delta P^*$ is the energetic interaction between components after equation-of-state effects have been stripped away.

If $B$ is assumed to be independent of temperature, the Flory–Huggins theory only predicts upper critical solution temperature (*UCST*)-type phase separation. It is possible to circumvent this deficiency by allowing $B$ to be temperature dependent $[B(T)=B^h-TB^s]$ in an extended Flory–Huggins treatment[38] but this form will not be used here. The Sanchez–Lacombe theory predicts lower critical solution temperature (*LCST*) behaviour stemming from equation-of-state terms that tend to destabilize the mixture at high temperature. The various interaction energies, $B(T)$, $B_{sc}$ and $\Delta P^*$, are related to each other by explicit equations discussed elsewhere[38,67].

At equilibrium, the change in chemical potential, $\Delta\mu_i$, must be equal in all phases, which for a binary mixture can be stated as:

$$\Delta\mu_1'=\Delta\mu_1'' \tag{10}$$

$$\Delta\mu_2'=\Delta\mu_2'' \tag{11}$$

where the single and double primes indicate the two different phases of a heterogeneous blend. These values can be calculated from the Flory–Huggins theory by:

$$\Delta\mu_1=RT\left[\ln\phi_1+\left(1-\frac{\tilde{V}_1}{\tilde{V}_2}\right)\phi_2\right]+B\tilde{V}_1\phi_2^2 \tag{12}$$

The change in the chemical potential for component 2 is obtained by interchanging all subscripts in equation (12). The compositions at each temperature where equations (10) and (11) are satisfied is the locus of the binodal or co-existence curve.

A simple binary interaction model[34–36] provides a simple expression for the Flory–Huggins interaction energy densities for mixing a random copolymer composed of units 1 and 2 with a homopolymer of 3 units in terms of monomer unit pair interactions, $B_{ij}$:

$$B=B_{13}\phi_1'+B_{23}\phi_2'-B_{12}\phi_1'\phi_2' \tag{13}$$

where $\phi_i'$ indicates the volume fraction of component $i$ in the copolymer. For mixing two random copolymers 1,2 and 3,4, the following applies:

$$B=B_{13}\phi_1'\phi_3''+B_{23}\phi_2'\phi_3''+B_{14}\phi_1'\phi_4''+B_{24}\phi_2'\phi_4''-B_{12}\phi_1'\phi_2'-B_{34}\phi_3''\phi_4'' \tag{14}$$

where the double primes denote the 3,4 copolymer composition. Corresponding equations for the Sanchez–Lacombe theory[68] can be written by analogy, e.g.

$$\Delta P^*=\Delta P_{13}^*\phi_1'+\Delta P_{23}^*\phi_2'-\Delta P_{12}^*\phi_1'\phi_2' \tag{15}$$

where the volume fractions are calculated from the hard core volumes.

### *Copolycarbonate approach*

The interaction energy between PC and SAN copolymers can be computed as a function of AN content via the binary interaction model (equation (13) or (15)) provided the appropriate interaction energies between the three monomer unit pairs $B_{ij}$ (Flory–Huggins formulation) or $\Delta P_{ij}^*$ (Sanchez–Lacombe equation-of-state formulation) are known. To obtain information about these parameters it is necessary to: (a) bring these units into intimate contact with each other (e.g. a homogeneous mixture) and (b) quantitatively probe some indicator of the free energy or chemical potential (e.g. phase boundary, melting-point depression, excess neutron or X-ray scattering, etc.). In this subsection we review results where objective (a) was met by blending copolycarbonates of bisphenol-A and tetramethyl bisphenol-A with SAN. In the next subsection we accomplish objective (a) by lowering the molecular weight of PC and SAN until miscibility is achieved. In both cases, objective (b) was met by observing (or bracketing) phase boundaries.

It is well known that tetramethyl bisphenol-A polycarbonate (TMPC) is miscible with PS at high molecular weights, and that these blends exhibit *LCST* behaviour[67]. It follows that miscibility can be maintained, within certain limits, as bisphenol-A PC units are randomly incorporated into TMPC and as AN is copolymerized with S. By following the changes in phase-separation temperatures and miscibility limits as a function of the amount of PC and AN units are changed in each copolymer, it has proved possible to obtain $B_{ij}$ or $\Delta P_{ij}^*$ information using the theories outlined earlier. The results from such a study are summarized in *Table 2*. The Flory–Huggins interaction energies were determined by forcing a quadratic curve, defined by

**Table 2** Interaction energies reported from copolycarbonate analysis[20]

| | S | | AN | | PC | |
|---|---|---|---|---|---|---|
| | $B_{ij}$ | $\Delta P_{ij}^*$ | $B_{ij}$ | $\Delta P_{ij}^*$ | $B_{ij}$ | $\Delta P_{ij}^*$ |
| PC | 0.49 | 0.43 | 3.80 | 4.4 | – | – |
| TMPC | −0.15 | −0.17[a] | 6.10 | 5.92[a] | −0.32 | −0.25 |
| S | – | – | 6.8[b] | 7.37[a] | 0.49 | 0.43 |

[a] Taken from the phase behaviour of TMPC/SAN blends by Kim and Paul[70]

[b] This interaction is from Nishimoto *et al.*[69]

equating equations (4) and (14), to pass between the miscible and immiscible data points determined by Kim and Paul[20]. A computer program was used to minimize the orthogonal distance between the curve and each experimental point. The parameters for the quadratic curve are a subset of an infinite number of sets which equally describe the curve by scaling the parameters by any non-zero real constant. Therefore, one of the parameters must be determined independently in order to scale the remaining parameters. Kim and Paul[20] chose the S–AN interaction ($B = 6.8$ cal cm$^{-3}$) reported by Nishimoto *et al.*[69].

The interaction energies determined from the Sanchez–Lacombe equation of state were extracted by using the binary interaction model ($\Delta P^*$ equivalent of equation (14)). The interaction energies, $\Delta P^*$, for the copolymer–copolymer blends were first calculated from the experimental cloud point data assuming they represent the spinodal curve. These values occupied the left-hand side of equation (14) while the other parameters, $\Delta P^*_{ij}$, can be varied. Three parameters were held fixed ($\Delta P^*_{\mathrm{TMPC/PS}} = -0.17$, $\Delta P^*_{\mathrm{PS/AN}} = 7.37$ and $\Delta P^*_{\mathrm{TMPC/AN}} = 5.92$ cal cm$^{-3}$ determined by analysing phase behaviour of TMPC–SAN blends[70]) while the other three $\Delta P^*_{ij}$ values were determined by minimizing the square of the errors between the computed and experimental $\Delta P^*$ values.

Once the interaction energies between each component are known, the change in the total interaction energy between PC and SAN blends with varying AN content can be predicted by the binary interaction model (equation (13) or (15)). The minimum interaction energy is predicted to occur around 28 wt% AN. The minimum value of the interaction energy is 0.04 cal cm$^{-3}$ at 140°C. Using this value in equation (4), PCs with molecular weights of 18 500 or less are predicted to be miscible with commercial SAN25.

### *Critical-molecular-weight approach*

While high-molecular-weight blends of PC and SAN are undoubtedly immiscible, as the molecular weight of the components decreases the entropy of mixing should become favourable enough to overcome any small endothermic mixing between the two components. By finding the critical molecular weights which define the border between miscibility and immiscibility, the critical interaction energy can be calculated from equation (4). To verify the calculations in the previous section, various molecular weights of PC and SAN25 were blended.

PC(9.9) blends with commercial SAN copolymers were found to be immiscible at all AN contents; however, blends from 15 to 25 wt% AN showed a maximum glass transition temperature, $T_g$, shift of 6°C for the SAN-rich phase. The molecular weight of SAN was then decreased in an attempt to obtain miscibility. A level of 25 wt% AN was chosen since this is approximately the azeotropic composition and because this is where the most favourable interaction between PC and SAN appears to occur. Blends of PC(9.9) with SAN25 of molecular weights down to 3137 were still immiscible, although at these low molecular weights the blends showed partial miscibility with shifts of 14 and 11°C in the $T_g$s for the PC and SAN phases, respectively. These blends were visually cloudy up to 300°C.

The PC(3.8) oligomer was then blended with the various low-molecular-weight SAN25 copolymers and was found to be totally miscible with SAN25(3.1) and immiscible with SAN25(6.0). The $T_g$ behaviour for the PC(3.8)–SAN25(3.1) blends is shown in *Figure 4* where the curve drawn is the $T_g$ predicted by the Fox equation. Blends with high PC content showed some crystallinity but were visually clear after PC crystals melted at ~220°C. The $T_g$s of PC(3.8) and SAN25(6.0) were too close to discern miscibility by ordinary scanning techniques so a sub-$T_g$ annealing technique described by various authors[71–75] was used. By annealing samples at 90°C for 24 h all blends clearly showed two enthalpy relaxation peaks and were judged immiscible. Blends were translucent or cloudy once the PC crystallinity had melted.

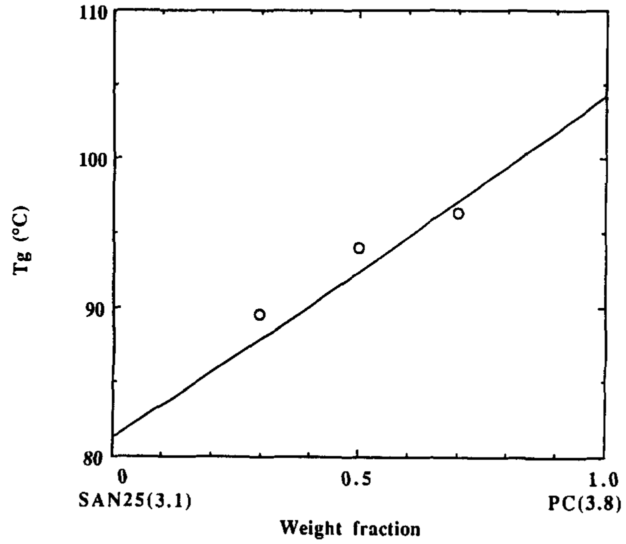


**Figure 4** $T_g$ behaviour of PC(3.8)–SAN25(3.1) blends determined by d.s.c. at 20°C min$^{-1}$ using mid-point method. The curve was calculated using the Fox equation and measured $T_g$ for the pure component polymers

Using these limits of miscibility the interaction energy for the PC–SAN25 pair is calculated to be $0.31 < B < 0.42$ cal cm$^{-3}$ using equation (4) with $T_c = 50$°C. The values of molecular weights for the miscible pair gives the upper limit on $B$ and the immiscible pair gives the lower limit. The synthesis of SAN25 oligomers (see Materials section) resulted in a t-Bu-S end group which is 4.25 and 1.94 vol% of the SAN25(3.1) and SAN25(6.0) copolymers, respectively. Since the interaction energy between just the butyl group and PC has been estimated at 8.1 and 9.0 cal cm$^{-3}$ for $B$ and $\Delta P^*$, respectively[38], even at these small concentrations the end groups can have a pronounced effect on the total net interaction energy. The effect of this end group can be taken into consideration by assuming the SAN25 oligomer to be a terpolymer composed of S, AN and n-butyl (Bu) units (sulfur is ignored and interactions with the t-butyl units are assumed to be equal to those of an n-butyl unit). In terms of the binary interaction model, the total interaction energy for a terpolymer of components 1–2–3 and a homopolymer of component 4 is:

$$B = B_{14}\phi'_1 + B_{24}\phi'_2 + B_{34}\phi'_3 - B_{12}\phi'_1\phi'_2 - B_{13}\phi'_1\phi'_3 - B_{23}\phi'_2\phi'_3 \qquad (16)$$

where the last two terms can be combined to give $-(B_{13}\phi'_1 + B_{23}\phi'_2)\phi'_3$. Using the interaction energies given in *Table 3* and setting 1 = B, 2 = S, 3 = AN and 4 = PC, these two terms become $-(0.30 + 4.9)0.224 = -(0.06 + 1.10)$.

**Table 3** Interaction energies used in the critical molecular weight analysis to determine the PC–AN interaction energies

| | $B_{ij}$ (cal cm$^{-3}$) | $\Delta P^*_{ij}$ (cal cm$^{-3}$) | Source |
|---|---|---|---|
| PC–Bu | 8.1 | 9.0 | Callaghan[38] |
| PC–PS | 0.43 | 0.44 | Callaghan[38] |
| Bu–PS | 4.0 | 4.5 | Callaghan[38] |
| Bu–AN | 11.6 | – | Ziaee[76] |
| PS–AN | 6.8 | 7.37 | Nishimoto *et al.*[69]<br>Kim and Paul[70] |

The first term inside the parentheses arises from the Bu–AN interaction energy. The interaction energy for the Bu–AN pair (see *Table 3*) was estimated from analogue calorimetry[76] using nonane and isobutyronitrile, and this value is considered to be an upper limit for this pair. Based on these estimates, the Bu–AN interaction makes only a minor contribution, relative to other terms, which is fortunate since we do not have a fully reliable estimate for this interaction. Equation (16), plus the $B_{ij}$ values in *Table 3*, can be ued to write two equations that express the upper and lower limits on $B$ established by blending PC(3.8) with the two lowest molecular weight SAN25 oligomers. Solving them for the unknown PC–AN interaction energy gives $4.4 < B_{\mathrm{PC/AN}} < 4.6$ cal cm$^{-3}$.

Using the same procedure to estimate the interaction energy from the Sanchez–Lacombe equation of state results in $0.36 < P^*_{\mathrm{PC/SAN25}} < 0.47$ cal cm$^{-3}$ from the PC(3.8)-SAN25 oligomer blends. Using the $\Delta P^*$ equivalent of equation (16) and the values from *Table 3*, the PC–AN interaction is estimated as $5.0 < \Delta P^*_{\mathrm{PC/AN}} < 5.2$ cal cm$^{-3}$. The characteristic parameters used in the equation of state have been reported elsewhere[70,77]. The equation of state predicts phase separation to occur by a *UCST*-type phase boundary. The value reported by Kim and Paul[20], $\Delta P^*_{\mathrm{PC/AN}} = 4.4$ cal cm$^{-3}$, is 13% less than that reported here.

The phase behaviour for any molecular weight combination of PC and SAN can now be predicted from the Flory–Huggins theory using the spinodal condition, equation (2), and the binary interaction model, equation (13). The shaded regions in *Figures 5* and *6* represent such calculations for various molecular weights of SAN25 with PC(3.8) and with PC(9.9), respectively. The solid points are for two-phase compositions while the open points indicate one-phase blends. In general, the fit to the experimental data is good.

The interaction energies for PC and SAN oligomers, with varying AN and end-group content, calculated from equation (16) are shown in *Figure 7*. The critical interaction parameters calculated from equation (4) (dashed lines) for the various PC–SAN25 oligomer blends are also indicated. Blends of high-molecular-weight SAN of any AN composition are predicted to be immiscible with PC(9.9) since the energy density never falls below the critical value for these molecular weights, as was confirmed experimentally. This is contrary to the claim by Nishi *et al.*[32] that PC with a weight-average molecular weight of 29 000 forms miscible blends with SAN25. These blends were prepared by hot casting from methylene chloride at temperatures of 60–100°C, well above the boiling temperature of the solvent. It is believed that the apparent miscibility reported for these blends is an artifact of a non-equilibrium preparation.

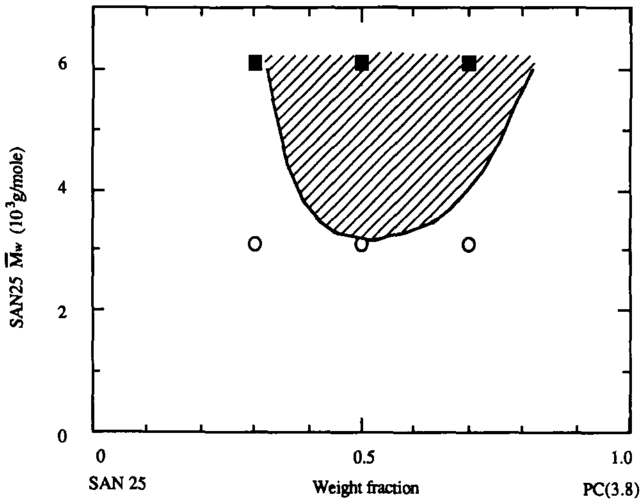


**Figure 5** Blends of PC(3.8) with SAN25 of different molecular weights: ○, one phase; ●, two phase. The curve is constructed using the Flory–Huggins spinodal condition and the binary interaction model with $B_{\mathrm{PC/S}} = 0.43$, $B_{\mathrm{PC/AN}} = 4.5$ and $B_{\mathrm{S/AN}} = 6.8$ cal cm$^{-3}$ at 50°C

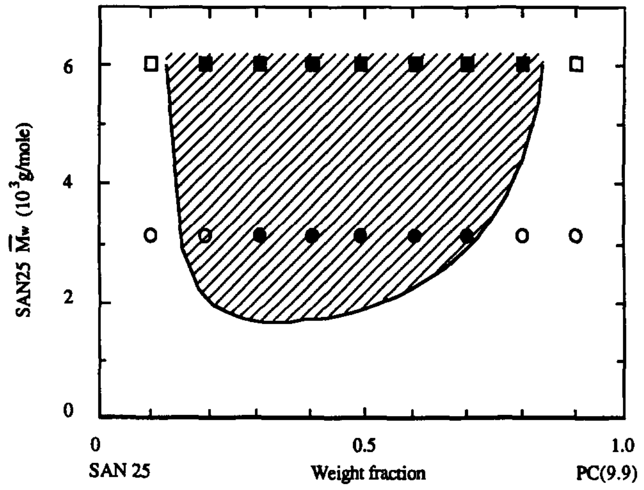


**Figure 6** Blends of PC(9.9) with SAN25 of different molecular weights: ○, one phase; ●, two phase. The curve is constructed using the Flory–Huggins spinodal condition and the binary interaction model with $B_{\mathrm{PC/S}} = 0.43$, $B_{\mathrm{PC/AN}} = 4.5$ and $B_{\mathrm{S/AN}} = 6.8$ cal cm$^{-3}$ at 50°C

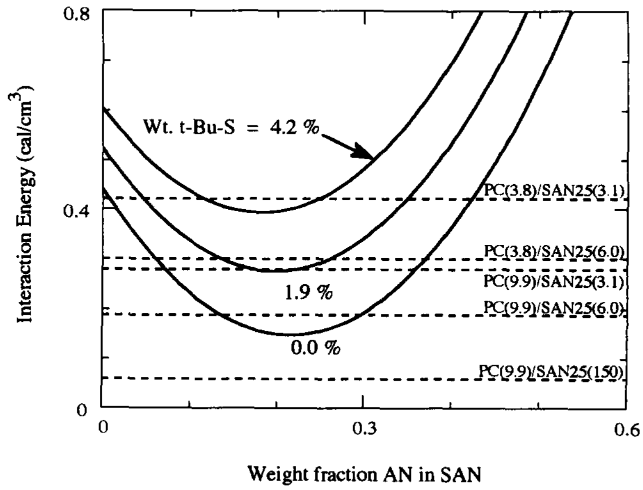


**Figure 7** Dependence of the PC–SAN Flory–Huggins interaction energy on the weight per cent of t-Bu-S end group on the SAN copolymer. The curves are drawn using equation (16) with the values given in *Table 3*. Dashed lines are the critical interaction energies calculated at 50°C

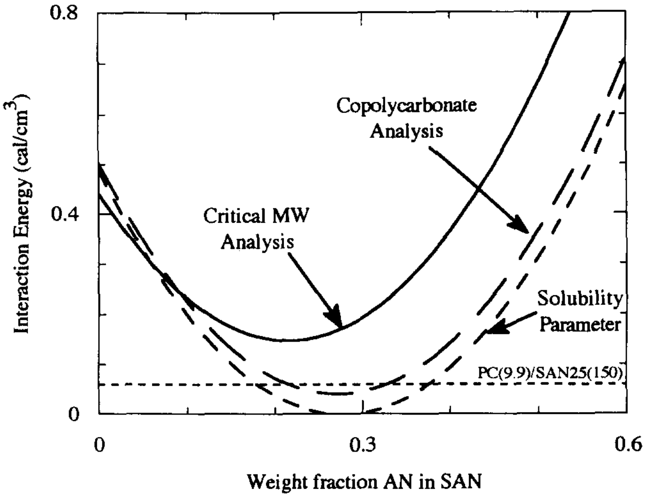


**Figure 8** Dependence of the PC–SAN Flory–Huggins interaction energy on the weight fraction of AN in the SAN copolymer. Curves are drawn using the binary interaction model with the interaction energies determined by the various analyses. The dashed horizontal line is the critical interaction energy calculated at 50°C

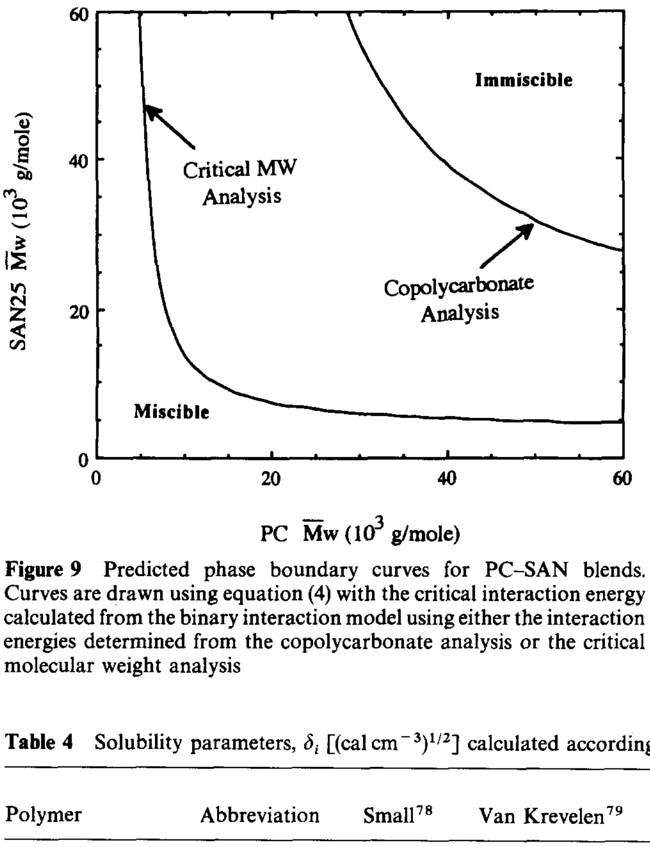


**Figure 9** Predicted phase boundary curves for PC–SAN blends. Curves are drawn using equation (4) with the critical interaction energy calculated from the binary interaction model using either the interaction energies determined from the copolycarbonate analysis or the critical molecular weight analysis

From *Figure 7*, the minimum in the curve for 0% end-group content occurs at ~22 wt% AN which agrees well with the lap shear studies[10] and impact strength measurements[11] described earlier. Additionally, using the PC–AN interaction energies from Kim and Paul[20] (copolycarbonate analysis) the middle curve in *Figure 8* is calculated. The values for the PC–AN interaction estimated by Kim and Paul must be somewhat low since their values predict that blends of PC(9.9) with SAN from 20 to 33% AN should be miscible (see dashed horizontal line in *Figure 8*), whereas these blends were found to be immiscible. This may be more clearly demonstrated by *Figure 9* which shows the region of miscibility for PC–SAN25 blends predicted from the Flory–Huggins interaction energies reported by Kim and Paul[20] and the critical molecular weight analysis reported here. Molecular weight combinations above and to the right of the curves are immiscible while those below and to the left are predicted to be miscible. Obviously, the net interaction energy predicted from the $B_{ij}$ values reported by Kim and Paul[20] is too low since miscibility is predicted when the molecular weights of both components are less than 39 000, which we have shown is not the case.

### *Solubility parameter approach*

The Flory–Huggins interaction energies can be computed from solubility parameters, $\delta_i = \sqrt{CED_i}$ ($CED$ = cohesive energy density), using[34]:

$$B_{ij} = (\delta_i - \delta_j)^2 \tag{17}$$

when the unlike *i,j* interaction is exactly the geometric mean of the two interactions between the like pairs *i,i* and *j,j*. Various group contribution methods are available for estimating the solubility parameter or the *CED* of polymers[78–83]. From the Sanchez–Lacombe theory[42] the *CED* is:

$$CED = \tilde{\rho}^2 P^* \tag{18}$$

Invoking the geometric mean approximation leads to:

$$\Delta P^*_{ij} = [\sqrt{P^*_i} - \sqrt{P^*_j}]^2 \tag{19}$$

Values for the solubility parameters according to the various methods are given in *Table 4*. Interaction energies estimated by these approximations are reported in *Table 5*. Only those predicted by the method of Fedors[82]

**Table 4** Solubility parameters, $\delta_i$ [(cal cm$^{-3}$)$^{1/2}$] calculated according to various methods

| Polymer | Abbreviation | Small[78] | Van Krevelen[79] | Van Krevelen and Hoftyzer[80] | Hoy[81] | Fedors[82] | Coleman *et al.*[83] | $\sqrt{P^*}$ |
|---|---|---|---|---|---|---|---|---|
| Polycarbonate | PC | 9.45 | 9.92 | 9.65 | 10.15 | 11.24 | 10.65 | 10.9 |
| Polystyrene | S | 9.14 | 9.66 | 9.32 | 9.20 | 10.55 | 9.48 | 9.74 |
| Polyacrylonitrile | AN | 12.75 | 15.30 | 12.57 | 12.77 | 13.18 | 13.83 | 11.3 |

**Table 5** Pair interaction energies calculated from the critical molecular weight analysis according to the Sanchez–Lacombe equation of state theory ($\Delta P^*_{ij}$) and the Flory–Huggins theory ($B_{ij}$) along with energies predicted from the Sanchez–Lacombe and solubility parameter theories

| Polymer | $\Delta P^*_{ij}$ | $B_{ij}$ | $[\sqrt{P^*_i} - \sqrt{P^*_j}]^2$ | Small[78] | Van Krevelen[79] | Van Krevelen and Hoftyzer[80] | Hoy[81] | Fedors[82] | Coleman *et al.*[83] |
|---|---|---|---|---|---|---|---|---|---|
| PC–S | 0.49 | 0.43 | 1.45 | 0.10 | 0.07 | 0.11 | 0.91 | 0.48 | 1.37 |
| PC–AN | 5.1 | 4.5 | 0.14 | 10.9 | 28.9 | 8.54 | 6.86 | 3.76 | 10.11 |
| S–AN | 7.37 | 6.8 | 2.48 | 13.0 | 31.8 | 10.6 | 3.57 | 6.92 | 18.94 |

All values are in cal cm$^{-3}$ and calculated according to $[\delta_i - \delta_j]^2$ unles otherwise stated give close quantitative agreement with the energies determined by the two experimental approaches under discussion. The solubility parameter approach predicts that the PC–SAN interaction energy goes to zero at about 28 wt% AN, which implies miscibility in this region for very high molecular weights. The predicted shape of the interaction energy *versus* AN content has the correct form (see *Figure 8*), but the actual interaction energies are obviously higher than this since the predicted miscibility is not observed. Clearly, the geometric mean rule is not followed closely enough for the PC–SAN system to predict the details of the phase behaviour.

### *PC–SAN interfacial characteristics*

Modern theories of the polymer–polymer interface[44–47] allow estimates of the interfacial tension, $\gamma$, and thickness, $\lambda$, provided the thermodynamic interaction energies between the two polymers are known. The interfacial tension is an important factor in determining the morphology generated during melt mixing[44,84,85] while the interfacial thickness relates to interfacial adhesion in the solid state[44]. Here we use the theory of Helfand and co-workers[46,47] to evaluate these interfacial parameters which are given by:

$$\lambda = \sqrt{\frac{2RT}{B}}\,(\beta_A^2+\beta_B^2)^{1/2} \tag{20}$$

$$\gamma = \frac{\sqrt{RTB}}{2}\,[\beta_A+\beta_B]\left[1+\frac{1}{3}\frac{(\beta_A+\beta_B)^2}{(\beta_A+\beta_B)^2}\right] \tag{21}$$

where

$$\beta_i = \sqrt{\frac{\rho_i\langle r_i^2\rangle}{6M_i}} \tag{22}$$

$B$ is the interaction energy density between components A and B, $\langle r_i^2\rangle$ is the mean square end-to-end distance and $M$ is the weight-average molecular weight. Equations (20)–(22) were derived by assuming: (1) random mixing; (2) no volume change on mixing; (3) small compressibility; and (4) that compressibility is independent of composition. Using estimates of $\langle r_i^2\rangle$ given by Brandrup and Immergut[86] at 30°C and the interaction energies from Kim and Paul[20] or from the critical molecular weight analysis at 0% t-Bu-S (see *Figure 7*), the interfacial thicknesses and tensions shown in *Figures 10* and *11*, respectively, were calculated by the theory of Helfand. The interaction energies from the critical-molecular-weight analysis and from the copolycarbonate analysis were determined at 50°C and at 140°C, respectively; nevertheless both predict a maximum in the interfacial thickness at around 22–28 wt% AN content. The interfacial tension prediction is also consistent with the experimental results discussed previously and shows a minimum at around 25 wt% AN.

Theories of polymer–polymer adhesion[44] assert that the interfacial fracture energy or stress increases with increasing interfacial thickness. Qualitatively, the experimental results in *Figure 1* and the calculated results in *Figure 10* conform to this expectation. According to Keitz *et al.*[10], the average failure stress forPC–SAN25 laminates is four times that for PC–PS laminates while the predicted interfacial thickness increases by 3.7 or 1.6 depending on the interaction energies used in the calculation. The adhesion data shown in *Figure 1* only provide a rough indication of the PC–SAN interface, and no quantitative comparisons are warranted until more proper adhesion measurements based on fracture mechanics methods are available for this system.

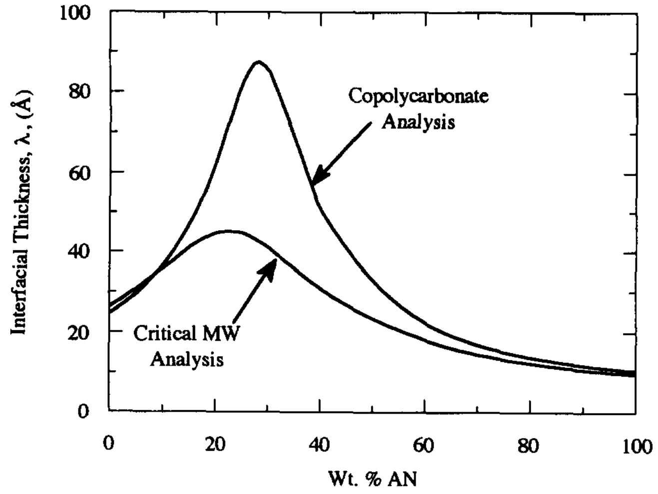


**Figure 10** PC–SAN interfacial thickness predicted by the theory of Helfand[46,47]

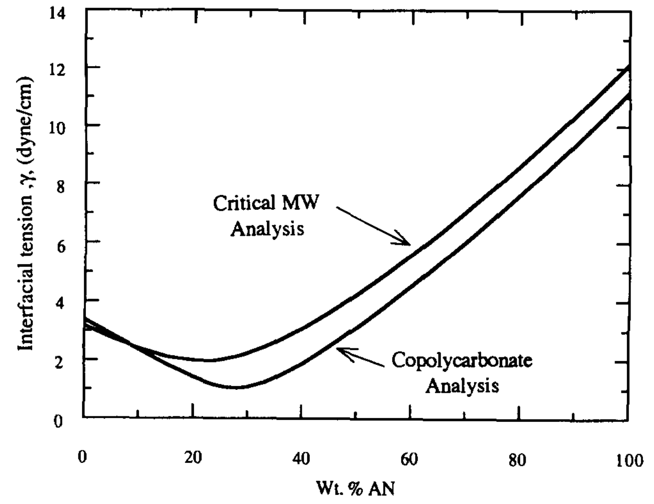


**Figure 11** PC–SAN interfacial tension predicted by the theory of Helfand[46,47]

## THE ISSUE OF PARTIAL MISCIBILITY

As part of their broader investigations of PC–SAN blends, Keitz *et al.*[10] and Mendelson[21] measured the $T_g$s of these mixtures as a function of the AN content. Both studies revealed that the $T_g$s for the two phases were shifted from those of the pure components towards each other by several degrees. Such shifts are frequently observed in two-phase blends that are not strongly segregated and are interpreted as a measure of partial miscibility[87–89]. This line of reasoning was used to estimate the extent that SAN is miscible in PC and vice versa. The results appeared to give semiquantitative support for the trends in PC–SAN adhesion and blend mechanical properties noted earlier.

More recently Guest and Daly[22] proposed that the $T_g$ shifts were due to partitioning of oligomers, formed during SAN polymerization, between the two phases. That is, loss of oligomer from the SAN phase will raise its $T_g$ while adding the oligomer to the PC phase will lower its $T_g$. They reported one experiment that supported their alternative explanation. It was decided to explore this proposition more fully.

Four commercial SAN copolymers, containing 18–33 wt% AN, were purified in the manner described earlier to remove oligomeric species. $T_g$s were measured before and after purification using a Perkin–Elmer DSC-7. The samples were first heated to 220°C to erase prior thermal history associated with preparation and storage and then quenched to 25°C. During the second scan at 20°C min$^{-1}$, the $T_g$ was recorded as the mid-point of the step change in heat capacity. The solid symbols in *Figure 12* represent the results obtained. The open symbols represent the results of Guest and Daly[22] while the solid line was calculated using the sequence distribution equation given by Johnston[90]. The present results agree very well with the data points of Guest and Daly and follow the trend in AN content predicted by Johnston. For each SAN copolymer, the $T_g$ of the purified material is 5–7°C higher than observed for the as-received material. This is consistent with removal of 1–2% oligomer as proposed by Guest and Daly[22].

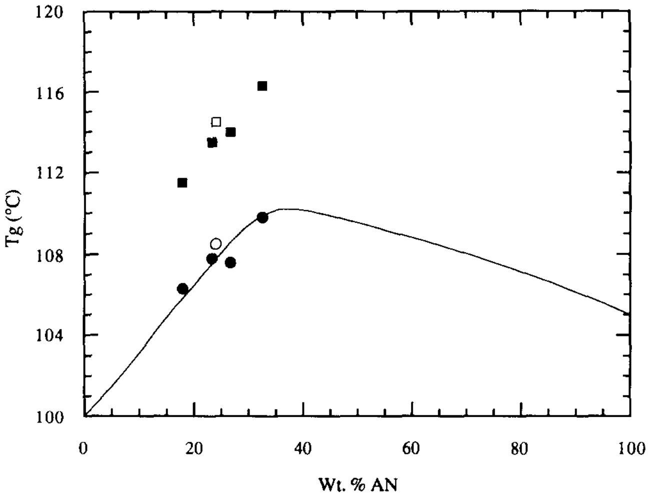


**Figure 12** Comparison of glass transition temperatures of as-received (○, ●) and purified (□, ■) SAN copolymers. Solid symbols represent current work while open symbols denote data by Guest and Daly[22]. The solid line was calculated using Johnston's sequence distribution equation[90]

Blends of these as-received and purified SAN copolymers with PC (Lexan 131-111) were made in a 50/50 weight ratio by both solvent casting and melt blending. Solutions of the two polymers in methylene chloride were stored in beakers at room temperature until most of the solvent evaporated. The resulting films were then placed in a vacuum oven for at least 3 days at 120°C. Similar blends were prepared by melt mixing at 250–280°C for 8 min in a small-scale Mini-Max moulder. $T_g$s were measured as before.

*Figure 13* shows the results for the solvent-cast blends while *Figure 14* gives corresponding data for the melt-mixed samples. Both series of experiments give equivalent results. Blending of as-received SAN copolymers with PC results in significant reductions in the $T_g$ of the PC-rich phase accompanied by a smaller increase in the $T_g$ of the SAN-rich phase. Blending of purified SAN copolymers leads to no measurable shifts in the $T_g$ of either phase. These results are the same as found by Guest and Daly[22] and support their proposal of oligomer partitioning rather than the earlier interpretation of partial miscibility[10,21].

The predicted shift in $T_g$s for the PC and SAN phases in the blend can be calculated by equating the chemical potentials (see equations (10)–(12)) to determine the weight fraction in each phase at equilibrium. The Fox equation can be used to estimate the shift in $T_g$. Using the interaction energies determined by the critical molecular weight analysis, the predicted $T_g$ shifts in both the PC- and SAN-rich phases at 250°C are shown in *Figure 15*. The $T_g$ shifts show a maximum in the 20–25 wt% AN content range. The maximum shift in $T_g$ for the PC-rich phase is 1.6°C while the maximum shift for the SAN-rich phase is only 0.15°C. Thus, these predicted shifts are extremely small, as found in *Figures 13* and *14*. The larger $T_g$ shift for PC indicates that the SAN is more soluble in PC than PC is soluble in SAN, which is confirmed by the slightly larger $T_g$ shifts in the PC-rich phases of *Figures 13* and *14*. When the interaction energies reported by Kim and Paul[20] are used to determine the shifts, maximum shifts of 11°C and 3°C are predicted for the SAN- and PC-rich phases, respectively. This is a result of the PC–AN interaction energy being underestimated, as shown in *Figures 8* and *9* and explained earlier.

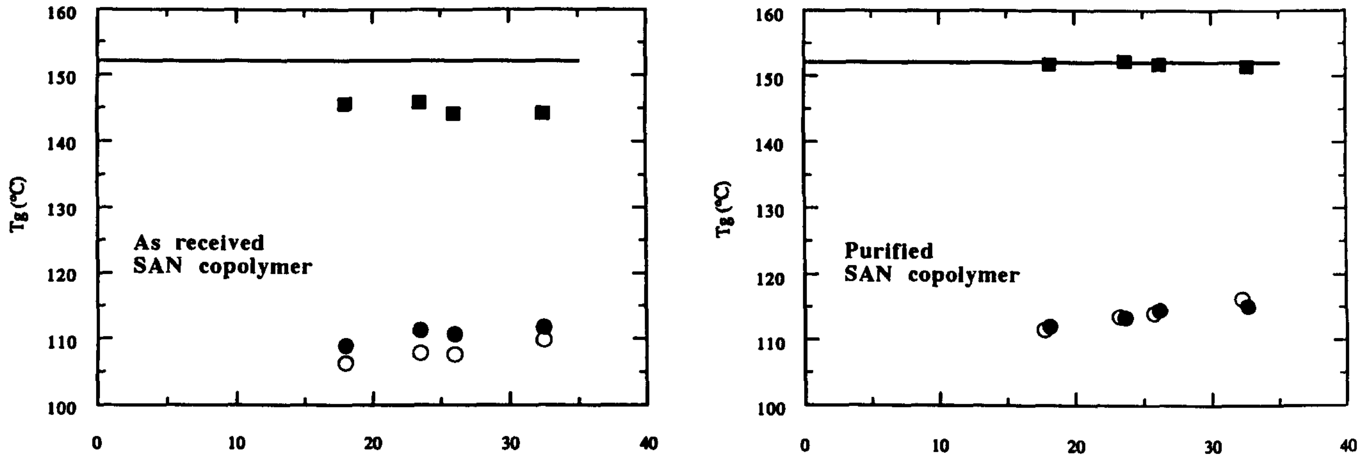


**Figure 13** Glass transition temperature behaviour of solvent-cast blends. Values prior to blending are given by solid line for PC and open circles for SAN copolymers. Values after blending are shown by solid symbols. Results for as-received SAN copolymers are shown on the left while those for the purified copolymers are on the right

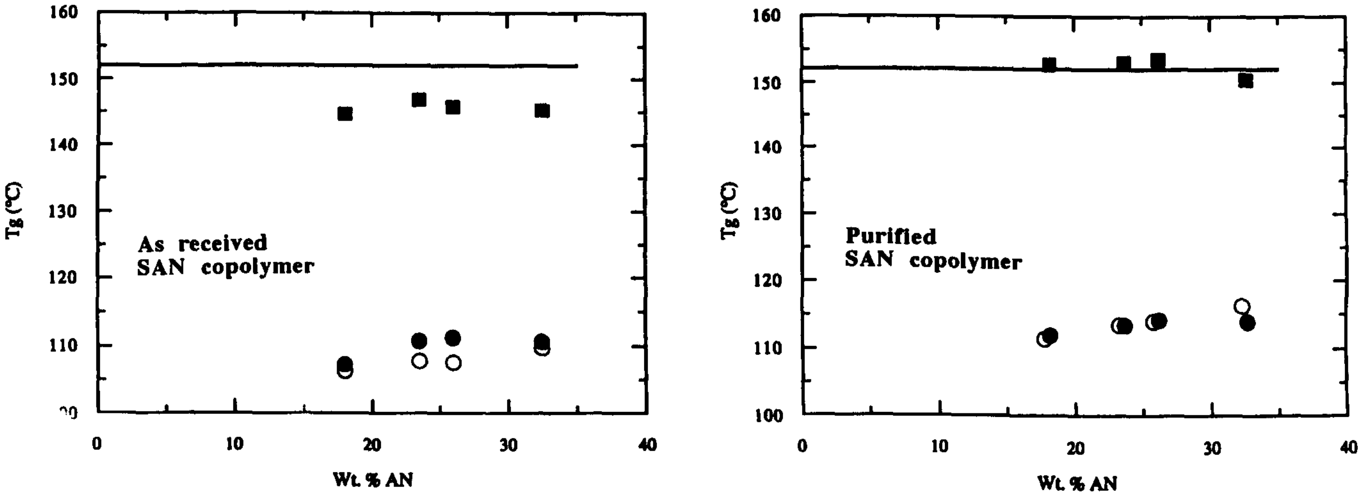


**Figure 14** Glass transition temperature behaviour of melt-mixed blends. Values prior to blending are give by solid line for PC and open circles for SAN copolymers. Values after blending are shown by solid symbols. Results for as-received SAN copolymers are shown on the left while those for the purified copolymers are on the right

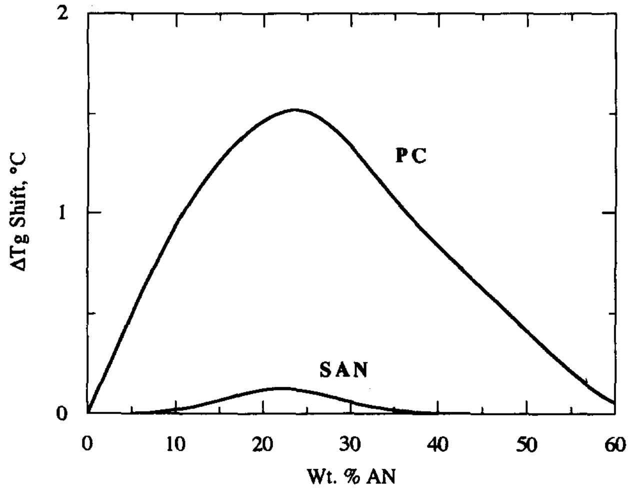


**Figure 15** Predicted shift in the glass transition temperatures for commercial molecular weight blends of PC and SAN using the interaction energies determined from the critical molecular weight analysis

## BLEND MORPHOLOGY

The phase morphology of multiphase blends is an important factor in their performance and is influenced by details of the mixing process, the rheological properties of the phases, and the nature of the interface between the phases[84,91–96]. The latter is a function of the thermodynamic interaction between the components, as discussed earlier. For idealized conditions where all these other factors can be held relatively fixed, a quantitative analysis of morphology can provide information about the interface[84] and, thus, the thermodynamic interaction. As noted earlier, Quintens *et al.*[27] have quantitatively analysed the morphology of injection-moulded 60/40 PC/SAN blends as a function of AN level. Their results show a remarkable trend with AN content in spite of the complexity of the mixing/moulding process and the resultant morphology, and the lack of any stated attempt to maintain consistent rheological properties among the SAN copolymers. They clearly show that the dispersion is finest at ~25 wt% AN, which is consistent with the mechanical properties described earlier.

Recently, we successfully used a simpler experimental design to gain insight about the nylon 6–SAN copolymer interfacial character[84], hence it was deemed appropriate to re-examine the PC–SAN system in a similar way. Mixtures of 75/25 PC/SAN were melt mixed in a Brabender Plasticorder for 10 min at 60 rev min$^{-1}$ and 270°C. A series of SAN copolymers of varying AN level were selected, attempting to maintain, as nearly as possible, a constant melt viscosity. A PC with a similar viscosity (H-3000 from Mitsubishi Gas Chemical) was selected for the matrix phase. Brabender torque at the mixing conditions was used as an indication of melt viscosity. As may be seen from the torque data in *Table 1*, the viscosity ratios varied from a low value of 0.51 for SAN 3.5 to a high value of 1.08 for SAN40, with most cases being near 0.8. Within this range the morphology should be relatively independent of rheological factors[44,84] and reflect the interfacial tension. Blend samples were microtomed and the PC extracted by exposing the samples to a 30% sodium hydroxide solution for 24 h. SEM and image analysis techniques, similar to those described previously[84], were used to determine the average diameter of the SAN particles dispersed in the PC matrix.

Results are shown in *Figure 16* as a function of AN content of the SAN copolymer. There is a minimum in average particle diameter in the range of ~25 wt% AN, consistent with the observations of Quintens *et al.*[27]. When the viscosities of the components and the shear rate of the mixing process are all fixed, as attempted here, correlations in the literature[84,91–96] indicate that particle size should be proportional to the interfacial tension. The particle diameters from *Figure 16* are plotted *versus* the estimates of interfacial tension from the critical molecular weight analysis given in *Figure 11* with the results shown in *Figure 17*. Within the accuracy of the information available, the data are well described by a direct proportionality between $\bar{d}_n$ and $\gamma$. Thus, the morphological observations are consistent in a semiquantitative sense with these estimates of the PC–SAN thermodynamic interaction.

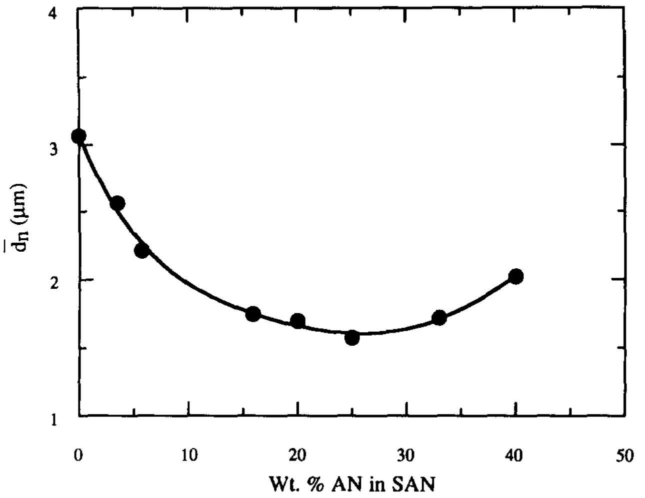


**Figure 16** Dependence of particle size on the AN content for PC–SAN blends determined from SEM image analysis

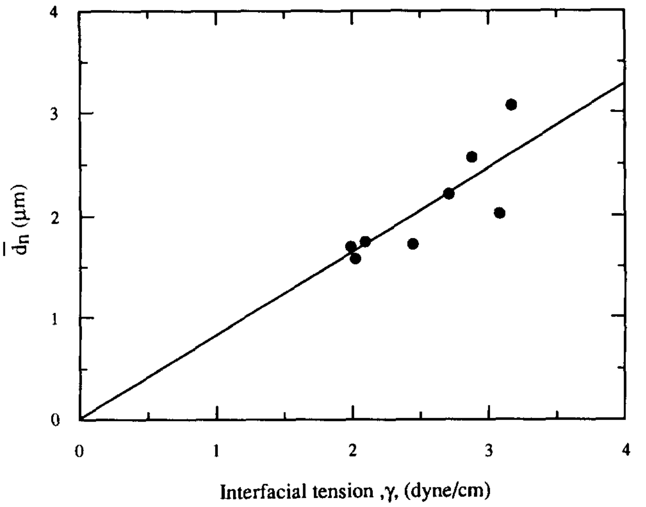


**Figure 17** Correlation of SAN particle size in PC matrix achieved by melt mixing with predicted PC–SAN interfacial tension

## SUMMARY

The literature contains considerable indirect evidence that is consistent with an optimum thermodynamic interaction of PC with SAN copolymers at about 25 wt% AN content[10,11,20,21,27,33]. This includes mechanical and morphological behaviour of blends as well as measurements of adhesion at the PC–SAN interface. A recent thermodynamic analysis based on both the Flory–Huggins and the Sanchez–Lacombe equation-of-state theories of the phase behaviour of blends of copolycarbonates of tetramethyl bisphenol-A and bisphenol-A with SAN copolymers provided an estimate for the PC–SAN interaction energy density[20]. It is predicted that the minimum interaction energy is indeed at ~25 wt% AN, but the absolute values proved to be too small to be consistent with other facts. This work presents results of a critical molecular weight analysis in which the molecular weights of PC and SAN materials were reduced until their blends became miscible. Because of the nature and amount of their end groups it was necessary to make corrections for their effects on the estimated interaction energy in the case of the SAN but not the PC oligomers. From these observations, another estimate of the PC–SAN interaction energy (both Flory–Huggins and Sanchez–Lacombe) was developed, which also predicts an optimum near 25 wt% AN with absolute values that appear to be consistent with all facts of phase behaviour known at this time. Clearly, more extensive studies could be used to refine these estimates. The estimates were used to calculate PC–SAN interfacial tensions and thicknesses by the Helfand theory[46,47]. The interfacial tension estimates are consistent with observations on blend morphology presented, i.e. the size of SAN particles in a PC matrix is minimum at ~25 wt% AN for a fixed melt mixing protocol and approximately equal PC and SAN viscosities. The interfacial thickness is at least qualitatively consistent with prior measurements of adhesion[10].

It was confirmed that the $T_g$ shifts in PC–SAN blends, previously attributed to partial miscibility[10,21], are in fact the result of partitioning of small amounts of oligomers in commercial SAN copolymers. The extent of $T_g$ shifts to be expected by theory, based on the PC–SAN interaction energy by the critical molecular weight approach, was found to be very small, which is consistent with experimental observations using purified SAN materials.

## ACKNOWLEDGEMENT

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