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## An IGC Study of Interactions in SAN/SMA Blends

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# An IGC Study of Interactions in SAN/SMA Blends*

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Inverse gas chromatography has generated surface energy and acid-base interaction data for copolymers of styrene/acrylonitrile (SAN) and styrene maleic anhydride, (SMA) at mole per-cent compositions of SAN-26, SMA-26, and SMA-18. Also measured were polymer pair interaction data for 1:1 weight ratio blends of the copolymers. Explicit values of the $\chi$ interaction parameter over wide temperature ranges also were obtained from these experiments. SAN was shown to be amphoteric, while SMA polymer surfaces interact as bases. The surface and bulk compositions differ both in single copolymers and polymer blends, with an excess of styrene moieties at surfaces and interfaces resulting from thermodynamic drives to minimize the relevant energies. Miscibility-immiscibility relationships in polymer blends are strongly temperature-dependent. Blends were shown to be miscible below glass transition temperatures, and again at temperatures above about 190°C, with immiscible conditions between these temperature ranges.

KEY WORDS Styrene-acrylonitrile; styrene-maleic anhydride; inverse gas chromatography (IGC); acid-base properties; copolymer blends; miscibility; immiscibility.

## INTRODUCTION

This paper is dedicated, affectionately, to James P. Wightman. Wightman has made notable contributions to the science of adhesion, both through his pedagogic activities and, with his coworkers, through his intensive research studies on adhesion in polymer-bonded systems.[1-3] He has underlined the importance of control over interactions at adhesive/substrate interfaces, *inter alia* by the attention paid to surface-modification procedures, such as rf-plasma treatments[2,3] applied to polymeric and metallic surfaces. The recognition of interaction phenomena as major contributors to events at surfaces, interfaces and interphases involving polymers is shared in our laboratories, and constitutes the motivation for the present communication. Its objective is to further the understanding of miscibility/immiscibility events in blends of

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the polymers styrene-co-acrylonitrile (SAN) and styrene-co-maleic anhydride (SMA). The methods of inverse gas chromatography (IGC) have been applied to this end, and have generated data which include dispersive contributions to the surface energy of the blends, their acid/base interaction potentials and Flory/Huggins $\chi$ values, all over substantial temperature ranges.

Binary blends of SAN/SMA have attracted considerable recent attention. Apart from their suitability as useful components of thermoplastic compositions, they arouse fundamental interest since they can display both miscible and immiscible behavior, depending on the relative AN and MA content. Kammer and coworkers[4] have used differential scanning calorimetry and light scattering data to map the miscibility area for wide ranges of AN and MA concentrations. Miscibility was observed for blends with roughly equal amounts of styrene in the two copolymers, a finding in agreement with reports by Hall,[5] among others. More detailed studies of phase behavior in SAN-SMA blends have been carried out by Paul and coworkers.[6,7] They showed that miscibility was to be expected for blends of copolymers with roughly equal weight fractions of MA and AN. Simple models, applicable to binary pairs of monomer units, were used[7,8] to attribute miscibility to weak exothermic interactions between AN and MA units. Values of thermodynamic interaction parameters were inferred from those obtained for small molecule analogues to the polymers in question. The phase behavior of certain of these polymer blends was also investigated by Inoue and coworkers,[9] who reported a lower critical solution temperature (LCST), exhibited as a slow demixing of SAN and SMA at higher temperatures. Demixing was stated to be due, in part, to a slow increase with temperature of the Flory-Huggins $\chi$, the parameter having been calculated from previously-published values for combinations of styrene, maleic anhydride and acrylonitrile monomers.[6]

Direct observations of the $\chi$ parameter for SAN/SMA blends would be a useful complement to the existing literature, particularly if such measurements were made over a temperature range spanning the defined miscibility/immiscibility boundary. The methods of inverse gas chromatography (IGC)[10] appear to be well suited for the task, and would, in addition, furnish data on the surface characteristics noted above.

## IGC BACKGROUND

The principles of IGC, frequently reviewed,[10-12] need not be elaborated here. Two applications of these principles relate particularly to the present work. One is the measurement of the dispersive component of polymer surface energy, $(\gamma_s)^d$, and of the acid/base interaction constants, $K_a$ and $K_d$. The other is the use of IGC to determine the thermodynamic interaction parameter, $\chi_{2,3}$, for mixed stationary phases (e.g. binary polymer blends).

### $\gamma_s^d$, $K_a$ and $K_d$

The route to these descriptors of polymer surfaces is based on the relationship between the specific retention volume, $V_n$, and the work of adhesion, $W_a$, between the polymer and the volatile probe molecules of the IGC experiment. When that relationship is

taken into account, then it has been shown[13,14] that

$$RT \ln V_n = 2N \cdot (\gamma^d_l)^{1/2} \cdot a \cdot (\gamma_s^d)^{1/2} + \text{const.} \tag{1}$$

where the subscripts $l$ and $s$ denote the liquid of the volatile and stationary phase materials, $a$ is the area of the adsorbed vapor molecule, N is the Avogadro number and R, T retain their usual meaning. The use of vapors able to interact with the solid by dispersive forces alone (e.g. those of alkanes), then leads to a convenient evaluation of $(\gamma_s^d)$. The acid/base interaction potential of a polymer solid is accessible through the use of vapor probes known to behave as electron donors and acceptors. This requires selecting an appropriate theory of acid/base behavior, such as that of Gutmann,[15] which has an assigned electron acceptor, AN, and donor, DN, numbers to several organic molecules. The retention characteristics of the specifically interacting probes, determined over appropriate temperature ranges, then identify the acid/base contribution to the adsorption enthalpy, $\Delta H^{ab}$. Following arguments presented elsewhere,[16] this can be expressed as a function of the solid's acid and base interaction constants, $K_a$ and $K_d$, via

$$-\Delta H^{ab} = K_a DN + K_b AN^* \tag{2}$$

where $AN^*$ is the acceptor number of the vapor probe, as corrected for dispersion-force contributions by the protocol of Riddle and Fowkes.[17] A rearrangement of eqn. (2) leads to the graphical determination of $K_a$ and $K_d$. Equations (1) and (2) are equally applicable to single and mixed stationary phases. In the latter case, when experiments are performed below the $T_g$ of the solid phase, values of the surface energy and acid/base interaction parameters may be used to infer the true composition of the blend surface. Due to entropic considerations and the requirement to minimize the surface free energy,[18,19] this will generally differ from the composition of the polymer bulk.[20,21] Information of this type may be useful to a better understanding of the SAN/SMA system.

## $\chi$ Parameters

IGC has been a particularly convenient method for the evaluation of $\chi$ for vapor-solid interactions. When a volatile probe (1) is injected in the conventional highly dilute amounts, the interaction with a polymer (2) is given by[22,23]

$$\chi_{1,2} = \ln \left[ \frac{RT v_2}{V_n V_1 P_1^\circ} \right]^{-1} + \frac{V_1}{M_2 v_2} - \left[ \frac{B_{11} - V_1}{RT} \right] P_1^\circ \tag{3}$$

where $V_1$ and $P_1^\circ$ are the molar volume and saturation vapor pressure of the volatile probe, $M_2$ and $v_2$ are the polymer molecular mass and the molar volume of the polymer repeat unit, and $B_{11}$ is the second virial coefficient, correcting for the non-ideality of the vapor probe.

If now $\chi$ is also determined for another polymer (3) interacting with the same vapors, it then follows[24] that for a mixed stationary phase of polymers 2 and 3 with known composition, the overall $\chi_{1(2,3)}$ can be written as

$$\chi_{1(2,3)} = (\chi_{1,2})\Phi_2 + (\chi_{1,3})\Phi_3 - (\chi_{2,3})\Phi_2\Phi_3 \tag{4}$$

where the $\Phi$ are volume fractions of the polymers. In principle, an explicit determination of $\chi_{2,3}$ follows and is accessible at any desired bulk composition and temperature. Substantial problems have been encountered, however, in the interpretation of $\chi_{2,3}$. These were recently discussed in some detail;[25] briefly, two main factors affect the interaction value for polymer mixtures. One is the discrepancy between bulk and surface compositions, not taken into account in the normal data processing procedure of IGC.[25] A second problem arises from non-random partitioning of the probe molecules. Thus, unless $\chi_{1,2}$ and $\chi_{1,3}$ are (at least roughly) equal, then $\chi_{2,3}$ will display a probe dependence. This problem is avoidable through the judicious selection of probes to be used for calculations of $\chi_{2,3}$, as in the present work.

## EXPERIMENTAL SECTION

### Materials

Three polymers were used in this work. All were supplied by DSM Research and used without further purification. The SAN-26 was a copolymer with 26 mol% AN content and a molecular weight, $M_n$, of 76 kg/mole. The SMA specimens had a MA content of 26 and 18 mol%. The molar masses of both were in the range of 110 kg/mole. Scanning calorimetric determinations (10°C/min. ramp) reported the following $T_g$ values:

SAN-26 $= 105°C$; SMA-26 $= 158°C$ and SMA-18 $= 145°C$; these are in reasonable agreement with the values to be inferred from the literature.[4]

Blends of SMA/SAN were of constant composition at equal weight ratios of the components. They were prepared by precipitation with n-hexane from 5% solutions in methylethyl ketone, recovery being quantitative in all cases. Solvent was removed by vacuum drying at 60°C, $10^{-2}$ torr, for more than 48 h. The 1/1 bulk composition, of course, was not necessarily reflected by the surface composition.

### Procedures

Columns for IGC determinations were of stainless steel tubing, 0.25 mm. i.d., which had been previously cleaned by standard procedures.[10,11] Individual polymers and polymer blends were deposited onto Chromosorb A/W (60/100 mesh) support from MEK solutions. The mass of supported polymer was evaluated by conventional ashing procedures.[10] Because of the broad temperature range over which data were collected (see below), two sets of columns were required for each stationary phase. For work below 100°C, a 1.0 meter column was used, while a column length of 1.6 m was needed to obtain reliable data above that temperature. The following were the masses of

supported polymer:

|  | 1.0 m column | 1.6 m column |
| --- | --- | --- |
| SAN-26 | 5.8 wt.% | 7.2 wt% |
| SMA-26 | 7.2 " | 6.6 " |
| SMA-18 | 6.5 " | 7.8 " |
| SAN-26/SMA-26 | 8.0 " | 5.9 " |
| SAN-26/SMA-18 | 7.7 " | 6.7 " |

A Varian 3400 chromatograph, equipped with both hot wire and ionization flame detectors, was used throughout. Experiments were conducted in the temperature range 40–190°C. The upper temperature limit for each material was determined by DSC experiments (Perkin-Elmer DSC-2B unit). In all cases at these temperatures, the time for first evidence of thermally-induced changes greatly exceeded the time requirements of IGC analyses. The carrier gas in IGC work was He, at a flow rate of 10 ml/min. Methane was used as a marker, the vapor probes were the n-alkanes from hexane to tetradecane, and the following were acid/base sensors: Chloroform and benzene, representing acids (Gutmann designation),[15] diethyl ether (base), ethyl acetate and acetone (amphoteric). Acid-base theories, including that of Gutmann,[15] are still controversial, so that the convention used here generates internally consistent, but not necessarily absolute indices of acidity/basicity for the stationary phases. Vapors were injected at very high dilution (estimated near $2 \times 10^{-4} \mu L$) at least in triplicate. Retention times were obtained from essentially Gaussian elution peaks with a reproducibility of better than 4%.

## RESULTS AND DISCUSSION

### Surface Characteristics of Individual Polymers

The route to both dispersive surface energies and to meaningful values of $K_a$ and $K_d$ relies on applicability to present materials of Eq. (1). Proof of that applicability is shown in Figure 1, for SAN-26 at 80°C. Use of n-alkane probes generates an excellent linear relationship, from which $(\gamma_s)^d$ is readily calculated, and which serves as a reference line for the determination of $\Delta G^{ab}$ for specifically interacting probes. The linearity shown here is typical of data for all stationary phases studied.

The use of acid/base probes at various temperatures led to determinations of $\Delta H^{ab}$, that parameter then being used to specify the acid/base interaction constants of polymers, according to Eq. (2). An illustration is given in Figure 2, again for SAN-26, in the 40–100°C range, that is, below the polymer $T_g$. The linearity is excellent, typical of all such representations in this work. Use of graphs such as illustrated in Figures 1 and 2 resulted in the accumulation of surface energy and $K_a$, $K_d$ parameters, reported in Table I. The Table in addition, lists, values of $I_{sp}$, the acid/base pair interaction parameter for the two polymer blends. The equation used to calculate $I_{sp}$, stated at the bottom of the Table, has been rationalized in a recent communication.[26] Dispersion
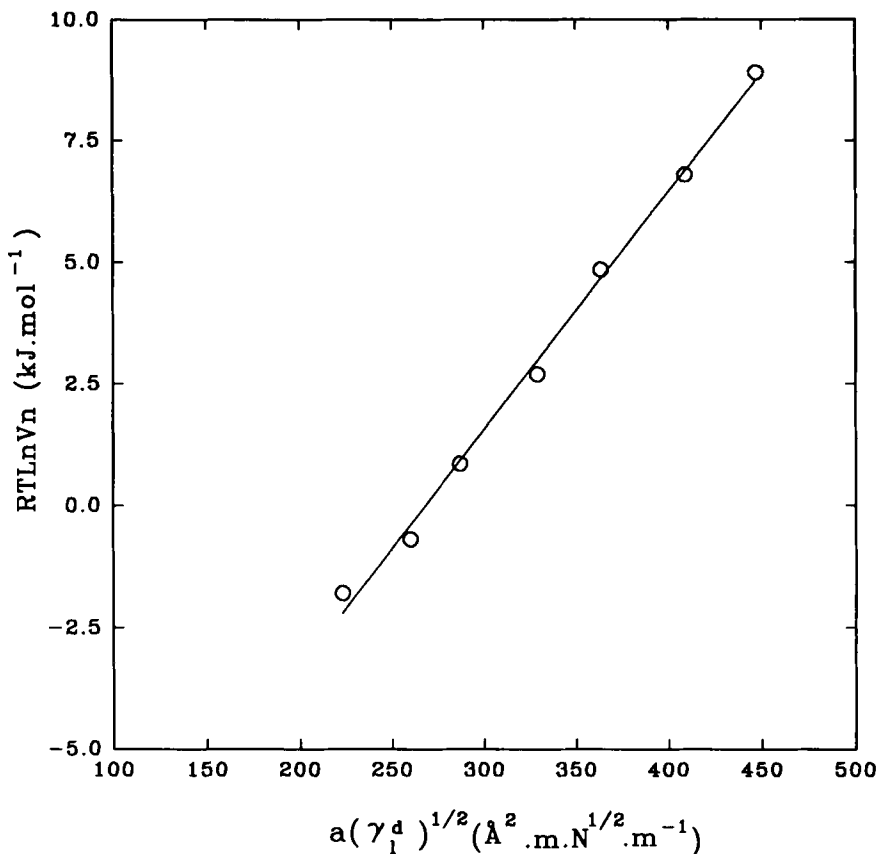
FIGURE 1    Retention volume variation with alkane probe size for SAN-26 at 80°C, showing adherence to the demands of Eq. (1).

surface energies are very similar for the three polymers, and display similar significant downward trends as temperature rises. These surface energies determine the spreading coefficient, and are a measure of the contribution to polymer miscibility made by dispersion forces. In these cases, spreading coefficients were near zero, suggesting that dispersion forces will not constitute a major drive for miscibility in blends of these materials. The $I_{sp}$ parameters, effectively zero for both blends, show that acid/base forces will also not be a significant factor favoring miscibility. The conclusion is consistent with the weak exothermic responses reported for combinations of MA and AN units.[6,7]

The $K_a$, $K_d$ values show the surface of SAN-26 to be amphoteric, but those of the two SMA copolymers are shifted significantly toward basicity. This would suggest a surface excess of basic styrene units, and a greater ability of SMA to accomodate the demands of surface energy minimization. We note here some subtleties associated with $K_a$, $K_d$ and $I_{sp}$ values obtained from experiments on either side of the polymer $T_g$. The convention in IGC[10–12] holds that below $T_g$, $V_n$ values are determined predominantly
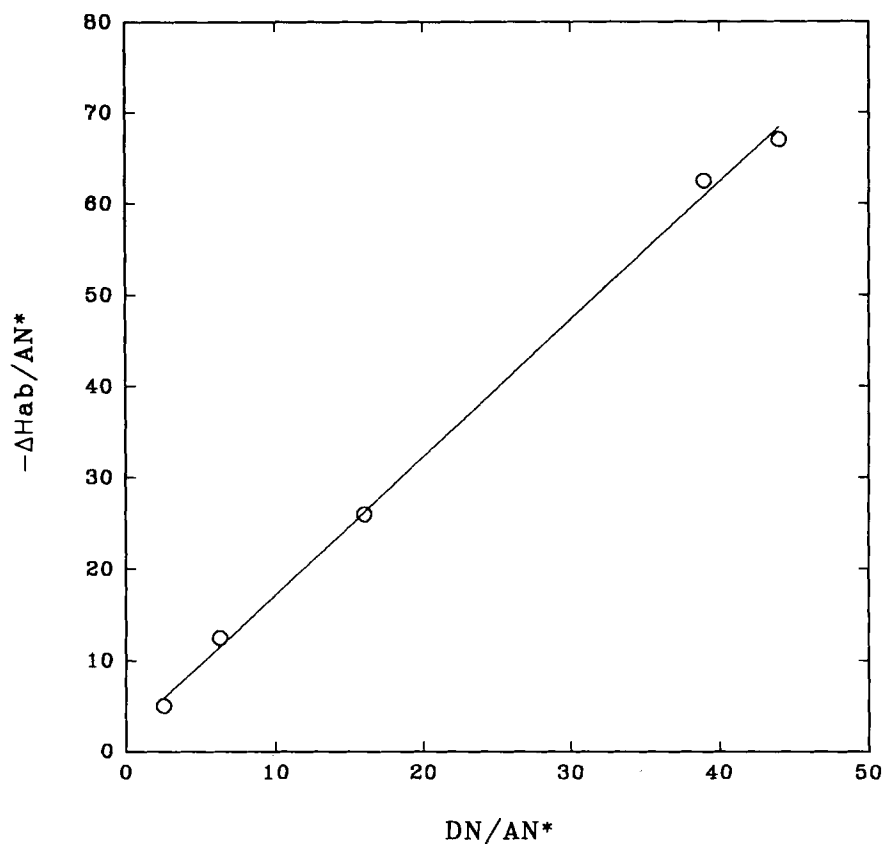
FIGURE 2   Graph leading to the determination of acid-base constants for polymer stationary phases; illustrated is SAN-26.

TABLE 1
Surface Energies, Acid/Base Interaction and Pair Interaction Data from IGC

| T (°C) | SAN-26 | | | SMA-26 | | | SMA-18 | | | $I_{sp}$ | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\gamma_s^{d*}$ | $K_a$ | $K_d$ | $\gamma_s^{d}$ | $K_a$ | $K_d$ | $\gamma_s^{d}$ | $K_a$ | $K_d$ | SAN26/ SMA26 | SAN26/ SMA18 |
| 40 | 28.8 | ↑ | ↑ | 29.3 | ↑ | ↑ | 28.1 | ↑ | ↑ | | |
| 60 | 26.1 | 2.4 | 2.4 | 25.1 | | | 24.1 | | | | |
| 80 | 23.2 | ↓ | ↓ | 21.1 | | | 22.0 | | | ↑ | ↑ |
| 100 | 20.9 | | | 20.5 | 1.5 | 4.5 | 18.8 | 2.2 | 8.5 | 0 | 0.1 |
| 120 | 14.6 | | | 20.0 | | | 16.7 | ↓ | ↓ | ↓ | ↓ |
| 140 | 14.2 | | | 17.0 | ↓ | ↓ | 14.1 | | | | |
| 160 | 16.0 | | | – | | | – | | | | |
| 170 | 16.5 | | | – | | | – | | | | |
| 180 | – | | | – | | | – | | | | |
| 190 | – | | | – | | | – | | | | |

$I_{sp} = (K_a)_1 (K_d)_2 + (K_a)_2 (K_d)_1 - (K_a)_1 (K_a)_2 - (K_d)_1 (K_d)_2$

* $\gamma$ in mJ. m$^{-2}$

by surface adsorption of probe molecules, while above $T_g$ the absorption of probe molecules makes the dominant contribution. Acid-base characteristics determined below $T_g$ then pertain to polymer surfaces. Above $T_g$, the acid-base and interaction parameters describe thermodynamics in the polymer bulk. The two sets of values may differ, since surface and bulk compositions may be significantly different. Moreover, since polymer surfaces will generally be heterogeneous, then, at high dilution of injected vapor, probe molecules will associate preferentially with high energy surface sites.[25] Data below $T_g$ then tend to characterize the surface energies and acid-base properties of this set of sites.

The $\chi$ for polymer/vapor interactions has been calculated over a broad temperature range for the alkane probes, with results shown in Figures 3 and 4 for SAN-26 and SMA-18, respectively. Formally, the application of Flory/Huggins concepts should be limited to isotropic bulk polymers. Thus, only the sections above about 100°C for SAN-26 and above about 140°C for SMA-18 (their $T_g$ values) may be considered as meeting this requisite. These are precisely the respective temperatures where we note
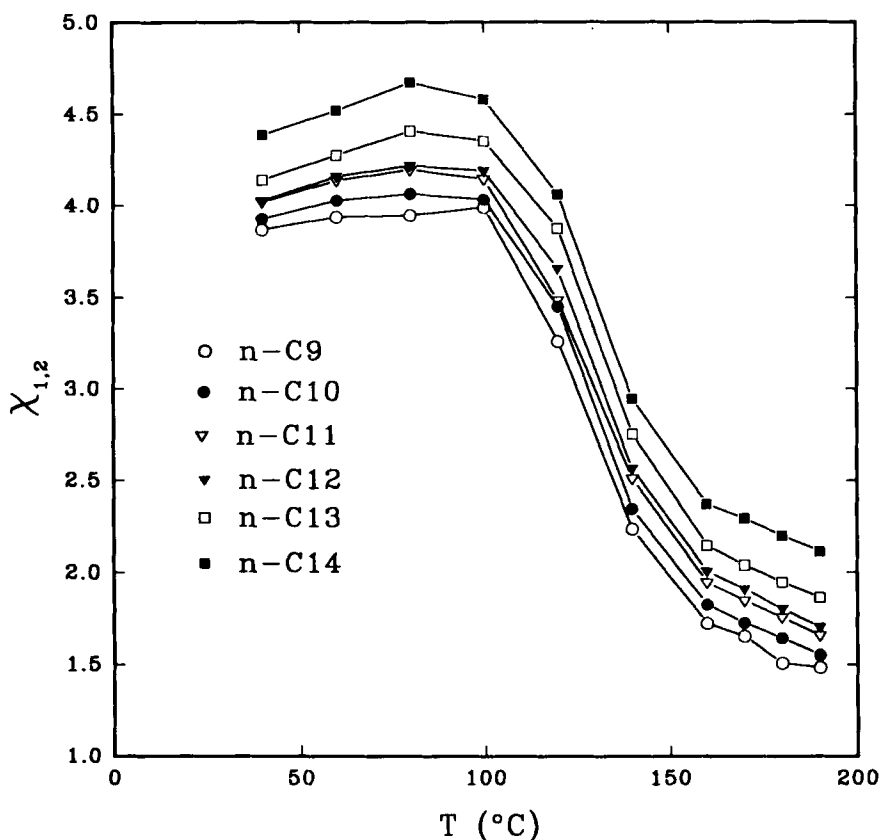


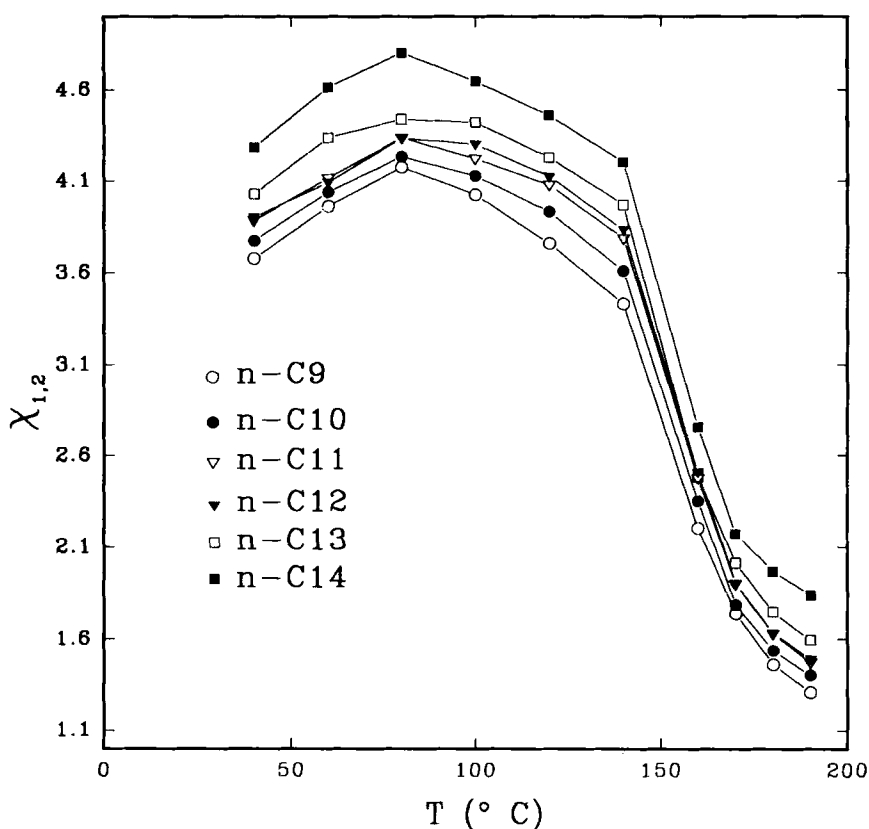FIGURE 3    Temperature dependence of $\chi_{1,2}$ for SAN-26.

FIGURE 4   Temperature dependence of $\chi_{1,2}$ for SMA-18.

major shifts from systematic variations in the $\chi$ values. Above $T_g$, alkane vapors are immiscible with the copolymers, though the decrease with rising $T$ toward the limit of miscibility ($\chi \sim 0.5$) is more pronounced for SMA than for SAN. Further, immiscibility becomes more pronounced with increasing molecular weight of the vapor probe. Although below $T_g$ the concept of measuring the response of isotropic bulk polymers cannot be sustained, it seems useful to report the computed data as a two-dimensional, or surface, analogue of the thermodynamic interaction number. The above remarks, about data accumulation below $T_g$ apply here also, so that these "$\chi$" values relate primarily to high energy sites of the polymer surface. The sharp rise in "$\chi$" below $T_g$ suggests a distinct difference between the interaction states of alkanes in contact with the surfaces and the bulk of these copolymers. This may be due to compositional differences between bulk and surface, as proposed above for SMA.

It was noted earlier that the estimate of the polymer/polymer interaction parameter, $\chi_{2,3}$, calls for the selection of probes which interact similarly with SAN and the SMA molecules. To assist in this, the computed differences between $\chi_{1,2}$ and $\chi_{1,3}$ have been entered in Table II. Clearly, the ideal of equality between these $\chi$ values is unattainable.

TABLE II

Vapor Probe Partitioning: Comparing $\chi_{12}$ and $\chi_{13}$ A: SAN-26/SMA-26: Datum $= 100 \dfrac{|\chi_{12} - \chi_{13}|}{1/2(\chi_{12} + \chi_{13})}$

| $T(°C)$ | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 170 | 180 | 190 |
|---|---|---|---|---|---|---|---|---|---|---|
| C6 | 0.3 | 0.8 | 5.3 | 11 | 59 | 88 | 59 | 38 | 27 | 45 |
| C7 | 2.7 | 7.4 | 5.2 | 0.1 | 38 | 67 | 56 | 32 | 27 | 7.7 |
| C8 | 0.9 | 7.4 | 7.2 | 12 | 36 | 68 | 56 | 42 | 29 | 2.1 |
| C9 | 0.2 | 7.1 | 11.4 | 9.2 | 32 | 61 | 57 | 41 | 27 | 9.0 |
| C10 | 0.2 | 6.1 | 9.0 | 19 | 27 | 60 | 59 | 51 | 33 | 16 |
| C11 | 0.1 | 6.6 | 8.9 | 11 | 29 | 55 | 60 | 50 | 32 | 19 |
| C12 | 0.1 | 7.8 | 7.7 | 10 | 23 | 53 | 60 | 51 | 29 | 19 |
| C13 | 0.2 | 8.5 | 9.8 | 9.5 | 20 | 49 | 59 | 51 | 34 | 20 |
| C14 | 0.4 | 8.7 | 9.9 | 9.7 | 20 | 50 | 56 | 45 | 33 | 19 |

B: SAN-26/SMA-18: Datum defined as in A.

| $T(°C)$ | 40 | 60 | 80 | 100 | 120 | 140 | 160 | 170 | 180 | 190 |
|---|---|---|---|---|---|---|---|---|---|---|
| C6 | 7.0 | 9.5 | 0.8 | 17 | 20 | 42 | 2.0 | 6.2 | 14 | 39.3 |
| C7 | 3.5 | 1.9 | 2.4 | 4.5 | 12 | 41 | 26.3 | 2.2 | 1.0 | 5.4 |
| C8 | 4.0 | 0.9 | 2.6 | 2.1 | 12 | 47 | 20.0 | 6.2 | 1.9 | 13 |
| C9 | 5.1 | 0.6 | 5.6 | 0.9 | 14 | 42 | 25.5 | 1.1 | 3.0 | 13 |
| C10 | 4.0 | 0.3 | 4.1 | 2.3 | 13 | 43 | 25.1 | 3.6 | 6.6 | 10 |
| C11 | 3.4 | 0.6 | 3.3 | 1.9 | 16 | 41 | 24.0 | 2.9 | 7.4 | 12 |
| C12 | 3.2 | 1.7 | 2.8 | 2.7 | 12 | 40 | 22.4 | 0.3 | 9.8 | 13 |
| C13 | 2.8 | 1.4 | 0.7 | 1.6 | 8.7 | 36 | 14.7 | 1.3 | 11 | 16 |
| C14 | 2.4 | 2.0 | 2.7 | 1.4 | 9.3 | 35 | 15.1 | 5.4 | 11 | 14 |

Accepting differences between the $\chi$ in the order of 10% as a compromise, useful values of $\chi_{2,3}$ may be obtained up to $\sim 100°C$, and then again near the upper temperature limit of current experiments. Of course, the earlier caveat about the applicability of theory to non-isotropic polymers also applies here; $\chi_{2,3}$ data below the $T_g$ of polymer blends are regarded as analogues to the conventional Flory/Huggins parameter, characterizing polymer/polymer interactions at the solid/vapor interface, as distinct from those occurring at SAN/SMA contacts within the bulk of the blends. The differences between $\chi_{1,2}$ and $\chi_{1,3}$ at $100 < T < 180(°C)$ are large and the consequent non-random partitioning of vapors between blend constituents must be expected to influence computed $\chi_{2,3}$ values.

## Polymer Blends

IGC data collected for 1:1 blends of SAN-26/SMA-26 and SAN-26/SMA-18 followed the statements of eqns. (1, 2) and resulted in surface energy and acid/base interaction numbers, summarized in Table III. The tabulation omits data at temperatures in the immediate vicinity of the calculated blend $T_g$. In addition to the experimental values of $\gamma_s^d$, $K_a$ and $K_d$, also listed are values of these parameters calculated by arithmetic averaging from data in Table I for single polymers. Certain disagreements between these sets reinforce the postulate that compositional differences exist between surface and bulk in these blends and/or in separate phases. At 180 and 190°C, well above the $T_g$

TABLE III
Experimental and Calculated Surface Characteristics of SAN/SMA Blends

| | | $\gamma_s^d$ (mJ/m²) | | $K_a$ | | $K_d$ | |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| **SAN-26/SMA-26 (1:1)** | | | | | | | |
| $T(°C)$ | 40 | 30 | 29.0 | ↕ | ↕ | ↕ | ↕ |
| | 60 | 26 | 25.1 | 2.1 | 2.0 | 6.3 | 3.5 |
| | 80 | 24 | 21.1 | ↕ | ↕ | ↕ | ↕ |
| | 100 | 19 | 19.4 | | | | |
| | 120 | 14 | 16.8 | | | | |
| | 180 | 13 | 12.8 | ↕ | ↕ | ↕ | ↕ |
| | | | | 2.0 | 2.4 | 7.7 | 6.6 |
| | 190 | 13 | 12.9 | ↕ | ↕ | ↕ | ↕ |
| **SAN-26/SMA-18 (1:1)** | | | | | | | |
| $T(°C)$ | 40 | 25.9 | 28.4 | ↕ | ↕ | ↕ | ↕ |
| | 60 | 21.4 | 25.1 | 1.8 | 2.3 | 6.9 | 5.5 |
| | 80 | 17.8 | 22.1 | ↕ | ↕ | ↕ | ↕ |
| | 100 | 15.7 | 18.5 | | | | |
| | 120 | 12.9 | 13.6 | | | | |
| | 180 | 15.5 | 15.2 | ↕ | ↕ | ↕ | ↕ |
| | | | | 2.4 | 1.8 | 8.5 | 6.2 |
| | 190 | 15.9 | 16.4 | ↕ | ↕ | ↕ | ↕ |

range for both blends, experimental and calculated values of $\gamma_s^d$ are in good agreement. At these temperatures and carrier gas flow rates in the IGC experiments, the vapor probes are able to penetrate into the polymer bulk[10,11,27] where the composition should not differ significantly from the stoichiometric value. Similarly, differences between sets of $K_a$ and $K_d$ values are considerably less than at lower temperatures. Below 100°C, however, the vapor probes interact largely with the polymer surface[27] and here differences between experimental and calculated values become evident. Experimental dispersion surface energies in SAN-26/SMA-26 are somewhat higher than expected, those in SAN-26/SMA-18 noticeably lower. $K_a$ for SAN-26/SMA-26 is roughly equal to the calculated datum, but $K_d$ exceeds its computed counterpart. The surface concentration of basic styrene moieties appears to be enhanced. The experimental $K_d$ for the SAN-26/SMA-18 blend is within the uncertainty limit of the corresponding 26-26 datum, suggesting a similar surface excess of styrene units in both blends. The $K_a$ is lower than forecast, supporting the earlier statement that the SMA-18 copolymer chain is more flexible than SMA-26, as also reflected in the respective glass transition temperatures.

The $T$-dependence of the overall $\chi_{1(2,3)}$, illustrated in Figure 5 for SAN-26/SMA-26, closely resembles the shape of Figures 3 and 4. None of these alkane probes is miscible with the polymer blend so that the interaction between blend components is not perturbed by the presence of the vapor. As was the case with single polymers, the degree of immiscibility rises with increasing chain length of the alkane probe. Calculations of
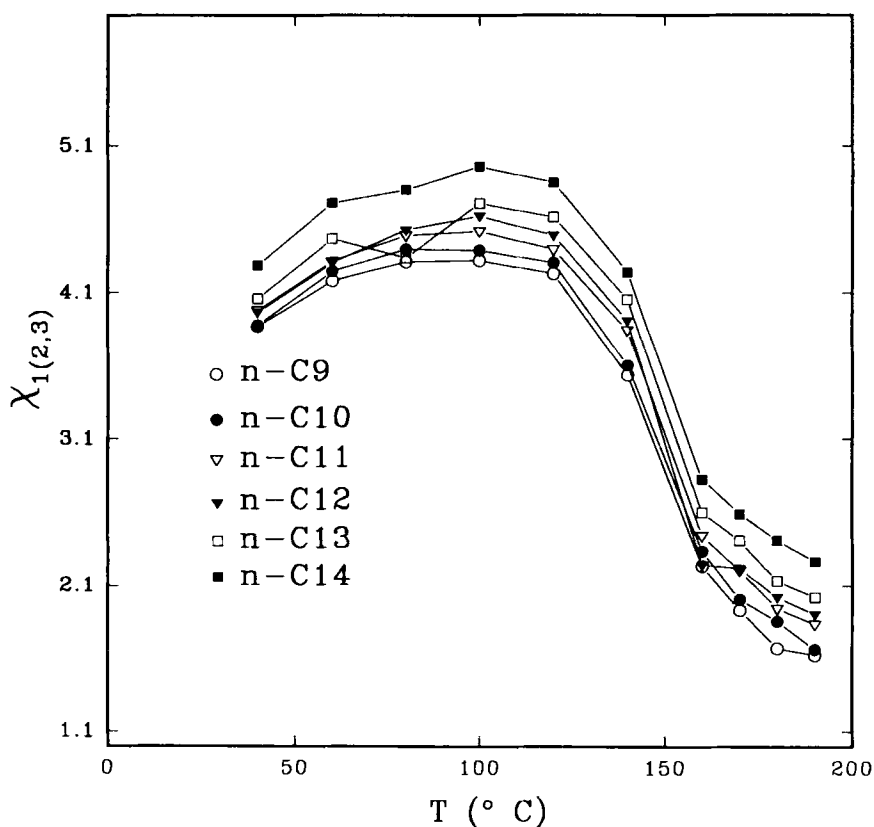
FIGURE 5    Temperature dependence of overall $\chi_{1(2,3)}$ for the 1:1 blend of SAN-26/SMA-26.

the thermodynamic interaction parameter $\chi_{2,3}$ can proceed, with the reservation noted in discussing results in Table II, that non-random partioning of the probes at various of the experimental temperatures is likely to take place. This is expected to affect the systematic trend in $\chi$ values. The relevant $\chi_{2,3}$ data are shown as functions of temperature in Figure 6 for SAN/SMA 26-26, and in Figure 7 for the 26-18 blend. The "spikiness" in these representations is at least partly a manifestation of the partitioning problem. The reservation notwithstanding, it is evident that the temperature-miscibility relation in these polymer blends is complex. Of the two systems, the SAN/SMA 26-18 blend (Fig. 7) has somewhat lower $\chi_{2,3}$ values, these being negative in the range $40 < T < 120°C$. Phase separation is predicted in the immediate vicinity of the $T_g$ range, but miscibility appears to be re-established at the high end of the present range of $T$ variation. Recalling earlier discussion, the $\chi_{2,3}$ values below $T_g$ indicate miscibility of an interface between SAN-26 and SMA-18, where the composition differs from that of the blends as originally compounded. Above $T_g$, the interaction parameter reports immiscibility within the bulk of the 1:1 compositions. The apparent return to miscible blends at $T \geq 180$–$190°C$ has not been reported previously, but seems reasonable in view of the discussion that follows.
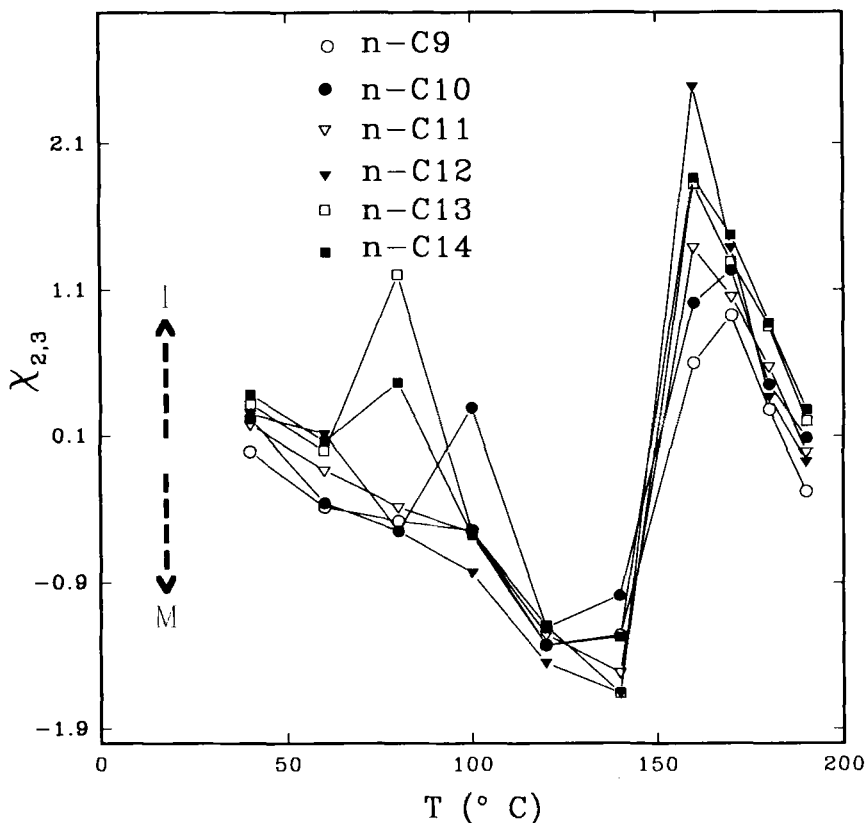
FIGURE 6    Temperature dependence of $\chi_{2,3}$ for 1:1 blend of SAN-26/SMA-26: I and M indicate immiscible and miscible regions, respectively.

In the 26-26 blend (Fig. 6), miscibility appears to be borderline at $T$ below about 60°C, but negative $\chi_{2,3}$ to 140°C indicate miscibility at these higher temperatures. Immiscibility near and above $T_g$, and a return to miscibility above about 190°C are features similar to those of the 26-18 blend. However, in practise there are indications that miscible melt blends of SAN-26/SMA-26 are obtained at compounding temperatures (200–250°C) where present $\chi_{2,3}$ data suggest immiscibility. The anomaly may originate in that contact surfaces in sheared melt blends and in IGC stationary phases may be quite different. In the rapidly-cooled melt blend, miscibility may be promoted by contacts between AN and MA moieties of the polymers. Under the static conditions of the IGC experiment, minimization of interfacial tensions may promote an excess of styrene moieties at interfaces, accounting for the disparate observations. All of the vapor probes report a sharp rise in $\chi_{2,3}$ into the positive range when the temperature rises into the range above 140°C. As in the case of the 26-18 blend, a return toward miscibility is evident at the highest temperatures of this study.

Comparison of our experimental $\chi_{2,3}$ data with calculated values reported in the literature is complicated by differences in the composition of the systems involved.
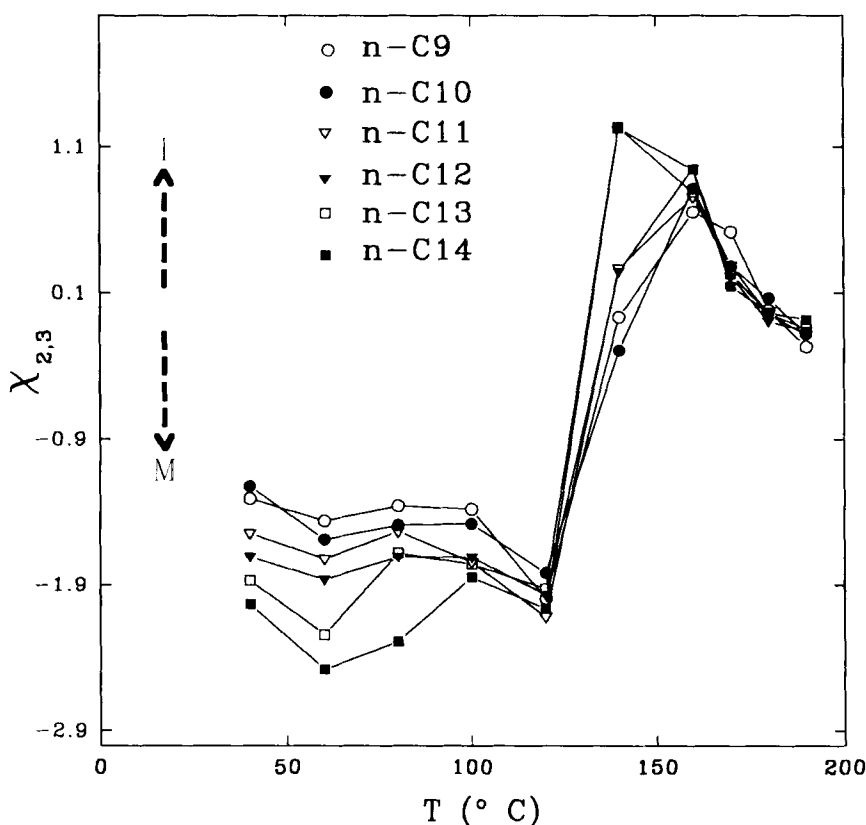
FIGURE 7   Temperature dependence of $\chi_{2,3}$ for 1:1 blend of SAN-26/SMA-18:I and M indicate immiscible and miscible regions, respectively.

A comparison may be made with the results of Inoue and coworkers,[9] who studied the SAN/SMA 20/15.5 blend at temperatures similar to ours. Their phase diagram indicates an LCST boundary between one and two-phase blends, which at the 1:1 composition falls at about 150°C, the blend being miscible below that $T$, and immiscible above. The results for the present 26-18 system in Figure 7 are in qualitative agreement, but the earlier report[9] does not show a return toward miscibility at higher temperatures. Cloud point data reported by Paul and coworkers,[6,7] however, report a LCST value of 250°C for the SAN/SMA 25-18 blend, indicating the existence of miscible conditions immediately below that temperature. Another consistency with the data in Reference 9 is in the order of miscibility; they state that higher AN contents in SAN restrict miscibility, a finding confirmed by a comparison of our data in Figures 6 and 7. Miscibility maps for various SAN/SMA compositions also are to be found in References 4, 5 and 6, but not absolute values of $\chi$ for pertinent $T$ ranges. Once more stressing the limitations discussed above, the presented data, therefore, help fill a void in the available data base for these interesting polymer combinations.

## CONCLUSION

- IGC experiments carried out over a wide range of temperatures have yielded dispersive surface energies and acid-base interaction constants for SAN-26 and SMA-26 and -18 copolymers and for 1:1 weight ratio blends of the copolymers. At $T < T_g$ surface properties are described; above $T_g$ the descriptions relate to the bulk polymers.

- Values of the dispersive surface energy and of the acid-base interaction constants for blends computed from data for the individual polymers, disagree with experimental observations. The suggested cause of the discrepancy is a difference in the composition of blend surfaces and bulk. The surfaces of single and blend polymers appear to be enriched in styrene moieties, consistent with thermodynamic drives of minimizing surface free energies.

- IGC data in the $T$ range from 40–190°C also lead to experimental values of the thermodynamic interaction parameter $\chi$ for SAN, SMA copolymers interacting with n-alkane vapors and for polymer-polymer interactions in blends. Above $T_g$ these interactions again relate to the bulk polymers, but below $T_g$ the thermodynamic parameters apply to a surface interphase, the composition of which differs from that of the bulk in single and blend polymers.

- Blends of both SAN-26/SMA-26 and SAN-26/SMA-18, at 1:1 weight compositions, display miscible and immiscible behavior. Miscibility is prevalent below the $T_g$ of components, with immiscibility prevalent to temperatures in the 180–190°C range. A reversion to miscibility is indicated at temperatures above 190°C.

## Acknowledgment

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