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FTIR and Calorimetric Analyses of the Specific Interactions in Poly(ϵ-caprolactone)/Poly(styrene-*co*-acrylonitrile) Blends Using Low Molecular Weight Analogues

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ABSTRACT: It has been known that blends of poly(ϵ-caprolactone) (PCL) and poly(styrene-*co*-acrylonitrile) (SAN) show a miscibility window in a relatively narrow range of copolymer composition in SAN. In order to study the interactions in this miscibility window in detail, FTIR and calorimetric measurements were carried out by using low molecular weight analogues corresponding to monomers of each polymer, because respective homopolymer pairs are not miscible. The FTIR study showed shifts of spectral peaks that is thought as a proof of presence of specific interactions. The acid−base self-interaction energies (E_{ii}) and association energies for respective pairs (E_{ij}) were also estimated by the detailed study of interactions by calorimetry. If the FTIR results were combined with the calorimetric ones, the acid−base spectral shifts of peaks, $\Delta\nu_{ab}$ (C═O stretch, C≡N stretch, and benzene ring out-of-plane C−H bending), indicated a linear relation with E_{ij} values that fits well with Drago's treatment based on quantum mechanics. The data of two independent experiments justified the presence of specific interactions. Finally the heats of mixing of homopolymer−copolymer pairs were calculated by using the self-interaction and association energies and compared with the behavior of miscibility window.

Introduction

In the field of polymer blends the detailed understanding of miscibility on a molecular level accompanied in many cases by lower and upper critical solution temperature (LCST and UCST) behavior has attracted many scientists. Two homopolymers are miscible only when there are favorable specific interactions between them leading to a negative contribution to the Gibbs free energy of mixing. These are usually associated with charge transfer or hydrogen-bonding between the components.[1] There have been reported a number of miscible blends containing random copolymer(s) that are miscible in a limited range of copolymer composition, the so called miscibility window.[2−13] In 1983 this behavior was explained by diluting repulsive interactions within the copolymer by less unfavorable interactions with another polymer "without any specific interactions".[5−7]

It has been found that poly(ϵ-caprolactone) (PCL) was miscible with poly(styrene-*co*-acrylonitrile) (SAN) random copolymer that contains from 8 to 28 wt % of acrylonitrile.[4] This behavior was interpreted by way of the miscibility window without any specific interactions and as being due to the repulsion between styrene and acrylonitrile comonomers. Recently, however, FTIR peak shifts in blends of PCL with SAN, suggesting the presence of the specific interactions, were observed.[14]

In order to investigate this phenomenon in detail, we carried out FTIR and calorimetric measurements. Because respective homopolymer pairs PAN/PS, PAN/PCL, and PS/PCL are immiscible, it was necessary to use the nearest low molecular weight analogues for the quantitative evaluation of all respective interactions. Analog calorimetry has been shown to be a successful tool for rationalizing and extending the results of polymer−polymer miscibility.[2,3,15,16]

Background

If the change of the Gibbs free energy ΔG is negative, the reaction can proceed spontaneously. Basically, in the case of mixing it is given by

$$\Delta G_M = \Delta H_M - T\Delta S_M \qquad (1)$$

where ΔH_M and ΔS_M are the enthalpy and entropy of mixing, respectively. In a binary polymer mixture it is convenient to start with Flory and Huggins expression for the Gibbs free energy of mixing per mole of lattice sites

$$\frac{\Delta G_M}{RT(V/V_r)} = \frac{\phi_A}{r_A}\ln\phi_A + \frac{\phi_B}{r_B}\ln\phi_B + \chi\phi_A\phi_B \qquad (2)$$

where V is the total volume, V_r is the molar volume of a segment, and r_i and ϕ_i denote the number of segments per chain and the volume fraction of component i, respectively. On the right side of eq 2, the first two terms means combinatorial entropy, while all noncombinatorial effects are represented by the χ parameter. The combinatorial entropy of mixing is related to the positional disorder in the system. Because the mixture is more disordered than the pure components, the combinatorial entropy of mixing leads to a negative contribution to ΔG_M, i.e., stabilization of the mixture. However, the combinatorial entropy for the polymer mixture consisting of high molecular weight components (large r_A and r_B) is virtually zero, and the negative contribution to ΔG_M is negligibly small compared with that due to mixtures of small molecules.[1]

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Usually, in literature based on the equation of state theories, two effects are mentioned that contribute to the interaction parameter χ: the exchange energy represented by parameter X_{AB}, and the free-volume effect arising from the different thermal expansion coefficients represented by the parameter Γ, which is always a positive contribution to ΔG_M and increases with increasing temperature. So the free-volume effect induces LCST behavior at elevated temperatures for miscible blends. Recently, it was mentioned that the size effect resulting from the difference in the segment sizes and represented by parameter ρ[17] is also always a positive contribution to ΔG_M but decreases with increasing temperature. A negative contribution to ΔG_M (except for very small combinatorial entropy) thus can be only coming from the exchange energy. So two polymers seem to mix on the molecular level only under the condition that mixing is exothermic (negative ΔH_M).

However, recently, an endothermic heat of mixing was reported in the case of a miscible blend.[18] The origin of positive ΔH_M was explained by strong self-association of one component (strong hydrogen bonding). By dilution of these interactions (disorientation), the polymer chain gains more freedom in the rotation of segments causing a gain in entropy (different from combinatorial). This increase in entropy gives a larger negative contribution to ΔG_M than the positive contribution to ΔH_M, so that the two polymers are miscible.

Homopolymer–Copolymer Mixtures. A simple binary interaction model offers one possible explanation for the miscibility window behavior, based on consideration of an intramolecular interaction within the copolymer in addition to intermolecular ones. The starting point is a parabolic expression of the heat of mixing, ΔH_M, of two components: a copolymer (AB) and a homopolymer (C)

$$\frac{\Delta H_M}{V_{AB} + V_C} = \mathbf{B}\phi_{AB}\phi_C \qquad (3)$$

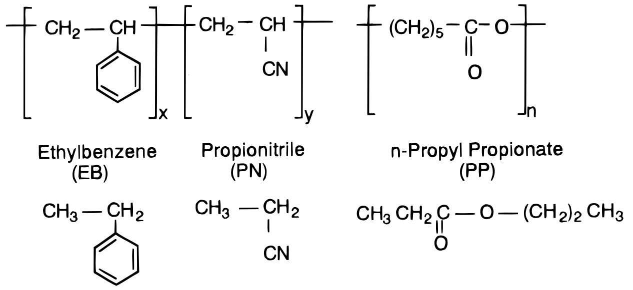
where V_i and ϕ_i are the volume and volume fraction of component i, respectively, ($\phi_{AB} + \phi_C = 1$), and $\mathbf{B}$ is a binary interaction energy density. Copolymer AB is composed of monomeric units A and B with volume fractions denoted ϕ_A and ϕ_B, ($\phi_A + \phi_B = 1$). Homopolymer C is comprised of different monomeric units C. Supposing quadratic function in dependence of copolymer composition, one can get a rather simple expression for the net interaction parameter for mixing AB + C

$$\mathbf{B} = \mathbf{B}_{AC}\phi_A + \mathbf{B}_{BC}\phi_B - \mathbf{B}_{AB}\phi_A\phi_B \qquad (4)$$

where $\mathbf{B}_{ij}$ are respective binary interaction parameters assumed to be independent of composition. If $\mathbf{B}_{AB}$ is positive and has a large enough value (compared to $\mathbf{B}_{AC}$ and $\mathbf{B}_{BC}$), the A and B segments do not attract, and this repulsion makes parameter $\mathbf{B}$ less than additive, changing at a certain composition from a positive to a negative value. When parameter $\mathbf{B}$ is negative, copolymers AB are miscible with homopolymer C. This simple result appears to explain the occurrence of miscibility window. Namely, addition of polymer C to the copolymer AB dilutes the most unfavorable interactions between A and B leading to a net exothermic mixing condition, even though no individual binary interactions are exothermic; i.e., no specific intermolecular interactions are involved.

Recently,[14] in contrast, it was reported that miscible PCL/SAN blends show shifts of nitrile and benzene C–H out-of-plane bending peaks in the IR spectrum. It means that specific interactions are present, and the binary interaction model approach is not correct in the statement that miscibility is possible without any specific interactions. This motivated the detailed study of interactions in these blends with FTIR spectroscopy and calorimetry.

Table 1. SAN, PCL, and Their Nearest Low Molecular Weight Analogues



Experimental Section

Materials. Low molecular weight analogues used in this work are shown in Table 1. These liquids were purchased from Tokyo Chemical Industry Co., Ltd. The purity is better than 99% (guaranteed reagent).

Calorimetric Measurements. Calorimetric measurements were carried out with a twin-type calorimeter (Tokyo Riko) regulated at 25.0 °C with a precision of 0.003 °C. Two Teflon-coated stainless steel vessels were inserted into an aluminum block, and the temperature difference between the sample and reference vessels was measured with thermistors. Signals from the thermistors were amplified and monitored by using a digital multimeter TR6861 (Advantest) with an accuracy ±0.02%. The arrangement within the vessel is illustrated in Figure 1. A couple of thermistors, a heater, a cooler, and a buret tip are dipped in each solution. By the use of the two thermistors in each vessel, the temperature changes could be measured with an error of ±0.03 mK. The titrant (0.25–1.0 cm^3) was injected into the vessel through a heat buffer by using an autoburet (Kyoto Electronics) with an accuracy ±0.003 cm^3. A computer controlled the autoburet, air pump (cooler), and current generator (heater) and received data from a voltmeter (thermistors). The evolved or absorbed heat was obtained directly in J.

FTIR Measurements. FTIR measurements were performed by using of Shimadzu FTIR-8100. Detector is high sensitivity pyroelectric ($LiTaO_3$). Calculated wavenumber accuracy based on the wavenumber of the He–Ne laser is ±0.01 cm^{-1}. A total of 50 scans were averaged. The tested liquid was placed between two KBr windows with adjustable spacing (0.01–0.5 mm).

Results and Discussion

In order to carry out the quantitative analysis of interactions we use the following assumptions:[19]

(1) A change of van der Waals intermolecular interactions accompaning mixing is negligible (for example, mixing of hexane–heptane).

(2) All contributions to the heat of mixing are due to specific acid–base interactions.

(3) All organic liquids (except for saturated hydrocarbons) make the specific self-association based on electron donor (basic) and electron acceptor (acid) sites of one molecule. Namely, molecules are self-associated in X–X pairs consisting of two molecules by the acid–base interaction.

(4) All X–X interactions are broken in the case of high dilution.

(5) All dissociated X molecules form new X–Y interactions.

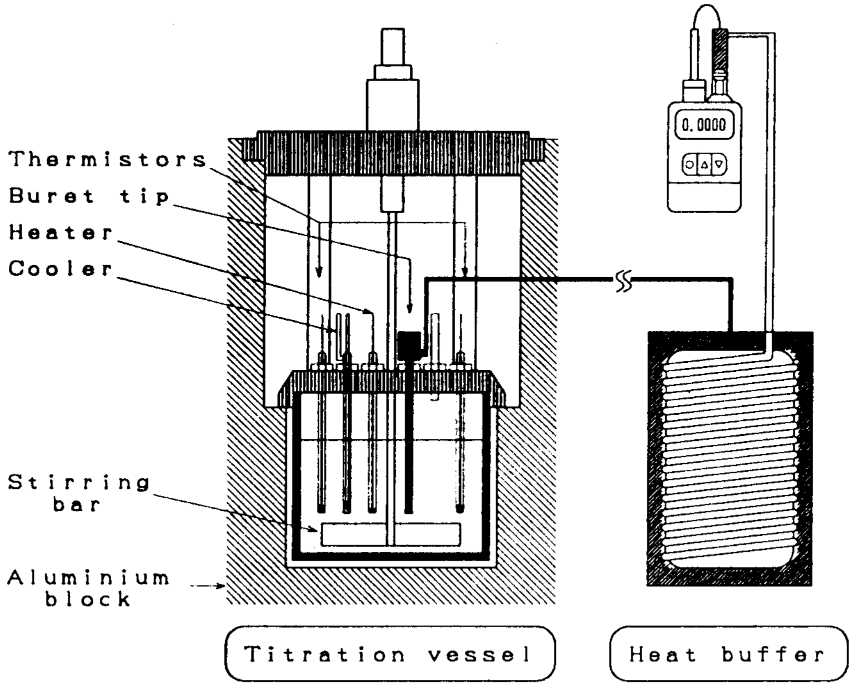


Figure 1. Diagram of the computer-controlled calorimeter.

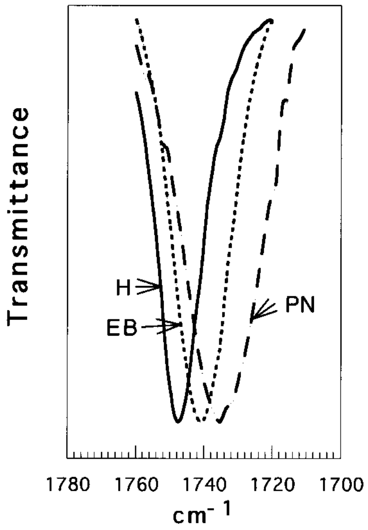


Figure 2. FTIR peaks of the carbonyl group C═O stretch of PP (1% solution) in H (hexane), EB, and PN.

Table 2. Peak Positions ν, Surface Tension, γ, and Shift of Peaks, $\Delta\nu_{ab}$, of 1% Solutions of PP, EB, and PN in the Listed Liquids

name	ν/cm^{-1}	γ/dyn cm^{-1}	$\Delta\nu_{ab}$/cm^{-1}
	C═O Stretch, 1% PP		
hexane	1747.2	18.4	0
decalin	1744.8	29.4	0
EB	1740.6	28.48	4.4
PN	1735.2	26.72	10.2
	Benzene Ring out-of-Plane C—H Bending, 1% EB		
hexane	697.1	18.4	0
decalin	696.6	29.4	0
PP	699.7	23.96	2.85
PN	702.2	26.72	5.48
	C≡N Stretch, 1% PN		
hexane	2250.8	18.4	0
decalin	2248.8	29.4	0
EB	2247.1	28.48	1.9
PP	2247.6	23.96	2.2

(6) Molecules Z (saturated hydrocarbons) do not have any acid—base self-association, neither do they form acid—base interactions with another molecule (X or Y).

FTIR Results. Figure 2 shows the carbonyl stretching peak of propyl propionate (PP) diluted up to 1 vol % concentration in *n*-hexane (H), ethylbenzene (EB), and propionitrile (PN), respectively. The positions of peak were determined at the center of the half-height and these values are given in Table 2. The shift of peak is bigger for PN than for EB. In the same way, the peak positions of the benzene ring out-of-plane C—H bending of EB diluted in H, PP, and PN and the nitrile C≡N stretch of PN diluted in H, EB, and PP are given in Table 2. These shifts gave qualitative evidence of the presence of specific interactions. In all of these three cases the peak shifts several cm^{-1} in the presence of another molecule compared with the position of the peak when the molecules are only diluted by hexane, but do not form any other interactions. Quantitative analysis of the magnitude of respective interactions is not possible just from these FTIR measurements. It is necessary to carry out other experiments, such as calorimetric measurement.

Calorimetric Results. Neat Liquid X (Low Molecular Weight Liquid). The total acid—base self-interaction energy E_{XX} (J mol^{-1}) is expressed as

$$E_{XX} = {}^1/_2\, N_{Avo}\epsilon_{XX} \tag{5}$$

where N_{Avo} is Avogadro's number (6.022×10^{23} (particles/mol)) and ϵ_{XX} is the contact energy of two molecules (or one pair) (J). E_{XX} can be experimentally obtained, when liquid X is diluted into a non-self-interacting liquid Z, such as hexane. This mixing can be described with a semichemical equation

$$N_X(X-X) + N_Z(Z) \xrightarrow{\Delta H_M} N'_X(X-X) + N''_X(X) + N_Z(Z) \tag{6}$$

where (i—i) means liquid i self-associated in i—i pairs, while (i) means liquid i in which molecules are isolated (or dissociated). N_i and N'_i are number of i molecules (that are associated in i—i pairs) before and after mixing, respectively. N''_imeans the number of i molecules that

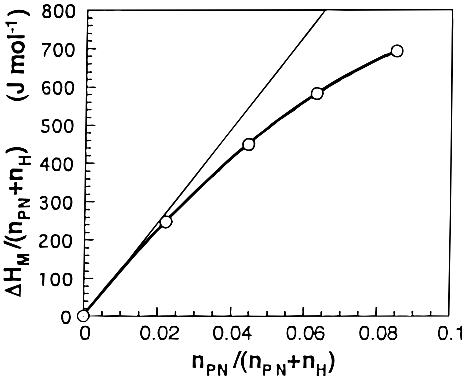


Figure 3. Heat of mixing vs molar fraction of PN diluted into hexane.

are isolated after mixing ($N_i = N'_i + N''_i$). ΔH_M means the heat of mixing. The number of i−i pairs before and after mixing NP_{ii} and NP'_{ii}, respectively, can be easily obtained ($NP_{ii} = {}^1/_2\, N_i$; $NP'_{ii} = {}^1/_2 N'_i$). Dividing eq 6 by N_{Avo} we get

$$n_X(X-X) + n_Z(Z) \xrightarrow{\Delta H_M} n'_X(X-X) + n''_X(X) + n_Z(Z) \quad (7)$$

where n_i means the number of moles of liquid i. Under condition that $n_X \ll n_Z$, $n'_X \to 0$ and $n''_X = n_X$. For $n_X = 1$, ΔH_M becomes E_{XX}. Equation 7 becomes more simple:

$$1(X-X) + n_Z(Z) \xrightarrow{E_{XX}} 1(X) + n_Z(Z) \quad (8)$$

Experimental data for the dilution of propionitrile into hexane can be seen in Figure 3.

Trying to describe the shape of the curve, it is convenient to set the names of axes:

$$x = \frac{n_X}{n_X + n_Z} \qquad y = \frac{\Delta H_M}{n_X + n_Z} \quad (9)$$

The shape of the curve can be described as a polynomial by ($y = k_1x + k_2x^2 + ...$). For $x \to 0$ higher terms are much smaller than the first term ($k_2x^2 \ll k_1x$), and the equation becomes linear ($y = k_1x$). The meaning of the initial slope can be expressed as

$$k_1 = \frac{\Delta y}{\Delta x} = \frac{\dfrac{\Delta H_M}{n_X + n_Z}}{\dfrac{n_X}{n_X + n_Z}} = \frac{\Delta H_M}{n_X} \quad (10)$$

Then the slope is equal to E_{XX}: that is the self-interacting energy of 1 mol of liquid X (J mol^{-1}). The contact energy of two molecules (one pair) of ϵ_{XX} can be obtained from eq 5.

Liquid X Mixed with Liquid Y. Both X and Y have some degree of acid−base self-interaction, E_{XX} and E_{YY}. The semichemical equation in this case is

$$N_X(X-X) + N_Y(Y-Y) \xrightarrow{\Delta H_M} N_{XY}(X-Y) + N'_X(X-X) + N'_Y(Y-Y) \quad (11)$$

where N_{ij} is the number of i and j molecules that are associated in i−j pairs. The total number of molecules is equal before and after mixing ($N_i + N_j = N_{ij} + N'_i + N'_j$). The number of i−j pairs is given by ($NP_{ij} = {}^1/_2 N_{ij}$) and the total number of pairs before and after mixing is given by ($NP_{ii} + NP_{jj} = NP_{ij} + NP'_{ii} + NP''_{jj}$). By dividing eq 11 by N_{Avo}, we can get

$$n_X(X-X) + n_Y(Y-Y) \xrightarrow{\Delta H_M} n_{XY}(X-Y) + n'_X(X-X) + n'_Y(n'_X(X-X) + n'_Y(Y-Y) \quad (12)$$

If $n_X \ll n_Y$, than $n'_X \to 0$. Setting $n_X = 1$ mol, we get

$$1(X-X) + n_Y(Y-Y) \xrightarrow{\Delta H_M} 2(X-Y) + (n_Y - 1)(Y-Y) \quad (13)$$

ΔH_M becomes ΔE_{XY} and the only changing quantities are

$$1(X-X) + 1(Y-Y) \xrightarrow{\Delta E_{XY}} 2(X-Y) \quad (14)$$

Description by self-interacting (E_{ii}) and by association (E_{ij}) energies gives

$$E_{XX} + E_{YY} + \Delta E_{XY} = 2E_{XY}\ (\mathrm{J\ mol^{-1}}) \quad (15)$$

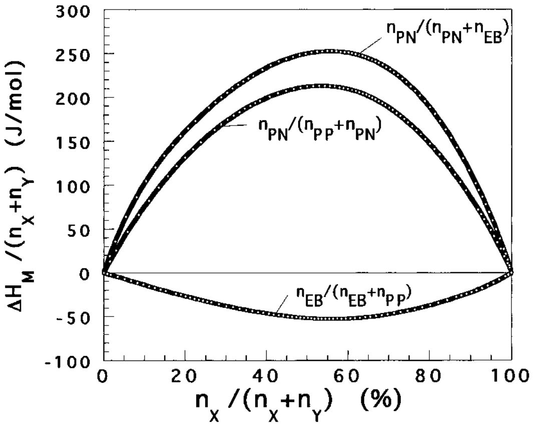


Figure 4. Heat of mixing vs molar fraction of respective pairs.

Self-interaction energies (E_{ii}) were obtained by diluting liquid i into hexane. The value ΔE_{XY} can be obtained from slope analysis similar to the case of diluting of liquid i into hexane, but in this case liquid i is diluted into liquid j, as can be seen in Figure 4. In this figure, the heat of mixing is plotted vs the molar fraction of respective pairs. For two pairs (PN + EB and PN + PP), the heat of mixing was found to be endothermic, that is consistent with immiscibility of PAN/PS and PAN/PCL respective pairs. Exothermic mixing of EB + PP was rather surprising, because high molecular weight respective polymers (PS/PCL) are not miscible. Possible reasons for this discrepancy will be discussed later. Continuing mathematical analysis, the respective interaction energy of 1 mol of X−Y pairs can be expressed as

$$E_{XY} = {}^1/_2(E_{XX} + E_{YY} + \Delta E_{XY}) \quad (16)$$

and the respective contact energy of one pair is

$$\epsilon_{XY} = \frac{2E_{XY}}{N_{Avo}} \quad (17)$$

Self-interaction (E_{ii}) and respective association energies (E_{ij}) obtained by calorimetry are listed in Tables 3 and 4, respectively. The highest value of E_{ii} was obtained for PN containing the C≡N nitrile group and then PP with a carbonyl group (C=O), and the smallest was for EB (benzene ring).

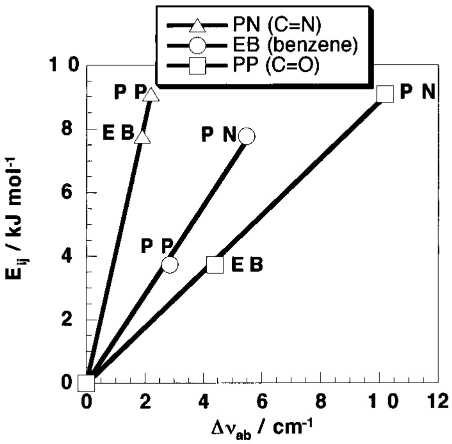


Figure 5. Association energies E_{ij} obtained by calorimetry vs shifts of peaks from FTIR.

Table 3. Self-Interaction Energies for Model Liquids

name	E_{ii}/J mol^{-1}
ethylbenzene (EB)	2395
propyl propionate (PP)	5199
propionitrile (PN)	12094

Table 4. Association Energies of Respective Pairs

pair	E_{ij}/J mol^{-1}
PN−PP	8220
EB−PP	3860
EB−PN	6524

FTIR + Calorimetry. Both FTIR and calorimetry lead to information about specific interactions. For example the shift of the carbonyl (C=O) stretch to lower frequencies is generally accepted as a result of specific interactions such as hydrogen bonding. For the quantitative analysis of the shift of the peaks it is necessary to use the following approach. The vibrating frequency of a certain group (such as C=O) is given by

$$\nu = \nu^{v} + \Delta\nu^{d} + \Delta\nu^{ab} \qquad (18)$$

where ν^{v} means the frequency in the vapor phase, $\Delta\nu^{d}$ is the frequency shift caused by dispersion force interactions between a certain group and its local environment (non-acid−base interacting liquid—such as hexane) and $\Delta\nu^{ab}$ means a frequency shift due to acid−base interactions. When the tested liquid was diluted in series of noninteracting liquids (like cyclohexane, heptane, octane, ...), a linear relationship of $\Delta\nu^{d}$ with the dispersion force contribution to the surface tension γ^{d} was found ($\Delta\nu^{ab} = 0$).[20] In our case the tested liquids were diluted in two noninteracting liquids (hexane and decalin) with an appreciably different surface tension in order to obtain the linear relationship ($\nu = \nu^{v} + a\gamma^{d}$). For the acid−base interacting liquids the exact values of $\Delta\nu^{ab}$ were calculated by the deviation from the linear relationship satisfied in noninteracting liquids[20] and are listed in Table 2. On the basis of quantum mechanics, Drago[21] explained the linear relationship between enthalpy of adduct formation and shift in the frequency of vibration ($\Delta H = k\Delta\nu^{ab}$). This simple relation offers a possibility of the confirmation of data obtained by two independent experiments. In Figure 5 the respective association energies E_{ij} are plotted vs shifts of peaks $\Delta\nu^{ab}$ (data from Table 2 and 4). For all three species a nice linear dependence was found that confirms the validity of data and calculations from two independent experiments.

Calculation for a Copolymer (AB)/Homopolymer (C) Mixture. In the sections above, it was explained how to obtain the self-interaction and respective association energies. In this section it will be explained how to use these values in order to calculate the heat of mixing of copolymer AB with homopolymer C. A and B indicate comonomer units in the copolymer while C is the monomer unit in the homopolymer. These correspond to X or Y in the previous part. In this section we also discuss the model disregarding chemical bonding between units for convenience.

For the easier calculation it is convenient to make assumption that $\phi_{AB} \ll \phi_{C}$ (ϕ is volume fraction) leading to a fact that all A−A, B−B and A−B interactions change into A−C and B−C, while nonbroken C−C are the same before and after mixing. Then the only changing quantities are

$$H^{ab}_{AB} + H^{ab}_{C} + \Delta H_{M} = 2H^{ab}_{ABC}\ (\mathrm{J\ mol^{-1}}) \qquad (19)$$

where H^{ab}_{AB}, H^{ab}_{C}, and H^{ab}_{ABC} are the overall acid−base association and self-interaction energies of copolymer, homopolymer, and blend, respectively.

Before Mixing—Copolymer AB. Before mixing, in the copolymer there are three kinds of interactions (A−A, B−B and A−B). The overall acid−base self-interaction energy is then described by

$$H^{ab}_{AB} = \epsilon_{AA}NP_{AA} + \epsilon_{BB}NP_{BB} + \epsilon_{AB}NP_{AB} \qquad (20)$$

and $NP_{COP} = NP_{AA} + NP_{BB} + NP_{AB}$. The total number of pairs in the copolymer, NP_{COP}, is given by

$$NP_{COP} = {}^{1}/_{2}N^{m}_{COP}x^{m}_{COP} \qquad (21)$$

where N^{m}_{COP} and x^{m}_{COP} means the number of macromolecules and the degree of polymerization of the copolymer, respectively.

For the following calculations it is convenient to use p_{ii} and p_{ij}, which are probabilities of the presence of an i−i or an i−j pair, respectively, and have values of 0−1. It follows that

$$p_{AA} = \frac{NP_{AA}}{NP_{COP}} \qquad p_{BB} = \frac{NP_{BB}}{NP_{COP}} \qquad p_{AB} = \frac{NP_{AB}}{NP_{COP}}$$
$$p_{AA} + p_{BB} + p_{AB} = 1$$

and

$$H^{ab}_{AB} = NP_{COP}(\epsilon_{AA}p_{AA} + \epsilon_{BB}p_{BB} + \epsilon_{AB}p_{AB}) \qquad (22)$$

For 1 mol of monomer or comonomer units, $NP_{COP} = {}^{1}/_{2}\,N_{Avo}$ and $E_{AA} = {}^{1}/_{2}\,N_{Avo}\,\epsilon_{AA}$.

It follows that

$$H^{ab}_{AB} = E_{AA}p_{AA} + E_{BB}p_{BB} + E_{AB}p_{AB} \qquad (23)$$

where $p_{AA} = (1-\beta)^{2}$, $p_{BB} = \beta^{2}$, and $p_{AB} = 2\beta(1-\beta)$. β means the mole fraction of B in copolymer AB and is given by

$$\beta = \frac{N_{B}}{N_{A} + N_{B}} \qquad (24)$$

where N_{i} means the number of comonomer unit i, and

$$N_{A} = (1-\beta)x^{m}_{COP}N^{m}_{COP}$$

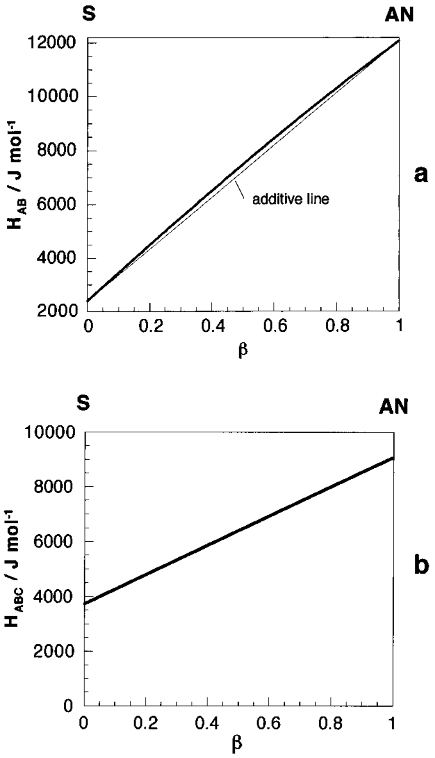


Figure 6. Calculated overall acid–base self-interaction and association energies vs copolymer composition β (mol % of AN in SAN): (a) copolymer AB (SAN); (b) blend ABC (PCL/SAN).

and

$$N_B = \beta\, x^m_{COP} N^m_{COP}$$

Equation 23 is obtained from

$$H^{ab}_{AB} = (1-\beta)^2 E_{AA} + \beta^2 E_{BB} + 2\beta(1-\beta)E_{AB} \tag{25}$$

$$= E_{AA}(1-\beta) + E_{BB}\beta + \Delta E_{AB}\beta(1-\beta) \tag{26}$$

where $E_{AB} = \frac{1}{2}(E_{AA} + E_{BB} + \Delta E_{AB})$.

In the case of copolymer AB, the condition $N_A \ll N_B$ is not met. The slope analysis is replaced by an investigation of the heat of mixing vs copolymer composition, which gives better fitting of data over all copolymer compositions β

$$\frac{\Delta H_M}{n_A + n_B} = \Delta E_{AB}\beta(1-\beta) \tag{27}$$

The overall self-interaction energy of the SAN copolymer, described by eq 26, is plotted as a function of copolymer composition in Figure 6a (β is mol % of AN in SAN). The first two terms in the right hand side of eq 26 is the additive line, and third term is the heat of mixing of A + B. The value of H^{ab}_{AB} in SAN is higher than the additive line. This indicates the endothermic mixing and repulsive interaction.

Before Mixing—Homopolymer C. There are only C–C interactions present, so that the self-interaction energy is given by

$$H^{ab}_{C} = NP_{CC}\epsilon_{CC}$$

For 1 mol of C

$$H^{ab}_{C} = E_{CC} \tag{28}$$

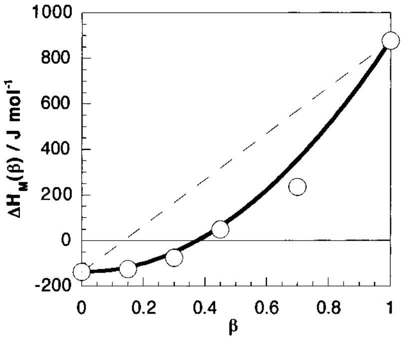


Figure 7. Enthalpy of mixing vs copolymer composition of PCL/SAN blend's low molecular weight analogues.

After Mixing—Blend AB/C. Because only a small amount of copolymer AB was diluted into large excess of homopolymer C, it can be supposed that all A–A, B–B and A–B interactions were after mixing replaced by A–C and B–C interactions:

$$H^{ab}_{ABC} = NP_{AC}\epsilon_{AC} + NP_{BC}\epsilon_{BC}$$

The total number of interacting pairs is $NP_{ABC} = NP_{AC} + NP_{BC}$ and $NP_{BC} = \beta\ NP_{ABC}$; $NP_{AC} = (1-\beta)NP_{ABC}$.

For 1 mol of blend, $NP_{ABC} = \frac{1}{2} N_{Avo}$, $\epsilon_{AC} = 2E_{AC}/N_{Avo}$, $\epsilon_{BC} = 2E_{BC}/N_{Avo}$, and then

$$H^{ab}_{ABC} = E_{AC}(1-\beta) + E_{BC}\beta \tag{29}$$

Figure 6b shows a plot based on eq 29 for SAN/PCL blend.

By expressing of heat of mixing from eq 19 we get

$$\Delta H_M = 2H^{ab}_{ABC} - (H^{ab}_{AB} + H^{ab}_{C}) \tag{30}$$

If eqs 25, 28, and 29 are inserted into eq 30, the copolymer composition dependence of heat of mixing $\Delta H_M(\beta)$ is expressed as

$$\Delta H_M(\beta) = 2[E_{AC}(1-\beta) + E_{BC}\beta] - [E_{AA}(1-\beta)^2 + E_{BB}\beta^2 + E_{AB}2\beta(1-\beta) + E_{CC}] \tag{31}$$

Equation 31 can be also obtained from the opposite case that only a small amount of homopolymer C was diluted into large excess of copolymer AB and all C–C interactions were after mixing replaced by A–C and B–C ones. Finally, eq 31 indicates an exchange energy for a case where self-interactions exist and corresponds to eq 4 which does not include the effect of self-interactions. If one sets the self-interaction energies (E_{AA}, E_{BB}, and E_{CC}) equal to zero in eq 31, an expression similar to eq 4 is obtained except for a coefficient.

Figure 7 shows the heat of mixing calculated for the PCL/SAN blend using eq 31 (solid curve) compared with points that were obtained experimentally by calorimetric measurement of premixtures of EB + PN (SAN) into PP (PCL). There is a good agreement of experimental values with calculated ones, which supports the validity of the model calculations.

Finally, we compare the phase diagram of PCL/SAN blends (Figure 8) with the heat of mixing results. The positive heat of mixing on the AN-rich side is in accordance with immiscibility of PCL with SAN that have a high content of AN. The position of boundary between positive and negative values of ΔH is in agreement with the right side of the miscibility window. In the left side of the miscibility window, however, the sign of ΔH does not change and is negative even for a

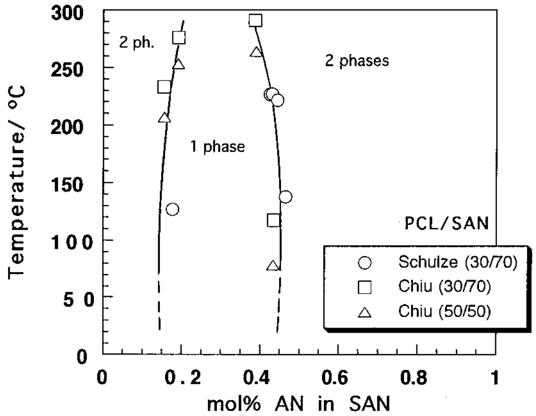


Figure 8. Miscibility window of PCL/SAN blends (phase diagram) taken from data in refs 4 and 24 (solid curve is hand drawn).

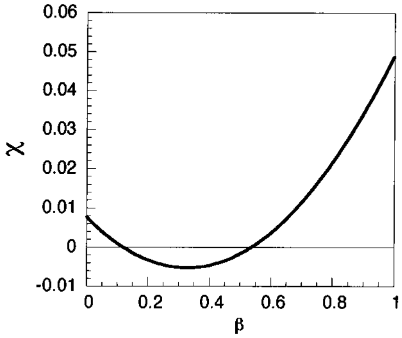


Figure 9. χ-parameter calculated by using three respective segmental χ-parameters ($\chi_{CL/S} = 0.0077$, $\chi_{CL/AN} = 0.049$ and $\chi_{S/AN} = 0.12$).

PCL/PS mixture ($\beta = 0$). High molecular weight PS and PCL are immiscible, while the heat of mixing of low molecular weight analogues was found to be negative. In the literature[16] another possible analogue for PCL, ethyl butyrate, mixed with ethylbenzene, also gives a negative heat of mixing of -0.28 cal cm^{-3} as the interaction energy density **B**. The negative sign for these mixtures seems to be correct. Moreover PS (M_n = 950 g mol^{-1}) and PCL (13 700) oligomers were found to be miscible.[22] The χ-parameter calculated from respective segmental χ-parameters shown in our previous work[23] is plotted in Figure 9, which gives a positive χ for the PCL/PS mixture. At present the reason for the discrepancy between Figures 7 and 9 is not clear. There are basically four contributions to the χ-parameter based on the equation of state theories: exchange energy, free volume, size effect,[17] and other noncombinatorial entropy effects. The other effects may be able to overcome the negative exchange energy term (the negative heat of mixing) for polymer–polymer mixtures, leading to immiscibility of high molecular weight PS with PCL. As another possibility, end-group effect in interactions may not be negligible for low molecular weight analogues.

Concluding Remarks

A detailed study of specific interactions in PCL/SAN blends was performed by using low molecular weight analogues. The FTIR measurements indicated the presence of the specific interactions from the shifts of spectral peaks. This means that the miscibility window in these blends cannot be interpreted as a "mixing without any specific interactions". From the calorimetric measurements, the existence of miscibility window in this blends was also shown to be mainly a result of breaking and formation of specific interactions, while the effects of free volume, different segmental size, and other noncombinatorial entropy cannot be overlooked. Comparing the binary interaction model using parameter **B** (binary interaction energy density) with this approach using self-interaction (E_{ii}) and association (E_{ij}) energies, it is possible to mention these advantages of the new calculation. The value **B** (or ΔE_{ij}) shows only the value of enthalpy of mixing (exothermic or endothermic), but does not make the presence of specific interactions clear. In other words, it cannot be compared with the FTIR results. In contrast, the respective association energies E_{ij} have a linear relationship with the shift of the FTIR peak. This connection of two independent experiments gives us confidence in the results for specific interactions.

The exothermic or endothermic mixing is a result of breaking of self-interactions (i–i) and formation of new respective interactions (i–j), where in the present study the ΔE_{ij} values were of 1 order of magnitude lower than E_{ii} and E_{ij} values. This also shows the importance of the measuring of self-interaction and association energies.

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References and Notes

(1) Kammer, H. W. *Acta Polym.* **1986**, *37*, 1.
(2) Cruz-Ramos, C. A.; Paul D. R. *Macromolecules* **1989**, *22*, 1289.
(3) Pfennig, J.-L. G.; Keskkula H.; Barlow J. W.; Paul, D. R. *Macromolecules* **1985**, *18*, 1937.
(4) Chiu, S. C.; Smith, T. G. *J. Appl. Polym. Sci.* **1984**, *29*, 1797.
(5) Kambour, R. P.; Bendler, J. T.; Bopp, R. C. *Macromolecules* **1983**, *16*, 753.
(6) ten Brinke, G.; Karasz, F. E.; MacKnight, W. J. *Macromolecules* **1983**, *16*, 1827.
(7) Paul, D. R.; Barlow, J. W. *Polymer* **1984**, *25*, 487.
(8) Stein, D. J.; Jung, R. H.; Illers, K. H.; Hendus, H. *Angew. Makromol. Chem.* **1974**, *36*, 89.
(9) Chiou, J. S.; Paul, D. R.; Barlow, J. W. *Polymer* **1982**, *23*, 1543.
(10) Hammer, C. F. *Macromolecules* **1971**, *4*, 69.
(11) Zakrzewski, G. A. *Polymer* **1973**, *14*, 347.
(12) Goh, S. H.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1982**, *22*, 34.
(13) Alexandrovich, P.; Karasz, F. E.; MacKnight, W. J. *Polymer* **1977**, *18*, 1022.
(14) Janarthanan, V.; Kressler, J.; Karasz, F. E.; MacKnight, W. J. *J. Polym. Sci., Polym. Phys. Ed.* **1993**, *31*, 1013.
(15) Harris, J. E.; Paul, D. R.; Barlow, J. W. *Polym. Eng. Sci.* **1983**, *23*, 676.
(16) Brannock, G. R.; Barlow, J. W.; Paul, D. R. *J. Polym. Sci., Polym. Phys. Ed.* **1990**, *28*, 871.
(17) Kammer, H. W.; Inoue, T.; Ougizawa, T. *Polymer* **1989**, *30*, 888.
(18) Painter, P. C.; Graf, J. F.; Coleman, M. M. *Macromolecules* **1991**, *24*, 5630.
(19) Mittal, K. L.; Anderson, H. R. *Acid-Base Interactions: Relevance to Adhesion Science and Technology*; VSP: Utrecht, The Netherlands, 1991.
(20) Fowkes, F. M.; Tischler, D. O.; Wolfe, J. A.; Lannigan, L. A.; Ademu-John, C. M.; Halliwell, M. J. *J. Polym. Sci.: Polym. Chem. Ed.* **1984**, *22*, 547.
(21) Drago, R. S.; Vogel, G. C.; Needham, T. E. *J. Am. Chem. Soc.* **1971**, *93*, 6014.
(22) Nojima, S.; Satoh, K.; Ashida, T. *Macromolecules* **1991**, *24*, 942.
(23) Kressler, J.; Svoboda, P.; Inoue, T. *Polymer* **1993**, *34*, 3225.
(24) Schulze, K.; Kressler, J.; Kammer, H. W. *Polymer* **1993**, *34*, 3704.

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