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Analog Calorimetry to Screen for Polyketone Blends

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Technical Progress Report **WRC 310–89**
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ABSTRACT

Polymers containing nitrile, phenol, anhydride, carboxylic acid, and ethylene oxide groups are excellent candidates to form miscible blends with CARILON® Polymer. Miscibile blends are of interest to shift the glass transition of polyketone away from ambient temperature and/or improve barrier properties. These candidate polymers have been identified through an analog calorimetry program. Low molecular weight compounds containing these functional groups mix exothermically with low molecular weight models of polyketone.

This report will be of interest to researchers concerned with a) mixtures of CARILON™ Polymer with additives and/or other polymers, and b) thermodynamics of polymer blends in general.

TECHNICAL PROGRESS REPORT WRC 310-89

ANALOG CALORIMETRY TO SCREEN FOR POLYKETONE BLENDS

by

R. N. French

SUMMARY

In 1987 we initiated an analog calorimetry program to evaluate the miscibility of polymer blends containing CARILON™ Thermoplastic Polymer. This work was done in conjunction with blending studies in the Exploratory Group of the Polymer Systems department. The incentive for this work was to a) identify/eliminate candidates for further testing, b) gain an understanding of how CARILON™ Polymer interacts with the functional groups on other polymers, and c) help develop the patent position on CARILON™ Polymer blends.

Underlying this project was the hypothesis that miscibility between two polymers requires exothmeric mixing. Therefore, we measured the heats-of-mixing of low molecular weight compounds, chosen to model the functional group interactions between various commercial polymers and polyketone.

We have identified several functional groups which show favorable specific interaction with ketones. The most important of these are the nitrile, phenol, carboxylic acid, ethylene oxide, and anhydride groups. The analog results are generally consistent with observations of actual polymer behavior. Miscible blends have been identified which may shift the glass transition of polyketone and improve the barrier properties.

This report comprises four sections. The Introduction discusses the importance of polymer blends and the thermodynamics of the mixing process. The Experimental section details the heat-of-mixing experiments used to derive interaction parameters. The Discussion section covers selection of analogs, chemical, composition and temperature effects, and interpretation of specific interactions. Modelling approaches and application to specific blends are also discussed. The Future section presents plans to extend the application and interpretation of these results.

INTRODUCTION

General Background

Polymer blends are of increasing commercial importance for three reasons. First they allow the "fine-tuning" of properties to match applications; a range of properties are accessible for a product by varying the composition. Second, blending can overcome processing problems. Third, an expensive polymer can be blended with an inexpensive material to obtain a cost effective product.

Excellent reviews on recent progress in polymer blending are available by Paul and Barlow[1] and in the Encyclopedia of Polymer Science and Engineering.[2]

The degree of mixing in polymer blends and the terms miscibility and compatibility are controversial subjects. When applied to small compounds, miscibility implies a thermodynamically stable state in which the components are intermingled on a molecular basis. However, polymer molecules are orders of magnitude larger. Slow diffusion rates make equilibrium difficult to achieve. Therefore, processing conditions influence the observed phase behavior in a sample. In addition, a fine dispersion of one polymer in a matrix of another often appears indistinguishable from a true "molecular" mixture.

Many popular tests for miscibility differ as to their detectable levels of mixing. Therefore more than one test should be run before drawing conclusions. Two widely used methods are optical techniques and Tg measurements. Cloudy blends at equilibrium are classified immiscible, although the converse can not be assumed. The presence of one Tg indicates a miscible blend. However, the scale of mixing to which Tg is sensitive remains unresolved.

From a practical standpoint, mixing on the molecular level is not necessary for a blend to have favorable properties. In fact, most commercial blends are immiscible. Their good properties arise from morphologies such as interpenetrating networks or the fine dispersion of one polymer in another. Compatibility is the term often applied to blends with favorable interactions regardless of whether the polymers are truly miscible.

However, true miscibility is necessary for blends to exhibit nonadditivity and even extrema in certain properties, such as sorption,

diffusion, and Tg. Most homopolymer blends are immiscible and consist of multiple amorphous phases, each being an essentially pure polymer.

Thermodynamic Approach

The thermodynamic basis for miscibility requires that the excess Gibbs energy of mixing, ΔG^M, be (-), and that the second derivative of this function with respect to composition be (+):

$$\Delta G^M < 0 \qquad (1)$$

and

$$\partial \Delta G^M / \partial \phi_1 > 0 \qquad (2)$$

Satisfaction of the first but not the second criterion indicates partial miscibility.

ΔG^M comprises enthalpic and entropic contributions:

$$\Delta G^M = \Delta H^M - T\Delta S^M \qquad (3)$$

Miscibility between small molecules is driven either by a negative heat-of-mixing or a positive entropy-of-mixing. However, mixing large molecules contributes only a very small favorable entropy. As the size of the polymer chains increases, the combinatorial entropy goes to zero. Therefore miscibility between polymers is determined almost exclusively by enthalpic effects. Polymer blend miscibility can be predicted from heat-of-mixing behavior.[3]

Direct heat-of-mixing measurements involving polymers are difficult. However, Don Paul and coworkers at the University of Texas have developed an alternative means of determining polymer-polymer heat effects.[4] They find that the heat-of-mixing low molecular weight compounds is related to the heat effect on mixing polymers containing the same functional groups as the small molecules. Interaction parameters derived from these measurements can be used to predict phase behavior in blends containing homopolymers and random copolymers. Walsh and coworkers at Imperial College in London have also used this technique.[5] The analog molecules to model a particular polymer must be carefully chosen to simulate the interactions

between functional groups in the polymers. Typically molecules containing at least two repeat units are used.

The heats-of-mixing are generally reported as B_{12} values through a van Laar expression:

$$\Delta H^M/V = B_{12}\,\phi_1\,\phi_2 \qquad (4)$$

where the interaction parameter, B_{12}, is related to the Flory-Huggins parameter, χ_{12},:

$$\chi_{12} = B_{12}V_{ref}/RT \qquad (5)$$

The B_{12} values can be combined in a binary interaction model[6] to predict ΔH^M for ternary blends and blends containing copolymers:

$$\Delta H^M = \Sigma\, B_{ij}\,\phi_i\,\phi_{ij} \qquad (6)$$

Paul at the University of Texas has applied this model successfully to numerous blends. This model offers two ways to achieve exothermic heats-of-mixing, and hence miscibility.

1. For blends of homopolymers to be miscible, specific interactions between different functional groups must outweigh those between the same functional groups.
2. Blends containing copolymers also can be miscible due to strong interactions between functional groups on different polymers. However miscibility can also result from strong unfavorable interactions between the functional groups on the copolymer. In this case the mixing process replaces these interactions with less unfavorable ones. The net result is a (-) ΔH^M, although there are no strong specific interactions in the system.

Application To The CARILON™ Thermoplastics Polymer Project

In 1987 we initiated an analog calorimetry program to evaluate the miscibility of polymer blends containing CARILON™ Thermoplastic Polymer. This work was done in conjunction with blending studies in the Exploratory

Group of the Polymer Systems department. The incentive for this work was to a) identify/eliminate candidates for further testing, b) gain an understanding of how CARILON™ Polymer interacts with the functional groups on other polymers, and c) help develop the patent position on CARILON™ Polymer blends.

This approach does not address such practical concerns as: a) whether the thermodynamic equilibrium state can be reached through realistic processing conditions, and b) how blending affects crystallinity. However the screening calculations are a useful tool to guide and understand the experimental blend program.

EXPERIMENTAL

Most chemicals used as analogs were obtained from Aldrich or Kodak as the highest purity available and used as received. The sulfone and triketone analogs were prepared by Bob Kluttz of the Polymer Systems department.

Heats-of-mixing and heats-of-dilution were measured using a HART flow calorimeter. The principle and method of operation are described in reference 7. All analog pairs were checked for miscibility prior to measurement.

For analogs which are liquids at room temperature direct heats-of-mixing were measured. For analogs which are solids at room temperature solutions of the solid analog in the liquid analog were prepared. These were made at as high a concentration as possible. The heat-of-mixing of this solution versus the pure liquid analog was measured. This effectively gives the heat-of-dilution from high to low concentration.

The pulse heater was calibrated using the recommended standard for heats-of-mixing at 25°C, cyclohexane - hexane.[8] At high temperature the ethanol - water system[9] was used to verify the calibration.

The data from the direct heats-of-mixing were reduced as:

$$B_{12} = \Delta H^M / \phi_1 \, \phi_2 \qquad (7)$$

For the heats-of-dilution an apparent interaction parameter was calculated:

$$B_{app} = \Delta H^M / \phi_A \phi_B \quad (8)$$

where solution B comprises analog 2 in analog 1 at composition ϕ_2. By assuming a parabolic shape to the heat-of-mixing curve we calculate B_{12} from B_{app}:

$$B_{12} = B_{app} / (\phi_2^2) \quad (9)$$

Tables 1, 2, and 3 list the B_{12} values derived from the heat-of-mixing and heat-of-dilution data.

DISCUSSION

Choice of Analogs

Our initial efforts addressed the appropriate analog for polyketone. Table 2 compares B_{12} values obtained with three polyketone analogs: mono-, di-, and tri- ketones. Only the heats with chloroethylmethylether (CEME) show qualitative differences for the three ketones; we have no explanation for these data. However, for the other three test systems all ketones show exothermic behavior.

In principle we would prefer to use an analog containing as many repeat groups as possible, in order to minimize "end group" effects. However, the triketone has a high melting point necessitating heat-of-dilution measurements. The low solubility of the triketone resulted in very small heat effects. This caused large uncertainty in its B_{12} values. This probably accounts for the quantitative differences between the triketone and the smaller analogs in the heats with TEGME and glutaronitrile.

The triketone is not commercially available, but is prepared by R. Q. Kluttz of the Polymer Systems Department. This limits the number of studies possible. Acetonyl acetone (AA) and acetone are commercially available. We selected AA as the primary polyketone analog since it contains two repeat units and is less volatile.

Chemical vs. Physical Effects

Both physical interactions and chemical reactions can contribute to heats-of-mixing. Acetonyl Acetone (AA) can react to form dimethyl furan or methylcyclopentenone in acid or base respectively. Since

heats-of-reaction are significantly higher than heats-of-mixing, small amounts of reaction can interfere with our measurements. At 25°C and for low residence times (<1 min) we do not expect significant reaction. However, to verify this, we consulted E. Smutny and S. Mullin of the Polymer Systems Department. G. C. analysis of our mixtures showed no discernible reaction products.

Interpretation of the Specific Interactions

It is well established that miscibility in high molecular weight homopolymers requires specific interactions between the functional groups on the two polymers. Exothermic mixing indicates strong specific interactions. To identify the nature of these interactons requires an understanding of the chemistry of the functional groups involved.

Ketones are classified as Lewis bases due to the electron donating ability of the carbonyl group. Therefore we expect ketones to interact exothermically with Lewis acids through charge transfer (i.e. electron donor/acceptor). Endothermic heats are expected for mixing two Lewis bases. This approach rationalizes many of the B_{12} values reported in Table 1.

However, some of the specific interactions are not so obvious. For example carbonyl, ether, phenyl and nitrile groups are usually considered Lewis bases (electron donors). Therefore, the exothermic mixing of AA with glutaronitile, TEGME, MSA, EPON 825, and DPC are unexpected. In these systems the carbon of the AA carbonyl may be acting as a Lewis acid site. However, the presence of multiple functional groups in proximity makes it difficult to predict acceptor/donor strength.

One must be careful not to relate B_{12} directly to the strength of interaction between the carbonyl of AA and the functional groups of the other analogs. Mixing involves a change from two pure liquids to a homogeneous combination of the two. The enthalpy change reflects the difference in enthalpy of the mixture from the average of the pure components. Therefore, the strength of interaction in the mixture must be viewed relative to the interactions between like molecules which it replaces.

The analogs which can hydrogen bond to the ketone are of extreme interest. The diols mix the most endothermically with AA. At 25°C they exist in the pure state as chains of H-bonded complexes. However, at the other extreme, the most exothermic mixing is with dimethyl glutaric acid

(DMG), a diacid which exists as H-bonded dimers at 25°C. The entropy of mixing undoubtedly plays a role in mixtures involving strongly self-associating components. Therefore, a strictly enthalpic approach to these systems is questionable. The mean field approximation is suspect as well.

The previous discussion highlights the importance of experimentally probing the nature and strength of interactions between functional groups. It is not currently possible to a priori predict the sign of the heat-of-mixing for many important systems.

Alternative Modelling

So far we have assumed that the Gibbs energy of mixing for polymers is predominantly determined by the heat-of-mixing. We have further assumed that these heats-of-mixing can be represented by a mean field expression:

$$\Delta H^M = B_{12}\,\phi_1\phi_2 \qquad (10)$$

where ϕ_1 and ϕ_2 are volume fractions of polymers 1 and 2 and B_{12} characterizes the difference between 1-2, 1-1, and 2-2 interactions.

When two polymers interact only through dispersive and/or weak specific interactions these are good assumptions. However, when strong specific interactions occur, random mixing of functional groups is not realistic. A more complex composition dependence is needed. Strong interactions also imply that the entropy-of-mixing term which is traditionally used, is inadequate.

Where strong interactions occur, ΔH^M should be split into dispersive and specific interaction contributions:

$$\Delta H^M = \Delta H^{disp} + \Delta H^{spint.} \qquad (11)$$

An estimate of $\Delta H^{spint.}$ can be obtained by estimating ΔH^{disp} using solubility parameters. $\Delta H^{spint.}$ should be proportional to the number of functional groups in the polymer. Handling the entropy effect of specific interactions is more difficult. However qualitatively it should oppose the enthalpy effect.

Coleman and Painter[10] have recently developed a model for polymer blends in which polymer A hydrogen bonds both to itself and to polymer B. They represent the H-bonding effect on ΔG^M through the competition of association equilibria. Their expression for ΔG^M is:

$$\frac{\Delta G^M}{RT} = \frac{\phi_A}{N_A} \ln\phi_A + \frac{\phi_B}{N_B} \ln\phi_B + \chi_{AB}\, \phi_A\, \phi_B + \frac{\Delta G^H}{RT} \qquad (12)$$

where ΔG^H reflects the entropy and enthalpy changes due to shifts in the hydrogen bonding equilibria. The key parameters in their model are the equilibrium constants and enthalpies for forming the hydrogen bonded species. Often these can be derived from FTIR experiments.

Coleman and Painter have modelled blends containing polymers of interest for blending with polyketone, such as nylons, urethanes, polyacids, polyalcohols, and polyphenols. We would like to understand how the hydrogen bonding ability of polyketone relates to that of the other electron donors such as polyethers and polyesters. This would allow us to relate the considerable information on blends of hydrogen bonding polymers with polyethers and polyesters to analogous blends with polyketone. This type of analysis will be necessary to rationalize the observed heat effects involving H-bonding systems. We plan to address this issue in a future report.

Composition Effect

As indicated above, the use of the van Laar expression to represent heats in strongly interacting systems such as those involving H-bonding is questionable. Therefore we attempted to measure heats-of-mixing at several concentrations for most systems. In general, we found the heat vs. composition curves to be reasonably parabolic.

Figures 1 and 2 show some heat curves for amide and carboxylic acid systems. The expected H-bonding in these systems does not seriously skew the curves. It appears that when heat effects are predominately endo- or exo-thermic the use of the van Laar expression is appropriate for our purposes. However, we have found that when the net heat effect is small, significant assymmetry can occur. For example, we have measured "S-shaped"

heat curves for an ether-urethane system where the endo- and exo-thermic contributions are closely balanced.

Temperature Effect

We have measured heats-of-mixing at high temperatures for several key systems. These were done to understand how interactions with polyketone analogs change with temperature. Most of our B_{12} values are at 25°C. These are applicable to blending by solution casting near room temperature but are removed from blend processing temperatures. We were interested to see if exothermic systems at 25°C could become endothermic at high temperatures. Such behavior would imply Lower Critical Solution Temperatures for the analogous polymer blends. These blends would be immiscible if processed above the LCST.

We are also interested in how changes in hydrogen-bonding with temperature affect heats-of-mixing. As temperature increases, self-association should decrease in these systems. One can speculate that at high temperature the enthalpy of mixing with acids, alcohols, amides, and urethanes will be governed not by the loss of self-association but by H-bonding with the ketone. This suggests that as temperature increases, the ΔH^M in these systems will become more exothermic and may go through minima. Therefore, blends with H-bonding polymers may be more miscible at high temperature than at 25°C.

Table 3 along with Figures 1 and 2 show the temperature dependence of heats for three classes of systems. We see no evidence of ΔH^M changing sign.

Relation to Observed Blend Behavior

In the following sections we discuss several specific systems of practical interest. Analog calorimetry shows a number of functional groups should interact favorably with polyketone. However, many of these are of limited interest to the blend program due to expected processing difficulties, limited commercial availability, and/or no expected benefit. Of immediate interest are blends which may improve toughness, barrier properties, shrinkage control, or melt stability.

1. Blends with poly(vinyl phenol) (PVPh).

The analog pair AA and 4-ethyl phenol (4EP) show the most exothermic mixing encountered in our calorimetry program. Previously reported FTIR results on AA + 4EP mixtures verify that the carbonyl of AA hydrogen-bonds to the phenol.

The analog behavior correctly predicts the observed miscibility of PVPh and polyketone. PVPh is a self-associating polymer. Upon mixing with polyketone, hydrogen bonds between hydroxyl groups are broken and reformed with carbonyls. In this system the net effect favors mixing. This is not always the case for mixtures of self associating polymers with polyketone.

2. Blends with poly(styrene co-acrylonitrile) (SAN).

Analog calorimetry shows evidence of favorable interactions between ketones and compounds containing nitrile groups. This strongly suggests that polyketone is miscible with polyacrylonitrile (PAN). However blends involving the homopolymer PAN are not commercially viable. Of much more interest are blends with copolymers containing nitrile groups. Application of the binary interaction model leads to the prediction that approximately 30% nitrile groups are required for a SAN to be miscible with CARILON Polymer.[11] J.M. Machado of Polymer Systems has confirmed miscibility between CARILON™ Polymer and a SAN containing 58% nitrile groups.[12]

3. Blends with polymers containing acid groups.

Blends with Nucrels (copolymers of ethylene and methacrylic acid) are being used to impact-modify and stabilize polyketone. We were interested in the degree of miscibility/compatibility between PK and the Nucrel family. To address this we have looked at heats for mixtures of AA with carboxylic acid analogs.

Don Paul at the University of Texas has used propionic acid (PA) unsuccessfully as an analog for poly(acrylic acid) (PAA). A copolymer of 92% styrene and 8% acrylic acid was found to be miscible with polymethylmethacrylate (MIB as analog) and showed strong interactions through FTIR. However the analog system of toluene (T), PA, and methyl

isobutyrate (MIB) showed no such interactions. Heats-of-mixing MIB with either PA or a PA/T premix were endothermic. This raised questions about the selection of analogs for strongly interacting systems such as carboxylic acids. Therefore, to verify our use of 2,4-dimethylglutaric acid (DMG) as a PAA analog we measured heats for MIB vs. DMG. Large exothermic heats indicate that DMG, with two carboxylic acid groups, behaves more like PAA than does the monofunctional PA.

The data in Table 3 shows that a high level of COOH produces exothermic mixing. This implies that polymers with high amounts of acid groups, such as poly(acrylic acid), are miscible with polyketone. However, as the COOH content decreases, the analogs mix endothermically implying that the corresponding polymers from immiscible blends with PK.

The amount of acid groups in Nucrels places them between octanoic acid and the limiting case of decane. The similar values for 2EHA and octanoic acid indicate that the location of the COOH is unimportant. Apparently steric and inductive effects do not noticeably affect ΔH^M. There are no significant changes with temperature except for DMGA. However the B_{12} values for DMGA may be misleading since they are based on heats-of-dilution. They are only applicable to AA rich compositions. Although the sign is certain, the magnitude of B_{12} is very sensitive to how well equation 4 represents ΔH^M across the entire range of mixture compositions.

In summary we can say that acid groups interact favorably with ketones. The number of acid groups in Nucrels is probably insufficient to give miscibility with PK. However favorable interactions between COOH and CO groups may affect the interface, and result in better adhesion between the phases.

4. Blends with nylons.

The B_{12} values for the AA/amide pairs show no evidence of favorable interaction at either low or high temperature. Although the CONH group

can undoubtedly hydrogen-bond to the CO of AA, the mixing process dilutes the self-association among amide groups. The loss in CONH-CONH interactions apparently outweighs the gain in CONH-CO interactions and yields a net (+) heat-of-mixing.

The calorimetry results imply that Nylon/PK blends are immiscible. Blends prepared by J.M. Machado of Polymer Systems are indeed two phase. However, there is evidence of a high degree of compatibility, probably due to chemical reactions at the interface.[13]

Small quantities of water probably convert some of the end amide groups of nylon to amine groups. The amine groups are suspected as the reactants with polyketone. To address this we measured the heat-of-mixing of pentylamine with AA. The exothermic effect was larger than can be expected from physical interaction alone. This implies that a chemical reaction occurs in this system. It appears that analog calorimetry can be a useful tool to screen for chemical as well as physical interactions.

5. Blends with polycarbonate (PC).

The heat of mixing a polyketone analog, acetonyl acetone (AA), with DPC is exothermic at 25, 100, and 190°C. Analysis of the melting point depression of DPC due to AA, using the Flory-Huggins theory, indicates that B_{12} is (-). This analog behavior clearly indicates a significant specific interaction. We would therefore predict that PC and polyketone should be miscible.

Melt extruded blends, prepared by W.P. Gergen of Polymer Systems, show no signs of compatibility. The behavior of PC and polyketone in the mutual solvent, HFIPA, also suggests incompatibility. Analysis of this polymer/polymer/solvent behavior using Flory-Huggins theory indicates a (+) value of B_{12}.

We have rationalized these conflicting indications through the structural difference between DPC and the PC repeat unit. DPC does not have the isopropyl group found in the PC repeat unit. This probably has

negligible effect on the specific interactions of the analog relative to the polymer. However, it does affect the dispersive forces.

Therefore, we expect the heat-of-mixing of PC with polyketone to have an additional endothermic contribution not found in the heat-of-mixing DPC and AA. This can rationalize endothermic mixing for the polymers given the exothermic mixing of the analogs.

In summary, we see no strong driving force for miscibility in polyketone blends with PC. However, we predict that these polymers should be close to miscibility due to the near balance of dispersive and specific interaction energies.

FUTURE WORK

In future reports we will discuss:

1. The application of the binary interaction model to miscibility predictions for blends with copolymers and ternary blends. Since such blends comprise at least three functional groups, additional B_{ij} values are needed.

2. The application of the Coleman-Painter H-bonding model to blends of CARILON™ Polymer and PVPh, polyurethanes, polyacids and polyalcohols.

3. The use of FTIR data in interpreting heat results.[14] Thermodynamic quantities of mixing express the change in state variables relative to the pure components. The presence or absence of specific interactions between groups must be inferred. For example, the net change in enthalpy for the mixing process can be treated as the sum of changes in dispersive forces, dipole-dipole, charge-transfer, and hydrogen-bonding interactions. However, the sign and magnitude of ΔH^M cannot be related a priori to any of these interactions in the absence of other information.

FTIR is a natural complement to thermodynamic measurements. It operates as a molecular probe of the state of individual groups on molecules. The characteristic frequencies of groups are very sensitive to

their environment and degree of interaction. The carbonyl (>C=O) stretching vibration in the 1600-1800cm^{-1} region is particularly well suited to study. Carbonyls involved in hydrogen-bonds generally appear at lower frequencies than "free" carbonyls. This shift in frequency can indicate the extent to which ketones hydrogen bond to alcohols, phenols, acids, and amides.

Care must be taken in interpreting spectral shifts since vibrational frequencies are sensitive to several parameters. However examination of spectra at several compositions, in conjunction with thermodynamic data, can give a good picture of what occurs in a mixture.

We are addressing three issues through FTIR:

A. detecting and identifying new interactions and changes in equilibria in mixtures.

B. comparing interactions in analogs to the interactions in their corresponding polymers.

C. understanding how the state of groups such as COOH change with temperature.

The FTIR spectra of PK blends are complicated by amorphous and crystalline bands. However AA is a liquid at 25°C and its spectra should resemble amorphous PK.

4. Analysis of the heats using group contribution approaches. This would allow estimation of the functional group content needed for miscibility. Such a solution-of-groups approach would not differentiate on the basis of heats among a blend of polymers, a random or block copolymer, a polymer solution, or a polymer/plasticizer. These systems would differ only through entropic and free volume contributions. Therefore this approach could be a powerful predictive tool and would indicate the importance of inductive and steric effects on interactions within and between polymers.

5. The application of information on interactions in polymer systems towards understanding transport and interfacial phenomena. Sorption in

polymer blends and copolymers depends on B_{ij}. Diffusion can also be related to B_{ij} through cohesive energy density. Statistical mechanical theories relate interfacial tension to B_{ij}. A set of B_{ij} values may be useful in explaining relative strengths of adhesion in immiscible blends.

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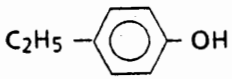
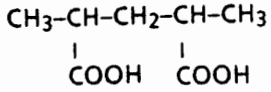
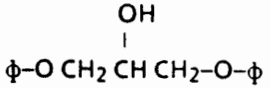
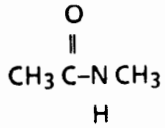
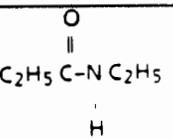
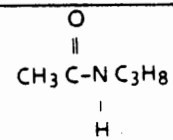
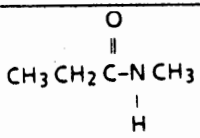
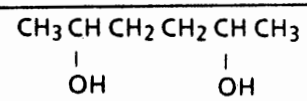
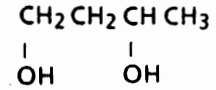
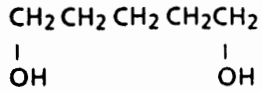
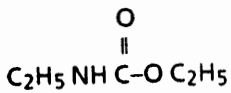
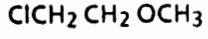
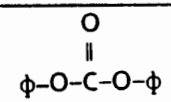
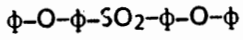
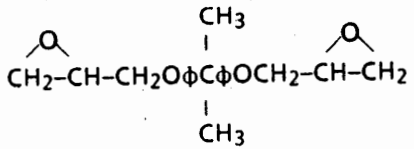
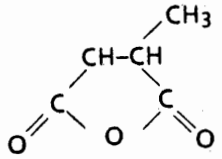
Table 1. Summary of Interaction Parameters for Analogs with Acetonyl Acetone at 25°C

Name	Structure	Polymer	B_{12}/Cal cm^{-3}	Specific Interaction	Comment
4 Ethyl Phenol (4EP)		PVP	-3.8	Ia	Cross outweighs self association
24 Dimethylglutaric Acid 24 DMG		Acrylic Acid Copolymers	-4.0	Ia	Cross outweighs self association
Diphenoxypropanol (DPP)		Phenoxy	-0.9	Ia Ic?	Cross outweighs self association
N Methylacetamide NMA		Nylon	+13.	Ia	Self outweighs cross association
N Ethylacetamide NEA		Nylon	+7.7	Ia	Self outweighs cross association
N Butylacetamide NBA		Nylon	~ +10.	Ia	Self outweighs cross association
N Methylpropionamide NMP		Nylon	+8 to +9	Ia	Self outweighs cross association
2,5 Hexanediol 25 HD		Polyalcohol PVA	~ +20	Ia	Self outweighs cross association

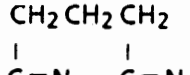
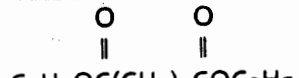
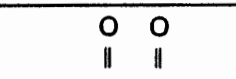
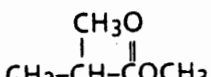
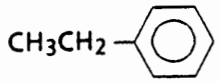
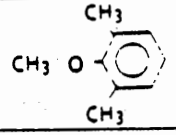
(continued)

Table 1 (Cont'd-1). Summary of Interaction Parameters for Analogs with Acetonyl Acetone at 25°C

Name	Structure	Polymer	B_{12}/Cal cm^{-3}	Specific Interaction	Comment
1,3 Butanediol 1.3 BD		PVA	~+13	Ia	Self outweighs cross association
1,5 Pentanediol 15 PD		PAA	~+10	Ia	Self outweighs cross association
Ethylurethane EU		"Hard" segment polyurethane	+6.1	Ia	Self outweighs cross association
2 Chloroethylmethylether CEME		PECH	-1.2	Ia	
Di phenylcarbonate DPC		PC	-1.9	Ic, III	
Ethersulfone S		PES	-1	Ic, III	
EPON 825			-0.7	II, IE	
Methylsuccinicanhydride MSA		Maleic anhydride copolymers	-2.5	III, II	

(continued)

Table 1 (Cont'd-2). Summary of Interaction Parameters for Analogs with Acetonyl Acetone at 25°C

Name	Structure	Polymer	B_{12}/Cal cm^{-3}	Specific Interaction	Comment
Tetraethyleneglycol dimethylether (TEGME)	$CH_3OC_2H_4OC_2H_4OC_2H_4OC_2H_4OCH_3$	PEO	-2.6	II	
Glutaronitrile (G)			-1.9	III	
Diethyladipate (DEA)		PCL	+2.0	III	Weak or absent outweighed by dispersive
Diethylterephthalate (DET)		PBT	+3.5	II, III	Weak or absent outweighed by dispersive
Methylisobutyrate (MIB)		PMMA	+1.8	III	Weak or absent outweighed by dispersive
Ethylbenzene (EB)		PS	+2.6	—	Weak or absent outweighed by dispersive
Hexane (H)	$CH_3(CH_2)_4CH_3$	PE	+6.0	—	Weak or absent outweighed by dispersive
Dimethoxymethane DMA	$CH_3OCH_2OCH_3$	Polyacetal	+0.4	II	Weak or absent outweighed by dispersive
26 Dimethylanisole		PPO	+0.9	Ic	Weak or absent outweighed by dispersive

TYPES OF SPECIFIC INTERACTIONS:

I. Electron transfer with O of C=O acting as donor

a) H-bonding with group capable of self association.

b) H-bonding with group that doesn't self associate

c) With πe- of aromatic

II. Electron transfer with C of C=O acting as acceptor

III. Dipole/dipole

TABLE 2

COMPARISON OF POLYKETONE ANALOGS

ANALOGS		B_{12}/CAL CM^{-3}
CEME	ACETONE	+0.1
	ACETONYLACETONE	-1.3
	TRIKETONE	+2.6
TEGME	ACETONE	-1.2
	ACETONYLACETONE	-2.5
	TRIKETONE	-8[a]
GLUTARONITRILE	ACETONE	-1.4
	ACETONYLACETONE	-1.9
	TRIKETONE	-4
DIPHENYLCARBONATE	ACETONE	-1.6
	ACETONYLACETONE	-1.9

a Due to the low solubility of the triketone in TEGME, this value has a larger than usual uncertainty.

TABLE 3. HEATS-OF-MIXING WITH ACETONYL ACETONE

Analog (Polymer)	Structure	CH_N/X	T/°C	$B_{12}/calcm^{-3}$
Dimethyl glutaric acid	$CH_3\text{-}CH(COOH)\text{-}CH_2\text{-}CH(COOH)\text{-}CH_3$	5/2	25	-4*
(Polyacrylic acid)			140	-14*
2-Ethyl hexanoic acid	$CH_3CH_2CH_2CH_2CH(COOH)CH_2CH_3$	7/1	30	7
(Nucrel)			100	10
			180	9
1-Octanoic acid (Nucrel)	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2\text{-}COOH$	7/1	180	9
1-Hexanoic acid (Nucrel)	$CH_3CH_2CH_2CH_2CH_2\text{-}COOH$	5/1	180	7
Decane	$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$	∞	180	13
Diphenylcarbonate (Polycarbonate)	$\phi\text{-}O\text{-}CO\text{-}O\text{-}\phi$		25	-1.9*
			100	-2.8*
			180	-3.4*
N-Methylpropionamide	$CH_3CH_2\text{-}CONH\text{-}CH_3$	3/1	25	8 to 9
			180	8 to 11

* Based on heats-of-dilution

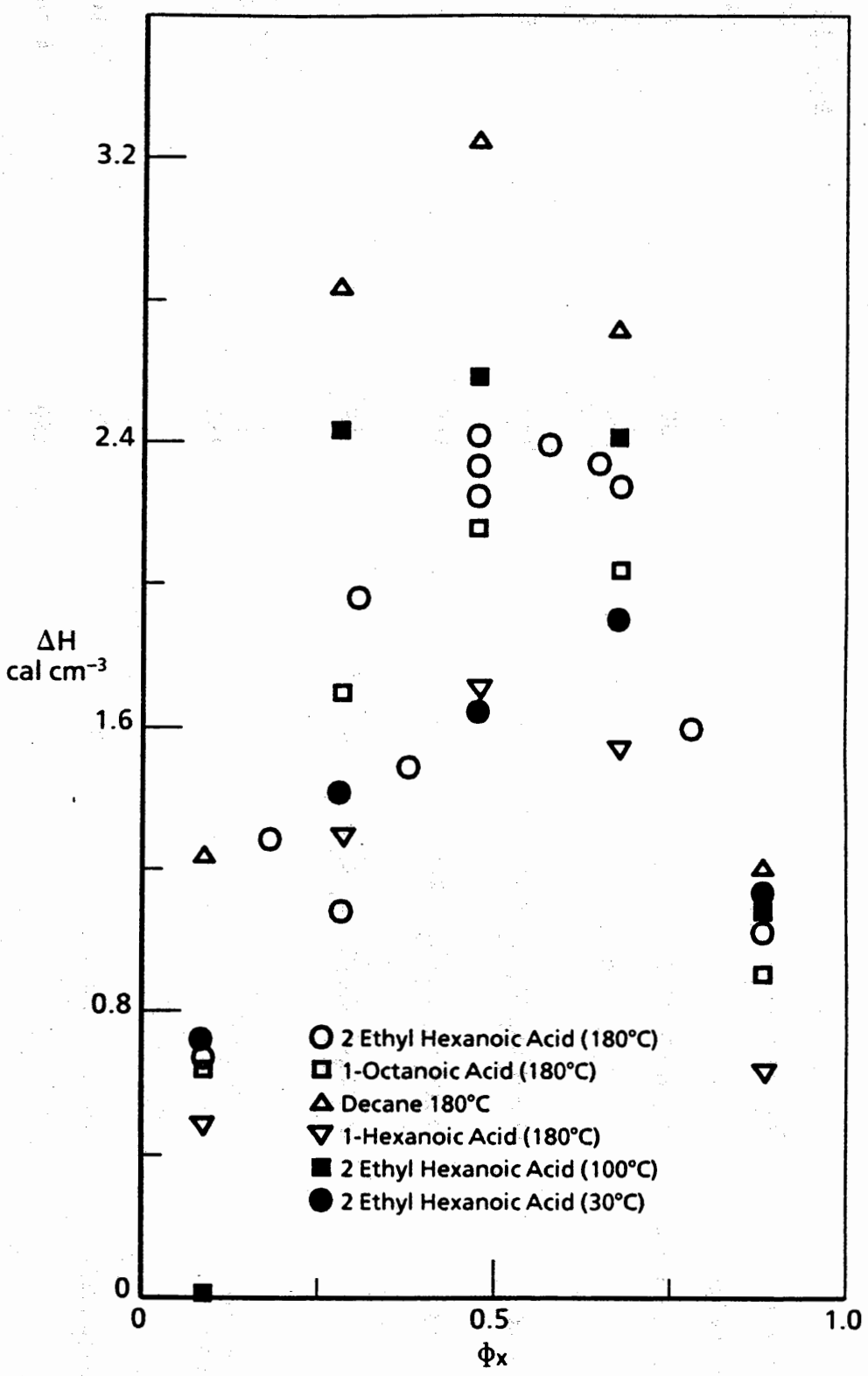


Figure 1. Heat-of-Mixing as a Function of Composition and Temperature for Acid Analogs with AA

014128-1

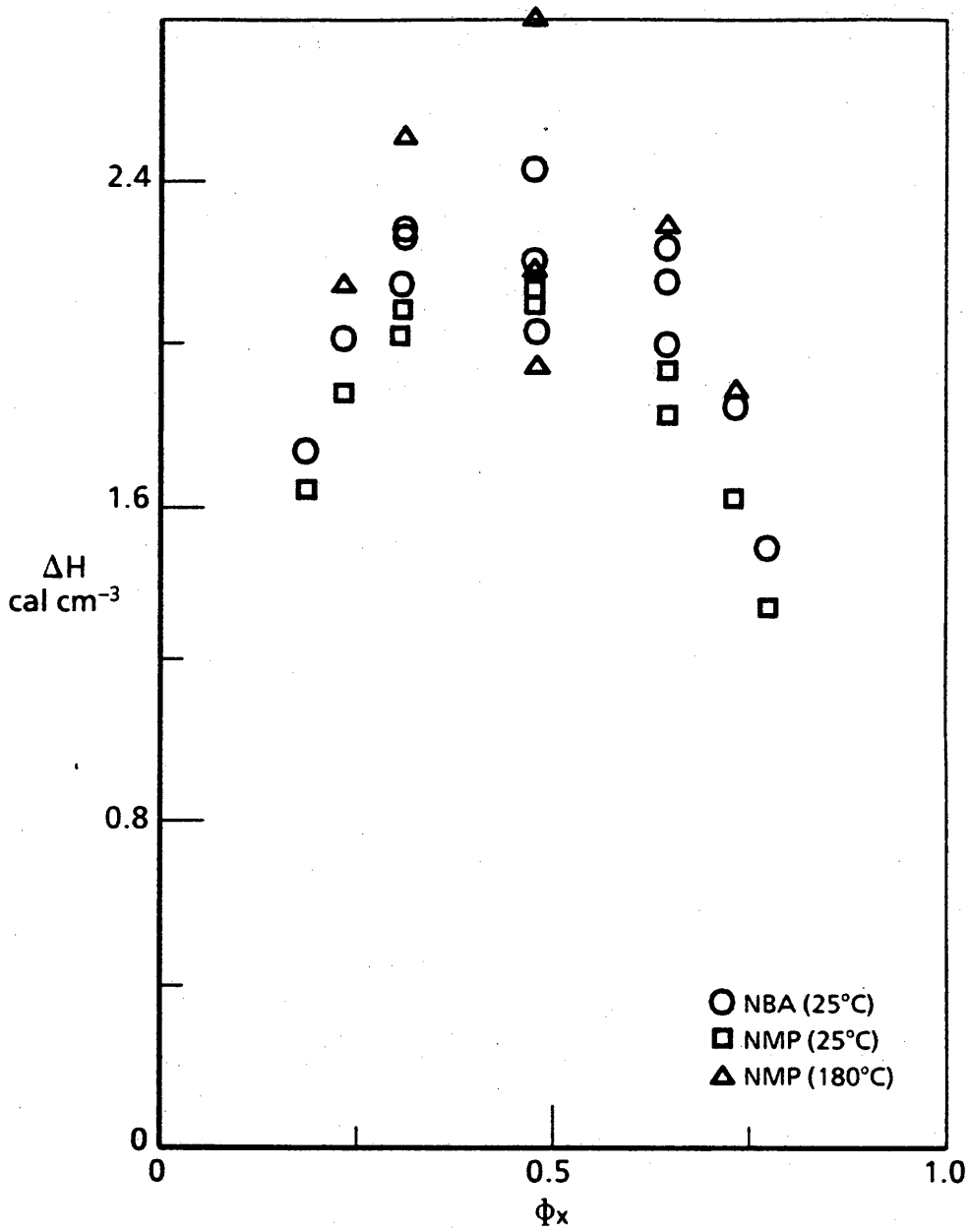
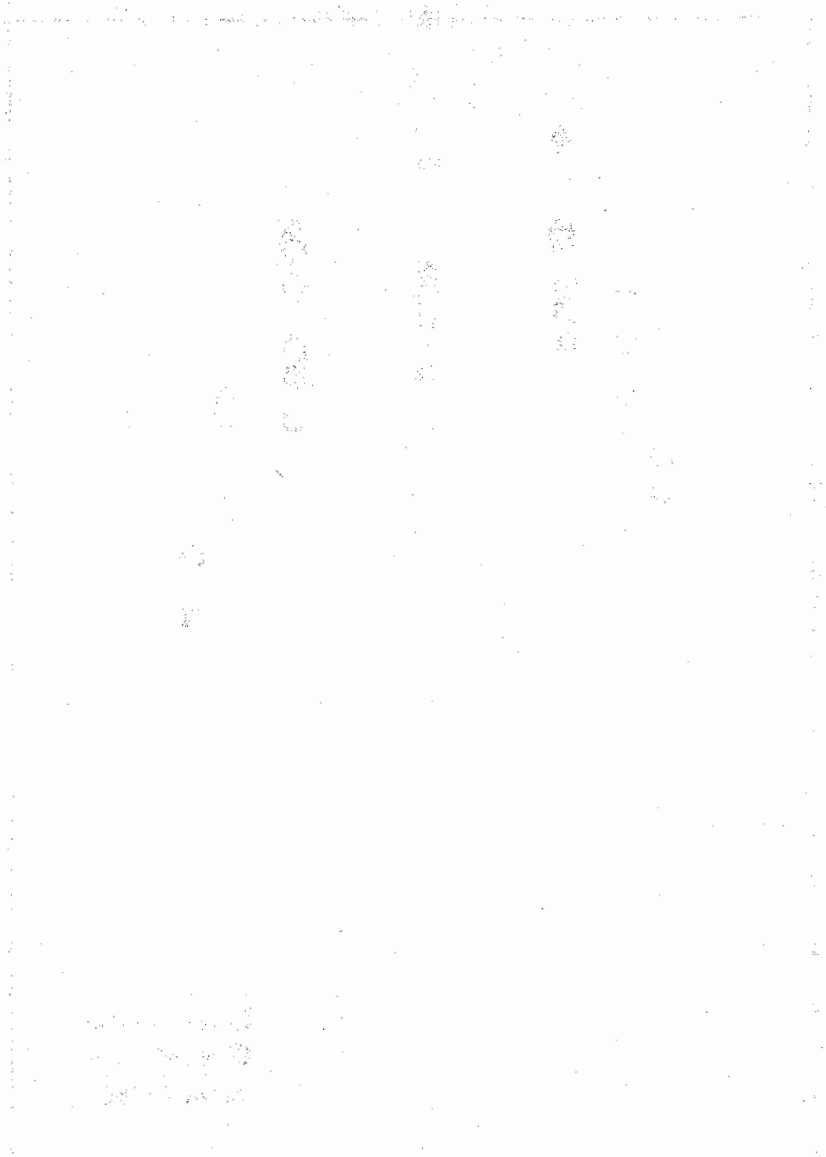


Figure 2. Heat-of-Mixing as a Function of Composition and Temperature for Nylon Analogs with AA

014128-2



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