Thermodynamics of the phase behaviour of poly(vinyl chloride)/aliphatic polyester blends

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A series of linear aliphatic polyesters having CH_2/COO ratios in their repeat units from 2 to 14 have been examined for miscibility with poly(vinyl chloride). There is a window of structures in the middle of this spectrum where miscibility is observed. At the low end there is a very sharp boundary lying between $CH_2/COO = 3$ and 4 dividing the polyesters which are immiscible with PVC from those which are miscible. At the high end the boundary is not so sharp but rather phase separation caused by a lower critical solution temperature occurs at progressively lower temperatures as CH_2/COO increases beyond 10. Thermodynamic interaction parameters for the miscible blends were obtained by analysis of the depression of the polyester melting point after correction for finite crystal thickness using the Hoffman–Weeks method. These results are compared with heats of mixing obtained directly using low molecular weight analogues of the polymers. The two results show very similar trends but are not quantitatively identical for reasons mentioned. A binary interaction model has been used to analyse the heat of mixing data, and it is concluded that there is a strong unfavourable intramolecular interaction between the $-CH_2-$ and $-COO-$ units in aliphatic polyesters which is an important factor in their miscibility with PVC and other polymers.

INTRODUCTION

It has been known for some time that poly(vinyl chloride), PVC, and poly(ε-caprolactone), PCL, form miscible blends[1,2]. More recently it has been shown that PVC is also miscible with other, but not all, aliphatic polyesters[3-11]. These findings can be conveniently organized in terms of the ratio of the number of aliphatic carbons, CH_2 or CH_x units depending on whether the structure is linear or branched, to the number of ester groups, COO, in the polyester repeat unit as found for blends of other polymers[12][18] with this homologous series. PVC does not appear to be miscible with any aliphatic polyester for which the CH_2/COO ratio is three or less but is miscible with those having this ratio equal to four or more; although, to date CH_2/COO ratios greater than seven have not been examined.

Ziska et al.[3] attempted to quantify this picture using thermodynamic interaction parameters estimated from the depression of the polyester melting points on blending with PVC. Limited results showed the interaction parameter becomes more negative as the CH_x/COO ratio increases and apparently is positive for values of three or less. These are unexpected results for two reasons. Firstly, it is obvious that this trend cannot continue indefinitely since PVC is not miscible with polyethylene. Based on the miscibility behaviour of PVC with copolymers of ethylene and carbon monoxide[19], it was reasoned that the in-

teraction parameters ought to be positive again at CH_2/COO ratios of about 12 or more[3]. Secondly, it has been suggested that the driving interaction for miscibility in these systems is one involving the polyester carbonyl with the PVC chlorine or the α-hydrogen based on spectroscopic observations[20-22] and, thus, it is curious that increasing the density of carbonyl in the structure would produce less favourable conditions for miscibility.

The issues mentioned above are important ones with respect to a general understanding of the influence of molecular structure on blend phase behaviour. Thus, an extensive study was undertaken to expand on the questions raised, and the results are reported here. This study has employed a wider range of aliphatic polyesters and additional techniques. Several commercially available polyesters with relatively low CH_2/COO ratios, not employed in the previous study[3], were examined to better define the boundary of miscibility at this end of the spectrum of the homologous series of aliphatic polyesters. To better define the limits of miscibility at the other end of the spectrum, several aliphatic polyesters having CH_2/COO ratios larger than those used in the previous study were synthesized for blending with PVC since these structures are not available from commercial sources.

Refined estimates of the blend interaction parameters were obtained from depression of the polyester melting points corrected for finite lamellar thicknesses[23,24]. This information was supplemented by direct calorimetry during mixing low molecular weight analogues of the various polymers[12,14]. These quantitative results are

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Table 1 Summary of polyesters used in this work

Polyester	Repeat unit	CH_2/COO	Abbreviation	Density (g cm^{-3})	$[\eta]$ (dl g^{-1})	T_m (°C)	T_g (°C)	Source
Poly(ethylene succinate)	$-(CH)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-$	2	PES	1.32	0.111[a]	100	−22	SPP[b]
Poly(propylene succinate)	$-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-$	2.5	PPS	1.29	0.163[a]	40	−38	SPP
Poly(ethylene adipate)	$-(CH_2)_2-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-$	3	PEA	1.21	0.11[c]	53	−50	SPP
Poly(propylene glutarate)	$-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-O-$	3	PPG	1.25	0.104[a]	39	−70	SPP
Poly(propylene adipate)	$-(CH_2)_3-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-$	3.5	PPA	1.28	0.097[a]	37	−69	SPP
Poly(butylene adipate)	$-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-$	4	PBA	1.13	0.157[c]	53	−70	SPP
Poly(ε-caprolactone)	$-(CH_2)_5-O-\overset{O}{\overset{\|}{C}}-$	5	PCL	1.095	0.67[d]	63	−71	Union Carbide (PCL-700)
Poly(butylene sebacate)	$-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-$	6	PBS	1.136	0.166[a]	62.6	−70[e]	Synthesized
Poly(hexamethylene sebacate)	$-(CH_2)_6-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-$	7	PHS	1.03	0.51[c]	68.9	−70	SPP
Poly(butylene dodecamethylene dicarboxylate)	$-(CH_2)_4-O-\overset{O}{\overset{\|}{C}}(CH_2)_{12}-\overset{O}{\overset{\|}{C}}-O$ — 8	8	PBDO	1.085	0.15[a]	76	−73[e]	Synthesized
Poly(dodecamethylene adipate)	$-(CH_2)_{12}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-$	8	PDOA	1.17	0.25[a]	77	−75[e]	Synthesized
Poly(decamethylene sebacate)	$-(CH_2)_{10}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_8-\overset{O}{\overset{\|}{C}}-O-$	9	PDS	1.15[e]	0.28[a]	75	−75[e]	Synthesized
Poly(decamethylene decamethylene dicarboxylate)	$-(CH_2)_{10}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-$ — 10	10	PDEDE	1.1[e]	0.28[a]	82.5	−77[e]	Synthesized
Poly(dodecamethylene decamethylene dicarboxylate)	$-(CH_2)_{12}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{10}-\overset{O}{\overset{\|}{C}}-O-$ — 11	11	PDODE	1.1[e]	0.30[a]	84.4	−78[e]	Synthesized
Poly(dodecamethylene dodecamethylene dicarboxylate)	$-(CH_2)_{12}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{12}-\overset{O}{\overset{\|}{C}}-O-$ — 12	12	PDODO	1.1[e]	0.29[a]	89.2	−78[e]	Synthesized
Poly(hexadecamethylene dodecamethylene dicarboxylate)	$-(CH_2)_{16}-O-\overset{O}{\overset{\|}{C}}-(CH_2)_{12}-\overset{O}{\overset{\|}{C}}-O-$ — 14	14	PHEDO	1.08[e]	0.30[a]	93.5	−79[e]	Synthesized

[a] Measured in chloroform at 25°C
[b] SPP = Scientific Polymer Products
[c] Measured in benzene at 25°C
[d] Measured in benzene at 30°C
[e] Estimated by group contribution method given in D. W. Van Krevelan, 'Properties of Polymers' Elsevier Scientific Publishing Co., 1976.

examined in terms of a binary interaction model recently proposed for blends involving copolymers[25] by subdividing the structure of PVC and the polyesters into small interacting units. The various experimental findings combine to form a consistent physical picture of the phase behaviour for these blend systems. The binary interaction model appears to provide a useful way of understanding the experimental observations.

MATERIALS AND PREPARATION PROCEDURES

The poly(vinyl chloride) used in this work was a commercial product of Diamond Shamrock with a density of 1.385 g cm^{-3} and a viscosity average molecular weight of 45 300 determined in THF at 25°C. Several polyesters with small CH_2/COO ratios, not examined in the previous study[3], were obtained from commercial sources and are listed in *Table 1* along with pertinent characterizing information. However, polyesters with higher CH_2/COO ratios were not available from any known sources so the needed polymers, shown also in *Table 1*, were synthesized and characterized as described below.

The appropriate diols and dibasic acids to form the polyesters in *Table 1* having CH_2/COO of 6 or greater (except PHS) were polymerized in the presence of *p*-toluenesulphonic acid catalyst using standard polycon-
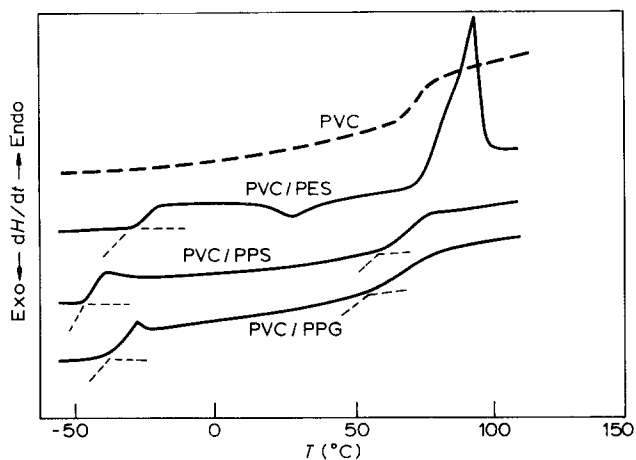
Figure 1 Thermograms for immiscible blends of the polyesters PES, PPS, and PPG with PVC, containing 50% by weight of PVC and the polyester indicated, and for pure PVC

densation procedures[26,27]. The reaction was continued until no further water condensate was collected. The products were purified by repeated dissolution and precipitation. Intrinsic viscosities were determined in chloroform at 25°C. Based on estimates of the Mark–Houwink parameters[16], these polyesters have molecular weights in the range of 5.0–5.5×10^3.

The thermal properties listed in *Table 1* were obtained, where possible, by differential scanning calorimetry. However, for most of the polyesters no glass transition temperature could be detected by d.s.c. owing to their very high crystallinity. For these cases, the glass transition temperature was estimated using a group contribution method[28].

Blends of PVC with the various polyesters were prepared in solution using tetrahydrofuran as solvent at elevated temperature as needed. Solvent was removed by heating in a vacuum oven for three to five days[28].

GLASS TRANSITION BEHAVIOUR

A central objective of this study was to determine which of the polyesters listed in *Table 1* form homogeneous blends with PVC at equilibrium in the amorphous state. The appearance of a single composition dependent glass transition is a useful means of demonstrating miscibility; however, for many of the present blends this approach is severely limited by the high level of polyester crystallinity which develops and makes this transition below the limits of detection because of the greatly reduced amount of amorphous material present. This section summarizes the information obtained using both thermal analysis and dynamic mechanical properties. These results, while less than completely conclusive in some cases, when combined with other observations presented subsequently allow definitive conclusions to be reached about the phase behaviour in every case. The instruments used were a Perkin-Elmer DSC-2 and a Rheovibron each outfitted with dedicated computers for automated operation and data analysis or display. Except where noted, the d.s.c. was used at a heating rate of 20°C min^{-1} for T_g determination. The Rheovibron was operated at 110 Hz and a heating rate of 1° to 2°C min^{-1}.

The discussion will concentrate first on establishing phase behaviour with PVC for polyesters having low

CH_2/COO ratios and then on the polyesters having high CH_2/COO ratios. *Figure 1* shows thermograms for each of the first three polyesters listed in *Table 1* when blended in equal weight proportions with PVC. The glass transitions noted correspond rather closely to those of the pure components, and this is the case for all other blend proportions. The melting endotherm for PES obscures the PVC glass transition. All three polyesters gave blends which were visually inhomogeneous and opaque at all temperatures. In view of these facts, the polyesters having CH_2/COO ratios of 2, 2.5 and 3 may be regarded as immiscible with PVC. This conclusion for PES is the same as that given by Ziska et al.[3]; however, the mixtures with PVC of the other two polyesters have not been studied previously. It is interesting to note that poly(propylene glutarate) has three aliphatic carbons per ester linkage just as poly(ethylene adipate)[3] does and both are immiscible with PVC despite the different ways in which these groups are located in the repeat unit. This suggests that miscibility with PVC is more a function of the CH_2/COO ratio than the arrangement of these units. Based on this, it is not surprising that poly(propylene succinate), $CH_2/COO = 2.5$, is immiscible with PVC.

Poly(propylene adipate) or PPA, $CH_2/COO = 3.5$, forms transparent blends with PVC when the PPA content is less than 25% and cloudy ones at higher concentrations. As seen in *Figure 2*, these regions correspond to miscible and partially miscible mixtures based on the T_g behaviour. Thus, PPA is right on the border of miscibility with PVC as the polyester structure is varied since polyesters having CH_2/COO equal to or greater than four form miscible systems while those with three or less form immiscible ones.

It is interesting to examine the effect of structural variations of PPS and PPA on miscibility with PVC. In each case, replacing the propylene unit with a neopentyl
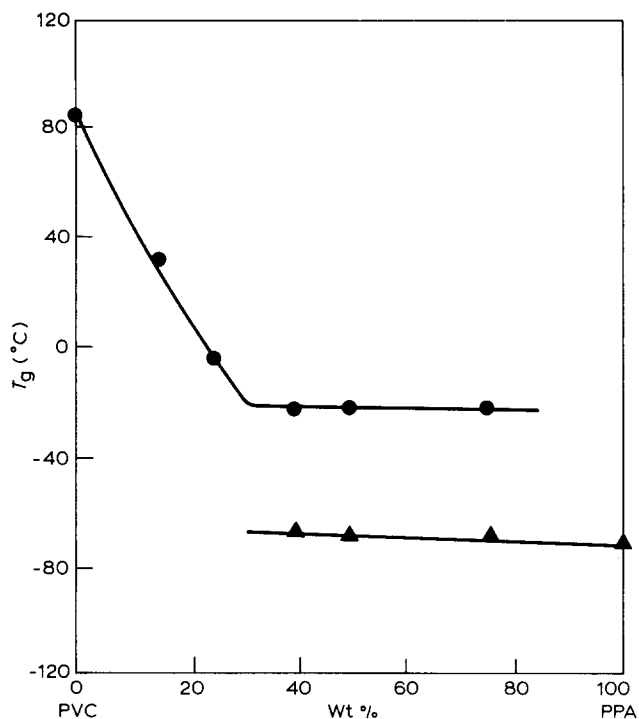

Figure 2 Glass transition behaviour of PVC–PPA blends showing miscibility over only a portion of the composition spectrum
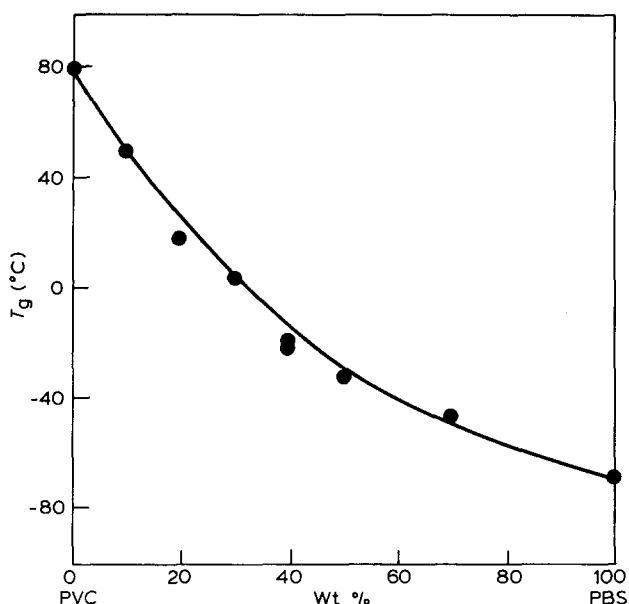
Figure 3 Glass transition behaviour for miscible PVC–PBS blends. Liquid N_2 quench, heating rate = 40°C min^{-1}

unit, i.e.

$$-CH_2CH_2CH_2- \quad \rightarrow \quad -CH_2-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2-$$

leads to miscibility with PVC as reported by Ziska et al.[3] and by Goh et al.[8]. Introduction of branching tends to decrease the propensity for aliphatic polyesters to be miscible with polycarbonate[12] and the polyhydroxy ether of bisphenol A[13]. However, for PVC it appears that the primary effect is the CH_x/COO ratio[3,4,7] rather than arrangement of these groups in the repeat unit. This suggests that specificity of the interactions involved is not very great.

In the previous study[3], polyesters with CH_2/COO ratios of 4, 5 and 7 were found to be miscible with PVC. Although no polyester with $CH_2/COO = 6$ was studied, it would be expected to also form miscible blends. This is confirmed here using poly(butylene sebacate), PBS. *Figure 3* shows the single composition dependent T_g expected. All glass transitions shown there were obtained after quenching the samples from the melt state at the fastest cooling rate possible with the cold finger of the d.s.c. dipping in liquid nitrogen. Samples quenched in this manner were almost totally amorphous, and their glass transitions do not show the complexities which accompany crystallization of the polyester component[18].

The remainder of the polyesters in *Table 1* have CH_2/COO ratios higher than those previously examined for miscibility with PVC. Because of their structure, they tend to have both high crystallinity and rapid crystallization rates which make experimental construction of diagrams like that in *Figure 3* very difficult[18]. *Figure 4* shows an attempt to establish such diagrams for three of these polyesters having $CH_2/COO = 8$, 9 and 10. Single composition dependent glass transitions were observed up to polyester contents of 20 to 30% after which no glass transitions could be detected by d.s.c. Rapid quenching failed to resolve this difficulty. The T_g's observed do extrapolate to the estimated T_g for the individual polyes-

ters in a reasonable fashion as seen in *Figure 4*. Similar behaviour was noted for the polyesters in *Table 1* having $CH_2/COO = 11$, 12 and 14.

Additional information about the glass transition behaviour was obtained for blends with selected polyesters using the Rheovibron. Results are shown in *Figure 5*. Data for the pure polyesters could not be obtained since each of them was too brittle for these mechanical measurements. Addition of polyester to PVC resulted in a decrease of the storage modulus, E'. In each case the α peak in the loss modulus E'', shifted to a lower temperature as polyester was added to PVC. The β peak in E'' diminished in magnitude, shifted to a lower temperature, or disappeared in every case as polyester was added to PVC. For all blends, the α peak or T_g is broader than it is for pure PVC. Broadening becomes greater as more polyester is added and as the CH_2/COO ratio for the polyester increases. Generally, this indicates larger composition fluctuations in the mixture. *Figure 6* shows the temperature location of the α peak in E'' versus blend composition for two of the polyesters, PBS and PDOA. The two curves drawn in each case attempt to show how these peak temperatures would be situated if the samples were completely amorphous or if they were semi-crystalline. Only in the former case would the data extrapolate to that estimated for the pure polyester since crystallinity will increase the PVC content of the amorphous phase[18] and probably will raise the T_g of amorphous phase even of the pure polyester[1] owing to motional restraints imposed on the amorphous segments by the crystallites. Blends having low polyester contents, 25% or less, were essentially amorphous and fall on the lower curves drawn in *Figure 6*. The appearance of crystallinity at higher polyester contents is the basis for the upper curves drawn.

While less conclusive than desired, the T_g behaviour of PVC blends with the polyesters having CH_2/COO in the range of 8 to 14 is consistent with these being miscible systems. More definitive evidence is described next.

LIQUID–LIQUID PHASE BEHAVIOUR

As noted previously[29], miscible polymer blends often undergo phase separation on heating owing to the existence of a lower critical solution temperature, LCST. The observation of such a cloud point curve is then direct evidence that complete thermodynamic miscibility exists at all lower temperatures provided an upper critical solution temperature, UCST, is not reached on cooling.
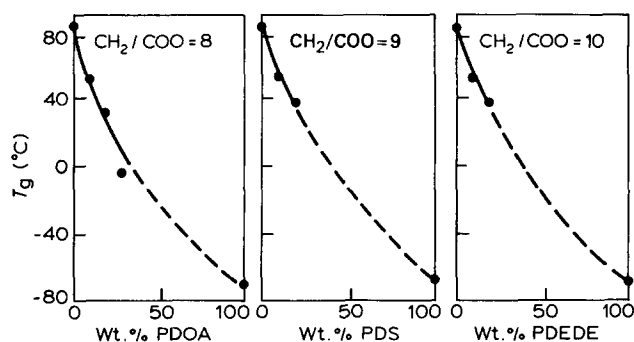

Figure 4 Glass transition behaviour obtained by d.s.c. for blends of PVC with PDOA, PDS and PDEDE. Polyester crystallinity prevented observation of blend T_g in region where curves are dashed
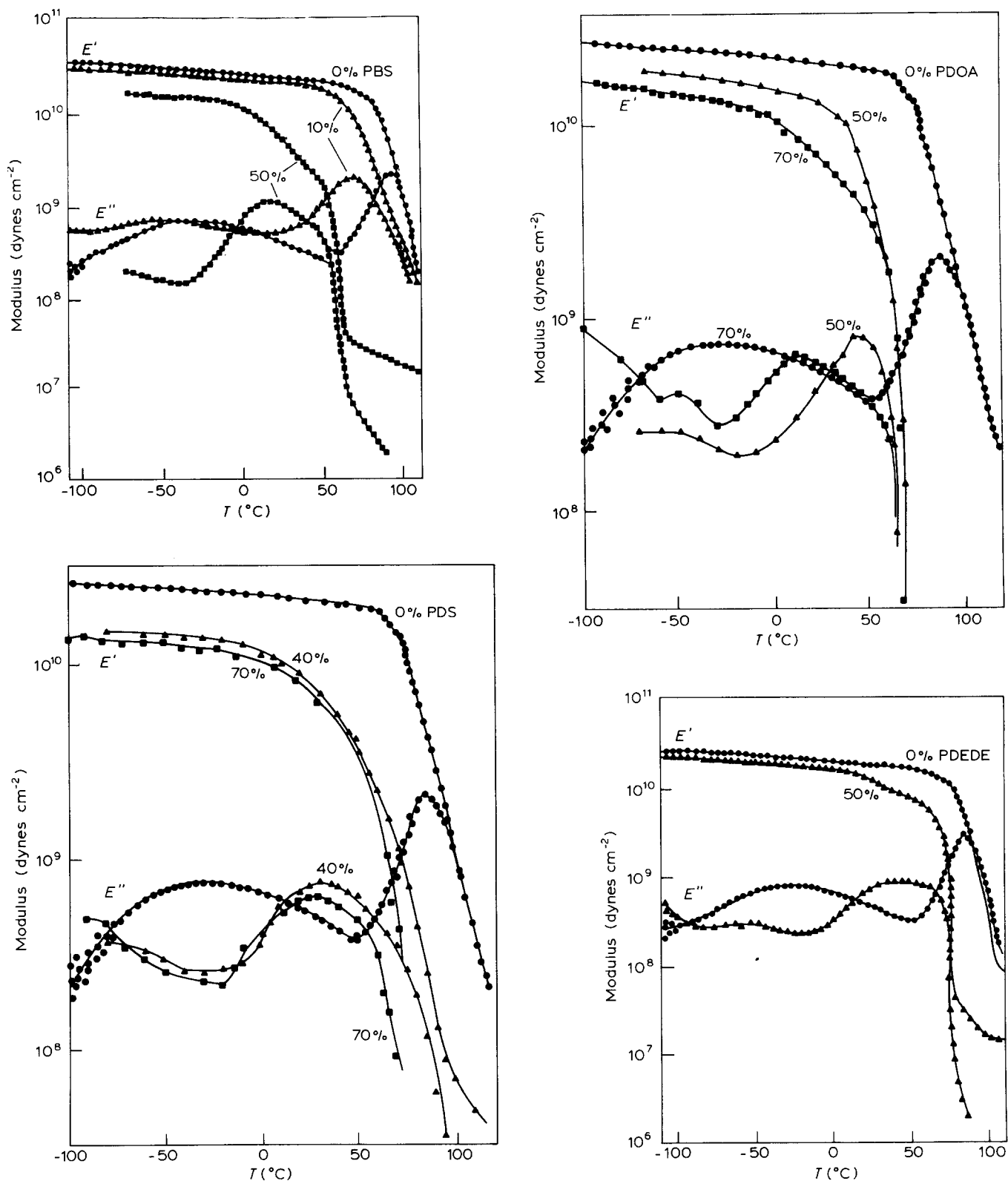
Figure 5 Dynamic mechanical properties of blends of PVC with four polyesters. Frequency = 110 Hz

Generally, the cloud point curve is lower the less negative the interaction parameter is but will be influenced by differences in the equation of state characteristics of the two components[30].

Nearly all of the blends examined here were cloudy to some degree at room temperature owing to the crystallinity of the polyester component. However, for $CH_2/COO \geqslant 4$, they all became transparent when heated above the melting point of the polyester. For those with CH_2/COO of ten or less, they remained clear on heating and did not show any evidence of phase separation prior to degradation at high temperatures. However, blends of PVC with the three polyesters in *Table 1* having the highest CH_2/COO ratios did turn cloudly on heating. The cloud point curves obtained at a heating rate of about $10°C\ min^{-1}$ using techniques described earlier[29] are shown in *Figure 7*. This phase separation was found to be reversible, i.e., the samples returned to a transparent state
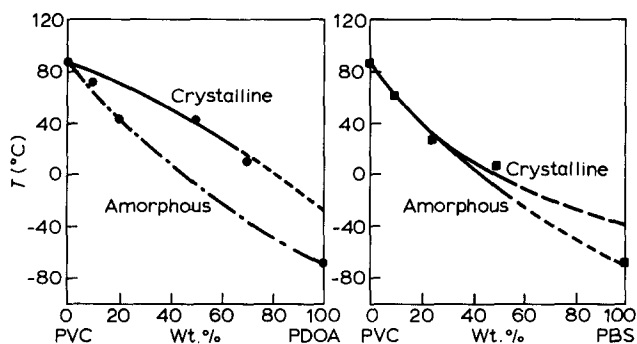
Figure 6 Temperature locations of main E'' maxima for PVC blends with PBS and PDOA. Curves are drawn to illustrate effect of crystallinity

upon cooling below the temperatures shown in *Figure 7*.

These observations confirm that PVC is completely miscible with all the higher CH_2/COO polyesters in *Table 1* by the arguments presented above. In the range $CH_2/COO = 4$ to 10, the interaction parameter is apparently sufficiently negative that no phase separation occurs on heating at temperatures attainable prior to degradation of the components. However, as CH_2/COO increases, the interaction parameter must become less negative such that phase separation occurs at lower temperatures the higher CH_2/COO is as shown in *Figure 7*. Continued increases in CH_2/COO beyond 14 should lower the cloud point further until it intersects the glass transition curve and formation of homogeneous blends becomes impractical[17].

So, there is a limited range of CH_2/COO values for which PVC is miscible with aliphatic polyesters as observed for their blends with some other polymers[12-18]. The division between immiscible and miscible mixtures is very sharp on the low end of the CH_2/COO scale; however, it is quite gradual at the higher end as *Figure 7* suggests.

MELTING POINT DEPRESSION ANALYSIS

The various polyesters used in this study all crystallize readily, and depression of their melting points in miscible blends with PVC has been used to obtain quantitative information about the thermodynamic interactions in these systems. The desired information is the interaction energy density, B, which is related to the heat of mixing, ΔH_{mix}, through:

$$\Delta H_{mix} = B\phi_1\phi_2 \qquad (1)$$

where ϕ_1 is the volume fraction of component i. Alternatively, an equivalent parameter related by the following:

$$\chi_{12} = \frac{BV_1}{RT} \qquad (2)$$

may be used where V_1 might be taken as the molar volume of the repeat unit for component 1 as done in the earlier study[3]. These parameters can, in general, be composition dependent and when deduced from phase equilibrium results, their values may include entropy effects in addition to the desired heat of mixing information. Equation

(1) combined with the Flory–Huggins estimate for the entropy of mixing gives the following expression for the equilibrium melting point, T_m, of the crystallizable component 2 when mixed with component 1

$$\left(\frac{1}{T_m}-\frac{1}{T_m^\circ}\right)\frac{(\Delta H_{2u}/V_{2u})}{R}+\frac{\ln\phi_2}{\tilde{V}_2}+\phi_1\left(\frac{1}{\tilde{V}_2}-\frac{1}{\tilde{V}_2}\right)=$$
$$-(B/RT_m)\phi_1^2 \qquad (3)$$

where T_m° is the melting point of pure 2, $\Delta H_{2u}/V_{2u}$ is the heat of fusion per unit volume of the 100% crystalline polymer, and $\tilde{V}_i$ is the molar volume of component i.

However, as Morra and Stein[23] have pointed out, the directly measured melting points are not equilibrium values since they represent finite lamellar thicknesses. This fact can be corrected for using the Hoffman–Weeks[24] approach wherein the melting points of specimens crystallized at a series of temperatures, T_c, are extrapolated to the limit of infinite lamellar thickness. *Figure 8* shows representative Hoffman–Weeks plots for PVC blends with two of the polyesters employed here, PBS and PHEDO. These results were obtained using the d.s.c. at a heating rate of $10^\circ C$ min^{-1} after crystallization of the samples for ~ 20 min at T_c. The observed melting points were extrapolated to the line $T_m = T_c$ to obtain the equilibrium melting point for each composition. These equilibrium values for various blend compositions formed a data base used to obtain B from equation (3) using a regression analysis program. Molar volumes were estimated from intrinsic viscosity data[15], and various literature sources were used to estimate $(\Delta H_{2u}/V_{2u})$ for each polyester[15,18]. Approp-
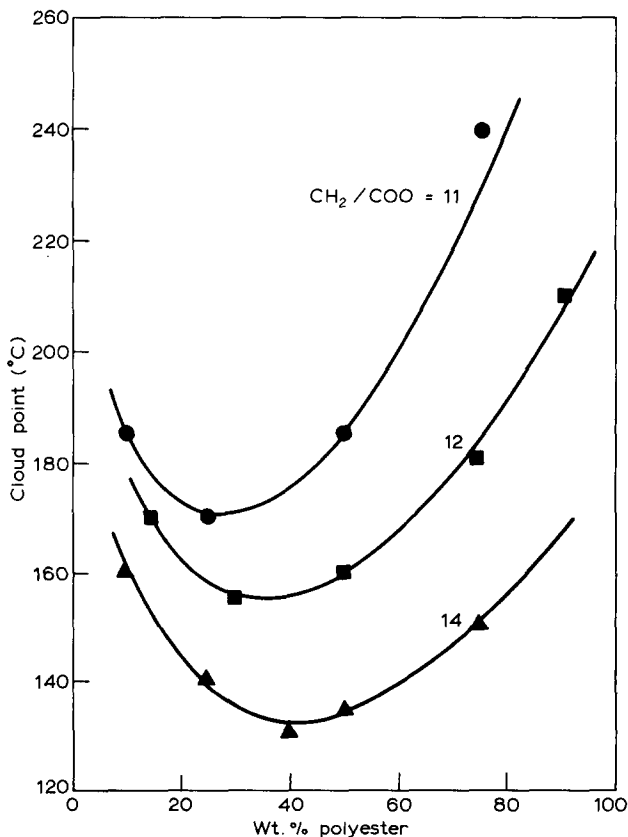

Figure 7 Cloud point curves for PVC blends with polyesters having high CH_2/COO ratios
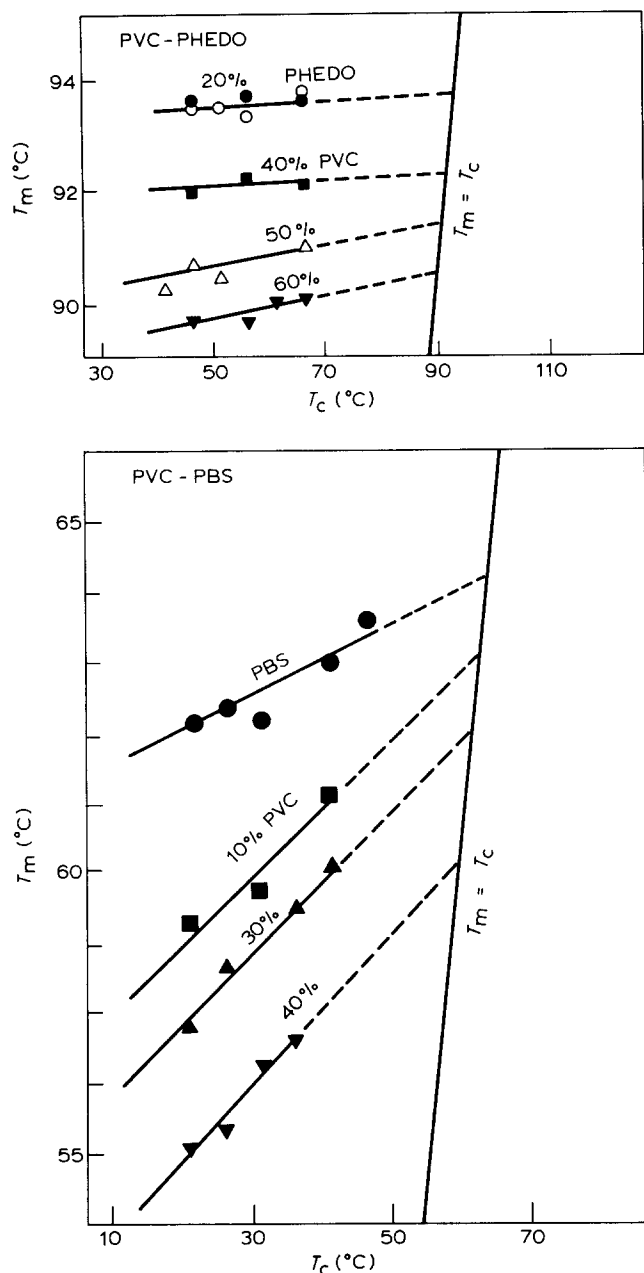
ANALOGUE CALORIMETRY

As described previously[12,14], another useful approach for obtaining quantitative thermodynamic information about polymer blends is direct measurement of the heat of mixing of low molecular weight analogues of the component polymers. This was done here using 1,3-dichlorobutane as the analogue for PVC and various symmetrical low molecular weight diesters to simulate the aliphatic polyesters. The heat of mixing was measured at 25°C using a calorimeter described previously[12,14] at roughly equal volume fractions of the model compounds used. Assuming that equation (1) describes the heat of mixing, the normalized quantity $\Delta H_{mix}/\phi_1\phi_2$ can be used as a measure of the interaction parameter B for comparison with the results obtained from the melting point depression analysis.

The normalized heats of mixing 1,3-dichlorobutane with the various low molecular weight ester model compounds are shown by the lower curve in *Figure 10* as a function of the number of aliphatic carbons per ester unit in the ester analogues. For this purpose, methyl and methylene units are regarded as similar in this count. The
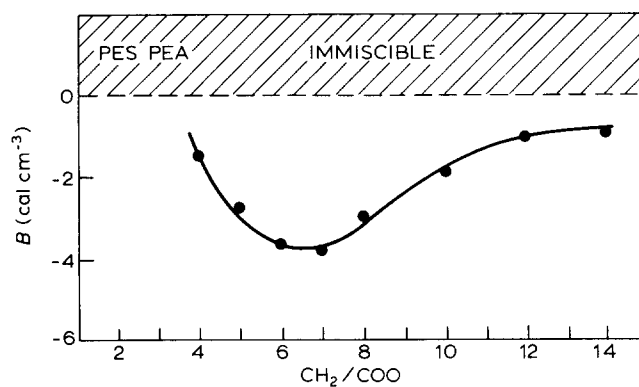

Figure 9 Interaction parameters for PVC–polyester blends obtained by melting point depression analysis
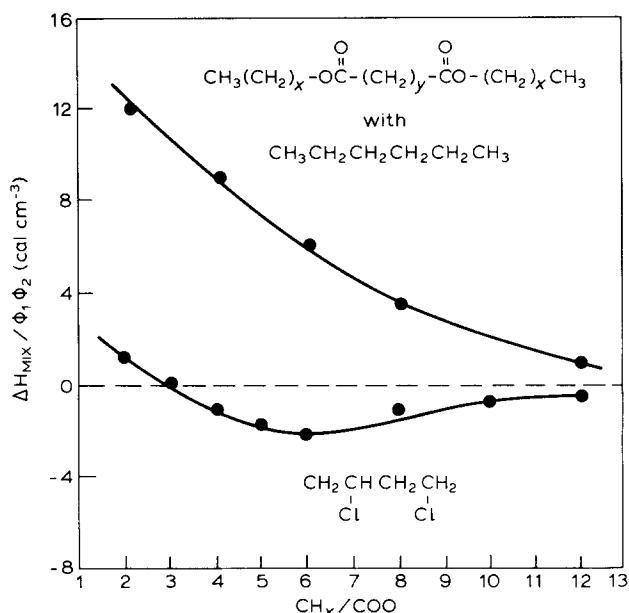
Figure 8 Typical Hoffman–Weeks plots for PVC blends with polyesters. Extrapolation of data to $T_c = T_m$ line gives equilibrium melting points

riate plots of this data did not show any suggestion of a significant composition dependence for B.

Figure 9 shows the values of B obtained for each polyester plotted *versus* the ratio of CH_2/COO groups in the repeat unit. These more precise data confirm the trend observed previously[3]. The interaction parameter becomes more negative as CH_2/COO increases in the range from 4 to about 7. However, as expected B goes through a minimum and increases at higher CH_2/COO ratios. At the low end of the scale, the values of B can be extrapolated to positive values for CH_2/COO ratios of about 3.5 or less in agreement with the observations on phase behaviour noted earlier. As mentioned before, this boundary is rather sharp. However, at the high end of the scale the values of B cannot be simply extrapolated to positive values. The slower approach to zero seen on this end is consistent with the gradual diminution of miscibility seen in *Figure 7* by the decreasing LCST as the hydrocarbon content of the polyester is increased.

Figure 10 Heat of mixing data for low molecular esters with hexane (upper curve) and 1,3-dichlorobutane (lower curve) at 25°C
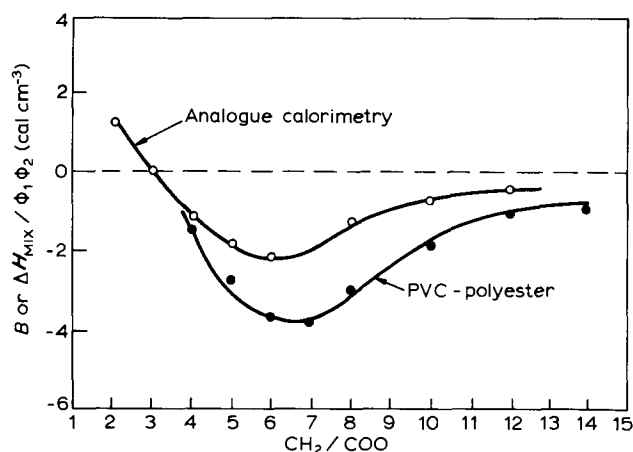
Figure 11 Comparison of interaction parameters obtained from analogue calorimetry (data from *Figure 10*) and from melting point depression analysis on blends (data from *Figure 9*)

response shown here is very similar to that observed in *Figure 9*. Interestingly, the heat of mixing does become positive at low CH_x/COO ratios as one might postulate from the melting point data. This effect cannot be directly observed for blends since they would be immiscible under these circumstances; however, the low molecular weight analogues can tolerate endothermic mixing because of the aid of entropy to their mutual solubility. This demonstrates clearly that immiscibility of PVC with polyesters having CH_2/COO equal to or less than three is not the result of issues related to accessibility or chain flexibility[7] but is caused by an unfavourable balance of interactions also present in corresponding low molecular weight molecules. *Figure 11* shows the data from *Figures 9* and *10* on the same scale so that a direct comparison can be made. The trends are quantitatively similar in every regard demonstrating that the same issues are involved in mixtures of low molecular weight species as in polymer blends. There is, however, a distinct quantitative difference between the information derived from these two approaches which may have several origins. Firstly, interaction parameters derived from phase behaviour may include entropic contributions not properly accounted for by the Flory–Huggins approach, i.e. *B* derived from melting point depression is actually a free energy parameter. Secondly, the model compounds are in a different volumetric state than the corresponding polymers, i.e. a difference in the free volume contribution to the enthalpy. Thirdly, there is the relatively high concentration of end groups in the model compounds not present in the polymer which may affect the heat of mixing. Finally, there is the possibility of systematic errors in the various techniques. It is not possible currently to determine which of these, or other factors, are most responsible for the differences seen. However, the good general agreement seen is both gratifying and instructive.

Figure 10 also shows the heat of mixing of the low molecular weight esters with hexane. These values are highly endothermic which must be the result of a strongly unfavourable interaction between ester units with hydrocarbon segments. This interaction also exists intramolecularly within the esters and the polyesters which as shown in the next section by a model may have a great deal to do with the miscibility of the aliphatic polyesters with other polymers.

APPLICATION OF BINARY INTERACTION MODEL

Various versions[25,31,32] of a binary interaction model have been introduced recently which show that intramolecular interactions are important considerations for understanding why certain random copolymers form miscible blends with other polymers when neither homopolymer derived from the monomers comprising the copolymer are similarly miscible. The contribution of intramolecular interactions introduced by these models is conceptually most easily visualized when applied to copolymers; however, it is not restricted to them. As demonstrated recently[25], homopolymers may also be divided into small interacting units analogous to 'monomers' in copolymers and the same approach may then be applied.

To illustrate this concept for the systems of interest here, the binary interaction model presented earlier[25] must be extended to a slightly different case involving blends of two 'copolymers' made from three 'monomers' 1, 2 and 3. Copolymer A is made up of monomers 1 and 2 with their volume fractions in the copolymer being ϕ_1' and ϕ_2', respectively, where $\phi_1' + \phi_2' = 1$. Copolymer B is made up of monomers 1 and 3 with their volume fractions being ϕ_1'' and ϕ_3'', respectively, where $\phi_1'' + \phi_3'' = 1$. By simple extension of the derivations shown previously[25], the net interaction parameter, *B*, for mixing copolymers A and B can be shown to be

$$B = B_{13}\phi_1'\phi_3'' + B_{12}\phi_1''\phi_2' + B_{23}\phi_2'\phi_3'' - B_{12}\phi_1'\phi_2' - B_{13}\phi_1''\phi_3''$$

$$= B_{23}\phi_2'\phi_3'' + B_{13}\phi_3''(\phi_1' - \phi_1'') + B_{12}\phi_2'(\phi_1'' - \phi_1') \qquad (4)$$

where the B_{ij} are the interaction energy densities for mixing the various *i* and *j* units. In equation (4) the terms with a plus sign stem from *intermolecular* interactions of the various groups between molecules of A and B while those with negative signs stem from *intramolecular* interactions of the different units within the molecules A and B. These are, of course, weighted according to the volume fraction each group represents in molecules A and B. The heat of mixing A with B is given by adaptation of equation (1) to the new subscript nomenclature, i.e.

$$\Delta H_{mix} = B\phi_A\phi_B \qquad (5)$$

with equation (4) representing the net interaction energy density in terms of the weighted interactions of the groups making up these molecules.

The PVC–aliphatic polyester systems can be adapted to the above description if we make the following identifications:

A = polyester   1 = –CH_x–

                      1 = –COO–

B = PVC   3 = –CHCl–
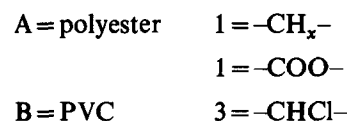
Group contribution information permits calculation of the volume fraction of each group in a molecule of known structure[14,28]. The problem, of course, is that there is no *a priori* means of knowing the three B_{ij} values needed in this case. One approach would be to obtain these values by fitting equation (4) to the melting point depression data in *Figure 9*, and this has been done[16]. However, an alter-
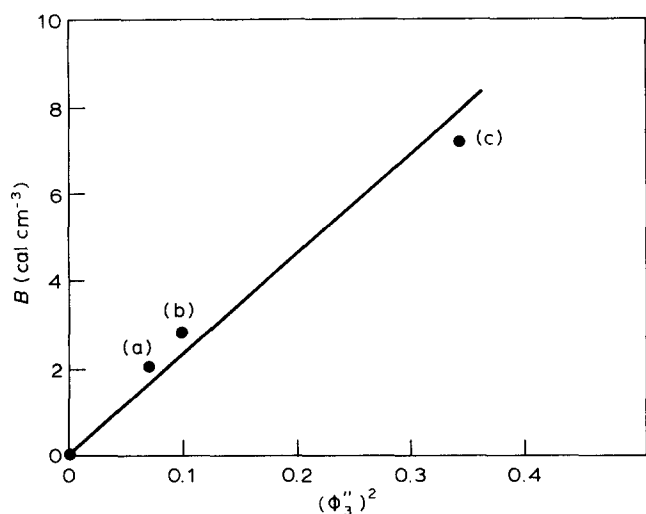
Figure 12 Interaction parameters for mixing hexane with (a) 2-chloro-2-methylbutane, (b) 2-chlorobutane, and (c) 1,3-dichlorobutane from calorimetry plotted as suggested by equation 6. Slope gives B_{13}
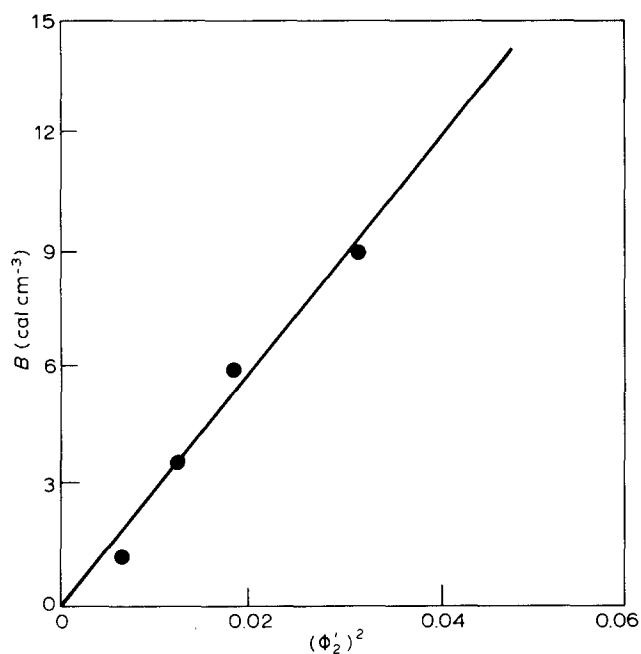

Figure 13 Interaction parameters for mixing hexane with a series of esters (data from *Figure 10*) from calorimetry plotted as suggested by equation 7. Slope gives B_{12}

native approach using information on the heats of mixing for various model compounds is presented here since this permits introduction of a wider range of experimental information and is somewhat more appealing and instructive than determining all three parameters from a single regression analysis.

The three B_{ij} parameters can be evaluated in a step-wise fashion using heat of mixing data for different series of model compounds. First, B_{13} is obtained from data for mixing hexane, A, with a series of chlorinated hydrocarbons, B, identified in the legend of *Figure 12*. In this case, $\phi_2' = 0$ and ϕ_3'' is variable so equation (4) reduces to:

$$B = B_{13}(\phi_3'')^2 \qquad (6)$$

The experimental values of $B \equiv \Delta H_{mix}/\phi_A\phi_B$ are plotted

versus $(\phi_2'')^2$, and as seen in *Figure 12* a reasonably good straight line results whose slope, B_{13}, is 23 cal cm^{-3}. Second, B_{12} is obtained from data for mixing a series of ester compounds, A, with hexane, B, which correspond to the results given by the upper curve in *Figure 9*. For this set of experiments, $\phi_3'' = 0$ and ϕ_2' is variable so equation (4) reduces to:

$$B = B_{12}(\phi_2')^2 \qquad (7)$$

The experimental values of B are plotted *versus* $(\phi_2')^2$ and again a reasonable straight line, omitting one extreme data point, is found whose slope, B_{12}, is 286 cal cm^{-3}. Finally, B_{23} is obtained from the data for mixing a series of ester compounds, A, with 1,3-dichlorobutane, B, corresponding to the information shown by the lower curve in *Figure 9*. Here, ϕ_3'' is fixed at a value of 0.65 and ϕ_2' varies. After substituting the known values for ϕ_3'', B_{12}, and B_{13} into equation 4 and rearranging, the following is obtained:

$$Y = B - (23)(0.65)(0.65 - \phi_2') - (286)\phi_2'(\phi_2' - 0.65)$$
$$\qquad (8)$$
$$= B_{23}(0.65)\phi_2'$$

Since for each ϕ_2' there is a value of B, then there is a value of Y for each ϕ_2'. Thus, a plot of Y *versus* $(0.65)\phi_2'$ should yield a straight line whose slope is B_{23}. Such a plot is shown in *Figure 14* and a good straight line is obtained; however, the best line through the data has a small finite intercept rather than going through the origin as expected. The slope of the line is 159 cal cm^{-3} and, if the non-zero intercept problem is ignored, this value can be equated to B_{23}.

Using the three B_{ij} values so obtained, the model can now be compared with the heat of mixing data for the analogues of PVC and the polyesters as shown in *Figure 15*. This is not a real test of the predictive capabilities of the model since the experimental results to which the comparison is made were part of the data base for obtaining one of the model parameters; however, this test
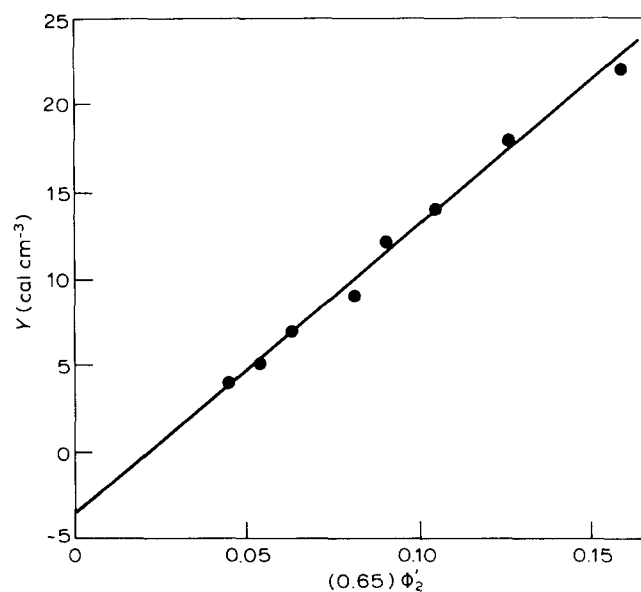

Figure 14 Interaction function plotted as suggested by equation 8. Slope gives B_{23}
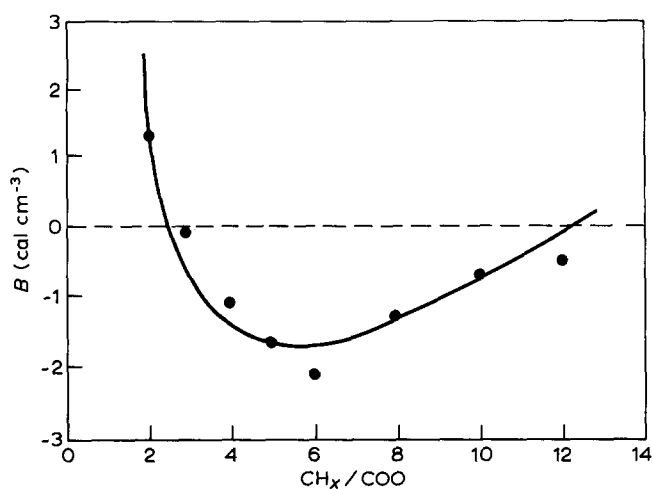
Figure 15 Comparison of model prediction (solid line) with experimental calorimetry data for mixing 1,3-dichlorobutane with various esters (data from *Figure 10*)

Table 2 Summary of binary interaction parameters

Interaction pair	Structure	B_{ij} (cal cm^{-3})
1↔2	CH$_x$ ↔ COO	286
1↔3	CH$_x$ ↔ CHCl	23
2↔3	COO ↔ CHCl	159

does show that the basic forms of the model and the data are similar. However, the model results indicate that B becomes zero at a CH$_x$/COO ratio just less than 13 while the experimental data suggests that B would not become zero until somewhat higher values are reached.

It is interesting to note that each of the B_{ij} values obtained in this way and summarized in *Table 2* are positive or that all the binary interactions between the various groups are individually endothermic. At the present time it is rather difficult to interpret what significance, if any, these values have. However, it is instructive to note that the B_{12} found here is rather similar to the value of 250 cal cm^{-3} obtained from different observations on mixing esters and polyesters with a system quite different from PVC or its analogues[14]. The value of this parameter is quite large, and perhaps larger than can be presently rationalized on any physical basis, but it does point to a strongly unfavourable interaction between the component groups, $-$CH$_2-$ and $-$COO$-$, in aliphatic polyesters—a fact that can be seen by the data in *Figure 10* without the aid of any model. This knowledge combined with the observations on copolymers[25,31] suggests that intramolecular 'repulsion' may indeed be a significant factor in the miscibility of aliphatic polyesters with so many other polymers[12-18].

CONCLUSION

It has been shown that PVC is miscible with a wide range of linear aliphatic polyesters but not all of them. The phase behaviour can be summarized according to the CH$_2$/COO ratio in the polyester repeat unit. Polyesters having CH$_2$/COO <4 are not completely miscible with PVC; whereas, those having CH$_2$/COO $\geqslant 4$ are completely miscible with PVC at all observable temperatures until CH$_2$/COO reaches 10 where LCST behaviour occurs with the temperature of phase separation gradually decreasing as CH$_2$/COO becomes larger. Ratios greater than 14 were not studied owing to the difficulty of obtaining monomers for synthesizing the polyesters.

Melting point depression and analogue calorimetry were used to obtain quantitative information about the thermodynamic interactions in this series of polymer blends. Heats of mixing of low molecular weight analogues of the polymers give trends comparable to that

obtained by studies on the polymer blends but there are quantitative differences in the values of the interaction parameters as might be expected for several reasons.

It is suggested that a strong unfavourable intramolecular interaction within the polyester molecules is an important factor in the phase behaviour of these systems just as it is known to be for blends involving certain random copolymers. A binary interaction model which has been used with some success for explaining miscibility windows in these copolymer blends is believed to contain the proper elements to rationalize the similar behaviour seen in the present systems as the structure of the polyester is systematically varied. This model can be used to fit heat of mixing data for related model compounds and thereby obtain values for the interaction energies for binary combinations of the units CH$_2$, COO and CHCl which comprise these polymers. However, there is presently no way to ascertain the physical significance or validity of these values (see *Table 2*). Hopefully additional investigations will be able to better deal with this issue and to ascertain the merits of this proposed approach to understanding the relation between blend phase behaviour and the molecular structure of the components.

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