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Evaluation of Interactions in Blends of Ethylene–Vinyl Acetate Copolymers with Poly(vinyl chloride) Using Model Compounds

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ABSTRACT: The interactions in blends of ethylene–vinyl acetate copolymers (EVA) with poly(vinyl chloride), PVC, have been examined by using low molecular weight analogues of the polymers. To simulate the different ethylene/vinyl acetate ratios in the copolymers, premixes of heptane with ethyl acetate or with 1,3-butanediol diacetate were used, as well as several alkyl acetates; 2,4-dichloropentane, 2,4-DCP, was chosen to model PVC. The heats of mixing of the EVA analogues with 2,4-DCP were found to be exothermic where their polymeric counterparts show miscibility. Hence, the miscibility window reported for the EVA–PVC system at one-to-one ratios of the two polymers can be approximately traced by these calorimetric results. The heats of mixing determined have a complex nature, and, in some cases, endothermic and exothermic behavior was found when mixing a single EVA analogue with the PVC model in different proportions. The weak endothermic portion in those cases was invariably located at high contents of 2,4-DCP; this agrees, at least qualitatively, with a trend toward immiscibility for blends in the PVC-rich region. Application of a binary interaction model to the calorimetric results allowed only a qualitative prediction of the miscibility window for EVA–PVC blends owing almost certainly to the nonparabolic behavior of the heats of mixing. Fourier transform infrared spectroscopy was used to follow the features of the carbonyl group when the analogues were placed in different molecular environments. This suggests three possible mechanisms govern phase behavior in the polymer blends, namely, dispersive forces, the disruption of carbonyl dipole–dipole interactions in EVA, and a specific interaction between the C=O and CHCl groups, which has been identified in the polymers. Only the latter mechanism contributes exothermically to the enthalpy of mixing. Apparently, the specific interaction contribution is able to counteract the other two components only within the limits of the miscibility window for the EVA–PVC system.

Introduction

Blends of poly(vinyl chloride), PVC, with ethylene–vinyl acetate copolymers, EVA, have been of continued interest for over 20 years.[1–17] From a technological standpoint, EVA copolymers of certain ethylene/vinyl acetate ratios are used as modifiers for PVC;[1] whereas, from a fundamental point of view, PVC–EVA blends constitute one of the first reported examples in the literature[2] in which copolymers form miscible blends with another polymer when the two homopolymers do not. In this case, PVC is not miscible with either polyethylene, PE, or poly(vinyl acetate), PVAc, but it does form miscible mixtures with some of their copolymers.

The existence of "miscibility windows" in homopolymer–copolymer blends has been rationalized in thermodynamic terms by means of a binary interaction model[18] and other similar approaches.[19,20] The essence of the former lies in the assumption that all segmental units in a homopolymer–copolymer blend interact with each other in a pairwise manner with an interaction energy density, B_{ij}, assuming parabolic behavior of the heat of mixing. If ϕ_1' and ϕ_2' are the respective volume fractions of units of type 1 and 2 in the copolymer, when these are mixed with the units of type 3 in the homopolymer, the net interaction energy density for the blend is

$$B = B_{13}\phi_1' + B_{23}\phi_2' - B_{12}\phi_1'\phi_2' \qquad (1)$$

If only endothermic interactions are present, i.e., all B_{ij} are positive, a large enough value of B_{12} can make the net interaction energy density negative and, thus, bring about miscibility through the existence of an exothermic heat of mixing.[18] In this manner, the miscibility of several homopolymer–copolymer blends can be explained.[19–21]

However, an interesting feature of the binary interaction model is that since the molecular interactions involved are calculated at the segmental level, these can be experimentally determined from suitable low molecular weight analogues of the polymer and, therefore, phase behavior predicted by combining calorimetric heat of mixing data with the binary interaction scheme.[21]

In this regard, the PVC–EVA system offers an excellent example of the above situation. Recently, Shiomi, Karasz, and MacKnight[17] presented a very detailed study of blend miscibility for homopolymers and copolymers containing vinyl chloride, ethylene, or vinyl acetate moieties. For the particular case of PVC–EVA blends, these authors were able to calculate a set of segmental Flory–Huggins interaction parameters and to correlate phase behavior within the thermodynamic framework of the binary interaction model. Therefore, it was of interest for us to compare the results obtained through analogue calorimetry with the phase behavior reported for PVC–EVA to gain a deeper understanding of the possible molecular interactions involved. Furthermore, since a number of spectroscopic studies have appeared in the literature[14,22,23] that characterize the type of specific interactions involved in miscible polymeric systems of this sort, it was also important to observe the spectroscopic features of the liquid mixtures selected as polymer models, as this might also be taken as a measurement of how well the polymer situation is mirrored by the analogues. Hence, Fourier transform infrared spectroscopic experiments were also carried out to address this point.

The main results reported in the literature for PVC–EVA blends are summarized to show the essential features of the phase behavior for this system. Then, an interpretation of this behavior in terms of calorimetric and spectroscopic results is presented.

Experimental Section

Analogue Selection. Table I shows the low molecular weight compounds used as models for the respective polymers. It is interesting to note that Meares[24] suggested in 1951 that either ethyl acetate (EA) or 1,3-butanediol diacetate (BDA) could be

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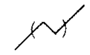
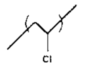
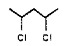
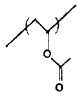
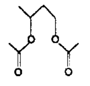
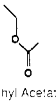
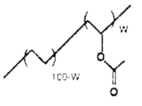
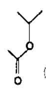
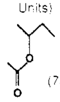
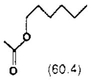
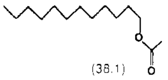
Table I
Structures of the Polymers and Their Low Molecular Weight Models

polymer	analogue
 Polyethylene (PE)	 Heptane (H)
 Poly(vinyl chloride) (PVC)	 2,4-Dichloropentane (2,4-DCP)
 Poly(vinyl acetate) (PVAc)	 1,3-Butanediol Diacetate (BDA) or  Ethyl Acetate (EA)
 Ethylene-Vinyl Acetate Copolymers (EVA) W = Wt % Vinyl Acetate Units	A) BDA-Heptane Premixes B) EA-Heptane Premixes C) Alkyl Acetates: (Wt % Vinyl Acetate Units)  (65.3) iso-Propyl Acetate  (75) sec-Butyl Acetate  (60.4) Hexyl Acetate  (38.1) Dodecyl Acetate

used as an analogue to study the energetics of PVAc interactions with other substrates, based on calorimetric and volumetric measurements, and they were chosen here to model PVAc segments.

On the other hand, 2,4-dichloropentane, 2,4-DCP, was selected as the PVC analogue on the grounds of greater structural similarity to the latter than other analogues previously used for PVC.[25,26] In fact, 2,4-DCP was recently used to study the conformational energy of PVC.[27] The infrared spectrum of 2,4-DCP in the fingerprint region appears to have a closer resemblance to that of PVC than, for example 1,3-dichlorobutane.

In this work, analogues having structural features of the copolymers, i.e., containing both repeat units in certain ratios, were also successfully used as model compounds. For instance, *sec*-butyl acetate can be visualized as an EVA analogue with 75 wt % (50 mol %) VA units (see Table I). Interestingly, 2-octyl acetate was used as an analogue for EVA in recent thermodynamic studies.[28]

Materials. Ethyl acetate (HPLC grade, 99+% purity), 1,3-butanediol diacetate (reagent grade, from a special lot with 99% purity), and the other acetates (all reagent grade with 99% purity) were obtained from the Aldrich Chemical Co. The 2,4-dichloropentane (95% purity) was purchased from Pfaltz and Bauer, Inc., and the heptane (HPLC grade, 99+% purity) was purchased from the Fisher Scientific Co. All were used without further purification.

Calorimetry. All calorimetric measurements were carried out at 25 °C in an LKB batch-type microcalorimeter Model 2107-111/112, connected to a Hewlett-Packard 63 integrator. At least 0.5 cm^3 of each component was used for each test, and, when needed, dilution runs were carried out in the case of binary mixtures at the composition ends. Reproducibility of the measurements was checked for several points and found to be within at least ±5%. Special mention must be made, however, of the mixtures in which ethyl acetate was used since because of the high vapor pressure of this component at 25 °C (about 90 mm Hg) some vapor premixing occurred through the interconnecting space between the two individual chambers. This condition, in general, tends to produce values of the heat of mixing that are too small in absolute magnitude. For instance, in the case of the ethyl acetate–heptane system, a difference of up to 20% was found when comparing the results obtained here with those reported by Nagata et al.,[29] who used a batch calorimeter with no vapor space. Reproducibility was poor when the samples to be mixed were left standing for a long time (>15 min) for temperature stabilization. Changing the alkane to dodecane did not improve this condition to a significant extent. We decided to direct our efforts to maintain data reproducibility for this system, while keeping the same temperature and PE analogue as for the BDA case. It was determined that short stabilization times (about 10 min) produced optimum reproducibility and the highest heats of mixing observed for this pair. Previous experiences with a number of other systems revealed that high volatility and viscosity of the components are the main factors affecting the accuracy of the measurements. However, when compounds with a very low vapor pressure are used, good reproducibility, as reported, was obtained even for long stabilization times. This is the case for all other compounds used here.

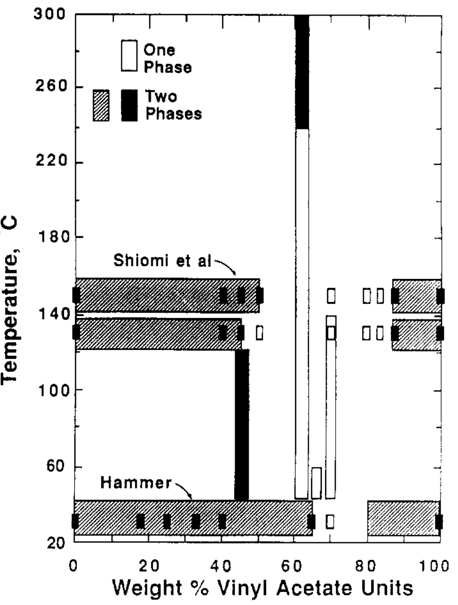


Figure 1. Phase behavior of EVA–PVC blends at equal weights of the polymers. Combined results of ref 2, 6, 13, 15, and 17.

Infrared Spectroscopy. Fourier transform infrared experiments (FTIR) were carried out with a Digilab FTS-15/90 FTIR spectrometer at room temperature. At least 100 scans at a resolution of 2 cm^{-1} were signal averaged and stored on magnetic disk for further analysis under scale-expansion conditions. The sample consisted of one or two drops tightly pressed between two KBr windows to form a thin liquid film.

Results and Discussion

Phase Behavior of PVC–EVA Blends. The complex nature of EVA–PVC blends is summarized in Figure 1, which illustrates the phase behavior for mixtures containing equal weights of PVC and EVA, at varying contents of VA in the copolymer and at different temperatures, as reported by independent investigators. The relevant aspect that clearly emerges from this picture is the intermediate miscibility region originally pointed out by Hammer.[2] More recent experiments by Shiomi, Karasz, and MacKnight[17] have revealed that the miscibility window is somewhat wider than initially reported, stretching from about 45 to almost 87 wt % (37 to 83 vol %) vinyl acetate in the copolymer or, in terms of mole percent of VA repeat units, between 21% and 68%. The immiscibility of PVC with either PE or PVAc, which constitute the two composition ends of the plot, is a point of total agreement in these reports. In what follows, the weight percent of vinyl acetate units in the copolymer is expressed as a number following the acronym; e.g., EVA45 has 45 wt % VA units.

Another important result worthy of mention is the appearance of a lower critical solution temperature (LCST) at about 240 °C for the blend prepared with EVA63. EVA50 also shows an LCST between 30 and 100 °C.[17] Although discrepancies might also arise due to different molecular weights used, the phase separation behavior

Table II
Miscibility Behavior of PVC–EVA45 Blends

polymer characteristics	method of preparation	conclusions	ref
PVC: [η] = 0.91 in cyclohexanone EVA: commercial sample[a]	not disclosed	miscible	5
PVC: T_g = 80 °C EVA: commercial sample[a]	solution casting from tetrahydrofuran	miscible at 40 and 80 wt % PVC (only compositions reported)	14
PVC: $\bar{M}_w$ = 83 000 EVA: commercial sample[a]	precipitation from solution	partially miscible	10
PVC: $\bar{M}_v$ = 110 000 EVA: $\bar{M}_w$ = 100 000–120 000	solution casting from tetrahydrofuran	immiscible between 10 and 75 wt % EVA, miscible elsewhere	15
PVC: $\bar{M}_n$ = 74 000 EVA: $\bar{M}_w$ = 170 000	milling and compression molding at 160 °C partially miscible	partially miscible	6
PVC: degree of polymerization: 800 EVA: commercial sample[a]	milling and compression molding at 160 °C immiscible	immiscible	3

[a] Bayer Levapren 450.

observed reveals that processing conditions may play a very important role in determining the phase structure of blends at room temperature. If a given PVC–EVA blend having an LCST is taken above the phase separation temperature during preparation, it might show either one- or two-phase behavior, depending on the relative rates of quenching and redissolution on cooling. For rapidly cooled samples, one might expect a two-phase blend at ambient conditions if the kinetics of redissolution are slow relative to the cooling rate, whereas slow cooling should allow the system to come to its equilibrium single-phase state at a comparable temperature.

LCST behavior may be the major reason for the varying degrees of miscibility for a PVC–EVA45 blend repeatedly mentioned by Elmqvist and Svanson.[8,9] Hence, the preparation method, as viewed in light of the thermally induced phase separation process, might also be one of the most important factors for explaining the extreme discrepancies in miscibility behavior reported for PVC–EVA45 blends. Table II shows that a full spectrum of possibilities, from complete miscibility to immiscibility at all compositions, has been reported for this system. Interestingly enough, phase separation at high temperatures for PVC/EVA45 has been reported for blends containing high (>75%) weight percentages of PVC.[14,15]

Yet another important feature of PVC/EVA systems away from the equal weight ratio region shown in Figure 1 is a trend toward immiscibility for PVC-rich blends. This is manifested as total immiscibility for blends of PVC/EVA65 with a PVC content above 50 wt %[6] or as a phase separation process in PVC/EVA70 at PVC contents of 85 wt %.[15] Also, Nolley, Paul, and Barlow[14] observed that the lowest phase separation temperature is located at the highest (around 90 wt %) PVC concentration. Moreover, the PVC/EVA45 system forms immiscible blends between 25 and 90 wt % PVC, but outside of this region, complete miscibility is observed at room temperature.[15] The PVC-rich blends in this system phase-separate at temperatures as low as 55 °C, whereas no LCST behavior is observed for the EVA-rich mixtures up to at least 120 °C.

To round out the picture for the PVC/EVA system, it should be mentioned that some blends may have a certain amount of crystallinity of the PE sequence. However, following the work of Salyer and Kenyon[3] on EVA, a crystalline phase is an issue only for those blends based on EVA copolymers containing less than about 40 wt % VA, which lies outside the region of miscibility observed for PVC/EVA mixtures. Moreover, Deanin et al.[16] addressed this point for several PVC/EVA blends and found that, in general, the melting features of the PE crystalline phase in EVA are not significantly affected by blending with PVC,[16] in contrast with the well-known melting behavior in miscible polymer blends.[31]

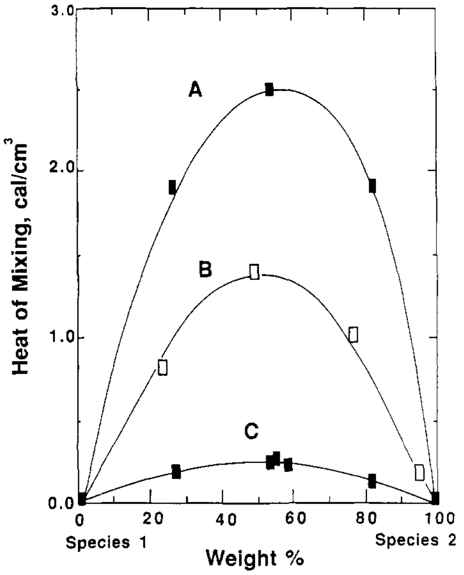


Figure 2. Heats of mixing at 25 °C for the systems (A) 1,3-butanediol diacetate/heptane, (B) 2,4-dichloropentane/heptane, and (C) 1,3-butanediol diacetate/2,4-dichloropentane.

Calorimetry. As a starting point to determine the relative interactions of the ethylene, vinyl chloride, and vinyl acetate segments in the blend, the heats of mixing for the binary systems heptane/BDA, heptane/2,4-DCP, and BDA/2,4-DCP were measured. The results obtained are shown in Figure 2. All three binary pairs exhibit endothermic behavior. Clearly, the heptane/BDA pair has the largest heat of mixing values whereas, the lowest magnitude corresponds to the BDA/2,4-DCP system. That all three pair interactions are endothermic is consistent with the fact that all three polymer pairs, PE/PVAc, PE/PVC, and PVAc/PVC, are immiscible, as already mentioned.

To model the energetics when a given EVA copolymer is mixed with PVC, a premixture containing BDA and heptane was prepared containing an equivalent of 75 wt % vinyl acetate units. Mixing this with 2,4-DCP resulted in exothermic behavior over essentially all of the composition range, as shown in Figure 3, except for a small region

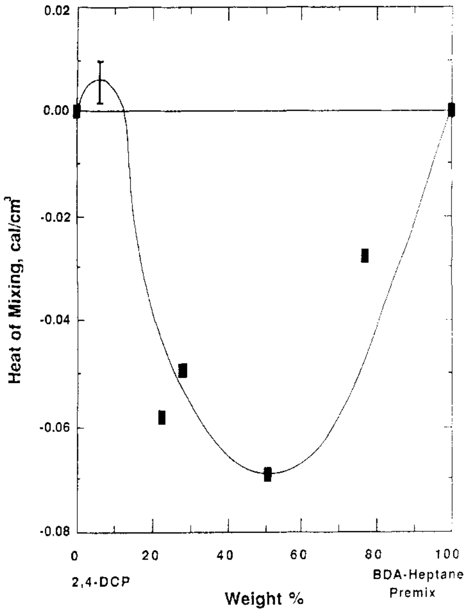


Figure 3. Heat of mixing at 25 °C of a BDA–heptane premix with 2,4-DCP. The premixture represents an EVA copolymer with 75 wt % VA units.

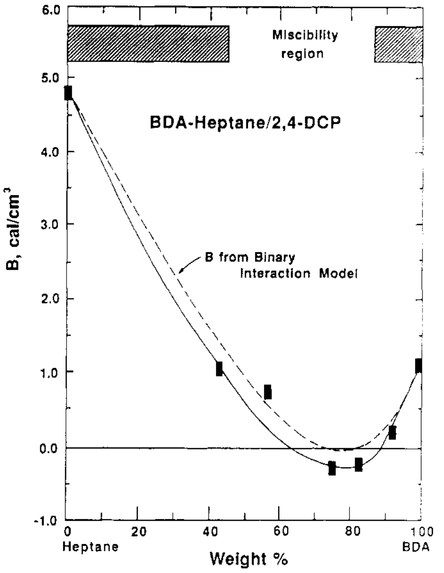


Figure 4. Interaction energy densities for BDA–heptane premixtures with 2,4-DCP. Weight ratio of premix to 2,4-DCP is 1 to 1. Miscibility region for PVC–EVA according to ref 17. See the text for binary interaction model calculation.

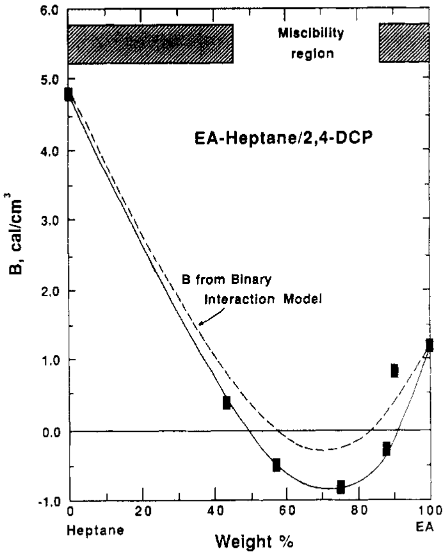


Figure 5. Interaction energy densities for EA–heptane premixtures with 2,4-DCP. Weight ratio of premix to 2,4-DCP is 1 to 1. Miscibility region for PVC–EVA as in Figure 4. See the text for binary interaction model calculation.

at very low amounts (<5 wt %) of the BDA–heptane premixture. Further elaboration on this point is made later. In correspondence with the exothermic nature of this particular system of analogues, PVC blends with EVA copolymers of similar compositions are found to be miscible, as seen in Figure 1.

These experiments clearly demonstrate that exothermic behavior can be observed in a system where all three pair interactions are endothermic. This can be rationalized as a result of coming down from a higher excess enthalpy state in the heptane/BDA system to a lower enthalpic state, on adding the 2,4-DCP. In essence, the latter functions as a diluent of the repulsive interactions between heptane and BDA.

An even more relevant conclusion here is that miscibility of certain EVA copolymers with PVC is predicted because of the negative heats of mixing. In fact, the "miscibility window" already discussed can be followed, in principle, by varying the relative amount of BDA in the premixture with heptane. Figure 4 shows the outcome of such an experiment in terms of the net interaction energy density for the mixture. Interaction energy densities were calculated as

$$B_{AB} = \Delta H_{mix}/\phi_A\phi_B \qquad (2)$$

where ϕ_A and ϕ_B are the volume fractions of the EVA analogue, in this case the premix of BDA and heptane, and 2,4-DCP, respectively. ΔH_{mix} is the heat of mixing at the midcomposition region. The correspondence between the exothermic region determined in this fashion and the miscibility region for the PVC–EVA system by Shiomi, Karasz, and MacKnight[17] is at least qualitatively close.

As a second alternative, ethyl acetate–heptane premixtures were tested with 2,4-DCP in the same manner as described for BDA-heptane/2,4-DCP, to confirm the above observations. Within the limitations stated in the Experimental Section for this system, Figure 5 was obtained showing again the existence of a region of exothermic behavior that also compares favorably to the miscibility window reported in the literature.[17] The magnitudes of the interaction energy densities, B, are more negative than when BDA is used instead of EA, and the region of exothermic mixing is wider. A more detailed discussion of this point is given in a later section.

A third approach for modeling the interaction in PVC–EVA blends was to mix 2,4-DCP with the four different acetates in Table I in which the "vinyl acetate" and "ethylene" moieties are chemically bonded in contrast to the premixes used above. The excess enthalpy–composition curves are shown in Figure 6 for the mixtures of 2,4-DCP with *sec*-butyl acetate and with *n*-dodecyl acetate.

Some major points regarding Figure 6a include the exothermic character of the 2,4-DCP/*sec*-butyl acetate mixtures in which the latter can be taken as a model compound for an EVA copolymer having 75 wt % VA, which is in the middle of the miscibility region for PVC–EVA. Endothermic behavior is also seen to occur at very low concentrations of *sec*-butyl acetate, as pointed out in the figure. Except for the higher magnitude of the heat of mixing in this case, the *sec*-butyl acetate/2,4-DCP system has a very close resemblance to the previously described BDA-heptane/2,4-DCP system shown in Figure 3.

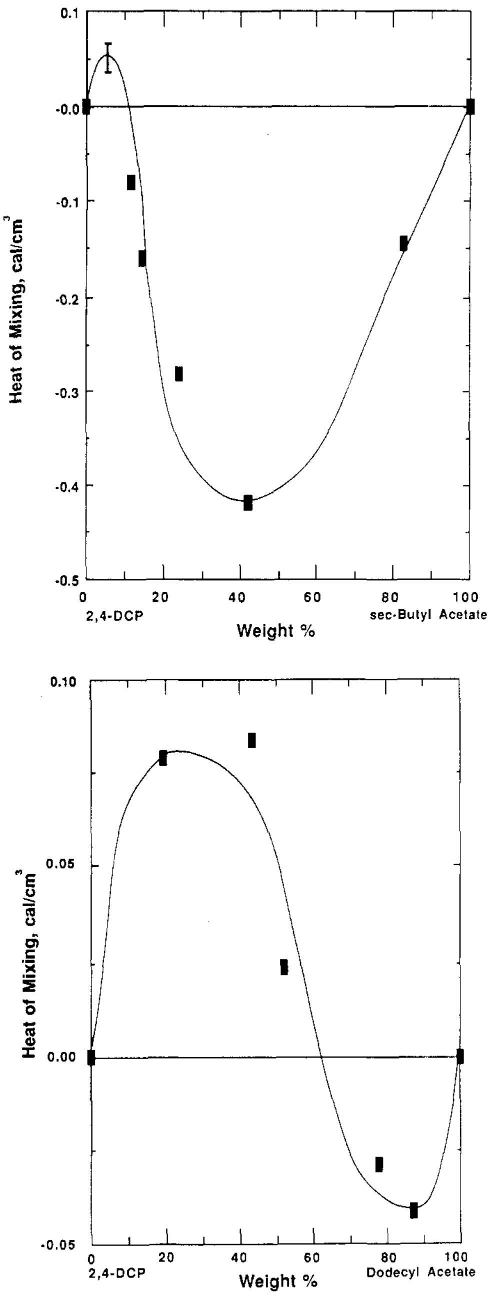


Figure 6. Heats of mixing at 25 °C for the binary mixtures (a, top) *sec*-butyl acetate/2,4-dichloropentane and (b, bottom) dodecyl acetate/2,4-dichloropentane (a represents EVA75, whereas b models EVA38).

The heat of mixing of *n*-dodecyl acetate, DDA, with 2,4-DCP is very small in magnitude and changes sign as the composition range is traversed (see Figure 6b). A fairly similar behavior is observed to occur in binary systems of ketones and carbon tetrachloride;[32] i.e., an endothermic region is seen to appear at high concentrations of the chlorinated compound, and exothermic mixing is observed elsewhere. The authors[32] attribute this to strong dipole–dipole interactions between the ketone molecules that are disrupted by incorporating a different molecule in the mixture, and the decrease in self-interaction of the ketone molecules generates an endothermic contribution that predominates in the ketone-poor range. However, new n–π interactions between the π electrons of the C=O double bond and the free electrons in the Cl atoms in CCl_4 presumably arise. Their formation provides an exothermic effect that is strong enough to balance the endothermic contribution mentioned and the dispersion forces in the system. As a consequence, exothermic behavior is observed.

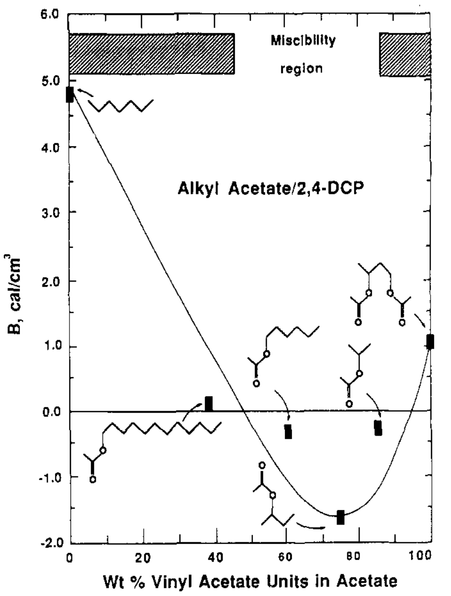


Figure 7. Interaction energy densities for binary mixtures of different alkyl acetates with 2,4-dichloropentane. Weight ratio of acetate to 2,4-DCP is 1 to 1. Miscibility region for PVC–EVA as in Figure 4.

Given the strong chemical similarity between the system just mentioned and ours, the above explanation applies in that strong dipole–dipole interactions of the carbonyl groups in DDA probably exist. When small amounts of 2,4-DCP are added, a favorable interaction between the two molecules is produced and generates exothermic behavior; however, when the dipole–dipole interactions are disrupted by the presence of large concentrations of 2,4-DCP, the endothermic contribution produced, coupled with the dispersive forces in the system, drives the net enthalpy of mixing to positive values.

Using only the heats of mixing observed in the mid-composition region for binary mixtures of 2,4-DCP with *sec*-propyl acetate, *sec*-butyl acetate, *n*-dodecyl acetate, *n*-hexyl acetate, *n*-heptane, and 1,3-butanediol diacetate, the value for the interaction energy density in each case was calculated as in eq 2. With this information, the diagram shown in Figure 7 was constructed. Once more, an exothermic region is detected for those mixtures with "vinyl acetate" contents around the middle of the composition range, and it is tempting to trace, empirically, a line correlating these results. When such an exercise is carried out, as indicated in the figure, an approximation of the miscibility limits based on the interaction energy densities is obtained, in which the lower limit agrees closely with that reported in the literature. On the other hand, the upper limit approximated in this fashion is displaced with respect to the one found by Shiomi, Karasz, and MacKnight,[17] making it the widest miscibility window predicted. The small magnitudes found for the heats of mixing of dodecyl acetate with 2,4-DCP appear to be reasonable from this perspective, since the number of vinyl acetate units in this model ester has been highly reduced in comparison with the other acetates.

After testing the three alternatives for analogue molecules to model the energetics of the EVA–PVC system, it is now possible to state that, irrespective of the type of analogue used for the EVA copolymer, i.e., premixes of heptane with ethyl acetate (or with 1,3-butanediol diacetate) or an alkyl acetate, a region of miscibility is always predicted at intermediate compositions, whereas immis-

Table III
Miscibility Window Limits

	vinyl acetate units, wt %: lower limit	vinyl acetate units, wt %: upper limit
predicted from model compounds		
BDA–heptane/2,4-DCP	63	86
EA–heptane/2,4-DCP	50	88
alkyl acetates/2,4-DCP	46	90
experimental[a]		
EVA/PVC	45	85

[a] Data of Shiomi et al. at low temperature.[17]

cibility of the EVA–PVC system is suggested at the two ends of the copolymer composition range. This is a valid statement for blends containing equal weight ratios of the two polymers. Some quantitative differences exist in the width of the miscibility window predicted by the calorimetric results, as presented in Table III. It is evident that the lower limit is better predicted by the EA–heptane premixtures with 2,4-DCP or the alkyl acetate/2,4-DCP approach, whereas the upper limit coincides more with the BDA–heptane premixtures with 2,4-DCP. A possible explanation for this result could be that the BDA-heptane premix is actually a closer analogue to EVA copolymers with high vinyl acetate contents that have a higher likelihood of containing interconnected vinyl acetate units, as opposed to those EVA copolymers rich in ethylene units, which dilute the vinyl acetate ones. Therefore, it is more likely to find the latter isolated from each other, as occurs in the ethyl acetate–heptane mixtures or the alkyl acetates.

Another distinction found for the three alternatives tested is the relatively low magnitude of the exothermic interaction energy densities of the BDA–heptane system with 2,4-DCP. For the 75 wt % vinyl acetate case, B is about one-fourth of the magnitude found when *sec*-butyl acetate is used and almost one-half the value for the same case when an EA–heptane mixture models the EVA copolymer. From a molecular viewpoint, this might be the result of the carbonyl groups not having the same freedom to interact with 2,4-DCP in all three cases. Hence, intuitively, the carbonyls attached to the same molecule in 1,3-butanediol diacetate would seem to possess lower flexibility for interaction than the other two cases. This is apparently valid as seen in the FTIR section. Also, it must be realized that equation of state effects, which arise from differences in free volume for the model compounds and the respective polymers, as well as temperature might cause part of the differences observed.

Another important issue from the calorimetric results is the tendency for endothermic heats of mixing on the 2,4-DCP-rich side of the binary mixtures when fixed ratios of the ester to aliphatic components are used, as seen in Figures 3 and 6a,b. Although not shown here, mixtures of *sec*-propyl acetate and *n*-hexyl acetate with 2,4-DCP show a slightly endothermic character in the 2,4-DCP-rich range. This phenomenon deserves special mention, since immiscibility tends to appear in the PVC-rich region in mixtures with EVA, whereas miscible blends are more often found when high proportions of the copolymer are present.[7,9,13] In terms of the possible energetic interactions and based on the previously described situation in ketone mixtures,[33] one might envision that three types of forces participate in the excess enthalpy generation: dispersive contributions from the contacts of alkyl units with ester units and with chlorinated units, dipole–dipole self-interactions among ester molecules, and an interaction between the carbonyl group in the esters and the CHCl group in 2,4-DCP. The dispersive component and the endothermic contribution from disruption of the C=O self-interaction predominate at the high 2,4-DCP end of the excess enthalpy–composition diagram. The interaction between 2,4-DCP and the carbonyl group generates an exothermic component that overcomes the other contributions only at certain contents of the ester. Nevertheless, it appears to be necessary for the carbonyl moieties to be somehow isolated from each other in order to fully interact with the chlorinated molecules. From this standpoint, the addition of heptane molecules to either EA or BDA disrupts the dipole forces between carbonyls and allows them to interact with the CHCl group. If small amounts of heptane are used, the dipole–dipole interactions are not eliminated, and adding 2,4-DCP produces a net endothermic effect because of the dissociation-like contribution of the carbonyls, even though some acetate/2,4-DCP interaction is present. On the other end, at high heptane concentrations, the majority of the carbonyls are able to interact with 2,4-DCP, but the dispersive component from the heptane/2,4-DCP contacts is also large enough to predominate as an endothermic effect. Thus, only at certain intermediate acetate to heptane ratios is the exothermic contribution dominant.

Table IV
Pair Interaction Parameters

	interaction energy densities, cal/cm^3: polymers[a]	interaction energy densities, cal/cm^3: analogues[b]
B_{12}	16.2	11.8 (10.3)
B_{13}	4.3	1.20 (1.02)
B_{23}	2.4	4.8

[a] From ref 17, calculated at 150 °C by using a reference volume of 52.5 cm^3/mol: 1 = vinyl acetate, 2 = ethylene, and 3 = vinyl chloride. [b] Experimental values from this work, determined at 25 °C: 1 = ethyl acetate (or 1,3-butanediol diacetate), 2 = heptane, and 3 = 2,4-dichloropentane.

Application of the Binary Interaction Model. It is interesting to analyze the data obtained for the binary interaction parameters, B_{ij}, in each system so that a more quantitative comparison in terms of polymer phase behavior can be made. Thus, the interaction parameters at midcomposition for the different binaries are first calculated from the experimental results already presented. These values are shown in Table IV. Assuming parabolic behavior, it is clearly seen that the inequality[18]

$$B_{12} > (B_{13}{}^{1/2} + B_{23}{}^{1/2})^2 \qquad (3)$$

which is the condition for a region of copolymer compositions showing exothermic values of B, is fulfilled for the pairs involving BDA as the PVAc analogue, as is the case if EA is used instead of BDA, provided that the value of B_{12} is that calculated from the results by Nagata et al.,[29] i.e., 11.8 cal/cm^3.

None of the other systems studied here, except for the already mentioned EA/H pair, have been previously reported in the literature. However, a comparison can be made at this point of the parameters obtained here as interaction energy densities with those calculated by Shiomi, Karasz, and MacKnight[17] through a mathematical correlation of their miscibility results and reported as Flory–Huggins-type parameters, χ_{ij}. The comparison is somewhat ambiguous,[33] since the value of χ_{ij} always depends on the reference volume, V_{ref}.

$$B_{ij} = \chi_{ij}(RT/V_{\text{ref}}) \qquad (4)$$

V_{ref} is generally chosen to be the molar volume of a repeat unit; however, in a polymer blend, the distinct repeat units usually have very different molar volumes, and selecting a value for V_{ref} becomes totally arbitrary.[33] The V_{ref} used in ref 17 is not specified; hence, we transformed the reported χ parameters into interaction energy densities taking $V_{\mathrm{ref}} = 52.5$ cm^3/mol, which is the average molar volume of the ethylene (32.7 cm^3/mol) and vinyl acetate (72.3 cm^3/mol) repeat units. This is only a reasonable approximation based on what appears to have been implicitly used by Shiomi et al.[17] to carry out their calculations for this particular system.

The values of B_{ij} obtained for the different pairs are reported in Table IV. It should be stressed that the interaction energy densities for the polymers were calculated by using miscibility data at 150 °C, and their accuracy is ±20%. The B_{ij} for the analogues are the values experimentally determined in the present work at 25 °C. Considering all the above limitations, the agreement of the two sets of values is at least fair.

Further use of the binary interaction parameters can be made by means of eq 1 (subscripts used are those assigned in Table IV). When the values in the latter table are substituted into this expression, fair agreement is found between the experimental and predicted values for the BDA–heptane 2,4-DCP system, with a one-to-one weight ratio of the components, as can be seen in Figure 4. Also, qualitative agreement is obtained for the system using EA instead of BDA, as shown in Figure 5, even though the higher value for B_{12} was used for the calculation. The calorimetric results shown in the previous section illustrate that the binary systems have a highly nonparabolic nature in several cases; hence, the assumption of parabolic behavior inherent in the above predictions may be an important source of difference with the experimental results.

The fact that BDA is essentially a PVAc dimer probably plays an important role here, since it is difficult to envision the two ester groups on the same molecule having the right orientation to simultaneously interact with 2,4-DCP, whereas in EA, each ester functionality operates independently from the others. Hence, it appears logical that there is a higher probability for attaining proper carbonyl orientation in each EA molecule to interact with the CHCl group and generate more negative heats of mixing. Although somewhat qualitative, this interaction scheme is confirmed by the spectroscopic results.

Fourier Transform Infrared Spectroscopy. A more mechanistic view of the interactions involved in these systems was sought by spectroscopic measurements. Previous studies of this type for mixtures of ester-containing polymers, including EVA with PVC, have appeared in the literature[14,22,23] as well as similar reports in which low molecular weight model compounds are used instead of the polymers.[23,26] Information involving the relevant interactions has been derived mostly from the carbonyl IR band of the ester group. A shift of this band toward lower frequencies ("red shift"), generally accompanied by some broadening, has been consistently observed in blends where the ester-containing polymer is miscible with PVC. However, essentially no modification of the carbonyl peak occurs when the mixture is not miscible.[35] Hence, the participation of the carbonyl group in the specific interaction is unquestionable and has been well documented, however, there has been some debate as to the functional group in PVC that is actually interacting with the ester carbonyl. Given the acidic nature of the α-hydrogen atom (or methine proton) in the PVC repeat unit, it appears logical to postulate that when the ester-containing segments are added a weak O···H hydrogen bond is formed that constitutes the main driving force for miscibility, as has been often stated.[23,36] Nevertheless, experiments involving carbon tetrachloride and carbonyl-containing compounds suggest that a dipole–dipole interaction between the chlorine atom and the C=O bond is possible. Kiyohara et al.[32] point out that such an interaction could be responsible for the observed negative heats of mixing for methyl ethyl ketone (MEK) and other ketones with CCl_4; on the other hand, IR experiments involving the methyl ethyl ketone/carbon tetrachloride system show a slight blue shift and sharpening of the C=O band, as is also observed with MEK–heptane mixtures.[37] Moreover, Varnell et al.[36] note that the carbonyl band from methyl acetate is seen to shift to a lower frequency in the presence of deuterochloroform, but no apparent change is observed when carbon tetrachloride is added instead. This would lead to the conclusion that there is probably no Cl···C=O interaction. Garton,[38] after carrying out similar spectroscopic experiments, concludes that, indeed, methyl acetate does not interact with CCl_4, but a strong interaction is detected with chlorinated molecules containing α-hydrogens. In the polymers, FTIR spectroscopic measurements have not aided in discriminating between the two interaction possibilities, because the methine vibration in the IR region has a very low intensity and overlaps with other bands, whereas the C–Cl band is conformation dependent and its analysis very complex.[14]

Notwithstanding the above features, the carbonyl band alone has a strong well-characterized IR absorption; hence, a great deal of information can be gained by analyzing its behavior under the distinct molecular environments tested here, since no interference from other bands is present. On the basis of this premise and the above reference frame, we proceed to analyze the FTIR results obtained.

Mixtures of BDA or EA with heptane follow similar trends in their carbonyl peak. As the amount of heptane in the solution increases, the carbonyl band is sharpened and shifts to a higher wavenumber, as illustrated for both model compounds in Figure 8. The band broadness of pure ethyl acetate is probably influenced by the sample size used. Dispersive interactions should predominate in these systems as confirmed by the endothermic heats of mixing already shown. In concomitance with this, the respective high molecular weight counterparts of these analogues, PE and PVAc, are immiscible.

At this point, one important question that deserves attention is why the carbonyl band shifts to higher frequencies when the ester group is placed in the heptane environment. Besides the differences in dielectric constants of the two compounds, which can be claimed as a reason for the shift of IR bands,[39] one other possibility involves dipole–dipole interactions of the carbonyl groups, as suggested by Kiyohara et al.[32] from calorimetric measurements. At least some degree of molecular aggregation has been reported in the literature for ethyl acetate even in the vapor phase,[40] and some departure from a nonassociated state has been determined for other aliphatic esters.[41] Hence, if the already mentioned dipole–dipole interactions are strong enough, two populations of carbonyls may exist: "free" and "self-interacting", having very similar vibration frequencies. By the means used here, the two resulting bands would not be separately observed but would appear as overlapping bands. The typical IR behavior of carbonyl in donor–acceptor situations suggests a "free" carbonyl would appear at a slightly higher wavenumber. When an inert solvent is added, the population of "self-interacting" carbonyls would tend to decrease in favor of keeping a quasi-chemical equilibrium situation, thus generating more free carbonyls. In the IR spectrum, the outcome of such a change in proportions of these two bands would then be the apparent blue shift observed. A

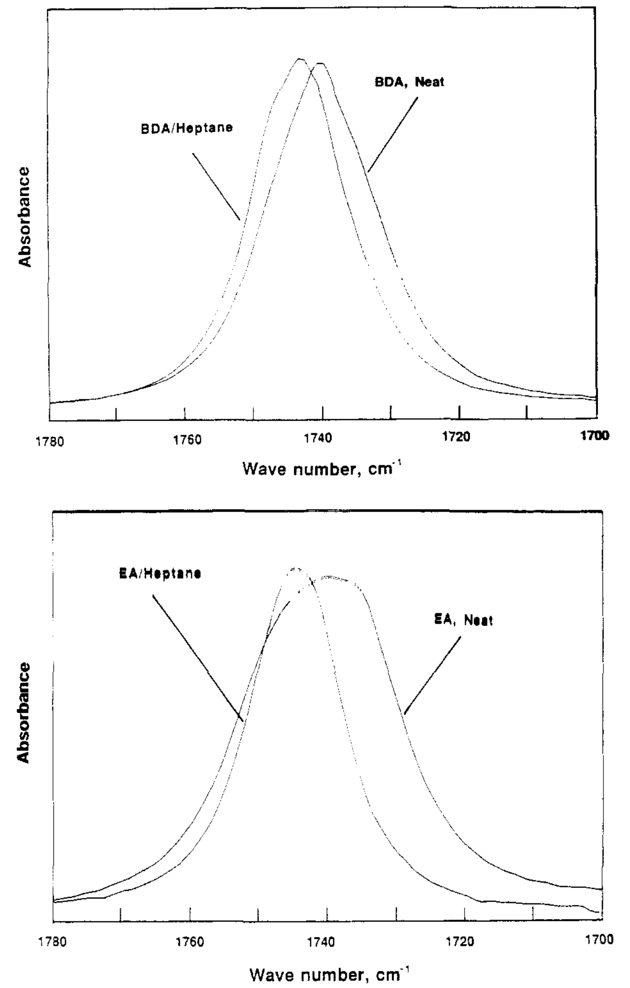


Figure 8. Behavior of carbonyl band in (a, top) 1,3-butanediol diacetate and (b, bottom) ethyl acetate and their mixtures with heptane. The weight percent of the acetates in heptane is, respectively, 60% and 57%.

similar phenomenon occurs in carbonyl-containing polymers[42] that are able to crystallize, in which the carbonyl population in the more closely packed crystalline phase has a clearly lower IR stretching frequency than the population in the amorphous phase, probably because the former is more prone to self-association. Finally, it should be mentioned that Fowkes et al.[43] have discussed the effects of molecular environment on the carbonyl shift in terms of acid–base interactions.

On the other extreme of the binary possibilities, Figure 9 illustrates how adding 2,4-DCP to either BDA or EA affects mainly the C=O bandwidth. In dilute solutions of BDA in 2,4-DCP, the peak maximum goes to a higher frequency; i.e., a slight "blue shift" is observed. In the case of EA, a very pronounced sharpening of the band is seen, while no shift in the maximum occurs. One might argue, in a very simplistic manner, that 2,4-DCP acts in an analogous fashion as an inert diluent, so it might be concluded that the ester and the chlorinated molecule interact to a very small extent. This result is indeed in line with the one obtained by calorimetry in that dispersive interactions predominate in these systems. However, both the spectroscopic and the calorimetric results might actually be the net outcome of different contributions, namely, the combination of dispersive forces, disruption of carbonyl dipole–dipole self-interactions, and an interaction between the C=O and CHCl groups, in which the first two components would cause a blue shift of the C=O peak while increasing the population of free carbonyls. The C=O interaction with the CHCl group would tend to decrease this effect, but its relative strength might not be large enough to compensate the other two components. The overall effect would then translate into endothermic heats of mixing for the 2,4-DCP/EA and 2,4-DCP/BDA systems, which correctly predicts immiscibility for PVC/PVAc blends.

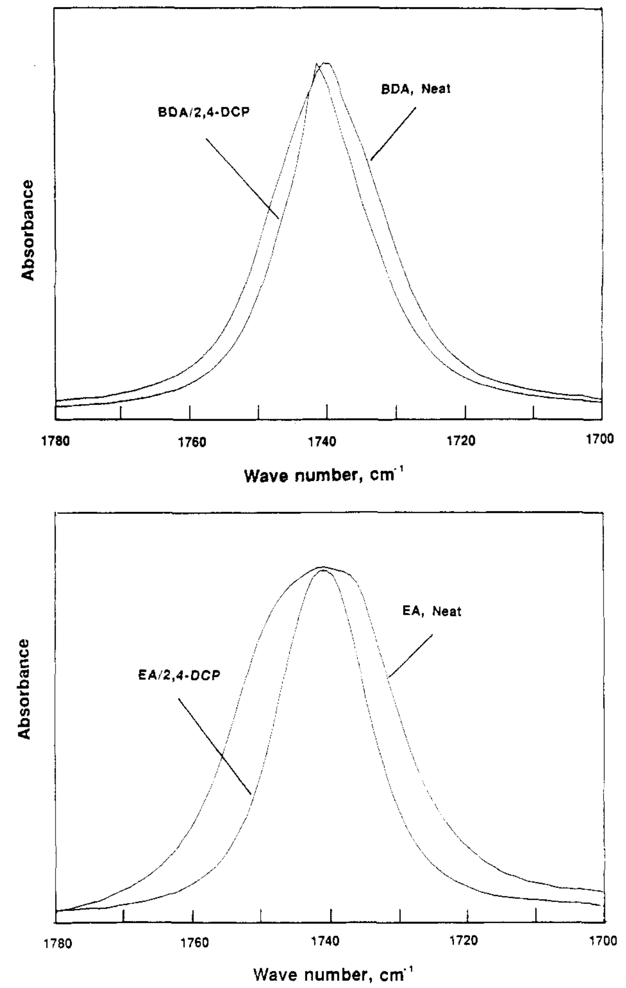


Figure 9. Behavior of carbonyl band in mixtures of (a, top) 1,3-butanediol diacetate and (b, bottom) ethyl acetate with 2,4-dichloropentane. The weight percent of the acetates in 2,4-DCP is, respectively, 17.5% and 42%.

Keeping in mind the self-interaction hypothesis, it is now interesting to monitor the behavior of the carbonyl band in BDA or EA premixtures with heptane, as models of EVA, when the PVC analogue is added. Parts a and b of Figure 10 show how, upon the addition of 2,4-DCP, the C=O band shifts slightly to a lower frequency and broadens in the case of BDA and that a clear red shift can be appreciated when adding 2,4-DCP to the EA/heptane mixture. The first conclusion from this experiment is that the carbonyls are now interacting with the PVC analogue, perhaps because the addition of heptane dilutes the dipole–dipole interactions of the carbonyls and makes them more accessible. Correspondingly, exothermic heats of mixing are obtained for some of these combinations.

Figures 11 and 12 further illustrate this point for mixtures of 2,4-DCP with *sec*-butyl acetate and with *n*-dodecyl acetate. Broadening and a red shift of the carbonyl band with respect to the neat acetates are clearly observed in each case, and, from this, there is additional evidence of the carbonyl interaction with the CHCl group. The *sec*-butyl acetate carbonyl band actually broadens considerably, and, as can be seen in Figure 11, a low-frequency

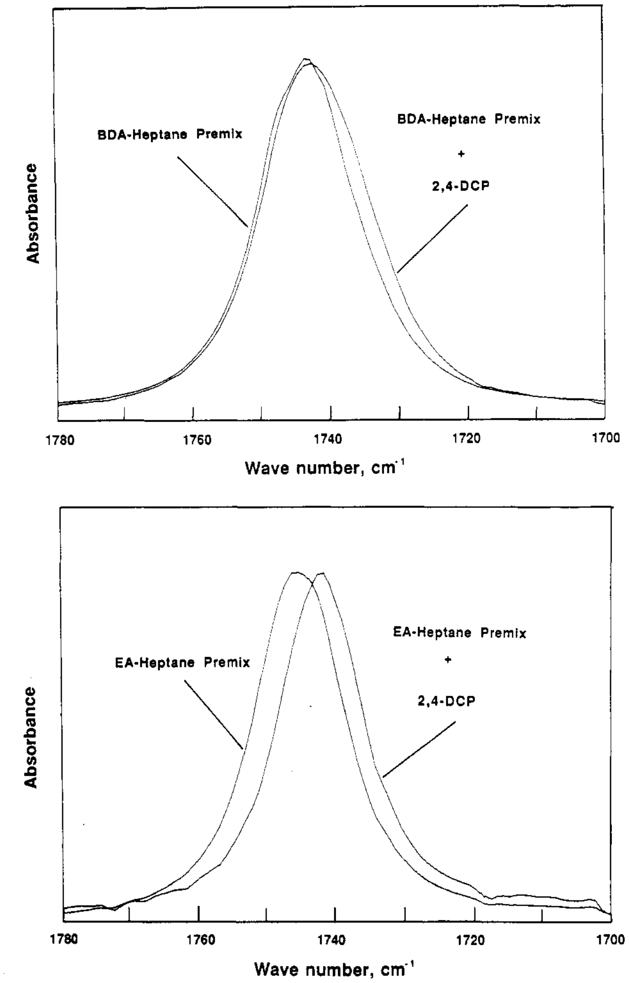


Figure 10. Effect of the addition of 2,4-dichloropentane to (a, top) BDA–heptane premix and (b, bottom) EA/H premix. Weight ratio of premix to 2,4-DCP is 1 to 1. Concentrations of BDA and EA in heptane are the same as in Figure 8.

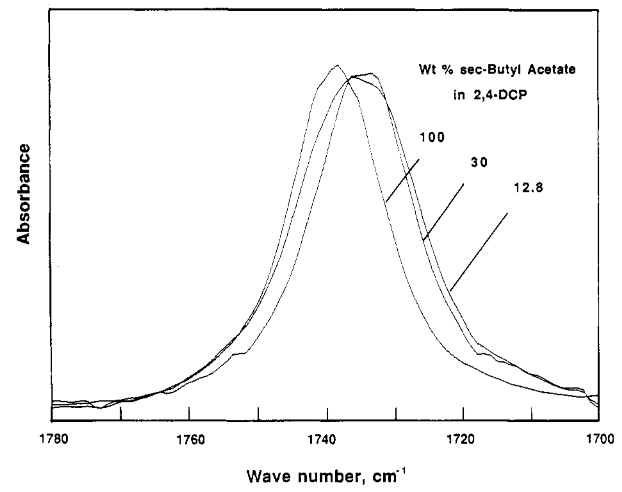


Figure 11. Behavior of the carbonyl band in *sec*-butyl acetate after successive additions of 2,4-dichloropentane.

shoulder is apparent at moderate concentrations, which becomes the main absorption peak at higher dilutions. The origin of this finding might be traced to the strength of the C=O interaction with the CHCl group. Garton[38] found that the carbonyl band splits into two components when methyl acetate is mixed with a 1,1,2,2-tetrachloroethane–heptane premix; the author assigns the higher frequency peak to the noninteracting carbonyls and the lower frequency component to the C=O population that interacts with the chlorinated molecule. Therefore, although the interaction in the present case may not be so strong to cause band splitting, the carbonyl absorption probably has a composite nature.

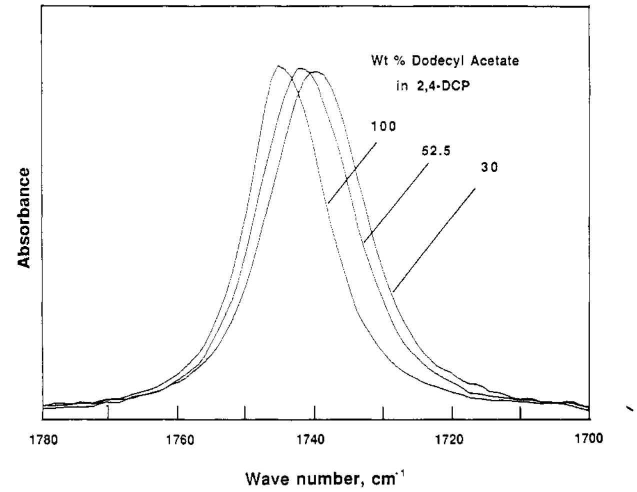


Figure 12. Changes in the carbonyl band peak position caused by dilution of dodecyl acetate with 2,4-dichloropentane.

Mixtures of 2,4-dichloropentane with *sec*-butyl acetate and with *n*-dodecyl acetate were examined to follow the trend of the band position as the ester is diluted with the chlorinated compound (see Figure 13a,b, where the peak maxima are plotted vs the acetate weight percentage). A monotonically decreasing carbonyl frequency is observed. At least in the *n*-dodecyl acetate case, it is tempting to say, even with the few data points presented, that less peak displacement is obtained as more dilute solutions of this compound in 2,4-DCP are used. Thus, a possible saturation of the interacting sites is reached at a certain concentration. For this particular case, the acetate-rich region is characterized by a small exothermic heat of mixing, as shown in Figure 6b, whereas the 2,4-DCP-rich portion is endothermic; hence, even having an evidently large degree of carbonyl interaction with the chlorinated compound does not guarantee that a negative heat of mixing is generated. In this particular instance, the balance of specific or negative interactions and dispersive forces is marginal. The region more concentrated in the ester has more carbonyls available for interaction with the 2,4-DCP molecules, which probably causes the exothermic effect, whereas it is likely that, if a point is reached where all carbonyls are already involved in an interaction, the further addition of 2,4-DCP is tantamount to increasing only the dispersive component in the heat of mixing and, hence, its endothermic behavior.

The more important aspects of this section can be presented most clearly by considering the change in position of the carbonyl band as the different EVA low molecular models are mixed in approximately equal weight proportions with 2,4-DCP to make the comparison more amenable with Figures 1, 4, 5, and 7. Figures 14–16 show the change in the band position of the carbonyl group for the three different analogue alternatives on adding 2,4-DCP. A shift of the carbonyl band toward lower frequencies if found as a result of the interaction between the polar acetate units and the CHCl groups. Moreover, plotting the difference between the original wavenumber of the carbonyl band and that seen after the addition of 2,4-DCP, as shown in Figure 17, clearly illustrates the red shift mentioned.

It must be remarked that the magnitude and sign of the C=O shifts found here closely agree with those for EVA–PVC blends.[14] Coleman et al.[14] report a shift of about 6

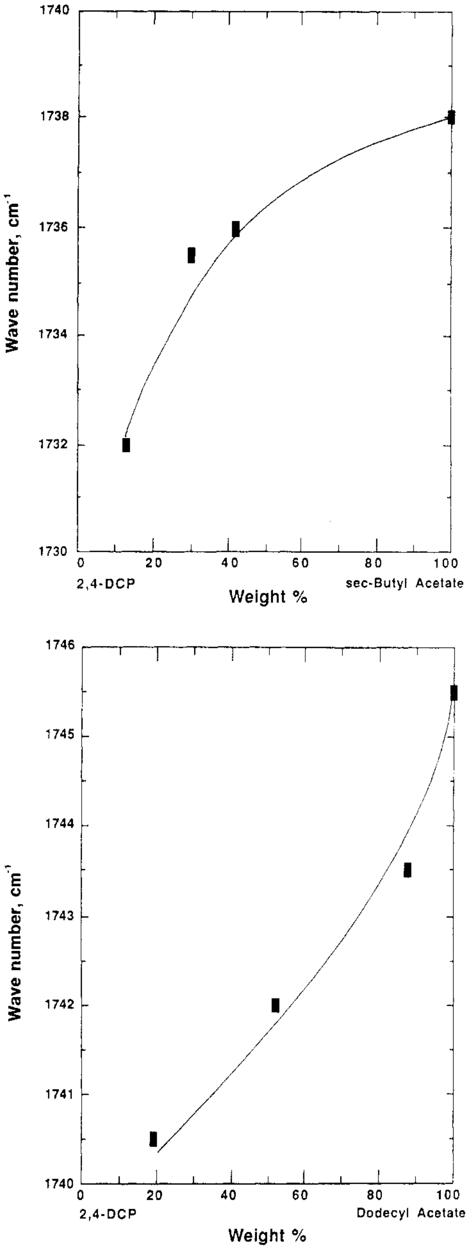


Figure 13. Concentration dependence of carbonyl band peak position of (a, top) *sec*-butyl acetate and (b, bottom) dodecyl acetate mixed with 2,4-dichloropentane.

cm^{-1} for a mixture of EVA45 with PVC in a weight ratio of 1 to 4, at room temperature, which would be similar to the shift obtained when ethyl acetate or an alkyl ester is used as the model compound for EVA.

The monotonic red shift of the carbonyl band in all cases illustrates that as the carbonyl-containing units are diluted more by the methylene environment they are more accessible to interact with the PVC model compound. Thus, when high concentrations of carbonyls are present, as in pure BDA and EA, perhaps some degree of interaction exists with 2,4-DCP but not enough to overcome the endothermic contributions from the dispersive component and the disruption of dipole self-interactions. However, as the carbonyl unit concentration is decreased by dilution, a greater degree of accessibility is attained, and the interaction of the C=O and CHCl groups becomes the dominant factor that drives the heat of mixing to negative values. This is characterized by an ever-decreasing wavenumber of the carbonyl band. Nevertheless, as the dilution of carbonyl groups proceeds further, even though the interaction is still present, the dispersive forces derived from the increased amount of ethylene segments in the mixture dominate the total energetics and produce the observed endothermic heat of mixing in the carbonyl-poor region. Finally, when no carbonyls are present, the ethylene and chlorinated moieties interact with the highest endothermic energetics. The above parallels the miscibility observed in the polymer systems and illustrates that an added advantage of the use of low molecular weight analogue mixtures is the possibility of probing compositions which are not accessible as homogeneous phases in polymer blends.

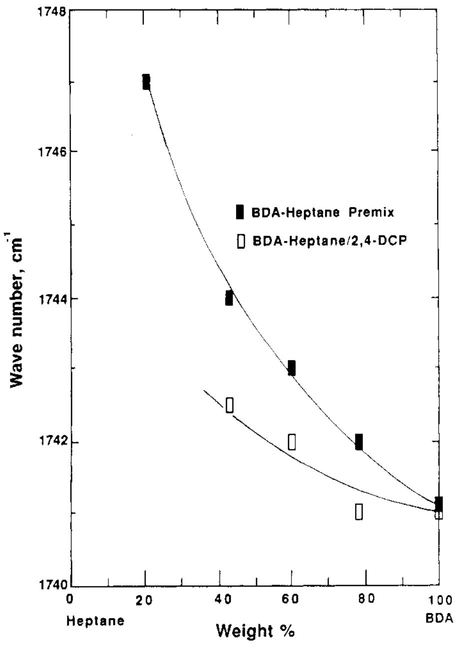


Figure 14. Position of carbonyl peak in BDA–heptane premixtures. Upper curve: binary BDA–heptane premixes. Lower curve: BDA–heptane premixes after adding 50 wt % 2,4-DCP.

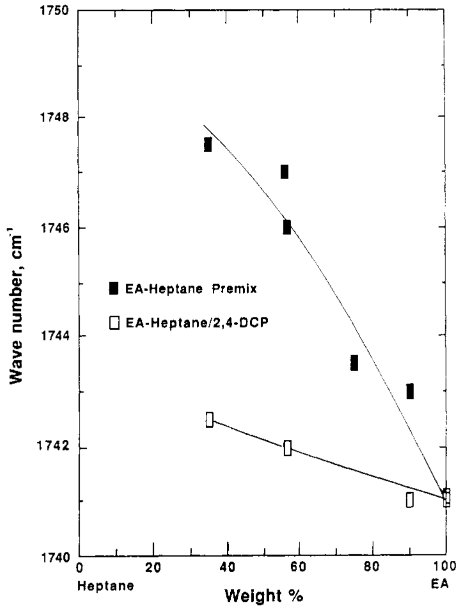


Figure 15. Position of carbonyl peak in EA–heptane premixtures. Upper curve: binary EA–heptane premixes. Lower curve: EA–heptane premixes after adding 50 wt % 2,4-DCP.

Conclusions

Low molecular weight analogue compounds appear to model closely the energetic behavior of blends of PVC with EVA copolymers. This has been confirmed based on the criterion that a negative enthalpy of mixing drives polymer

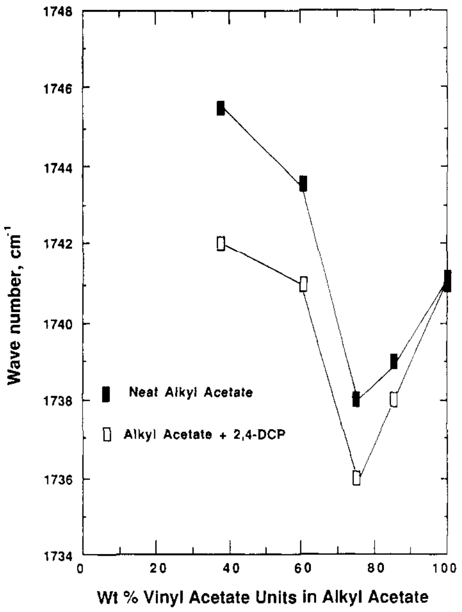


Figure 16. Position of carbonyl band in alkyl acetates before (upper curve) and after (lower curve) the addition of 2,4-DCP.

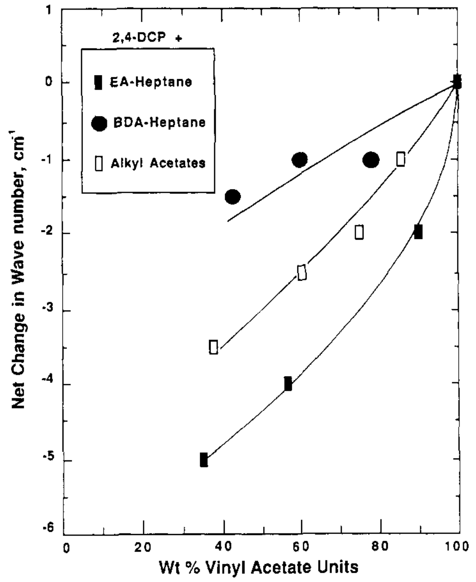


Figure 17. Net change in the carbonyl peak maximum after the addition of 2,4-DCP to BDA–heptane and EA–heptane premixes and to alkyl acetates. Differences taken from the points in Figures 14–16.

miscibility. Calorimetric measurements in the analogues predict the existence of a miscibility window in PVC–EVA systems at intermediate compositions of ethylene and vinyl acetate in the copolymer that are close to those reported in the literature.

FTIR spectroscopy gives evidence of the interaction involving the carbonyl groups in the copolymer with the CHCl group in PVC. A shift similar in magnitude and direction as detected in EVA–PVC systems is seen for the carbonyl band of the EVA analogue in the presence of the chlorinated model compound.

On the basis of previous results,[14,17,32] one might speculate that miscibility in this system can be rationalized by considering three mechanisms that contribute to the enthalpy of mixing. Two of these are of an endothermic nature, namely, a dispersive van der Waals type contribution and the energy required to disrupt dipole–dipole carbonyl "self-interactions" when the acetates are placed in a new molecular environment. No direct evidence for the latter is offered here, but previous investigations point out its existence.[32] The C=O interaction with the CHCl group is the exothermic component. The balance between these three forces is delicate and produces a net exothermic enthalpy at intermediate acetate to ethylene ratios, whereas the endothermic components overcome the exothermic contribution at the acetate-rich and ethylene-rich ends.

All three different pairs of analogues used here, i.e., heptane, 2,4-dichloropentane, and ethyl acetate or 1,3-butanediol diacetate, produce endothermic enthalpies of mixing when taken in pairs at 1 to 1 weight ratios. The interaction energy densities calculated from these results, when used in a thermodynamic binary interaction model[18,20] predict, at least qualitatively, a region of exothermic excess enthalpy and consequent polymer miscibility in the intermediate composition range.

The calorimetric measurements obtained here represent experimental determinations of the energetic effects at play in the polymer systems considered and reflect their phase behavior. Such good correspondence requires careful selection of the liquid analogues for polymer segments; for some systems, the energetic interactions in the polymer blend can be substantially different than those for the mixtures of structurally analogous low molecular weight species.[44,45]

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Registry No. BDA, 1117-31-3; EA, 141-78-6; heptane, 142-82-5; isopropyl acetate, 108-21-4; hexyl acetate, 142-92-7; *sec*-butyl acetate, 105-46-4; dodecyl acetate, 112-66-3.

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Addition of Dichlorocarbene to Poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) and Poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene). Characterization of Microstructures by ^{13}C and ^{29}Si NMR

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ABSTRACT: Dichlorocarbene generated under phase-transfer catalysis conditions was added to poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I). Catalytic isomerization of I by photochemically generated phenylthio radicals gave poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II). Dichlorocarbene was also added to II. The microstructures of these dichlorocarbene adduct polymers were characterized by ^{1}H, ^{13}C, and ^{29}Si NMR. Their thermal stabilities were determined by thermogravimetric analysis. They were found to be considerably less stable than the starting polymers I or II. These dichlorocarbene adduct polymers slowly undergo spontaneous depolymerization at room temperature. The mechanism of this process is considered.

There is considerable interest in the chemical modification of polymers.[1,2] Dichlorocarbene, efficiently generated by reaction of concentrated aqueous solutions of potassium or sodium hydroxide with chloroform in the presence of catalytic amounts of quaternary ammonium salts phase-transfer catalysts (PTC), has been added stereospecifically to the carbon–carbon double bonds of the backbones of *cis*- and *trans*-1,4-polybutadiene.[3-6] Difluorocarbene has also been added to the carbon–carbon double bonds of 1,4-polybutadienes.[7]

We should like to report the addition of dichlorocarbene, generated under PTC conditions, to poly(1,1-dimethyl-1-sila-*cis*-pent-3-ene) (I) and to poly(1,1-dimethyl-1-sila-*cis* (and *trans*)-pent-3-ene) (II). Anionic ring-opening polymerization of 1,1-dimethyl-1-silacyclopent-3-ene as previously reported gave I.[8] Stereospecific cis addition of dichlorocarbene to the carbon–carbon double bonds of I produces a polymer (III) whose microstructures can be analyzed by ^{13}C and ^{29}Si NMR spectroscopy. Two signals are observed in the ^{29}Si NMR at 3.88 and 3.76 ppm. The first results from the microstructure in which two consecutive dichlorocyclopropane rings are on the same side of the polymer backbone, while the second arises from the microstructure in which one cyclopropane ring is on one side while the next is on the opposite side of the polymer chain. Similarly, two signals are observed in the ^{13}C NMR for the methyl groups bonded to the silyl centers at −2.77 and −2.86 ppm (see Figure 1).

Neither the ^{13}C NMR chemical shifts of the methine carbons (29.90 ppm) nor those of the dichloro-substituted carbons (68.14 ppm) are sensitive to the neighboring units' microstructure. Triad analysis predicts three distinct microenvironments: one in which three adjacent cyclopropanes are on the same side of the polymer chain (s,s,s), one in which two adjacent cyclopropanes are on the same side while the next is on the opposite side (s,s,o), and finally one in which the one cyclopropane is on one side, the next on the opposite, and the last on the same side of the polymer chain as the first (s,o,s). Analysis of these situations leads to the prediction that the two symmetrical triads (s,s,s) and (s,o,s) will each give rise to a distinct ^{13}C NMR resonance for the methylene carbons, while the unsymmetrical triad (s,s,o) will give rise to two unique methylene carbon signals for a total of four distinct methylene resonances. In fact, only two signals are observed for the methylene carbons. This may be explained if fortuitously one of the methylene resonances for the unsymmetrical triad is coincident with the signal for the first symmetrical triad while its other ^{13}C methylene signal is coincident with that of the other symmetrical triad (see Figure 2).

An alternative way to analyze these data is to assume that the ^{13}C chemical shifts of the methylene carbons of the central unit of each triad are only affected by the stereochemical orientation of the nearest-neighbor cyclopropanes. Application of this approach to the unsym-

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