Macromolecules **1983,** *16,* 391-396

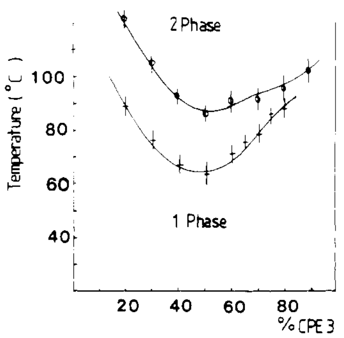

Figure 10. Phase diagrams for blends CPE3-EVA40 (+) and CPE3-EVA45 (O).

the CPE3 has a higher LCST than H48, which has a higher LCST than H40. Hence the CPE3 is more compatible than H48, which is more compatible than H40. For both sets of polymers this coincides with a higher concentration of interacting groups, resulting in a higher degree of compatibility as would be expected. In many cases the phase diagrams show indications of asymmetry or even bimodality. This is not an unusual phenomenon in polymer/polymer phase diagrams[8] and various explanations of it have been given.

Conclusions

Various chlorinated polyethylenes and ethylene-vinyl acetate copolymers have been found to be compatible at all compositions at room temperature. They all show evidence of an LCST, phase separating at temperatures between room temperature and 100 °C. The polymers with a higher concentration of functional groups, chlorine or acetate, respectively, show the higher LCST and are hence more compatible. This shows the importance of the specific interaction in causing compatibility and of the relative concentrations of interacting groups in determining the degree of compatibility and the temperatures of the phase separation boundaries. In a further paper we proceed to explore the detailed thermodynamics of the system.[9]

Registry No. EVA, 24937-78-8.

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Compatibility of Ethylene-Vinyl Acetate Copolymers with Chlorinated Polyethylenes. 2. Investigation of the Thermodynamic Parameters

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ABSTRACT: An investigation was made into the thermodynamic parameters of the compatible polymer system ethylene-vinyl acetate copolymer/chlorinated polyethylene. The heats of mixing of low molecular weight analogues were measured and found to be negative, favorable for mixing. The interaction parameter was measured by inverse gas chromatography and this was found to be negative, changing to positive at higher temperatures, consistent with the observed phase separation on heating. The effect of pressure on the phase boundary was also measured. The phase boundary moved to higher temperatures with increasing pressure, which predicts a densification on mixing. It was concluded that it would be necessary to invoke an unfavorable noncombinatorial entropy contribution to the free energy of mixing in order to accommodate the heat of mixing measurements with the observed phase separation on heating.

Introduction

The compatibility of polymers, as of any other materials, is determined by the free energy of mixing ΔG. A favorable free energy of mixing is a necessary but not sufficient requirement for compatibility, but if one can predict the free energy of mixing as a function of composition, then one can predict whether the two polymers are compatible under those conditions of temperature and pressure.

The theoretical problem is therefore to predict ΔG from known or measurable properties of the substances. Various theories have been developed to deal with this problem in the case of polymer solutions and mixtures. Most are basically Flory-Huggins, or lattice, models, which assume a lattice on which the polymer molecules can be arranged and therefore calculate an entropy of mixing. This combined with a heat of mixing, depending on an interaction function and some function of composition, gives ΔG. These models have been very successful in explaining many properties of polymer solutions but have some shortcomings, especially in that they do not take account of possible volume changes on mixing. Corresponding-state and equation-of-state models seek to overcome this. The parameters of pressure, temperature, and volume are expressed in a reduced form by dividing them by reduction parameters, and volume changes are allowed. The calculations are much more complicated, and a great deal of information (often not available) about the materials is required. In many circumstances despite all this effort

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they do not fit the experimental results much better than the simpler theories. All the theories have been reviewed many times,[1-3] and here we only describe those parts that directly relate to our results. In the case of polymer mixtures the thermodynamics are often dominated by the specific interactions between the polymers, and none of the theories can adequately describe these phenomena.

In its simplest form the Flory–Huggins model is unable to deal with the miscibility of high molecular weight polymers. The combinatorial entropy is favorable for mixing but tends toward zero as the molecular weights tend toward infinity. A single interaction parameter (which can be related to the heat of mixing) therefore gives miscibility or immiscibility, depending on its sign. Mixtures of polymers often show phase separating on heating. This could only be explained in terms of this simple model if the heat of mixing varies markedly with temperature. Knowledge of how the heat of mixing (or interaction parameter) varies with temperature could therefore give us valuable information about any system being studied.

Phase diagrams also often are asymmetrical[4,5] or even bimodal. This can only be explained by a concentration dependence of the interaction parameter, and therefore information about the dependence of heat of mixing on composition is also of use.

In order to apply an equation-of-state model, one requires values of the reduction parameters. These can be derived from knowledge of the thermal expansion coefficient, $\alpha = [(\partial V/\partial T)_P]/V$, and the thermal pressure coefficient, $\gamma = (\partial P/\partial T)_V$. Experimentally, a direct or indirect estimate of the volume change on mixing can give useful information in terms of this model.

In all cases one must also consider the importance of various noncombinatorial entropy terms that can affect the result. This may be especially true for systems where there are specific interactions. These imply a preferred orientation of one polymer with respect to the other and a corresponding loss of entropy. None of the theories can describe this effect adequately.

The direct experimental determination of heats of mixing of high polymers is hindered by their viscosity. Oligomer mixtures have been used to overcome this problem[6] and should give reliable results as long as there are not pronounced end group effects.[6] Other workers have attempted to obtain values from measurements of mixing in solution.[7] This requires great experimental accuracy and many suffer from specific effects such as nonrandom mixing. Low molecular weight analogues can also be used[8] but these must be chosen carefully and can probably never model the system as well as oligomers. For any given system practical considerations often dictate the choice of alternative.

Inverse gas chromatography can also be used to determine values of interaction parameters for two polymers. For reasons discussed elsewhere,[9] we do not consider this a very reliable technique. However, the results are useful for comparative purpose and can give information concerning trends within a series of related polymer mixtures.

Direct measurement of the volume changes on mixing are difficult due to the inaccuracy of solid density measurements. Related information can, however, be obtained by measurement of the effect of pressure on phase separation behavior. Pressure changes the phase separation temperature and we can calculate $(\partial T/\partial P)_c$. The effect of pressure on polymer solutions has been reported,[10] and the effect on oligomers has also been examined.[11]

In this paper we report an investigation of the various thermodynamic parameters of mixtures of chlorinated polyethylene with ethylene–vinyl acetate copolymer. In the previous paper of the series we showed such polymers to be partially compatible, with lower critical solution temperatures depending on the composition of the polymers concerned.[12] We report measurements of the heat of mixing and interaction parameters as a function of temperature and composition as well as measurements of the effect of pressure on the phase boundaries.

Table I
Properties of Low Molecular Weight Analogues

	Cereclor 45	Cereclor 52	2-octyl acetate
wt % Cl	45.7	53.1	
$\overline{M}_n$	395	437	
density, g cm^3			
65 °C	1.1355	1.2319	0.8173
77 °C	1.1180	1.2140	0.8087
84 °C	1.1079	1.2039	0.8037

Experimental Section

Materials. The chlorinated polyethylene and ethylene–vinyl acetate copolymer, their sources, and their analysis were as described in the previous paper of this series. Blends of these polymers were also prepared as previously described. In this paper, the results are mostly concerned with blends of CPE3 (52.65% Cl) and EVA45 (45% vinyl acetate).

Two commercial chlorinated paraffins, Cereclor 45 and Cereclor 52 (ICI), were used as low molecular weight analogues of chlorinated polyethylene. The degrees of chlorination were determined by elemental analysis, the molecular weights by vapor phase osmometry at 37 °C using butanone as a solvent, and the densities by use of a pycnometer. The results of these measurements are shown in Table I.

1-Methyheptyl acetate (2-octyl acetate) was used as a low molecular weight analogue for the ethylene–vinyl acetate copolymers. It was prepared by the reaction of octan-2-ol with acetic anhydride. The octan-2-ol (AR) was distilled at 64 °C (20 mmHg) before use; all other reagents were AnalaR grade and were used as supplied.

Octan-2-ol (100 cm^3, 0.77 mol) and pyridine (80 cm^3, 1.0 mol) were placed in a flask fitted with a stirrer and reflux condenser. Acetic anhydride (86 cm^3, 0.91 mol) was slowly added to the flask via a dropping funnel while the contents were refluxed. The mixture was then refluxed for a further 4 h. Ether (100 cm^3) and distilled water (100 cm^3) were added to the contents of the flask. The organic layer was separated and washed successively with 10% sulfuric acid (40 cm^3) and sodium carbonate solution. The ether solution was dried over anhydrous sodium sulfate, the ether evaporated off, and the product distilled. The ester product was collected at 68–70 °C (20 mmHg).

Gas chromatography showed the product to be greater than 98% pure, the only observable impurity being unreacted octan-2-ol. Elemental analysis: C, 69.25 (69.77); H, 11.20 (11.63); O, 18.61 (18.60). The density was determined by pycnometry and the results are shown in Table I.

Heats of Mixing. The heats of mixing were measured with a modified NBS batch-type calorimeter.[13] The machine has an accuracy of ±0.02 J/g as determined by an acid–base reaction. However, the viscosity of our materials makes mixing more difficult and we estimate an error of ±0.05 J/g for our system. The machine was calibrated with a heating coil immersed in the particular systems under investigation.

Inverse Gas Chromatography. These measurements were carried out on a Pye GCD series chromatograph fitted with a flame ionization detector. Nitrogen was used as a carrier gas and the flow rate was controlled by a needle valve coupled to a pressure controller. The pressure was measured by a mercury manometer and the flow rate by a soap bubble flow meter.

The column support was 30–60 mesh PTFE (phase separation). The two polymers were weighed in the required quantity and ratio and dissolved at 5% (w/v) in THF. The beads were added and the solvent was evaporated with agitation to dryness. The resulting coated beads were dried under vacuum at 10^{-1} mmHg for 1 week. The product was then sieved through a 15-mesh sieve

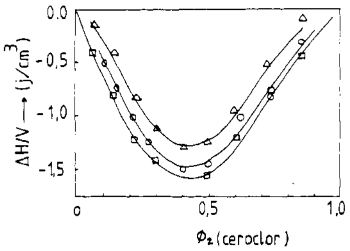

Figure 1. Plot of heat of mixing against composition for mixtures of 2-octyl acetate with Cereclor 52 at (□) 64.5, (○) 73.08, and (△) 84.5 °C.

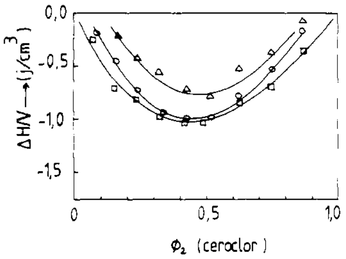

Figure 2. Plot of heat of mixing against composition for mixtures of 2-octyl acetate with Cereclor 45 at temperatures as in Figure 1.

and packed into glass coiled columns (150 cm × 4 mm i.d.). The coating weights used were 0.12 g/pg of support. This measured coating was determined by weighing the beads after extracting the polymer.

The columns were installed and heated to the appropriate temperature for 6 h while nitrogen was passed through the packings in order to achieve equilibrium. Injections of 0.1 μL of various solvent probes were made using a 1-μL syringe. Retention times were measured three times at each of three flow rates and the results extrapolated to zero flow rate. Values of the "noninteraction" retention time were obtained by injections of methane gas.

Measurement of the Effect of Pressure on the Phase Diagram. These were carried out with a bomb capable of withstanding 1500 atm and 100 °C as described elsewhere.[14] It was further modified by placing a thermocouple inside the bomb and by instrumentation of the system with a microcomputer.[15] Light could be passed through the sample and focused onto a photodiode; a drop in transmitted intensity was indicative of the cloud point. The background scattering from the oil as a function of temperature was linear and fairly constant over the range studied and therefore it was not necessary to subtract it in order to observe the cloud point.

The bomb was filled with paraffin oil, which must be changed frequently due to contamination reducing its clarity. A solvent-cast sample of the blend approximately 0.3 mm thick was placed in a sample tube, which was then filled with silicone oil (Dow Corning 200/350 cs). The tube was inverted over a trough of mercury, which transmitted the pressure to the sample when inside the bomb. The possible effect of silicone oil on the sample and on the cloud point was checked by measurement of the cloud point at atmospheric pressure both inside the bomb and in the turbidimeter described in the previous paper. The cloud point was found in each case to be identical with that of a sample in the absence of silicone oil.

A sample of a 50/50 blend of EVA45/CPE3 was used and cloud points were measured between atmospheric pressure and 750 atm.

Results and Discussion

The results for the heat of mixing of 2-octyl acetate with Cereclor 45 and with Cereclor 52 at three different temperatures are shown in Figures 1 and 2, respectively. At all temperatures and compositions the Cereclor 52 has a more favorable (more negative) heat of mixing with the ester than Cereclor 45. This corresponds with our observation in the previous paper of this series that chlorinated polyethylenes with a higher percentage of chlorine are more compatible (have a higher LCST) with ethylene–vinyl acetate copolymers. For both Cereclor mixtures the heat of mixing is less favorable at higher temperatures. This corresponds with our previous observation that the polymer mixtures phase separate on heating. The heat of mixing is, however, negative at all temperatures and compositions tested although the analogous polymers phase separated over this temperature range. The low molecular weight analogues may not be chemically identical with the polymers but it is probable that the heat of mixing is indeed negative and a large unfavorable noncombinatorial entropy of mixing causes them to be incompatible.

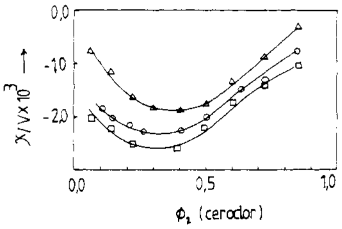

Figure 3. Plot of the interaction parameter χ/V^0 against composition for mixtures of 2-octyl acetate with Cereclor 52 at temperatures as in Figure 1.

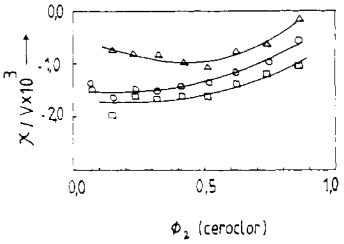

Figure 4. Plot of the interaction parameter χ/V^0 against composition for mixtures of 2-octyl acetate with Cereclor 45 at temperatures as in Figure 1.

The heat-of-mixing results can be presented alternatively in terms of an interaction parameter χ using $\Delta H/V = RT(\chi/V^0)\phi_1\phi_2$, where ϕ_1 and ϕ_2 are the volume fractions of each component. V^0 is an arbitrary segment volume that we cannot specify for analogues or a series of different copolymers. We will therefore discuss our results in terms of an unnormalized quantity in order to allow comparison of the various quantities.

The results for mixtures of ester with Cereclor 45 and Cereclor 52 are shown in Figures 3 and 4, respectively. The χ/V^0 values are negative for all compositions and temperatures but show a composition dependence being less favorable for compatibility at higher Cereclor contents. This corresponds to the asymmetrical cloud point diagrams for mixtures of chlorinated polyethylene with ethylene–vinyl acetate copolymers, which showed less compatibility (a lower phase separation temperature) for higher volume fractions of chlorinated polyethylene.

If there is a specific interaction between two polymers, there is no reason for the heat of mixing to be adequately described by the above equation, which is more appropriate for dispersion forces. The heat of mixing could be expected instead to depend on the concentrations of the interacting groups and the energetics of the process as well as interactions of other sorts within and between the two polymers concerned.

Samples of the various polymers were examined by inverse gas chromatography using several solvent probes in order to calculate the polymer–solvent interaction parameters, and from these and measurements using polymer blends, values of the polymer–polymer interaction parameters could be found.

Table II
Polymer–Solvent Interaction Parameters and Polymer–Polymer Interaction Parameters for EVA45, CPE3, and Three of Their Blends at 70 °C

				EVA45		CPE3		25% (w/w) CPE3		50% (w/w) CPE3		75% (w/w) CPE3	
solvent	P_1^0, atm	V_1, cm^3	B_{11}	$V_{g\,2}^0$, cm^3/g	χ_{12}	$V_{g\,3}^0$, cm^3/g	χ_{13}	$V_{g\,23}^0$, cm^3/g	χ_{23}/V_2	$V_{g\,23}^0$, cm^3/g	χ_{23}/V_2	$V_{g\,23}^0$, cm^3/g	χ_{23}/V_2
acetone	1.578	79.204	−1200	16.00	1.548	15.05	1.329	14.56	−0.0060	15.00	−0.0015	15.64	0.0011
methanol	1.208	42.920	−950	10.01	2.867	5.23	3.236	9.02	0.0049	6.00	−0.0211	5.973	−0.0070
ethyl acetate	0.785	104.886	−1300	37.37	1.083	23.55	1.265	30.147	−0.0063	26.00	−0.0060	26.55	−0.0010
tetrahydrofuran	1.145	84.936	−1005	43.25	0.776	34.02	0.737	36.26	−0.0089	32.1	−0.0089	32.99	−0.0058
diethyl ether	3.032	113.450	−768	10.28	1.000	3.66	1.752	7.58	−0.0049	7.2	−0.00353	5.878	0.0066
chloroform	1.336	47.625	−860	72.75	0.677	24.34	1.493	52.71	−0.0124	37.00	−0.0166	32.42	−0.0046
n-pentane	2.788	125.020	−830	8.00	1.237	1.96	2.362	6.07	0.0006	4.00	−0.0025	4.02	0.0107
2-butanone	0.689	95.621	−1508	41.38	1.204	38.20	0.822	35.2	−0.0097	30.00	−0.0118	32.42	−0.0093
dichloromethane	1.909	40.021	−558	33.37	1.273	13.74	1.881	27.00	−0.0355	15.90	−0.0356	15.17	−0.0201
average									−0.0119		−0.0142		−0.0079
χ/V^0 (from ΔH)									−0.0022		−0.0024		−0.0015

Table III
Polymer–Solvent Interaction Parameters and Polymer–Polymer Interaction Parameters for EVA45, CPE3, and Three of Their Blends at 100 °C

				EVA45		CPE3		25% (w/w) CPE3		50% (w/w) CPE3		75% (w/w) CPE3	
solvent	P_1^0, atm	V_1, cm^3	B_{11}	$V_{g\,2}^0$, cm^3/g	χ_{12}	$V_{g\,3}^0$, cm^3/g	χ_{13}	$V_{g\,23}^0$, cm^3/g	χ_{23}/V_2	$V_{g\,23}^0$, cm^3/g	χ_{23}/V_2	$V_{g\,23}^0$, cm^3/g	χ_{23}/V_2
acetone	3.606	82.820	−790	8.00	1.7383	6.00	1.7549	8.85	0.0123	6.00	0.0207	4.74	−0.0180
methanol	3.615	44.820	−543	3.86	3.0889	1.30	3.9060	4.80	0.0610	2.70	0.4982	2.21	0.0294
ethyl acetate	1.996	110.386	−1030	11.10	1.6865	8.25	1.712	17.00	0.0275	9.00	0.0012	11.50	0.0107
tetrahydrofuran	2.183	87.209	−780	13.01	1.6607	11.76	1.4906	22.00	0.0391	13.50	0.0042	15.20	0.0126
diethyl ether	6.388	121.212	−607	3.64	1.6218	1.63	2.1541	5.50	0.0296	3.00	0.0055	2.30	0.0042
chloroform	3.124	48.946	−690	21.4	1.3960	8.30	2.072	25.70	0.0480	11.90	0.0446	15.00	0.0300
chloroform	3.124	48.946	−690	21.4	1.3960	8.30	2.072	25.70	0.0480	11.90	0.0446	15.00	0.0300
n-pentane	5.803	133.904	−700	3.00	1.8175	1.00	2.6450	4.00	0.0238	1.90	0.0024	2.01	0.0131
2-butanone	1.661	98.754	−1100	11.90	1.9023	12.00	1.6228	18.02	0.0262	12.00	0.0006	14.00	0.0078
dichloromethane	3.190	41.395	−467	9.60	2.3222	4.85	2.7339	11.5	0.0420	6.9	0.0117	10.20	0.0004
average									0.0344		0.0108		0.0135

The quantity measured is the time taken for a pulse of solvent to pass through the column (t_s) and the volume flow rate of carrier gas (Q). These are related to the specific retention volume at 273.15 K by

$$V_g = (t_s - t_m)Q\frac{j}{W}\frac{273.15}{T}$$

where t_m is the retention time for a noninteracting material, methane, W is the weight of stationary phase, T is the operating temperature, and j is the correction factor for gas compressibility, given by

$$j = \frac{3}{2}\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}$$

where P_i is the inlet pressure and P_o is the outlet pressure. The values of V_g are extrapolated to zero flow rate to give V_g^0.

The polymer–solvent interaction parameter can be found from [16]

$$\chi_{12} = \ln\frac{273.15Rv_2}{P_1^0V_g^0V_1} - 1 - \frac{P_1^0}{RT}(B_{11} - V_1)$$

where v_2 is the specific volume of the polymer, P_1^0 is the vapor pressure of the solvent, V_1 is the molar volume of the solvent, and B_{11} is the second virial coefficient of the solvent, all these values being at column temperature. Values for these parameters were obtained or calculated from results from various sources. The densities of the solvents were found from Timmermans[17] as were values of P_1^0 except for THF and butanone, which were calculated by the method of Ambron.[18] Second virial coefficients were taken from Dymond and Smith,[19] those for THF and butanone being estimated from critical constants by the method of McGlashan and Potter.[20]

The data, measurements, and results for the polymer–solvent interaction parameters for EVA45 (ethylene–vinyl acetate copolymer) and CPE3 (chlorinated polyethylene) for a series of solvents at 70 and 100 °C are shown in Tables II and III, respectively. It can be seen that EVA45 has the most favorable interaction with the electron-acceptor hydrogen-bonding solvent chloroform whereas CPE3 has the most favorable interaction with electron-donor hydrogen-bonding solvents. This demonstrates the complementary dissimilarity between the two polymers.

Provided that χ_{12} and χ_{13} are known, measurements of the interaction between a solvent and a column containing a homogeneous mixture of the two polymers can be used to determine the interaction parameter χ_{23} between the two polymers:

$$\left[\left(\frac{\chi_{12}}{V_1}\right)\phi_2 + \left(\frac{\chi_{13}}{V_1}\right)\phi_3 - \left(\frac{\chi_{23}}{V_2}\right)\phi_2\phi_3\right]V_1 = \ln\frac{273.15R(W_2v_2 + W_3v_3)}{P_1^0V_{g\,23}^0V_1} - \left(1 - \frac{V_1}{V_2}\right)\phi_2 - \left(1 - \frac{V_1}{V_3}\right)\phi_3 - \frac{P_1^0}{RT}(B_{11} - V_1)$$

Alternatively, χ_{23} can be obtained directly from values of

$V_g{}^0$ obtained from single polymers

$$\frac{1}{V_1}\left[\frac{1}{\phi_3}\ln\frac{v_2}{V_g{}^0{}_2}+\frac{1}{\phi_2}\ln\frac{v_3}{V_g{}^0{}_3}-\frac{1}{\phi_2\phi_3}\ln\frac{W_2v_2+W_3v_3}{V_g{}^0{}_{23}}\right]=\frac{\chi_{23}}{V_2}$$

where ϕ_2 and ϕ_3 are the volume fractions and W_2 and W_3 are the weight fractions of polymers 2 and 3 in the mixed column. V_1, V_2, and V_3 are the molar volumes and v_2 and v_3 the specific volumes of the components; $V_g{}^0{}_2$, $V_g{}^0{}_3$ and $V_g{}^0{}_{23}$ refer to the single-component and mixed-column values.

Values of $V_g{}^0{}_{23}$ and the calculated values of χ_{23}/V_2 for columns prepared at three different polymer mixture compositions at 70 and 100 °C are also shown in Tables II and III, respectively. We also show an average value over all the solvents. The values of χ_{23} should be independent of solvent probe used but because of effects such as specific interactions and nonrandom mixing this is not the case, though the results are not very different and most show the same general trend with composition.

The estimated error in measurements of $V_g{}^0$ is between 1.5 and 5%. This translates into an error in χ_{12} and χ_{13} values of 1.6-6.6%, depending on the total value of $V_g{}^0$. This gives an error in χ_{23} ranging from ±0.001 to ±0.005. Values of χ_{23} derived from solvent probe such as pentane, methanol, and diethyl ether, which give lower retention volumes, are much less reliable.

The results shows more unfavorable interaction parameters for measurements at higher temperatures as would be expected, as these are close to the observed phase separation temperature noted for these two polymers in the previous paper. They also show less favorable interactions at higher fractional compositions of CPE3, which coincides with the asymmetry observed in the phase boundary.

The values of χ_{23}/V_2 are directly comparable with the values of χ/V^0 from the heat-of-mixing experiments with certain reservations. First, χ/V^0 was derived from heat of mixing per unit volume of two low molecular weight analogues; therefore they are only valid as far as 1 cm^3 of that mixture is equivalent to 1 cm^3 of the polymer mixture containing the same ratio of the respective components. Second, for reasons discussed in detail elsewhere,[9] we have reservations about the quantitative reliability of inverse gas chromatography because of the problem of removing the effects of surface adsorption and diffusion limitation in the stationary phase. Third, the heat-of-mixing data depend solely on the enthalpy of mixing whereas the inverse gas chromatography results depend on the free energy of mixing. The commonly used equations already have the Flory–Huggins equation built into them, which means that the χ values derived from them have any noncombinatorial entropy contributions built into them. We have included estimates of χ/V^0 interpolated to match the conditions of temperature (70 °C) and composition (weight percent, Cereclor 52) of the gas chromatography experiments in Table II. The χ/V^0 values extracted from heats of mixing are smaller but show a similar dependence on concentration. If the larger values from the gas chromatography results are attributed to a noncombinatorial entropy contribution, then this must be favorable for mixing. This is unlikely for a system with specific interactions. It is more likely that this is due to the oligomers not being exactly equivalent to the polymers or to the quantitative unreliability of the inverse gas chromatography results. The change to positive interaction parameters for inverse gas chromatography at 100 °C is also inconsistent with a favorable and noncombinatorial entropy contribution. The variation of the interaction parameter with temperature is much greater than the variation of the heat of mixing and this requires another explanation.

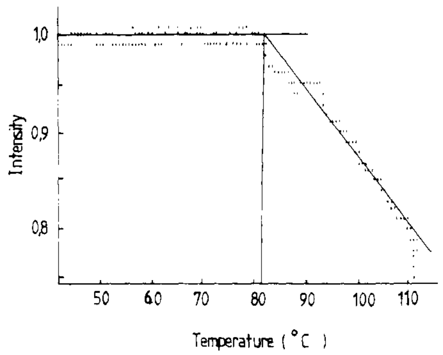

Figure 5. Plot of transmitted intensity against temperature for a 50/50 (w/w) mixture of EFA45 and CPE3 obtained using the pressure rig.

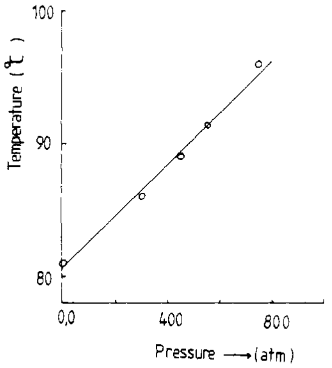

Figure 6. Plot of temperature of phase separation against pressure for a 50/50 (w/w) mixture of EVA45 and CPE3.

The cloud points for a 50/50 blend of EVA45/CPE3 were measured at a series of pressures. An example of the plots of transmitted intensity against temperatures is shown in Figure 5. At the cloud point the intensity begins to drop and in this way the cloud point temperature can be determined to within ±2 K. A plot of cloud point temperature against pressure is shown in Figure 6. A best-straight-line fit gives a value for dT/dP of $18 \times 10^{-3} \pm 3 \times 10^{-3}$ K atm.$^{-1}$

This can be related to the volume change on mixing by[21]

$$\left(\frac{\partial T}{\partial P}\right)_c = -\frac{(\partial\chi/\partial P)_T}{(\partial\chi/\partial T)_P} \simeq \frac{T\Delta V_m}{\Delta H_m}$$

Using $T = 355$ K and $\Delta H_m = -1.3$ J cm^{-3} (×9.869 atm), we find the fractional change in volume $\Delta V_m = -7 \times 10^{-4}$.

The negative sign is expected because if pressure increases the phase separation temperature, there must be a densification on mixing. This densification is generally favorable for mixing of the two polymers.

Conclusion

We have shown that the compatibility of ethylene–vinyl acetate copolymers with chlorinated polyethylenes can be understood because low molecular weight analogues have negative heats of mixing. Variation in the heat of mixing with composition has also been shown to coincide with the asymmetry in the phase diagrams of the polymers.

Measurements of polymer–polymer interaction parameters by inverse gas chromatography gave results consistent with phase separation over the temperature range observed within the limits of accuracy of the method.

The change in the phase separation temperature with pressure predicts a densification on mixing, which is also generally favorable for compatibility.

The phase separation at higher temperatures could be qualitatively explained by the variation of heat of mixing with temperature. The heat of mixing of the low molecular weight analogues does not change sign over the temperature range studied, which suggests that an unfavorable noncombinatorial entropy contribution is responsible for the phase separation in the high-polymer systems.

Registry No. EVA, 24937-78-8; 2-octyl acetate, 2051-50-5; octan-2-ol, 123-96-6.

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A Method for Studying the ^{13}C NMR Relaxation Time as a Function of Position along the Polymeric Chain

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ABSTRACT: A combination of selective deuteration and rapid pulse sequences in FT NMR allows one to determine ^{13}C T_1 in various portions of a polymeric molecule. This procedure has been applied to polystyrene. By preparing atactic polystyrene molecules selectively deuterated in the central portion of the chain, we have shown that carbons in the terminal portion have significantly greater T_1 than the average values determined in undeuterated and randomly deuterated molecules of comparable average molecular weights. These results indicate that the effective correlation times of the backbone carbons in long chains decrease from the center toward the terminals.

The use of NMR to investigate molecular dynamics in solution has been gaining in importance during the past decade. As can be seen from the recent review by Heatley,[1] the ^{13}C relaxation times (T_1 and T_2) in polymers are the most widely used NMR measurements for this purpose. In all such studies to date, the T_1's of various carbons in a polymer were measured as composite or effective relaxation times involving all carbons of any given type in the chain, without any attempt to separate the specific contribution of the relaxation times of terminal carbons or carbons in any particular portion of the chain. Such attempts were made only for some chain molecules of intermediate length, in which several distinct ^{13}C signals at the end of a chain can be resolved. Thus Levine et al.[2] and Lyerla et al.[3] measured the ^{13}C T_1 for resolved carbons in neat n-alkanes (n not exceeding 20). They found that the T_1's of the terminal carbons were considerably higher than those corresponding to the carbons in the central portion of the chain. Resonances of four terminal carbons could be resolved, and the indication was that there is a progressive increase in T_1 and corresponding decrease in τ_{eff} (effective correlation time) from the central to the terminal portion of the chain. Whether there is a corresponding monotonic increase in T_1 of macromolecules in general or whether this increase is largely limited to only a few terminal atoms in longer chains has never been experimentally answered. The purpose of this work was to devise an experimental procedure that will address the problem of variation of τ_{eff} of polymeric segments located in the different portions of the chain. It consists of a combination of selective deuteration and rapid pulse sequences in FT NMR. This procedure is described below.

Description of the Method

The ^{13}C relaxation times (T_1 and T_2) in polymers of protonated carbons are predominantly associated with a dipolar mechanism.[1] If any particular carbon is completely deuterated, its ^{13}C relaxation time (T_1) becomes considerably longer. In the case of isotropic rotational motion with a correlation time τ_C in the extreme narrowing limit ($\omega_0^2\tau_C^2 \ll 1$, ω_0 being the magnetic resonance frequency), the ratio of relaxation time of deuterated ^{13}C, $T_1^{\text{C-D}}$, to that of protonated ^{13}C, $T_1^{\text{C-H}}$, which we shall denote by Γ, is given by

$$\Gamma = \frac{T_1^{\text{C-D}}}{T_1^{\text{C-H}}} = \frac{\gamma_H^2}{\gamma_D^2}\,\frac{S(S+1)}{I(I+1)}$$

where γ_H and S are the magnetogyric ratio and spin

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