Compatibility in a Blend of Poly(2,3-Dichloro-1-Propyl Acrylate) and Poly(glycidyl Methacrylate-*co*-Ethyl Acrylate)

D. D. DAVIS, G. N. TAYLOR, and T. K. KWEI, *Bell Laboratories, Murray Hill, New Jersey 07974*

Synopsis

The compatibility of mixtures of poly(2,3-dichloro-1-propyl acrylate) and poly(glycidyl methacrylate–*co*–ethyl acrylate) has been investigated by measurement of the following properties: density, light transmission, glass transition temperature, vapor absorption, and NMR relaxation times. To varying degrees, all results provided evidence supporting the contention that these mixtures are compatible.

INTRODUCTION

The increasing importance of polymer blends is reflected in the growing volume of literature on this topic. In this article, we study the compatibility of mixtures of poly(2,3-dichloro-1-propylacrylate), DCPA, with a 65:35 copolymer of glycidyl methacrylate and ethyl acrylate, named COP for convenience. The resulting mixtures are of current interest as resist materials in x-ray lithography.[1,2]

Five different types of measurements were employed in this study to evaluate compatibility: (1) density, (2) optical clarity, (3) glass transition temperature, (4) vapor absorption, and (5) NMR.

EXPERIMENTAL

Materials

The GMA–EA copolymer was synthesized by the Mead Chemical Co. Its intrinsic viscosity was 0.47 dl/g in 2-butanone at 30°C. By GPC the $\overline{M}_w$ was 1.5 × 10^5 g/mol and the M_w/M_n was 2.5. The DCPA polymer was prepared as previously described.[1] Its intrinsic viscosity was 1.95 dl/g in ethyl acetate at 30°C. The $\overline{M}_w$ was found to be 2.47 × 10^6 g/mol by light scattering; and $\overline{M}_n$ as determined by osmometry was 8.57 × 10^5 g/mol.

Films of DCPA and COP and their mixtures were cast from chlorobenzene solutions and dried in vacuum at 50°C overnight. Quantitative analysis for chlorine revealed that the three mixtures used in the density and NMR experiments contained 28.9, 56.8, and 78.2% DCPA.

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Densities

Densities were measured using a $Ca(NO_3)_2$ density gradient column calibrated at eight densities over the range of 1.10–1.50 g/cm^3.

Optical Clarity

We conducted optical clarity experiments in order to investigate whether the polymer mixtures would undergo phase separation at high temperatures. Such separation is a phenomenon associated with the "lower critical solution temperature," and has been observed in many compatible polymer mixtures.[3-5] In our experiments, the intensity of light transmitted through a mixture as the temperature was increased to 290°C was monitored by recording the voltage generated as the light impinged on a photoresistor mounted on a Reichert zetopan microscope.

Glass Transition Temperatures

The glass transition temperatures of DCPA and COP and their mixtures were measured by differential scanning calorimetry using a du Pont thermal analyzer, model 990. The sample size was 12–15 mg and the heating rate was 10°C/min throughout our experiments. The reproducibility of the T_g measurement was ±1°C.

Vapor Absorption

Films of DCPA, COP, and a 56.8% DCPA mixture having thicknesses of about 0.005 cm were evacuated for several days at 65°C and then exposed to benzene vapor in a Cahn electric balance. The increases in weight at sorption equilibrium were measured at several vapor pressures at 50 and 60°C.

Nuclear Magnetic Resonance

Samples of DCPA, COP, and a 56.8% DCPA mixture were degassed in their NMR tubes for four days at 60°C followed by several more days at room temperature prior to being sealed. The pulsed NMR method was utilized at a frequency of 30 MHz to determine the spin–spin relaxation time, T_2, by a 90° pulse and the spin–lattice relaxation time, T_1, by a 180°–90° pulse sequence. To evaluate T_2, the nuclear free induction decay, FID, was analyzed by a computer program, although in some instances a manual analysis was done on a computer generated semilogarithmic plot of the FID.

RESULTS

Densities

The observed densities of DCPA and COP, 1.441 and 1.235 g/cm^3, respectively, agree within 0.002/g cm^3 of the values calculated by the addition of group contributions to the molar volume.[6] A plot of film density versus composition results in a straight line as shown in Figure 1.
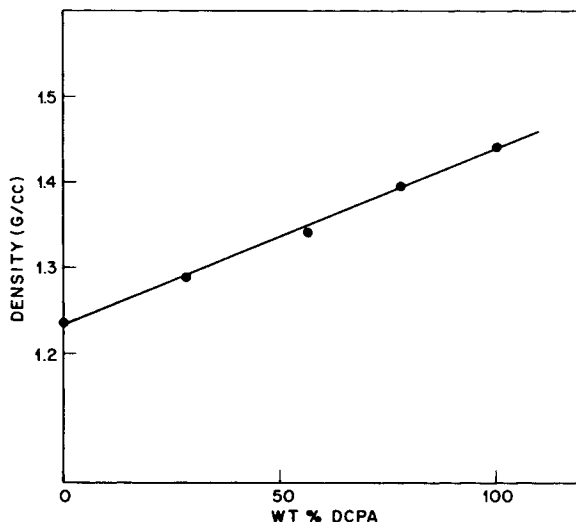
Fig. 1. Density vs. mixture composition. Linear relationship indicative of volume additivity.

Optical Clarity

All the films prepared for this study were initially transparent. As the temperature was increased, no change in either the intensity of the transmitted light or the visual appearance occurred. Hence, this topic will not be discussed further in our text.

Glass Transition Temperatures

The T_g values for DCPA and COP were 1.5 and 40°C, respectively. Each of the mixtures showed a single T_g. When the observed T_g values were plotted versus weight, mole, or volume fractions of the constituent polymers, a straight line was not obtained, nor did the Fox equation[7,8] apply. However, the Gordon–Taylor equation[9] appeared to give a reasonable fit with our data (Fig. 2). In the Gordon–Taylor equation:

$$T_g = k(T_{g1} - T_g)W_1/W_2 + T_{g2} \tag{1}$$

W is the weight fraction and k is a constant for the polymer pair. From the slope of the straight line, k is calculated to be 0.47.

Vapor Sorption

Figure 3 shows the absorption isotherm of benzene by DCPA at 50 and 60°C. The curves for the other films were equally smooth. Therefore, the curves for all three films are shown in a composite plot, without the experimental points, in Figure 4. The vapor absorption is seen to increase with the temperature for each material. At 50°C, the amount of vapor absorbed by the mixture is either equal to or slightly less than that predicted by the rule of additivity. At 60°C the difference is larger.
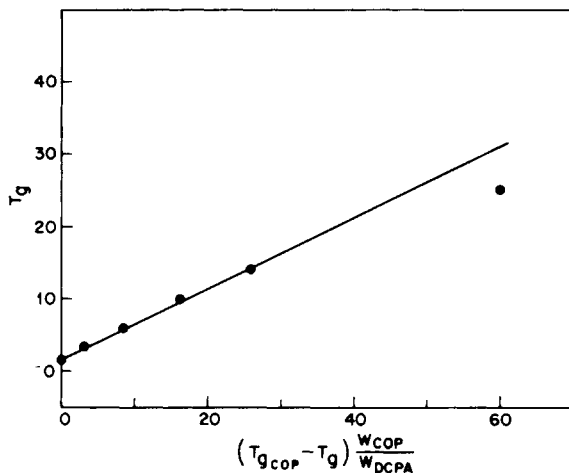
Fig. 2. T_g's of polymer mixtures plotted with Gordon–Taylor equation [eq. (1)].

Nuclear Magnetic Resonance

The dependencies of T_1 on temperature are shown in Figure 5 for the two component polymers and their mixture. Table I lists the temperatures at which T_1 minima occur. For COP, the T_1 assignments are as follows. The partial minimum in T_1 at about $-120°C$ is due to the methyl protons on the ethyl side chain of the ethyl acrylate portion of the copolymer. In poly(ethyl acrylate) homopolymer, this motion is seen by NMR at about the same temperature.[10,11]
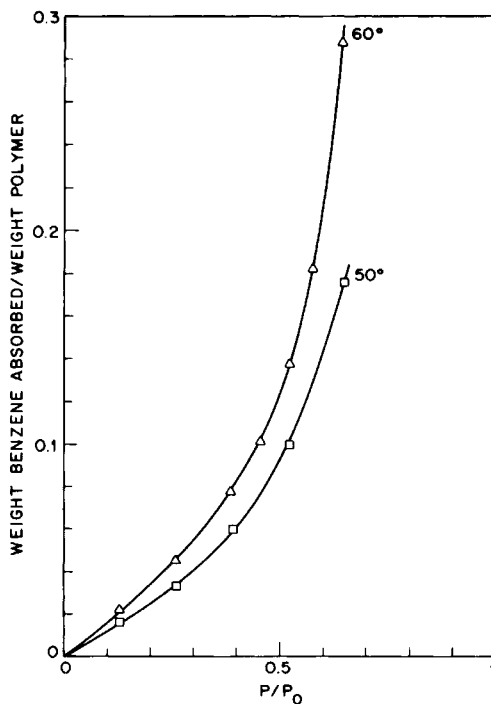

Fig. 3. Vapor absorption of DCPA vs. benzene partial pressure.
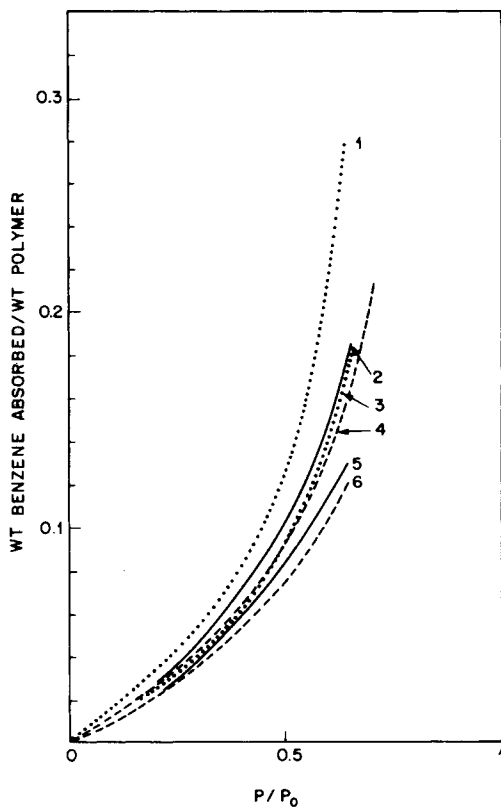
Fig. 4. Benzene vapor absorption for all three materials: (1) DCPA, 60°C; (2) mixture, 60°C; (3) DCPA, 50°C; (4) COP, 60°C; (5) mixture, 50°C; (6) COP, 50°C; DCPA, ...; mixture, —; GOP,

TABLE I
Temperatures of T_1 Minima, °C

	COP ester methyl	DCPA chain-end methyl	COP α-methyl	DCPA side chain	Main chain
DCPA (using results of calculated fit)		−105		+90	180
COP	−120		−20		195
Mixture 56.8% DCPA	−120		0	85	175

Surprisingly then, the neighboring bulky glycidyl ester side chain imposes no additional hindrance to this side-chain methyl motion. It has been demonstrated by Hatada, et al.,[12] that the side-chain protons in a methacrylate polymer are the least dependent of all protons in the polymer on contributions to its T_1 from the remaining protons. The T_1 minimum at −20°C arises from rotation of the methyl group bonded to the main chain, the α-methyl group of COP. Though freer than the α-methyl rotation in poly(methyl methacrylate), it occurs at the same temperature as does the α-methyl motion in poly(ethyl methacrylate). This is not unexpected as the α-methyl motion has been found to be insensitive
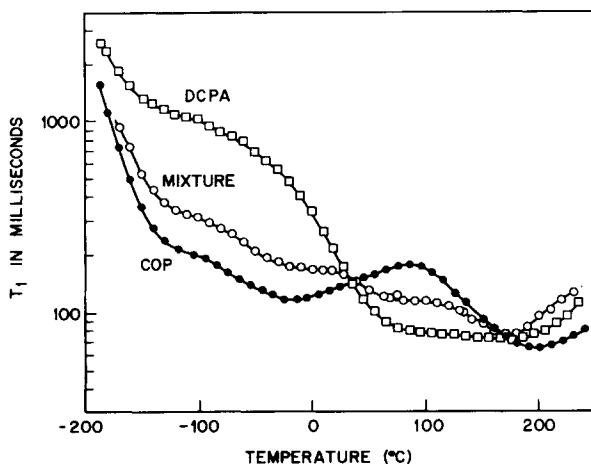
Fig. 5. T_1 vs. temperature dependence for DCPA, COP, 56.8% DCPA mixture. Table I lists temperatures of T_1 minima.

to further increase in ester group length.[11] The minimum in T_1 around 195°C is, of course, attributed to the large-scale chain mobility above the glass transition. An α-methyl group increases chain stiffness, but in the case of COP its concentration is less than in a methacrylate homopolymer. Also, though a longer side chain tends to decrease T_g, the glycidyl side chain of COP imparts additional polarity which tends to increase T_g. In view of these considerations, the occurrence of the upper T_1 minimum of COP at a temperature slightly lower than that of poly(ethyl methacrylate)[10] appears reasonable.

For DCPA, the T_1 assignments are as follows. The partial minimum around -100°C must arise from the methyl groups situated on chain ends. The T_1 minimum in the 80–180°C temperature region is unusual in its breadth and flatness. This is very likely the result of the near merging of two strong T_1 minima, those associated with DCPA side-chain and main-chain processes. For most polymers at NMR frequencies, the low activation energy side-chain motion and the higher activation energy main-chain motion have already merged. But the chlorine laden side groups in DCPA retard the main-chain motion. An attempt was made to fit the T_1 data to a combination of three motional modes labeled as α, β, and γ. The assumption was made that each motion was characterized by a single correlation time, and that the correlation time was governed by the Arrhenius relationship. The T_1 temperature behavior was calculated by applying the T_1 expression of BPP[13] as modified by Kubo and Tomita[14] which is

$$\frac{1}{T_1} = \frac{1}{1.41 T_{1_{min}}} \left[\frac{\nu_r/\nu_c}{1 + (\nu_r/\nu_c)^2} + \frac{4\nu_r/\nu_c}{1 + (2\nu_r/\nu_c)^2} \right] \tag{2}$$

Here ν_r is the NMR frequency and ν_c is the calculated correlation frequency which at the minimum in T_1 is 1.62 ν_r, for the case of a single correlation time. The best fit is shown in Figure 6 where the continuous line is the calculated composite T_1 magnitude and the circle symbols represent the experimental points. Table II contains the parameters for the three assumed motions. The activation energy of the β process calculated from the fit is in good agreement
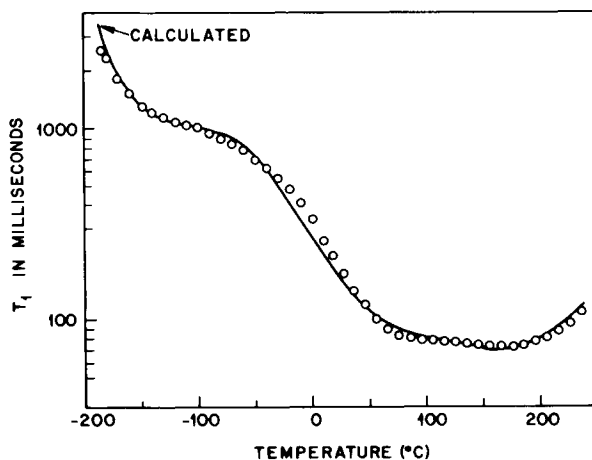
Fig. 6. Comparison of calculated single relaxation time model T_1 temperature behavior of DCPA, —, with one observed data, O.   Table II contains parameters for three assumed motions.

with the value of 3.9 kcal/mol computed from the experimental data in the range 0–50°C by means of a $ln\ T_1$–$1/T$ plot. A similar calculation for the γ process in the region −185 to −150°C yields 0.4 vs. 0.7 kcal/mol from the fit. For a single relaxation time model, the fit is pleasing. The indication is strong that the broad minimum in T_1 does arise from two overlapping motions.

For the mixture, only one T_1 was observed throughout the temperature range investigated, −170 to 230°C. The T_1 value is always intermediate between those of the pure components, reflecting the features of the component lower in T_1 magnitude, until 165°C, when it rises higher than the T_1 of both the pure components. The T_1 minimum at 175°C appears to be about equal to that of the unresolved DCPA minimum. (The T_1 fitting calculation placed the α process minimum for DCPA at 180°C.)

The spin–spin relaxation time, T_2, for the two polymers and their mixture are given in Figure 7, and the mobile fractions are given in Figure 8. Both the DCPA and the COP exhibit bicomponent FIDs from the onset of their glass transitions up to temperatures where both T_2 and mobile fraction have increased to such an extent that a second component is no longer resolvable. Since two T_2's were observed for each polymer, a complex T_2 behavior for their mixture is anticipated. Our computer programs handle only one or two FID components, since to seek more than two components in a decay response would be prone to error. Owing to the bicomponent nature of the FID of the polymers as well as their mixture, the use of T_2 as a means of determining the degree of mixing is not well suited to the present system and will not be elaborated further.

TABLE II
Parameters for the BPP T_1 Fit to DCPA

	γ	β	α
Temperature of T_1 minimum, °C	−105	90	180
T_1 at minimum, sec	1.07	0.100	0.135
Apparent activation energy, kcal/mol	0.7	4.4	10

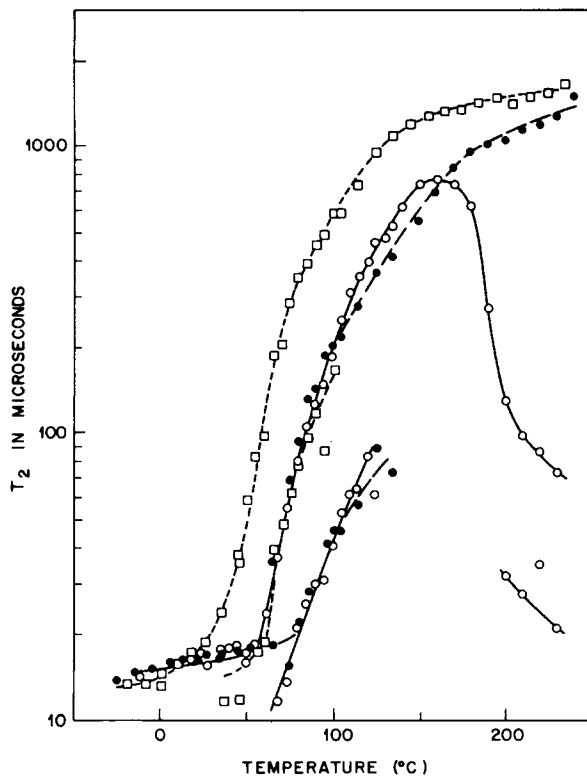Fig. 7. T_2 vs. temperature for DCPA, COP, 56.8% DCPA mixture. □, DCPA; ○, mixture; ●, COP.

DISCUSSION

Densities

The linearity of the density–composition relationship indicates that the rule of volume additivity is observed upon mixing the two polymers. The appropriate corrections in this calculation, as made in ref. 15, are too small to be detected in our experiment.

Glass Transition

Since a single well-defined glass transition was found in the thermogram for each mixture, the mixtures can be considered compatible by this commonly used criterion.

Interaction Parameter

From the vapor sorption data the polymer–polymer interaction parameter can be determined[15] by separately measuring the interaction parameters of each polymer, and also their mixture, with the same solvent (subscript $_1$). The three interaction parameters are linked by the following expression:

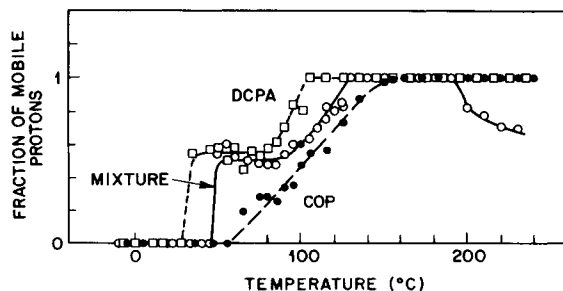$$\chi'_{23} = \frac{v_2\chi_{12} + v_3\chi_{13} - \chi_{1-mix}}{v_2v_3} \tag{3}$$

Fig. 8. Mobile fractions from analysis of the NMR FIDS.

In eq. (3), the prime symbol, χ'_{23}, denotes the interaction parameter per segment to avoid confusion in nomenclature when compared with other symbols commonly used in the literature. Each of the three χ's can be obtained by means of vapor sorption experiments in which the Flory–Huggins equation[16] is implemented

$$ln\ a_1 = ln\ v_1 + v_p + \chi_{1p}v_p^2 \tag{4}$$

In eq. (4), a_1 is the activity of the solvent which, for the chosen solvent, benzene, is nearly equal to its partial pressure, and p represents a polymer (or a mixture). The interaction parameters for the three films, as calculated from the smoothly drawn curves through the vapor absorption data (Fig. 4), are shown in Figures 9–11 as a function of the benzene volume fraction. Weighing errors are most significant at low solvent concentration. Accordingly, obvious deviations were ignored in drawing the straight lines in these figures. For all three materials, the solvent–polymer interaction parameter decreases with temperature and with benzene volume fraction.
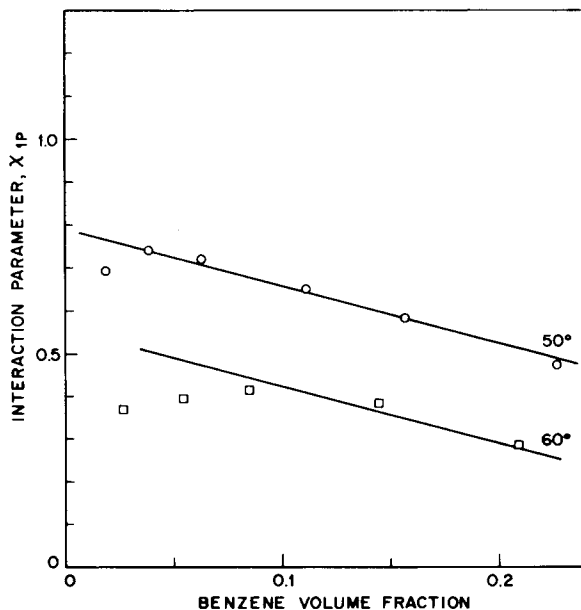

Fig. 9. Interaction parameter for DCPA vs. benzene volume fraction calculated from Fig. 3 data using eq. (4).
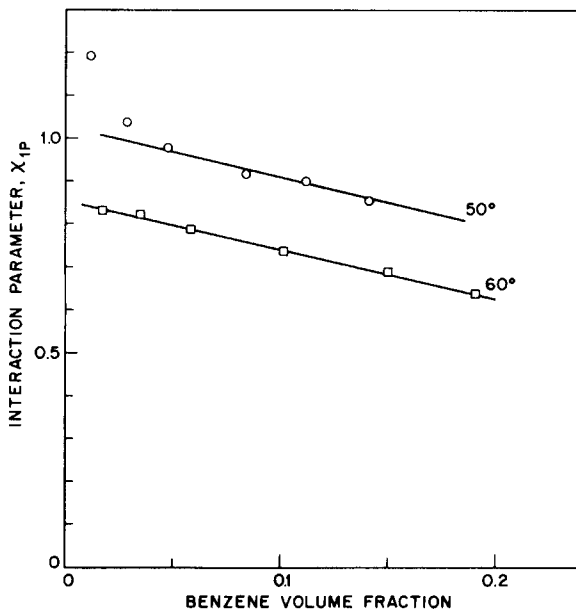
Fig. 10. Interaction parameter for COP vs. benzene volume fraction calculated from Fig. 4 data using eq. (4).

An excellent discussion on the proper use of eqs. (3) and (4) in order to preserve internal consistency was given by Hopfenberg and Paul.[17] We believe that a legitimate procedure to apply eqs. (3) and (4), when the χ values are concentration dependent, is to carry out the calculation at a fixed value of vapor activity. For the purpose of the present calculation, we have chosen a benzene activity of 0.45, corresponding to a benzene volume fraction of about 0.1. The calculated χ_{1p} values at $a_1 = 0.45$ (not smoothed values from Figs. 9–11) are listed in Table III.

Except for benzene–DCPA at 60°C, the χ_{1p} values for the two component polymers and their mixture exceed 0.5. Therefore, benzene is a poor solvent for the polymers. The value of $|\Delta\chi|$, i.e., $|\chi_{12} - \chi_{13}|$, is not as small as we would like (see benzene–PS–PVME[18]), but neither is it excessive in magnitude (see chloroform–PS–PVME[18]). The value of χ'_{23} obtained at 50°C is 0.04 and is larger than the critical value of χ'_{23} (0.0006–0.002) estimated from the molecular weights of the two component polymers. Since the amount of vapor absorbed by the mixture at 50°C is generally equal to or slightly less than the amount predicted from the rule of additivity (by weight), one would expect the χ'_{23} value to be closer to zero. However, the combined inaccuracy in the many steps involved in the computation of χ'_{23} is estimated to be at least ±0.02 units. Although our calculated value of 0.04 exceeds the critical value of interaction parameter, the difference is sufficiently small so that the polymer pair can be considered to be on the verge of compatibility. The negative χ'_{23} value found at 60°C satisfies the sufficient condition of thermodynamic miscibility in the context of Flory's equation, although the absolute value may be too large.

In this connection, we have also calculated χ'_{23} from Hildebrand solubility parameters, δ. The δ values were obtained at 25°C by employing Hoy's Table[19] of molar attraction constants for each of the various molecular groups of the

repeat unit according to Small's relationship.[20]   The calculated value of χ'_{23} is about 0.002.

Nuclear Magnetic Resonance

Over the entire temperature range the mixture exhibited only one T_1.   This implies that the mixing is sufficiently thorough so that all the protons can magnetically interact through the mechanism of spin diffusion to dissipate their spin energy via whatever sites are relaxing effectively.   An expression based on a simple spin diffusion model involving the observed T_1 has been formulated by McBrierty, Douglass, and Kwei[21] for judging whether spin diffusion is extant in a mixture such as studied here.   When applied to the DCPA–COP system at $-20°C$, the appropriate relationship is given by eq. (5):

$$\frac{1}{T_1}(w_1 - 2.43) = 0.415K_2^0 - 0.892\,K_1^0 w_1 - 0.415K_2^0 \tag{5}$$

In eq. (5), T_1 is the observed value for a mixture having a weight fraction of DCPA of w_1 and K_1^0 and K_2^0 are the intrinsic relaxation rates for a DCPA side-chain proton and a COP α-methyl proton, respectively.   This relationship was applied to the mixture (56.8% DCPA), using the observed T_1 at $-20°C$, where the two relaxations cited should be dominant in the system.   Although only three points are available, they do follow the linear relationship as depicted in Figure 12. Accepting this, one can follow the aforementioned authors and calculate, using the same formula for spin diffusion length, an approximate maximum size of the heterogeneities of the mixture.   The result obtained is that the heterogeneities are not more than about 100 Å.
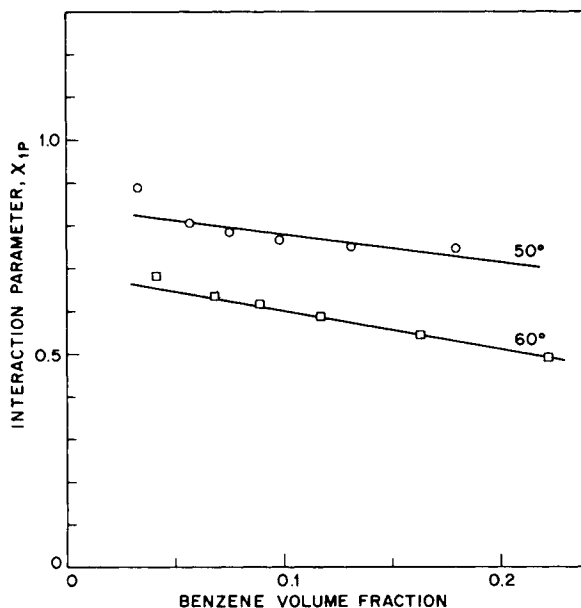

Fig. 11. Interaction parameter for 56.8% DCPA mixture vs. benzene volume fraction calculated from Fig. 4 data using eq. (4).
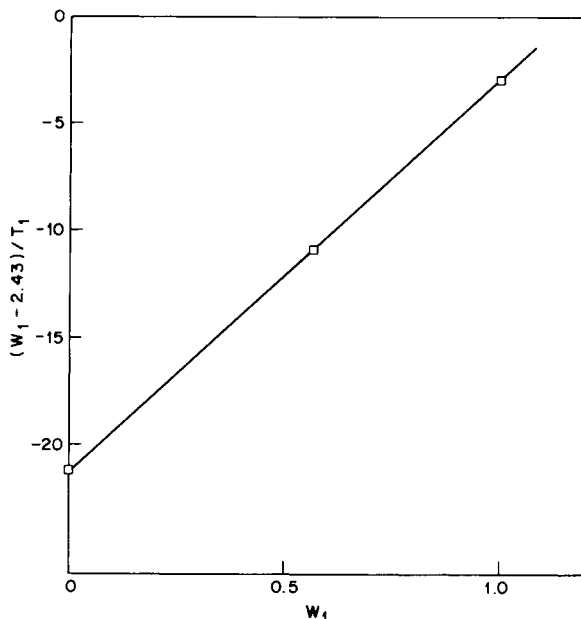
Fig. 12. Application of McBrierty–Douglass–Kwei spin diffusion model, eq. (5), to T_1 data at $-20°C$.

CONCLUSION

That the DCPA–COP mixture is a compatible blend is corroborated by all five types of experiments used. The observed χ'_{23} values, if taken literally, suggest that the mixture is compatible at $60°C$, though perhaps only marginally so around room temperature. The NMR results place the level of heterogeneity at less than 100 Å.

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