Compatibility of Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/Poly(styrene-*co*-4-chlorostyrene) Blends. I. Differential Scanning Calorimetry and Density Studies

J. R. Fried,* F. E. Karasz, and W. J. MacKnight

Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003. *Received July 20, 1977*

ABSTRACT: Blends of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and random copolymers of styrene and 4-chlorostyrene have been studied by differential scanning calorimetry and density measurements. DSC results suggest that copolymers with compositions ≤67.1 mol % of 4-chlorosytrene are compatible with PPO as judged by the detection of a single glass-transition intermediate in temperature between the T_g's of the unblended copolymer and PPO. Conversely, blends of PPO and copolymers ≥67.8 mol % of 4-chlorostyrene or with the homopolymers of 4-chlorostyrene or 2-chlorostyrene exhibit two glass transitions. Although this transition from one to two-phase behavior occurs in blends of PPO and copolymers which may differ by less than 1% in composition, more subtle differences in blend homogeneity are evident over a wider range of copolymer compositions. The width of the glass transition of the compatible blends increases as copolymers with higher 4-chlorostyrene compositions are blended until a maximum is reached just prior to phase separation at 67.1 mol %. The two-phase blends of PPO and copolymers of 67.8 and 68.6 mol % of 4-chlorostyrene exhibit transitions which are both shifted in temperature and reduced in intensity (ΔC_p) from those of the unblended component polymers. These latter results are interpreted as evidence of partial miscibility in intra- and interphase regions, respectively, for these critical composition blends. In addition, there is evidence of partial phase separation upon annealing of the compatible 67.1 mol % of 4-chlorostyrene blends which suggests the existence of an upper critical consolute temperature. Measurements of blend densities indicate that the compatible blends and those two-phase blends of copolymer compositions of 67.8 and 68.6 mol % of 4-chlorostyrene have a small negative excess volume of mixing. These results are indicative of weak intermolecular interactions favoring better packing between molecules in the compatible or semicompatible state and suggests athermal or mildly exothermic heats of mixing for these blends. No increase in density upon blending was observed for the incompatible blends of PPO and the homopolymers of 4-chlorostyrene and 2-chlorostyrene.

Only a few examples exist of pairs of mutually miscible high molecular weight polymers. In a recent review article, Krause[1] has examined the literature for several hundred polyblends, of which less than one dozen can be classified as compatible by the criterion of a single, compositionally dependent glass-transition temperature (T_g). Those blends that satisfy this criterion for blend homogeneity can be molded or cast into transparent films and produce clear, single-phase solutions even at high polymer concentrations.

Blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) meet all criteria for compatibility. A single T_g has been detected at each blend composition by thermal optical analysis (TOA),[2,3] differential scanning calorimetry (DSC),[2,6] and dielectric,[4] thermomechanical,[5] and dynamic mechanical[6,7] techniques.

Recent studies[7-10] have shown that while poly(4-chlorostyrene) (PpClS) and PPO are *not* compatible, random copolymers of styrene (S) and 4-chlorostyrene (pClS) may be compatible depending only on the copolymer composition. Shultz and Beach[7] have shown that the critical copolymer composition for compatibility is between 65 and 68 mol % of pClS. Below 65 mol % of pClS, a single T_g increasing in temperature with increasing PPO blend composition was detected by DSC, TOA, and dynamic mechanical measurements. Above 68 mol % of pClS, two transitions, those of the copolymer and PPO, were evident. An intermediate copolymer composition of 66.6 mol % of pClS appeared to be incompatible with PPO but results from DSC and TOA were ambiguous.

In the case of the incompatible blends of PPO and those copolymers near the critical 65 to 68 mol % of pClS range, Shultz and Beach noted that the T_g of the minor component by weight in the blend could not be detected by the DSC technique. This was attributed by the authors to insufficient instrumental sensitivity. DSC measurements were made on small samples, 10 mg or less, by means of a Perkin-Elmer DSC I. In a study of heterogeneous copolymers of butadiene and acrylonitrile which separate into two phases having T_g's so close in value that they ordinarily appear superimposed, Landi[11] has employed larger samples, 25 to 35 mg, and a point-wise correction of relative heat absorption to optimize the signal-to-noise ratio and permit better DSC resolution.

In the present study, large sample sizes, the Landi technique of baseline correction and improved instrumentation have been used to follow quantitative and qualitative changes in the glass transitions of blends of PPO and copolymers of S and pClS whose compositions cover the range from compatibility to incompatibility, particularly those within the critical region between 65 and 68 mol % of pClS. The parameters of the glass transition reported here are the width and the height (ΔC_p) of the T_g region from which information on the extent of both intra- and interphase mixing has been deduced. In addition, blend densities have been measured and are compared to those observed for other compatible blends in the literature. Results of dielectric measurements of those PPO/poly(S-*co*-pClS) blends with copolymer compositions near the critical region marking the compatibility–incompatibility region are presented in the accompanying paper.[12] In a forthcoming paper, conclusions on the dependence of mechanical (tensile) properties on blend compatibility will be given for the same blends for which DSC and density data have been presented here.

Experimental Section

A. Materials. PPO was obtained as an additive-free powder through the courtesy of A. Katchman of General Electric. It was purified by filtering and precipitating a dilute toluene solution (3–5 w/v %) of the PPO powder into a large volume of methanol (10:1 methanol–toluene). Molecular weights of the purified PPO were determined in chloroform by gel permeation chromatography (GPC) at 25 °C, courtesy of C. Orlando of General Electric. GPC results were $\overline{M}_n = 16\,900$, $\overline{M}_w = 34\,800$, $\overline{M}_z = 54\,300$ with polydispersities of 2.05 ($\overline{M}_w/\overline{M}_n$) and 1.56 ($\overline{M}_z/\overline{M}_w$).

---

* Address correspondence to this author at the Corporate Research Department, Monsanto Company, St. Louis, Mo. 63166.

0024-9297/78/2211-0150$01.00/0

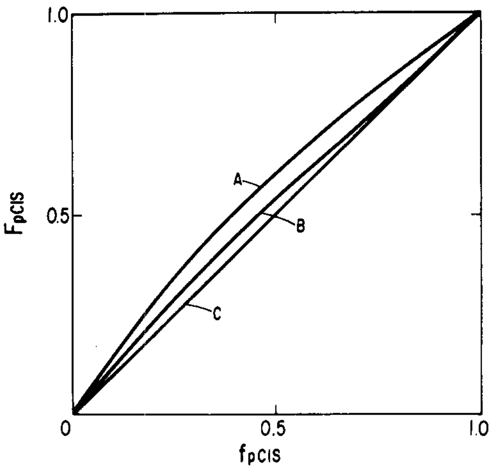

Figure 1. Copolymer composition (F_{pClS}) in mole fraction of 4-chlorostyrene (pClS) vs. mole fraction of pClS in monomer mixture (f_{pClS}). Curve A, calculated from the reactivity ratios of Okumoto et al. ($r_s = 0.62$; $r_{pClS} = 1.35$); curve B, calculated from the reactivity ratios of Lewis et al. ($r_s = 0.74$; $r_{pClS} = 1.03$); curve C, ideal copolymerization line (if $r_s = r_{pClS} = 1$).

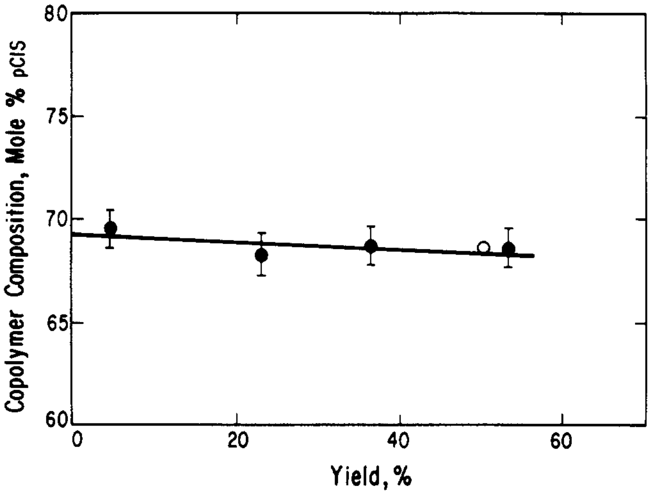

Figure 2. Copolymer composition in mol % of pClS vs. % yield for a monomer batch containing 64.3 mol % of pClS. Solid line represents a least-squares fit of experimental points (●); (○) denotes composition of copolymer E from a 15× larger batch with the same monomer composition.

Monomers for the polymerizations were styrene (Eastman, lot C28), 4-chlorostyrene (Aldrich, lot 110137), and 2-chlorostyrene (Aldrich, lots 051817 and 090347). These were purified prior to polymerization by washing with 10% aqueous sodium hydroxide in equal volumes with the monomers. The washed monomers were dried by decanting them over activated molecular sieves and were then distilled under vacuum (15–25 mmHg).

B. Polymerizations. With the exception of one thermal polymerization at 110 °C (Copolymer F), all polymerizations were free radical in toluene solution at 60.0 °C. The initiator was 2,2′-bis(azoisobutyronitrile) (AIBN) which was purified by crystallization from methanol. Quantities of the purified monomer(s) and toluene were pipetted into predried 250-mL round-bottom flasks containing 0.400 mol % (by monomer composition) of AIBN. These were then immersed in a controlled temperature shaking water bath after bubbling dried nitrogen into the reaction mixture for 5 min. Polymerization time was typically 15 h.

At the end of the polymerization, the reaction mixtures were diluted with additional toluene to a total polymer concentration of about 4% and precipitated into a 10:1 ratio of rapidly stirred methanol. The white precipitates were washed with methanol and dried at 100 °C for 48 h (80 °C for PS). They were then weighed to determine yield and purified by reprecipitating as above.

C. Copolymer Drift Study. As a result of the evidence[7] indicating that the transition from compatible to incompatible PPO/copolymer blends occurs within a narrow range of copolymer compositions (65 and 68 mol % of pClS), effort was made to obtain copolymers which themselves were narrow in compositional distribution. In an ideal or totally random batch copolymerization as illustrated by line C in Figure 1, the copolymer composition depends only on the initial composition of the monomer mixture (f_{pClS}). During a nonideal copolymerization, the composition of the initial batch will continuously change as one monomer is used at a preferential rate over the other. The final average copolymer composition will then represent a continuous distribution of copolymer compositions. The breadth of this distribution will be determined by values of the monomer reactivity ratios and the percent conversion to which the copolymerization is allowed to proceed. Reactivity ratios near the ideal values of unity and low conversions favor narrow copolymer composition distributions. In the case of the copolymerization of S and pClS, reactivity ratios given in the literature predict only minor deviations from ideality. Copolymer compositions in mole fraction pClS (F_{pClS}) calculated from the instantaneous copolymerization equation[13] and sets of reactivity ratios given by Lewis et al.[14] and Okumoto et al.[15] for S and pClS are plotted vs. monomer batch composition in Figure 1 with comparison to the ideal copolymerization line.

To evaluate experimental drift of copolymer composition with conversion, samples were removed at different times from a batch containing 64.32 mol % of pClS (35.68 mol % of S). Yields were determined and the composition of the copolymer at each yield (or conversion) was obtained from chlorine analysis. Further details of the drift study are given elsewhere.[10] Copolymer composition as a function of copolymerization yield is plotted in Figure 2. The solid line represents a least-squares fit of the experimental data. As suggested by the slope of the line, drift is small (0.89 mol % of pClS) provided conversion is limited to about 50%. Equivalent drift (1–2 mol %) was calculated by using the Lewis or Okumoto reactivity ratios in the copolymerization equation with the assumption that composition is constant within a 10% conversion interval. Even better fit of experimental copolymer composition with calculated values was obtained by using the reactivity ratios ($r_S = 0.667$ and $r_{pClS} = 1.203$) calculated from the empiral Q-e scheme of Alfrey and Price.[16] At 40% conversion, these values predict a drift of 1.20 mol % of pClS which is within experimental error of the observed drift of 0.89 mol %. Based upon these values, conversion was limited to about 50% in the four free-radical copolymerizations (B, C, D, and E) used in this study.

Table I
Copolymer Compositions and Molecular Weights of Blend Polymers

Sample	Mol % of pClS	Mol wt × 10^{-3} $\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_z/\overline{M}_w$
PS	0	38.0	81.8	2.16	1.53
B	58.5	94.7	208	2.19	1.92
C	67.1	88.1	145	1.69	1.41
D	67.8	100	192	1.92	1.42
E	68.6	81.0	177	2.19	1.53
F	75.4	270	487	1.80	1.50
PpClS	100	128	217	1.69	1.46
PoClS	0	235	658	2.81	1.61

D. Polymer Characterization. In addition to PS, PpClS, and poly(2-chlorostyrene) (PoClS), five copolymers varying in composition between 58.5 and 75.4 mol % of pClS were synthesized. The polymer compositions were determined from chlorine analysis using a double procedure of a potentiometric titration of chloride followed by a gravimetric determination of silver chloride with a reported precision of ±0.1 wt %.[42] An average of these two determinations is reported in mol % of pClS as copolymer composition in Table I. Molecular weights and molecular weight distributions were determined in tetrahydrofuran by GPC at 25 °C. Except for PS, all GPC molecular weights were corrected for different copolymer compositions by the method used by Shultz and Beach[7] with the assumption that molecules of equal contour lengths elute at equal volumes. A summary of molecular weight data is given in Table I.

E. Blend and Film Preparation. The copolymers and homopolymers given in Table I were blended with PPO by coprecipitation from dilute toluene solution (3–4 w/v %) into a large quantity of methanol (10:1). The precipitates were dried under vacuum at 100 °C for 48 h. Blends containing 20, 40, 60, and 80 wt % of PPO were prepared in this manner. In addition, blends containing 50 wt % of PPO were prepared for copolymer E and PpClS.

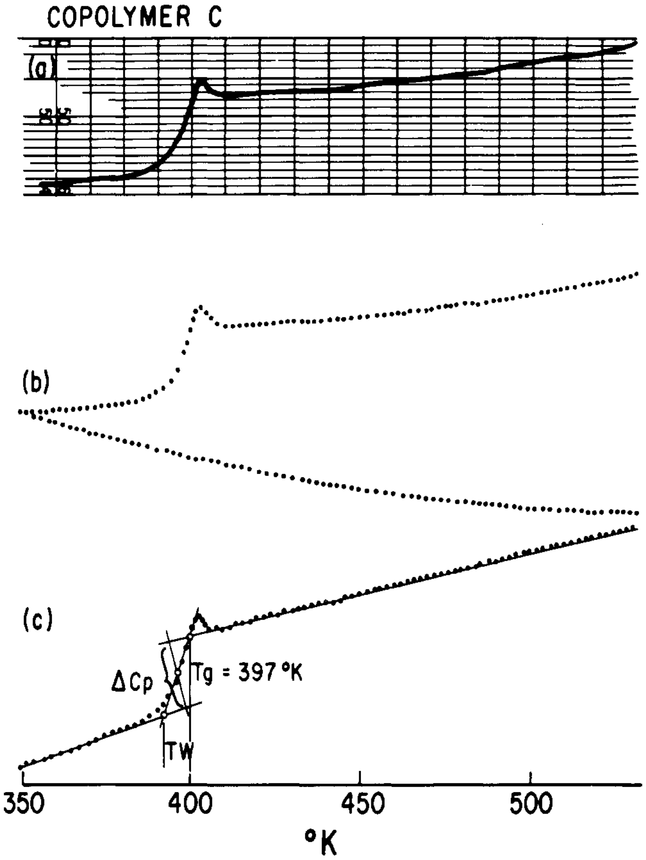

Figure 3. Example of the point-correction technique used to analyze the DSC thermograms. (a) DSC thermogram of copolymer C (unblended); (b) point traces of copolymer C and blank pan thermograms; (c) final adjusted point trace with indicated parameters of the glass transition temperature (T_g), width (TW), and height (ΔC_p).

The dried, precipitated blends were compression molded at 10 000 psi into square films approximately 3 in. along a side and 0.12 in. in thickness. All unblended components except PPO (PS, PpClS, PoClS, and the five copolymers) were molded at 180 °C while all the blends and unblended PPO were molded at 280 °C under a nitrogen purge stream. Films used for DSC and density measurements were allowed to cool under pressure for about 90 min until the mold temperature was just below T_g before removal from the press. Films prepared in this manner were free of voids and air bubbles.

F. Differential Scanning Calorimetry. A Perkin-Elmer DSC II was used to study the glass transitions of the blends and the blend components. DSC samples were punched from the compression molded films. Two disks from each film were pressed into aluminum DSC pans which were then sealed. The combined weight of the two disks, typically between 20 and 30 mg, was measured by a Perkin-Elmer AD-2 autobalance to a precision of 0.01 mg. A heating rate of 20 °C min^{-1} and a range of 5 mcal s^{-1} was used for each sample while chart settings (Perkin-Elmer model 56 recorder) were 10 mV at a speed of 20 mm min^{-1}. Samples were heated from 330 to 530 K under a nitrogen purge at 20 psi and were immediately cooled back to 330 K at 80 °C min^{-1}. After several minutes of equilibration at 330 K, the samples were then reprogrammed to 530 K at 20 °C min^{-1} and again cooled to 330 K. A blank (sealed, empty pan) was then run to 530 K at 20 °C min^{-1} with identical instrumental settings except for changes in the zero positioning of the pen.

The DSC thermograms for the sample (the second of two runs) and the blank were placed one over the other on an illuminated screen for intersection at 350 K. A piece of millimeter graph paper (10 mm cm^{-1}) was placed over the two thermograms so that each mm division coincided with 1 °C on the DSC traces. The two thermograms were then traced on the graph paper by placing points at each 2 °C interval along the curves while at the glass transition these intervals were reduced to 1 °C for better accuracy in determination of T_g. When the vertical distance between corresponding points on the sample and blank thermograms was plotted against temperature on another piece of graph paper, the shape of the original sample thermogram was accurately reproduced and deviation from baseline linearity was automatically corrected. The entire procedure is illustrated in Figure 3 for a 22.93-mg sample of copolymer C selected as an example. The uncorrected DSC thermogram for copolymer C is shown in Figure 3a, while the point traces for this thermogram and for the blank and the final corrected trace (vertical distance vs. temperature) are illustrated in Figures 3b and 3c, respectively. The above procedure improves accuracy in the determinations of T_g defined as the temperature at the half-height of the transition, the transition width (TW), and the transition height (ΔC_p) through better extrapolation of the linear portions of the thermogram through the glass transition. These parameters are indicated in Figure 3c.

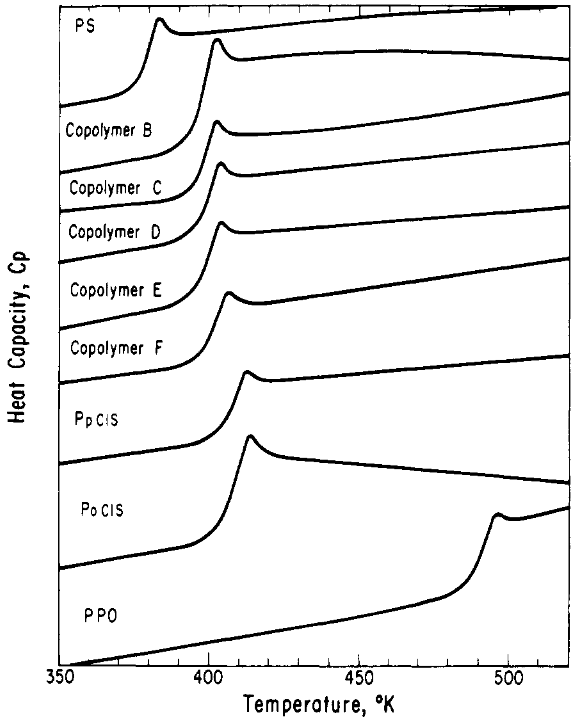

Figure 4. Traces of DSC thermograms of unblended polymers.

Before each series of DSC measurements, the baseline was optimized by conventional DSC techniques and the temperature calibration was checked by reference to the standard melt temperatures of indium (429.78 K), tin (505.06 K), and occasionally lead (600.65 K). Any small curvature in baseline remaining after optimization was automatically corrected by the point-tracing method outlined above, and minor deviations from the standard reference temperatures were accommodated by either adding or subtracting the appropriate error, 1 or 2 °C, from the T_g measured for each sample. This error was obtained from a linear plot of the difference between the measured and true melt temperatures for each of the standard reference materials (tin and indium) vs. temperature.

G. Density Measurements. The densities of the blends and the unblended materials were measured at room temperature in gradient columns of sodium nitrate in distilled water. Several columns with different density ranges were used. In each case, the gradient between densities at the top and the bottom of the column was about 0.04 g/cm^3. These columns were calibrated by three or four glass bead standards whose positions within the 1000-mL graduate columns were determined by means of a Gaertner cathetometer. The best linear relation between column position and density was obtained by the method of least squares. The positions of four to six disks punched from different locations on the same film sample were used to calculate a mean density for all samples except PPO for which 19 samples taken from different films were used. Error bounds for density measurements are reported as the standard deviations of the mean.[10]

Results and Discussion

A. Differential Scanning Calorimetry. DSC traces obtained for nine unblended samples of PS, copolymers B–F, PpClS, PoClS, and PPO are shown in Figure 4. With the exception of the location of T_g, the thermograms appear identical. For each unblended polymer, the width of the glass transition defined in Figure 3c as TW was 6 °C at the heating

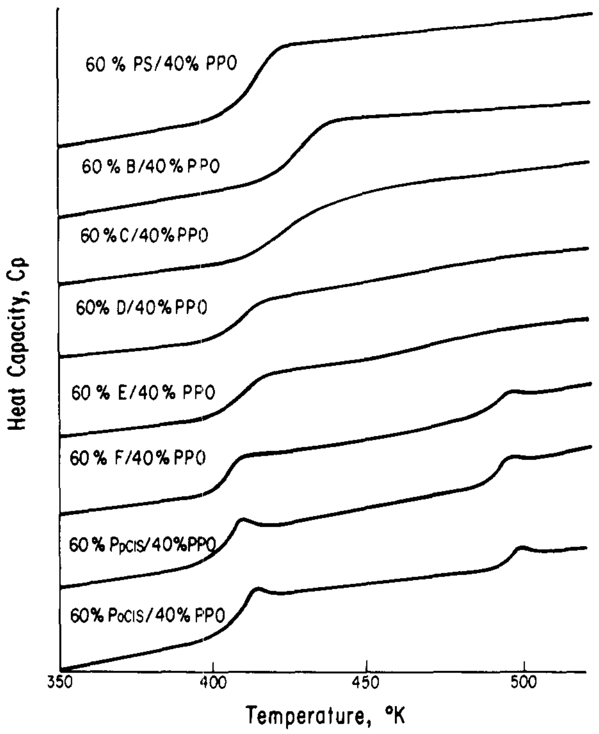

Figure 5. Traces of DSC thermograms of blends containing 40% of PPO by weight.

rate of 20 °C min^{-1} used for all DSC scans. In addition, all the unblended polymers display small peaks at the high temperature side of the transition. These are typical of annealed or slow cooled polymers which have reached a state of excess enthalpy in the glass.[17,18] Upon rapid heating through T_g, the equilibrium enthalpy state is overshot resulting in an apparent excess enthalpy peak as the polymer molecules quickly relax to their equilibrium thermodynamic state.

DSC traces for blends of the above polymers with 40% of PPO by weight are given in Figure 5. Dielectric measurements of many of these same blends are reviewed in the accompanying article.[12] Several features of these thermograms are immediately evident. First, only a single transition is apparent for the blends of PS, copolymer B, and copolymer C. Two transitions are observed for the remaining blends of copolymer D, copolymer E, copolymer F, PpClS, and PoClS; however, the high temperature glass transition, that corresponding to the PPO component, of both copolymer D and copolymer C blends is highly broadened and reduced in relative magnitude (ΔC_p) as compared to the PpClS/PPO blend, for example. Were it not for the large sample size, these weak transitions of the copolymer D and copolymer E blends would have been obscured by ordinary instrumental noise as was the case in the DSC study of similar copolymer blends by Shultz and Beach.[7]

Systematic changes in both the width and the height (ΔC_p) of the glass transition of blends of PPO and copolymers of increasing pClS content are evident from analysis of the DSC thermograms of all the blend formulations. The most noticeable of these changes is in the transition width as shown for example in the 40% PPO blends given in Figure 5. The width of the single glass transition of the compatible PPO/PS blend is broad in comparison to that of either PS or PPO alone under identical DSC conditions. In the example of the 40% PPO/60% PS blend given in Figure 5, the transition width as defined by Figure 3c is 13 °C compared to 6 °C for either unblended PS or PPO. The blend transitions continue to increase in width as copolymers with higher pClS content are blended. For example, the widths for the 40% PPO copolymer B and copolymer C blends are 18 and 34 °C, respectively. The two transitions that are evident for blends of PPO and copolymers with higher pClS contents are also broad but begin to narrow with increasing pClS composition. At the extremes of composition, the two transitions of the incompatible PpClS and PoClS blends are the same width as the unblended components and appear as if the thermograms of PpClS or PoClS and PPO had been superimposed.

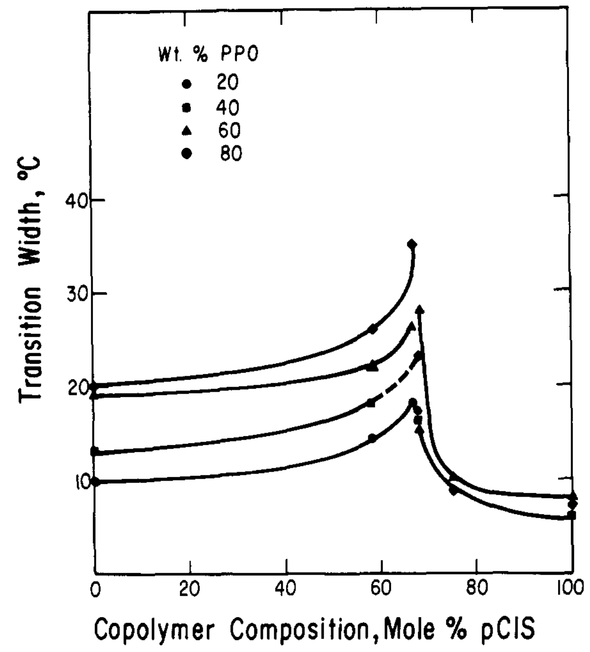

Figure 6. Width of the glass transition of blends of 4-chlorostyrene copolymers and PPO as a function of both copolymer and blend composition. Widths of the two-phase blends (≥67.8 mol % of pClS) are indicated for the major component transition only.

This trend in transition width is illustrated in Figure 6 in which width is plotted against pClS composition of the copolymer. The extremes of the abscissa represent PPO blends with PS and PpClS. As shown, the width increases with increasing copolymer composition to a sharp maximum at 67.1 mol % of pClS (copolymer C blends). Above that composition, two-phase blends are observed. The width of each of the two glass transitions of these blends (plotted in Figure 6 as the width of the major component transition) rapidly decreases with increasing pClS copolymer composition.

The observed transition width behavior may be explained on the basis of phase homogeneity. The validity of this argument is supported by the work of Nielsen[19] who found that the width of the logarithmic decrement in the dynamic mechanical spectrum of several vinyl copolymers of broad compositional distribution increased with the chemical heterogeneity of the system although the position of the maximum remained unchanged. Such broadening has been attributed to fluctuations in the interaction of a chain segment with its nearest neighbors in excess of normal thermal fluctuations.[20] In the accompanying article, analysis of the width of the dielectric spectra of the PPO/copolymer blends has shown that large fluctuations in local compositions occur in the compatible blends and in the two-phase blends of PPO and copolymers whose compositions are near the range marking the compatibility–incompatibility region where broadening is observed to be the greatest. This continuous range of blend compositions in the compatible blends (PS, B, and C) and edge of compatibility blends (D and E) leads to a continuous distribution of glass transitions appearing as a broad single transition. At the end of each small transition in the distribution the molecules of the local region participating in the

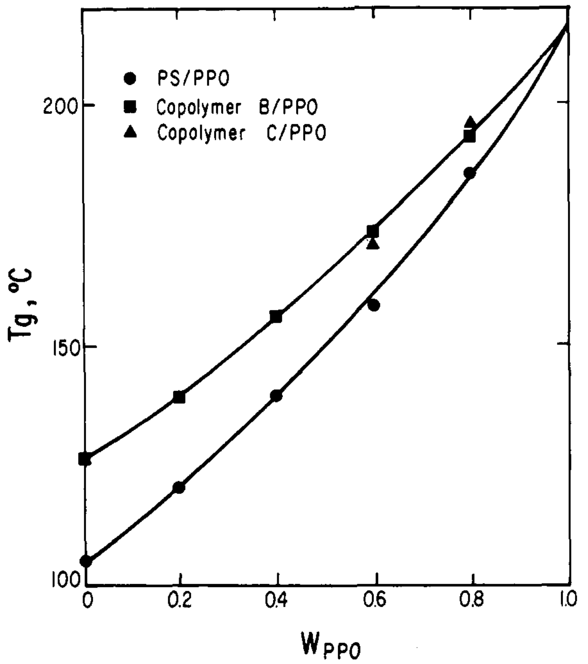

Figure 7. Glass transition temperatures (T_g's) of compatible blends vs. blend composition in weight fraction PPO (W_{PPO}). Curves indicate T_g's calculated from the Wood equation, eq 1, using $k = 0.679$. A single curve represents T_g's predicted for blends of both copolymer B and copolymer C whose T_g's are nearly equivalent at 125 and 127 °C, respectively.

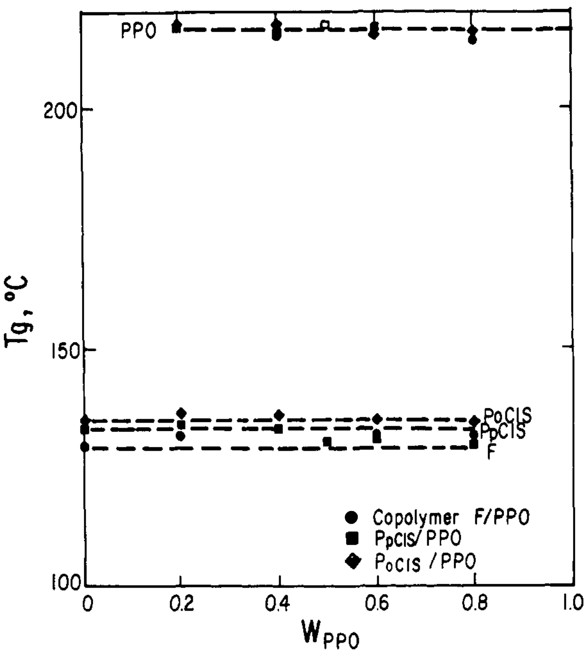

Figure 8. T_g's of incompatible blends vs. weight fraction PPO (W_{PPO}).

transition are free to relax out of a lower enthalpy state to the equilibrium enthalpy state. Since small molecular regions are relaxing over a large temperature range, no excess enthalpy peak appears at the end of the broad transitions of the compatible and edge of compatibility blends. As the blends separate into two phases which are pure in one component (copolymer F, PpClS, and PoClS) the transitions narrow and the characteristic excess enthalpies of the pure components reappear.

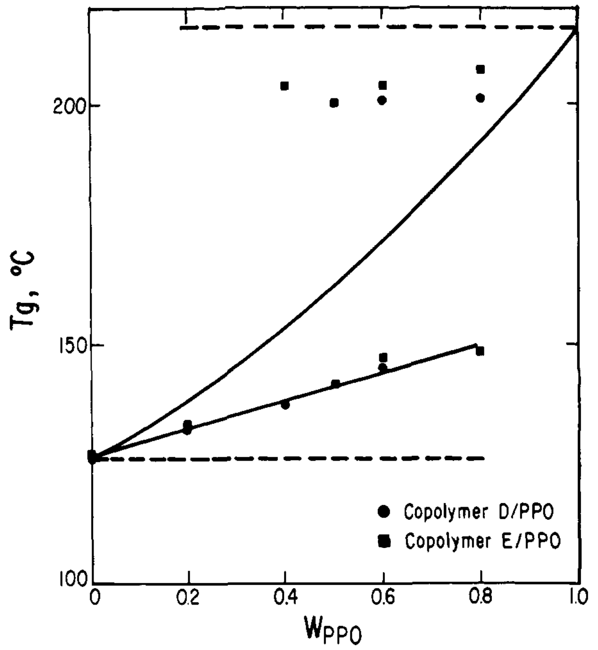

Figure 9. T_g's of edge of compatibility blends (those of copolymers D and E) vs. weight fraction PPO (W_{PPO}). Solid line represents a least-squares fit of the dependence of the T_g's of the copolymer-rich phases on W_{PPO}. Broken lines represent T_g's expected for incompatible blends. Curve gives T_g's expected for these blends (from Wood equation) if they were totally compatible.

The broadening of the transitions of the two-phase copolymer D and copolymer E blends suggests that each of the two phases contains some of the other component. In other words, there exists copolymer-rich phases containing some PPO and PPO-rich phases containing some copolymer. Confirmation of these conclusions comes from measurement of the T_g's of each phase as defined by Figure 3c.

The T_g's of the three compatible blends are plotted against weight fraction PPO (W_{PPO}) in Figure 7. In all three cases the blend T_g can be predicted from the Wood[21] equation represented by the curves drawn in Figure 7. This equation is given by

$$W_1(T_g - T_{g,1}) + kW_2(T_g - T_{g,2}) = 0 \qquad (1)$$

where W_1, W_2, and $T_{g,1}$, $T_{g,2}$ are the weight fractions and T_g's of components 1 and 2, respectively, T_g is the blend T_g, and k is an empirical constant which for the PPO/PS and PPO/copolymer blends was found to be 0.679 for best fit with the experimental data.

In contrast, the T_g's of the two phases of the incompatible blends of PPO/PpClS, PPO/PoClS, and PPO/copolymer F are unchanged from those of the corresponding unblended components as indicated by the broken horizontal lines in Figure 8. As shown in Figure 9, the T_g's of both phases of the edge of compatibility blends of PPO/copolymer D and PPO/copolymer E are shifted from the corresponding T_g's of the unblended components. There is a depression of between 9 and 16 °C in the T_g of the PPO-rich phase from the T_g of unblended PPO which is represented by the broken line and a linear increase in T_g of the copolymer-rich phase with increasing weight fraction of PPO in the blend. The solid line was drawn from a least-squares fit of the copolymer-rich phase T_g's of both the edge of compatibility blends. For comparison with the observed T_g dependence, a curve representing expected T_g's for compatible PPO/copolymer D blends has been drawn in Figure 9 from values calculated using the Wood equation and the 0.679 parameter. True compositions of the copolymer-rich and PPO-rich phases of the PPO/copolymer D and PPO/copolymer E blends have been calculated from the observed T_g of each phase and the Wood equation using the same 0.679 parameter. Results indicate that the PPO-rich phase in each of these blends is composed of about 86 wt % of PPO or 14 wt % of copolymer and is roughly independent of overall blend composition while the composition of the copolymer-rich phase increases to about 37 wt % of PPO at an overall blend composition of 80 wt % of PPO.

The above-mentioned dissimilar phase-composition relationships of the copolymer-rich and PPO-rich blends with overall blend composition suggest an assymmetry in the phase diagram of the PPO/copolymer blends. This behavior may arise from differences in the molecular weights of the copolymer and PPO components. As Table I indicates, the molecular weights of copolymers D and E are in the range of 80–100 000 $\overline{M}_n$ which is significantly larger than the 16 900 $\overline{M}_n$ determined by GPC for PPO. Skewness of the phase diagram toward the low molecular weight component has been discussed by Koningsveld.[22,23] Simple thermodynamic considerations suggest that partial mixing of the low molecular weight PPO molecules in the high molecular weight copolymer phase would be favored as a result of increased mixing entropy as the overall molecular weight of that phase decreases with increasing PPO content. This is supported by the observed trend of the phase T_g data.

An additional trend previously mentioned in comparison of the blend thermograms is the diminished transitions of particularly the minor component transitions of the edge of compatibility blends. The observed behavior may be expressed quantitatively by comparing the observed transition heights of all the blend transitions with the heights expected on the basis of blend sample weight and composition. The change in heat capacity at the glass transition or ΔC_p is given for DSC measurements by the relation

$$\Delta C_p = FS/MR \tag{2}$$

where F is the fractional increase in the ordinate at T_g, S is the full scale value of the power (ordinate) in mcal s^{-1}, M is the DSC sample mass in mg, and R is the heating rate in deg s^{-1}. For the particular DSC settings given previously, eq 2 becomes[10]

$$\Delta C_p = 0.0652(H/M) \tag{3}$$

where H is the transition height in mm and M is the sample weight in mg as before. Knowing the ΔC_p of the unblended component polymers from measurement of their transition heights and use of eq 3, the ΔC_p of the blend can be calculated from the relationship

$$(\Delta C_{p,B})_{\text{calcd}} = W_1 \Delta C_{p,1} + W_2 \Delta C_{p,2} \tag{4}$$

The ratio of the measured to calculated ΔC_p of the compatible (PS, B, and C) and incompatible (PpClS and PoClS) blends is plotted in Figure 10. For these blends, this ratio lies within a range of 84 to 105% of unity. In Figure 11, this same ratio has been plotted against weight fraction PPO for the PPO/copolymer F and two edge of compatibility blends of PPO/copolymer D and PPO/copolymer E. The ratios calculated for these blends lie in the range between only 54 to 94% of unity. This apparent decrease in transition intensity is more pronounced as the composition of the copolymer is closer to that of copolymer C (67.1 mol % of pClS) or in other words as the blends approach a compatible state. Thus, the largest decrease is found for the blends of copolymer D (67.8 mol % of pClS) for which the observed transition heights are only 54–67% of unity. These results suggest that only a fraction of the blend molecules are participating in the two observed transitions of these blends. This supports the qualitative observation made earlier that the transitions of the minor components by weight in these blends are particularly difficult to detect.

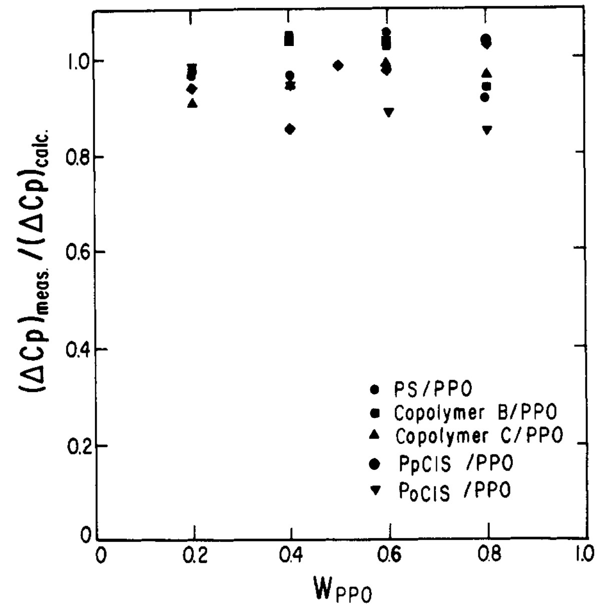

Figure 10. Ratio of measured to calculated transition heights (ΔC_p) of the compatible and incompatible blends vs. blend composition in weight fraction PPO (W_{PPO}). Those of the incompatible blends are averages of both transitions.

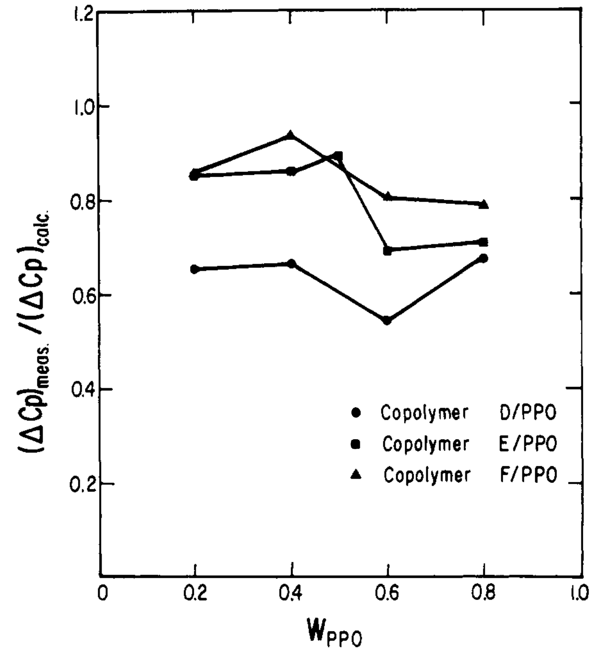

Figure 11. Ratio of measured to calculated ΔC_p of the edge of compatibility blends and incompatible copolymer F blends vs. W_{PPO}. Ratios are averages of both transitions.

One possible explanation for the reduction in transition height may be the size of the dispersed phase.[24] The transition of a minor component may appear reduced in intensity if some of the dispersed phases are too small for detection by DSC as has been suggested in other studies.[25] From analysis of the ΔC_p of both the major and minor components in these blends, phase size in these blends cannot be judged the sole or even the important factor contributing to the observed reduction in ΔC_p. This is suggested by Figure 12 in which the ratio of measured to calculated ΔC_p of both the copolymer-rich and PPO-rich transitions has been plotted vs. weight fraction PPO of the copolymer D/PPO blends. If phase size was the only contributing factor to reduced ΔC_p, then the transitions of the

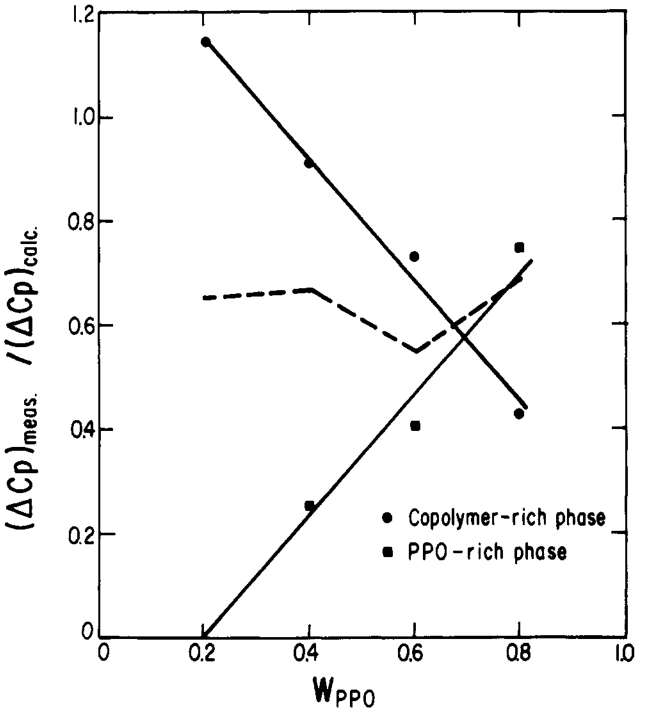

Figure 12. Ratios of measured to calculated ΔC_p of the copolymer-rich and PPO-rich phases (solid lines) of the copolymer D blends. Lines were drawn from a least-squares fit of measured ratios. Broken curve connects averages of both transitions (from Figure 11).

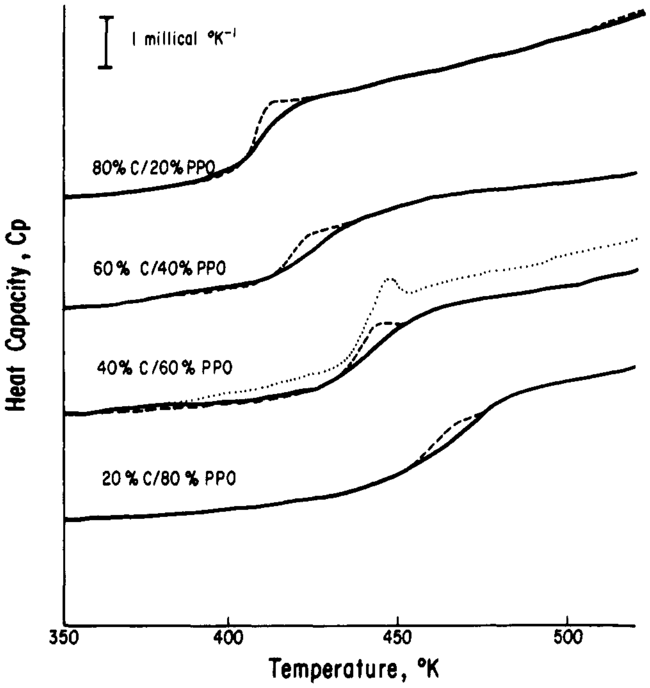

Figure 13. Traces of DSC thermograms of copolymer C blends: (—) unannealed; (- - -) annealed for 30 min at 20 °C below T_g; (···) annealed for 90 min at 20 °C below T_g.

major component or continuous phases would be expected to be unaffected. The observed behavior is quite different as shown by Figure 12.

At low W_{PPO} (0.20) where copolymer D would be expected to form the matrix material, its transition appears enhanced while no transition is evident of the PPO-rich phase. This suggests that the PPO is dissolved in the copolymer phase as previously deduced from the elevation in T_g observed for that phase. From the rise in T_g alone, the Wood equation indicates that only 35% by weight of the total PPO in the blend is participating in the copolymer transition. The remaining PPO is totally unaccounted for. It may be present as dispersed phases too small for detection by DSC as suggested above but further analysis of both transitions at the other blend compositions infers that this may not be a full explanation. At the other end of the composition range, i.e., at 80% of PPO, the transitions of *both* the expected continuous PPO phase and dispersed copolymer phase are reduced. The PPO transition is reduced to only about 70% of its expected ΔC_p. The phase size argument cannot be applied here because no discrete domains of PPO would be expected at such high PPO concentrations. At intermediate blend compositions similar reasoning may be applied.

If reduced phase size is not the most important contributing factor to reduced ΔC_p, then the simplistic two-phase model of a dispersed and continuous phase must be modified to include a diffuse interfacial region. There has been some direct experimental evidence confirming the existence of diffuse boundary regions between the dispersed phase and matrix components in some incompatible polymer blends.[26-29]

In a recent study, Letz[29] has found that if two incompatible polymers are allowed to interdiffuse either by bonding two films together or mixing powders in suspension and then evaporating the suspending medium and compacting the powdered mixtures, an interphase region is formed at elevated temperatures. Interdiffusion at first proceeds by Fick's law but after 20 min, diffusion was retarded and finally stopped. Letz proposed that the equilibrium thickness of the interphase layer can be used as a quantitative criterion of polymer compatibility. More compatible polymer pairs would be expected to have larger interphase regions while highly incompatible pairs would have very small interphase layers and therefore sharp phase boundaries. At 160 °C, equilibrium thicknesses of 28 000 and 89 600 Å were measured by phase contrast microscopy for mixtures of isotactic polypropylene/polyethylene and PVC/polyethylene, respectively.

The results of Letz would suggest that for the most incompatible pair, that of PpClS and PPO, the interphase layer should be relatively small. Therefore, the majority of PpClS and PPO molecules exist in separate, well-defined phases characterized by sharp, quantitative glass transitions of the pure materials. As the copolymer compositions and PPO become more compatible, some miscibility probably occurs in the region between phases. It is probable that this interphase mixing occurs between low molecular weight molecules of the polydisperse components for which the thermodynamic restrictions for compatibility are less severe. As the pClS content of the copolymer is decreased, interphase mixing extends to larger molecular weight molecules and therefore the amount of material (or the size of the diffuse interphase layer) between phases increases. If the size and composition of these interphase regions varies throughout the sample, then the T_g corresponding to these regions may be so small or broad that detection is not possible. This means that the dominant transitions of the principal phases are the only detectable ones and these appear small due to depleted material participating in the interphase regions.

Figure 13 shows traces of DSC thermograms of four blend compositions of copolymer C obtained following the usual procedure of heating at 20 °C min^{-1} from 330 K after rapid (80 °C min^{-1}) cooling from 530 K. These are compared with the superimposed thermograms of the same blend samples which had been annealed for 30 min at 20 °C below the blend T_g. Upon annealing for 30 min, the broad glass transitions of the copolymer C blends appear to split into two sharper transitions whose T_g's are narrowly separated. Longer periods of annealing result in an apparent excess enthalpy peak which partially obscures the higher temperature transition as for example in the case of the 40 wt % of copolymer C blend annealed for 90 min (Figure 13). These changes in transition behavior are completely reversible. Cycling the annealed sample through 530 K causes the broken transition to revert to the original broad glass transition of the unannealed blend. Rapid cooling to below T_g appears to freeze in the more homogeneous structure but annealing below T_g allows the molecules to relax into a more heterogeneous equilibrium condition.

B. Density Measurements. Blend densities may be calculated from the sum of the products of component weight fractions and specific volumes (reciprocal densities),[31,35] i.e.,

$$\frac{1}{\rho} = \frac{W_1}{\rho_1} + \frac{W_2}{\rho_2} \qquad (5)$$

where W and ρ are weight fractions and densities, respectively.

In the case of the PS/PPO blends, densities at ambient temperature were found to be approximately 0.8% larger than calculated on the basis of simple additivity from eq 5. This result agrees with values reported in other studies.[32–34] Increases in blend density observed for the other compatible and edge of compatibility copolymer blends are slightly smaller. These are in the range of 0.5–0.6%. Densities become additive as the blend components are incompatible as for example in the PpClS and PoClS/PPO blends. This trend is illustrated for three representative blends in Figure 14 where the reciprocal of density or specific volume is plotted vs. weight fraction PPO for the compatible PS and copolymer B/PPO blends and the incompatible PpClS/PPO blends. As shown, the measured specific volumes agree with the additivity values for the PpClS/PPO blends but are lower for the compatible blends, implying negative excess volumes of mixing.

A negative excess volume of mixing or increases in density upon blending has been observed in several other blend systems. For example, approximately the same value of density increase, about 0.01 gm cm^{-3}, as found here for the PS/PPO blends has been reported for a compatible blend of PVC and a terpolymer of ethylene, vinyl acetate, and sulfur dioxide.[31] Somewhat larger density increases have been reported for three other compatible blends: PVC/poly (butadiene-*co*-acrylonitrile);[35–37] PVC/poly(ethylene-co-vinyl acetate);[36] and PS/poly(vinyl methyl ether).[38] The largest density increase for any blend so far studied is that of 0.05 gm cc^{-1} or about 5% for PVC in a 50/50 blend with a copolymer of butadiene and acrylonitrile containing 41 wt % of acrylonitrile reported by Rånby.[36,37]

The magnitude of the density increase, or alternately the negative excess volume of mixing in compatible polymer blends, may be taken as a relative measure of compatibility, though it should be noted that a quantitative analysis of this point should involve comparisons of the respective volumes above the T_g's of the blends and constituent polymer. Alekseyenko[39] has defined a packing coefficient, K, for this purpose. This parameter, expressed as the ratio of actual to additive mixing volumes, is ≥ 1 for incompatible blends and <1 for compatible blends.

Hickman and Ikeda[31] and Zakrzewski[35] have suggested that the observed density increase or negative excess volume of mixing for compatible blends is a result of strong molecular interaction favoring better packing between molecules. This is reasonable because the largest density increases are observed for the more polar polymer pairs, e.g., PVC/poly(butadiene-*co*-acrylonitrile), for which intermolecular interactions are the strongest. By contrast, the nearly nonpolar pair of PS and PPO exhibits a much smaller density increase as a result of correspondingly smaller intermolecular interactions. Evidence for such weak interactions, possibly dipolar in nature, exists in the NMR results of Otocka.[40] These weak interactions are manifested in a near-zero value of the Flory interaction parameter as reported by Shultz and McCullough.[41] This means that the enthalpy of mixing for PS and PPO should be also nearly zero or slightly negative. As a result, the free energy of mixing attains a favorable negative value.

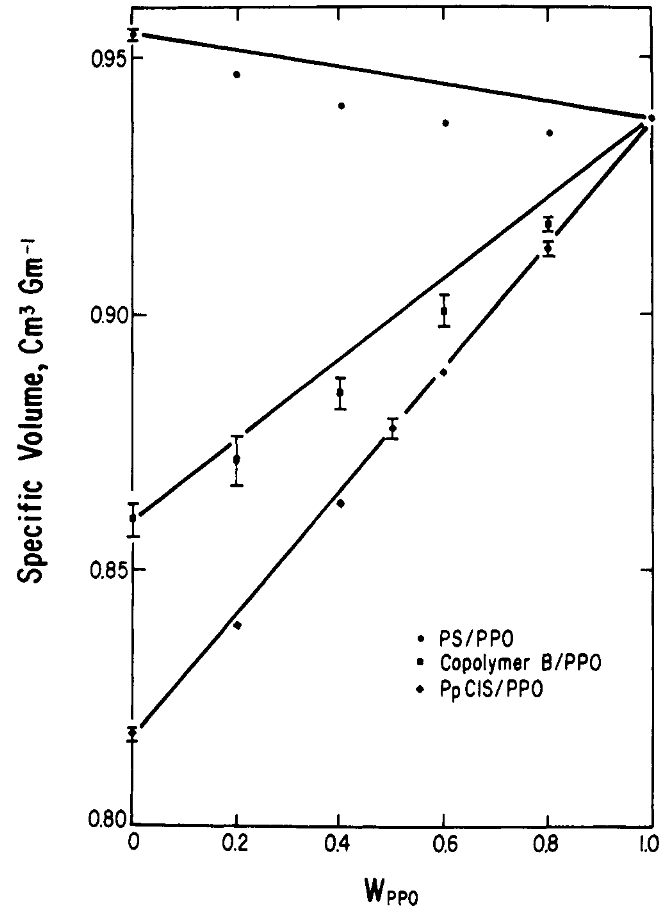

Figure 14. Specific volume vs. blend composition in weight fraction PPO (W_{PPO}). Solid curves, calculated from additive relationship, eq 5. Standard deviations from the mean falling outside the data points are indicated by error bars.

The observed small density increases for the copolymer D/PPO and copolymer E/PPO blends are not surprising because as noted previously these blends appear partially compatible. The more incompatible blend of copolymer F/PPO would be expected to have a zero density increase; however, a small increase in density (ca. 0.3%) was observed. As Figure 8 indicated, the copolymer F/PPO blends exhibited a small depression (perhaps 2–3 °C) in the T_g of the predominantly PPO phase and a small elevation in the T_g of the copolymer F phase. In addition, there were indications from the quantitative measurements of the glass transition heights of these blends as shown in Figure 11 that substantial quantities of copolymer F and PPO molecules may be involved in interphase mixing. These results suggest that copolymer F and PPO may be compatible to a very small extent. This can probably be attributed to copolymer heterogeneity as a result of the technique of the polymerization. As mentioned in the Experimental Section, copolymer F was the only one that was thermally polymerized. As a result of the higher polymerization temperature (110 °C) coupled with a rapid nitrogen purge through the system, the monomer mixture may have become richer in the higher boiling monomer, i.e., pClS. This means that the overall copolymer composition of 75.4 mol % of pClS was probably an average of a broader distribution of compositions than was the case for the other copolymers polymerized by free-radical initiation at a lower temperature (60 °C). As a result of this probable compositional heterogeneity, copolymer F no doubt has a portion of its molecular population with compositions in the compatible range below 67.8 mol % of pClS.

Acknowledgment. One of us (F.E.K.) gratefully acknowledges support from AFOSR Grant 76-2983.

References and Notes

(1) S. Krause, *J. Macromol. Sci., Rev. Macromol. Chem.*, **7**, 251 (1972).
(2) A. R. Shultz and B. M. Gendron, *J. Appl. Polym. Sci.*, **16**, 461 (1972).
(3) A. R. Shultz and B. M. Gendron, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **14**, 571 (1973); *J. Macromol. Sci., Chem.*, **8**, 175 (1974).
(4) W. J. MacKnight, J. Stoelting, and F. E. Karasz, *Adv. Chem. Ser.*, **No. 99**, 29 (1971).
(5) W. M. Prest, Jr., and R. S. Porter, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 1639 (1972).
(6) J. Stoelting, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **10**, 133 (1970).
(7) A. R. Shultz and B. M. Beach, *Macromolecules*, **7**, 902 (1974).
(8) J. J. Tkacik, Ph.D. Dissertation, University of Massachusetts, 1975.
(9) F. E. Karasz, W. J. MacKnight, and J. J. Tkacik, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 415 (1974).
(10) J. R. Fried, Ph.D. Dissertation, University of Massachusetts, 1976.
(11) V. R. Landi, *Rubber Chem. Technol.*, **45**, 222 (1972).
(12) R. E. Wetton, W. J. MacKnight, F. E. Karasz, and J. R. Fried, *Macromolecules*, following paper in this issue.
(13) S. I. Rosen, "Fundamental Principles of Polymeric Materials for Practicing Engineers", Barnes and Noble, New York, N.Y., 1971, p 123.
(14) F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and R. F. Mayo, *J. Am. Chem. Soc.*, **70**, 1519 (1948).
(15) T. Okumoto, T. Takeuchi, and S. Tsuge, *Macromolecules*, **6**, 922 (1973).
(16) T. Alfrey, Jr., and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947).
(17) A. S. Marshall and S. E. B. Petrie, *J. Appl. Phys.*, **46**, 4223 (1975).
(18) S. E. B. Petrie in "Polymeric Materials: Relationships between Structure and Mechanical Behavior", E. Baer and S. V. Radcliffe, Ed., American Society of Metals, Metals Park, Ohio, 1974.
(19) L. E. Nielsen, *J. Am. Chem. Soc.*, **75**, 1435 (1953).
(20) R. Buchdahl and L. E. Nielsen, *J. Polym. Sci.*, **15**, 1 (1955).
(21) L. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).
(22) R. Koningsveld, *Chem. Zvesti*, **26**, 263 (1972).
(23) R. Koningsveld, L. A. Kleintjens, and H. M. Schoffeleers, *Pure Appl. Chem.*, **39**, 1 (1974).
(24) R. E. Wetton, J. D. Moore, and P. Ingram, *Polymer*, **14**, 161 (1973).
(25) J. W. Schurer, A. de Boer, and G. Challa, *Polymer*, **16**, 201 (1975).
(26) S. S. Wojuzkij, A. N. Kamenskij, and N. M. Fodimann, *Kolloid Z. Z. Polym.*, **215 (1)**, 36 (1967).
(27) G. N. Avgeropoulos, F. C. Weissert, P. H. Biddison, and G. G. A. Bohm, *Rubber Chem. Technol.*, **49**, 93–104 (1976).
(28) V. Ye Lebedev, S. Yu Lipatov, and V. P. Privalko, *Polym. Sci. USSR (Engl. Transl.)*, **17(1)**, 171 (1975).
(29) J. Letz, *J. Polym. Sci., Polym. Phys. Ed.*, **7**, 1987–1994 (1969).
(30) C. F. Hammer, *Macromolecules*, **4**, 69 (1971).
(31) J. J. Hickman and R. M. Ikeda, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 1713 (1973).
(32) C. H. M. Jacques and H. B. Hopfenberg, *Polym. Eng. Sci.*, **14**, 441 (1975).
(33) H. B. Hopfenberg, V. T. Stannett, and G. M. Folk, *Polym. Eng. Sci.*, **15**, 261 (1975).
(34) A. F. Yee, *Polym. Eng. Sci.*, **17**, 213 (1977).
(35) G. A. Zakrzewski, *Polymer*, **14**, 347 (1973).
(36) B. G. Ranby, *J. Polym. Sci., Polym. Symp.*, **51**, 89 (1975).
(37) Y. J. Shur and B. Ranby, *J. Appl. Polym. Sci.*, **19**, 2143 (1975).
(38) T. K. Kwei, T. Nishi, and R. F. Roberts, *Macromolecules*, **7**, 667 (1974).
(39) V. I. Alekseyenko, *Vysokomol. Soedin.*, **2**, 1449 (1960); *Polym. Sci. USSR*, **3**, 367 (1962).
(40) E. P. Otocka, Bell Telephone Laboratories memorandum for record, 1968.
(41) A. R. Shultz and C. R. McCullough, *J. Polym. Sci., Polym. Phys. Ed.*, **10**, 307 (1972).
(42) Performed as a commercial service by Schwarzkopf Microanalytical Laboratory, New York, N.Y.

Compatibility of Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)/Poly(styrene-*co*-4-chlorostyrene) Blends. 2. Dielectric Study of the Critical Composition Region

R. E. Wetton,[1] W. J. MacKnight,* J. R. Fried, and F. E. Karasz

Polymer Science and Engineering Department, Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01003. *Received July 20, 1977*

ABSTRACT: Random copolymers of styrene and 4-chlorostyrene bridging the composition range from compatibility to incompatibility with poly(2,6-dimethyl-1,4-phenylene oxide) have been blended with the latter polymer. Dielectric constant and loss data are reported for the key blends containing 60% by weight of the copolymers. Dielectric relaxation spectra were found to be far broader for the blends than for the parent copolymers and this is interpreted primarily as arising from a wide range of local concentrations which are present even in the "compatible" blend. Phase separation produces a characteristic shoulder on the high-frequency side of the relaxation which is interpreted in terms of a Maxwell–Wagner–Sillars loss process. Dipole correlation parameters are derived in all cases and found to be relatively constant when due allowances have been made for the true phase compositions. The dielectric evidence indicates the existence of an upper consolate temperature (~180 °C) for the copolymer of critical composition. Fast cooling from above this temperature produces some differences in relaxation behavior compared to a sample annealed at lower temperatures.

A number of compatible polymer pairs have now been reported in the literature.[2a] The most studied system is that of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and poly(styrene) (PS), but the reasons for compatibility are still poorly understood. Compatibility of polymer systems is only to be expected if specific favorable interactions (such as hydrogen bonding) occur between the pair of polymers as entropy of mixing terms are predicted to be very small between chain molecules.[2b] The origin of the enhanced intermolecular attraction between PPO and PS molecules is unknown. Direct calorimetric evidence for the expected exothermic heat of mixing has now been obtained,[3a] although the experimental uncertainty involved in obtaining this data is too large for complacency. Indirect evidence for its existence lies in the negative deviation of specific volumes from simple additivity predictions as shown in the accompanying paper.[3b] The en-

0024-9297/78/2211-0158$01.00/0