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.

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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

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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-

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hancement of intermolecular attraction can be reduced by copolymerization of PS with 4-chlorostyrene and in the limit of blends of PPO with poly(4-chlorostyrene) (PpClS) no density deviation from ideality is observed and two clear-cut phases co-exist. This observation was first made on a relatively coarse scale by Shultz and Beach[4] and a more detailed account of compatibility changes is presented in the accompanying paper.[3b]

In the PPO–PS system, as with other studies of polymer blends, two main criteria have been adopted to assess compatibility of components. They are: (1) a single glass transition temperature or mechanical loss peak and (2) optical clarity, usually judged by eye rather than in a proper scattering experiment. There seems little reason to doubt that the existence of two glass transitions or related relaxation processes (provided that they are genuine glass transitions) and the presence of optical turbidity must indicate the presence of two phases at the temperature of the highest observed glass transition. Once one phase has entered a genuinely glassy state, further compositional changes in the mobile phase are precluded unless a third phase is generated on cooling. Unfortunately the phase compositions at any observation temperature are thus not normal equilibrium states at that temperature. There is no way in which DSC or temperature plane mechanical or dielectric relaxation can be easily used to obtain information on phase equilibrium at any temperature other than the highest glass transition of the blend.

Observations of a single T_g and optical clarity are less reliable indicators of a homogeneous single-phase blend. As well as the obvious difficulties of resolution with components of similar T_g's and refractive indices, there are the more basic problems associated with very small phases and the freezing in of very nonequilibrium structure. When polymers are only weakly incompatible, the interfacial free energy between two phases will be small and the surface free energy of a system containing small phases will not be prohibitively high. At a phase size ~50 Å diameter, molecular relaxation must be grossly influenced by interfacial segments, which comprise the bulk of the particle. T_g and relaxation data will thus be indicative of parameters other than phase structure. Even in large phase structures in highly incompatible systems, mechanical loss peaks have been found to decrease in amplitude with decreasing phase size because of increasing mechanical isolation of the smaller phases.[5] In the limit of very small phase size this problem could lead to a complete lack of sensitivity in the ability of the mechanical (and DSC) techniques to detect the dispersed phase. The optical technique is also insensitive at small particle size, unless a proper light or small-angle x-ray scattering experiment is carried out. The problem of quenched-in structures is very severe in systems of near compatibility. Irreversible thermodynamic principles state that the rate of a particular process (in this case phase separation) is proportional to the free energy difference of the beginning and end states. If this is small, then even relatively slow cooling from the melt may give a structure in the glassy state characteristic not even of T_g but of some relatively high melt temperature.

More refined techniques are required to probe structures of small particle size and marginal incompatibility. An interesting development in this area is the NMR spin diffusion measurement as utilized by Kwei and co-workers.[6] In the present paper, we report the use for the first time of dielectric frequency plane measurements as a definitive probe of the relaxational characteristics of phases present. As the relaxation process is scanned with variable frequency at a series of constant temperatures, data can in principle be obtained which are characteristic of the equilibrium properties of the system at any temperature above the highest T_g. Below the highest T_g the effect of quenching and annealing can be investigated.

Table I
Copolymer Synthesis and Characterization Details

Copolymer	Molar feed ratio, mol % pClS	Anal., mol % pClS	Yield	$\bar{M}_n$
B	55.8	58.5	58.1	95 000
C	62.5	67.1	48.9	88 000
D	63.5	67.8	55.4	100 000

Experimental Section

The aim of the present work was to study the critical compatibility region between PPO and appropriate random copolymers of styrene and 4-chlorostyrene (S, pClS). The copolymer compositions were therefore chosen to bridge the critical composition region from compatible (58.5% chlorostyrene) to incompatible (67.8% chlorostyrene). The random copolymers were synthesized by Fried using conventional free radical methods and full details can be found in the accompanying paper.[3b] The pertinent details are extracted in Table I. An important point in the synthesis of random copolymers of nonidentical reactivity ratios is the composition drift of chains formed at different stages of reaction. By keeping the conversion to about 50%, the composition change was both measured and calculated to be ~1% during the batch polymerizations. Even this may be significant as the similar copolymers C and D will have overlapping composition ranges. Blends were produced by coprecipitation of a 3% toluene solution of each copolymer with purified PPO into a 10:1 excess of methanol. Each of the copolymers listed in Table I was blended with 40% PPO (by weight) to give three blends for dielectric measurement. Glass-transition data are reported over the complete blend composition range by Fried et al.[3b] The powders were dried finally at 100 °C under moderate vacuum for 48 h before compression molding into sheets approximately 0.3 mm thick. From these sheets 56-mm diameter disks were scribed for dielectric specimens, which were stored under vacuum until use.

Dielectric measurements were performed in a conventional three-terminal cell with working electrode diameter 53 mm allowing adequate overlap of the guard ring by the centrally placed specimen. A General Radio transformer ratio arm bridge, with external excitation and detection, was used to measure the dielectric constant (ϵ') and loss factor ($\tan \delta$) over the frequency range 0.03 to 100 KHz. The cell was of all steel construction with PTFE insulated electrodes. All measurements were performed well above ambient and under these conditions good temperature control could be achieved by surrounding the cell by two heating mantles with power input regulated manually by a variac. Temperature control was ±0.2 °C on any given frequency scan. The procedure normally used was to raise the temperature in steps of approximately 5 °C over a period of 30 min followed by a further 10-min period of equilibration before data were obtained by varying frequency. This procedure was varied somewhat in annealing experiments as documented in the relevant Results and Discussion section, but dielectric data were always obtained in the frequency plane with temperature held constant.

Results and Discussion

Copolymers of Chlorostyrene and Styrene. The three PS–pClS copolymers studied in the present work differed by only 9% in chlorostyrene content. No major change in relaxation characteristics has been reported in previous studies of related copolymers[7] and thus only the two extreme copolymers B and D were measured in the unblended state. The data were similar in characteristics for both samples and the full dielectric constant (ϵ') and loss (ϵ'') results are thus shown for copolymer D only in Figure 1. Normalized curves for dielectric loss can be produced by plotting $\epsilon''/\epsilon''_{max}$ vs. $\log (f/f_{max})$, where the peak value of maximum dielectric loss (ϵ''_{max}) in any frequency scan occurs at f_{max}. Figure 2 shows the normalized dielectric loss curve for both copolymers B and D over a range of temperatures. No shape change occurs with changing temperature or composition. This is in agreement with previous studies of similar copolymers.[7,8] This constancy of shape

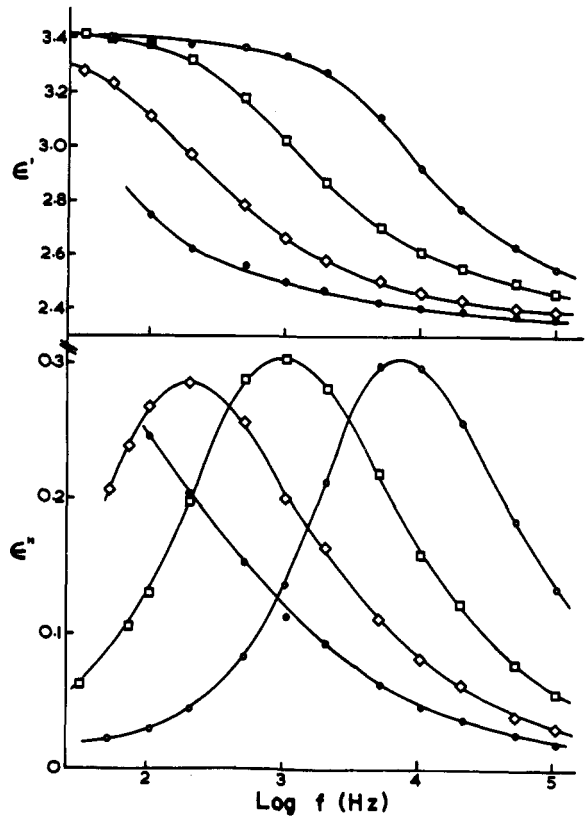

Figure 1. Dielectric constant (ϵ') and loss (ϵ'') for unblended copolymer D (see Table I) in the frequency plane at temperatures: (●) 142 °C, (◇) 147.4 °C, (□) 153.5 °C, and (○) 163.8 °C.

is reflected in the Cole–Cole[9] plot of ϵ' vs. ϵ'' where α in the relation

$$\epsilon' - i\epsilon'' = \epsilon_\infty + \frac{\epsilon_0 - \epsilon_\infty}{1 + (i\omega\tau_0)^{1-\alpha}} \quad (1)$$

may be determined from the angular depression of the arc center below the ϵ' axis. The data were well fitted at the low frequency end with $\alpha = 0.029$ for each copolymer. Not unusually, the high frequency end was observed to be nearly linear rather than circular.[10]

The strengths of the T_g relaxation process ($\epsilon_0 - \epsilon_\infty$) for the incompatible copolymer D and the compatible copolymer B are 1.03 and 1.16, respectively, from the Cole–Cole plots and 1.22 and 1.37, respectively, from inspection of ϵ' plateaus at different temperatures. These strengths are in opposite order to their chlorostyrene content and indicate a changing dipole correlation with changing mole fraction of strong dipole. In order to be more specific, values of $\mu_e^2(x_2)$, the *average* dipole moment squared per monomer unit, were evaluated from the Onsager[11] equation:

$$\mu_e^2(x_2) = \frac{9kT}{4\pi N} \frac{(2\epsilon'_R + \epsilon'_u)(\epsilon'_R - \epsilon'_u)}{\epsilon'_R(\epsilon'_u + 2)^2} \quad (2)$$

where ϵ'_R and ϵ'_u, the relaxed ($\epsilon'_R \equiv \epsilon_0$ in eq 1) and unrelaxed ($\epsilon'_u \equiv \epsilon_\infty$) dielectric constants at 423 K, were obtained from extrapolations of the Cole–Cole plots to $\epsilon''(\omega) = 0$. The combined number of dipoles (N) per cubic centimeter of chlorostyrene and styrene was evaluated as $\rho L/(x_1M_1 + x_2M_2)$ where x and M refer to mole fractions and monomer molecular weight respectively, ρ is the overall density, and L is Avogadro's number. The experimental values of $\mu_e^2(x_2)$ are then 1.07 and 1.17 D^2 for copolymers B and D, respectively.

Correlation parameters (g) can be evaluated in two ways but their significance is not the same in both calculations. In the present system, the chlorostyrene dipole strength is large,

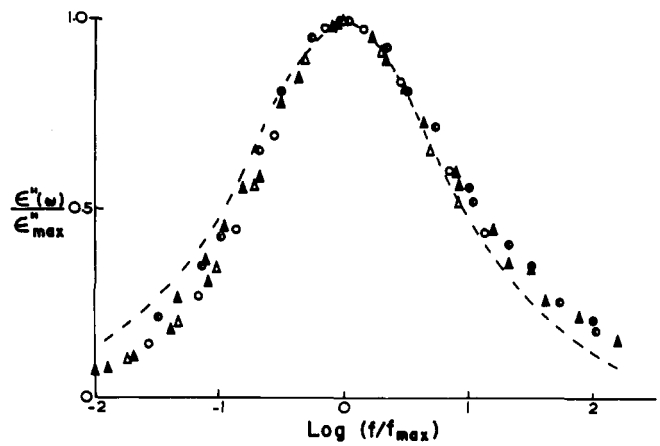

Figure 2. Normalized dielectric loss curves, $\epsilon''(\omega)/\epsilon''_{max}$ vs. log (f/f_{max}) for unblended copolymer B at (▲) 150 °C, (▲) 156 °C, and (△) 163.2 °C and D at (●) 147.1 °C, (◐) 153.5 °C and (○) 163.8 °C. The Fuoss–Kirkwood theoretical curve (eq 6 with $m = 0.6$) is shown (- - -) for comparison.

2.0 D,[12] while the styrene dipole strength is low, ~0.3 D. The dielectric relaxation strength and hence $\mu_e^2(x_2)$ is dominated by angular correlations of the chlorostyrene dipoles. This may be assessed empirically by defining an effective local correlation parameter[13] and assuming additivity of orientational polarizability to give:

$$\mu_e^2(x_2) = x_1g_1\mu_1^2 + x_2g_2\mu_2^2 \quad (3)$$

At the mole fractions used in this work, the first term will not have great significance. Thus in order to obtain a value of g_2 we take $g_1 = g_2$, which will probably not be far from the truth anyway in the present random system of chemically similar structural units. For the lowest chlorostyrene containing copolymer (B) the value of $g_2 = 0.46$ and for the highest chlorostyrene copolymer (D) $g_2 = 0.38$. As is intuitively obvious from the dielectric strength data, the spatial correlation between chlorostyrene dipoles (not necessarily from a single chain) is stronger for the higher chlorostyrene copolymer. For no spatial correlation $g = 1$ and the data indicate that the chain or local liquid structure is encouraging orientations with canceling dipole vectors, the effect being greater at higher dipole concentrations.[14]

In a more refined approach, Work et al.[8] with a chemically similar system (4-chlorostyrene, 4-methylstyrene copolymers) were able to describe the experimental dipole moment with a single orientation parameter. Rewriting their equation 12 in terms of absolute values rather than ratios and dropping the last term we have:

$$\mu_e^2(x_2) = x_1\mu_1^2 + x_2\mu_2^2 + 2(x_1\mu_1 + x_2\mu_2)^2\Sigma\eta_k \quad (4)$$

where η_k is the average cosine between two dipole vectors separated by $(k - 1)$ monomers in a random copolymer with η_k's independent of the types of monomers in the sequence. All the dipole correlations are assumed to arise from in-chain effects and the Kirkwood parameter is then given by[8]

$$g = (1 + 2\Sigma\eta_k) \quad (5)$$

Substituting the previously discussed values in eq 4 rather than eq 3 yields values of g of 0.66 and 0.62 for copolymers B and D, respectively. These are considerably closer than the g_2 ratios from (3) but still indicate more dipole correlation in the higher chlorostyrene copolymer. The lack of constancy of g makes eq 4 less attractive for the present system than it was for the chlorostyrene–methylstyrene copolymers where its approximate constancy validated the assumptions made in its derivation. It is tempting to assume that "typal" correla-

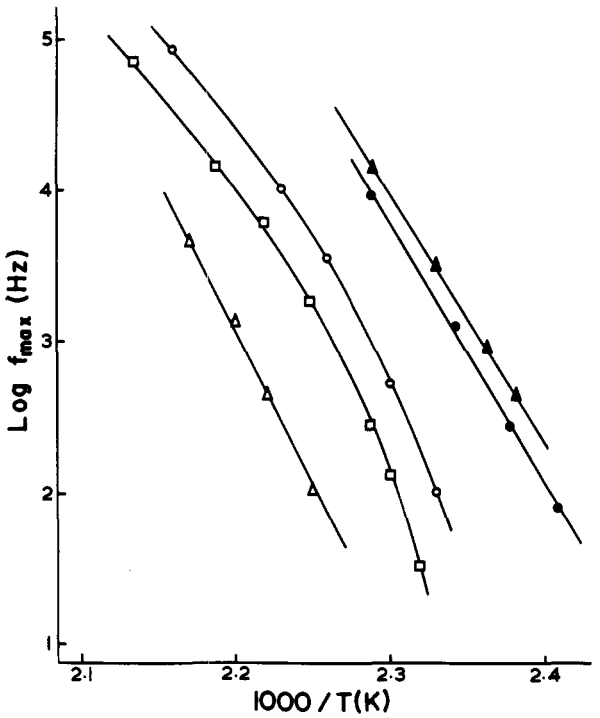

Figure 3. Locus of log frequency of dielectric loss maximum against reciprocal temperature for all the systems studied: (▲) copolymer B, (●) copolymer D, (△) blend 40% PPO/B, (□) blend 40% PPO/C, (○) blend 40% PPO/D.

tions, i.e., preferential sequence distributions of the monomers, is the reason for the breakdown in the present case. However, in related work in very compatible PpClS–PS copolymers[14] blended with PPO, correlation parameters (similar to g_2) have always been found to increase toward unity with decreasing copolymer concentration in the blend. Thus, fairly generally with the present copolymers the rule seems to be that decreasing chlorostyrene dipole concentration, whether by mole fraction reduction in-chain or by dilution with compatible chains, gives correlation parameters increasing toward the free dipole value of unity.

Plots of log f_{max} (for a peak in ϵ'') vs. $1/T$ are shown for copolymers B and D in Figure 3. The data can be adequately represented by straight lines in this region giving activation enthalpies of 318 and 326 kJ/mol for B and D. These figures are the same within experimental uncertainty and indicate no dramatic change in relaxational characteristics, as evidenced also by the constancy of relaxation shape (Figure 2) and closely similar T_g's (125 and 126 °C, respectively).

Copolymer Blends with PPO. (a) Widths of Relaxation Spectra. Copolymer B is compatible with PPO in the present composition range as judged by the DSC data of Fried et al.[3b] The dielectric loss and constant data originating from the single glass transition relaxation region of the 40% PPO blend are shown in Figure 4. This relaxation spectrum (approximated by the ϵ'' vs. log f plot with relaxation time $\tau = 1/2\pi f$) is much broader than that of any of the unblended copolymers. This is obvious just from inspection of the curves in Figures 4 and 1 and by comparison of the normalized curves for the copolymer alone in Figure 2 with that for the blend in Figure 5. Quantifying the breadth of the compatible blend spectrum via the Cole–Cole parameter α (eq 1) we obtain α(compatible blend) = 0.077 compared with α(all unblended copolymers) = 0.029.

In a system which is molecularly homogeneous, the increase in relaxation spectrum breadth would have to be attributed to gross changes in conformation characteristics of the relaxing chains. Flexible polymer chains as pointed out by Johari and

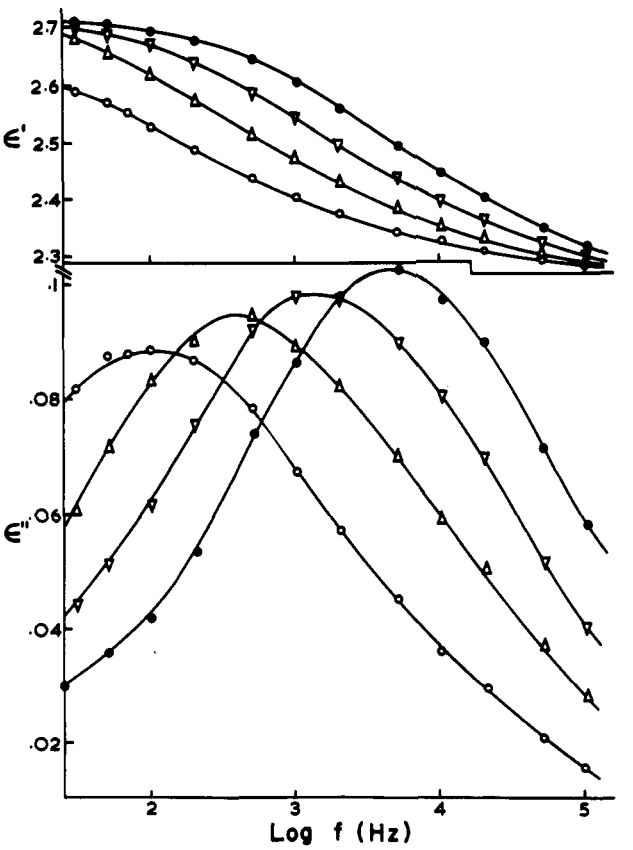

Figure 4. Dielectric constant (ϵ') and loss (ϵ'') for the compatible blend 40% PPO/copolymer B in the frequency plane at temperatures (○) 170 °C, (△) 177 °C, (▽) 182 °C, and (●) 188 °C.

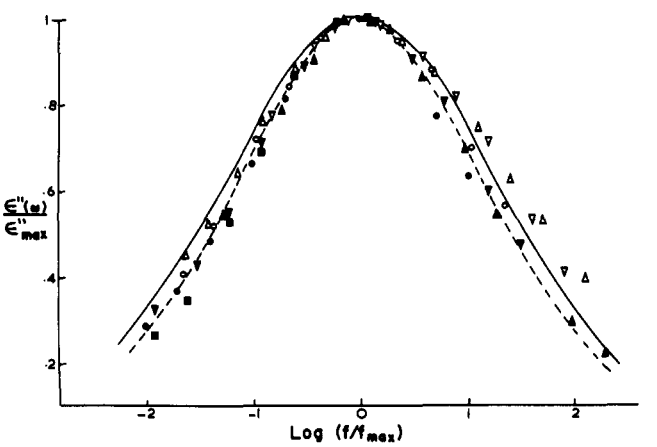

Figure 5. Normalized dielectric relaxation curves $\epsilon''(\omega)/\epsilon''_{max}$ vs. log (f/f_{max}) for a blend of 40% PPO/copolymer B at (△) 177 °C, (▽) 182 °C, and (○) 188 °C and for a blend of 40% PPO/copolymer D at (▲) 161 °C, (▼) 169.4 °C, (●) 175.4 °C, and (■) 188.5 °C. Theoretical curves based on a distribution of local concentrations and hence relaxation times (eq 8) are shown with $\beta = 0.8$ (—) and 1.0 (- - -).

Goldstein[15] and by Williams et al.[16] exhibit relaxation spectra which are no broader than those exhibited by low molecular weight glass forming dipolar liquids. As the latter authors correctly pointed out, this indicates the dominance of cooperative relaxation processes between large numbers of monomers on the relaxation spectrum, rather than any correlation with chain connectivity phenomenon and dipole cross-correlations along the chain. The unblended copolymers certainly all fall into this flexible chain category with relaxation half-widths ~1.96, similar to values found for glass forming liquids.[16] Conversely, the relaxation spectrum of the

compatible copolymer B in the PPO blend is so broad that it would signify the presence of equilibrium conformational correlation lengths greater than or at least comparable to the dimension of the cooperative relaxing regions. The present copolymers show no change in relaxation shape with composition, despite changing conformation parameter (g in eq 3 and 5). Similarly, comparing the data of Leffingwell and Bueche[7] on 2-chlorostyrene–styrene copolymers with the results of Work et al.[8] on 4-methylstyrene–4-chlorostyrene copolymer no significant change in relaxation shape occurs despite differing conformational parameters. Changes in conformational stiffness with blending are thus a very unlikely explanation of the large relaxation breadths observed in Figures 4 and 5.

Broadening of relaxation spectra in mutual solutions of certain glass forming liquids has been ascribed[17] to concentration fluctuations which persist for longer times than those required for dipole polarization. As PpClS homopolymer is incompatible with PPO it is very reasonable to expect that regional fluctuations in concentration will exist on a local scale. Chain segments having a statistically high chlorostyrene monomer content will exist in regions of low PPO concentration and conversely segments with high styrene content will exist in conjunction with high PPO concentrations. These distinctions will not be clear cut and a continuous range of local chlorostyrene concentrations is to be expected because of the statistically random nature of the chlorostyrene/styrene placements in the chain. Knowledge of the monomer reactivity ratios permits the calculation of the probability of occurrence of different types of monomer sequences.

In the present work we wish to test whether a variable concentration model can satisfactorily explain the observed dielectric relaxation spectrum. We note first that the Fuoss–Kirkwood empirical relation[18]

$$\epsilon''(\omega) = \epsilon''_{max} \text{ sech } (m \ln \omega\tau) \tag{6}$$

gives an adequate mathematical description of the normalized curves for the nonblended copolymers. The dashed line in Figure 2 is a plot of eq 6 with $m = 0.6$. Because eq 6 is symmetrical on a logarithmic scale and the actual relaxation curves are asymmetric, the best curve will underestimate the data on the high frequency side and overestimate them on the low frequency side. This systematic deviation will persist through the following calculations, but use of better approximations such as the Cole–Davidson[19] expression leads to unwarranted difficulties in locating the average relaxation time which is no longer given by $1/\omega_{max}$ for the peak in ϵ''.

A distribution of relaxation times is considered to arise from the distribution of chlorostyrene segment/PPO concentrations locally present. The probability $P(ln\,\tau)$ of finding a region of different central relaxation time (τ) is assumed to decrease symmetrically on a ln τ scale on both sides of the average value with the Gaussian error curve

$$P(ln\,\tau) = [\beta/\pi^{(1/2)}]\, exp[-\beta^2(ln\,\tau)^2] \tag{7}$$

where β is an adjustable width parameter. Each region will contribute the basic relaxation spectrum of the copolymer given by eq 6 centered on a relaxation time which is a function of concentration, and eq 7 is used only to define the spread of central relaxation times arising from concentration differences throughout the material. Thus, the resultant dielectric loss curve of the material is given by

$$\epsilon''(\omega)/\epsilon''_{max} = K \sum_{ln\tau=-\infty}^{ln\tau=+\infty} P(\tau) \text{ sech } (0.6 \ln \omega\tau) \tag{8}$$

where K is a normalization constant adjusted to make $(\epsilon''(\omega)/\epsilon''_{max})$ unity at the observed peak maximum. Figure 5 shows the agreement between a curve computed from the above model with $\beta = 0.8$ and the data for the blend of copolymer B. The agreement is quite satisfactory when the deficiencies of the original spectrum representation (eq 6) are considered. The small skewed disagreement is a consequence of the use of this symmetrical expression as discussed earlier.

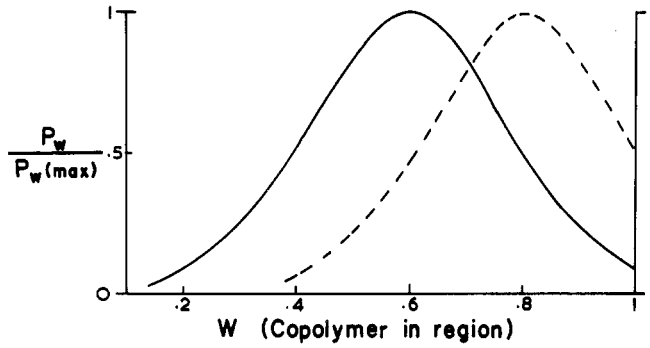

Figure 6. The relative probability of occurrence $[P_w/P_w(max)]$ of regions with copolymer weight fraction W, in blends of 40% PPO/copolymer D (- - -) and 40% PPO/copolymer B (—) as calculated from eq 8.

It is instructive to estimate what degree of concentration fluctuation is present to give rise to the spectrum of central relaxation times. This can be obtained by assuming that $(\partial T_{max}/\partial C)_{f,P} = (\partial T_g/\partial C)_{R,P} = Y$ where the first term denotes the variation of loss peak position with concentration at constant measuring frequency and $(\partial T_g/\partial C)_{R,P}$ refers to constant rate of heating DSC data.[3b] As $[\partial(\log f_{max})/\partial T]_{C,P} = Z$ is known from Figure 3, the required term $[\partial(\log f_{max})/\partial C]_{T,P} = YZ$. This enables the abscissa in Figure 5 to be transposed to concentration units (weight fraction of copolymers present in the region) and produces the concentration variation shown in Figure 6 for a blend of copolymer B with PPO (40%). No significance must be placed on the exact shape or extremes of these concentration fluctuation curves but the analysis does show that a wide range of copolymer concentrations is present. Any analysis of the above type leads to the conclusion that for the compatible copolymer (B) at average weight fraction 0.6 in PPO significant local concentrations exist as widely different as 0.4 and 0.8 as a conservative estimate.

The other extreme in terms of blend behavior is represented by the clearly two-phase blend of copolymer D with 40% PPO (by weight). Dielectric constant and loss in the temperature region above the lower T_g exhibited by this system are shown in Figure 7. Meaningful results could not be obtained in the region above the upper T_g of the system (>200 °C) because of massive pseudoconductivity (space charge) effects. However, as will be shown later, most of the relaxation strength is present in the lower T_g relaxation region. Two features are apparent in these data. First, there is an overall reduction in relaxation width, with the normalized dielectric loss curves lying inside that for the compatible blend (of copolymer B) in Figure 5. Second, the dielectric loss at low temperatures exhibits a distinct shoulder on the high frequency side, which rapidly merges into the main peak as temperature is raised. Considering the width characteristics of the incompatible blend first, it is seen that increasing the chlorostyrene content of this polymer has narrowed the relaxation width compared to the compatible blend even without any subtraction of the high frequency shoulder. By treating the spectrum in the same way as the compatible system, the distribution of central relaxation times required to fit the data is narrower with $\beta = 1.0$ in eq 7 and the resultant theoretical curve from eq 8 is also compared with the experimental curve in Figure 5. The derived concentration fluctuations are shown in Figure 6. The

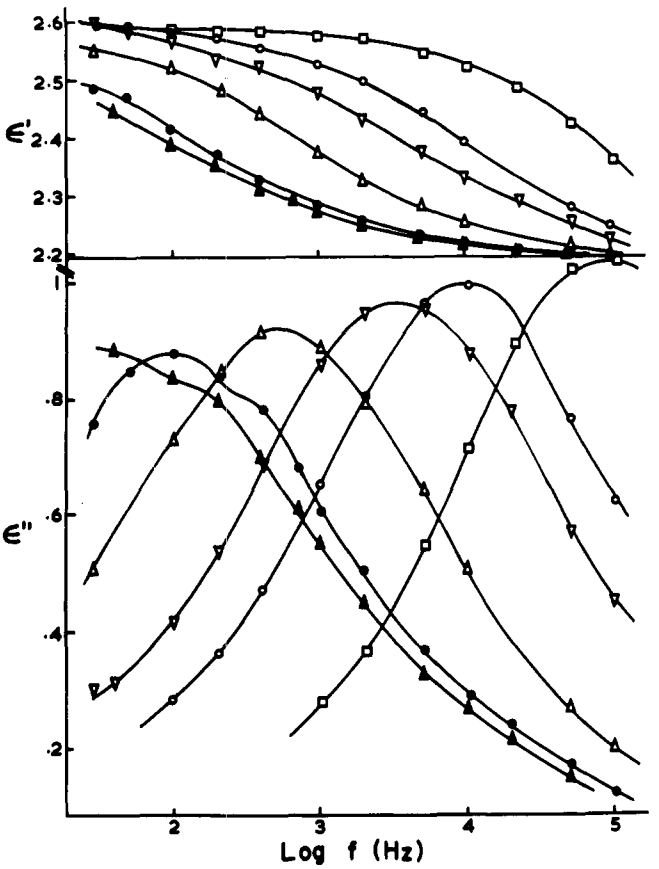

Figure 7. Dielectric constant (ϵ') and loss (ϵ'') for an incompatible blend of 40% PPO/copolymer D in the frequency plane at temperatures (▲) 152 °C, (●) 155 °C, (△) 161 °C, (▽) 169.4 °C, (○) 175.4 °C, and (□) 188.5 °C.

weight distribution half-width is reduced by 0.036 even without allowance for the presence of the shoulder on the relaxation curve. It is significant that the relaxation spectrum (best Cole–Cole $\alpha = 0.075$) has not narrowed to anything like that of the nonblended copolymer ($\alpha = 0.029$). Assuming that this copolymer D/PPO system is two phase, the present dielectric evidence demonstrates that the major part of the copolymer component still exists in a range of differing local concentrations. Thus the relaxation spectrum discussed above arises from a copolymer-rich phase of varying PPO concentration coexisting with a PPO-rich phase of high T_g with a dielectric relaxation at higher temperatures than those of the present measurements. As mentioned previously, meaningful dielectric data cannot be obtained in this region.

(b) Phase-Separated Blends. Maxwell–Wagner–Sillars Process. The presence of a high frequency shoulder on the dielectric loss curves correlates with the existence of a phase-separated system. It is not observed in the nonblended copolymers or in polystyrene itself or in any rigidly para-substituted styrenes.[20] Figure 8 compares the loss curves for the range of polymers studied for peak positions at the low frequency end of the measurement range. The verge of compatibility blend (copolymer C/PPO 40%) is seen to have a clearly resolved high frequency peak and must be considered as phase separated rather than homogeneous, but in this case the data are dependent to some extent on the thermal history as discussed later. A possible interpretation of this additional relaxation process is that it originates in the phase boundary from a polystyrene segment rich sheath between the PPO-rich and PPO-poor phases. This seems molecularly improbable and unlikely to give such a discrete process within the range of concentrations present.

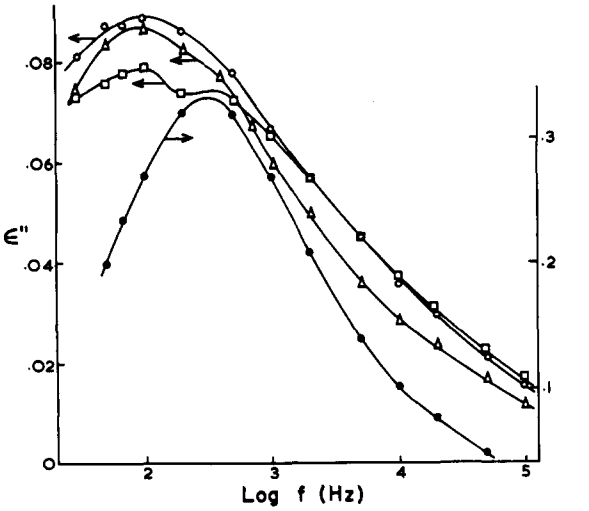

Figure 8. Comparison of shapes of dielectric relaxation curves for the three blends compared with the unblended copolymer B (right-hand axis), all in the low frequency region of maximum resolution. Curves as follows: (○) 40% PPO/B at 170 °C, (□) 40% PPO/C at 161 °C, (△) 40% PPO/D at 155 °C, and (●) unblended copolymer B at 140.5 °C.

In any two-phase dielectric system, a nonmolecular relaxation process is predicted by the theories of Maxwell,[21] Wagner,[22] and later Sillars.[23] This originally described the effective polarization contributed by conducting particles in an insulating medium, but the principle applies quite generally for any two-phase system of nonidentical dielectric properties. The geometrical[23] and interaction[24] effects can be very significant and without a detailed knowledge of the morphology of phase separation, a quantitative analysis is not possible. However, the basic relation for the position of the peak in dielectric loss from the M–W–S theory,

$$f_{max} = (1.8 \times 10^{12}\sigma_2)/(2\epsilon_1' + \epsilon_2') \quad (9)$$

can be used to estimate the region in which loss from such a process could be expected. Here the conductivity σ_2 is in units of ohm^{-1} cm^{-1} and ϵ_1' and ϵ_2' are the relative dielectric constants of the continuous and dispersed phases. The denominator in eq 9 is noncritical. The main problem arises in selecting a value of σ_2. The maximum value should be obtained as $3.6\pi\omega\epsilon_2''_{max}$. Substituting the peak value for the dielectric loss (0.3) of the copolymer D at 1000 Hz gives the M–W–S loss center as 40 Hz. This should be compared with the observed shoulder position of 400 Hz. Considering the crudeness of the calculation involving application of eq 9 at high second-phase concentration and the ignoring of geometrical factors associated with the phase morphology, agreement is as good as could be expected. The shoulder is therefore interpreted in the above way and is a definitive indication of a phase-separated system in the present case and probably more generally.

A notable new feature in the verge of compatibility blend (copolymer C/PPO 40%) is the variation in dielectric spectra with varying thermal history. The resolution reported in Figure 8 was the best achieved in the present work and in this case annealing was carried out at the measurement temperature (161 °C). By comparison, the sample fast cooled (10 min from 195 °C) from above its highest T_g to the same measurement temperature gives loss data not very different from the compatible blend with only a trace of a shoulder and very broad total relaxation spectrum. The indication is that both loss processes are broad in this sample. This observation can still be explained in terms of concentration variations in the phases because σ_2 in eq 9 will exhibit a range of values to give a broadened M–W–S relaxation, each individual component

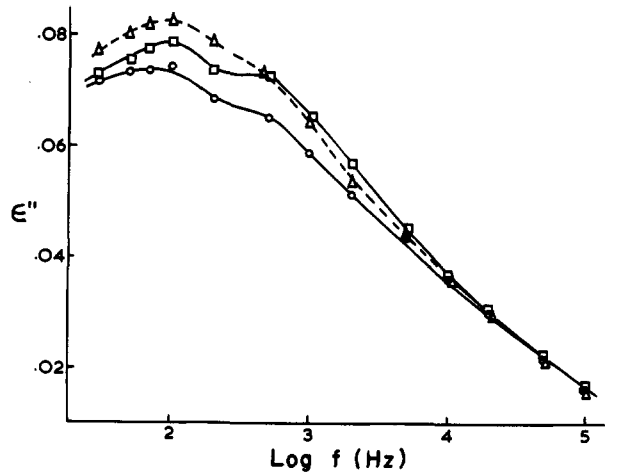

Figure 9. Effect of thermal history of the dielectric frequency plane data for the marginally incompatible blend 40% PPO/copolymer C: (○) T = 161 °C after annealing 1 day at 120 °C, (□) T = 161.3 °C after annealing 1 h at 161 °C, (△) T = 159.5 °C after "quenching" (10 min cooling) from 195 °C.

of which should be a Debye-type process. The effect of various thermal histories is shown in Figure 9. Annealing at low temperature (120 °C) before measuring at 161 °C produces better resolution of the two loss processes than annealing at 195 °C before measuring at the same temperature. This suggests that there is an upper consolute temperature ~180 °C giving a compatible system for copolymer C/PPO above this temperature. On fast cooling phase separation is only able to occur to a minor extent, while annealing at a temperature well below the consolute point gives more clearly defined phase structure.

An important implication of the above compatibility information is that observation of two T_g's in a sample annealed at 120 °C compared to the single broad transition in a quenched sample is a consequence of inherent incompatibility at low temperatures and compatibility at high temperatures. The production of two distinct T_g processes is not just a consequence of the annealing of the structures of the glassy states present to give sharper transitions. The resolved T_g has not been observed as a shoulder on the low-frequency side of the main peak (15 °C resolution in the DSC ≡ 1.8 separation in log frequency). This temperature region starts to be confused by pseudoconductivity effects.

The locus of the maximum dielectric loss against log frequency can be described by a simple Arrhenius activation energy law for the nonblended copolymers and also for the compatible blend. Figure 3 shows, however, that the phase-separated systems, blends of copolymer C and of copolymer D with PPO, show pronounced curvature. This is largely explicable in terms of the two overlapping relaxations as the central portion of the locus will be pulled to higher frequencies by the overlapping M–W–S relaxation. At high frequencies the two processes have completely merged and at low frequencies there is sufficient separation that peak positions are not much distorted. In fact, if the first and last points are joined, the slopes are in line with those of the homogeneous systems. The activation energy of copolymer B in the blend with PPO is 381 kJ/mol which is an increase over the nonblended value of 318 kJ/mol. This increase arises because of the stiffer nature of the PPO chain which gives rise also to the elevation of T_g for compatible blends.

(c) Correlation Parameters (g_2) in the Blends. The dielectric relaxation strengths for the blends can be analyzed in the same manner as employed for the unblended copolymers. Table II gives the limiting dielectric constants obtained

Table II
Dielectric Relaxation Data for Blended and Unblended Copolymers

System	Temp, °C	ϵ'_u	ϵ'_R	$\Delta\epsilon'$	μ_e^2	g_2
Copolymer B	150	2.60	3.76	1.16	1.07	0.46
Copolymer D	153.5	2.40	3.42	1.02	1.09	0.38
Copolymer B/40% PPO	182	2.24	2.74	0.50	1.07	0.44
Copolymer C/40% PPO	177.5	2.265	2.71	0.445	0.97[a]	0.36
					1.06[b]	0.44
Copolymer D/40% PPO	161	2.18	2.62	0.44	0.95[a]	0.35
					1.04[b]	0.43

[a] Assuming all copolymer present in relaxing phase. [b] Value for 92% of copolymer in relaxing phase.

via extrapolation of the best Cole–Cole type plots (noncircular) to $\epsilon''(\omega) = 0$. Using the Onsager relation (eq 2) together with eq 3 a value of g_2 can again be obtained.

Additional provisos and uncertainties arise in this case and they will be dealt with below. The first impression is that $\Delta\epsilon'$ for the blends are all lower than expected on the grounds that 0.6 weight fraction of copolymer is present. This is, however, an artifact of the effect of the limiting relaxed dielectric constant (ϵ'_R) and to a lesser extent the differing temperatures. The value of the effective square of the dipole moment per average monomer unit of the copolymer is found to be unexceptional. However, the figures in Table II are derived assuming that all the 0.6 weight fraction of copolymer contributes toward the observed relaxation. This is believed to be true for blends of B (compatible) and C (verge of compatibility, small separation in T_g's) but not for the blend with D. In this case, from the DSC data[3b] it can be estimated that only 0.55 weight fraction of copolymer (out of the total 0.6) is contributing to this phase. Allowance for this gives the value with footnote *b* rather than the value with footnote *a* in the table.

The correlation parameter g_2 is seen to be significantly different only for the blend of copolymer C (very similar to D in composition). If the same calculation as from footnote *b*, Table II, is performed, assuming the same weight and composition of a second phase as for D, then the result is in line. The explanation may well then be that there is a second phase containing the missing ~0.05 weight fraction of copolymer. This substantiates the conclusions, concerning phase separation in copolymer C/PPO, from relaxation spectra considerations.

A possible source of error in considering the dielectric relaxation strengths of a two-phase system is lack of homogeneity of the local field. The magnitude of possible discrepancies can be assessed using Kerner's equation,[25]

$$\epsilon_b = \left[\frac{v_1\epsilon_1}{e} + \frac{v_2\epsilon_1\epsilon_2}{2\epsilon_1 + \epsilon_2}\right] \Big/ \left[\frac{v_1}{3} + \frac{v_2\epsilon_1}{2\epsilon_1 + \epsilon_2}\right] \qquad (10)$$

where the dielectric constant of a blend is given in terms of two components of dielectric constant, ϵ_1 (PPO) and ϵ_2 (copolymer) in our case. The appropriate volume fractions are v_1 and v_2. Taking the dielectric constant of PPO = 2.5 throughout the whole spectral region, and taking ϵ_2 values for copolymer D as an example equal to 2.4 below the relaxation and 3.42 above gives ϵ_b(unrelaxed) = 2.442 and ϵ_b(relaxed) = 3.019. Thus, $\Delta\epsilon'$(Kerner) = 0.58 as opposed to 0.61 from a simple additivity (parallel) model calculation. Errors in this sense are thus likely to be small provided the overall *average* sphericity of phases holds. We have no direct evidence of the morphology present in these systems.

Conclusions

Copolymers of styrene with pClS exhibit relaxation spectra, due to cooperative main-chain rotation above their T_g's, of widths characteristic of many flexible chain polymers and glass-forming liquids. Cole–Cole circular arc parameters do not change with composition but there is a slight increase in dipole correlation parameters (Kirkwood "g") with decreasing chlorostyrene content.

On blending copolymers of compositions (58.5–67.8% pClS) with PPO very broad relaxation spectra are obtained. In general this is interpreted as arising from a range of local environments differing in concentration. The range of local concentrations required to cause this spectral broadening is evaluated and model calculations then give good agreement with experimental results. In addition to the broadening, a characteristic higher second peak or shoulder is observed in phase-separated systems. This is interpreted as a Maxwell–Wagner–Sillars process. In the copolymer of critical composition (67.1% pClS) this second peak and the overall breadth are dependent on thermal history. The inference is that an upper consolute temperature (~180 °C) exists for this particular copolymer blend. Fast cooling from above this temperature produces less well defined phase structure.

The locus of maximum dielectric loss is linear against log frequency for the copolymers alone and the compatible blend, but curvature results in the case of incompatible blends. This is primarily due to the presence of the high frequency overlapping dispersion region.

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Dielectric Relaxation Studies of Bisphenol A–Diphenyl Carbonate/Lexan Polycarbonate Solid Solutions

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ABSTRACT: The T_g and sub-T_g relaxations in solid solutions of Lexan polycarbonate and bisphenol A–diphenyl carbonate (MLEX) have been studied dielectrically. The T_g's of the mixed system obey the Fox equation and act as a polymer/diluent system exhibiting a single correlated motion. The $\alpha(T_g)$ relaxation appears Arrhenius activated. These apparent activation energies are composition dependent for 0 to 50 vol % MLEX and exhibit plasticization effects. Above 50% MLEX, the energies are composition independent. These results are discussed in terms of intra- and intermolecular interactions. The solid solution cannot be described as a mixture of high and low molecular weight polymers. The sub-T_g relaxations reflect the T_g analysis. The addition of either component to the other causes the β relaxation (phenylcarbonyl motion) to disappear with the γ relaxation (carbonyl motion) being a molar averaging of the γ relaxation of the pure components. The sub-T_g relaxations are uncorrelated.

The effect of plasticizers on polymer properties is industrially important and forms the subject of a variety of dynamic studies.[1-14] In these studies, various plasticizer–polymer combinations have been used, including polar polymer–nonpolar plasticizer, polar plasticizer–nonpolar polymer, etc. The studies typically show the glass-transition temperature, T_g, of the polymer to be plasticized. In some cases involving a polar plasticizer, the dynamic T_g exhibits uncorrelated structure where the relaxations of the individual components are perturbed by their counterpart.[3,5,6,11] An example is the system poly(vinyl acetate)/benzyl benzoate[3] where (1) at low plasticizer concentrations a plasticized polymer T_g occurs, (2) at low polymer concentrations an antiplasticized plasticizer T_g occurs, and (3) at intermediate compositions overlapping but independent relaxations from both components occur. Würstlin[3] proposed that at low plasticizer concentrations, the plasticizer molecules were bound to the polymer chains via dipole–dipole interactions. He further postulated that a critical composition exists where the polymer becomes completely "solvated" by the plasticizer and that above this composition relaxations due to pure plasticizer became evident. Luther and Weisel[6] and Thurn and Würstlin[5] were later

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