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Dielectric Study of Polymer Compatibility: Blends of Polystyrene/Poly-2-chlorostyrene

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ABSTRACT

The dielectric constant and loss have been monitored isothermally in the frequency plane in the α relaxation region for a series of amorphous compatible and phase separating polymer blends comprising one polar and one relatively non-polar component. Differential scanning calorimetry has been employed for preliminary assessment of the miscibility of a given pair. The system polystyrene/poly-2-chlorostyrene (PS/PoCS) has been found to exhibit miscibility highly dependent on molecular weight and temperature. High molecular weight blends display wide loss spectra; phase separation above a lower critical solution temperature (LCST) results in the narrowing of the loss curves. Low molecular weight polystyrene yields blends which remain homogeneous up to degradation temperatures and exhibit narrow loss peaks. Comparison between PS/PoCS blends and random copolymers of styrene and 2-chlorostyrene is made.

INTRODUCTION

There exists a growing body of literature on the subject of compatible polymer blends [1]. From this extensive body of work some general observations have arisen concerning the properties of such blends. To the early criteria for compatibility such as optical clarity of films or the existence of a single compositionally dependent glass-transition temperature T_g have been added densification [2], a negative enthalpy of mixing [3], and the existence of a lower critical solution temperature (LCST) [4]. The LCST is also predicted to occur by several of the more modern theories of polymer solutions [5, 6]. The intimacy of mixing in such apparently one phase systems has not been established, in general. It is not apparent whether a blend of two high molecular weight components is homogeneous on a segmental scale or on a scale somewhere between the segmental and the molecular. We have previously studied blends of poly(2,6-dimethyl-1,4-phenylene oxide) with poly(styrene-co-4-chlorostyrene) using the dielectric relaxation technique [7]. Dielectric relaxation spectra were found to be much broader for the blends than for their components. This was interpreted as arising from a wide range of local concentrations which are present in the ostensibly single phase mixture. This work demonstrated that dielectric relaxation studies are sensitive to the intimacy of mixing and can be used as a tool to investigate compatible polyblends.

We have discovered a compatible polyblend consisting of the components polystyrene (PS) and poly-2-chlorostyrene (PoCS) which provides many advantages for study by the dielectric relaxation technique. These include a relatively nonpolar component, (PS), and a relatively polar component, (PoCS); the existence of an LCST in a convenient temperature range; and the possibility of studying random copolymers of the two components to establish a basis for comparison with the blends. In addition, complicating effects such as crystallinity, or the occurrence of thermal degradation can be avoided. Finally a range of PS molecular weights is conveniently available to investigate the effect of this important parameter on blend properties.

In this paper we report the dielectric relaxation behavior of PS/PoCS blends in the relaxation region associated with T_g , here labeled the α relaxation. Random copolymers, poly(styrene-co-2-chlorostyrene) are also studied. The results indicate that the local

environment of the high molecular weight blends in the one phase region (below the LCST) is quite heterogeneous but that the low molecular weight blends are much more intimately mixed. However, in the two-phase region (above the LCST) it appears that both phases are more homogeneously mixed than the single phase below the LCST.

EXPERIMENTAL

Materials

Atactic polystyrene (PS) in pellet form was obtained from the Monsanto Company (HH 101 resin), courtesy of T. Boyd. Purification was accomplished by reprecipitation from toluene into methanol. Molecular weight averages by GPC are $\bar{M}_n = 1.2 \times 10^5$, $\bar{M}_w = 2.8 \times 10^5$. Narrow distribution low molecular weight atactic polystyrenes were purchased from the Pressure Chemical Company, and used without further treatment. Samples with molecular weights of 10,000 and 20,000 are denoted PS10K and PS20K, respectively.

Poly-2-chlorostyrene was prepared by free-radical techniques with 0.5 mole % azobisisobutyronitrile as initiator. Monomers were purchased from the Aldrich Chemical Company and purified by distillation under vacuum. Polymerization was carried out for 10 hr at 60°C, with 40 mole % toluene added as solvent and chain-transfer agent. Polystyrene equivalent molecular weight averages by GPC were $\bar{M}_n = 5.8 \times 10^4$, $\bar{M}_w = 1.2 \times 10^5$. All chlorostyrene polymers were purified by precipitation.

Poly(styrene-co-2-chlorostyrenes) were prepared in the same manner as poly-2-chlorostyrene. Copolymer compositions were determined by elemental analysis for chlorine.

Blends were prepared by coprecipitation. Solutions, 2% in toluene, were added dropwise to a 12:1 excess of stirred methanol. Films for differential scanning calorimetry and dielectric measurements were compression-molded from the vacuum-dried powders at temperatures dictated by the T_g of the polymers.

Dielectric Measurements

The dielectric constant ϵ' and loss factor ϵ'' of pure materials and blends were determined isothermally at 16 discrete frequencies spanning the range 50 Hz to 100 kHz. A General Radio model 1620A capacitance measuring assembly was employed in the dissipation factor mode. Samples of thickness approximately 0.04 cm were held in a three-terminal Balsbaugh model LD-3 cell, with an active electrode diameter of 5.3 cm. The temperature of the sample assembly was maintained to within $\pm 0.2^\circ\text{C}$. by use of a specially constructed oven employing a Versatherm proportional controller. Approximately 1 hr was required for the temperature to reach equilibrium between measurements.

Calorimetric Measurements

Differential scanning calorimetry experiments were conducted with a Perkin-Elmer model DSC-2 instrument. Sample sizes of approximately 20 mg were used, and a heating rate of $20^\circ\text{C}/\text{min}$ was employed. The DSC glass-transition values (T_g) were determined as the temperature at which the heat capacity achieved one half the total step change associated with the transition.

RESULTS AND DISCUSSION

Calorimetric Studies of PS/PoCS Blends

Coprecipitated PS/PoCS blends were compression-molded at 135°C into films for calorimetric and dielectric studies. At this temperature, the resultant samples were optically clear and thus apparently single phase. DSC measurements confirmed the compatibility of the system; a single compositionally dependent glass transition was observed for the as-molded specimens. Figure 1 presents the DSC T_g 's obtained as a function of blend composition. An identical curve to that shown in Fig. 1 is obtained if a plot of T_g vs. weight fraction 2-chlorostyrene is made for the random copolymer series poly(styrene-co-2-chlorostyrene).

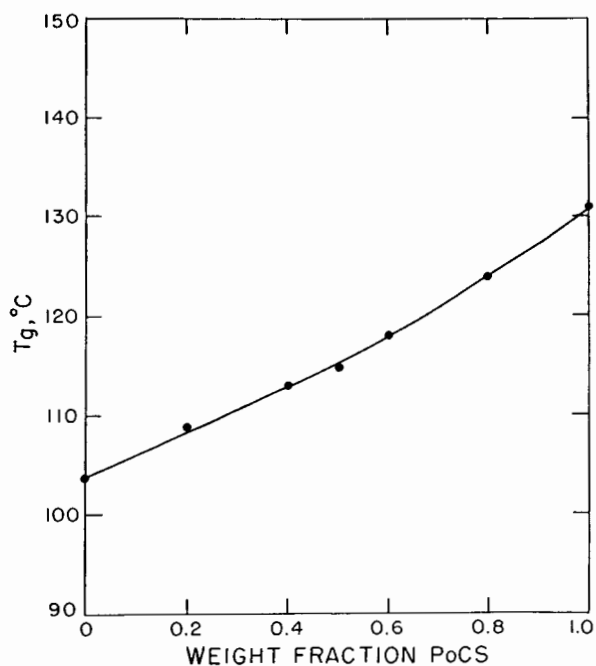


FIG. 1. Composition dependence of the glass-transition temperature for PS/PoCS blends measured by DSC.

Annealing the blends at elevated temperatures in the calorimeter, with subsequent quenching and rescanning, induced phase separation as evidenced by the observation of two glass transitions. Figure 2 shows DSC thermograms obtained from a 50/50 by weight PS/PoCS blend. The top trace is that of the as-molded sample, the bottom trace exhibits the two transitions produced by annealing 15 min at 170°C. Annealing 15 min at 135°C (the molding temperature) produced no change in the transition from that of the as-molded sample.

Blends of the same PoCS with the 10,000 and 20,000 molecular weight polystyrenes were also observed to be compatible by DSC. Remarkably, 50/50 by weight PS10K/PoCS blends were found to be stable to over 320°C. Phase separation at a LCST was also not observed for 50/50 PS20K/PoCS blends. A similar 37,000 molecular weight "monodisperse" polystyrene/PoCS blend phase separated at 150°C.

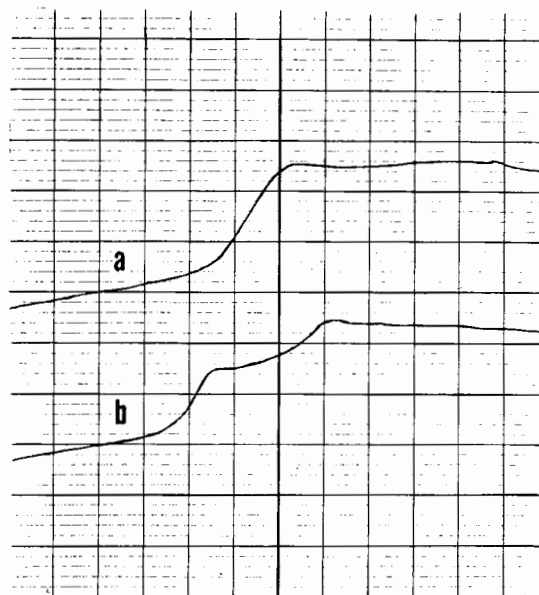


FIG. 2. DSC thermograms illustrating phase separation of a 50/50 PS/PoCS blend: (a) as-molded sample (molding temperature = 135°C); (b) after annealing for 15 min at 170°C.

It remains to establish the complete phase diagram for PS/PoCS blends using either the DSC technique or a light scattering technique such as cloud point determinations. The results of such a study will be reported subsequently.

Dielectric Relaxation in Poly(styrene-co-2 chlorostyrene)

Representative raw data for the homopolymer PoCS are presented in Figs. 3 and 4. These data are then replotted in Fig. 5 as ϵ'' versus ϵ' , according to the method of Cole and Cole [8]. Extrapolations to limiting low and high frequency dielectric constants, ϵ_R and ϵ_u , respectively, were made from plots such as that shown

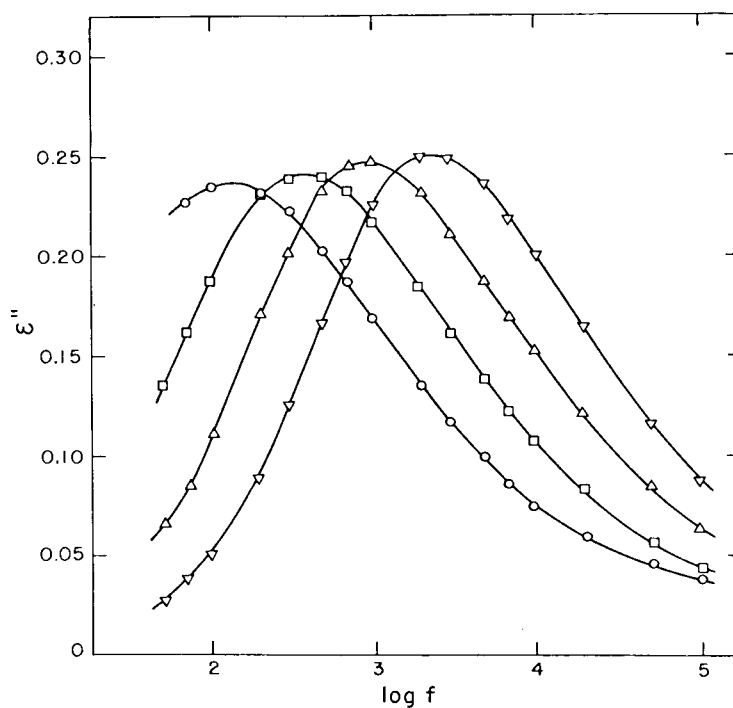


FIG. 3. Frequency dependence of the dielectric loss factor ϵ'' at various temperatures for PoCS: (○) 151.4°C; (□) 155.3°C; (Δ) 160.2°C; (▽) 165.0°C.

in Fig. 5. Effective dipole moments μ_e per repeat unit were calculated from the Onsager equation [9]:

$$\mu_e^2 = (9kT/4\pi N)[(2\epsilon_R + \epsilon_u)(\epsilon_R - \epsilon_u)/\epsilon_R(\epsilon_u + 2)^2] \quad (1)$$

where N is the number of dipoles per unit volume, k is the Boltzmann constant, and T is the absolute temperature. Densities of PoCS and PS were obtained from density gradient column measurements. The copolymer densities were obtained on the assumption of volume additivity. That is:

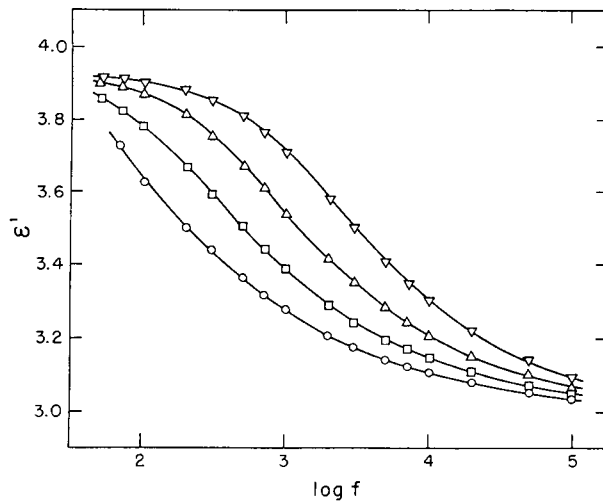


FIG. 4. Frequency dependence of the dielectric constant ϵ' at various temperatures for PoCS: (○) 151.4°C; (□) 155.3°C; (Δ) 160.2°C; (▽) 165.0°C.

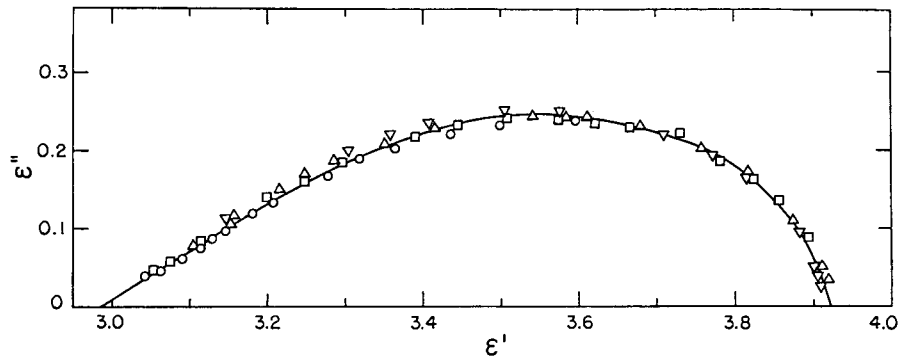


FIG. 5. Cole-Cole plot of the α relaxation region in PoCS: (○) 151.4°C; (□) 155.3°C; (Δ) 160.2°C; (▽) 165.0°C.

$$1/\rho = (w_1/\rho_1) + (w_2/\rho_2) \quad (2)$$

where the w are the weight fractions and the ρ the densities of the homopolymers. N then follows from

$$N = N_0 \rho / (X_1 M_1 + X_2 M_2) \quad (3)$$

where N_0 is Avogadro's number, the X are mole fractions, and M are repeat unit molecular weights of the comonomers. The Kirkwood-Frohlich dipole correlation factor [10], g , was determined from

$$g = \mu_e^2 / \mu_0^2 \quad (4)$$

where μ_0 is the dipole moment of the isolated repeat unit. μ_0 was obtained from the gas-phase dipole moments of toluene and 2-chlorotoluene according to Eq. (5):

$$\mu_0^2 = X_1 \mu_1^2 + X_2 \mu_2^2 \quad (5)$$

where X_1 and X_2 are the mole fractions of styrene and 2-chlorostyrene in the polymer and μ_1 and μ_2 are the gas-phase dipole moments of toluene (0.36 Debyes) and 2-chlorotoluene (1.56 Debyes), respectively.

The dependence of g on copolymer composition is shown in Fig. 6. The increase in g with increasing styrene content can be attributed to a loss of cancelling correlations among the polar 2-chlorostyrene units as they are "diluted" by the relatively nonpolar styrene units. These angular correlations among dipoles are dependent on the copolymer sequence distribution. It has been shown elsewhere [11] that most of the observed effect can be explained on the basis of a simple dyad correlation model assuming a random copolymer.

Figure 7 shows a normalized dielectric loss curve for PoCS obtained from the data in Fig. 3. Figure 8 shows the half and three

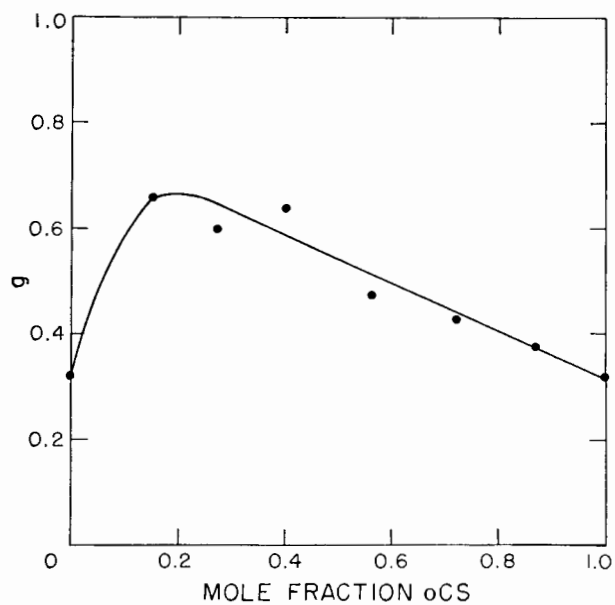


FIG. 6. Composition dependence of g for poly(styrene-co-2-chlorostyrene) copolymers.

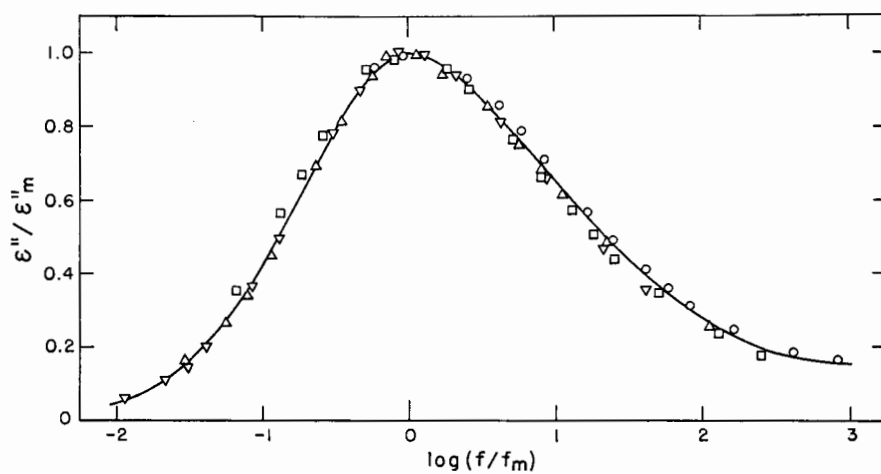


FIG. 7. Normalized frequency dependence of the dielectric loss factor for PoCS: (\circ) 151.4°C; (\square) 155.3°C; (Δ) 160.2°C; (∇) 165.0°C.

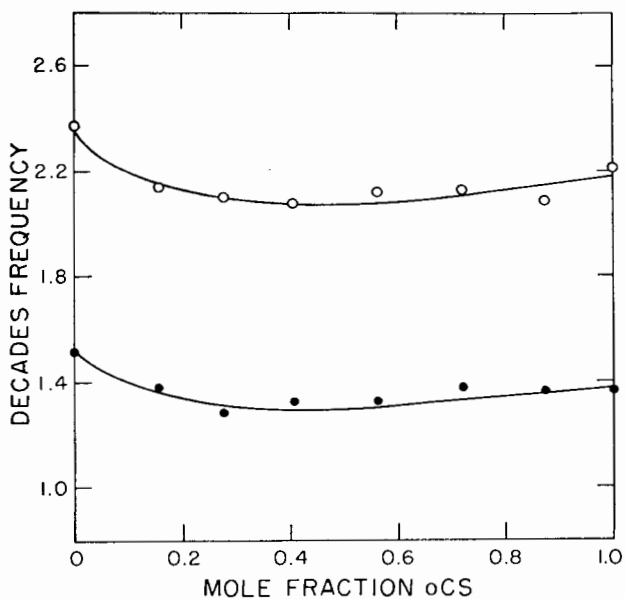


FIG. 8. Composition dependence of the loss width for poly(styrene-co-2 chlorostyrene) copolymers: (○) 0.5 width; (●) 0.75 width.

quarter widths of such normalized loss curves as a function of composition for the copolymers studied. It is clear from Fig. 8 that the widths are essentially independent of composition.

Dielectric Relaxation in Blends of PS/PoCS

The dielectric relaxation behavior of the blends is quite distinct from that of the corresponding copolymers. The data were treated in a similar manner to those for the copolymers discussed above. In this case g values were obtained from the relationship

$$\mu_e^2 = g_1 X_1 \mu_1^2 + g_2 X_2 \mu_2^2 \quad (6)$$

where g_1 and g_2 are the g factors for the homopolymer components of the blends, X_1 and X_2 are the mole fractions of repeat units of each component in the blend and μ_1 and μ_2 have the same meaning as in Eq. (5). μ_e^2 is measured from Eq. (1).

In this particular case, the contribution of PS to μ_e^2 is negligible because of its much lower polarity than PoCS. The blend composition dependencies of μ_e^2 and g are plotted in Fig. 9 for two different PS molecular weights. In contrast to the copolymer results (Fig. 6), g is independent of composition. This means that the local conformational states of the PoCS chain are unperturbed by blending with PS. Put another way, the observed behavior of g argues against the occurrence of chain expansion in the blends as would be the case for a polymer dissolved in a "good" low molecular weight solvent.

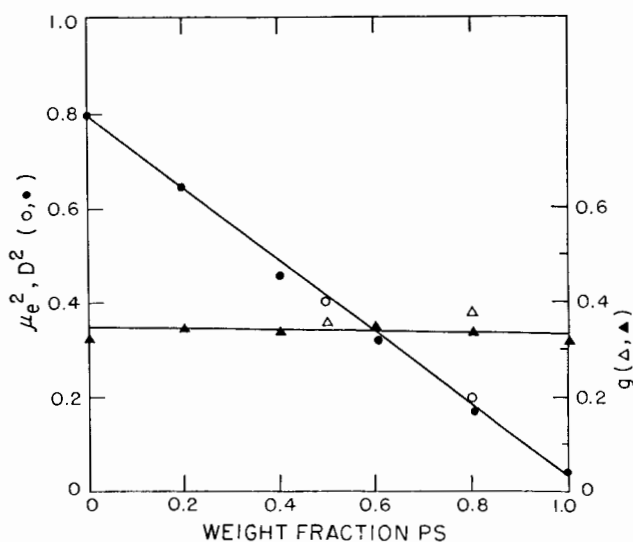


FIG. 9. Composition dependence of (○, ●) dipole moments and (Δ, ▲) g factors for PS/PoCS blends: (○, Δ) PS10K blends; (●, ▲) HH101 blends.

The foremost effect of mixing on the dielectric loss spectra is an increase in the breadths of the curves. Figure 10 presents the widths in decades at 0.5 and 0.75 height of the normalized loss plots as a function of blend composition. All such widths were inferred from data at the lowest temperatures of measurement, presumably below the LCST. Both PS and PoCS display nearly identical widths as do the copolymers (Fig. 8), that of PS being slightly broader possibly due to the no longer negligible effects of any intrinsic background loss for this nearly nonpolar material. At a composition of 0.6 weight fraction PS the loss half-width is a decade larger. Values for the very compatible PS10K/PoCS blends are included in Fig. 10. Only a slight increase in width is observed compared to the homopolymers. A 50/50 PS20K/PoCS blend exhibited identical behavior. The increased breadth of dielectric loss curves of compatible blends has been taken by Wetton et al. [7] and Bank et al. [12] as evidence for a distribution of molecular environments. Other authors have also reported the observation of broadened dielectric loss curves for compatible polyblends [13, 14]. Similar phenomena occur in dynamic mechanical experiments. Nielsen observed damping curves to widen with increased chemical heterogeneity of random copolymers [15] and with decreased compatibility of plasticizers [16]. In these studies, such findings point to a fundamental difference between the higher and lower molecular weight mixtures. Not only does a decrease in chain length lead to an increase in the phase separation temperature (LCST), but also to more intimate mixing on the molecular scale. However, this does not affect the g factor which is identical for both the high molecular weight blends and the low molecular weight blends.

Dielectric Observation of PS/PoCS Phase Separation

Calorimetric studies demonstrated the phase separation of PS/PoCS blends at elevated temperatures, inferring the existence of a LCST for the system. The frequencies employed for dielectric measurements were such that the temperatures of observation of the α relaxation were high enough to cause phase separation of PS/PoCS blends containing 0.4, 0.6, and 0.8 weight fraction PoCS. This phenomenon was manifested in a number of ways. Figure 11

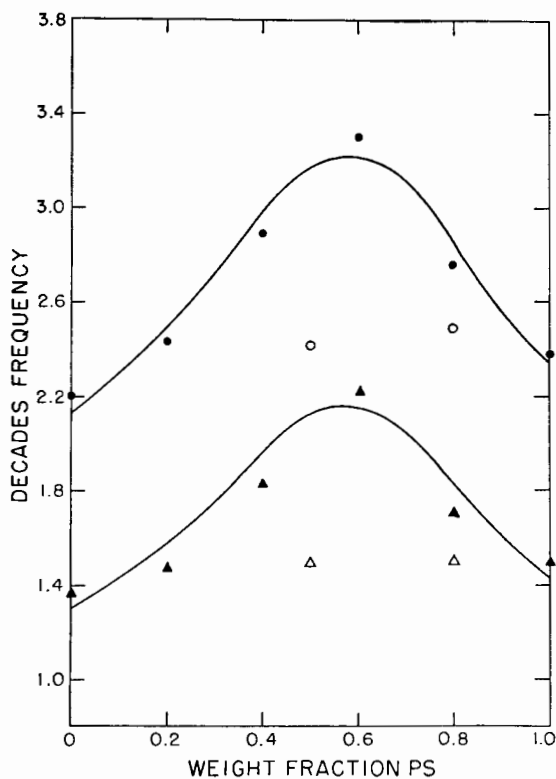


FIG. 10. Composition dependence of the loss width for PS/PoCS blends: (○, △) PS10K blends; (●) HH101 blends, 0.5 width; (▲) HH101 blends, 0.75 width.

illustrates the normalized loss behavior of the 0.6 weight fraction PoCS blend. The broad outer curve is that obtained at 150.3 °C as the sample was just beginning to separate; the inner data points are those of the same material at 171.8 °C. At the latter temperature, the loss curve width is seen to have become identical to that of the pure PoCS, indicated by a dotted line. At intermediate temperatures there is a gradual narrowing. The phase separation process is thus indicated to result in a surprising decrease in the local microheterogeneity of the separated phases.

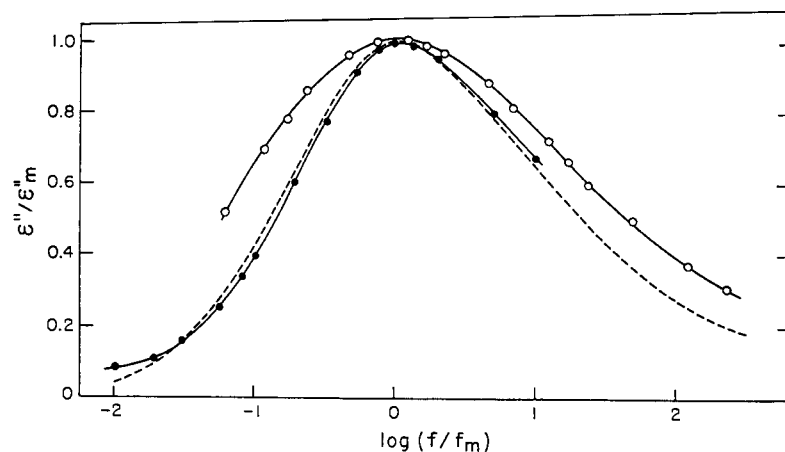


FIG. 11. Normalized frequency dependencies of the dielectric loss factor for a 40/60 PS/PoCS blend above and below the LCST: (○) 40/60 PS/PoCS, 150.3 °C; (●) 40/60 PS/PoCS, 171.8 °C; (--) PoCS, unblended, 151–165 °C.

CONCLUSIONS

PS and PoCS form compatible polyblends which exhibit a LCST. The LCST is a strong function of molecular weight.

The composition dependence of the Kirkwood-Frohlich g factor in the copolymers poly(styrene-co-2-chlorostyrene) may be rationalized on the basis of copolymer sequence distribution and reflects local chain conformations.

The Kirkwood-Frohlich g factor in the blends is independent of blend composition thus indicating that local chain conformations are unaffected by blending. This is true of both high molecular weight PS blends and low molecular weight PS blends.

The broadening of dielectric loss curves for the high molecular weight PS blends compared to the copolymers indicates a heterogeneous local environment in such blends. The low molecular weight PS loss curves are not broadened indicating a more intimate level of mixing in such blends compared to the high molecular weight blends.

The occurrence of the LCST may be detected by the dielectric technique. It is manifested by a sudden narrowing of the dielectric loss curves.

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REFERENCES

- [1] S. Krause, J. Macromol. Sci.-Revs. Macromol. Chem., **C7**, 251 (1972).
- [2] A. F. Yee, Polym. Eng. Sci., **17**, 213 (1977).
- [3] N. E. Weeks, F. E. Karasz, and W. J. MacKnight, J. Appl. Phys., **48**, 4068 (1977).
- [4] R. E. Bernstein, C. A. Cruz, D. R. Paul, and J. W. Barlow, Macromolecules, **10**, 681 (1977).
- [5] L. P. McMaster, Macromolecules, **6**, 760 (1973).
- [6] R. H. Lacombe and I. C. Sanchez, J. Phys. Chem., **80**, 2568 (1976).
- [7] R. E. Wetton, W. J. MacKnight, J. R. Fried, and F. E. Karasz, Macromolecules, **11**, 158 (1978).
- [8] K. S. Cole and R. H. Cole, J. Chem. Phys., **9**, 341 (1941).
- [9] L. Onsager, J. Am. Chem. Soc., **58**, 1486 (1936).
- [10] N. G. McCrum, B. E. Read, and G. Williams, Anelastic and Dielectric Effects in Polymeric Solids, Wiley, London, 1967.
- [11] P. Alexandrovich, F. E. Karasz, and W. J. MacKnight, Polymer, **21**, 488 (1980).
- [12] M. Bank, J. Leffingwell and C. Thies, J. Polym. Sci. A-2, **10**, 1097 (1972).
- [13] W. J. MacKnight, J. Stoelting, and F. E. Karasz, Adv. Chem. Ser., **99**, 29 (1971).
- [14] S. Akiyama, Y. Komatsu, and R. Kaneko, Polym. J., **7**, 172 (1975).
- [15] L. E. Nielsen, J. Am. Chem. Soc., **75**, 1435 (1953).
- [16] L. E. Nielsen, Mechanical Properties of Polymers, Reinhold, New York, 1962.