The Rheooptical Properties of Polymer Blends: Polystyrene and Poly(2,6-Dimethyl-1,4-Phenylene Oxide)*

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Synopsis

The stress-optical coefficients (SOCs) of miscible polystyrene (PS)/poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) blends were measured in the melt state over a wide range of compositions. The flow birefringence measurements were performed with a slit die rheometer using a simplified procedure which eliminates the need to specify the distribution of extinction angles in the flow space. The SOC of the PS/PPO system at $\sim T_g + 110°C$ follows a linear blending law and full optical compensation (SOC = 0) is observed at ~ 61 wt % PS. This value is lower by $\sim 10\%$ relative to values obtained by film stretching techniques. Measurements of SOC in the glassy state also yield linear dependence of SOC on composition but no compensation is obtained in this case because of the sign reversal in the SOC of PS in the glass transition range.

INTRODUCTION

Polymeric materials are playing an increasingly important role in a host of optoelectronic systems and devices. In many applications the optical properties of the polymer, and particularly its intrinsic optical anisotropy, are of critical importance. The intrinsic anisotropy controls the level of birefringence in an article produced from the bulk polymer, and its desired value is dictated by the nature of the application. Birefringence is often undesirable (e.g., in optical disk substrates, plastic lenses, and waveguides[1-3]), and it must be eliminated or drastically reduced in order to achieve acceptable performance. The birefringence is related to the molecular (segmental) anisotropy of the polymer chain through the stress-optical coefficient C_m, which is defined, by way of the stress-optical law, as

$$C_m \equiv \frac{\Delta n}{\Delta \sigma} \tag{1}$$

where Δn is the birefringence and $\Delta \sigma$ is a colinear principal stress difference applied on (or "frozen" in) the polymer matrix. For crosslinked rubbery or molten polymers this coefficient can be related to the segmental optical anisotropy by[4,5]

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* Portions of this work were presented at the Xth International Congress on Rheology, Sydney, Australia, August 1988.

$$C_m = \frac{2\pi}{45} \frac{(n^2 + 2)^2}{nkT} (\alpha_1 - \alpha_2)_s \qquad (2)$$

where $(\alpha_1 - \alpha_2)_s$ is the difference in the principal polarizabilities of Kuhn's statistical segment, T is the temperature, k is Boltzmann's constant, n is the average refractive index, and the subscript m denotes the molten or rubbery state. Thus C_m, through the stress-optical law, relates the segmental anisotropy to the macroscopic anisotropy of the bulk polymer, and through manipulation of this property, along with the applied (or frozen-in) stress, one can control the birefringence level in the processed polymer. The effect of C_m on the residual birefringence in a molded plastic article has been evaluated and discussed in a recent study.[6]

C_m can be reduced either by adjusting the level of $(\alpha_1 - \alpha_2)_s$ via synthetic means, or by physical blending of two miscible polymers with widely different coefficients to achieve effective compensation of the segmental anisotropies.[7-11] The apparent birefringence of a multicomponent polymer system can be expressed by a simple linear additivity law of the form [12]

$$\Delta n = \sum_i \phi_i f_i \Delta n_i^0 + \Delta n_F \qquad (3)$$

where ϕ_i is the volume fraction of the ith component, f_i is its Hermans orientation function, and Δn_i^0 its intrinsic birefringence. Δn_F is a form birefringence expressing the contribution of the phase boundaries and is expected to be negligible for miscible blends. The intrinsic birefringence can be derived from differentiation of the Lorentz–Lorenz equation to give

$$\Delta n^0 = \frac{2\pi}{9} \frac{(n^2 + 2)^2}{n} N_s \Delta \alpha_0 \qquad (4)$$

Here $\Delta \alpha_0$ is the polarizability difference for a repeat unit, N_s is the number of monomer units per volume, and the close correspondence to eq. (2) is evident. Equation (3) can be written alternatively in terms of the stress-optical coefficients C_i of the pure components:

$$\Delta n = \sum_i \phi_i C_i \Delta \sigma_i + \Delta n_F \qquad (5)$$

where $\Delta \sigma_i$, the stress applied on component i, is given by

$$\Delta \sigma_i = \kappa_i \Delta \sigma \qquad (6)$$

where κ_i is a stress–concentration factor representing the fraction of the total stress borne by the ith component. Thus, for $\Delta n_F = 0$,

$$\Delta n = \left(\sum_i \phi_i C_i \kappa_i \right) \Delta \sigma \qquad (7)$$

and the apparent stress-optical coefficient of the blend is given by

$$C = \sum_i \phi_i C_i \kappa_i \tag{8}$$

Although this relation has been tested for both miscible and immiscible blends in the glassy and rubbery states,[9,10,13–15] its validity for polymer melts well above the glass transition temperature has not been strictly verified.

In this study we present rheooptical data for blends of polystyrene (PS) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) that are known to be miscible at all proportions.[16,17] Effective optical compensation of the PS/PPO blend in a molded disk has been recently demonstrated in a study by Manabe et al.,[18] who show that for a particular blend composition one can obtain a birefringence-free disk. Usually, determination of C_m (or Δn^0) from birefringence measurements in the solid state is somewhat ambiguous because of the need to decouple the intrinsic birefringence from the orientation function [cf. eq. (3)]. This requires independent measurements, usually by IR dichroism, to determine the orientation of the various components (phases) in the system. Also, in this procedure the material is deformed at relatively low temperatures ($> T_g$), and it must be cooled rapidly in order to prevent relaxation of orientation. Flow birefringence measurements in the melt, on the other hand, yield C_m directly. In the present study, the coefficients of the PPO/PS blends were determined by a flow birefringence technique based on a general procedure proposed by Wales.[19] Our overall aim was to establish independently a general blending law for C_m and test the birefringence additivity assumption [eq. (3)] for miscible blends in the melt state. Some data on the stress-optical coefficients of the PS/PPO blends in the glassy state are also presented.

EXPERIMENTAL

Materials. The pure polymer components are commercial resins listed in Table I. The PS-rich ($> 60\%$) blends were prepared by coprecipitation from chloroform into methanol followed by drying for 1 week at 120°C to remove residual solvent. Two additional blends, 80/20 and 34/66 PPO/PS, were obtained from General Electric Co. and used as received to prepare other PPO-rich blends by coextrusion with PS. All the PPO-rich blends contained a thermal stabilizer to prevent degradation at the high temperatures used in the flow birefringence experiment. Miscibility was established by DSC measurements to confirm the existence of a single T_g. These measurements were run on the DuPont 990 thermal analyzer and T_g was extracted from second heating scans

TABLE I
List of Materials

Material	Grade	$M_n^a \times 10^{-3}$	$M_w^a \times 10^{-3}$	T_g^b (°C)
PS	Styron 685D (Dow)	124	312	106
PPO	691-111 (GE)	17	49	210

[a] PS equivalent.
[b] Midpoint, scan at 10°C/min.
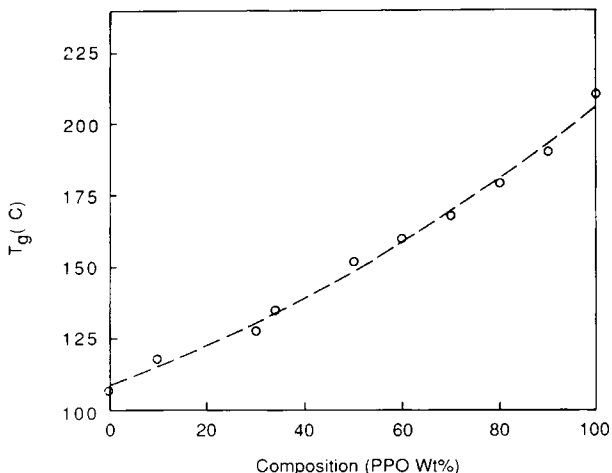
Fig. 1. T_g vs. composition for the PS/PPO blends of this study.

at 10°C/min. T_g vs. composition, based on these measurements, is plotted in Figure 1.

Flow Birefringence. The experimental system is shown schematically in Figure 2. The system consists of a thermostated slit die, a melt drive, and an optical train. The dimensions of the rectangular slit are: $L \times W \times H = 9.50 \times 1.20 \times 0.080$ cm; with an aspect ratio of 15 the flow in the slit is effectively a rectilinear simple shear flow.[20] The slit is equipped with a strain-gauge transducer located at the die entry and round quartz windows 6.5 mm in diameter positioned on both sides of the rectilinear channel, 7.2 cm downstream from the entrance. Also, to minimize end effects, the die has a conical entry zone with a converging angle of 36°. The die block is mounted at the bottom of the barrel of a Gottfert Rheograph 2001 rheometer which is used as a hot melt reservoir. The hydraulic drive of the rheometer is used to extrude the molten polymer through the die at a fixed rate. As shown in Figure 2, the optical train
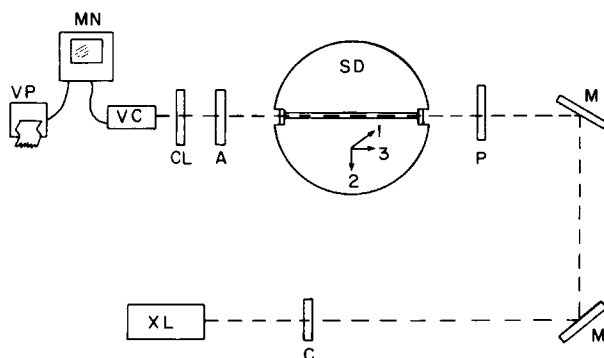

Fig. 2.   The flow birefringence setup: (XL) light source; (C) collimator; (M) mirror; (P) polarizer; (SD) slit die block; (A) analyzer; (CL) condensing lens; (VC) CCD camera; (MN) monitor; (VP) printer; (1) flow direction; (3) neutral axis.

consists of a xenon light source, crossed polars, collimating and focusing lenses, mirrors, and a CCD camera. The polarized beam is directed through the quartz windows along the neutral ("3") axis of the flow field, i.e., perpendicular to the shearing plane. The birefringence pattern generated by the flowing melt is recorded on a video monitor and analyzed to obtain the birefringence distribution across the shearing (12) plane. A typical isochromatic fringe pattern is shown in Figure 3. Typically, for a given composition and temperature the run is repeated at several extrusion rates.

For simple shear flows the stress-optical law reduces to[21]

$$\Delta n \sin 2\chi = 2C_m \tau_{12} \tag{9}$$

and

$$\Delta n \cos 2\chi = C_m N_1 \tag{10}$$

where χ is the extinction angle, τ_{12} is the shear stress, and N_1 is the first normal stress difference. For a 1-dimensional slit flow the shear stress is given by

$$\tau_{12} = \Delta P \, y / L \tag{11}$$

where ΔP is the pressure drop, y is the gapwise position ($y = 0$ at midplane), and L is the die length. In our system the birefringence is related to the measured retardation R by
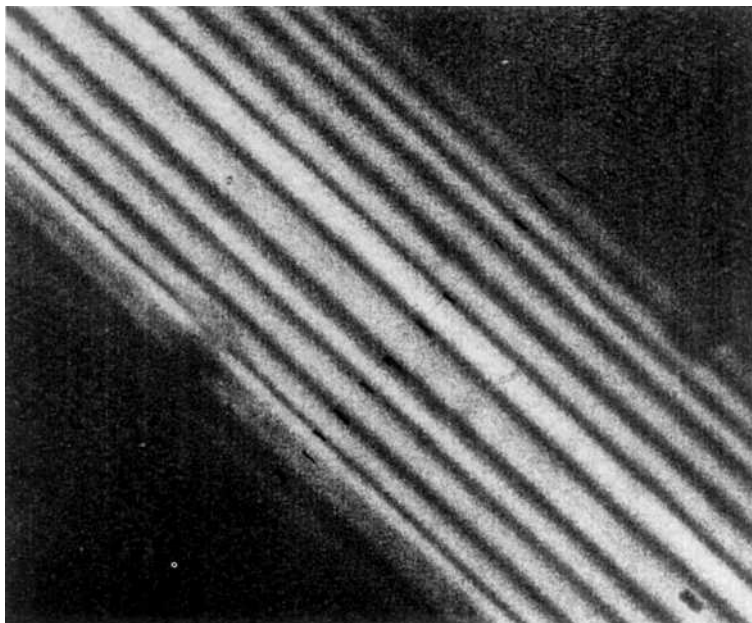

Fig. 3. Isochromatic fringe pattern across the shearing (12) plane for PS at 210°C and a pressure drop (ΔP) of 63 bars.

$$\Delta n = R/W = m\lambda/W, \qquad m = 0, 1, 2, \cdots \qquad (12)$$

where m is the fringe order, λ is the wavelength of the light beam, and W is the slit width. Combining eqs. (9), (11), and (12) gives

$$m = 2C_m W \,\Delta P \, y/L \,\lambda \,\sin[2\chi(y)] \qquad (13)$$

Since at low stresses (shear rates) $\chi = 45°$,

$$\lim_{y \to 0} \frac{dm}{dy} = C_m \frac{2W\Delta P}{L\lambda} \equiv C_m A \qquad (14)$$

and C_m can be estimated from the initial slope of the m vs. Ay curve without measuring χ directly. This simplification, first proposed by Wales,[19] is especially useful in a slit die system where a band spreading effect is known to introduce some uncertainty in locating the position of the isoclinics (iso-χ fringes).[21,22] This effect has been attributed to the positional dependence of the shear stress in the vicinity of the viewing windows, which leads to a range of positions along the channel depth at which a given stress may exist.[22]

Strain Birefringence. The stress-optical coefficients of the various blend compositions in the glassy state, C_g, were measured using a standard photoelastic method. Blends at various compositions were solvent-cast by a blade onto a smooth glass plate to form ca. 50 μm thick films. After drying in a vacuum oven for 24 h, the films were mounted on a rigid straining frame and subjected to uniaxial tension. The films were strained to varying degrees and the corresponding force was measured by a strain gauge transducer (Model P-3500, Measurements Group) attached to the lower clamp in the frame. The unstrained films were birefringence-free when viewed in normal incidence. The birefringence in the strained films was measured by a white light polariscope based on the Tardy method. The stress-optical coefficient of the glassy polymer was then extracted from the linear portion of the force–birefringence curve based on eq. (1).

RESULTS AND DISCUSSION

The values of C_m for the PS/PPO blends were obtained based on the linearized procedure discussed above. A typical curve of m vs. Ay, for PS at 210°C, is shown in Figure 4. The curve was fitted to a parabola by linear regression and its initial slope was used to estimate C_m [cf. eq. (14)]. The values of C_m obtained in this manner were generally in good agreement with literature values for several commercial polymers (see Table II). In order to assess the linearized procedure more fully, we compared the coefficient obtained with this technique to a value obtained with the complete procedure whereby the distribution of χ is extracted from the isoclinic pattern. The isoclinic fringes for various values of χ were generated by rotating the crossed polarizer–analyzer assembly in the range 0–45° relative to the flow direction. Because of the band spreading effect noted above, locating the positions of the isoclinics was not straightforward. Essentially, we followed the recommendations of McHugh et al.[22] in specifying
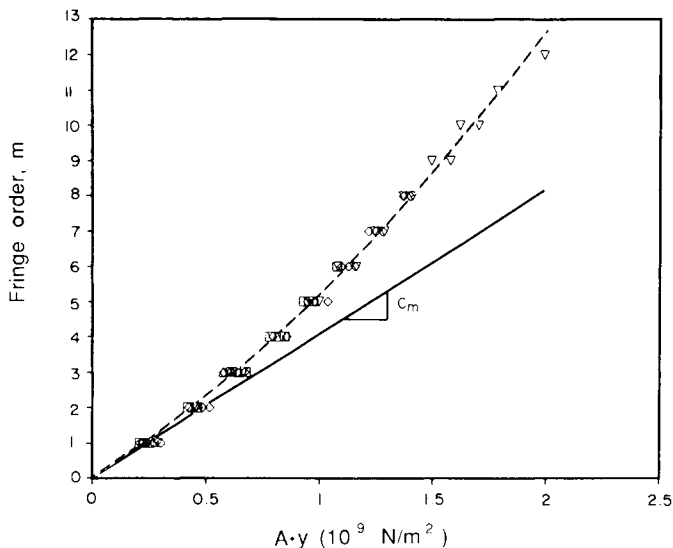
Fig. 4. m vs. Ay [cf. eq. (14)] for PS at 210°C under various pressures (in bars): (○) 21; (△) 41; (□) 63; (◇) 91; (▽) 124. The broken curve is a parabola fitted by linear regression and the solid line is its initial slope.

the positions of the isoclinic fringes, and the results are plotted in Figure 5 in the form of m vs. $Ay/\sin(2X)$. This clearly removes the nonlinearity in the curve in Figure 4 as expected from eq. (13), and the value of C_m thus obtained is in essential agreement with the value obtained by the linearized procedure. It should be noted that the nonlinearity in the curve in Figure 4 is directly related to the rheological nonlinearity of the polymer melt. PS, being a strongly shear thinning melt, yields a highly nonlinear curve whereas polycarbonate, which is Newtonian over a wide range of shear rates, gives an essentially linear curve of m vs. Ay.

TABLE II
Stress-Optical Coefficients

| | | C_m (10^{-9} m^2/N) | |
Polymer[a]	Temperature (°C)	This study	Literature[b]
PS	190	—	−4.1
PS	200	—	−4.4
PS	210	−4.1	−4.2
PS	220	−4.2	−4.2
PS	230	−3.9	—
HDPE	150	2.1	2.35, 2.4
LDPE	150	2.6	2.0, 2.1

  [a] PS, Styron 685D; HDPE, Phillips 424; LDPE, Phillips 808A.
  [b] Reference 21, p. 113. The polymer grades in this reference are different from those used in this study.
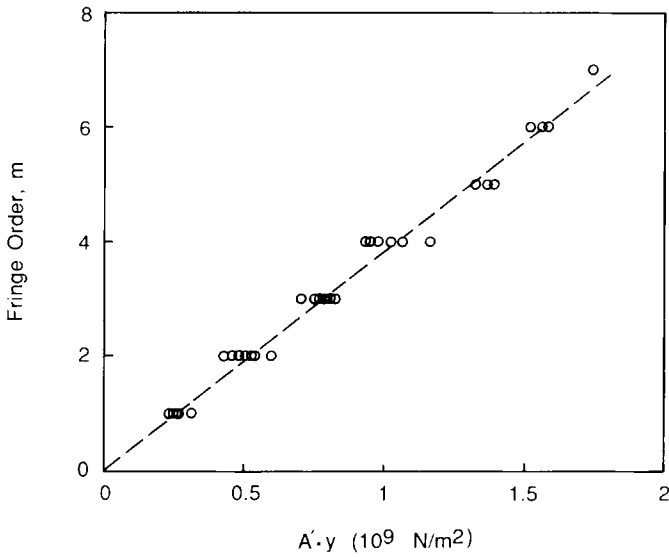
Fig. 5. m vs. $A'y$ for PS at 210°C under various pressures. $A' \equiv A/\sin[2\chi(y)]$.

The stress-optical coefficients of the PS/PPO blends are plotted vs. composition in Figure 6. The data indicate that physical blending is indeed an effective means of manipulating the stress-optical coefficient of polymer melts and, as was noted elsewhere,[7-11,18] one can achieve full optical compensation if
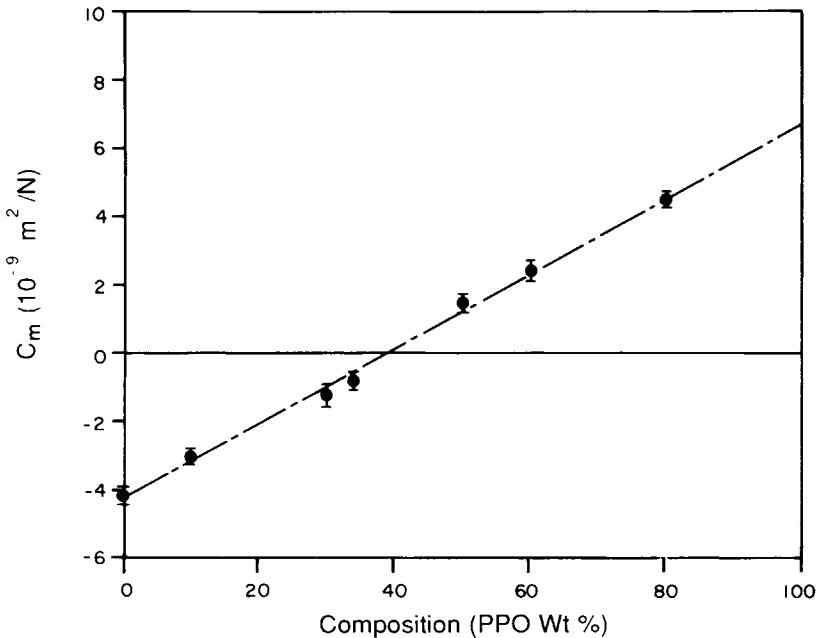

Fig. 6.   Stress-optical coefficient vs. composition for PS/PPO blends at $T \cong T_g + 110°C$. Line fitted by linear regression.

the coefficients of the pure components are opposite in sign. The zero-birefringent composition obtained in this study ($\sim 61 \pm 2$ wt % PS) is $\sim 10\%$ lower than the value reported by Saito and Inoue,[10] but is in somewhat better agreement with the data of Prest[7] and Manabe et al.[18] In the studies of Saito and Inoue and Lefebvre et al.[15] on the PS/PPO system, intrinsic birefringence values were determined from birefringence and IR dichroism measurements on stretched films, whereas Manabe et al. have obtained the zero-birefringent composition from birefringence measurements on molded disks (not a direct method!). In a recent study,[23] we have shown that the intrinsic birefringence of amorphous polymers can be estimated from measurement of the transverse birefringence in solvent-cast films. This approximate method yielded a zero-birefringent composition of ~ 67 wt % PS for the PS/PPO system which is closer to the value of Saito and Inoue. Using birefringence and dichroism measurements on stretched films, Lefebvre et al.[15] obtained intrinsic birefringence values for PS and PPO. Based on eqs. (2) and (4), these values should scale like the stress-optical coefficients of the pure components. Indeed, we get a coefficient ratio of -1.6, using an extrapolated value for PPO, compared to -2.1 obtained by Lefebvre et al. for the intrinsic birefringence ratio. This discrepancy is well within the experimental uncertainties in both studies. If the intrinsic birefringences of Lefebvre et al. are used to calculate the zero-birefringent composition, then, assuming linear additivity and identical orientation for both constituents, a value close to the one found by Saito and Inoue[10] is obtained. The apparent difference between the value obtained in this study and in those of Prest and Manabe et al.[18] and the values reported by Saito and Inoue,[10] Machell et al.,[23] and Lefebvre et al.[15] may be partly due to the temperature dependence of C_m; in the former studies (except for Prest's) the polymer is deformed at high temperatures whereas in the latter the polymer films are stretched at temperatures close to T_g.

The curve in Figure 6 is linear within the composition range tested. This implies that linear additivity [eq. (3)] is followed and that the stress concentration factors κ_i for PS and PPO are unity, in line with the observations of Livingston and Brown,[13] who studied the effect of composition on the stress-optical coefficients of blends of two styrene–butadiene rubbers with different comonomer compositions. They observed a linear dependence of C_m on composition for compatible blends of these copolymers, whereas the dependence was nonlinear for incompatible blends of copolymers in this series. It should be noted that the data in Figure 6 were generated at $T \cong T_g + 110°C$ for the respective blends since performing all the measurements at the same temperature was impractical due to substantial differences in T_g and melt rheology. This, however, should not influence the results qualitatively owing to the weak dependence of C_m on temperature (at high temperatures!). Indeed, if the temperature dependence is removed by plotting $C_m \cdot T$ [cf. eq. (2)] vs. composition, as shown in Figure 7, the curve remains linear and the zero-birefringent composition is identical to the one obtained in Figure 6. Lefebvre et al.[24] reported that, in spite of the compatibility of PS and PPO, the two polymers orient differently when subjected to uniaxial strain. This effect, if extended to the melt state, should yield different extinction angles for PS and PPO and may contribute to some nonlinearity in the C_m–composition curve. Such behavior, however, was not observed within the range of the data or perhaps was not
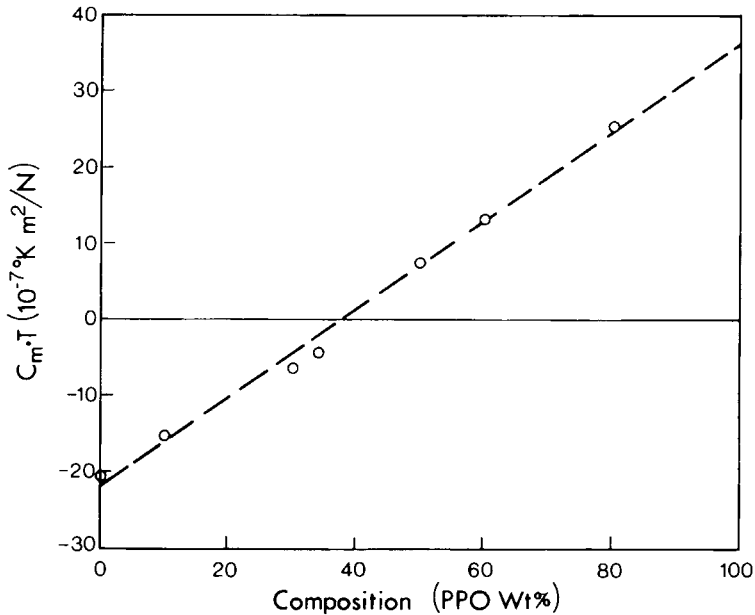
Fig. 7. The data of Figure 6 replotted in terms of $C_m \cdot T$ vs. composition.

significant enough to induce nonlinearity, but it may also account in part for the disparity in the values of the zero-birefringent composition noted above.

Werumeus Buning and Gijsen,[11] in a study on the rheooptical properties of tetramethylpolycarbonate/PS blends using the film stretching method, have obtained a nonlinear dependence of SOC on composition. The observed zero-birefringent composition for this blend system was substantially different from the value expected from linear additivity. (The difference is somewhat smaller if the composition is expressed in volume fractions.) They also observed, for some blend compositions, a strong dependence of SOC on elongation, which violates the stress-optical law [eq. (1)]. This effect as well as the nonlinearity in the SOC–composition curve was attributed to poor miscibility and the possibility of phase separation in some compositions, which may lead to different stress concentration factors for the pure components as well as to finite form birefringence [cf. eq. (5)].

If linear additivity is the rule rather than the exception, then the simplified method of Saito and Inoue[10] can be used to estimate the zero-birefringent composition ϕ^0. For a miscible binary (A/B) blend [cf. eqs. (3) and (4)],

$$\phi^0 = \frac{-\Delta n_B^0}{\Delta n_A^0 - \Delta n_B^0}$$

$$\cong \frac{-\Delta \alpha_{0,B}}{\Delta \alpha_{0,A} - \Delta \alpha_{0,B}} \tag{15}$$

where the monomeric polarizability difference $\Delta \alpha_0$ is given by

$$\Delta\alpha_0 = \alpha_x - \frac{\alpha_y + \alpha_z}{2} \tag{16}$$

x being the chain axis and α_i the principal polarizabilities of the repeat unit. These polarizabilities can be derived from proper transformation of the polarizability vectors of the constituent bonds to the coordinate system of the polymer chain, assuming certain conformation.[25] This method is not exact since $\Delta\alpha_0$ and $(\alpha_1 - \alpha_2)_s$ [cf. eqs. (2) and (4)] are generally not identical, especially for stiff backbone polymers, but it can provide a general guide for selecting the zero-birefringent composition for a given binary blend system.

The PS/PPO blend at the zero-birefringent composition (61 wt % PS) is not expected to be a truly nonbirefringent polymer inasmuch as its rheooptical response in the glassy state is likely to be different from its response in the melt state. Indeed, the compositional dependence of C_g is fundamentally different from that of C_m (Fig. 8). Generally, the values of C_g are orders of magnitude lower than those of C_m (C_g of PS is in close agreement with a value reported by Nielsen and Buchdahl[26]). However, more importantly, since both PS and PPO have positive coefficients, full compensation of optical anisotropies in the glassy state is not feasible for the PS/PPO system. This underscores the different nature of the stress-optical mechanisms above and below T_g. The dependence of C_g on composition appears to be linear within the range of the data, thus suggesting that linear additivity is obeyed in the glassy state as well as in the melt state.

It was recently claimed[6] that C_g, rather than C_m, controls the level of the transverse (in-plane) birefringence in injection-molded substrates for optical memory disks, whereas the normal birefringence component is controlled by
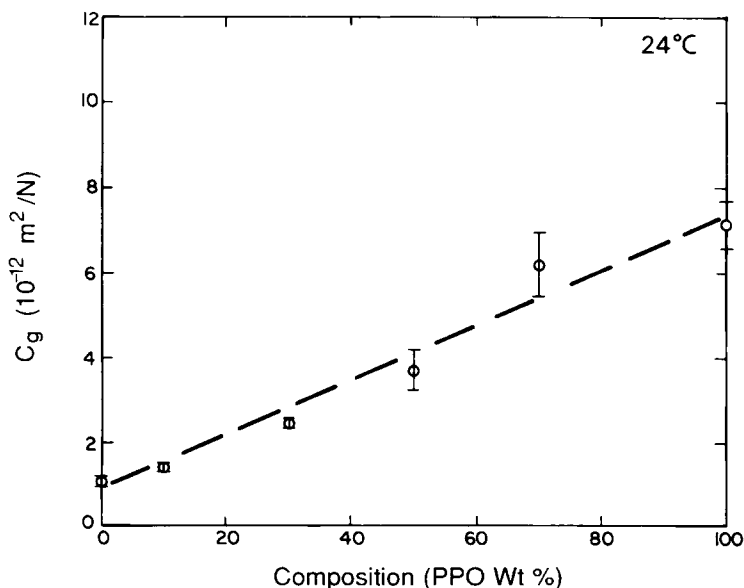

Fig. 8.   Stress-optical coefficient vs. composition for PPO/PS blends at $T \simeq 25°C$. Line fitted by linear regression.

C_m. If this claim is proven valid, then compensation by blending may not achieve the goal of obtaining birefringence-free substrates since even at the zero-birefringent composition, the disk may possess finite transverse birefringence if $C_g \neq 0$. This should limit the general attractiveness of blending as a means for achieving optically isotropic polymers unless the contribution of C_g is insignificant in a particular application.

SUMMARY

The SOCs of several compositions of PS/PPO blends were measured in the melt using a novel flow birefringence technique; through linearization of the flow birefringence equations, this technique allows determination of C_m without specifying the extinction angles in the flow space, which considerably simplifies the experimental procedure. The values of C_m obtained in this way are generally in agreement with literature values.

We have shown that the SOC of the PS/PPO system at temperatures well above T_g follows linear additivity, and full compensation ($C_m = 0$) is observed at ~ 61 wt % PS. This value is $\sim 10\%$ higher than values obtained elsewhere using film stretching methods. The latter measurements are usually conducted at temperatures only slightly above T_g, which may account for some of the difference. In the glassy state, compensation is not feasible since both constituent polymers have positive stress-optical coefficients. This generally limits the utility of blending as a tool for achieving low optical anisotropy in amorphous polymer systems.

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