Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Thermo-Optical Analysis of Poly(2,6-disubstituted-1,4-phenylene Oxide) Blends

A. R. Shultz[a]; B. M. Gendron[a]
[a] General Electric Corporate Research and Development, Schenectady, New York

To cite this Article Shultz, A. R. and Gendron, B. M.(1974) 'Thermo-Optical Analysis of Poly(2,6-disubstituted-1,4-phenylene Oxide) Blends', Journal of Macromolecular Science, Part A, 8: 1, 175 — 189
To link to this Article: DOI: 10.1080/00222337408065823
URL: http://dx.doi.org/10.1080/00222337408065823

J. MACROMOL. SCI.—CHEM., A8(1), pp. 175-189 (1974)

Thermo-Optical Analysis of Poly(2,6-disubstituted-1,4-phenylene Oxide) Blends

A. R. SHULTZ and B. M. GENDRON

General Electric Corporate Research and Development
Schenectady, New York 12301

ABSTRACT

Mobility transitions closely related to the glass transitions of three binary polymer-polymer blend systems have been determined by thermo-optical analysis (TOA). TOA in this instance consists of the automated observation of birefringence relaxation in scratched transparent polymer and polymer blend films during their programmed heating. The blend systems studied were: I. polystyrene (PS) + poly(2,6-dimethyl-1,4-phenylene oxide)(PMMPO); II. poly(2-methyl-6-phenyl-1,4-phenylene oxide)(PMPPO) + PMMPO; and III. PS + PMPPO. Blend Systems I and II display a single TOA transition temperature at each blend composition indicating homogeneity and true thermodynamic compatibility of the polymer pairs. Blend System III displays two TOA transition temperatures at each blend composition indicating incompatibility and resultant liquid-liquid phase equilibration in molten mixtures of PS and PMPPO.

The shapes of the transmitted light intensity vs temperature curves for scratched PS + PMMPO films between 90° crossed plane polarizer and analyzer are examined at three heating rates of the microscope hot stage. The use of green light rather than

white light in the analysis was examined briefly in System II blends. Glass transitions T_g(DSC) obtained by differential scanning calorimetry are also reported.

INTRODUCTION

The use of thermo-optical analysis (TOA) to determine mobility transitions in amorphous blends of polystyrene (PS) + poly(2,6-dimethyl-1,4-phenylene oxide) (PMMPO) [1], poly(co-styrene/p-chlorostyrene) + PMMPO [2], and poly(2-methyl-6-benzyl-1,4-phenylene oxide) (PMBPO) + PMMPO [3] has been reported. TOA as presently employed is a rather empirical, automated observation of birefringence relaxation in stressed/strained transparent polymer films during heating as an indicator of molecular mobility onset. The TOA transition temperature, T_{TOA}, defined as the temperature at which scratch-induced birefringence in the sample completely disappears, is slightly higher than the glass transition temperature, T_g, of the sample. The operational simplicity and sensitivity of the TOA method recommend its expanded use as a detector of glass transitions. The complexity of the factors contributing to the absolute form and substance of TOA data makes detailed analyses of the controlling molecular and supermolecular physical properties difficult.

The present study was undertaken to provide a further demonstration of the utility of TOA, to examine the effect of heating rate on the TOA curves of Blend System I (PS + PMMPO), and to examine the nature of two new blend systems: System II, poly(2-methyl-6-phenyl-1,4-phenylene oxide) (PMPPO) + PMMPO; and System III, PS + PMPPO.

EXPERIMENTAL

Materials and Film Preparation

The polystyrene used was Lot PS4a (Pressure Chemical Co.), an anionically-polymerized polystyrene having a nominal molecular weight 97,200 and an $M_w/M_n = 1.06$. The PMMPO (an experimental PPO resin, General Electric Co. registered trademark) was prepared by the oxidative coupling of 2,6-xylenol [4-7]. Its intrinsic viscosity at 30° in chloroform is 0.49 dl/g, $M_n = 18,500$ by osmotic pressure and $M_w = 37,200$ by light scattering. The PMPPO was prepared by the oxidative coupling of 2-methyl-6-phenyl phenol. Its $[\eta]$ at 30° in chloroform is 0.88 dl/g.

Polymer blend films were prepared as follows. One-gram mixtures of polymer were dissolved in 10 ml toluene by stirring at 40°. The clear, homogeneous solutions were then precipitated into 200 ml methanol in a Waring blender. The fine, fibrous precipitates were collected on a sintered-glass frit filter, air-dried, and dried overnight at 80° in a vacuum oven. The blends thus obtained were then compression molded into films of about 5 to 8 mil thickness. The molding temperatures ranged from 180 to 270° C for the PS + PMMPO and PS + PMPPO blends. The PMPPO + PMMPO blends were molded at 240° C. Prior to precipitation of the toluene solutions of the PS + PMPPO mixtures, a drop of each solution was placed on a microscope slide and allowed to dry in air under an inverted Petri dish. This gave two sets of films for Blend System III, one compression molded and the other solution cast.

Measurement of Transition Temperatures

For comparison with TOA, some T_g measurements were made by differential scanning calorimetry. A Perkin-Elmer DSC Model 1B was used at a 20°/min heating rate. Its temperature scale was calibrated by observation of the melting points of indium, tin, and lead.

TOA measurements were performed as previously described [1]. Scratches scribed in the sample films with a steel stylus at room temperature provided stress/strain birefringent regions for monitoring during heating at constant rate in the hot stage (Mettler FP2 plus FP21) of a Zeiss standard WL polarizing microscope. The light that was transmitted through a plane polarizer, the sample, and a 90° crossed plane analyzer was picked up by a photocell. The amplified photocurrent was fed through a voltage divider and the voltage difference was plotted continuously against time (temperature) on a strip chart recorder (Leeds and Northrup, AZAR-Speedomax). The normal heating rate for TOA was 10°/min. Heating at 2 and 1°/min was also investigated for Blend System I. The temperature control unit reading was calibrated at each heating rate by observing the disappearance of light transmission during melting in the hot stage of small samples of naphthalene, adipic acid, and 2-chloroanthraquinone between the crossed polarizers. The results are presented in Table 1. In reporting temperatures in the TOA runs the control dial readings were adjusted by -2, -0.8, and -0.7° for the 10, 2, and 1°/min heating rate runs, respectively. White light from the incandescent tungsten lamp was normally used. A rather broad-band green light was obtained by insertion of a Zeiss #27316 filter for one series of runs on Blend System II. Normal TOA procedure at 10°/min heating rate involved scribing the film, making a run from 60 to 250°, removing the film on its slide, allowing it to cool to room temperature with the slide in contact with a

TABLE 1. Calibration of Hot-Stage Control Unit

Compound	Triple point (°C)	T(apparent) - T(actual) (deg.)		
		1°/min	2°/min	10°/min
Naphthalene	80.24	0.4	0.7	2.3
Acipic acid	151.46	0.7	0.8	2.5
2-Chloroanthraquinone	208.95	0.8	1.0	2.6

stone bench top, re-scribing the film, and making a second run. In some instances a third run was made. For runs at 2 and 1°/min the films were heated at 10°/min to a temperature 30° below the T_{TOA} at 10°/min heating rate, and then the control was switched to the slower heating rate.

RESULTS

The TOA results will first be presented for each blend system individually. A summary discussion concerning all three blend systems will then follow.

I. Polystyrene (PS) + Poly(2,6-dimethyl-1,4-phenylene Oxide) (PMMPO)

TOA and DSC measurement results on this blend system were presented in a previous publication [1]. The II blend films of this series covered the total composition range in weight fraction increments of 0.100. This seemed a good series to examine with regard to the effect of heating rate on the form of the apparent transmitted light intensity vs temperature curve and on the observed transition temperature.

Figure 1 represents the strip chart recording for the PS + PMMPO film having weight fraction composition $w_{PMMPO} = 0.800$ being heated at 1°/min. The six temperatures T_s, T_u, $T_{1/2}$, T_i, T_{TOA}, and T_E indicated on the plot were tabulated, when possible, for each TOA curve of the 11 sample films at each of the three heating rates. The accuracy of determining the starting and end temperatures, T_s and T_E, was low due to the low-angle approach of the curves to the initial and final

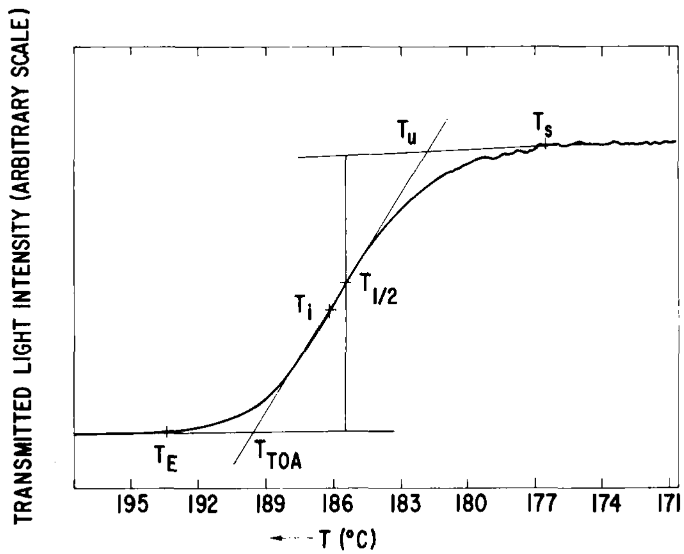

FIG. 1. TOA curve indicating possible characteristic temperatures. PS + PMMPO film having $w_{PMMPO} = 0.800$. Heating rate, 1°/min.

tangents. T_u, the temperature of intersection of the initial tangent with the tangent through the inflection point, suffered in accuracy due to the difficulty of locating the initial tangent. The temperatures T_i and T_{TOA}, denoting the temperature at the curve's inflection point and the temperature of intersection of the tangent through this point with the final tangent, respectively, were the most readily determined temperatures. These temperatures are plotted in Figs. 2 and 3. As one might expect, the transition temperatures observed at the slower heating rates are in general displaced to slightly lower temperatures. In the composition range $0.500 \leq w_{PMMPO} \leq 1.000$, the T_{TOA} and T_i behaviors at the three heating rates are quite orderly and consistent. No sample of the $w_{PMMPO} = 0.400$ film was available for the 2 and 1°/min measurements. The film having $w_{PMMPO} = 0.300$, for which at 10°/min the transmitted light intensity vs temperature curve exhibited a drop and rise before the final disappearance of birefringence [1], yielded no satisfactory transition temperatures at the 2 and 1°/min heating rates. The transmitted light intensities had dropped to very low values at the start of the slow heating runs (i.e., at 100°, which is 30° below the T_{TOA} at the 10°/min heating

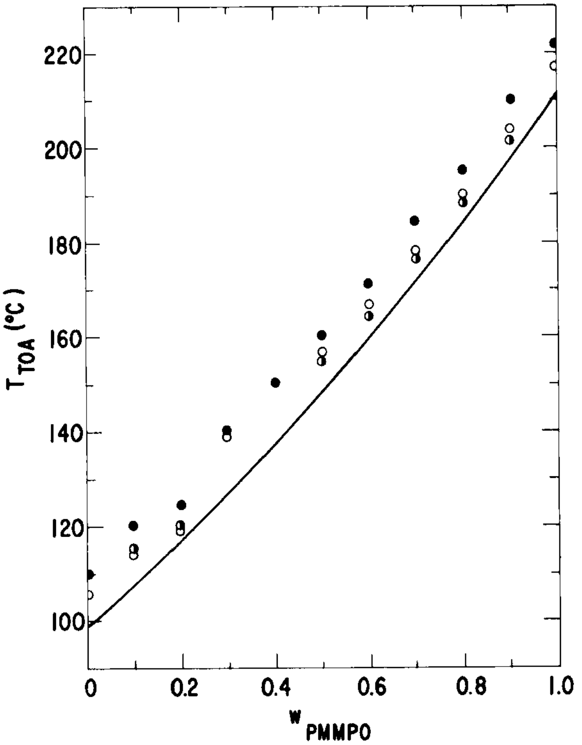

FIG. 2. TOA transition temperatures of PS + PMMPO blend films plotted against weight fraction of PMMPO. Heating rates: (●) 10°/min; (○) 2°/min; (◑) 1°/min. The solid curve represents T_g(DSC) measured at 20°/min heating rate.

rate). Although there were slight increases and declines in the transmitted light intensities, no T_i or T_{TOA} could be assigned for w_{PMMPO} = 0.300. It is believed that the measurement difficulty lies in the opposite signs of the stress optical and strain optical coefficients in PS plus a compensating birefringence contribution by the PMMPO. At w_{PMMPO} = 0.200, 0.100, and 0.000 the films display consistent T_{TOA} at the three heating rates. The T_i at 10°/min for the films having w_{PMMPO} = 0.100 and 0.000 are low, reflecting the observed rather gradual decrease in transmitted light intensity with temperature prior to the final disappearance.

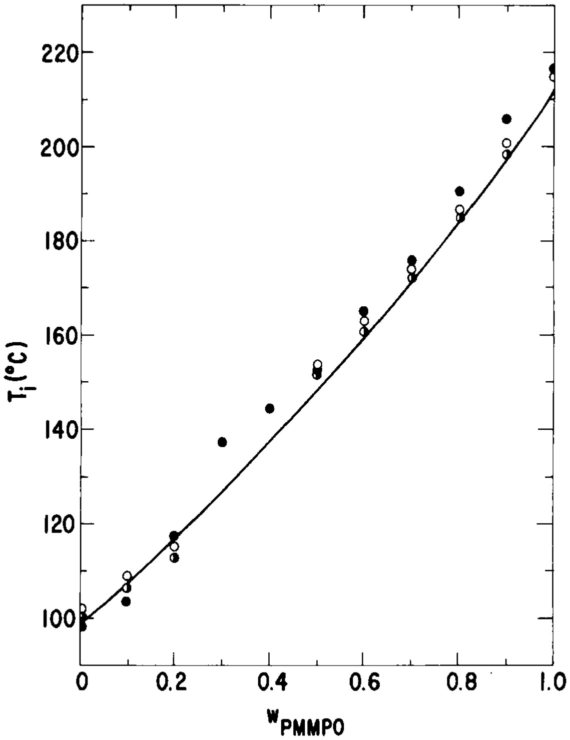

FIG. 3. Temperatures, T_i, at the inflection points of PS + PMMPO TOA curves plotted against weight fraction of PMMPO. Symbols as in Fig. 2. Solid curve represents T_g(DSC).

The curves in Figs. 2 and 3 represent the glass transition temperatures T_g(DSC) obtained by differential scanning calorimetry at a 20°/min heating rate [1]. The T_i at 2 and 1°/min approach rather closely to these T_g(DSC).

II. Poly(2-methyl-6-phenyl-1,4-phenylene Oxide) (PMPPO) + Poly(2,6-dimethyl-1,4-phenylene Oxide) (PMMPO)

Figure 4 presents the TOA plots obtained for the compression molded films of Blend System II using white light. Figure 5 presents the TOA

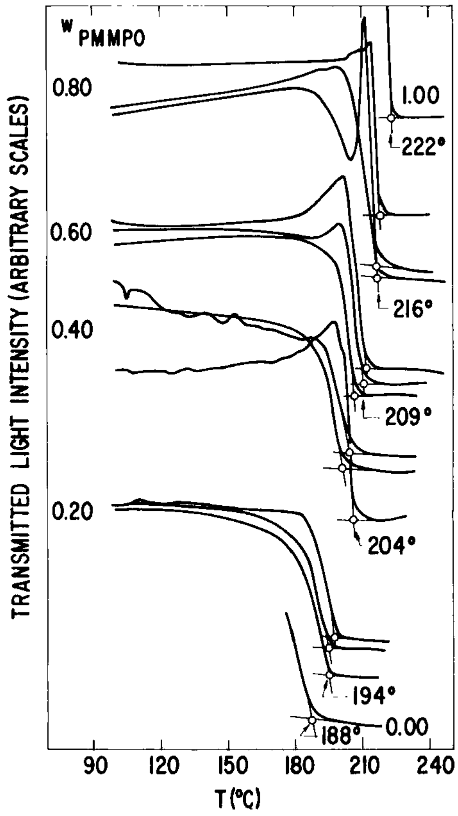

FIG. 4. TOA curves for System II (PMPPO + PMMPO) blend films. Transmitted white light; 10°/min heating.

plots (first runs only) obtained using green light. The latter were slightly smoother, but no significant differences are noted between the TOA curve shapes or the T_{TOA} values obtained with white light or green light transmission.

The measured T_{TOA} (10°/min) are listed in Table 2. Also listed are the T_g(DSC) observed for these blend films. Both the TOA and DSC data exhibit single transition temperatures, indicating the films to be homogeneous, single-phase blends.

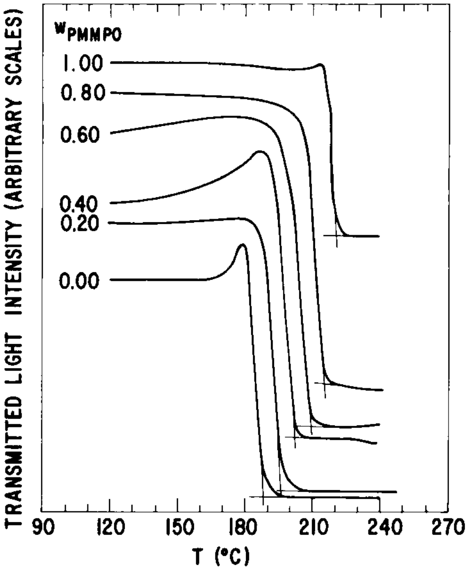

FIG. 5. TOA curves for System II blend films. First run; green light; 10°/min heating.

TABLE 2. Thermo-optical and Glass Transition (DSC) Temperatures in PMPPO(1) + PMMPO(2) Blends

	T_{TOA}(°C)		
w_2	White light TOA	Green light TOA	T_g(DSC) (°C)
0.000	190, 188,[a] 187[a]	188, 186	169, 170
0.200	194, 192, 196	197, 193	177, 175
0.400	206, 202, 204	202, 203	182, 181
0.600	206, 210, 210	210, 210	190, 189
0.800	215, 216, 217	215, 215	203, 203
1.000	222, 222	221, 221	211, 213

[a] Annealed at 200° for 3 min.

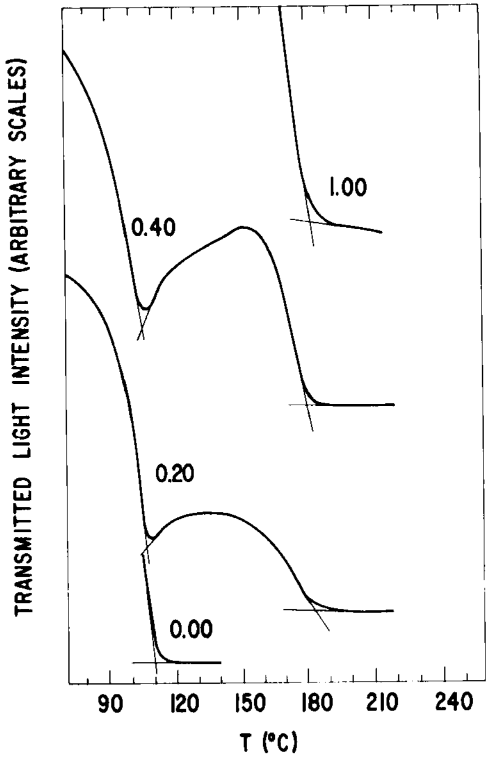

FIG. 6. TOA curves for System III (PS + PMPPO) blend films. Pure PS, pure PMPPO, and blends having weight fraction of PMPPO equal to 0.20 and 0.40. Heating rate, 10°/min.

III. Polystyrene (PS) + Poly(2-methyl-6-phenyl-1,4-phenylene Oxide) (PMPPO)

The blend films of System III all exhibited turbidities ("milky" or "cloudy") which were visually indicative of inhomogeneous, two-phase structures. TOA curves for pure PS4a, pure PMPPO, and solution cast films having weight fractions PMPPO of 0.20 and 0.40 are represented in Fig. 6. The shapes of the TOA curves for these blend films are quite similar to those observed for the incompatible blend films of PMMPO + poly(p-chlorostyrene) [2]. Two distinct T_{TOA} are noted. These correspond approximately to the T_{TOA} of the individual polymers which comprise the blends.

TABLE 3. Thermo-optical and Glass Transition (DSC) Temperatures in PS(1) + PMPPO(2) Blends

	T_{TOA} (°C)			T_g (DSC) (°C)	
w_2	Compression molded film	Compression molded film; annealed 3 min at 200° C	Thin film cast from toluene solution	Compression molded film	Fibrous co-precipitated blend
0.00	110		(116)	91	
	116		110	99	
0.20	- , -	114, 185	100, 185	103, -	108, 175
	113, 185	114, 181	109, 181	105, 154	103, 162
0.40	114, 193	108, 181	91, 180	107, -	94, -
	110, 182	107, 181	107, 182	104, 166	106, 160
0.60	- , 178	98, 184	(108), 176	- , -	106, -
	- , 185	103, 183	(121), 182	- , 168	105, 168
0.80	- , 186	(101), 183	- , 181	- , 172	(113), 177
	- , 187	(99), 182	(121), 180	- , 172	(99), 168
1.00	190	188	175	169	
		187	182	170	

The T_{TOA} and T_g(DSC) for Blend System III are given in Table 3. The T_{TOA} were measured on the compression molded films, on these same films annealed for 3 min at 200°C, and on the thin, solution cast films. The T_g(DSC) were measured on the compression molded films and on the coprecipitated blends from which these films were formed. It is somewhat difficult to detect the transitions, T_{TOA} and T_g(DSC), of the minority phase in the nonannealed, compression molded blend films. This is especially true in the detection of the lower temperature transition, and it is similar to the difficulty of detecting the T_g of a semicrystalline polymer.

DISCUSSION

The observed thermo-optical transition temperatures for the three polymer blend systems are summarized in Fig. 7. The T_{TOA} of Blend System II (PMPPO + PMMPO) are seen to increase linearly with increasing PMMPO content in the blends. The relation may be expressed as

$$T_{TOA}\ (^\circ C) = 189 + 33w_2 \qquad (1)$$

where w_2 is the weight fraction of PMMPO.

The T_g(DSC) (cf. Table 2) for System II may be fairly well represented by a least-squares fitted relation

$$T_g(DSC)\ (^\circ C) = 170 + 43w_2 - 20w_2(1 - w_2) \qquad (2)$$

The T_{TOA} dependence on w_2 does not, therefore, exactly parallel the T_g (DSC) dependence, but ranges from 19° above T_g(DSC) at $w_2 = 0$ to 9° above T_g(DSC) at $w_2 = 1.0$. There is evidence of only one T_{TOA} and one T_g(DSC) at each blend composition. Poly(2-methyl-6-phenyl-1,4-phenylene oxide) therefore joins polystyrene [1], various styrene/p-chlorostyrene statistical copolymers [2], and poly(2-methyl-6-benzyl-1,4-phenylene oxide) [3] on the list of polymers thermodynamically compatible with poly(2,6-dimethyl-1,4-phenylene oxide).

System III (PS + PMPPO) blends exhibit incompatibility as demonstrated by two T_{TOA} and two T_g(DSC) at given blend compositions.

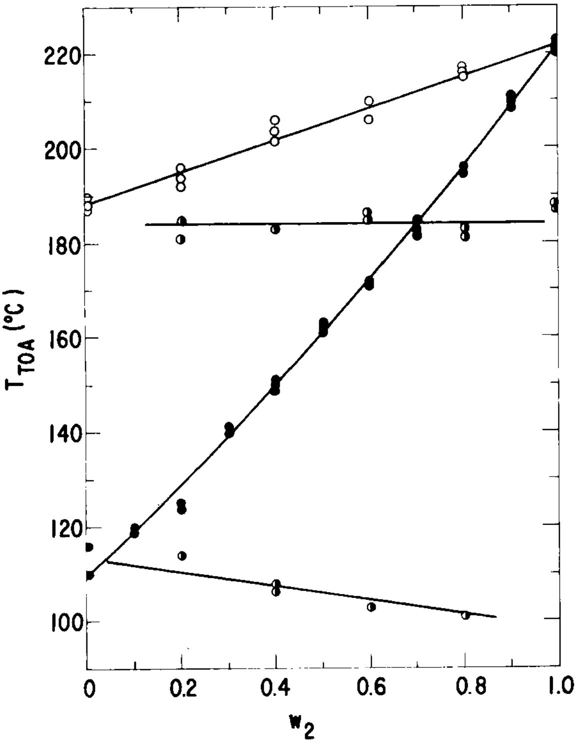

FIG. 7. Thermo-optical transition temperatures plotted against the weight fraction of Component 2. Blend systems: (●) I, PS(1) + PMMPO(2); (○) II, PMPPO(1) + PMMPO(2); and (◑) III, PS(1) + PMPPO(2).

There is some indication (Fig. 7) that the T_{TOA} of the phase rich in PMPPO is lowered slightly by the PS. Since the equilibrating phases in such "quasi-binary" polymer blends should contain molecules of each polymer distributed between them, there is reason to expect this [8, 9]. The effect, however, is slight in the present system. One also expects the T_{TOA} and T_g(DSC) of the phase rich in PS to be elevated by the PMPPO molecules equilibrated into it. Although the data scatter precludes a firm estimate of this effect, the T_g(DSC) data (Table 3) do indicate a possible 5 to 7° elevation of the PS glass transition by the PMPPO contained therein. Any elevation of the T_{TOA} of the phase rich in PS by PMPPO is obscured by the onset of increasing light transmission in approach to the second transition, producing an apparent shift of the transition to lower temperatures.

TOA and DSC provide complementary evidence of compatibility in polymer blends. Although TOA depends upon light as a probe, it is not limited by a need for any refractive index difference between separated phases, nor is it limited by the requirement that the domain dimensions in inhomogeneous blends be comparable to or exceed the wavelength of the light. The T_{TOA} of the matrix of a clear inhomogeneous blend can be determined without regard to the dimensions of the internal phase. The effect of orientation relaxations within and at the boundaries of very small domain internal phases upon the light transmission in the TOA measurement as presently constituted deserves theoretical and experimental exploration. As an empirical tool TOA is providing a very useful service in the examination of certain polymer blend systems. The use of birefringence observations to examine changes in submolecular and supermolecular mobility of single-component and multicomponent systems has a considerable history. The development of novel ways to apply such observations to polymer characterization remains a fertile field in polymer physicochemical research.

ACKNOWLEDGMENTS

The authors wish to acknowledge helpful discussions with Dr. G. D. Cooper concerning his early work on DSC of PMPPO + PMMPO blends. Thanks are also due to Dr. D. M. White and Mr. H. J. Klopfer who supplied the PMPPO and to Mr. R. W. Beers for assistance in film molding operations.

REFERENCES

[1] A. R. Shultz and B. M. Gendron, J. Appl. Polym. Sci., 16, 461 (1972).

[2] A. R. Shultz and B. M. Gendron, Paper Presented at the 6th Biennial Polymer Symposium, University of Michigan, Ann Arbor, Michigan, June 12-15, 1972.

[3] A. R. Shultz and B. M. Gendron, Paper Presented at the 2nd International Symposium on Polymer Characterization, Battelle Seattle Research Center, Seattle, Washington, August 21-23, 1972; J. Polym. Sci., Polym. Symp., 43, 89 (1973).

[4] A. S. Hay, U.S. Patent 3,306,875 (February 28, 1967), assigned to General Electric Co.

[5] A. S. Hay, H. S. Blanchard, G. F. Endres, and J. W. Eustance, J. Amer. Chem. Soc., 81, 6335 (1959).
[6] A. S. Hay, J. Polym. Sci., 58, 581 (1962).
[7] D. M. White and H. J. Klopfer, Ibid., A-1, 8, 1427 (1970).
[8] R. Koningsveld, H. A. G. Chermin, and M. Gordon, Proc. Roy. Soc., Ser. A, 319, 331 (1970).
[9] R. Koningsveld, Chem. Zvesti, 26, 263 (1972).