Phase Behavior of Polyarylate Blends

L. M. ROBESON, *Union Carbide Corporation Research and Development Department, Specialty Polymers and Composites Division, Bound Brook, New Jersey 08805*

Synopsis

Melt mixtures of a polyarylate based on bisphenol A and tere/isophthalates were made with poly(ethylene terephthalate), several cyclohexane dimethanol-based polyesters, polycarbonate, and the poly(hydroxy ether) of bisphenol A. The phase behavior was determined using classical methods. With minimum time and temperature exposure, polyarylate exhibits phase separation with poly(ethylene terephthalate) (PET) at >30 wt % PET. With moderate time and temperature exposure, adequate ester exchange occurs with polyarylate/PET blends to yield single-phase behavior. The activation energy of the ester-exchange reaction was determined to be 37.0 kcal/mole.

Under minimum time and temperature exposure conditions, miscibility of polyarylate with three different cyclohexane dimethanol-based polyesters was observed. A polyarylate-polycarbonate 50:50 mixture was shown to be phase separated under minimum mixing conditions but capable of exchange reactions to yield single-phase behavior with proper time and temperature exposure. Likewise, a 70:30 polyarylate-poly(hydroxy ether of bisphenol A) blend was phase separated as mixed, but with further elevated temperature exposure, a cross-linked single-phase system resulted.

The density versus composition of the polyarylate-PET blends was linear with the phase-separated systems but exhibited a slight densification with the miscible systems produced by higher temperature exposure. The glass transition of the miscible polyarylate-polyester blends exhibited a significant deviation (lower) than predicted by a linear or Fox equation prediction. This was attributed to the low value of ΔC_p (specific heat difference between the glass and rubber states) of polyarylate as noted by the Couchman equation to be a major factor in the T_g versus composition relationship. The optical characteristics of the blends paralleled the observed phase behavior as single-phase blends were all transparent (in the amorphous state) whereas phase-separated blends were translucent to opaque. These results clearly demonstrate the importance of ester-exchange or transesterification reactions in the phase behavior of blends of polymers capable of these reactions.

INTRODUCTION

Polyarylates based on bisphenols and tere/isophthalates have been recognized as an important class of polymeric materials for over two decades.[1,2] Specifically, the polyarylate based on bisphenol A and tere/isophthalates is now commercially available offering a high heat distortion temperature (174°C), excellent toughness, high resilience from deformation, and excellent mechanical property retention after long-term ultraviolet (UV) exposure.[3,4,5] Blends of polyarylates with other polymers have been mentioned in various patents and several references in the technical literature.

The polyarylate based on bisphenol A and tere/isophthalates was noted to be miscible with bisphenol A polycarbonate by Mondragon et. al.[6] Blends

CCC 0021-8995/85/104081-18$04.00

of a polyarylate based on bisphenol A, terephthalate, and neopentyl glycol with poly(butylene terephthalate) were noted to be miscible by Slagowski et al.[7]

A French patent assigned to N. V. Order Zoekingsinstitut Research is the earliest reference discussing blends of poly(alkylene terephthalates) with bisphenol A-based polyarylates.[8] An intermediate glass transition was noted for a blend of poly(ethylene terephthalate) and bisphenol A-based polyarylates (thus suggesting miscibility). More recent patent references discuss miscible blends of polyarylates with cyclohexane dimethanol-based polyesters[9] and ternary blends of polyarylate and polyesters and a number of other polymers.[10] Binary blends of polyarylate-poly(ethylene terephthalate) have been discussed in several patents[10-12] with data that suggest the possibility of miscible behavior. Polyarylate-poly(etherimide) blends were noted to exhibit a narrow range of miscibility [$\geq$ 75 wt % poly(etherimide)].[13]

The most complete study reported in the technical literature on polyarylate-polyester blends involved studies by Kimura et al. on polyarylate-poly(butylene terephthalate) (PBT)[14] and polyarylate-poly(ethylene terephthalate)[15] blends. These blends were prepared by dissolving the polymers (2 g per 100 ml solvent) in a tetrachloroethane-phenol 40–60 solution followed by coagulation in methanol. Polyarylate-PBT blends were shown to be miscible before and after transesterification, whereas polyarylate-PET blends were phase separated before ester exchange and single phase after ester exchange.

A study by Eguiazabal et al.[16] noted miscibility for polyarylate-PET and polyarylate-PBT blends coagulated from phenol-methanol. Miscibility was also noted for polyarylate-polycarbonate blends prepared by casting from chloroform.
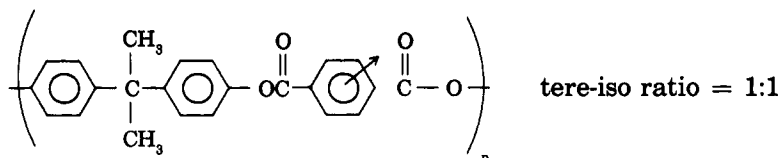
The literature studies are primarily based on coagulated or solution-cast samples. With polyarylate-PET blends, the two literature references disagree[15,16] on the phase behavior. Differences in the time and temperature exposure between these references are believed to be responsible for the results reported, as will be noted by the results reported in this paper.

This paper will primarily discuss the phase behavior of polyarylate-polyester blends prepared by melt mixing. Poly(ethylene terephthalate) will be specifically considered, as well as cyclohexane dimethanol-based polyesters. Additional data will be presented on melt blends of polyarylate and polycarbonate. The phase behavior depends on a number of factors, including the type of polyester, concentration of the mixture, temperature, tere-iso ratio, and molecular weight of the constituents. The mixing conditions were found to be of prime importance since potential ester exchange between polyarylate and the polyester (or polycarbonate) can lead to block copolymer formation and improved miscibility. The miscibility enhancement due to the introduction of covalent bonds between the constituents of a blend to form block, graft, or cross-linked moieties is well known experimentally and predicted by various theories.[17-20]

The transparency, in particular, and the property profile, in general, will be dependent upon the phase behavior of the polyarylate-polyester blend. The crystallization kinetics of the crystalline polyester will also be dependent upon the phase behavior, with slower crystallization rates observed with increased miscibility of a particular blend.

EXPERIMENTAL

The polyarylate utilized for these studies was Ardel D-100 (Union Carbide Corp.) with the structure

$$\left(\!\!\left\langle\bigcirc\right\rangle\!-\!\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}\!-\!\left\langle\bigcirc\right\rangle\!-\!O\overset{\overset{\displaystyle O}{\|}}{C}\!-\!\left\langle\bigcirc\right\rangle\,\overset{\overset{\displaystyle O}{\|}}{C}\!-\!O\right)_{\!\!n}\qquad \text{tere-iso ratio} = 1{:}1$$

The poly(ethylene terephthalate) was Cleartuf 104 with an intrinsic viscosity of 1.04 (measured in 60:40 phenol-tetrachloroethane at 23°C; Goodyear Co.) A polyester based on cyclohexane dimethanol, ethylene glycol, and terephthalic acid in a molar ratio of approximately 1:2:3, termed PETG-6763 (Tennessee Eastman Co.), with a molecular weight (MW) of about 26,000, was utilized for blend studies. The polycarbonate used in a blend with polyarylate was Lexan 101 (General Electric Co.).

All samples were well-dried in a heated vacuum oven prior to blending. The blends described herein were prepared via extrusion under conditions to minimize the time and temperature exposure but sufficient to provide for uniform mixtures. Generally, extruder settings of 265–270°C were utilized with a maximum exposure time of 3 min at those temperatures. Extruded blends were compression molded at 260–270°C under minimum exposure times. Samples containing poly(ethylene terephthalate) were quenched in ice water to prevent crystallization.

A torsion pendulum based on the design of Nielsen[21] was utilized for dynamic mechanical characterization. This apparatus was preferred over the more common forced vibration instruments as free vibration is more sensitive and allows better resolution of low-temperature relaxations. The frequency of the test was in the range of 1 Hz for the glassy state of the samples.

EXPERIMENTAL RESULTS

A series of polyarylate-PET blends differing by 10 wt % were prepared via extrusion at 265–270°C. The samples were compression molded at 265–270°C with a minimum cycle time (<3 min) followed by quenching in ice water. Another set of samples was compression molded at 300°C with a cycle time of approximately 10 min followed by quenching in ice water. The results indicated miscibility above 70 wt % polyarylate and partial miscibility below that level for compression molding at 265–270°C. Below 70 wt % polyarylate, the blends were translucent to opaque, thus visually confirming the phase separation. All samples molded at 300°C exhibited single-phase behavior as judged by a dynamic mechanical single T_g. These samples were all transparent. The dynamic mechanical results are illustrated for Ardel D-100 polyarylate, 80:20 by weight polyarylate-PET, 60:40 by weight polyarylate-PET, 40:60 by weight polyarylate-PET, and Cleartuf 104 poly(ethylene terephthalate), respectively, in Figures 1–5.

As illustrated by the data, the 80 wt % polyarylate blend exhibited no sign of phase separation, but at both 60 wt % and 40 wt % polyarylate,
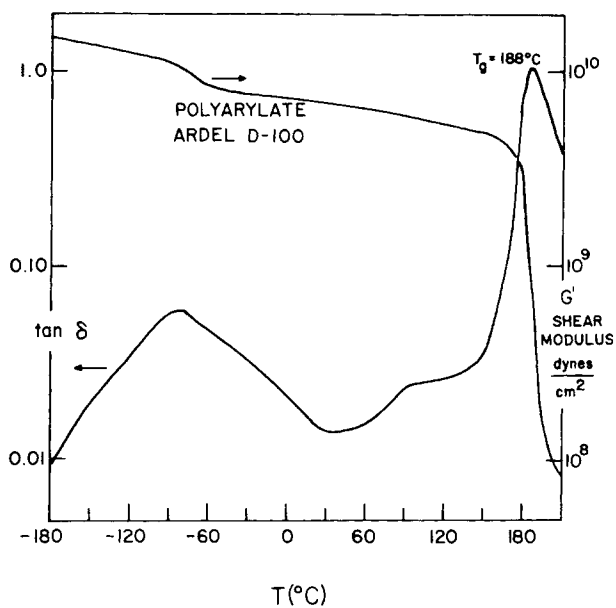
Fig. 1. Dynamic mechanical results for polyarylate Ardel D-100.

the samples molded at 270°C were phase separated with two distinct transitions resulting from a polyarylate-rich phase and a PET-rich phase. Note that complete phase separation was not observed as each phase exhibited a T_g shifted in the direction of the other component.
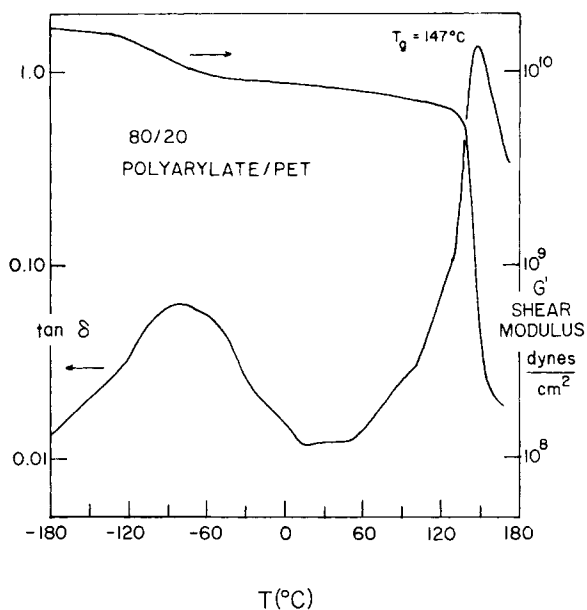

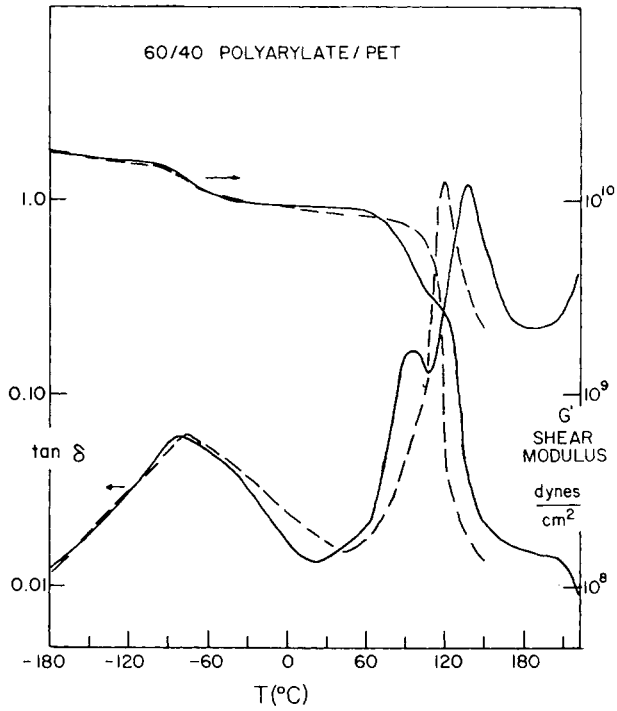Fig. 2. Dynamic mechanical results for 80:20 polyarylate-PET blend (by weight).

Fig. 3. Dynamic mechanical results for 60:40 Polyarylate-PET blend (by weight): (——) molded at 270°C; (- - -) molded at 300°C.
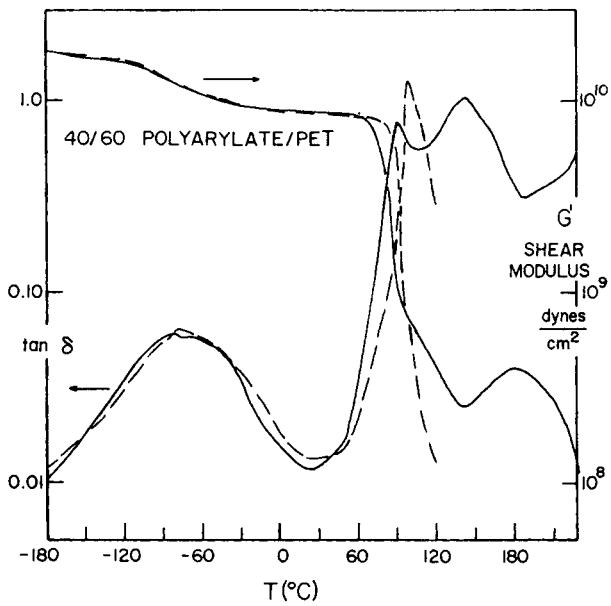

Fig. 4. Dynamic mechanical results for 40:60 polyarylate-PET blend (by weight): (——) molded at 270°C; (- - -) molded at 300°C.
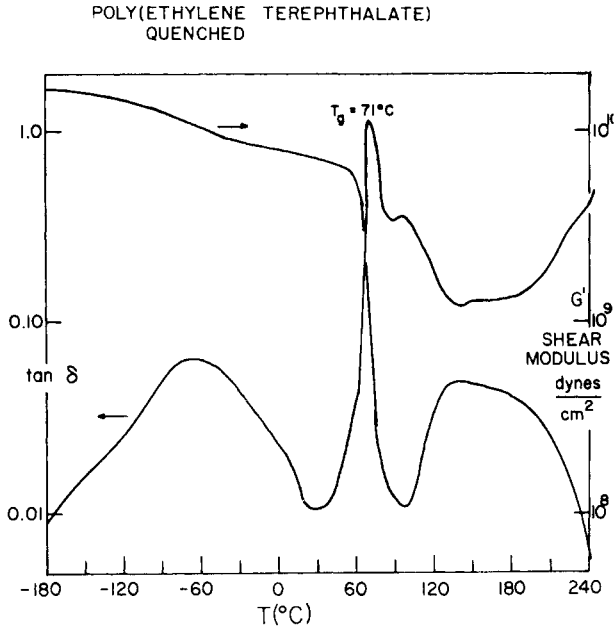
POLY(ETHYLENE TEREPHTHALATE)
QUENCHED

Fig. 5. Dynamic mechanical results for Poly(ethylene terephthalate)-Cleartuf 104 (quenched).

The glass transition of the miscible blends (e.g., 300°C molding) versus composition is shown in Figure 6. The nonlinearity of T_g versus composition is even lower than predicted by the empirical Fox equation[22]

$$\frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}}$$

where W_i = weight fraction of i and $T_{gi} = T_g$ of component i (undiluted state). The prediction of the Couchman equation[23]

$$\ln T_g = \frac{W_A \, \Delta C_{pA} \ln T_{gA} + W_A \, \Delta C_{pB} \ln T_{gB}}{W_A \, \Delta C_{pA} + W_B \, \Delta C_{pB}}$$

where ΔC_{pi} = difference in C_p between glass and rubber states for component i, is also given in Figure 6. The prediction of the Couchman equation lies below the experimental data. The ΔC_p value for polyarylate (0.0275 cal/g-°C) is considerably lower than most polymers, including the value for Cleartuf 104-PET (0.0680 cal/g-°C). This mismatch of ΔC_{pi} values is presumably responsible for the minimum deviation of the T_g versus composition data for polyarylate-PET blends.

The calorimetric results on the same series of quenched samples just noted are listed in Table I for the samples compression molded at 270°C and, in Table II, for the samples compression molded at 300°C. The samples were heated at 10°C/min from 23 to 275°C to determine T_g, heating T_c, ΔH_c
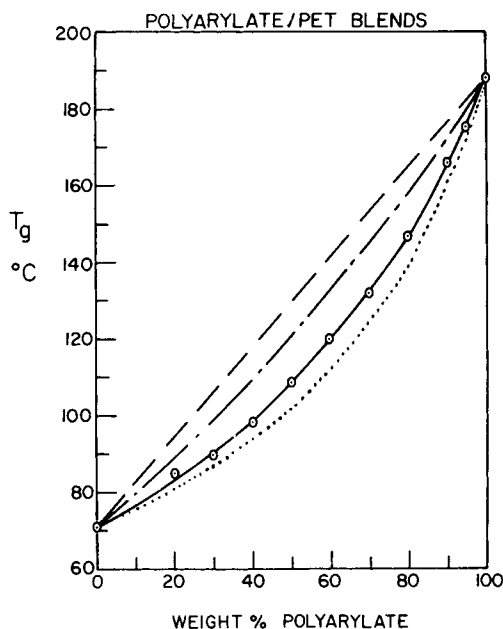
Fig. 6. Glass transition temperature (T_g) versus composition for polyarylate-PET blends:
(—) Linear; (- - -) Fox Equation; (-○-) Experimental; (· · ·) Couchman equation.

(heat of crystallization), T_m, and ΔH_f (heat of fusion). The samples were then cooled at 5°C/min to determine T_c and ΔH_c. The samples were then reheated to 275°C followed by cooling at 160°C/min to 180°C to determine the crystallization time t_c, defined as the time to reach maximum crystallization rate at 180°C. The T_g results in Table I are for the PET-rich phase up to 60% polyarylate and for the polyarylate-rich phase above that point. The values are somewhat indeterminate at intermediate compositions since the resolution of the calorimetry measurement is significantly lower than that for dynamic mechanical characterization.

As with the dynamic mechanical results, the calorimetric data show that mixtures of low to intermediate polyarylate content exhibit phase separation for samples compression molded at 270°C, whereas the data indicate increased miscibility for the blends molded at 300°C. The addition of polyarylate to PET leads to decreased crystallization rate for PET. The miscible blends exhibit even a further decrease in crystallization rate as compared with the phase-separated blend. An increase in the T_g of PET, dilution with polyarylate, and covalent bond formation (due to ester exchange) between the constituents are all contributory factors leading to decreased crystallization rates, as has been previously documented in miscible polymer blends.[17,24]

The density versus composition for phase-separated blends would be expected to exhibit linear behavior. Many miscible polymer blends, however, exhibit densification over that expected from an additivity relationship.[17,25] Density data for the polyarylate-PET blends (molded at 270 and 300°C) are

TABLE I
Calorimetry (DSC) Results on Polyarylate-PET Blends[a]

Sample description	T_g (°C)	T_m (°C)	ΔH_f (cal/g)	T_c^b (°C)	ΔH_c^b (cal/g)	T_c^c (°C)	ΔH_c^c (cal/g)	t_c at 180°C
PET Cleartuf 104	77	252	8.5	153	6.1	190	9.7	156 s
90% PET, 10% polyarylate	75	254	8.2	146	4.4	188	8.0	160 s
80% PET, 20% polyarylate	78	250	6.9	159	5.6	172	6.6	360 s
70% PET, 30% polyarylate	82	247	5.1	179	4.6	141	—	>1800 s
60% PET, 40% polyarylate	80	247	4.4	180	3.8	117	—	
50% PET, 50% polyarylate	86	245	1.4	—	—	—	—	—
40% PET, 60% polyarylate	85	—	—	—	—	—	—	—
30% PET, 70% polyarylate	110	—	—	—	—	—	—	—
20% PET, 80% polyarylate	130	—	—	—	—	—	—	—
10% PET, 90% polyarylate	152	—	—	—	—	—	—	—
Polyarylate Ardel D-100	187	—	—	—	—	—	—	—

[a] Samples extruded and compression molded at 270°C.
[b] T_c and ΔH_c from heating cycle.
[c] T_c and ΔH_c from cooling cycle.

illustrated in Figure 7. The highest molding temperatures resulted in slight increases in density, as expected from increased miscibility. The greatest deviation from linearity is observed at high polyarylate levels at which the dynamic mechanical results had indicated the best miscibility.

TABLE II
Calorimetry (DSC) Results on Polyarylate-PET Blends

Sample description	T_g (°C)	T_m (°C)	H_f (cal/g)	T_c^b (°C)	ΔH_c^b (cal/g)	T_c^c (°C)	ΔH_c^c (cal/g)	t_c at 180°C
90% Cleartuf 104 PET, 10% polyarylate Ardel D-100	78	248	6.9	157	5.9	176	7.0	240 s
80% Cleartuf 104 PET, 20% polyarylate	83	238	4.7	190	2.4	—	—	944 s
70% Cleartuf 104 PET, 30% polyarylate	87	235	0.16	—	—			>1320 s
60% Cleartuf 104, 40% polyarylate	93	—	—					
50% Cleartuf 104, 50% polyarylate	98	—	—					

[a] Samples extruded and compression molded at 300°C.
[b] T_c and ΔH_c from heating cycle.
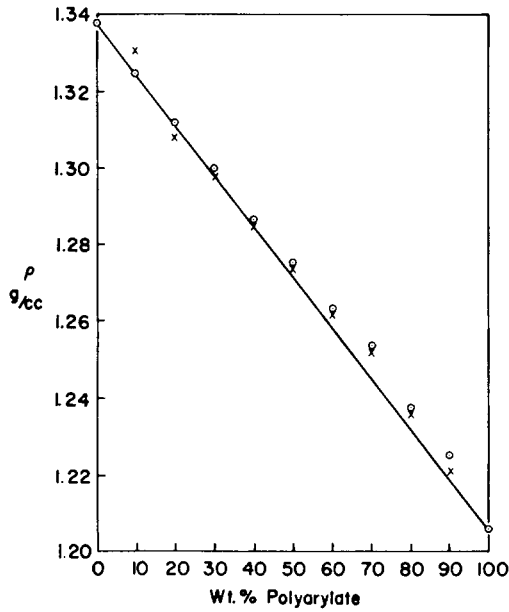[c] T_c and ΔH_c from cooling cycle.

Fig. 7.   Density results on polyarylate PET Blends: (x) molded at 270°C; (○) molded at 300°C.

Thermogravimetric data of polyarylate, PET, and several blends are illustrated in Figure 8. The calculated curve shown in Figure 8 is a composite curve of both constituents acting independently of the other. The initial weight loss for the blend occurs at a higher temperature than the predicted curve, indicating polyarylate stabilizes poly(ethylene terephthalate) in air. In N_2, the predicted and experimental data overlapped up to ~35% weight loss.
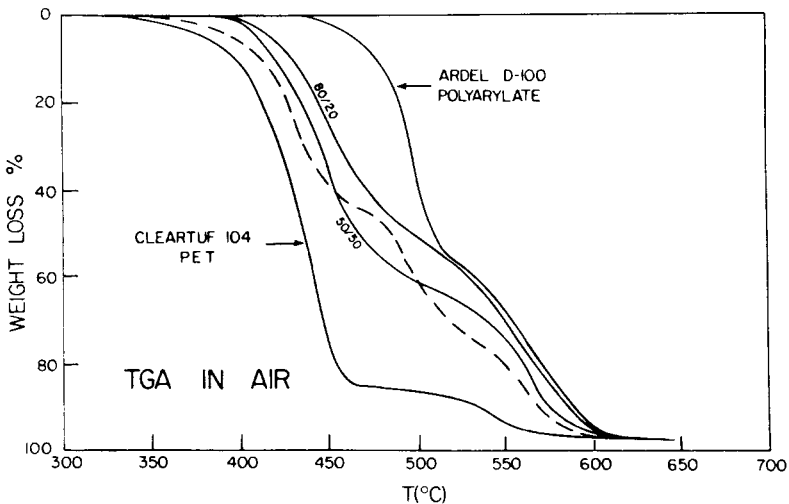

Fig. 8.   Thermogravimetric data for polyarylate-PET blends in air (heating rate = 10°C/min): (- - -) 50/50 calculated.

Polyarylate-PETG blends were extruded and compression molded at 265–270°C, and as single T_g values were observed over the entire composition range, no higher molding temperatures were investigated. The dynamic mechanical results for PETG and several polyarylate-PETG blends are illustrated in Figures 9 and 10. A solution cast film (from methylene chloride) of a 50:50 by weight PETG-polyarylate blend exhibited phase separation and T_g values of 100 and 160°C (via resilience minimum determination; see Reference 17 for procedure). Compression molding of the cast film yielded phase behavior best described as microheterogeneous without sharp T_g values. Chloroform cast films of the same composition gave a very broad T_g in the range of 120°C. These results indicate the solvent may affect the phase behavior, and the polyarylate-PETG is miscible under minimum melt mixing conditions in which only minimal ester exchange would be expected. The T_g versus composition data for polyarylate-PETG blends are given in Figure 11. Although not shown, the Couchman equation prediction was lower than the experimental data as also observed with polyarylate-PET blends.

A polyarylate-polycarbonate 50:50 by weight blend was prepared via extrusion at 265–270°C. Samples were compression molded at 260, 320, and 350°C. The modulus-temperature and resilience-temperature data are illustrated in Figure 12. At 260°C, reasonably complete phase separation is observed, whereas at 320°C, partial miscibility is observed as evidenced by two T_g intermediate between component values. At 350°C, miscibility is observed based on a single T_g. This increasing miscibility with increasing molding temperature is believed due to ester-exchange reactions leading to
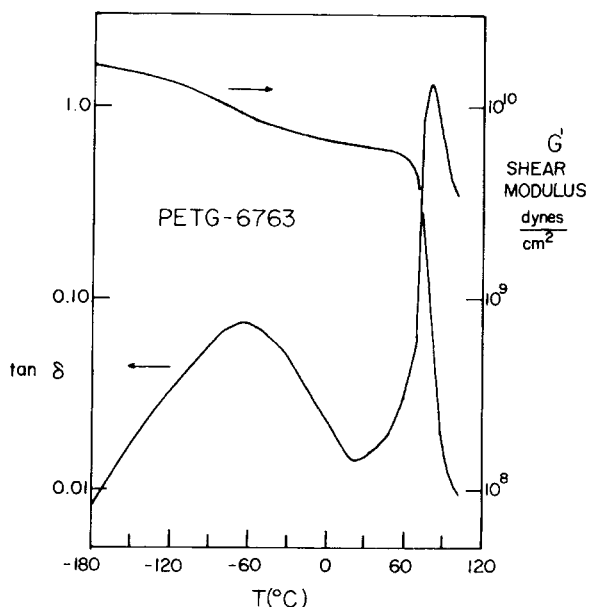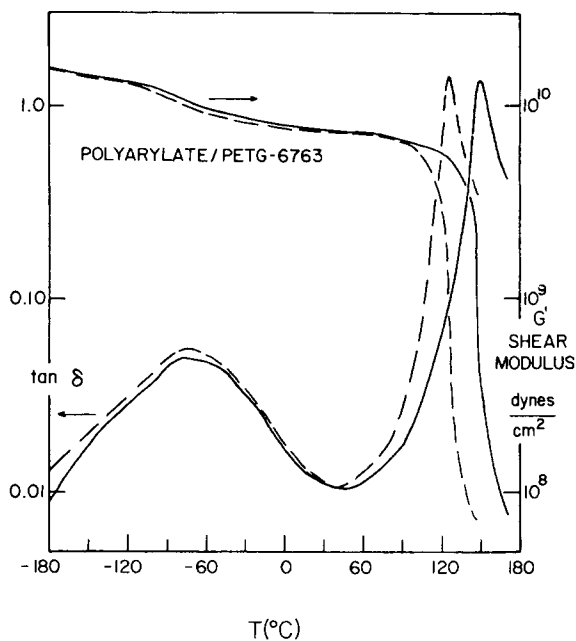

Fig. 9. Dynamic mechanical results for PETG-6763.

Fig. 10.   Dynamic mechanical results for polyarylate-PETG blends (75:25 and 60:40) (by weight): (—) 75/25; (- - -) 60/40.
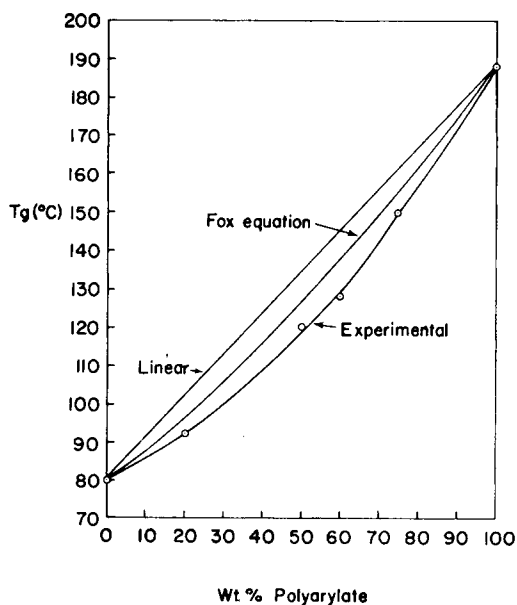

Fig. 11.   Glass transition temperature (T_g) versus composition for polyarylate-PETG-6763 blends.
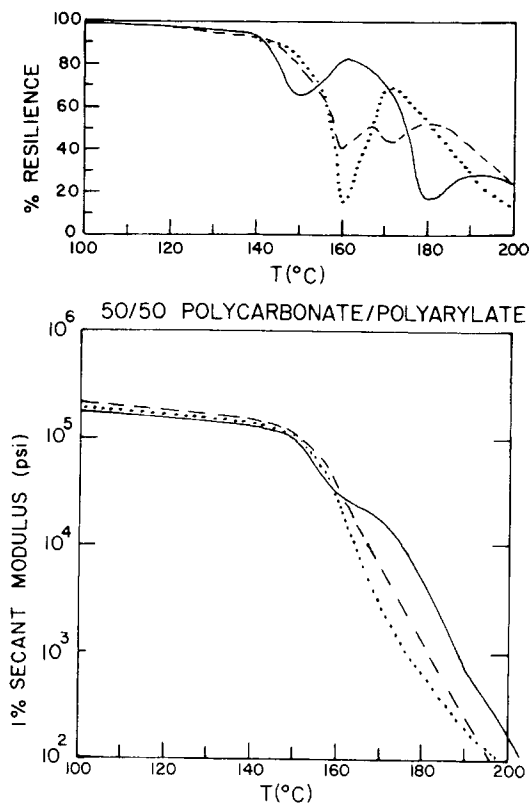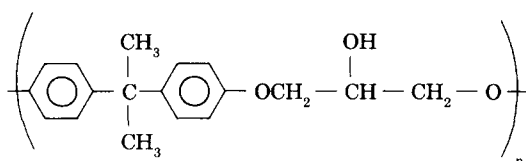
Fig. 12. Modulus-temperature and resilience-temperature results for 50:50 (by weight) po-
lyarylate-polycarbonate blend: (—) 260°C; (- - -) 320°C; (· · ·) 350°C.

block copolymer formation. Visual observation of the samples paralleled
the phase behavior as the 260°C molded sample was opaque, the 320°C
molded sample was translucent, and the 350°C molded sample was trans-
parent. In order to assure that the mixing condition (265–270°C) was ade-
quate, a sample of the same composition was dissolved in chloroform and
cast into thin films and devolatilized in a vacuum oven. The films were
rapidly compression molded at 265°C. The resilience-temperature data gave
two T_g similar to that observed with the extruded samples. The modulus-
temperature data indicated negligible crystallization of either component
as the modulus above the T_g of both components (e.g., > 190°C) indicated
no significant plateau. This demonstrates that the polyarylate-polycarbon-
ate blend is phase separated unless conditions to yield ester exchange are
employed.

Two additional polyesters were melt blended with polyarylate at 265–
270°C under minimum time exposure conditions followed by rapid compres-
sion molding at 260°C. The polyesters were Kodar A-150 (cyclohexane di-
methanol-tere/isophthalic acid copolymer; (~80–87% tere)[26] and a similar
copolymer with a tere-iso ratio of 70:30. The blends (50:50 by weight
polyarylate-polyester) were both transparent and exhibited single T_g values
(125°C for blend based on copolyester with tere/iso ratio of 70:30; 130°C for
blend based on Kodar A-150).

The poly(hydroxy ether) of bisphenol A (phenoxy)

$$\left(\!\! \bigotimes - \underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}} - \bigotimes - OCH_2 - \underset{\underset{}{}}{\overset{\overset{OH}{|}}{CH}} - CH_2 - O \right)_{\! n}$$

has a secondary hydroxyl that may be amenable to transesterification re-
actions with polyarylate yielding a cross-linked structure. A 70:30 polyary-
late-phenoxy blend was prepared in an extruder at 265–270°C followed by
rapid compression molding at 270°C. The dynamic mechanical results (Fig-
ure 13) clearly show phase separation for a sample molded at 270°C.
Compression molding of the same material at 320°C (20 min) yielded a single-
phase system with a modulus plateau above the glass transition tempera-
ture indicative of cross-linking. This demonstrates the potential of tran-
sesterification of polyarylate and phenoxy. It is interesting to note that
sufficient molecular mobility is present to allow reaction of the two-phase
system to ultimately yield single-phase behavior.

In order to assess the relative rate of ester exchange between polyarylate-
PET, samples of 20:80 polyarylate-PET were exposed to 260, 270, 280, 290,
300, and 310°C for various time intervals followed by determination of the
crystallization temperature T_c by cooling from 260°C at 5°C/min. The dif-
ferential scanning calorimeter was utilized to expose the sample to the
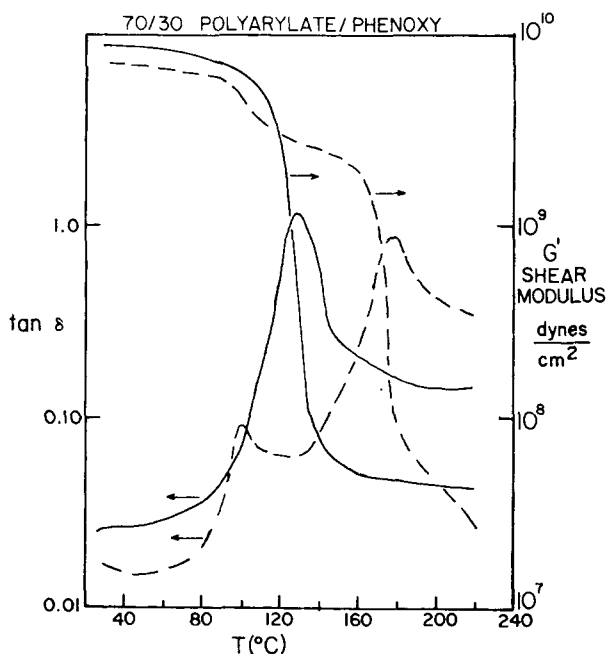

Fig. 13. Dynamic mechanical results for 70:30 by weight polyarylate-phenoxy blend: (- - -)
270°C; (—) 320°C (20 min.).

predetermined time-temperature conditions. The samples were rapidly heated at ~100°C/min to the exposure temperature, held at a specific time interval, cooled to 260°C at ~100°C/min, and cooled at 5°C/min to determine T_c. From a plot of T_c versus exposure time, the time required to yield a T_c value of 165°C was determined. The reciprocal time required to yield $T_c = 165$°C will be proportional to the ester exchange rate ($k \sim 1/t$), and thus,

$$k = k_0 e^{-Ea/RT} \quad \sim \frac{1}{t}$$

The plot of ln $(1/t)$ versus $1/T$ (Figure 14) yields an activation energy of 37.0 kcal/mole for the ester-exchange reaction of polyarylate-PET.

In order to provide more direct proof of ester exchange resulting in the polyarylate-PET blend, a single screw (30:1 L/D) Killion extruder was utilized to prepare 50:50 Ardel D-100–Cleartuf 104 blends at various temperatures. The pellet appearance was compared to the solubility characteristics in 1,1,2,2-tetrachloroethane at 80°C. The lower temperatures yielded opaque to translucent pellets that were only swollen in tetrachloroethane, but not dissolved (except for extracted polyarylate). At the point where transparent pellets were obtained (by raising extrusion temperatures), the pellets totally dissolved in tetrachloroethane. The results are noted in Table III. Only the highest temperature extruded product was soluble in methylene chloride (except for 1.5 wt %). As methylene chloride has much poorer solvency for PET than tetrachloroethane, solubility of the blend is not achieved until a high level of randomization has occurred. The methylene chloride extract-
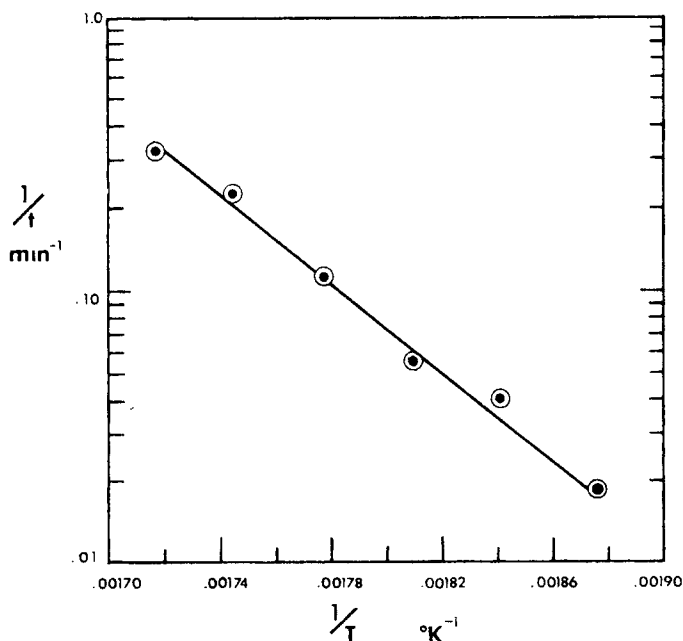

Fig. 14. Arrhenius plot to determine activation energy for polyarylate-PET ester-exchange reaction: Ea = 37.0 kcal/mole.

TABLE III
Qualitative Analysis of Solubility Characteristics of a 50:50 Polyarylate-PET Blend

Extruder setting temperature (°C)	Stock temperature (°C)	Pellet transparency	Tetrachloroethane pellet solubility[a] (80°C)	Methylene chloride pellet solubility[a]	IR results on methylene chloride extractables (presence of PET)[b]
260	247	Translucent to opaque	Not soluble	Not soluble	Not observed
280	259	Translucent to opaque	Not soluble	Not soluble	Not observed
300	276	Translucent	Not soluble; gelatinous product	Not soluble	Trace
320	292	Transparent	Soluble	Not soluble; gelatinous product	Minor
340	308	Transparent	Soluble	Not Soluble; gelatinous product	Significant
360	323	Transparent	Soluble	98.5% Soluble	—

[a] Solubility refers to the total system; polyarylate is, of course, extracted.
[b] IR results on CH_2Cl_2 extractables from pellets (observation of peaks at 1100–1120 cm^{-1}. Stock temperature measured by a melt probe at the end of the extrusion section.

ables from the pellets were subjected to infrared (IR) analysis. No evidence of PET was observed at the two lower mixing temperatures. A trace of PET was noted at the borderline temperature for miscibility, and increasing amounts of PET were then observed as the temperature was increased. These results demonstrate a reaction is occurring in the polyarylate-PET system at the position where the phase behavior goes from two-phase to single-phase.

DISCUSSION OF RESULTS AND CONCLUSIONS

Melt blends of polyarylate [derived from bisphenol A and tere/iso (50:50) phthalates] are miscible with poly(ethylene terephthalate) above 70 wt % polyarylate when mixed under minimum time and temperature exposure conditions. Below that level, a two-phase composition results, with a polyarylate-rich phase and a PET-rich phase. Moderate time-temperature exposure leads to a single-phase system for all compositions due to ester-exchange reactions. The crystallization kinetics of PET are quite dependent upon the phase behavior as well as the degree of ester exchange. In essence, the crystallization kinetics can be utilized to qualitatively follow the ester exchange of the constituents as well as to determine the activation energy of the ester-exchange reaction. The ester-exchange reactions lead to block copolymer formation, and thus, improved miscibility is expected as predicted by the theoretical development by Meier[18] and Krause.[19] The phase behavior parallels the optical characteristics as translucent to opaque blends exhibit two-phase behavior whereas transparent blends are single phase (as determined by glass transition measurements). The T_g behavior versus composition is lower than predicted by the Fox equation but is higher than the prediction of the Couchman equation. The large difference in ΔC_p (glass-rubber transition) between polyarylate and PET is presumably the reason for the large deviation from linearity or the empirical Fox equation T_g predictions. Polyarylate exhibits a very low ΔC_p value relative to many other polymers. The T_g data by Aharoni[27] on poly(ester-carbonate)–PET blends also exhibit lower T_g values than the Fox equation prediction. The polyester part of the poly(ester-carbonate) copolymer employed by Aharoni is a polyarylate based on terephthalate and bisphenol A.

The copolyester of cyclohexane dimethanol, ethylene glycol, and terephthalic acid (PETG-6763) is miscible with polyarylate over the entire composition range when mixed in the melt, even under minimum time and temperature exposure conditions. Solution cast films gave mixed results, with definite two-phase behavior when cast from methylene chloride and a very broad transition when cast from chloroform. In certain cases, the solvent has been found to be critical in regard to phase behavior of solution cast films.[28,29] The T_g versus composition for the polyarylate-PETG blends gave a significant deviation from linearity, presumably due to a low ΔC_p value for polyarylate. Two other polyesters [cyclohexane dimethanol-tere/iso phthalates (at 84:16 and 70:30 tere-iso)] were determined to be miscible with polyarylate under minimum time and temperature exposure conditions during melt mixing. All three cyclohexane dimethanol-based polyesters gave transparent molded specimens.

The results on blends of polyarylate and polycarbonate clearly demonstrate phase separation under conditions of minimum time and temperature exposure during melt processing. Increasing time and temperature exposure resulted in transformation of a phase-separated system to a miscible blend. This transformation was accompanied by a change from opaque to translucent to transparent blends as the time-temperature exposure was increased.

As previously noted, polyarylate-PET blends were noted to be phase separated when coagulated from a common solvent in work by Kimura et al.[15] Results reported by Eguiazabal indicated miscibility for the polyarylate-PET blend (also coagulated).[16] It must be pointed out, however, that the study by Eguiazabal et al.[16] reported results on polyarylate-PET blends after annealing at 277°C for 20 min for PET contents of > 20 wt %. The results reported in this paper indicate (see Figure 14) that a significant level of ester exchange has resulted under these conditions. It is interesting to point out that Eguiazabal et al.[16] reported that 80:20 and 90:10 polyarylate-PET blends exhibited single T_g values when the coagulated blends were annealed at 167°C for 20 min. With these considerations, the results reported in this paper agree with the results of the previous investigations,[15,16] and the time-temperature exposure of the extrusion technique employed here did not yield a significant level of ester exchange.

Both papers by Eguiazabal et al.[16] and Mondragon et al.[6] concluded that blends of polyarylate and polycarbonate were miscible, thus not in agreement with the results reported here. The study by Eguiazabal et al. reported a single T_g for a 50:50 polyarylate-polycarbonate blend prepared by casting from chloroform and heating at 277°C for 20 min. The results of Mondragon et al.[6] were reported on polyarylate-polycarbonate blends prepared by both melt mixing at 300°C and solution cast from chloroform. In both cases, the blends were annealed at 300°C for 10 min. The time-temperature exposure conditions of both investigations are significantly higher than the minimum conditions reported here. It is therefore concluded that the prior investigations observed single-phase behavior due to exchange reactions of polyarylate and polycarbonate. Note that the polyarylate employed in the prior investigations is virtually identical to the polyarylate used in this study. The chloroform cast 50:50 polyarylate-polycarbonate blend of this study gave two distinct transitions, further demonstrating phase separation where exchange reactions are minimal. A recent reference[30] on polycarbonate-polyarylate blends reached the same conclusions as this paper. Blends prepared in chloroform followed by drying and compression molding were two-phase. Heating at 250°C for over 4 h yielded single-phase blends.

The results on a polyarylate blend with the poly(hydroxy ether) of bisphenol A demonstrate the potential for polymeric transesterifications even with phase-separated systems. The uncross-linked, phase-separated blend of phenoxy and polyarylate is transformed into a single-phase cross-linked blend with adequate time and temperature exposure. Similar results were reported by Eguiazabal et al.[16] for solution cast films of phenoxy and polyarylate. Similar cross-linking reactions have been noted for poly(butylene terephthalate) and phenoxy[31] and for poly(ethylene terephthalate) and phenoxy.[32]

In several miscible polymer blends, the low-temperature secondary relaxation transitions (commonly attributed to rotational modes) have been shown to be significantly reduced in magnitude.[33-35] No evidence exists for this behavior in the polyarylate-polyester blends reported here.

References

1. G. Bier, *Polymer.*, **15**, 527 (1974).
2. V. V. Korshak and S. V. Vinogradova, *Polyesters*, Pergamon Press, Oxford, 1965.
3. J. D. Domine, 37th ANTEC of SPE, p. 655, New Orleans, LA, May 7–10, 1979.
4. D. Freitag and K. Reinking, *Kunststoffe*, **71**(1), 46 (1981).
5. H. Sakata, S. P. E., 32nd ANTEC, p. 459, April 13–16, 1974, San Francisco, California.
6. I. Mondragon, M. Cortazar, and G. M. Guzman, *Makromol. Chem.*, **184**, 1741 (1983).
7. E. L. Slagowski, E. P. Chang, and J. J. Tkacik, *Polym. Eng. Sci.*, **21**, 513 (1981).
8. French Patent No. 1,392,883, assigned to N. V. Order Zoekingsinstitut Research, Feb. 8, 1965.
9. L. M. Robeson, U.S. Pat. No. 4,246,381, assigned to Union Carbide Corp., Jan. 20, 1981.
10. L. M. Robeson, U.S. Pat. No. 4,259,458, assigned to Union Carbide Corp., March 31, 1981.
11. L. M. Robeson, U.S. Pat. No. 4,231,922, assigned to Union Carbide Corp., Nov. 4, 1980.
12. H. Sakata, T. Okamoto, and H. Hasegawa, U.S. Pat. No. 3,946,091 assigned to Unitika Ltd.), March 23, 1976.
13. L. M. Robeson, M. Matzner, and L. M. Maresca, U.S. Pat. No. 4,250,279, assigned to Union Carbide Corp., Feb. 10, 1981.
14. M. Kimura, R. S. Porter, and G. Salee, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 367 (1983).
15. M. Kimura, G. Salee, and R. S. Porter, *J. Appl. Polym. Sci.*, **29**, 1629 (1984).
16. J. I. Eguiazabal, M. E. Calahorra, M. M. Cortazar, and J. J. Irwin, *Polym. Eng. Sci.*, **24**, 608 (1984).
17. O. Olabisi, L. M. Robeson, and M. T. Shaw, in *Polymer-Polymer Miscibility*, Chapter 2, Academic Press, New York, 1979.
18. D. J. Meier, *J. Polym. Sci., Part C*, **26**, 81 (1969).
19. S. Krause, *Macromolecules*, **3**, 84 (1970).
20. L. M. Robeson, M. Matzner, L. J. Fetters, and J. E. McGrath, in *Recent Advances in Polymer Blends, Blocks, and Grafts* (L. H. Sperling, ed.), Plenum, New York, 1974, p. 281.
21. L. E. Nielsen, *Rev. Sci. Instrum.*, **22**, 690 (1951).
22. T. G. Fox. *Bull. Amer. Phys. Soc.*, **1**, 123 (1956).
23. P. R. Couchman, *Macromolecules*, **11**, 1156 (1978).
24. L. M. Robeson, *J. Appl. Polym. Sci.*, **17**, 3607 (1973).
25. L. W. Kleiner, F. E. Karasz, and W. J. MacKnight, *Polym. Eng. Sci.*, **19**, 519 (1979).
26. R. N. Mohn, D. R. Paul, J. W. Barlow, and C. A. Cruz, *J. Appl. Polym.*, **23**, 575 (1979).
27. S. M. Aharoni, *J. Macromol. Sci.-Phys.*, **B22**(5,6) 813 (1983).
28. M. Bank, J. Leffingwell, and C. Thies, *Macromolecules*, **4**, 43 (1971).
29. J. Leffingwell, C. Thies, and H. Gertzman, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **14**(1), 596 (1973).
30. M. Kimura and R. S. Porter, *Anal. Calorim.*, **5**, 25, (1984).
31. L. M. Robeson and A. B. Furtek, *J. Appl. Polym. Sci.*, **23**, 645 (1979).
32. L. M. Robeson, in *Polymer Compatibility and Incompatibility: Principles and Practices*, (K. Solc, ed.), MMI Press Symposium Series, Vol. 2, Harwood Academic, New York, 1982, p. 177.
33. N. Sundgren, G. Bergman, and Y. J. Shur, *J. Appl. Polym. Sci.*, **22**, 1255 1978).
34. G. Bergman, H. Bertilsson, and Y. J. Shur, *J. Appl. Polym. Sci.*, **21**, 2953 (1977).
35. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci., Part A-2*, **7**, 795 (1968).