

Halato-Telechelic Polymers. 12. Block Copolymerization of Polystyrene and Polybutadiene via Ionic Interactions

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INTRODUCTION

Multiphase polymeric systems (polymer blends, block and graft copolymers, ion-containing polymers, and filled polymers) are now receiving much interest as an efficient means of achieving technological progress in the field of synthetic organic materials: some deficient properties of commodity polymers can be improved, it is possible to reduce the cost of engineering polymers without damage to their useful properties, and new and sometimes unexpected behavior may arise from well-chosen polymer combinations.¹⁻⁴

Combining miscible polymers promotes the same general behavior as that of the corresponding random copolymers, whereas additivity in the properties of each component is observed when the associated polymers are immiscible and form multiphase systems. In the latter case, the ultimate mechanical properties are strongly dependent on the interfacial adhesion. The situation is of course ideal in block and graft copolymers owing to the covalent bonding between the immiscible components. Immiscible polymer blends generally suffer from a high interfacial tension that is responsible for a disappointing mechanical behavior. However, suitable block or graft copolymers used in moderate amounts are recognized as efficient interfacial agents or adhesion promoters; their beneficial effect has been reported by independent investigators.^{1,5-8} The mutual interactions of functional groups attached, one on each immiscible polymer of a binary blend, is another means of enhancing the interfacial adhesion.⁹ In that respect, ionomeric blends recently described by Eisenberg et al. deserve interest.¹⁰⁻¹³ This method of miscibility enhancement consists of the incorporation, into the two polymers to be mixed, of different acid and base moieties that, upon mixing, become ionic as a result of the transfer of a proton from the acid to the base. The electrostatic interactions between these two ions force the two chains to remain in close proximity. For instance, polystyrene can be made miscible with poly(ethyl acrylate) when polystyrene is sulfonated to the extent of 5% and the poly(ethyl acrylate) actually contains a similar percentage of vinylpyridine units.¹⁰ The same is true for the polystyrene-polyisoprene pair,¹¹ whereas strong interactions occur between sulfonic acid groups attached onto polystyrene and urethane or urea moieties on polyurethane chains.¹²

Blending two immiscible telechelic polymers capped with acid and tertiary amine functions, respectively, is also expected to promote coulombic interactions between the end-groups and to engage the individual chains in a kind of multiblock copolymer. This work deals with the feasibility of block "copolymerizing" polystyrene and polybutadiene by means of ionic interactions between the chains extremities. Since these materials are immiscible, their combination has to form a multiphase system; the main question is to know whether the electrostatic interactions between two end-ions are able to overcome the thermodynamic repulsion of the related polymeric backbones. If the answer is yes, then a structure reminiscent of a multiblock copolymer may be predicted.

EXPERIMENTAL

The main features of the ω - and α,ω -functional polymers used in this study are summarized in Table I. PB1 and PB3 were kindly supplied by B.F. Goodrich. PS1 and PS2 were prepared by living anionic polymerization in tetrahydrofuran (THF) at -78°C .¹⁴ α -methylstyrene sodium oligomer was used as a difunctional initiator, and sec. butyllithium as a monofunctional one. The living macroanions were deactivated by anhydrous carbon dioxide. PB2 was prepared by converting the carboxylic acid end-groups of PB1 into carboxyl chloride groups, which then reacted with *N,N*-dimethylaminoethanol. A large excess of freshly distilled thionyl chloride was added into a solution of PB1 in toluene (5–10 wt % PB1) that had been previously dried by azeotropic distillation of toluene. After stirring at room temperature for 12 h, the carbonyl stretching band of the acid groups (1710 cm^{-1}) had completely disappeared in favor of a new absorption band at 1790 cm^{-1} , assigned to acid chloride groups. The unreacted thionyl chloride was distilled off, before adding pyridine and the freshly distilled and carefully dried (over CaH_2) *N,N*-dimethylaminoethanol used in a fivefold molar excess. After stirring at 25°C for 24 h, the infrared (IR) absorption at 1790 cm^{-1} was completely substituted by an absorption band at 1730 cm^{-1} characteristic of ester groups. PB2 was recovered by precipitation into methanol. The functionality (f , mean number of functional groups per chain) was determined by potentiometric titration of the acid end-groups with tetramethylammonium hydroxide, and of the tert-amino end-groups by *p*-toluene-sulfonic acid in a 9/1 benzene-methanol mixture.

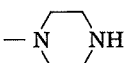
Polymer blends were prepared by solvent casting. Each polymer was separately dissolved in toluene (10 wt %), and a solution was slowly added into the other one under an efficient stirring. Two hours later, toluene was allowed for slow evaporation and the final product dried under vacuum at 50°C up to constant weight.

IR spectroscopy was performed with a model 197 Perkin Elmer apparatus. Differential thermal analyses were performed with a Du Pont 990 thermal analyzer (heating rate, $20^{\circ}\text{C}/\text{min}$). Molecular weights were determined by gel permeation chromatography in THF at 25°C (Waters 200 apparatus).

RESULTS

As a reference, polystyrene and polybutadiene bearing the same carboxylic acid end-groups (PS1 and PB1) were blended and investigated by DSC. Two separate changes in the specific heat, characteristic of immiscible polymer blends, were visible at the glass transition temperature (T_g) of the corresponding homopolymers (Tables I and II). However, T_g is surprisingly high for the low molecular weight polystyrene

TABLE I
Symbols, Molecular Weights, Functionality, and Glass Transition of Polymers

Polymer	Symbol	M.W.	Functional Group(s)	Functionality	$T_g(^{\circ}\text{C})$
Polystyrene	PS1	5000	— COOH	0.97	104
Polystyrene	PS2	6000	— COOH	1.95	114
Polybutadiene	PB1 ^a	4600	— COOH	2.00	-76
Polybutadiene	PB2	4600	— $\text{N}(\text{CH}_3)_2$	1.95	-76
Polybutadiene	PB3 ^a	4000 ^b		—	-77

^a Kindly supplied by B. F. Goodrich.

^b As determined from titration of the amino end-groups, while assuming an ideal functionality of 2.

TABLE II
Glass Transition Temperature (T_g) of Telechelic Polystyrene and Polybutadiene Blends

Polymer Blends	First DSC Run			Second DSC Run		
	T_{g1}	T_{g2}	T_{g3}	T_{g1}	T_{g2}	T_{g3}
PS1/PB1	-78	—	108	—	—	—
PS1/PB2	-78	22	62	-80	—	72
PS1/PB3	-75	—	62	-76	—	72
PS2/PB2	-74	—	54	-74	—	71
PS2/PB3	-75	—	60	-79	—	73

investigated in this study (PS1 and PS2). This could result from the short central α -methylstyrene segment derived from the initiator, and/or the possible hydrogen bonding between the carboxylic acid end-groups. Mixing α,ω -diamino polybutadiene with ω - or α , ω -carboxylic acid polystyrene results again in a heterophase system since two separate T_g 's are clearly observed (Table II). Nevertheless, two unexpected features are worth noting. The PS1/PB2 blend exhibits three distinctive T_g 's; an intermediate transition (or T_{g2}) is indeed visible between the glass transition of polybutadiene (T_{g1}) and polystyrene (T_{g3}). Furthermore, in the limits of the experimental errors, T_{g1} is not significantly modified, whereas T_{g3} is systematically decreased to a large extent. The drop in T_{g3} is dependent on the sample history. Blends reported in Table II were indeed prepared by dissolution in a common solvent (toluene), followed by the slow evaporation of the latter. The first DSC run was thus performed with blends resulting from this solution casting procedure. After heating up to 150°C , the blends were allowed for cooling ($\sim 5^{\circ}\text{C}/\text{min}$) in the DSC cell down to -120°C and a second run was performed. The same scenario is reported: T_{g1} remains largely unmodified, but T_{g3} decreases to reach a value approximately 10°C higher than the previous one. It is also meaningful that T_{g2} completely disappears, once the PS1/PB2 blend is heated beyond T_{g3} (Figure 1). No modification results from any further DSC run.

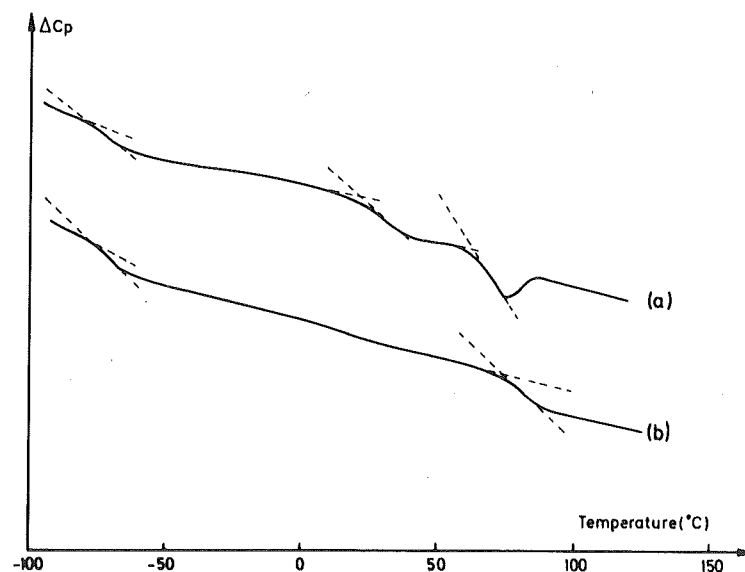


Fig. 1. DSC curves of the PS1/PB2 blend: (a), as obtained from solution; (b), after annealing at 150°C for 10 min.

The nature of the amino end-groups of polybutadiene (PB2 or PB3) has no significant incidence on T_g of polystyrene (Tg_3), at least after the first DSC run.

The possible dependence of the mixing state on the nature of the common solvent used in the blending process deserves interest. Figure 2 convincingly illustrates the influence of this parameter on Tg_3 for the PS2/PB2 blend: 54°C for toluene, about -8°C (broad transition) for tetrahydrofuran, and +12°C for CCl_4 . After a first heating run up to 150°C, this disagreement disappears and a unique and constant value of Tg_3 is reported.

Finally, it is of great interest to investigate whether the aging of the polyblends has an effect on their thermogram or not. In this regard, each polyblend was divided into two separate samples and kept at 25°C in the dark. After 6 months, one sample was analyzed as such by DSC, whereas the second sample was dried under vacuum for a week at room temperature before thermal characterization. In both cases, the DSC curve (first run) was the same as that reported for the freshly prepared polyblend during the second DSC run (Table II). No further modification was detected if the DSC analysis was repeated. This means that the features exhibited by the polyblends immediately after mixing (first DSC run, Table II) correspond to non-equilibrium situations, whereas a stable state is reached either rapidly by heating above Tg_3 or progressively by aging at 25°C. This is also assessed by the behavior of the PS2/PB2 blend cast from THF: after aging for 6 months at 25°C, the broad transition at -8°C decreases at the advantage of a new transition at 68°C (Figure 3). All these observations support that the differences in T_g noted during the first and the second DSC run for each polyblend (Table II) or during the first DSC run for the PS2/PB2 blend cast from different solvents (Figure 2) cannot be attributed to residual solvent in the samples. This claim can also be supported by the high value of Tg_3 reported for the reference PS1/PB1 polyblend during the first DSC run. If polyblends were contaminated by residual solvent, a decrease in Tg_3 in PS2/PB2 blend (Figure 2) would be expected to be more important in the presence of toluene, which is the less volatile solvent used in this series of experiments.

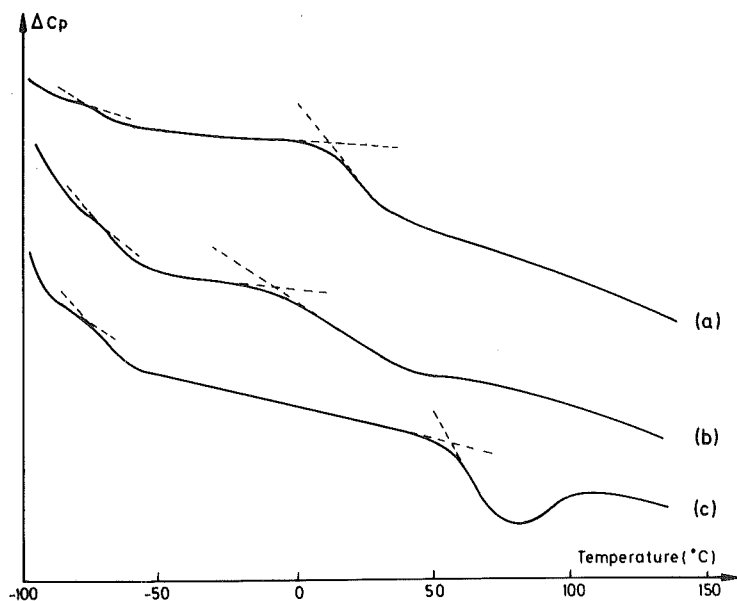


Fig. 2. DSC curves of the PS2/PB2 blend cast from different solvents: (a), CCl_4 ; (b), THF; (c), toluene.

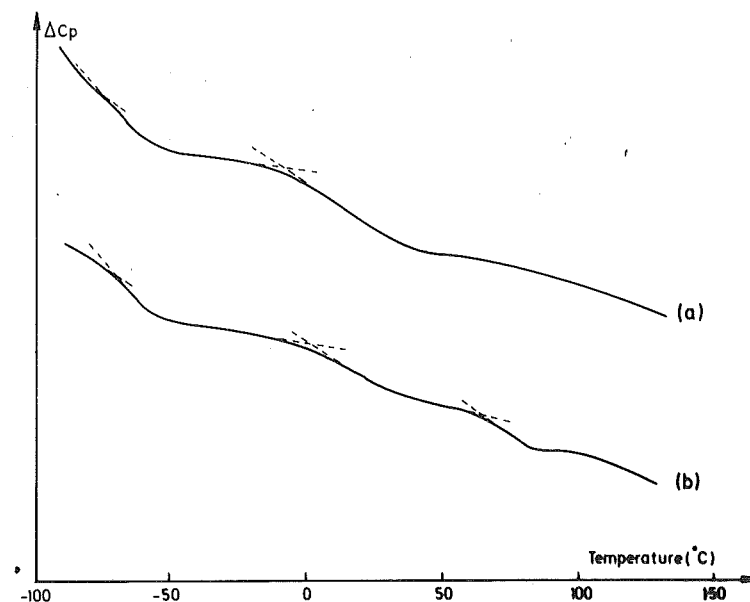


Fig. 3. DSC curves of the PS2/PB2 blend cast from THF: (a), after mixing; (b), after a six months period of aging.

DISCUSSION

It is worth recalling that the end-neutralization of ω - or α , ω -carboxylic acid polystyrene and poly(α -methylstyrene) by metal ions is responsible for a dramatic decrease in T_g .¹⁵ This effect is related to the nature of the metal carboxylate end-groups and, in the series of alcalino-earth cations, to the atomic radius of the metal. Furthermore, the T_g depression is dependent on the sample history; it is more pronounced when the halato-telechelic poly(α -methylstyrene) is recovered from solutions by solvent evaporation rather than obtained by cooling from the melt. All these features are similarly observed when ω - or α , ω -carboxylic acid polystyrene is blended with α , ω -diamino polybutadiene. At first sight, it could be concluded that a proton transfer occurs from the carboxylic acid to the amino group, resulting in the formation of a carboxylate anion and an ammonium cation attached to the polystyrene and polybutadiene chains, respectively. According to Eisenberg et al., this phenomenon takes place between sulfonic acid randomly attached onto polystyrene and vinylpyridine containing poly(ethylacrylate); thus, electrostatic interactions between these two ions can trigger the polymer compatibilization.¹⁰ Substituted for sulfonic acids, carboxylic acids do also improve compatibilization, but not quite to the same extent because only hydrogen bonding should be involved. In order to prove this claim, IR spectra of carboxylic acid-terminated polystyrene and its blends with amino-terminated polybutadiene were recorded (Figure 4). The 1710 cm^{-1} absorption in the IR spectrum of the unneutralized polystyrene has to be assigned to the carbonyl stretching band of the carboxylic acid end-groups. After mixing with a dimethyl amino-terminated polybutadiene, this characteristic absorption completely disappears in favor of a 1550 cm^{-1} absorption assigned to the carbonyl stretching of carboxylate anions. As a consequence and within the limits of the IR sensitivity, the proton transfer does indeed occur between the carboxylic acid and the dimethylamino end-groups. The situation is less clear-cut in the case of PB3, which ends in an aliphatic ring containing a secondary and a tertiary amine as well. This end-group has itself a characteristic and broad absorption around 1550 cm^{-1} , i.e., the wavelength at which the absorption of the carboxylate anion is

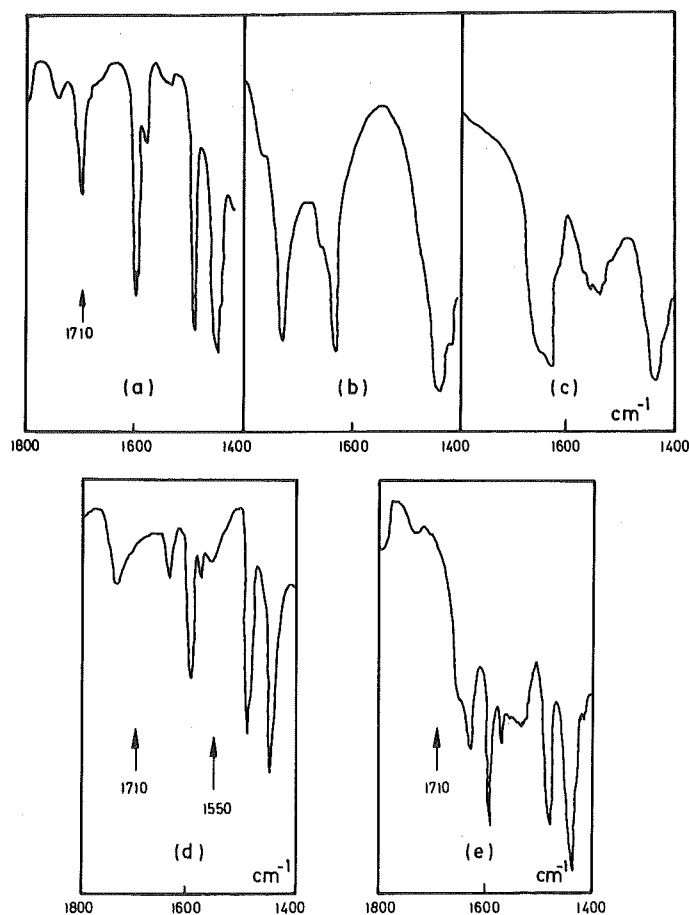


Fig. 4. Infrared spectra of homopolymers and polymer blends: (a), PS2; (b), PB2; (c), PB3; (d), PS2/PB2; (e), PS2/PB3.

typically observed. Accordingly, the proton transfer between the carboxylic acid end-groups in polystyrene and PB3 can only be visualized by the disappearance of the 1710 cm^{-1} absorption. A careful examination of the 1550 cm^{-1} band reveals, however, a slight modification when PB3 is mixed with PS2. Contrary to Eisenberg's expectation for the carboxylic acid-pyridine pair, the proton transfer is quite easy for carboxylic acid-aliphatic amine pairs, in agreement with the difference in basicity of aliphatic and aromatic tertiary amines. In that respect, Rees has demonstrated that carboxylic acid-containing polyethylene could be neutralized with aliphatic diamines. Whereas aromatic diamines were too weak to react with these polymeric acids.¹⁶ Similarly, Weiss and Agarwal partly neutralize a propylene-acrylic acid copolymer with tributylamine.¹⁷

That a proton transfer occurs between the acid end-groups of polystyrene and the amino groups capping polybutadiene means that these complementary end-groups come into close contact. Furthermore, the resulting formation of carboxylate anions and ammonium cations, and their mutual attraction, provide a means of stabilizing the cross-interaction of the polystyrene and polybutadiene chain ends, engaging these polymers in a spatial arrangement as do block copolymers. The analogy between polystyrene-polybutadiene block copolymers and blends of telechelic polysty-

rene and polybutadiene terminated with carboxyl and amino groups, respectively, can find support in the glass transition behavior of poly(styrene-*b*-diene) copolymers.¹⁸⁻²⁵ Several authors have shown, independently, that the glass transition temperature of the hard phase decreases much more rapidly with decreasing molecular weight than predicted for homopolystyrene. In a series of poly(styrene-*b*-isoprene-*b*-styrene) (SIS) copolymers containing 30% polyisoprene, T_g of the hard phase decreases about 30°C as the total molecular weight decreases from 90,000 to 25,000.²¹ In another investigation, a poly(styrene-*b*-isoprene) copolymer of low molecular weight (M_n : 8500) and containing 0.5 styrene weight fraction exhibits a decrease in T_g of the polystyrene phase as high as 56°C .²⁰ It is also reported that T_g of the softer phase moves slightly and irregularly toward higher temperatures with decreasing molecular weight.^{20,21} The explanations offered for this phenomenon are still at variance. Some authors suggest it is the consequence of some phase mixing at the border of the microdomains, the volume of the interlayer increasing at the expense of the two pure phases when their molecular weight decreases.²¹ Another explanation relies upon strong dynamical interactions between the chains in the hard and the soft phases. It is proposed that the highly mobile chains in the polydiene microphase induce premature molecular motions in the polystyrene microphase.²⁰ It is worth noting that these two models require a strong dependence between polystyrene and polydiene segments in order to allow either their partial mixing or the direct transmission of segmental motions from soft to hard microphases. If the glass transition behavior observed in this work has the same origin as that reported in block copolymers, no doubt that the ionic interactions should promote a strong interdependence between the polystyrene and polybutadiene end-groups. Of course, the main question is to know whether the T_g depression results from the existence and the possible aggregation of carboxylate-ammonium ion pairs as observed in halato-telechelic polystyrene and poly(α -methylstyrene)¹⁵ or from the association of polystyrene and polybutadiene into a block structure via ionic interactions. The evidence for an intermediate, while transitory, T_g (T_g2) would be in favor of the second hypothesis. Indeed, depending on molecular weight and composition of SIS triblock copolymers, one, two or three T_g 's have been reported²¹ and related to the morphology going from a single phase to a completely organized two-phase structure through intermediate states where phases are merely segregated. Nevertheless, the authors admit that the interphase region cannot be differentiated from the pure phases by electron microscopy. Beecher et al. have also put in evidence an intermediate transition in SIS copolymers, as investigated by dynamic mechanical testing.¹⁸ Quite interestingly, this transition is very sensitive to the blend history, and especially to the solvents from which films of the copolymers are cast. By comparison, T_g2 observed in the PS1/PB2 blend as cast from toluene and its disappearance after a first DSC run could support a direct analogy with classic triblock copolymers of the same chemical nature. Furthermore, it is well-known that solvent and thermal treatment have a decisive influence on the degree of phase separation and the morphological details of block copolymers.²⁶⁻²⁸ Therefore, the strong dependence of T_g3 on thermal history (Figure 1) and solvent treatment (Figure 2) could give consistency to the analogy with block copolymers. But the slight and irregular variation in T_g1 , instead of a slight increase as observed in block copolymers, prevents a definitive acceptance of the suggested model.

Further investigation is planned in order to evaluate the effect of both the molecular weight of each prepolymer and the presence of the acid (or amino) group at the ends of either the soft or the hard prepolymer. The mechanical evaluation of these blends stabilized through ionic interactions of the chain-ends would also be of great significance.

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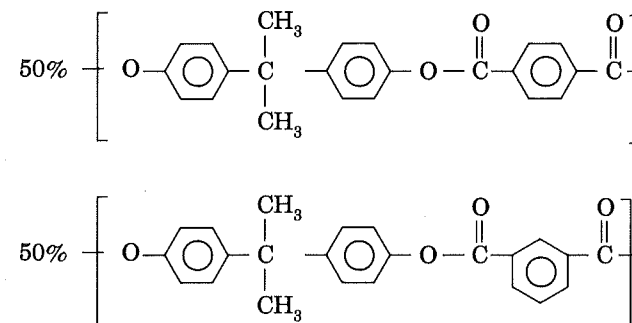
Thermal Degradation of a Polyarylate Polymer

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INTRODUCTION

It is known that polymers consisting of linear molecules with largely aromatic repeat units have generally good heat resistance.¹

The polymer which is the subject of this research, polyarylate (PAR), is a copolyester of bisphenol-A and an equimolar mixture of isophthalic and terephthalic acids. It has, therefore, a great amount of aromatic rings:



So, we have found interesting to carry out a study of the thermal degradation of this polymer by using thermogravimetric analysis in order to obtain the kinetic parameters involved in this process.

As the values reported in most of the thermogravimetric studies are dependent not only on factors such as carrier gas, sample quantity and shape, flow rate, heating rate, etc., but also upon the mathematical treatment used to evaluate the data, several methods reported in the literature have been applied.

EXPERIMENTAL

Polyarylate (ARILEF U-100) was kindly supplied by SOLVAY & Cie. The polymer was purified by solution in chloroform and precipitated over an excess of methanol. Then, the isolated polymer was dried in a vacuum oven. The average molecular weights, determined by GPC in THF at 25°C, were $\bar{M}_n = 21,500$ and $\bar{M}_w = 51,400$.

Thermogravimetric analyses were carried out by using a DuPont 951 Thermobalance attached to a DuPont 990 module. All the thermogravimetric curves were obtained under the following conditions: the nitrogen flow was kept constant at 30 ml/min, the sample weight was being about 10–12 mg. The chromel-alumel sample thermocouple used to monitor the sample temperature was positioned within 2 mm of the sample pan. Heating rates were 2, 5, 10, 20, and 50°C/min.