

# Ternary Polymer Mixtures: Polyarylate/ Phenoxy / Poly(Butylene Terephthalate)

J. I. EGUIAZABAL,\* J. J. IRUIN, M. CORTAZAR,  
and G. M. GUZMAN, *Departamento de Química-Física y  
Macromoléculas, Facultad de Ciencias Químicas,  
Universidad del País Vasco  
P. O. Box 1072, San Sebastian, Spain*

## Synopsis

The intended objective of this work was to bring together two immiscible polymers, polyarylate (PAr) and Phenoxy [poly(hydroxy ether of bisphenol-A)], preparing ternary mixtures with a third component, poly(butylene terephthalate) (PBT). Experimental results showed that ternary mixtures containing 30% or more PBT gave single glass transition temperatures by DSC. Moreover, the PBT melting point depended on the composition of the mixtures. These results, which could be indicative of the existence of a single amorphous phase in these blends, have been discussed. Nevertheless, results must be considered with caution, given the peculiarities of the  $T_g$ -composition diagrams for the miscible pairs PAr/PBT and Phenoxy/PBT. Hypothetic interchange reactions during melting have been found to be unimportant.

## INTRODUCTION

Polymer blends containing polyesters have received great attention in the patent and paper literature.<sup>1-14</sup> Many polyesters have been found to be miscible with other polymers. Generally, the formation of these miscible blends has been attributed to specific interactions between polymer molecules, such as hydrogen bonding,<sup>11</sup> dipole-dipole interactions,<sup>15</sup> or, when the second component of the blend is aromatic, a  $n-\pi$  complex formation between free electrons of the ester group and the aromatic ring.<sup>16</sup> However, factors other than specific interactions may affect the miscibility of a polymer blend, for example, the density of interacting groups,<sup>10,11</sup> steric effects,<sup>8,16</sup> or flexibility in the polymer chain.<sup>17</sup>

Some of these factors may originate the observed immiscibility in mixtures of a commercial polyarylate (PAr) (copolyester of bisphenol-A with an equimolar mixture of isophthalic and terephthalic acids) and the poly(hydroxy ether of bisphenol-A) (Phenoxy). Despite the potential capacity of the pendant hydroxyl groups of Phenoxy in miscibilizing its mixtures with other polymers containing ester and ether groups,<sup>18,19</sup> PAr/phenoxy blends of different compositions show two glass transition temperatures by DSC, indicating the existence of two amorphous phases.<sup>20</sup>

Although PAr and Phenoxy are immiscible, both polymers are miscible with poly(butylene terephthalate) (PBT).<sup>17,19</sup> Therefore, we wish to explore the

\*To whom correspondence should be addressed.

possibility of rendering PAr and Phenoxy compatible, using PBT as a common "solvent," to obtain ternary compatible mixtures. The notion of bringing together two incompatible polymers by means of the use of a third material is practiced with low molecular weight polymers in coating formulations. On the other hand, Kwei et al.<sup>21</sup> have suggested that two incompatible polymers, poly(methyl methacrylate) and poly(ethyl methacrylate), form with poly(vinylidene fluoride) ternary mixtures which are miscible over a wide range of compositions.

This work is devoted to the study of the PAr/Phenoxy/PBT mixtures, by using differential scanning calorimetry (DSC), in order to obtain glass transition and melting temperatures in mixtures of different compositions and subjected to several thermal treatments.

### EXPERIMENTAL

Polyarylate (Arilef U-100) was supplied by Solvay et Cie. Its average molecular weights, determined by GPC in THF at 303 K were  $\bar{M}_n = 21,500$  and  $\bar{M}_w = 51,400$ . Phenoxy (PKHH, Union Carbide) was obtained from Quimidroga, Barcelona, Spain. Its reported molecular weights<sup>22</sup> were  $\bar{M}_n = 25,000$  and  $\bar{M}_w = 80,000$ . Poly(butylene terephthalate) (Polysciences, cat. no. 6511) has a viscosity average molecular weight  $\bar{M}_v = 32,000$  determined at 298 K in a phenol/tetrachloroethane mixture (60/40 by weight).

Ternary mixtures were prepared by solution/precipitation. The desired amounts of the polymers were dissolved in phenol at 333 K to give a concentration of approximately 10% in the solution. These solutions were added dropwise to an excess of methanol at 273 K, causing a rapid coprecipitation. The precipitate was filtered off and washed with methanol. The final precipitate was dried *in vacuo* for 48 h at 363 K.

Thermal analysis was performed using a Perkin-Elmer DSC-2C differential scanning calorimeter at a heating rate of 20 K/min. Sample weights were about 10 mg. A nitrogen flow was maintained through the sample chamber. An empty sample pan was used as reference. The glass transition temperature ( $T_g$ ) was determined as the intersection of the lower temperature specific heat and the transition region data. The crystallization temperature ( $T_c$ ) was considered to be the maximum of the exothermic peak of crystallization and the melting temperature ( $T_m$ ) that of the endothermic peak of fusion.

Samples with two different thermal histories were studied:

(a) Samples which have been quenched in dry ice/acetone (200 K) after melting at 523 K for 5 min were used in the study of the effects of quenching in the thermal behavior of the blends.

(b) Samples crystallized at 423 K for 10 min after melting at 523 K for 5 min were studied to verify the effect of the PBT crystallization on the blend behavior.

### RESULTS AND DISCUSSION

The thermodynamics of polymer mixtures have gained in interest during the last few years. However, complications inherent in the experimental determinations and theoretical treatments make it difficult to get well-defined conclusions. The introduction of a third component in the mixture com-

plicates the problem even further. Two aspects of ternary mixtures may be considered. In some polymer/polymer systems, stated to be immiscible from a thermodynamical point of view, the presence of a third component, either monomeric or polymeric can render the mixture compatible but not miscible. It is well known that considerable efforts are being made in the study of the compatibilizing effect caused by AB block copolymers in mixtures of two incompatible A and B homopolymers.<sup>23,24</sup> But, despite their unique and technologically useful physical properties, these materials are microphase-separated systems, where the emulsifying effect of the third component alleviates the very poor mechanical properties of most polymer blends. Consequently, this compatibilization effect, which is a consequence of the interfacial activity of block copolymers, does not attain a thermodynamically stable one-phase mixture.

The second problem in which our interest is focused is the true, thermodynamic miscibilization effect due to the third component. Some related problems have been recently reported in the literature dealing with this subject. For instance, the presence of a common solvent in a polymer/polymer mixture may be the cause of picturesque behavior. Casting of a blend from a solution in the common solvent is the simplest mixing procedure available and is widely practiced. However, the nature of the cast film when the solvent is removed strongly depends on the solvent used.<sup>25</sup> The classical example is the polystyrene/poly(vinyl methyl ether) system, which at temperatures below 373–393 K is a miscible blend. Films cast from toluene are single phase in the extended DSC experiments. However, the use of chloroform or other chlorine compounds give cloudy films. Apparently, the chloroform is capable of seriously modifying the interactions between polystyrene and poly(vinyl methyl ether), even at low concentrations. An opposite situation is the possibility of obtaining metastable miscible blends, when the common solvent is removed. Polystyrene and poly(methyl methacrylate) are two immiscible polymers which may be obtained in a metastable miscible state when a freeze drying process is carried out with a polystyrene/poly(methyl methacrylate)/naphthalene mixture.<sup>25</sup> The blend, annealed to allow equilibration at a given temperature, gives two glass transition temperatures, indicative of a situation of immiscibility. Recent interest<sup>26</sup> has been paid to mixtures of a random AB copolymer with a C homopolymer, in which C is immiscible with the A and B homopolymers and miscible with some compositions of the copolymer. This peculiar situation has been explained on the basis of the unfavorable intramolecular interactions between the A and B monomers in the copolymer chains. These unfavorable interactions are diluted by the addition of C homopolymer.

With the above-mentioned ideas in mind, it is possible to consider a system in which two immiscible polymers may be miscibilized by the presence of a third polymeric component miscible with each of these two immiscible polymers.

Polyarylate (PAr) is an amorphous thermoplastic polycondensate, with a high glass transition temperature, characterized by a remarkable toughness. However, the solvent resistance of this polymer is very poor. PAr is stable at its processing temperatures if dried.

Poly(butylene terephthalate) (PBT) is a fast-crystallizing thermoplastic polyester with a high melting point, excellent solvent resistance, but a low  $T_g$ ,

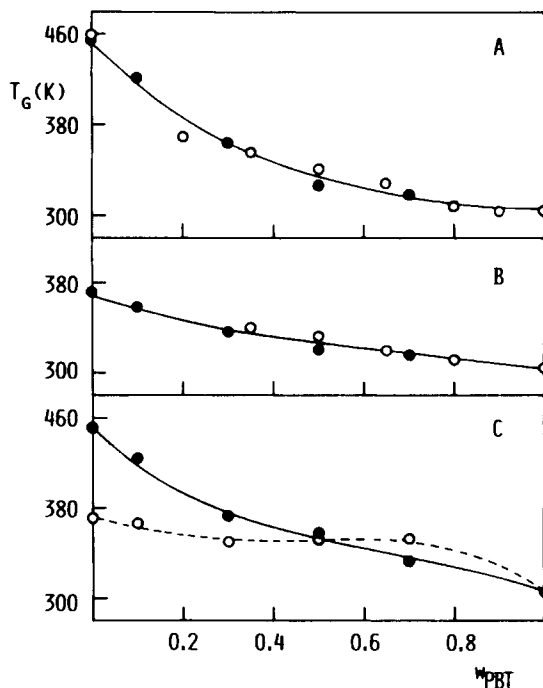


Fig. 1.  $T_g$ 's of the PAr/PBT and Phenoxy/PBT binary blends; (A)(●) PAr/PBT, quenched (this work); (○) PAr/PBT, Kimura et al.<sup>17</sup>; (B)(●) Phenoxy/PBT, quenched (this work); (○) Phenoxy/PBT (Robeson and Furtek)<sup>19</sup>; (C) (●) PAr/PBT isothermally crystallized; (○) Phenoxy/PBT isothermally crystallized.

which induces a noticeable decrease in some mechanical properties. Like other polyesters, it is unstable within the range of its processing temperatures.

The poly(hydroxy ether) from the condensation of bisphenol-A and epichlorohydrin (Phenoxy, Union Carbide) has been found to be miscible with a variety of polyesters. This miscibility is believed to be the result of specific interactions between the hydroxyl of Phenoxy (proton donor) and the carbonyl of the polyesters (proton acceptor).

As we previously pointed out, PBT is miscible with PAr and Phenoxy. Figures 1(A) and 1(B) show our results of the  $T_g$ -composition behavior in PAr/PBT and Phenoxy/PBT quenched binary blends, in conjunction with those obtained by Kimura and co-workers<sup>17</sup> and Robeson and Furtek,<sup>19</sup> in the same mixtures. In both cases, experimental results agree considerably and can be reproduced by means of the Gordon-Taylor equation<sup>27</sup> if we previously adjust the  $k$  semiempirical parameter. This parameter has to be 0.258 in the PAr/PBT blend and 0.471 in the case of Phenoxy/PBT mixture. Following Prud'homme and co-workers,<sup>28,29</sup> this Gordon-Taylor parameter can be considered as a measure of the interacting intensity of the blend components. The higher the parameter, the stronger the interaction. According to this criterium, interactions seem to be more pronounced in the Phenoxy/PBT case.

Another set of binary samples was prepared by allowing an isothermal crystallization of PBT at 423 K. This set was prepared in order to study the influence of the PBT crystallization on the miscibility of binary and ternary

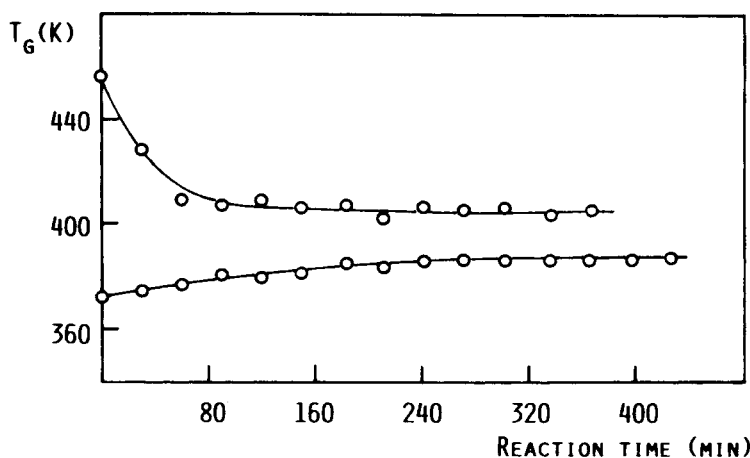


Fig. 2.  $T_g$ 's of the PAr/Phenoxy (50/50) blend vs. reaction time at 550 K.

blends. As a consequence of crystallization, PBT concentration in the amorphous phase decreases, altering the behavior of the blend. Figure 1(C) shows  $T_g$ -composition diagrams corresponding to PAr/PBT and Phenoxy/PBT blends, both isothermally crystallized. As predicted, the obtained  $T_g$  values are now higher than those of the quenched samples. The lower PBT concentration in the amorphous phase and mobility restrictions imposed by PBT crystallites are responsible for this behavior.

Despite the claimed capacity of the specific interactions between the Phenoxy hydroxyl group and ester groups for stabilizing polymer mixtures, PAr and Phenoxy are immiscible. DSC results showed two  $T_g$ 's in all the investigated compositions. The  $T_g$ 's were only slightly shifted with respect to those of the pure components. However, when the mixtures were heated at 550 K and different times, the two  $T_g$ 's grew closer, and a single glass transition appeared when the treatment was continued. Figure 2 shows the evolution of the  $T_g$ 's of the PAr/Phenoxy (50/50) blend vs. time at 550 K. A similar behavior was obtained with other blend compositions. This behavior seems to be a consequence of some type of interchange reactions. A second evidence of

TABLE I  
Solubility of PAr/Phenoxy (50/50) blend vs. time at 550 K

Time at 550 K (min)	Solubility (%)
0	100
30	98
60	76
90	64
120	68
150	42
210	28
240	20
270	24
360	19

the existence of interchange reactions can be inferred from the solubility tests carried out on the samples which have been subjected to different heating times. Mixtures without treatment are fully soluble in chloroform, and the solubility decreases with heating time. Table I shows the results for a 50/50 blend, as an example.

All phenomena here described seem to confirm the existence of interchange reactions between PAr and Phenoxy at 550 K. The most plausible idea is that, during heating, a mixture of a crosslinked copolymer, a branched copolymer, and the original polymers is generated. The interchange reaction should arise from an alcoholysis between the lateral hydroxyl groups of the Phenoxy and the ester groups of PAr. These interchange reactions are clearly influenced by the reaction temperature. For instance, after heating treatments at 523 K, DSC experiments on PAr/Phenoxy blends do not detect  $T_g$  changes up to 20 min, glass transition temperatures being 456 K ( $\pm 2$ ) (PAr) and 370 K ( $\pm 1$ ) (Phenoxy).

Similar transesterification reactions have been reported in both PAr/PBT<sup>17</sup> and Phenoxy/PBT<sup>19</sup> mixtures. Kimura and co-workers<sup>17</sup> have studied the transesterification process at 523 K in the case of PAr/PBT blends. As an important conclusion to our work, they found by  $T_g$ 's and intrinsic viscosities measurements that there is an induction time of about 100 min before the reaction proceeds. Robeson and Furtek<sup>19</sup> studied the transesterification reaction in Phenoxy/PBT blends by measuring the evolution of the relative torque in a Brabender at 523 K with time. In all the investigated mixtures, there is an induction time of about 8–12 min. Given that in our thermal treatments we have maintained the samples for 5 min at 523 K for melting PBT, the results resumed above allow us to discard the possible influence of the interchange reactions in the evolution of the  $T_g$ 's observed in our DSC experiments with ternary mixtures.

Figure 3 summarizes  $T_g$  values corresponding to the quenched PAr/Phenoxy/PBT ternary blends. Each part of the figure summarizes results with a constant PAr/Phenoxy ratio, showing the variation of the  $T_g$  with the PBT concentration. In all cases, at 0% PBT, i.e., in PAr/Phenoxy binary blends, two  $T_g$ 's appear, as a consequence of the above-mentioned immiscibility of this binary mixture. Incorporation of 10% PBT provokes a different behavior depending on the PAr/Phenoxy composition in the blend. In those of 75/25 and 50/50 ratios, two  $T_g$ 's are still observed, both lower than those appearing in the binary mixture. These transitions must correspond to two separated phases, one PAr/PBT and the other Phenoxy/PBT. In both cases it can be supposed that the incorporation of 10% PBT is incapable of miscibilizing PAr and Phenoxy. However, in the PAr/Phenoxy 25/75 ratio, the addition of 10% PBT gives a single glass transition which would indicate the presence of a unique phase constituted by the three polymers. At PBT contents higher than 30%, only one glass transition has been always observed, irrespective of the PAr/Phenoxy ratio in the blend. These results seem to confirm the PBT capacity in miscibilizing Phenoxy and PAr. However, this apparent conclusion must be considered with caution, as we will see later.

Scans of the quenched samples present an exotherm corresponding to the PBT crystallization during the scanning, followed by the melting endotherm. In general, the endotherm area is slightly higher than that of the crystalliza-

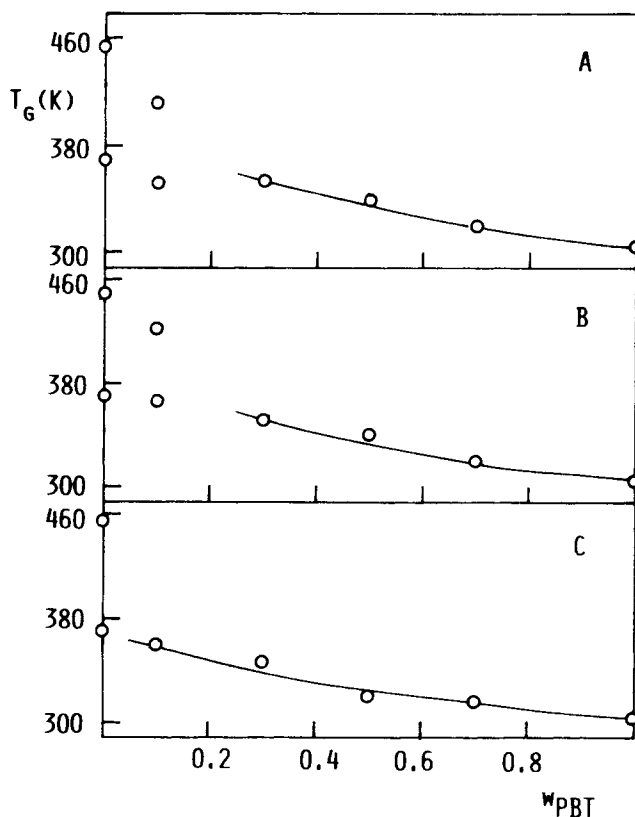


Fig. 3.  $T_g$ 's of the PAr/Phenoxy/PBT-quenched blends with different PAr/Phenoxy ratios: (A) 75/25; (B) 50/50; (C) 25/75.

tion exotherm. At 10% PBT contents, exotherm does not appear, but endotherm is still observed. Both experimental results seem to indicate that these quenched samples are not fully amorphous. Consequently, the reported  $T_g$  data may not be strictly correct.

The position of the crystallization peak depends on the mixture composition as can be seen in Figure 4. At constant PAr/Phenoxy ratio, this peak tends towards higher temperatures when the PBT percentage decreases. Similar behavior has been found by Kimura et al.<sup>17</sup> and Robeson and Furtek<sup>19</sup> for quenched PAr/PBT and Phenoxy/PBT blends, respectively. Nishi and Wang<sup>30</sup> have reported a similar variation in quenched poly(vinylidene fluoride)/poly(methyl methacrylate) blends. In our opinion, these results may be attributed to the increase in the glass transition temperature of the blend as the PBT percentage decreases. The higher the  $T_g$ , the lower the blend mobility, the PBT crystallization being hindered. For the same reason, at constant PBT percentage, the crystallization peak shifted to higher temperatures when PAr contents increased.

In the quenched samples, the PBT melting temperature is, in all cases, lower than that of the pure crystalline polymer (494 K), undergoing the same treatment. Within the experimental error, the melting temperatures encountered are independent, or nearly independent of the PBT concentration. The

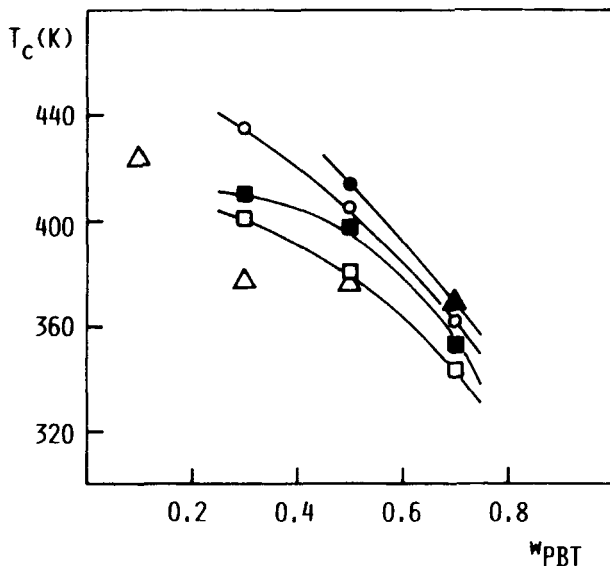


Fig. 4. Crystallization temperatures of PBT in PAr/Phenoxy/PBT blends with different PAr/Phenoxy ratios: (●) 100/0; (○) 75/25 (■) 50/50; (□) 25/75; (△) 0/100.

PAr/Phenoxy ratio has also a slight influence on the melting temperature. The results have been summarized in Table II, where an average temperature has been taken as representative for each PAr/Phenoxy ratio, irrespective of the PBT proportion.

In the isothermally crystallized mixtures, the PBT concentration in the amorphous phase decreases, altering the behavior of the ternary blends. Figure 5 summarizes the experimental results concerning the samples investigated. The main difference with the quenched samples is that the mixture 35/35/30 showed two  $T_g$ 's, whereas in the corresponding quenched blend only one  $T_g$  had been observed. This difference is a consequence of the segregation of the crystalline PBT, which reduces the PBT percentage in the amorphous phase. It is also interesting to point out that the  $T_g$ 's of these blends are nearly independent of the PAr/Phenoxy ratio. This is an unexpected result if we take into account the higher  $T_g$  of the polyarylate. A possible explanation arises from the decreasing of the mobility when the PAr percentage increases. Consequently, the PBT crystallization rate is lower, and, using identical crystallization times, the PBT contents in the amorphous phase is higher, compensating for the expected higher  $T_g$  because of the higher PAr concentra-

TABLE II  
Average PBT Melting Points in Ternary Blends at Different PAr/Phenoxy Ratios

PAr/Phenoxy ratio	PBT melting temperature (K)
100/0	491
75/25	489
50/50	488
25/75	492
0/100	492



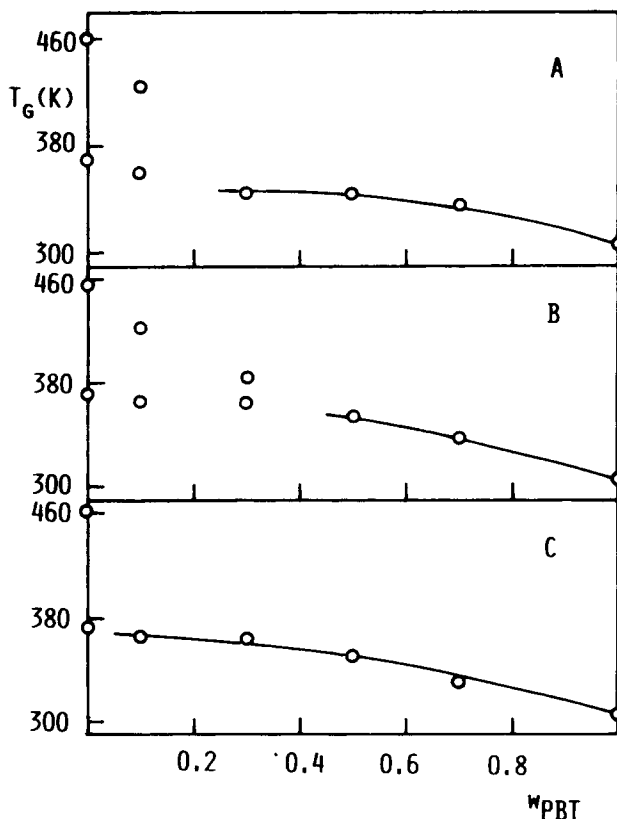


Fig. 5.  $T_g$ 's of the PAr/Phenoxy/PBT blends isothermally crystallized, at different PAr/Phenoxy ratios: (A) 75/25; (B) 50/50; (C) 25/75.

tion. Finally, the melting behavior of the isothermally crystallized samples is more complicated than in the quenched ones. Depending on the composition, two or three melting peaks may be observed. Similar behaviors have also been reported in pure crystalline polymers and blends.<sup>31-34</sup> The explanation of these results has usually been given on the basis of melting-recrystallization processes, secondary crystallization, etc. But the clarification of these aspects implies a deeper study of the influence that factors such as crystallization time and temperature heating rate, etc., have on both the position and the area of the different endotherms.

Apart from the phenomenological results summarized above, an important and basic question arises from the  $T_g$  behavior in ternary blends: is the PBT capable of miscibilizing, thermodynamically speaking, the two-phase PAr/Phenoxy mixture? In other words, is it possible to have some concentrations where the ternary mixture coexists in a single stable phase? We think that calorimetric data, as presented here, must be considered with caution. A single inspection, for instance, of Figures 1 and 3 shows that in the region where ternary blends exhibit one glass transition, binary mixtures have two close  $T_g$ 's. It is well known that even in binary mixtures there are some problems associated with the  $T_g$  test for miscibility. In practice, one may anticipate

problems if the  $T_g$ 's lie within 20 K or less of each other. The problem may be somewhat alleviated by the use of the differential representation  $dC_p/dT$  vs.  $T$ ; but insufficient evidence is as yet available regarding this point. Other traditional experimental criteria, such as film clarity, becomes invalid in this case, given the difficulties encountered in obtaining appropriate films. We also think that this is the case of another ternary system reported in the literature,<sup>21</sup> that constituted by poly(vinylidene fluoride), poly(methyl methacrylate), and poly(ethyl methacrylate). Poly(vinylidene fluoride) is a crystalline polymer, miscible separately with the two acrylic polymers which, in turn, are immiscible. A close inspection of Kwei and co-workers' data<sup>21</sup> shows that ternary mixtures exhibited only one  $T_g$  in concentrations where binary  $T_g$ -composition diagrams presented close glass transition temperatures. No data were reported about the clarity of the films.

In conclusion, it is our opinion that the miscibilization of an immiscible blend in a common polymeric "solvent" is an objective that is more difficult to attain than in the case of a homologous solvent. Moreover, as pointed out by Pfenning et al.<sup>35</sup> the small contribution of combinatorial entropy to the free energy of mixing in a polymeric ternary mixture precludes, in general, the miscibility observed in a low molecular weight version of the same mixture.

This research was supported by the U.S.-Spanish Joint Committee for Scientific and Technological Cooperation (Grant Register Number CCB8401071).

## References

1. G. Salee, U. S. Pat. 4,221,694 (1980).
2. K. Hazama, Y. Asai, and K. Yasue, Jpn. Kokai, 7534, 342 (1975).
3. M. L. Doerr (to Fiber Industries), U. S. Pat. 3,752,866 (1973).
4. K. Sakai, S. Matsunaku, and S. Masuda, Jpn. Pat. 78, 255 (1973).
5. L. M. Robeson and M. Matzner (to Union Carbide Corporation), Eur. Pat. EP 73,067 (1983).
6. Union Carbide Corp., Jpn. Kokai Tokkyo Koho JP 5807, 445, (1983).
7. C. A. Cruz, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **24**, 2101 (1979).
8. C. A. Cruz, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **24**, 2399 (1979).
9. C. A. Cruz, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **25**, 1549 (1980).
10. J. J. Ziska, J. W. Barlow, and D. R. Paul, *Polymer*, **22**, 918 (1981).
11. J. E. Harris, S. H. Goh, D. R. Paul, and J. W. Barlow, *J. Appl. Polym. Sci.*, **27**, 839 (1982).
12. R. E. Prud'homme, *Polym. Eng. Sci.*, **22**, 1138 (1982).
13. E. M. Woo, J. W. Barlow, and D. R. Paul, *J. Appl. Polym. Sci.*, **28**, 1347 (1983).
14. M. Aubin and R. E. Prud'homme, *Polym. Eng. Sci.*, **24**, 350 (1984).
15. D. Allard and R. E. Prud'homme, *J. Appl. Polym. Sci.*, **27**, 559 (1982).
16. C. A. Cruz, J. W. Barlow, and D. R. Paul, *Macromolecules*, **12**, 726 (1979).
17. M. Kimura, R. S. Porter, and G. Salee, *J. Polym. Sci., Polym. Phys. Ed.*, **21**, 367 (1983).
18. L. M. Robeson, W. F. Hale, and C. N. Merriam, *Macromolecules*, **14**, 1644 (1981).
19. L. M. Robeson and A. B. Furtek, *J. Appl. Polym. Sci.*, **23**, 645 (1979).
20. J. J. Iruin, J. I. Eguiazabal, M. E. Calahorra, and M. Cortazar, Proceedings of the International Symposium on Polymer Alloys: Structure and Properties, Brugge, Belgium, June, 1984.
21. T. K. Kwei, H. L. Frish, W. Radigan, and S. Vogel, *Macromolecules*, **10**, 157 (1977).
22. O. Olabisi, L. M. Robeson, and M. T. Shaw, *Polymer-Polymer Miscibility*, Academic, New York, 1979.
23. R. Fayt, R. Jerome, and Ph. Teyssie, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 2209 (1982).
24. D. J. Meier, in *Polymer Blends and Mixtures*, D. J. Walsh, J. S. Higgins, and A. Maconnachie, Eds., NATO ASI Series, Applied Sciences No. 89, Nijhoff, Boston, 1985.

25. M. T. Shaw, in *Polymer Blends and Mixtures*, D. J. Walsh, J. S. Higgins, and A. Maconnachie, Eds., NATO ASI Series, Applied Sciences No. 89, Nijhoff, Boston, 1985.
26. G. ten Brinke, F. E. Karasz, and W. J. MacKnight, *Macromolecules*, **16**, 1827 (1983).
27. M. Gordon and J. S. Taylor, *J. Appl. Chem.*, **2**, 493 (1952).
28. G. Belorgey, M. Aubin, and R. E. Prud'homme, *Polymer*, **23**, 1051 (1982).
29. G. Belorgey and R. E. Prud'homme, *J. Polym. Sci., Polym. Phys. Ed.*, **20**, 191 (1982).
30. T. Nishi and T. T. Wang, *Macromolecules*, **8**, 909 (1975).
31. R. Groeninckx, H. Reynaers, H. Berghmans, and G. Smets, *J. Polym. Sci., Polym. Phys. Ed.*, **18**, 1311 (1980).
32. P. J. Lemstra, T. Kooistra, and G. Challa, *J. Polym. Sci., Part A-2*, **10**, 823 (1972).
33. A. Eshuis, E. Roerdink, and G. Challa, *Polymer*, **23**, 735 (1982).
34. J. Plans, W. J. MacKnight, and F. E. Karasz, *Macromolecules*, **17**, 810 (1984).
35. J. L. G. Pfenning, H. Keskkula, J. W. Barlow, and D. R. Paul, *Macromolecules*, **18**, 1937 (1985).

Received February 28, 1986

Accepted March 3, 1986