Polymer Bulletin 29, 415–422 (1992)

Polymer Bulletin

Crystallization and melting behaviour of poly(butylene terephthalate) in poly(butylene terephthalate)/polyarylate blends

M. Cortázar, J. J. Iruin, and J. I. Eguiazábal*

Dpto. de Ciencia y Tecnología de Polímeros, Facultad de Química, UPV/EHU P.O. Box 1072, San Sebastian, Spain

Summary

The crystallization and melting behaviour of poly(butylene terephthalate) has been studied in the pure state and in its blends with a polyarylate of bisphenol A and isophthalic/terephthalic acids. Differential scanning calorimetry has been used as experimental technique and the effects of different thermal treatments have been analyzed. Results show the hindrance for the crystallization of poly(butylene terephthalate) imposed by the presence of polyarylate, as well as the existence of multiple melting after isothermal crystallization. Explanations are given for the observed behaviours.

Introduction

Polymer blends are at the present time an important investigation field in polymer science, because they provide an useful way for the development of new polymeric materials.

Among the different aspects to be studied concerning polymer blends, those related to their thermal behaviour are very important, as they determine in a great extent the processing and properties of the blends. This is particularly true in the case of systems containing a crystallizable polymer. In this case, those effects related to the amorphous-crystalline nature of the blends determine the mechanical properties and are greatly influenced by the processing conditions.

Blends composed of poly(butylene terephthalate) (PBT) and a polyarylate of bisphenol A and 50/50 isophthalic/terephthalic acids (PAr) have been recognized as miscible in the whole compositional range (1,2). As PBT is a semicrystalline polymer, while PAr is amorphous, some effect of PAr on the crystallization-melting behaviour of PBT may be expected. It has been reported recently (3) that the spherulitic grow rate of PBT decreases when this polymer is blended with a polyarylate of bisphenol A and isophthalic acid/terephthalic acid (75/25).

It has been reported (4-8) that PBT shows a multiple melting behaviour after different thermal treatments. Generally (4,6-8) two melting endotherms are found although Marrs et al. (5) found up to four endotherms depending on the crystallization temperature. Different explanations are given for the origin of the multiple endotherms observed.

In this work we have studied the crystallization-melting behaviour of PBT in blends with PAr at different compositions, using differential scanning calorimetry (DSC) as experimental technique. Several thermal treatments have been applied to the samples, which give rise to different crystallization-melting behaviours.

Experimental

The polymers used in this work were commercial products. PBT was a product from Polysciences (cat. N. 6511) and had a viscosity average molecular weight M_v=32,000, determined at 25°C in a phenol/tetrachloroethane mixture (60/40 by weight). PAr was Arilef U-100 and was kindly supplied by Solvay. Its average molecular weights determined by GPC in THF at 30°C were M_n=21,500 and M_w=51,400.

PBT/PAr blends in 100/0, 90/10, 70/30 and 50/50 compositions were prepared by solution/precipitation in phenol/methanol, as has been described in previous papers (2).

---

*Corresponding author

All the thermal treatments on the samples, as well as the calorimetric scans, were carried out in a PERKIN-ELMER DSC-2 differential scanning calorimeter equipped with a PERKIN-ELMER TADS 3700 system. The thermal treatments were carried out after melting for 5 min at 523 K. With these melting conditions, no transesterification reactions take place, as it has been reported by Porter et al. (1). The heating rate during the scans was 20 K/min, except when the effect of this parameter on the melting endotherms was studied. A nitrogen flow was maintained through the sample and reference chambers. The temperature and the enthalpy were calibrated with reference to indium and tin standards. The crystallization and melting temperatures were measured at the maxima of the corresponding peaks.

Results and Discussion

Our first study on the crystallization-melting behaviour of PBT and of the blends was that concerning their non-isothermal crystallization from the melt. Non-isothermal crystallization was carried out at a cooling rate of 10 K/min. After non-isothermal crystallization, a heating scan was carried out up to 523 K to study the melting behaviour of PBT.

In Figure 1 we show the crystallization temperatures from the melt, which decrease as the PBT content in the blends decreases. This variation is accompanied by a widening of the crystallization peaks, as observed in Figure 2. Both phenomena indicate the difficulties for the PBT crystallization as a consequence of the presence of PAr, as would be expected given the miscibility of the blends.

During the heating scan, pure PBT and PBT/PAr blends showed a melting endotherm with one or two shoulders, a first indication of the existence of a multiple melting behaviour. The melting temperatures measured at the maxima of the main endotherms for the different compositions are also represented in Figure 1. A decrease of the melting temperature with the increase of the PAr content in the blends is observed. This behaviour is different from that found by Porter et al. (1) who observed a constant melting temperature irrespective of the blend composition. This difference may be possibly due to the different thermal treatments applied to the samples in both works.

In Figure 3 we show the melting heat of PBT in PBT/PAr blends as a function of composition. As it is observed, the values obtained are near the linear relationship between the values of the pure components. This indicates a small influence of PAr on the final crystallinity level of PBT and dissagrees with the results obtained by Porter et al. (1). These authors observed increased crystallinity levels in PBT-rich PBT/PAr blends. The different behaviours may be attributed once again to the different thermal treatments applied to the blends.

Our second study was that concerning the isothermal crystallization of the blends from the melt state. This crystallization was carried out primarily at 460 K. In Table I we show the

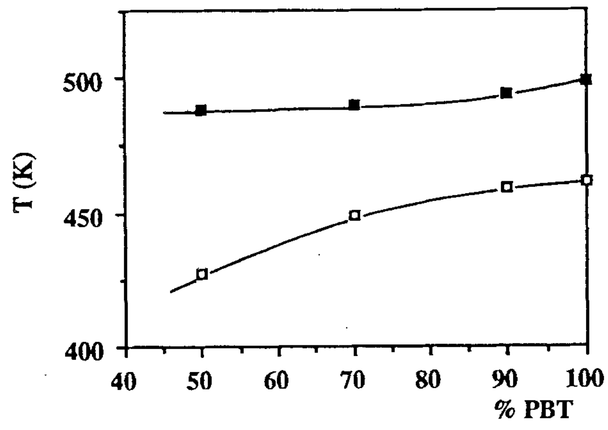

Figure 1.- Crystallization temperatures during cooling (☐) and melting temperatures in the second heating scan (■) for PBT/PAr blends.

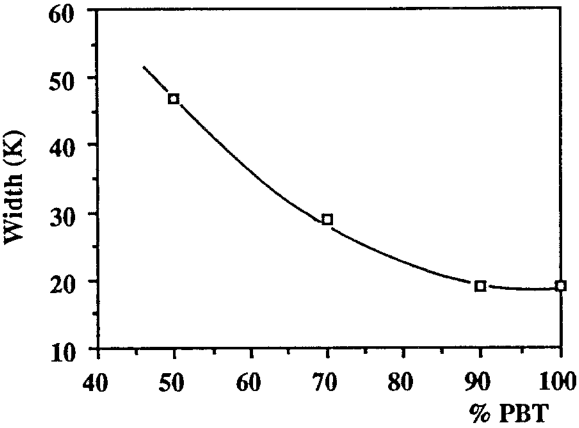

Figure 2.- Width of the crystallization exotherm during cooling of PBT/PAr blends.

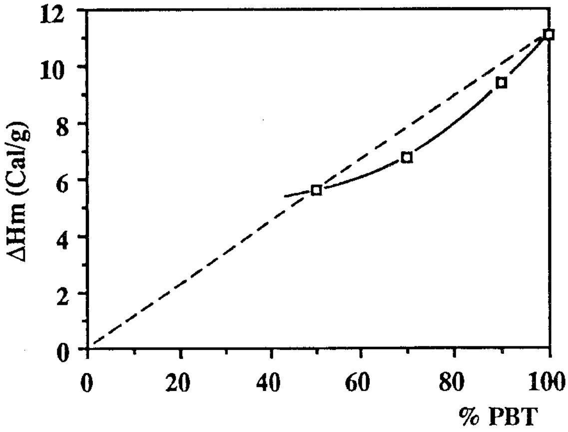

Figure 3.- Melting heat of PBT in PBT/PAr blends.

Table I.- Times at the maxima of the crystallization exotherms of PBT/PAr blends. (Crystallization temperature: 460 K).

Composition (PBT/PAr)	Time (sec)
100/0	27.0
90/10	37.5
70/30	124.5
50/50	375.0

times corresponding to the maxima of the crystallization exotherms. As it is observed, a clear increase of this parameter takes place as the PAr content in the blends increases. This clearly indicates that PAr retards the PBT crystallization from the melt, in good agreement with the results obtained by Runt et al. (3).

Figure 4 shows the melting endotherms of pure PBT and of this polymer in the blends after isothermal crystallization for 10 min at 460 K. As it is observed, three endotherms appear.

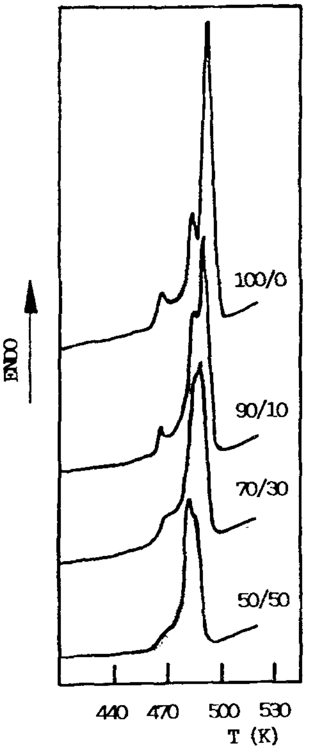

Figure 4.- Melting endotherms of PBT/PAr blends crystallized at 460 K.

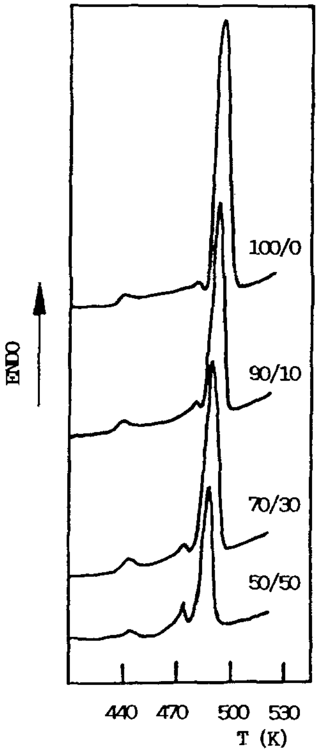

Figure 5.- Melting endotherms of PBT/PAr blends crystallized at 430 K.

These endotherms will be called endotherms I, II and III from lower to higher temperature. An overlapping of the endotherms is observed in some cases. This behaviour is similar to that observed by several authors for poly(ethylene terephthalate) (9,10) and may be related to that observed by Marrs et al. (5) for PBT and for tetramethylene terephthalate-tetramethylene sebacate copolymers. However, the behaviour observed for the pure crystalline polymer is somewhat different in our work and in that of Marrs et al. On the other hand, the three endotherms observed dissagree with the results obtained in other works carried out on the melting of isothermally crystallized PBT, in which only two endotherms were observed (7). In the works on poly(ethylene terephthalate) the three melting endotherms were attributed (9,10) to the melting of crystals formed by a secondary crystallization process (endotherm I), to the melting of crystals grown by normal primary crystallization (endotherm II) and to the melting of crystals formed by a recrystallization process during the DSC scan (endotherm III). In the work of Marrs et al., endotherm II and III are explained on the basis of the same melting-recrystallization processes, while it is suggested that endotherm I corresponds to the melting of crystals of low molecular weight polymer, formed by a fractionation process during crystallization.

As it is also observed in Figure 4, the three melting endotherms are affected by the blend composition. In pure PBT the lower endotherm (I) appears approximately 10 K above the crystallization temperature. Endotherm II appears at 486 K and finally, endotherm III is observed at 496 K. $T_{m,\,I}$ shows a small increase as the PAr content in the blend increases. However, this variation cannot be considered representative because endotherm I overlaps with endotherm II in the 70/30 and 50/50 compositions of PBT/PAr blends and this may affect the position of the maximum of the first endotherm.

The peak temperature of endotherm II is approximately 486 K irrespective of the blend composition except in the 70/30 blend in which it appears as a shoulder and cannot be

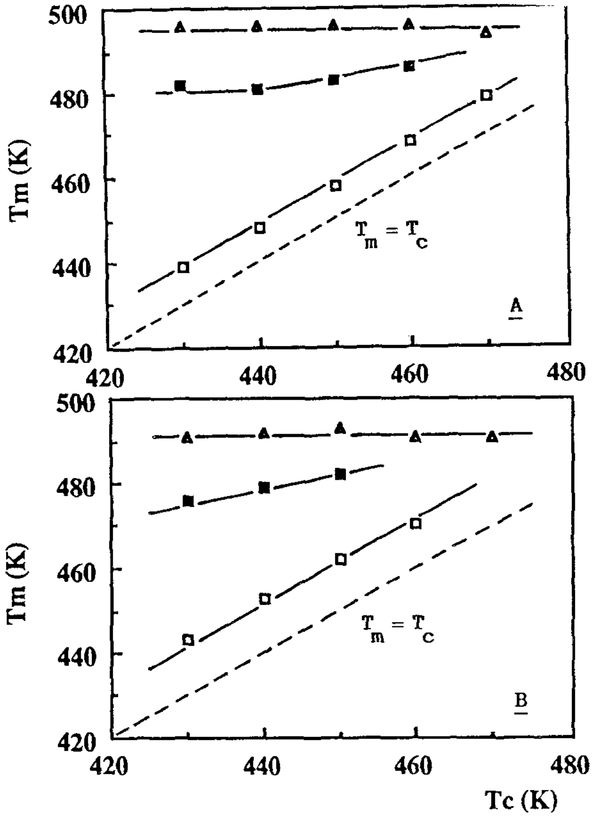

Figure 6.- Melting temperatures of PBT (A) and of the PBT/PAr (70/30) blend (B) as a function of crystallization temperature.

accurately determined. Finally, endotherm III tends to lower temperatures as the PAr content in the blends increases. All these results seem to indicate that PAr does not affect the perfection of the PBT crystals which give rise to endotherm II, while the crystals which melt at the higher temperatures are less perfect at high PAr contents in the blends.

Although the melting heats of the different endotherms cannot be calculated due to their overlapping, a qualitative comparison of the areas of the endotherms can be made readily. Thus, no clear effect of the blend composition on the area of endotherm I can be found. However, it clearly appears that the area of endotherm II increases with respect to that of endotherm III as the PAr content in the blends increases. This observation may be explained if we suppose that endotherm II corresponds to crystals formed during isothermal crystallization while endotherm III is due to the melting of crystals formed by recrystallization during the DSC scan. PAr makes difficult the recrystallization of PBT and this effect is more pronounced the higher the PAr content. Thus, the higher the PAr content, the smaller the PBT fraction which undergoes recrystallization during the scan.

Isothermal crystallization was also carried out in a range of temperatures, from 430 K to 470 K. As an example, Figure 5 shows the melting endotherms obtained after crystallization at 430 K for 10 min. Intermediate crystallization temperatures give rise to intermediate results. It can be observed in Figure 5 that a small endotherm (endotherm I) appears at approximately 440 K (once again 10 K above the crystallization temperature). On the other hand, endotherms II and III are also observed. The effect of the blend composition on the melting endotherms is similar to that found after crystallization at 460 K, i. e., the area of the

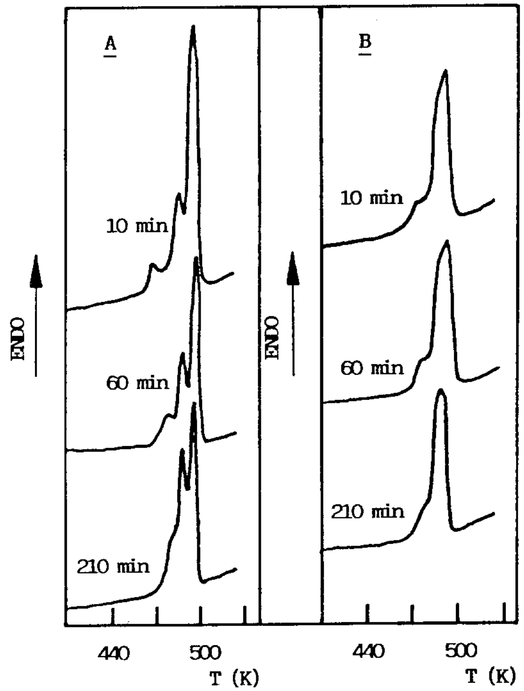

Figure 7.- Effect of crystallization time on the melting endotherms of PBT (A) and of the PBT/PAr (70/30) blend (B).

intermediate endotherm increases with respect to that of the high-temperature endotherm as the PAr content in the blends increases. However, several differences exist between the results obtained at 430 K and at 460 K. First, in pure PBT, a small exothermic response seems to appear between endotherms II and III after crystallization at 430 K. This observation is similar to others in the literature (5,6) and would substantiate the above mentioned explanation for the multiple melting behaviour of PBT, i. e., endotherm II corresponds to the melting of crystals obtained after isothermal crystallization while endotherm III corresponds to crystals formed by recrystallization during the calorimetric scan. The exothermic response should thus correspond to this recrystallization of the original PBT crystals.

Another interesting difference between the calorimetric behaviours observed in Figures 4 and 5 is the fact that the ratio $\mathrm{Area}_{II}/\mathrm{Area}_{III}$ is clearly higher at higher crystallization temperature.

If the melting-recrystallization mechanism is accepted, this result would indicate that the PBT fraction which undergoes recrystallization during the scan is greater the lower the crystallization temperature, as would be expected taking into account that the isothermally formed crystals are less perfect after crystallization at lower temperatures.

In Figure 6 we show the variation of the three melting temperatures of PBT in the pure polymer and in the PBT/PAr (70/30) blend as a function of the crystallization temperature. As it is observed the difference between the peak temperature of endotherm I and the crystallization temperature is approximately constant in each case. As far as endotherm II is concerned, it appears approximately at the same temperature for PBT and for the 70/30 blend after crystallization at the same temperature. This indicates that the presence of PAr does not affect the perfection of the crystals obtained by isothermal crystallization. Finally, endotherm III appears at a temperature which is approximately independent of the crystallization temperature for each composition, indicating that the crystallization temperature does not

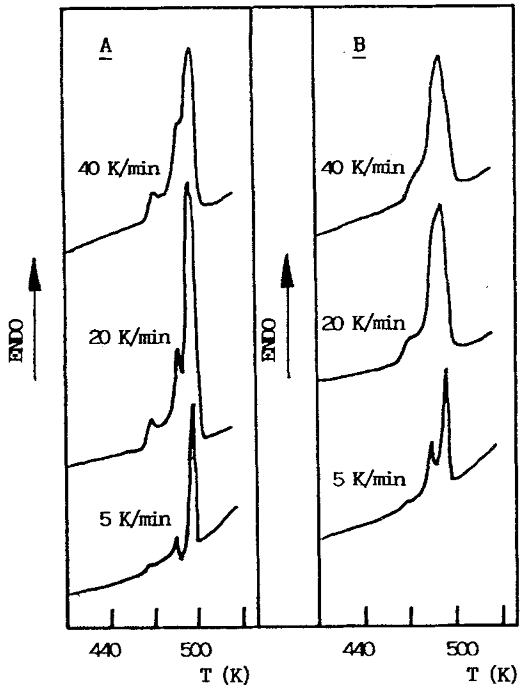

Figure 8.- Effect of heating rate on the melting endotherms of PBT (A) and of the PBT/PAr (70/30) blend (B).

affect the perfection of the corresponding crystals. However, the melting point of endotherm III for pure PBT is higher than that in the blends. Once again, if the melting-recrystallization mechanism is accepted, it appears that PAr makes difficult the recrystallization of PBT, and hence, less perfect crystals are obtained in the blends.

The existence of melting-recrystallization phenomena during the DSC scans carried out on PBT and on PBT/PAr blends can be confirmed by studying the effect of the crystallization time and of the heating rate on the different melting endotherms. In Figure 7 we show the effect of crystallization time on the endotherms of PBT and of the PBT/PAr (70/30) blend crystallized at 460 K. The other compositions studied show intermediate behaviours. Several features are evident from Figure 7. First, the lower endotherm appears at a higher temperature the higher is the crystallization time, and becomes a shoulder on endotherm II. This indicates that crystals formed by secondary crystallization are more perfect at higher crystallization times. Moreover, we can observe that, the higher the crystallization time, the greater the area of endotherm II with respect to that of endotherm III in the case of PBT. This indicates that recrystallization is less favoured at high crystallization times. This behaviour coincides with that observed for poly(ethylene terephthalate) (10). There is not practically effect of the crystallization time on the melting temperatures of endotherms II and III in the case of pure PBT, a behaviour which is coincident with that observed for PET (10).

In the case of the PBT/PAr (70/30) blend, the effect of the crystallization time on the melting endotherms is much less clear due to the overlapping which is observed in Figure 7. However, a tendency similar to that explained for pure PBT seems to appear.

Finally, in Figure 8 we have represented the effect of heating rate on the melting behaviour. The more interesting effect of this parameter is that concerning endotherms II and III. As it is observed in Figure 8, the higher the heating rate, the greater the ratio $\mathrm{Area}_{II}/\mathrm{Area}_{III}$. This effect is evident in all compositions studied, in spite of the overlapping of the endotherms which exists in some compositions at high heating rate. These effects support the explanation of melting-recrystallization phenomena during the DSC scans as responsible for the appearance of endotherms II and III. The reason is that the higher the heating rate, the smaller the time available for recrystallization, and this causes the decrease in the area of endotherm III with respect to that of endotherm II. The effect seems to be more important in the case of the 70/30 blend, possibly due to the negative effect of PAr on the recrystallization of PBT.

The results reported in this work show the existence of an important effect of PAr on the crystallization-melting behaviour of PBT when PBT/PAr blends are subjected to different thermal treatments. This effect should be due to the thermodynamic interaction between both polymers and also to kinetic effects present in the blends. It is also observed that three melting endotherms exist after isothermal crystallization, which are due to secondary crystallization and to melting-recrystallization phenomena.

Acknowledgements: This work has been supported by the CICYT (Project n. MAT 89/0187) and the Gipuzkoako Foru Aldundia.

References

1. Kimura, M., Porter, R. S. and Salee, G. (1983) J. Polym. Sci., Polym. Phys. Ed., **21**: 367
2. Eguiazabal, J. I., Iruin, J. J., Cortazar, M. and M. Guzman, G. (1986) J. Appl. Polym. Sci., **32**: 5945
3.- Runt J., Miley, D. M., Zahng, X., Gallagher, K. P., McFeaters, K. and Fishburn, J. (1992) Macromolecules, **25**: 1929
4. Hobbs, S. Y. and Pratt, C. F. (1975) Polymer, **16**: 462
5. Marrs, W., Peters, R. H. and Still, R. H. (1979) J. Appl. Polym. Sci., **23**: 1077
6. Ludwig, H.- J. and Eyerer, P. (1988) Polym. Eng. Sci., **28**: 143
7. Yeh, J. T. and Runt, J. (1989) J. Polym. Sci., Polym. Phys. Ed., **27**: 1543
8. Cheng, S. Z. D., Pan, R. and Wunderlich, B. (1988) Makromol. Chem., **189**: 2443
9. Zhou, C. and Clough, S. (1988) Polym. Eng. Sci., **28**: 69
10. Eguiazabal, J. I., Cortazar, M. and Iruin, J. J. (1991) J. Appl. Polym. Sci., **42**: 489

Accepted August 12, 1992 C