

Poly(ethylene Terephthalate)/Polyarylate Blends: Influence of Interchange Reactions on the Melting Behavior of Poly(ethylene Terephthalate)*

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SYNOPSIS

The influence of the interchange reactions of poly(ethylene terephthalate) (PET)/polyarylate (PAr) blends on the melting behavior of isothermally crystallized PET has been studied. PET shows three melting endotherms in the pure state and also when mixed with PAr. These endotherms are explained in terms of primary and secondary crystallization processes as well as recrystallization during the calorimetric scan. It is also shown that interchange reactions hinder the crystallization processes of PET.

INTRODUCTION

Much work has been devoted in the literature to the explanation of the melting behavior of poly(ethylene terephthalate) (PET) isothermally crystallized from the melt state.^{1–11} Depending on the authors, two or three melting endotherms were found, and they were explained in terms of primary and secondary crystallization processes and recrystallization during the scan. Different polymers, such as isotactic polystyrene,^{12,13} isotactic poly(propylene oxide),¹⁴ nylon 8,¹⁵ and PET itself¹¹ have shown the existence of three melting transitions during heating subsequent to isothermal crystallization. In all cases, it is assumed that the lower temperature endotherm observed in the DSC analysis corresponds to the melting of crystals formed by a secondary crystallization process, while the intermediate endotherm reflects the melting of crystals grown by normal primary crystallization. Finally, the higher temperature endotherm corresponds to crystals formed by a reorganization process during the DSC scan.

The mixtures composed of PET and a polyarylate of bisphenol A and 50/50 isophthalic and terephthalic acids (PAr) have been studied^{16–18} and recognized as miscible or partially miscible depending on the blend composition. Mixtures with a PAr content equal to or lower than 70% showed partial miscibility.

The PET/PAr mixtures have an additional and very interesting feature, such as the occurrence of interchange reactions between functional groups of both polymers when they are exposed to high temperatures.^{16–18} In this work we have studied the influence of the interchange reactions on the melting behavior of isothermally crystallized PET.

EXPERIMENTAL

The polymers used in this work were poly(ethylene terephthalate) (PET) from Polysciences (cat. n. 4301) and polyarylate (PAr), Arilef U-100 from SOLVAY, a copolyester of bisphenol A and 50/50 isophthalic/terephthalic acids. The characterization data of the polymers are given in Table I and were obtained by means of viscometry in the case of PET and by GPC in the case of PAr. A PET/PAr (80/20) blend was prepared by the procedure previously described.¹⁸ Pure PET was exposed to the same treatment.

* Dedicated to Professor Gonzalo Martín Guzmán on the occasion of his nomination as Emeritus Professor of the University of the Basque Country.

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Table I Characterization Data for Poly(ethylene Terephthalate) and Polyarylate

	\bar{M}_n	\bar{M}_w	\bar{M}_v
Poly(ethylene terephthalate)	—	—	18,000
Polyarylate	21,500	51,400	—

All the isothermal crystallizations as well as the calorimetric scans were carried out in a Perkin-Elmer DSC-2 calorimeter. The crystallizations were carried out after melting for 15 min at 570 K. TGA and DSC data indicated that no appreciable degradation that would affect the crystallization and melting of PET occurs in these conditions. The heating rate during the scans was 20 K/min, except when the influence of this parameter on the melting behavior of PET was investigated.

The interchange reactions during the melting of the mixture were investigated by NMR, with a Varian VXR 300 spectrometer at room temperature. The chloroform-insoluble fractions of the mixture before and after melting were studied using a mixture of deuterated chloroform and deuterated trifluoroacetic acid as a solvent. Tetramethylsilane was the internal reference standard.

RESULTS AND DISCUSSION

Figure 1 shows the 8- to 9-ppm region of the NMR spectra of the chloroform-insoluble fractions of the PET/PAr (80/20) mixture before and after melting 15 min at 570 K. As could be expected, the spectrum of the untreated sample in the represented region only shows the signal corresponding to the terephthalate protons of poly(ethylene terephthalate),

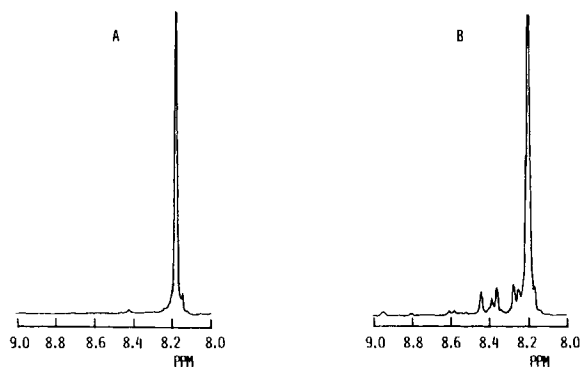
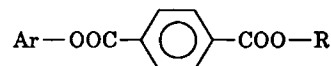


Figure 1 ^1H -NMR spectra of the chloroform-insoluble fractions of the PET/PAr (80/20) blend (a) without thermal treatment and (b) after 15 min at 570 K.

which appears at 8.18 δ . On the contrary, the spectrum of the chloroform-insoluble fraction of the sample treated at 570 K shows several new signals that appear at 8.26 and 8.38 ppm, and also at 8.44 ppm. This last signal can be attributed to the aromatic protons of the terephthalate units of polyarylate, whereas the signals at 8.26 and 8.38 ppm can be attributed to the aromatic protons of the terephthalate unit asymmetrically substituted, i.e., to the structure



which is formed as a consequence of the interchange reactions.^{19,20}

The interchange reactions affect the melting behavior of PET, as we shall see. This influence should be due to the inclusion of PAr segments in PET chains, which is demonstrated by means of NMR analysis, and hinders PET crystallization, and produces less perfectly formed crystals.

Figure 2 shows the melting endotherms of PET after isothermal crystallization for a period of 10 min at different temperatures. It can be observed that three melting endotherms appear generally in pure PET as well as in the PET/PAr (80/20) mixture. The three endotherms will be called, respec-

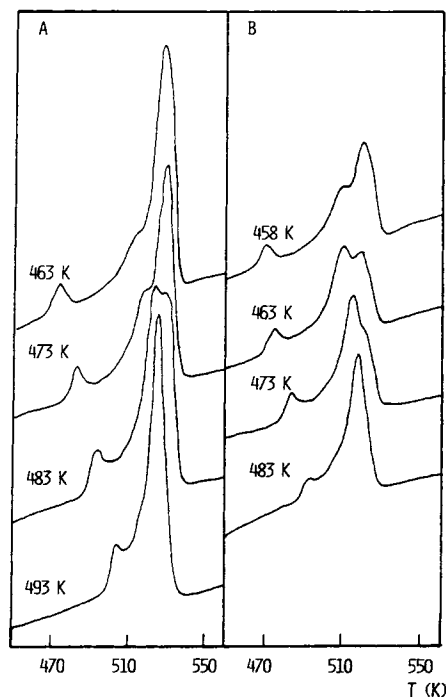


Figure 2 Melting endotherms of (a) pure PET and (b) of the PET/PAr (80/20) blend after isothermal crystallization at different temperatures.

tively, from lower to higher peak temperature, I, II, and III. As can be seen in Figure 3, endotherm I appears at a temperature that is approximately 10 K higher than the crystallization temperature and is attributed to the melting of crystals grown during a secondary crystallization process.¹¹ No influence of the presence of PAr on this endotherm is seen from the thermograms obtained. The two other endotherms show a different behavior with the crystallization temperature. The melting temperature of endotherm II follows a linear relationship with T_c (Fig. 3). $T_{m,II}$ is higher in pure PET than in the mixture. This seems to indicate that more perfect crystals are obtained during isothermal crystallization of the pure crystalline polymer, i.e., PAr hinders the PET crystallization as a consequence of interchange reactions.

The extrapolation of the T_m-T_c relationships to the line $T_m = T_c$ to obtain the equilibrium melting temperature gives $T_m^o = 542$ K for pure PET and $T_m^o = 538$ K for PET in the mixture. The slopes of the $T_m - T_c$ representations are 0.391 and 0.386, respectively. According to Nishi and Wang²¹ the slope of the T_m-T_c relationships is related to the stability of the crystals generated during isothermal crystallization. Thus, the values obtained indicate that the stability of crystals is similar in pure PET and in the mixture.

The values of T_m^o and of the slope obtained for pure PET are in very good agreement with those obtained by Zhou and Clough.¹¹ The differences between pure PET and the same polymer in the 80/20 mixture indicate once again that PAr hinders PET crystallization.

The peak temperature of the higher melting endotherm (III) remains constant with the crystallization temperature, as can be seen in Figure 3, indicating that the crystals that give rise to this en-

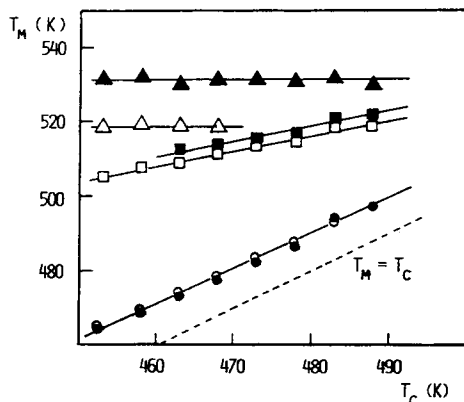


Figure 3 T_m versus T_c for PET (solid symbols) and PET/PAr (80/20) blend (open symbols).

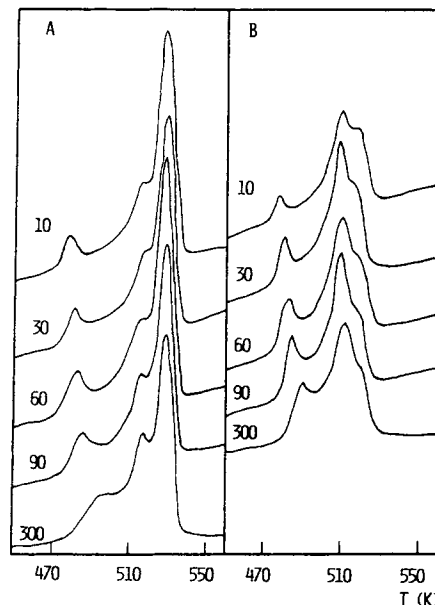


Figure 4 Melting endotherms of (a) pure PET and (b) of the PET/PAr (80/20) blend crystallized at 468 K, as a function of crystallization time in minutes.

dotherm are independent of those formed during the isothermal crystallization. This endotherm is attributed to the melting of crystals grown and improved during the calorimetric scan by means of a recrystallization process.¹¹ Although $T_{m,III}$ is constant with the crystallization temperature, its value is 18 K lower in the blend than in the pure crystalline polymer. This indicates that the recrystallization during the scan is hindered by PAr and gives rise to less perfect crystals with respect to pure PET.

The melting heats corresponding to each endotherm cannot be adequately determined because of the overlapping of the endotherms, as can be seen in Figure 2. However, a qualitative comparison between the pure crystalline polymer and PET in the mixture can be made from the traces shown in Figure 2. Thus, no clear influence of the crystallization temperature or of the presence of PAr on the endotherm I can be distinguished. As far as the areas of endotherms II and III are concerned, it clearly appears that the higher the crystallization temperature, the greater the area corresponding to endotherm II with respect to that of endotherm III, i.e., the greater the heat of fusion of the crystals generated during isothermal crystallization. It can also be observed in Figure 2 that endotherm III disappears at a crystallization temperature that is higher in the pure PET than in the 80/20 mixture. Above these crystallization temperatures, recrystallization does not take place during the scan. If we compare the areas of endotherms II and III for pure PET and

for this polymer in the mixture after crystallization at the same temperature (473 K, for example) it clearly appears that the ratio of $\text{area}_{\text{II}}/\text{area}_{\text{III}}$ is lower in the pure polymer. All these results can be explained if we take into account that the higher the crystallization temperature, the more perfect the crystals obtained during isothermal crystallization, and, consequently, the lower the recrystallization tendency during the scan. On the other hand, it appears that the presence of PAR units in the PET chains as a consequence of interchange reactions hinders recrystallization in the mixture with respect to pure PET.

The origin of the three melting endotherms and the influence of PAR on the crystallization processes of PET can be further clarified by studying the influence of the crystallization time and of the scan rate on the different peaks.

In Figures 4 and 5, the effect of the crystallization time is represented for PET and PET/PAR (80/20) crystallized at 468 K. It clearly appears that $T_{m,\text{I}}$ increases as the crystallization time increases (Fig. 5). This indicates that the crystals formed by means of the secondary crystallization process are more perfect when the crystallization time is greater. A slightly more pronounced increase of $T_{m,\text{I}}$ with the crystallization time is found in pure PET, showing once again the effect of the interchange reactions on the crystallization of PET. As far as the endotherm II is concerned, the $T_{m,\text{II}}$ values are practically constant with crystallization time, at least in the time range used and at the selected crystallization temperature. Only a slight increase is found at the shortest times for PET. The comparison between this behavior and those found in other works is difficult to make because some confusion exists in the available literature about the nature of the different endotherms that appear in DSC analysis of iso-

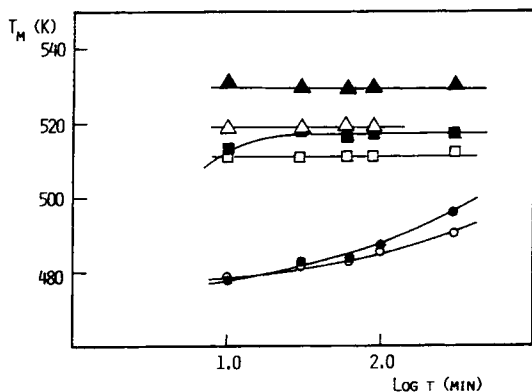


Figure 5 Effect of crystallization time at 468 K on the melting temperatures of PET (solid symbols) and PET/PAR (80/20) blend (open symbols).

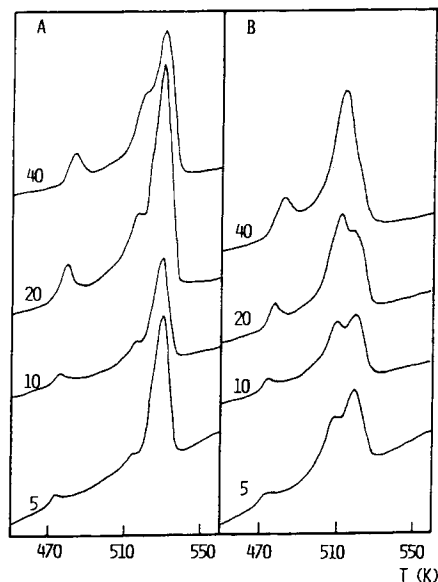


Figure 6 Effect of the heating rate (K/min) on the melting endotherms of (a) PET and (b) PET/PAR (80/20) blend.

thermally crystallized PET, and thus, as has been mentioned by Zhou and Clough,¹¹ some authors have not observed endotherm II and in other cases, the relation between the lower temperature endotherm and the I and II peaks observed in our work as well as in that of Zhou and Clough is not clear because of the different crystallization conditions used in the different works. Zhou and Clough do not mention the influence of the crystallization time on the peak temperature of endotherm II.

The peak temperature of endotherm III remains constant with the crystallization time. This result is in good agreement with those previously reported,^{3,8} taking into account the crystallization temperature and times used in our work, and indicates once again that the crystals that give rise to this peak are independent of the isothermal crystallization process.

The area of endotherm II increases with respect to that of endotherm III as the crystallization time increases, as can be observed in Figure 4. This seems to indicate that the greater the crystallization time, the more material crystallizes during isothermal crystallization. This result is consistent with the increase in the density of PET with annealing time, which has been observed by different authors,^{8,10} and is also in good agreement with the results of Zhou and Clough.¹¹

As can be observed in Figure 4, in pure PET the area of endotherm II is much smaller than that of endotherm III. On the contrary, in PET/PAR (80/20), endotherm II is greater than endotherm III.

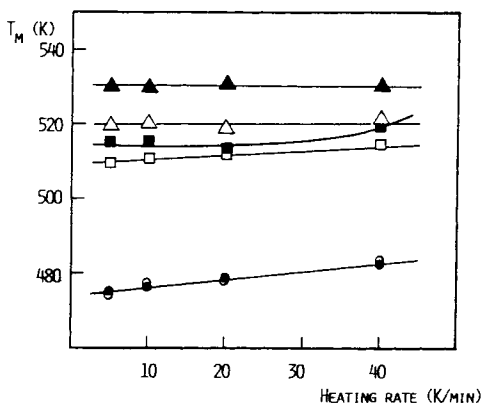


Figure 7 Effect of the heating rate on the melting temperatures of PET (solid symbols) and PET/PAr (80/20) blend (open symbols), crystallized for 10 min at 468 K.

This is additional evidence that recrystallization is much less favored in the blend, as a consequence of interchange reactions.

Finally, the scan rate also affects the melting endotherms of PET in the pure state and when mixed with PAr. In Figures 6 and 7 this influence can be observed. It is seen that $T_{m,I}$ increases along with an increase in the heating rate. The increase is somewhat more pronounced in the pure crystalline polymer. Although similar behavior has been found in some cases,¹² no explanations have been given.

However, the influence of the heating rate on endotherms II and III is more interesting. The melting temperature $T_{m,II}$ increases slightly along with the heating rate, whereas $T_{m,III}$ remains approximately constant. A similar behavior was found by Fakirov et al.,⁶ whereas other authors have found a somewhat different behavior.

The influence of the heating rate on the ratio of areas of endotherms II and III also points to the nature of the endotherms. As can be seen in Figure 6, as the heating rate increases, the area of endotherm II increases with respect to that of endotherm III. Although this effect would be a consequence of a poorer resolution of the peaks, we think that in this case, it arises from the lesser amount of time during which the original PET crystals are able to undergo recrystallization at a higher heating rate. Otherwise, a broader endotherm should be observed at 40 K/min. This explanation is coincident with that given by other authors on the same subject.¹¹⁻¹³

From the aforementioned results, it clearly appears that the interchange reactions between PET and PAr during melting hinder the isothermal crystallization of PET as well as the recrystallization

during the scan. This effect should be a consequence of the incorporation of PAr units in the PET chains, which decrease the crystallizable segment length of the crystalline polymer.

The financial support of the Gipuzkoako Foru Aldundia and of the University of the Basque Country (1987 Research Programme) is gratefully acknowledged.

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Received October 26, 1989

Accepted March 8, 1990