Chemical Heterogeneity of Poly(ethylene terephthalate) As Revealed by Temperature Rising Elution Fractionation and Its Influence on Polymer Thermal Behavior: A Comparison with Poly(ethylene terephthalate-*co*-isophthalate)

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ABSTRACT: The chemical heterogeneity of poly(ethylene terephthalate) (PET) and of poly(ethylene terephthalate-*co*-isophthalate) (PETI) was investigated using temperature rising elution fractionation (TREF). NMR and SEC results of the TREF fractions of the two polymers are compared. Both polymers show the same trend upon fractionation, confirming that diethylene glycol units (DEG) can be considered as a statistical comonomer in PET which influences the crystallizability of PET. PET and PETI were finally analyzed by the stepwise isothermal segregation technique (SIST). The occurrence of multiple melting peaks for both polymers, when crystallized isothermally by step from the melt, is related to the statistical inclusion of the comonomers in the chains.

Introduction

Most semicrystalline engineering polymers have been reported to exhibit multiple melting behavior.[1−3] Despite the large number of studies dedicated to poly(ethylene terephthalate),[4−12] the exact origin of the multiple melting phenomenon is still often debated for this polymer.

For polyolefins and essentially ethylene/α-olefins copolymers, the multiple melting has been related to the chemical structure.[13,14] It has been shown that the α-monomer sequence distribution along a polymer chain (intrachain heterogeneity) and between polymer chains (interchain heterogeneity) plays an important role in the melting behavior, morphology, and properties.[15] The low-temperature melting peaks are associated with chains containing more comonomer than the chains with low comonomer content that form crystals melting at higher temperatures.

For aromatic polyesters, like PET, the chemical heterogeneity of the chain is usually neglected when not completely denied. It is, in fact, well-known that commercial PET contains a small amount of diethylene glycol units (DEG) that are produced by the transetherification of monomeric ethylene glycol during the synthesis.[16] PET can thus be considered as a copolymer of terephthalic acid, ethylene glycol, and diethylene glycol.

The effect of DEG on PET crystallization was first studied by Frank and Zachmann.[17] They investigated the effect of diethylene glycol content on the rate of crystallization of PET with DEG contents up to 15%. They observed, as others later,[18,19] that increasing the concentration of DEG causes the rate of crystallization to decrease when PET is isothermally crystallized from the melt. Fakirov[20] et al. analyzed the influence of DEG content on the crystal lattice parameters and small-angle X-ray scattering of isothermally crystallized PET. They showed that unit cell dimensions are unaffected but that the long period increases with increasing DEG content. They concluded that most of the DEG units are rejected in the amorphous layers.

A recent study conducted by Medellin-Rodriguez[21,22] illustrates the thermal behavior of PET containing a small amount of 1,4-cyclohexylene units as comonomer. In these studies, the influence of PET molecular weight and incorporation of 1,4-cyclohexylene units were investigated in the view of relating the melting behavior of the polymer to the concentration of chain defects. Medellin-Rodriguez demonstrated that the amplitude of the lower temperature melting peak was increasing when the molecular mass or the concentration of 1,4-cyclohexylene units was increasing. This work is the first one to draw a link between the chemical structure of PET and its complex melting behavior.

The aim of the present study is to elucidate further the role of DEG in PET thermal behavior. We will show that PET contains indeed some defects that lead to a thermal behavior similar to an isophthalate−terephthalate copolyester (PETI) and that its chemical heterogeneity may thus play a role in its multiple melting behavior *when crystallized under specific conditions.*

In this paper, we report the preparative fractionation of PET with temperature rising elution fractionation (TREF) and the subsequent analysis of the samples using nuclear magnetic resonance (NMR) and size exclusion chromatography (SEC). TREF has been recently proved to successfully fractionate copolyesters as a function of their crystallizability.[23] Differences in crystallizability are related, in this case, to the existence of a distribution of crystallizable sequences of different lengths. As we demonstrated[23] by both simulation and experimental results, TREF sorts chains in categories characterized by the length of the greater regular sequence of the chains. Hence, all chains whose greater regular sequence length is comprised in a narrow interval will be eluted at the same temperature. Because of the intrachain distribution of sequences lengths in copolyesters, TREF is not capable of producing purely homogeneous fractions.

We will thus present the results obtained when the polymers are submitted to the stepwise isothermal segregation technique (SIST) whose ability to reveal

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Table 1. Molecular Weight of PET and PETI Calculated by SEC[a]

SEC values	PET	PETI
M_n	16 000	11 000
M_w	50 000	50 000

[a] Values are expressed in equivalent PET.

inter- and intrachain heterogeneity has already been demonstrated.[23]

At last, the results of a numerical simulation of sequence length in the chains will be described in order to give a better understanding of the statistical character of both PET and PETI.

Experimental Section

Materials. All the polyesters used in this study were supplied by ICI Melinex. The copolyester has an isophthalate content of 21%. Molecular weights calculated by SEC for PET and PETI are reported in Table 1.

Size Exclusion Chromatography. Size exclusion chromatography (SEC) was performed with a mixture of hexafluoro-2-propanol (HFIP) and chloroform as solvent (98/2 $CHCl_3$/HFIP). The flow rate was 0.8 mL min^{-1}. Two Waters HR 5E styragel columns were used in series. The chromatograph was completed with a Waters 2486 UV detector working at 254 nm.

Calibration was made using various polystyrene (PS) standards. The Mark−Houwink coefficients for PS and PET were taken as given by Fox et al.,[24] in order to build a universal calibration curve for PET in [$CHCl_3$/HFIP].

Temperature Rising Elution Fractionation. The TREF was carried out in a homemade column containing an inert support (iron mesh). The temperature of the column was controlled using a Julabo F32 thermal controller (30−200 ± 0.05 °C). The polymer (5 g) was first dissolved in 300 mL of trichlorobenzene (TCB) containing 0.2% Irganox 1010 to prevent any oxidative degradation and then poured into the column at 200 °C. After 1 h the oil bath temperature was programmed to decrease from 200 to 30 °C at a rate of 1.5 °C h^{-1}. After crystallization of the polymer on the support, the temperature of the column was gradually raised in a stepwise manner (from 30 to 200 °C by 10 °C steps) and flushed with TCB at the same temperature. Samples eluted at different temperatures were recovered by precipitation in a large excess of methanol, filtered, and vacuum-dried.

Differential Scanning Calorimetry. The stepwise isothermal segregation technique (SIST) experiments were carried out in a Perkin-Elmer DSC7 calorimeter. The apparatus was calibrated against indium and tin for the temperature and against indium for the heat flow.

The polymer samples were heated in the DSC instrument from room temperature to 280 °C and maintained at this temperature for 5 min and then rapidly cooled (80 °C/min) to 215 °C and maintained for 1 h. The sample was successively kept at each of the following temperatures: 200, 175, 160, 145, 130, and 115 °C for 1 h and then cooled to 30 °C at a rate of 80 °C min^{-1}. A usual scanning reheating experiment at 10 °C min^{-1} was then performed to reveal multiple melting peaks.

Nuclear Magnetic Resonance. ^{13}C NMR and ^1H NMR spectra were recorded on a Brucker 500 MHz FT-NMR instrument at room temperature. Polymers were dissolved in a mixture of chloroform-*d* and HFIP (10% v/v). The polymer concentration was 2.5 g L^{-1}, and chemical shifts are quoted in ppm from TMS. The DEG content was estimated using a method previously described by Golike and Cobbs.[19]

For PETI copolyesters, the calculation of the isophthalic content was performed on the basis of the aromatic protons of terephthalic (8.21 ppm) and isophthalic acid (8.81 ppm).

Results and Discussion

Before performing any fractionation, a PET sample was submitted to dissolution and crystallization steps.

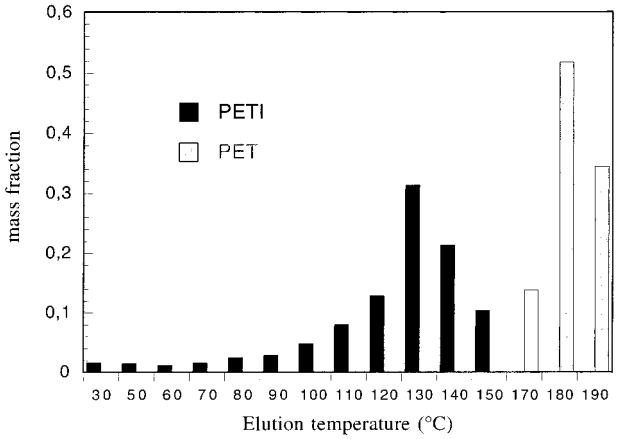

Figure 1. Mass distribution of PETI (black) and PET (gray) TREF fractions as a function of elution temperature.

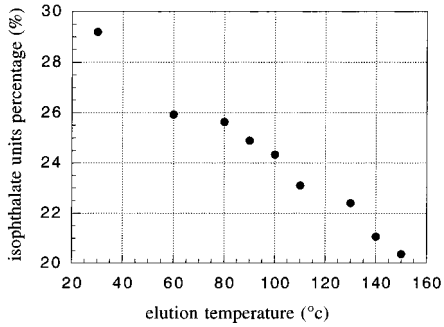

Figure 2. Isophthalic units percentage determined by ^1H NMR as a function of elution temperature for PETI TREF fractions.

After crystallization the full sample was eluted with TCB at 200 °C and precipitated in methanol. The analysis of the polymer by SEC reveals that no significant molecular weight degradation occurs during these first two steps. Hence, we can safely assume in the following that our TREF conditions do not modify the structure of the polymer.

A preparative TREF fractionation was performed on both PETI and PET to fractionate the polymers (or copolymers). TREF results show that three fractions were collected for PET between 170 and 190 °C plus a low temperature (30 °C) fraction containing mainly PET oligomers, while for PETI the polymer was eluted between 30 and 150 °C. Fractions were collected at three different temperatures for PET and 14 different temperatures for PETI. After weighting of the dried fractions, the mass distribution of the dry fractions are shown in Figure 1. A last fraction eluted at 195 °C representing about 25% of the sample was not analyzed for PET.

The temperatures of elution of PET and PETI are quite different. This indicates longer average crystalline sequence lengths in PET, which is in agreement with the much lower comonomer content than for PETI copolyesters. Figure 1 demonstrates for both PET and PETI the existence of species of different crystallizability.

The chain structure of the TREF fractions of PET and PETI was investigated by ^{13}C NMR for the quantification of DEG units in PET and by ^1H NMR for the quantification of isophthalic units in PETI. Figure 2 and Figure 3 show the evolution of comonomer content as a function of elution temperature.

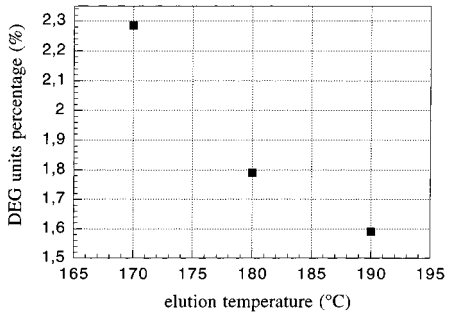

Figure 3. DEG units percentage determined by ^{13}C NMR as a function of elution temperature for PET TREF fractions.

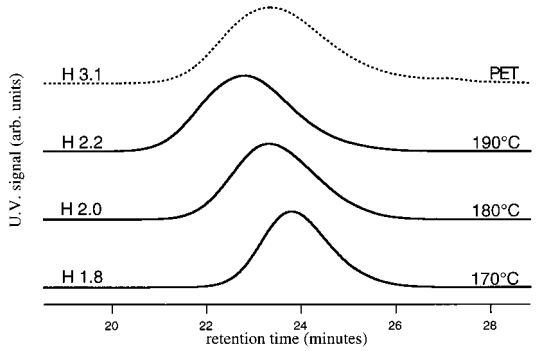

Figure 4. SEC chromatographs of PET (dotted line) and PET TREF fractions (plain lines). The curves have been shifted vertically for clarity. The polydispersity of the samples is reported on the left side of the graphs (*H*) and the elution temperature on the right side.

Figure 2 shows that fractions of PETI collected at higher temperatures contain less isophthalic moieties than fractions collected at lower temperatures. The observation of a decreasing isophthalic content with increasing elution temperature is consistent with usual TREF results were the concentration of defects decreases with increasing elution temperature and is also consistent with the results reported by Berghmans et al.[25] for the crystallinity of isophthalic/terephthalic copolymers. The values of DEG content reported on Figure 3, which are expressed as number of DEG units by 100 constitutive units, show clearly that the fractions collected at lower temperatures of elution contain fewer DEG units. This is in good agreement with Zachmann's results which indicate a decrease of crystallizability of PET upon DEG content increase. The evolutions with elution temperature of isophthalic content in PETI or DEG content in PET are similar, which supports the view that PET behaves actually as a copolymer. Of course, PETI contains DEG units, but the percentage of DEG units within PETI (1.5%) is much lower than the percentage of isophthalic units and is therefore neglected in this study.

The molecular weight distributions of the PET and PETI fractions were analyzed by SEC. The results are reported in Figure 4 (PETI) and Figure 5 (PET). Both figures show the same behavior. The average molecular weight increases with elution temperature. Although the polydispersity (*H*) of the fractions is narrower than for raw polymers, the *H* values are still high. As demonstrated elsewhere,[23] the increase of molecular weight with elution temperature is due to the fact that the probability of finding long crystallizable sequences increases with molecular weight. This results in an enrichment of the high-temperature fractions in longer chains. As long chains may statistically contain a long

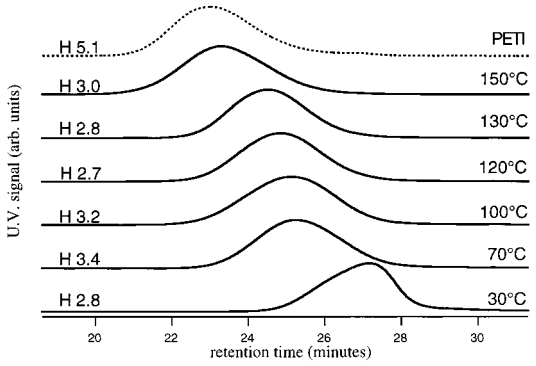

Figure 5. SEC chromatographs of PETI (dotted line) and PETI TREF fractions (plain lines). The curves have been shifted vertically for clarity. The polydispersity of the samples is reported on the left side of the graphs (*H*) and the elution temperature on the right side.

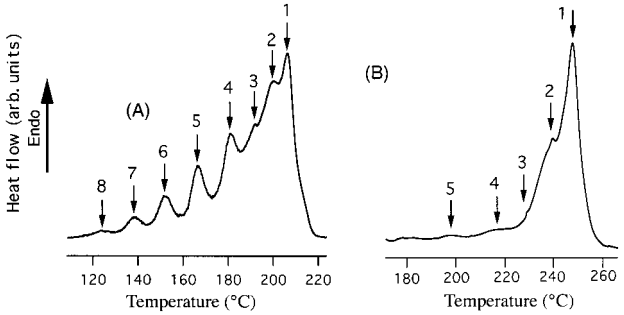

Figure 6. DSC melting curve (10 °C/min) of PETI (A) and PET (B) after SIST treatment. The peaks have been numbered for clarity.

crystallizable sequence plus a series of shorter ones or only a greater number of shorter ones which will be collected at lower temperature of elution, chains of identical molecular weight will be distributed among different fractions. This explains the molecular weight polydispersity of the TREF fractions.

Moreover, Wild[26] et al. have shown for a linear polyethylene that, providing that the molecular is greater than 1000, the elution temperature is not molecular weight dependent and that a narrow polydisperse linear polyethylene is eluted in a narrow temperature range.

The SIST technique has been found efficient to reveal the inter- and intramolecular heterogeneity of copolyesters as has already been demonstrated some years ago for poly(ethylene/α-olefins).[15] If we now turn to the thermal behavior of unfractionated PETI and PET as revealed by SIST, one should also expect similarities between the two polymers.

Figure 6 (A and B) shows the DSC melting curve of PETI and PET after SIST treatment. PETI exhibits multiple peaks ranging from 120 to 215 °C. They reflect the presence of species that crystallize at different temperatures during the cooling (i.e., that have different crystallizability) and that melt at different temperatures. The various peaks can be assigned to the melting of crystals containing terephthalate sequences of different lengths.

The melting thermogram of PET after SIST shows, like PETI, various peaks. The low-temperature melting peaks are less important than for PETI. These peaks should be attributed the same origin than for PETI: the existence of shorter regular sequences due to the DEG content, which can only crystallize in thinner crystals

generated at lower temperature during the SIST cooling. This indicates that multiple melting peaks observed for PET after its complex cooling from the melt result from its copolymer nature. We have to point out that multiple melting may also occur when polymers are crystallized from the glassy state. This multiple melting has to be distinguished from the one observed after SIST when cooling from the melt. For cold crystallized PET and other aromatic polymers, it is indeed usually agreed that melting−recrystallization mechanisms[27−29] play a major role in the apparition of multiple melting peaks.

We have compared, in this paper, the thermal properties of PET and PETI considering both polymers as statistical copolymers. The statistical character of PETI, which contains about 21% of defects, does not need to be discussed. However, we may wonder about the meaning "statistical" for PET, considering that its defects content is as low as 1.5%. An answer to this question can be given by numerical simulations. The principles of the simulation have been previously described;[23] in essence, it consists of generating a large number of copolymer chains by successively selecting randomly one or the other monomer from a mixture of monomers whose relative amounts are initially fixed.

In this paper, we present results obtained on monodisperse PET and PETI of identical molecular weight (16 000 M_n). The effect of molecular weight distribution has already been described elsewhere[23] and is not relevant within the purpose of this paper. The DEG percentage was fixed at 1.88% (weight average of the three TREF fractions), and the isophthalic content was fixed at 21% as given by ^{1}H NMR for PETI. As the DEG content of PETI is very low compared to the isophthalic content, this value was not taken into account. As we mentioned before, the sorting criterion when performing TREF on PETI is the greater sequence length existing in a single chain (GSLC). As the GSLC decreases, the crystallizability of the chain is decreased. As a consequence, chains with long GSLC will be collected in high-temperature TREF fractions. It may be thus interesting to compare the simulated and calculted distributions of GSLC of PET and PETI. For PET, the sequence length calculated corresponds to the successive number of ethylene glycol/terephthalate groups interrupted by a diethylene glycol/terephthalate unit; for PETI the sequence length corresponds to the successive number of ethylene glycol/terephthalate groups interrupted by a diethylene glycol/isophthalate unit. Figure 7 reports the number of chains as a function of their GSLC, for both polymers. The curves show that for PETI the GSLC's are between 10 and 25 terephthalate units; for PET the range of GSLC's lies between 20 and 82 ethylene glycol/terephthalate units. The peak at 82 consists of PET chains that do not carry any DEG unit; i.e., they are pure PET chains. We observe for PET a large distribution of GSLC that depends on the position of the DEG unit and of the number of DEG units in the chain. In terms of sequence length distribution, PET behaves only partially like a statistical copolymer because at low defects concentration some chains do not carry any defect. The chains carrying one or more DEG units form a distribution of GSLC similar to the one observed for copolymers such as PETI. The main differences between PETI and PET are the size of the sequences and the existence for PET of chains carrying no defects. The absolute relationship between the length of the sequences and the TREF separation will not be discussed herein. However, we expect, given the limited thickness of crystals usually reported for PET, that the separation of PET by TREF will only be effective for the shorter sequences. As the length of the sequence is increased, the influence of defects on the crystals formation will decrease.

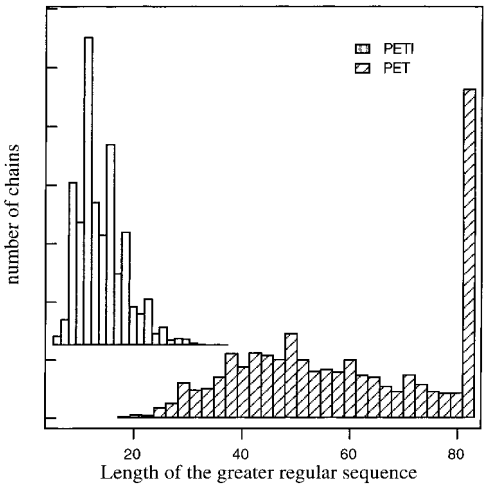

Figure 7. Number of chains (from simulation) as a function of the greater sequence length in the chain: PETI (gray filling) and PET (crosshatched). The PETI distribution is shifted vertically for clarity.

Real copolyesters are not homodisperse, and adding polydispersity to the simulation will "smooth" the curve by introducing shorter sequences of pure PET and larger sequences of PET containing DEG units in addition to the actual distribution. However, the contribution of polydispersity does not bring any new element to the discussion and will not be developed here.

Conclusions

From this, we conclude that TREF separates PET and PETI in a qualitatively identical manner. The molecular characteristics of the fractions vary with elution temperature in a similar way. The main differences are the origin of the segregation (i.e., the chemical nature of the defects interrupting regular sequences) and the percentage of defects. For PET the factor affecting the TREF fractionation process is the presence of different DEG contents on different chains in the polymer. Hence, PET has to be considered as a partially statistical copolymer with a low comonomer content. This statistical character is sufficient to explain the apparition of multiple peaks when crystallizing PET by steps from the melt, exactly in the same way as for PETI copolymers containing a larger comonomer content.

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