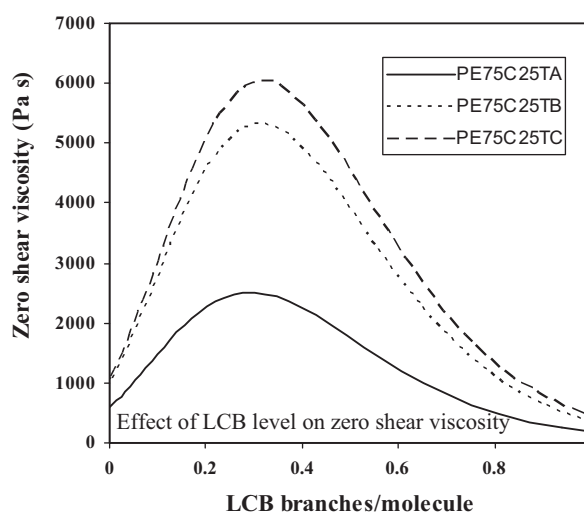


# Rheological Features and Flow-Induced Crystallization of Branched Poly[ethylene-co-(1,4-cyclohexanedimethylene terephthalate)] Copolyesters

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A set of amorphous poly[ethylene-co-(1,4-cyclohexanedimethylene terephthalate)] (PECT) copolymers containing 25 and 30% of 1,4-cyclohexane dimethylene (CHDM) units and small amounts of branching agent pentaerythritol (PER) is investigated. The level of long chain branching was estimated by analyzing the positive deviation from  $\eta_0 \bar{M}_w^{3.54}$  law. Branching also produced melt elasticity enhancement which is desirable for certain processing methods. Capillary extrusion experiments at 180 °C generated flow-induced crystallization in PECT containing 25% of CHDM. Crystallization increased with the amount of PER added, which was explained by the favorable effect of branching to increase elongational rate at the entrance of the capillary. Linear and branched PECTs containing 30% of CHDM did not crystallize.



## Introduction

Poly(ethylene terephthalate) (PET) is the polyester thermoplastic most extensively utilized nowadays.<sup>[1,2]</sup> It is mostly produced by step-growth melt polymerization of tere-

phthalic acid (PTA) and ethylene glycol (EG), which is followed by solid-state polycondensation when higher viscosity indexes are desired.<sup>[3,4]</sup> Several grades of PET usable for a wide range of applications including melt spinning, blow molding and injection molding are thus accessible.<sup>[5]</sup>

Poly(ethylene terephthalate) copolymers in which about 30 mol-% of EG is replaced by 1,4-cyclohexane dimethanol (CHDM) have been recently developed to cover applications where low crystallinity and high glass transition temperature ( $T_g$ ) are a priority.<sup>[6–8]</sup> These CHDM containing copolyesters poly[ethylene-co-(1,4-cyclohexanedimethylene terephthalate)] (PECT) are usually produced by copolymerization of PTA or dimethyl terephthalate

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(DMT) and mixtures of EG and CHDM in a continuous process that uses large-scale screw reactors. In this way, PECT with adequate melt strength and viscosity for processing may be obtained. PECT produced from PTA in vertical batch reactors is an alternative procedure of interest that has not been industrially exploited until now. The main reason is that this procedure is unable to afford PECT with the molecular weight necessary to attain the rheological properties suitable for melt processing.

Technical assessments of PECT copolyesters require an adequate rheological response to satisfy the correlation *Rheology–Processing–Properties*. This implies to select the most suitable molecular architecture for each PECT grade. Indeed a certain number of papers have been published on the improvement of the rheological properties of PET prepared in the presence of a variety of branching agents.<sup>[9–22]</sup> A description of the synthesis of a dozen of branched polyesters *via* different tri- and tetrafunctional comonomers is given in the review paper of McKee et al.<sup>[9]</sup> Modification of polyesters by introducing long chain branching has received significant attention as an efficient method to enhance melt strength and melt viscosity. Randomly branched polyesters are often prepared by step-growth polymerization in the presence of multifunctional comonomers. Both polycarboxylic (trimesic and pyromellitic acids)<sup>[14,15]</sup> and polyhydroxylic [glycerol and pentaerythritol (PER)]<sup>[11,12]</sup> monomers have been extensively explored to prepare high-melt viscosity PET with improved performance. However, to the best of our knowledge, no study on the influence of branching on the properties of PECT copolyesters has been made so far.

In this paper, PECT copolyesters containing small amounts of the tetrafunctional alcohol PER are synthesized. The thermal, mechanical and rheological behavior of these long chain branched PECTs are examined and the occurrence of flow-induced crystallization in some of these amorphous copolyesters is reported.

## Experimental Part

### Materials

Purified terephthalic acid, EG, 90% aqueous solution of CHDM (30:70 *cis/trans* mixture), PER and germanium dioxide catalyst were all supplied by La Seda de Barcelona SA (Catalonia, Spain) and used as received. Solvents employed for characterization such as trichloromethane (TCM), dichloroacetic acid (DCA) and hexafluoro-2-propanol (HFIP) were all of high-purity grade.

### Measurements

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 25.0 °C on a Bruker AMX-300 spectrometer operating at 300.1 and 75.5 MHz, respectively. 10 and 50 mg of polymer sample dissolved in 1 mL of deuterated

TCM were used for <sup>1</sup>H and <sup>13</sup>C, respectively. 64 scans were acquired for <sup>1</sup>H and 1000–10 000 for <sup>13</sup>C with 32 and 64 K data points, and relaxation delays of 1 and 2 s, respectively. Spectra were internally referenced to tetramethylsilane (TMS).

Intrinsic viscosities of the polymers dissolved in DCA were measured with an Ubbelohde viscometer at 25 ± 0.1 °C. Molecular weight analysis were performed by gel permeation chromatography (GPC) using HFIP containing 6.8 g·L<sup>-1</sup> of sodium trifluoroacetate as mobile phase. Separation was carried out using a Waters linear Styragel HR 5E (styrene-divinylbenzene) column, protected with a precolumn. Flux was 0.5 mL·min<sup>-1</sup> and 100 µL of 0.1% w/v sample solutions were injected. Molecular weight averages and distributions were calculated after calibrating the system against PMMA standards using an RI Waters 410 detector or a MiniDawn (Wyatt) light scattering detector ( $d_n/d_c$  was estimated from sample amount injected).

The thermal behavior of the polyesters was examined by differential scanning calorimetry (DSC) with a PerkinElmer Pyris1 instrument calibrated with indium. DSC data were obtained from 4 to 6 mg samples under nitrogen circulation. Heating and cooling rates of 10 °C·min<sup>-1</sup> were routinely used, except for the determination of the  $T_g$ s, which implied a heating rate of 20 °C·min<sup>-1</sup>. Thermogravimetric analysis (TGA) was carried out with a Perkin-Elmer TGA-6 thermobalance at a heating rate of 10 °C·min<sup>-1</sup> under a nitrogen atmosphere.

Tensile tests were performed on rectangular specimens (40 × 5 mm<sup>2</sup>) cut from 200 µm-thick films that were obtained by melt compression. The material was sandwiched between two steel platens covered with Teflon-coated aluminium foil and provided with appropriate spacers to control the thickness of the film. The platens were placed in a press and heated at 180 °C for 5 min. Successive increase in pressures of 13, 25 and 50 kg·cm<sup>-2</sup> were then applied, the platens being held at each pressure for 1 min. Finally, the pressure was released and the platens quenched in cold water. The probes were stored in vacuum for 48 h before use. The tensile tests were conducted at room temperature on a Zwick B22.5/TN1S universal tensile testing apparatus operating at a constant crosshead speed of 10 mm·min<sup>-1</sup> with a 0.5 N preload and a grip-to-grip separation of 20 mm. All reported tensile data were averaged from at least five independent measurements.

Oscillatory experiments were performed in a stress controlled rotational rheometer ARG2 (TA Instruments) at  $T = 230$  °C. Dynamic viscoelastic functions such as storage modulus  $G'$ , loss modulus  $G''$  and complex viscosity  $\eta^* = \eta' - i\eta''$  were determined over a frequency range of 0.01–100 Hz. The linear viscoelastic conditions were established by a torque sweep test. Cylindrical samples of diameter  $D = 25$  mm and thickness  $h = 2$  mm prepared by compression molding ( $P = 150$  bar and  $t = 4$  min) were employed.

Extrusion flow measurements were carried out in a Göttfert Rheograph 2002 rheometer at 180, 190 and 230 °C. The diameter of the barrel was  $D_b = 9.5$  mm and the dimensions of the tungsten made capillary were  $L_c = 30$  mm and  $d_c = 1$  mm. The entry angle was flat (180 °). Experiments at successively increased constant shear rates (constant piston velocity) were carried out, covering the interval 30–400 s<sup>-1</sup>. The piston force, which is proportional to the shear stress, was recorded as a function of time for each piston velocity to detect steady-state conditions or, eventually, flow-induced crystallization.

## Reaction Equipment

The batch pilot plant equipment used in this work is similar to that described for PET process by James and Packer.<sup>[23]</sup> The reactor is a nominally 1.5-L jacketed stainless steel vessel (Karl Kurt Juchheim Laborgeräte GmbH) fitted with an anchor agitator and an EUROSTAR power control-visc P7 overhead stirrer (IKA) with an RS232 connection able to register and monitor both speed and torque readings. The reactor is oil heated using a high-temperature circulator. The final product is removed from a valve on the bottom of the reactor. A rectification column for separating water from glycols during esterification is fitted to the outlet port.

## Linear and Branched Copolyesters Synthesis

Purified terephthalic acid (2.11 mol), EG (1.90 mol) and CHDM (0.63 mol) in a molar ratio of PTA/glycols = 1:1.2 and germanium dioxide catalyst (150 ppm Ge based on polymer) were charged into the reactor. The amount of CHDM in the feed was equal to the desired CHDM content of the copolyester, with the diol exceeded in the feed being EG. Various amounts of PER (0–0.2 mol-%) were added to the initial feed. After venting the whole reaction system per triplicate with nitrogen, the pressure was set at 3 bar abs and the esterification was conducted for 70 min at an average temperature of 260 °C under stirring at 60 rpm. At this stage, most of the water added with CHDM and that generated in the esterification reaction was distilled-off. Additional amounts of water were removed under atmospheric pressure for a period of 35 min. At this point, the stirrer speed was set at 30 rpm, the vacuum gradually lowered and temperature slowly increased up to 285 °C; this period took around 50 min. The increase in the torque applied to the stirrer was used to follow the progress of the polycondensation reaction, which was completed after 80 min. After relieving the vacuum using nitrogen, the polymer was extruded and quenched in a bath of iced water. Samples for analysis and characterization were taken from the product extruded after the first minute of output.

## Results and Discussion

### Synthesis and Characterization of PECT Copolyesters Containing PER

Two series of PECT containing PER copolyesters with contents of 25 and 30 mol-% in CHDM, respectively each one comprising PER compositions of 1.0, 1.5 and 2.0 mol-% (named as A, B and C), were synthesized. The insertion of a PER unit in the copolyester chain is reasonably assumed to create a branching point from which four long arms protrude. The polymerization reaction was carried out by feeding the reactor with PTA, the mixture of glycols and PER in the selected composition, and GeO<sub>2</sub> catalyst. The reaction proceeded similarly for all the compositions used, although the viscosity of the mixture was noticed to increase exceptionally for contents of PER of 1.5 and 2.0 mol-%. Nevertheless, the evolution of the torque

indicated that polymerization was completed after about 75 min irrespective of the concentration of PER was used.

The composition in glycols of the resulting copolyesters was determined by <sup>1</sup>H NMR; contents in CHDM units of 29 and 25 mol-% were found for the series PE<sub>70</sub>C<sub>30</sub>T and PE<sub>75</sub>C<sub>25</sub>T, respectively, indicating that incorporation of this glycol in the copolyester was essentially complete in both cases. The content of the copolyester in diethylene-glycol (DEG), which is generated by uncontrolled side etherification reactions, was found to be less than 2 mol-%. Unfortunately, the amount of PER incorporated in the copolyester could not be assessed by NMR, since the small amount added (1.5–2.0 mol-%) is out of the sensitivity of the method. All the copolymers were readily soluble in chloroform without detectable signs of gel-like formation, indicating that the occurrence of crosslinking reaction can be neglected.

Characterization data for PE<sub>70</sub>C<sub>30</sub>T and PE<sub>75</sub>C<sub>25</sub>T series including molecular size, thermal properties and mechanical parameters are given in Table 1. In the two series, the intrinsic viscosity [ $\eta$ ] determined in DCA solutions was observed to increase with the amount of added PER. The almost linear dependence of [ $\eta$ ] on PER concentration is displayed in Figure 1a for PE<sub>70</sub>C<sub>30</sub>T series. Although values of [ $\eta$ ] for this series are comparatively higher than those of PE<sub>75</sub>C<sub>25</sub>T series, the effect exerted by PER on polymer viscosity is similar for both.

Molecular weights were determined by GPC using two evaluation methods. Elution volumes estimated against PMMA standards rendered the average molecular weights as well as polydispersities, whereas light scattering measurements afforded absolute values of the weight-average molecular weights. In both cases and for the two series, molecular weight values were observed to increase with the amount of PER. This behavior is consistent with the increase in molecular size that is expected to result from the incorporation of the branching unit into the copolyester chain. As it also should be expected from an increase in the branching degree, the distribution of molecular sizes broadened in the same sense. Changes taking place in the GPC profiles with the concentration in PER are illustrated in Figure 1b for PE<sub>70</sub>C<sub>30</sub>T series. Similar results are observed for PE<sub>75</sub>C<sub>25</sub>T series. It should be noticed that significantly lower molecular weight values resulted in the analysis using light scattering. An over-estimation due to the use of the PMMA standards is a possible explanation for such divergence. At any case, the increment obtained in molecular weights as determined by GPC is clearly smaller than for PET containing similar amounts of PER reported previously by other authors.<sup>[13,24]</sup> This is interpreted as the logical consequence of the higher conversion attained in the synthesis of PET homopolyester when compared to PECT copolyester. Actually, according to our own experience, copolymerization with CHDM makes

Table 1. Composition, molecular size and thermal and mechanical properties of copolyesters.

	$[M]^a$	$[\eta]^b$	$\overline{M}_w^c$	$PDI^d$	$M_w^d$	$T_g^e$	$T_d^f$	$T_d^f$	$RW^f$	$E$	$\sigma_{max}$	$\epsilon_{break}$
		$dL \cdot g^{-1}$	$g \cdot mol^{-1}$		$g \cdot mol^{-1}$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	%	MPa	MPa	%
PE <sub>70</sub> C <sub>30</sub> T	0.00	0.70	46 800	2.0	39 800	81	416	439	10	125 (42)	52.7 (0.5)	15.1 (9.6)
PE <sub>70</sub> C <sub>30</sub> T-A	1.00	0.77	53 240	2.2	45 300	81	410	440	9	107 (34)	57.0 (2.3)	21.5 (11.7)
PE <sub>70</sub> C <sub>30</sub> T-B	1.50	0.79	60 000	2.5	46 700	81	409	440	9	99 (31)	48.4 (7.1)	14.5 (4.7)
PE <sub>70</sub> C <sub>30</sub> T-C	2.00	0.84	71 120	2.8	50 700	81	416	440	10	127 (8)	56.9 (0.7)	10.5 (0.7)
PE <sub>75</sub> C <sub>25</sub> T	0.00	0.62	46 600	2.1	36 200	80	412	438	9	—	—	—
PE <sub>75</sub> C <sub>25</sub> T-A	1.00	0.69	44 700	2.1	37 800	81	409	435	9	—	—	—
PE <sub>75</sub> C <sub>25</sub> T-B	1.50	0.69	55 250	2.5	43 400	81	408	438	9	—	—	—
PE <sub>75</sub> C <sub>25</sub> T-C	2.00	0.72	64 500	2.7	44 200	81	408	438	10	—	—	—

<sup>a</sup>)PER in the feed in  $mmol \cdot mol^{-1}$  PTA; <sup>b</sup>)Intrinsic viscosity determined in DCA at 25 °C; <sup>c</sup>)Absolute weight-average molecular weight determined by light scattering; <sup>d</sup>)Weight-average molecular weight ( $\overline{M}_w$ ) and polydispersity index (PDI) estimated by GPC against PMMA standards; <sup>e</sup>) $T_g$  in °C taken as the inflection point of the heating DSC traces registered at  $20^{\circ}C \cdot min^{-1}$  from melt-quenched samples; <sup>f</sup>)Decomposition temperatures measured by TGA for 10% of weight loss ( $T_d$ ) and for the maximum decomposition rate ( $T_d$ ). RW is the percentage of residue left after heating at 550 °C; Elastic module ( $E$ ), maximum tensile stress ( $\sigma_{max}$ ) and elongation to break ( $\epsilon_{break}$ ) measured in stress-strain tensile essays. Standard deviations in brackets.

the chain growth difficult at high conversions so that attaining high branching degrees is less probable.

Thermal and mechanical data measured for the copolyesters are compared in Table 1. None of the copolyesters studied in this work showed sign of melting when analyzed by DSC. This is a much anticipated result since PECT with contents in CHDM in the 25–30% range is known to be amorphous, a feature that should not be expected to change with branching. No significant change in the glass transition was either detected by the incorporation of PER with  $T_g$  values kept invariable at 80–81 °C. As depicted in Figure 2 for the representative case of PE<sub>70</sub>C<sub>30</sub>T-B, the thermal decomposition of these copolyesters takes place in one single step leaving less

than 10% of residue. The TGA data collected for the two series reveals that the onset of decomposition temperature slightly decreases and the maximum rate decomposition temperature remains practically unchanged with the addition of PER. It can be concluded, therefore, that the thermal stability of our PECT copolyesters is unaltered by branching and that all the samples start to decompose at temperatures well above those involved in industrial processing.

The mechanical behavior of the PE<sub>70</sub>C<sub>30</sub>T copolyesters in tensile tests was also evaluated. The results of Table 1 indicate that no significant changes in the elastic modulus, stress strength and elongation to break were produced by the introduction of branches in PECT copolyesters.

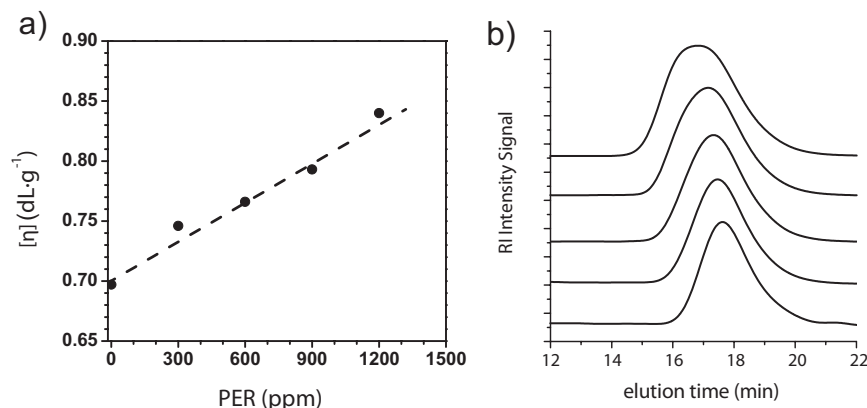


Figure 1. Evolution of the intrinsic viscosity (a) and elution times (b) in GPC of PECT copolyesters with the addition of PER (PE<sub>70</sub>C<sub>30</sub>T series).

### Rheological Characterization Using Oscillatory Flow Measurements

The real part  $\eta'$  of the complex viscosity  $\eta^*$  is shown as a function of frequency in Figure 3 for PE<sub>75</sub>C<sub>25</sub>T series. Similar results (not displayed) are obtained for PE<sub>30</sub>C<sub>30</sub>T series. The experimental data, obtained at a temperature of 230 °C were fitted to the Briedis and Faltelson model (mentioned in the book of Vinogradov and Malkin),<sup>[25]</sup> which is actually an

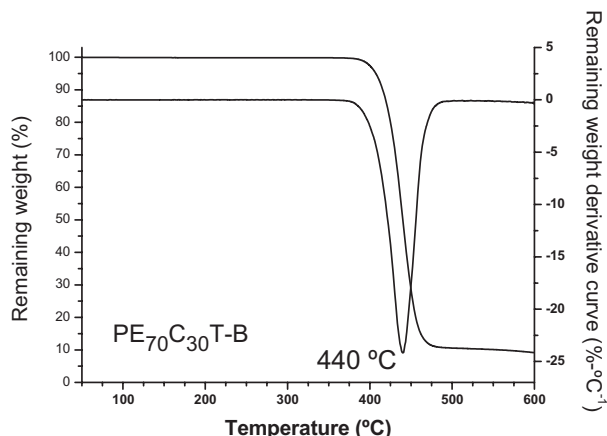


Figure 2. TGA trace of PE<sub>70</sub>C<sub>30</sub>T-B registered under inert atmosphere and its derivative curve.

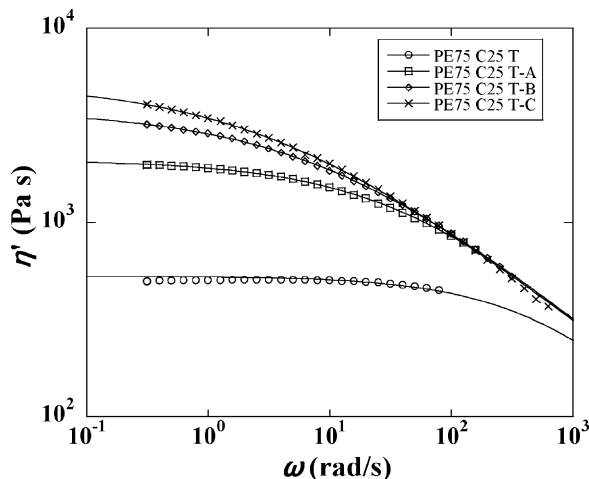


Figure 3. The real part of the complex viscosity as a function of frequency at 230 °C for PE<sub>75</sub>C<sub>25</sub> series. The lines correspond to the fits to Equation (1).

adaptation of the Cross model<sup>[26]</sup> to oscillatory viscosity results.

$$\eta' = \frac{\eta_0}{1 + (\omega\tau_0)^\alpha} \quad (1)$$

where  $\eta_0$  is the viscosity in the Newtonian plateau, named zero shear viscosity,  $\tau$  the relaxation time and  $\alpha$  is the nonlinearity index. Zero shear viscosity values are given in Table 2, showing a considerable increase as the amount of PER increases. Another rheological effect of the incorporation of PER units into PECT was the shift of the onset of the nonlinear behavior to lower frequencies. The observed results may be due to either molecular weight enhancement or to long chain branching. Besides, a certain broadening of the molecular weight distribution was detected (Table 1). Certainly, since branching and molecular weight growth can be induced by the addition of PER

to the polymerization reaction, it is difficult to separate the influence of each of the molecular parameters on the viscosity function of PECT containing PER. Notwithstanding our paper, constitutes the first report on the rheology of branched PECT, some results have been already published in the literature about the effect of branching on melt viscosity of PET. In contrast to the viscosity enhancement that can be seen in Figure 3, Hudson et al.<sup>[13]</sup> observed a viscosity reduction for modified PET samples. Using a fixed level of PER and varying levels of benzyl alcohol as an end-capper they concluded that the fall in their zero shear viscosity values was due to branching. Other authors<sup>[13–17,27,28]</sup> also found zero shear viscosity for branched species to be lower than that of linear PET analogues. In contrast, a reactive extrusion process of PET with polyanhydride and polypoxide modifiers gave rise to increased viscosities,<sup>[18–22]</sup> attributed to a combination of long chain branching, molecular weight increase and

Table 2. Zero shear viscosity  $\eta_0$ , crossover frequency  $\omega_x$ , relaxation time  $\tau$  and steady-state compliance  $J_e^0$  at 230 °C. Number of branches per molecule  $\lambda$  calculated by Janzen and Colby model.

	$\eta_0$	$\omega_x$	$\tau$	$J_e^0$	$\lambda$
	Pa·s	rad·s <sup>-1</sup>	s	Pa <sup>-1</sup>	
PE <sub>70</sub> C <sub>30</sub> T	860	880	0.0017	$1.97 \times 10^{-6}$	–
PE <sub>70</sub> C <sub>30</sub> T-A	2 800	330	0.02696	$9.62 \times 10^{-6}$	0.08
PE <sub>70</sub> C <sub>30</sub> T-B	4 200	316	0.1629	$3.87 \times 10^{-5}$	0.11
PE <sub>70</sub> C <sub>30</sub> T-C	5 500	304	0.2389	$4.34 \times 10^{-5}$	0.15
PE <sub>75</sub> C <sub>25</sub> T	530	–	0.0012	$2.26 \times 10^{-6}$	–
PE <sub>75</sub> C <sub>25</sub> T-A	2 100	566	0.0192	$9.14 \times 10^{-6}$	0.19
PE <sub>75</sub> C <sub>25</sub> T-B	3 770	432	0.10	$2.65 \times 10^{-5}$	0.16
PE <sub>75</sub> C <sub>25</sub> T-C	5 250	371	0.26	$4.95 \times 10^{-5}$	0.21

broadening of the molecular weight distribution. In the previous research carried out by some of the authors on rheological effects of long chain branching in polyethylenes<sup>[29–32]</sup> and poly(propylenes),<sup>[33–34]</sup> a very clear positive deviation from the general approximate scaling law of linear polymers  $\eta_0 \bar{M}_w^{3.4}$  was observed for slightly branched samples. We recall that although moderate or high levels of LCB in polyethylene produce a decrease in viscosity, because of a reduction of the hydrodynamic volume,<sup>[35]</sup> low levels of LCB slow the diffusion of the chains resulting in a viscosity increase. In Figure 4, a double logarithmic plot of the zero shear viscosity  $\eta_0$ , against molecular weight is presented. We assumed that the higher viscosity values of PECT-containing PER were due to long chain branching. Actually, as an approximation, the scaling law  $\eta_0 \bar{M}_w^{3.54}$  proposed by Manaresi<sup>[14]</sup> for linear polyethylene terephthalates was used to fit linear PECT samples, whereas  $\eta_0$  values of PECT containing PER scaled reasonably well with  $\bar{M}_w^6$ , which according to Lusignan et al.<sup>[36]</sup> would correspond to the expected behavior of branched polyesters.

The model proposed by Janzen and Colby<sup>[37]</sup> represents a significant advance for the evaluation of LCB level, using zero shear viscosity data. The method takes into account the extreme sensitivity of the melt viscosity to random branching architecture. The predictive methodology treats branching in an average and random way, representing the branched polymer as blends of linear chains with chains containing a single entangled branch. The approach is applicable to polymers with sparse-to-intermediate levels of LCB and with reasonably narrow molecular weight distributions. These materials have branched chains with molecular weight not much greater than their linear counterparts, thus making it very difficult to

estimate the extent of branching from dilute-solution analytical techniques like <sup>13</sup>C NMR and size exclusion chromatography (SEC) pair with multi-angle laser light scattering (MALLS)<sup>[37]</sup>.

The dependence of  $\eta_0$  on  $\bar{M}_w$  is well established for linear and flexible chains. Two regimes are separated by a critical molecular weight,  $M_c$  below which  $\eta_0$  scales directly with  $\bar{M}_w$  and above which  $\eta_0$  generally scales with  $\eta_0 \bar{M}_w^{3.4}$ . Chains with molecular weight below  $M_c$  are too small to entangle, while the high molecular weight chains are topologically constrained due to entanglement coupling. Several parameters influence rheological properties including branch length, degree of branching and chain architecture (random, star branched, comb and H-branched). The Janzen and Colby method summarizes the dependence of zero shear viscosity on molecular weight and on average chain length adjacent to random branch points, when present, as follows:

$$\eta_0 = \begin{cases} AM_w & \text{for } M_b < M_c \\ AM_w \left[ 1 + \left( \frac{M_w}{M_c} \right)^{2.4} \right] & \text{for } M_c < M_w < M_b \\ AM_b \left[ 1 + \left( \frac{M_b}{M_c} \right)^{2.4} \right] \left( \frac{M_w}{M_b} \right)^{s/\gamma} & \text{for } M_c < M_b < M_w \end{cases} \quad (2)$$

where,  $M_c$  is the critical molecular weight for entanglement of random branches,  $\bar{M}_w$  the weight-average molecular weight and  $M_b$  is an average molecular weight between a branch point and its adjacent vertexes, either chain ends or other branch points. The numerical prefactor  $A$  carries the dimensions of viscosity, and is specific for a chosen polymer system at a given temperature. The second line on the right hand side of equation gives the usual 3.4 power dependence of  $\eta_0$  on  $\bar{M}_w$  for linear polymers with  $M_w \gg M_c$ . The general behavior observed in branched polymers, namely viscosities either greater or less than those of linear counterparts with the same  $\bar{M}_w$ , is taken into account in the third line of equation through a dependence of the exponent  $s/\gamma$  on  $M_b$ .

$$\frac{s}{\gamma} = \max \left[ 1, \frac{3}{2} + \frac{9}{8} B \ln \left( \frac{M_b}{90 M_{Kuhn}} \right) \right] \quad (3)$$

Equation (2) and (3) comprise the general descriptive model to be employed below. If  $A$ ,  $B$ ,  $M_c$  and  $M_{Kuhn}$  are known constants, then, given measured values of  $\eta_0$  and  $\bar{M}_w$ , it is possible to solve these equations to obtain  $M_b$  in cases where  $M_c < M_b < M_w$ . In Table 3, the parameters used to calculate the viscosity dependence on  $\bar{M}_w$  and level of branching for PECT randomly branched samples are shown. The selected  $B$  value should be compatible assuming that the insertion of a PER unit in the copolyester chain creates a branching point. Accordingly, the most logical branching levels were obtained considering  $B = 6.2$ .

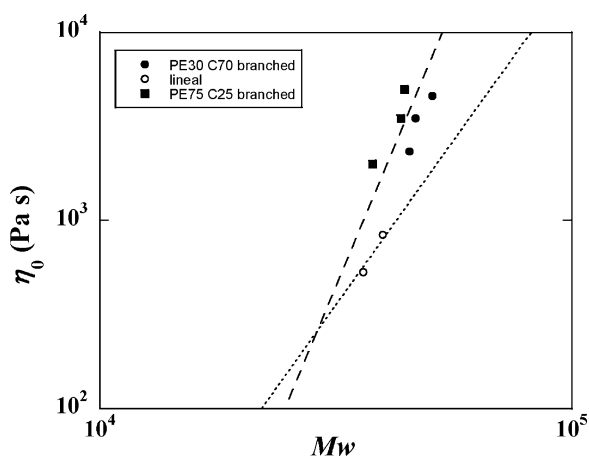


Figure 4. Double logarithmic plot of the zero shear viscosity  $\eta_0$  (Table 2) against molecular weight for all the investigated samples (Table 1). The lines are drawn considering the literature results on  $\eta_0$ - $\bar{M}_w$  correlation for linear and branched polyesters (see text).



**Table 3.** Parameters for randomly branched PECT, used to calculate the number of branches per molecule applying Janzen and Colby model.

Parameter	Value	
A (Pa · s)(g · mol <sup>-1</sup> )	3.85 × 10 <sup>-5</sup>	This work
B	6.2	This work
M <sub>0</sub> (g · mol <sup>-1</sup> )	218	–
M <sub>c</sub> (g · mol <sup>-1</sup> )	3300	[37]
M <sub>1</sub> (g · mol <sup>-1</sup> )	34	Molecular weight per bond
M <sub>Kuhn</sub> (g · mol <sup>-1</sup> )	138	Referred to PET <sup>[38,39] a)</sup>
M <sub>b</sub> /M <sub>c</sub>	Varied independently	–
s/γ	Varied	–

a)From  $M_{Kuhn} = pb_2\rho N_A$ ;  $p = 1.99 \text{ \AA}^{[39]}$ ,  $\rho = 0.989 \text{ g} \cdot \text{cm}^{-3}^{[38]}$ ,  $b = 1.07 \text{ nm}^{[40]}$ .

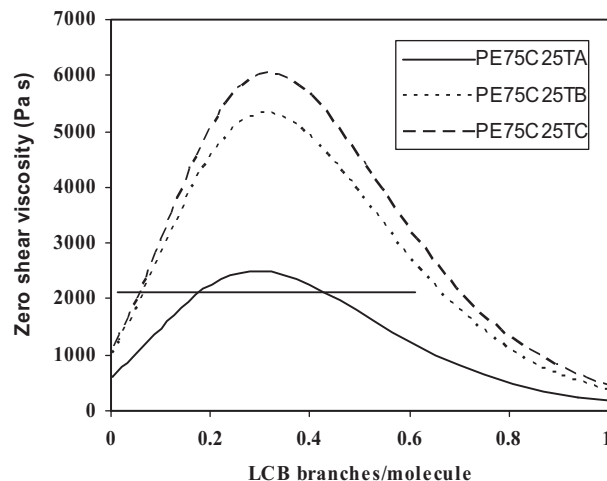
Lussignan et al.<sup>[36]</sup> estimated  $B = 2.1$  for copolyesters, although re-analysis of data by Janzen and Colby<sup>[37]</sup> indicated  $B = 3.9$ ; in both papers a functionality  $f = 3$  was contemplated. The higher  $B$  value required to deduce reasonable branching levels from our calculations should be due to the use of PER as a tetrafunctional branching agent ( $f = 4$ ). In fact, Lussignan et al. considered  $f = 3$  for a  $M_b = 40\,000 \text{ g} \cdot \text{mol}^{-1}$ , calculated directly from experimental data, but this value is unrealistic for our samples which have a weight-average molecular weight  $\bar{M}_w$  close to  $50\,000 \text{ g} \cdot \text{mol}^{-1}$ . Since  $B$  and  $M_b$  are inversely proportional, the higher  $B$  value estimated in our case is related to a lower  $M_b$  value.

For a randomly branched polymer chain, the average number of branches per chain and the branch length  $M_b$  are coupled for a given molecular weight<sup>[41]</sup>

$$M_b = \frac{M_w}{2\lambda + 1} \quad (4)$$

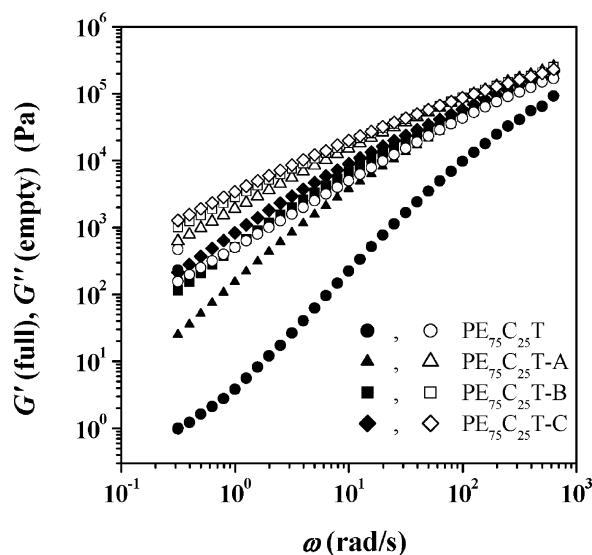
Varying  $\lambda$ , and so  $M_b/M_c$ , while holding  $\bar{M}_w$  fixed, the model predicts  $\eta_0$  passing through a maximum, as can be seen in Figure 5 for PE<sub>75</sub>C<sub>25</sub>T series. According to the results shown in Figure 5 the measured viscosity value of sample PE<sub>75</sub>C<sub>25</sub>TA  $\eta_0 = 2\,100 \text{ Pa} \cdot \text{s}$ , stands for two numbers of branches values:  $\lambda = 0.19$  and  $\lambda = 0.44$  branches/molecule. Only the value  $\lambda = 0.19$  can reasonably account for the PER concentration of this sample and, therefore, the second value should be rejected.

In Table 2, the values of the branches per molecule of our samples, deduced using the described procedure are presented.



**Figure 5.** Zero shear viscosity values,  $\eta_0$ , given by the Janzen and Colby model (Equation 2) varying  $M_b/M_c$  and therefore  $\lambda$ , for samples PE<sub>75</sub>C<sub>25</sub>T-A ( $\bar{M}_w = 37\,800$ ), PE<sub>75</sub>C<sub>25</sub>T-B ( $\bar{M}_w = 43\,400$ ) and PE<sub>75</sub>C<sub>25</sub>T-C ( $\bar{M}_w = 44\,200$ ). As an example, the crossing line taken at  $\eta_0 = 2\,100 \text{ Pa} \cdot \text{s}$  (viscosity of PE<sub>75</sub>C<sub>25</sub>T-A sample) gives two  $\lambda$  values (see text).

In Figure 6 and 7, the storage  $G'$  and loss  $G''$  moduli as a function of frequency for the two PECT-containing PER series are presented. A noticeable increase in the storage or elastic modulus  $G'$  as the percent of PER increased was remarked. Significantly, the crossover frequency  $\omega_x$  (given by the frequency at  $G' = G''$ ) decreased as PER concentration increased, indicating an enhancement of melt elasticity. A parameter most commonly used to evaluate the elasticity of liquids is the steady-state compliance  $J_e^0$ . Using the general model of linear viscoelasticity<sup>[42]</sup>, this



**Figure 6.** Storage and loss moduli of PE<sub>75</sub>C<sub>25</sub> series as a function of frequency at 230 °C.

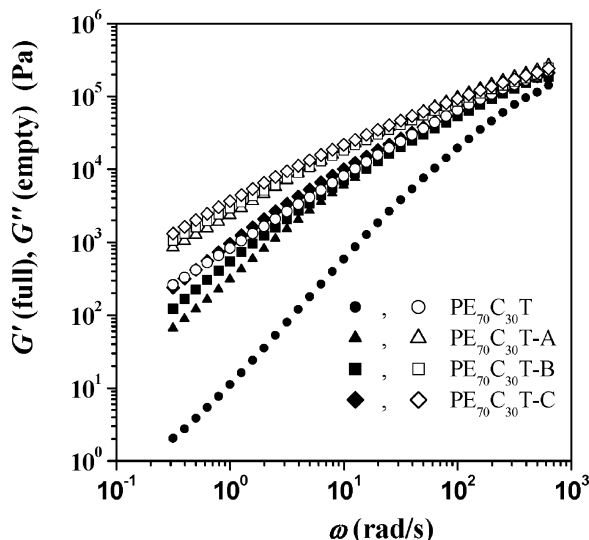


Figure 7. Storage and loss moduli of PE<sub>70</sub>C<sub>30</sub> series as a function of frequency at 230 °C.

viscoelastic function can be expressed as  $J_e^0 = \tau_d / \eta_0$ , where  $\tau_d$  is the longest relaxation time. As stated by Doi and Edwards,<sup>[43]</sup> the longest relaxation time corresponds to the reptation or disengagement time experimentally given by the inverse of the shear rate or frequency which marks the onset of shear thinning. Accordingly, the relaxation time  $\tau_0$  of Equation (1) is used in our case to obtain the steady-state compliance  $J_e^0$ . The corresponding values of  $\eta_0$ ,  $\omega_x$ ,  $\tau$  and  $J_e^0$  are presented in Table 2. It is well known that the steady-state compliance of linear polymer melts increases with the polydispersity of the molecular weight distribution, rather than with the molecular weight,  $\bar{M}_w$ .<sup>[25,35,44]</sup> But in our case, the slight broadening of the molecular weight distribution as PER concentration augmented (Table 1) could not account for the severe increase in the steady-state compliance seen in Table 2. Consequently, the role played by long chain branching should be contemplated. As a matter of fact, enhanced melt elasticity was reported years ago for long chain branched polyethylenes, compared to linear samples.<sup>[45–49]</sup> More recently, the same effect has been recalled for isotactic and syndiotactic poly(propylene).<sup>[32,49–50]</sup> According to these results, we assumed that long chain branching caused by the incorporation of PER to polymerization process produced the observed melt elasticity increase. This reflected the favorable effect of long chain branching to improve the structural stability of the melt. Actually, viscosity and melt elasticity enhancement allows widening the processing window of PECT to methods which require melt strength such as calendering, blow molding and extrusion foaming. An excessively low viscosity coupled with low melt elasticity can produce instabilities and sagging. For instance, the correlation between melt elasticity and

bubble stability in blow-molding of polyethylenes was analyzed by Leal et al.<sup>[51]</sup> In the case of polyesters, the incorporation of chain modifying agents by reactive extrusion was employed by Forsythe (2006)<sup>[18]</sup> to promote the formation of hyperbranched PETs and, hence, improve the melt strength of the samples.

#### Capillary Extrusion Measurements: Flow-Induced Crystallization

The capillary flow developed in pressure driven extrusion rheometers offers the advantage of giving viscosity results under conditions similar to those involved in polymer processing. In the particular case of the investigated samples, we focused our attention in the shear rate ranging from 20 to 200 s<sup>-1</sup>. This interval is typically implied in extrusion blowing and calendering processes. The viscosity results of our PECT samples at a suitable temperature for polyesters ( $T = 230$  °C) are shown in Figure 8 and 9. Although the shear thinning effect gave rise to a certain viscosity convergence at the highest shear rates, the viscosity enhancement as PER was added was significant. Therefore, a stability improvement of the calendering process of a linear PECT can be expected with the addition of a branching agent such as PER.

One of the potential advantages of the PECT samples is their *a priori* amorphous character, which make them suitable to be processed at temperatures approximately 100 °C above the  $T_g$ . Considering this circumstance, the viscosity of the samples was also measured at 180 °C (approximately  $T_g + 100$ , see Table 1) in the capillary extrusion rheometer described in the Experimental Part. For PE<sub>70</sub>C<sub>30</sub> series normal results, steady-state viscosities

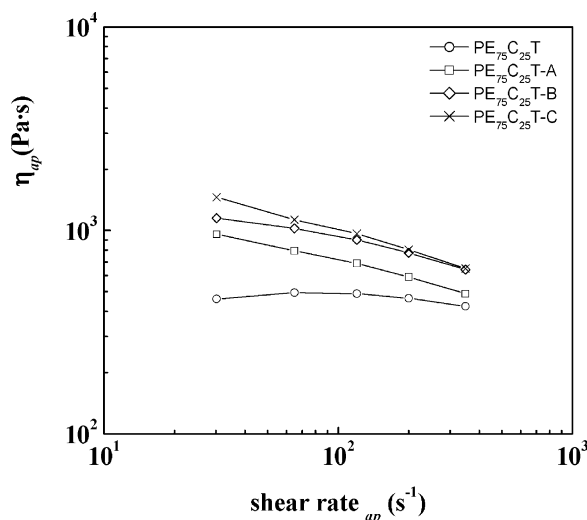


Figure 8. Viscosity of PE<sub>75</sub>C<sub>25</sub>T series as a function of the apparent shear rate obtained in capillary flow at  $T = 230$  °C. Lines are drawn to guide the eye.



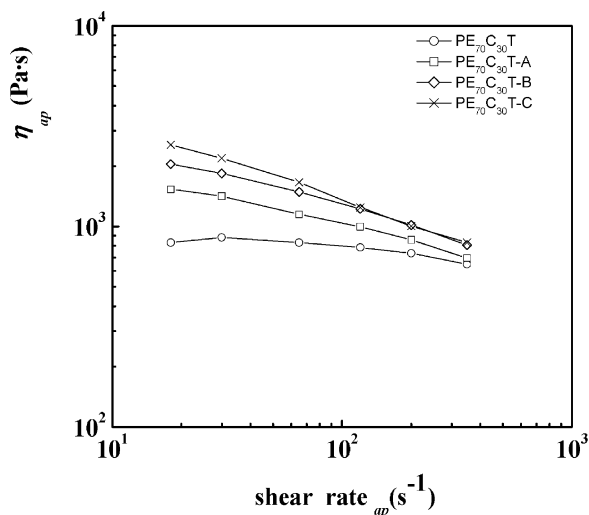


Figure 9. Viscosity of PE<sub>70</sub>C<sub>30</sub>T series as a function of the apparent shear rate obtained in capillary flow at  $T = 230\text{ }^{\circ}\text{C}$ . Lines are drawn to guide the eye.

and transparent extrudates (not shown) were obtained. Measurements carried out with a linear PE<sub>75</sub>C<sub>25</sub>T sample at  $180\text{ }^{\circ}\text{C}$  also gave steady-state flow and transparent extrudates, although a peculiarity, which is described below, was remarked. However, in the case of branched PE<sub>75</sub>C<sub>25</sub>T-A, PE<sub>75</sub>C<sub>25</sub>T-B and PE<sub>75</sub>C<sub>25</sub>T-C samples, steady-state flow curves could only be obtained up to  $\dot{\gamma} = 30\text{ s}^{-1}$ , since at higher values the piston force increased with time for a constant shear rate. Under this unstable flow, opaque extrudates were obtained, which lead us to consider the hypothesis of an incipient crystallization. Combined rheological and DSC analysis confirmed this theory. In Figure 10, the piston force (directly proportional to the melt viscosity) necessary to produce a shear rate of  $60\text{ s}^{-1}$  is presented as a function of extrusion time, at  $T = 190\text{ }^{\circ}\text{C}$  and  $180\text{ }^{\circ}\text{C}$ . The required piston force remained stable at  $190\text{ }^{\circ}\text{C}$ , indicating steady-state conditions (constant viscosity for a given constant shear rate) at any considered time. However, at  $180\text{ }^{\circ}\text{C}$ , after 13 min the piston force increased suddenly as flow was blocked. DSC analysis of the extrudates obtained, respectively at 180 and  $190\text{ }^{\circ}\text{C}$  were conclusive. In contrast to the completely amorphous extrudate obtained at  $190\text{ }^{\circ}\text{C}$ , Figure 10 shows the melting peak of a crystalline phase in the extrudate obtained after 13 min at  $180\text{ }^{\circ}\text{C}$ . The time at which the force began to increase (Figure 10) was taken as the onset time for induced crystallization. The corresponding melting temperatures, enthalpies of melting and crystallization onset times for branched PE<sub>75</sub>C<sub>25</sub>T-A, PE<sub>75</sub>C<sub>25</sub>T-B and PE<sub>75</sub>C<sub>25</sub>T-C extrudates are presented in Table 4. The peculiar response of linear PE<sub>75</sub>C<sub>25</sub>T at  $180\text{ }^{\circ}\text{C}$  is also considered in this table. No crystallinity was detected in the extrudates of this polymer, but the analysis of a sample

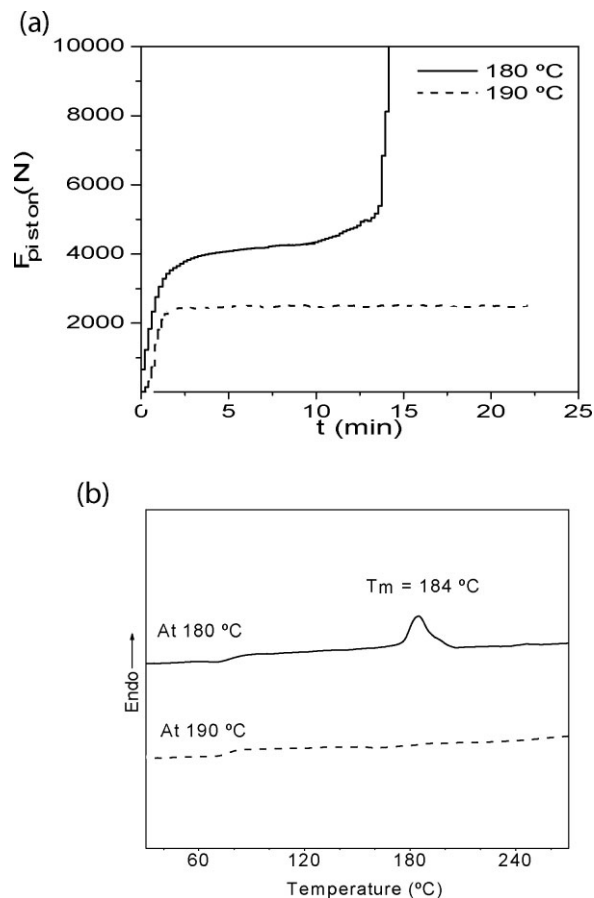


Figure 10. Extrusion flow results and DSC analysis of PE<sub>75</sub>C<sub>25</sub>T-A sample. (a) evolution with time of the piston force necessary to produce an apparent shear rate of  $60\text{ s}^{-1}$  at  $T = 190\text{ }^{\circ}\text{C}$  and  $180\text{ }^{\circ}\text{C}$ . (b) DSC results of the extrudates obtained at 180 and  $190\text{ }^{\circ}\text{C}$ , respectively: A completely amorphous extrudate is obtained at  $190\text{ }^{\circ}\text{C}$ . However, the melting peak of a crystalline phase is observed in the extrudate obtained after 13 min at  $180\text{ }^{\circ}\text{C}$ .

removed from the toroid shaped at the rheometer reservoir, at the entrance of the capillary die, showed the presence of a certain degree of crystallinity.

Before discussing the effect of long chain branching and CHDM concentration on crystallinity level, we analyze the mechanism of flow induction.

The pioneering work about induced crystallinity in polyethylene in an extrusion capillary rheometer, published by Southern and Porter almost 40 years ago,<sup>[52]</sup> was developed and extended to the case of PET by Cuculo and coworkers<sup>[53–56]</sup> in the late 1970s and early 1980s. These authors focused on the role played by converging flows at the entrance of the capillary die, concluding that the formation of crystals should be attributed to elongational rate in the converging stream. These crystals can migrate to die flow zone giving rise to opacity of the extrudates, as well as to a rapid piston force increase, like that observed

**Table 4.** Crystallization onset time  $t_i$ , melting temperature  $T_m$  and enthalpy of melting  $\Delta H_c$  of the extrudates obtained at 180 °C. For linear PE<sub>75</sub>C<sub>25</sub>T copolymer, data correspond to a piece of sample taken from the toroid formed at the entrance of the capillary (see text). No crystallization was observed in the case of PE<sub>70</sub>C<sub>30</sub> series.

	$t_i$	$T_c$	$\Delta H_c$
	min	°C	J · g <sup>-1</sup>
PE <sub>75</sub> C <sub>25</sub> T	>35	191	2.6
PE <sub>75</sub> C <sub>25</sub> T-A	13	186	14.2
PE <sub>75</sub> C <sub>25</sub> T-B	3	184	17.2
PE <sub>75</sub> C <sub>25</sub> T-C	<1	184	20.3

in Figure 10. The DSC result of the linear PE<sub>75</sub>C<sub>25</sub>T sample (Table 4) indicated that small crystals were formed, presumably by elongational flow, at the entrance of the capillary die. To confirm that converging stream at the entrance of the capillary was responsible for the observed crystallization and discard the possibility of shear-induced crystallinity, a 2 h continuous shear flow measurement in a plate–plate torsion mode rheometer at  $T=180$  °C and  $\dot{\gamma}=60$  s<sup>-1</sup> was performed with PE<sub>75</sub>C<sub>25</sub>T series samples; not a single symptom of crystallization was observed, all the samples remained amorphous, as in their original state. The possibility of pressure-induced crystallization was also judged, submitting the samples to pressures equivalent or higher than those developed during flow, in a pressure–volume–temperature, PVT Haake equipment. No variation in the amorphous state of the samples was observed. Therefore, we assumed that the explanation offered by Cuculo and coworkers holds for the flow-induced crystallization process of linear and branched PE<sub>75</sub>C<sub>25</sub>T series. In the particular case of linear PE<sub>75</sub>C<sub>25</sub>T, no crystals were observed in the extrudate, which would indicate that crystals formed at the entrance were not able to migrate to the capillary flow.

According to the enthalpies of melting and crystallization onset times shown in Table 4, induced crystallinity increased with long chain branching. This constituted an initially unexpected result, since it is known that owing to the irregularity of their structure, crystallization is more difficult in branched polymers, than in linear equivalent polymers. In particular, this was verified for PET containing PER.<sup>[14]</sup> However, to the difference with most commonly thermodynamically investigated quiescent crystallization processes, flow conditions may play a major role in flow-induced crystallization. In this sense, although the applied shear rate was the same for all our samples ( $\dot{\gamma}=60$  s<sup>-1</sup>), the viscosity and, consequently, the shear stress augmented with LCB level, which resulted in an increase in the elongational rate. This is based on the

analysis of the converging flows, initiated by Cogswell (1972),<sup>[57]</sup> that shows a direct proportionality between the elongational velocity gradient developed at the entrance of a capillary and the shear stress produced in the capillary flow. In consequence, contemplating the rheological prevailing effect on flow-induced crystallization, our results were not surprising; as long chain branching level augmented, the developed elongational rate in the converging flow increased, which produced a reduction of the crystallization induction time and an increase of the enthalpy of melting.

Another outcome of our research was that neither linear nor branched PE<sub>70</sub>C<sub>30</sub>T series samples crystallized, at least under the conditions considered in this work. Certainly, 30% CHDM concentration lies exactly in the middle of the 20–40% amorphous copolyesters window (see Figure 1 of Turner<sup>[7]</sup>), which can be linked to the slowest crystallization process. This was at a certain extent confirmed when we analyzed the scarce literature results about crystallization of PECT under special conditions. In a patent presented by Schiraldi et al. (2001)<sup>[6]</sup> it was claimed that annealing an amorphous PE<sub>75</sub>C<sub>25</sub>T sample at 150 °C for 2 h results in a partially crystalline sample of melting peak 185 °C and melting enthalpy 25.2 J · g<sup>-1</sup>. The authors remarked the much lower degree of crystallinity observed for a PE<sub>65</sub>C<sub>35</sub>T sample (melting enthalpy 2.2 J · g<sup>-1</sup>) which was attributed to the high amount of CHDM. On the other hand, a strain-induced crystallization of an amorphous commercial PE<sub>80</sub>C<sub>20</sub>T was investigated by Kattan et al. (2001),<sup>[58]</sup> but significantly not similar studies were reported for more central CHDM percents of the amorphous 20–40% window. We, therefore, believe that the suppression of induced crystallization process observed for PE<sub>70</sub>C<sub>30</sub> series is probably associated with the shift to a 'more amorphous' character, as CHDM augments from 25 to 30%.

## Conclusion

A set of amorphous PECT containing 25 and 30% of CHDM units and small amounts of branching agent (PER, 1, 1.5 and 2 mol-%) were obtained. These long chain branched PECTs displayed increase in intrinsic viscosities with increase in contents in the tetrafunctional agent, but no significant change in their thermal and mechanical properties was observed.

The effect of long chain branching on zero shear viscosity and on melt elasticity was revealed. Following the method proposed by Janzen and Colby, based on  $\eta_0$  results, the level of long chain branching was estimated to be between 0.08 and 0.21 branches/molecule. On the other hand, it was seen that long chain branching also produces a melt elasticity enhancement. Both viscosity and

elasticity enhancement are desirable for certain processing methods, such as blow molding and calendering.

Capillary extrusion experiments at 180 °C produced a flow-induced crystallization process which was proven to be originated by elongational flow at the entrance of the capillary. Surprisingly enough, crystallization level increased as the amount of LCB augmented. This unexpected result is explained by analyzing the favorable influence of long chain branching to increase elongational rate. Linear and branched PECT containing 30% of CHDM did not crystallize, at least under the experimental conditions considered in this work.

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