Solid-State Polycondensation of Poly(Ethylene Terephthalate) Recycled from Postconsumer Soft-Drink Bottles. I.

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SYNOPSIS

Poly(ethylene terephthalate) (PET), taken from postconsumer soft-drink bottles, was subjected to solid-state polycondensation, as received or after dissolution in various solvents and precipitation in methanol. The solvents used were: benzyl alcohol, phenol/tetrachloroethane 60/40, or o-chlorophenol. The effect of various reaction parameters, such as reaction temperature (180, 200, 220, and 230°C), and time on intrinsic viscosity [η] and carboxyl and hydroxyl end-group content have been investigated. During the solid-state polycondensation of PET that was used as received, both esterification and transesterification took place at all temperatures, while in PET samples, used after dissolution, the transesterification was observed only at 230°C. The highest number average molecular weight, $\bar{M}_n$ = 60,200, was obtained from PET with initial $\bar{M}_n$ = 20,300, dissolved in o-chlorophenol, after solid-state polycondensation at 230°C for 8 h. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET), a linear thermoplastic polyester, known as one of the major synthetic fibers, has become an important commercial material with many other applications, for example, soft-drink bottles, photographic films, recording audio and video tapes, films for food packaging, and insulating material for capacitors. For each application, a certain number average molecular weight ($\bar{M}_n$) is needed, for example, PET for audio or video tapes usually has an intrinsic viscosity [η] of 0.55; as the requirements of mechanical properties become more stringent, higher molecular weight becomes necessary, for example, the PET for fibers has an [η] of 0.65, for carbonated soft-drink bottles, an [η] of 0.73, and for industrial tire cords, an [η] higher than 0.85. This high number average molecular weight PET is usually produced by "solid-state polycondensation" of a prepolymer and not by con-

tinuation of the melt polymerization, because longer time in the melt state causes an excessive degradation of the final product. On the other hand, many attempts are directed toward recycling of PET bottles, which are used in secondary end use applications. The recycling rate for PET containers was 18% in 1987, 28% in 1989,[1] and 35% in 1993 in the USA.

The present work is concerned with the solid state polycondensation of PET, recycled from postconsumer Coca-Cola bottles. These bottles, free from their polyethylene base and cups and polypropylene labels, were dissolved in a solvent such as: benzylic alcohol (BA), phenol/tetrachloroethane mixture (PTCE), or o-chlorophenol (OCP). The dissolved PET, after isolation by precipitation in methanol, was subjected to solid-state polycondensation. The aim of this dissolution of PET bottles was to provide PET samples with a high surface area, which facilitates the process of polycondensation.[2]

The properties of PET samples, obtained after dissolution and solid-state polycondensation, were found to be dependent on the nature of the solvent used.

EXPERIMENTAL

Materials

Postconsumer PET bottles from Coca-Cola, free from polyethylene bases and cups and polypropylene labels, were washed with detergent, were rinsed with hot water, and were vacuum dried at 110°C for 12 h. The average thickness of the bottle wall was 0.28–0.30 mm. This material was cut in a mill into small pieces, was sieved, and the particle size fraction −0.80 + 0.40 mm was chosen. The dried, granulated material was subjected to solid-state polycondensation, or it was dissolved first in a solvent (BA, PTCE, or OCP), was precipitated in methanol, was dried, and was then subjected to solid-state polycondensation under the same conditions. PET samples, obtained after dissolution, were fibrous.

Solid-State Polycondensation

The reaction apparatus involved six volumetric flasks (100 mL), which were connected to a vacuum line and were immersed in a potassium nitrate/sodium nitrite thermostated bath, having a precision within ±0.5°C. A thermometer was introduced in the first flask, which, when touching the bottom of the flask, showed a difference of only 0.5–1.0°C under vacuum.

Two g of the PET sample was introduced in each flask and the vacuum stabilized between 3 and 4 Pa. The reaction temperature was kept constant at 180, 200, 220, or 230°C. The reaction flasks were withdrawn successively from the bath after 1, 2, 4, 6, and 8 h, and were allowed to be cooled to room temperature. The resulting samples were measured for the intrinsic viscosity, hydroxyl, and carboxyl content.

Measurements

All viscosity measurements were conducted at 25.0 ± 0.1°C in an Ubbelohde-type viscometer on solutions in 60/40% w/w PTCE, at a polymer concentration of 0.25%. The intrinsic viscosity of each sample was calculated by using the Solomon–Ciuta[3] equation of a single point measurement.[4-6]

$$[\eta] = [2(\eta_{sp} - \ln n_{rel})]^{0.5}/c \qquad (1)$$

The number average molecular weight ($\bar{M}_n$) of the samples was calculated from $[\eta]$ values, using the Berkowitz[11] equation, which is shown in "Re-

sults and Discussion." The $\bar{M}_n$ was also calculated from the end-group content of the samples as

$$\bar{M}_n = 2/(OH) + (COOH) \qquad (2)$$

where the concentration of hydroxyl and carboxyl groups is expressed in mol/g.

The carboxyl end-group content was determined according to Pohl's method.[7] The hydroxyl end group content was determined according to the method proposed by Zimmermann and Kolbig,[8] reported also by Weisskopf.[9] The latter method is based on the reaction of the hydroxyl end-groups of PET with o-sulfobenzoic acid cyclic anhydride.

The thermal behavior of solid-state polycondensated samples was studied using a differential scanning calorimeter DSC-2 (Perkin–Elmer). Measurement conditions (DSC) were: Sample weight = 8 ± 0.1 mg, heating rate = 20°C/min, cooling rate = 2.5°C/min, and sensitivity = 5 mcal/sec.

RESULTS AND DISCUSSION

Solubility

In this work, PET derived from postconsumer Coca-Cola bottles was dissolved in a certain solvent and was precipitated in methanol in order to produce a fibrous PET sample, a form which is more convenient for solid-state polycondensation. PET is generally insoluble in most common organic solvents at room temperature, and only at higher temperatures does a slight solubility appear in certain solvents, such as BA, PTCE, or OCP. The solubility behavior of PET in these solvents was determined and the results are shown in Table I. The solutions were heated at a temperature of about 15°C lower than the boiling point of the solvent for 15 min. The dissolved PET was isolated by precipitation in methanol and was characterized by determination of the intrinsic viscosity [η] and the end-group content in order to check if chemical reactions also occurred during the dissolution of PET.

Benzylic alcohol (BA), although permitted the use of the highest temperature, showed the lowest solubility effect on PET and also caused an alcoholysis reaction; the $\bar{M}_n$ of the recovered PET was decreased from 20,200 to 15,000. Phenol/tetrachloroethane (PTCE) showed a slightly higher solubility effect than BA and a smaller effect on $\bar{M}_n$, but this mixture is difficult to handle and is not recyclable. o-Chlorophenol (OCP) is shown to be the best solvent.

Table I Solubility Data of PET in Different Solvents[a]

Solvent	Solubility (%)	Temperature (°C)	Yield[b] (%)	$[\eta]$ (dL/g)	$\bar{M}_n$
Blank	—	—	—	0.73	20,300
BA	8.9	190	96	0.60	15,000
PTCE	10.0	130	100	0.70	19,000
OCP	10.4	160	98	0.73	20,300

[a] After heating with stirring for 15 min.
[b] This is the yield of the recovered PET after precipitation in methanol.

Viscometry

In order to find the $\bar{M}_n$ of postpolycondensated samples by viscometry, a suitable Mark–Houwink equation was looked for in the literature (Table II).

The Moore equation[10] relates the inherent viscosity η_{inh} (at a polymer concentration of 0.25%) with the weight average molecular weight ($\bar{M}_w$):

$$\eta_{inh} = 4.68 \times 10^{-4} \, \bar{M}_w^{0.68} \qquad (3)$$

For PET, $\bar{M}_w = 2 \, \bar{M}_n$ and, therefore,

$$\eta_{inh} = 7.50 \times 10^{-4} \, (\bar{M}_n)^{0.68}$$

or

$$\bar{M}_n = 3.92 \times 10^4 \, \eta_{inh}^{1.47} \qquad (4)$$

The Hergenrother and Nelson equation[6] relates the intrinsic viscosity $[\eta]$ with the viscosity–average molecular weight, ($\bar{M}_v$):

$$[\eta] = 2.37 \times 10^{-4} \, (\bar{M}_v)^{0.73} \qquad (5)$$

Using an average value of 1.86 for $\bar{M}_v/\bar{M}_n$, one can obtain a good approximation of $\bar{M}_n$ for all PET sam-

ples with a dispersion factor near 2.0 by the appropriate substitution,

$$[\eta] = 2.37 \times 10^{-4} \, (1.86 \, \bar{M}_n)^{0.73}$$

or

$$[\eta] = 3.73 \times 10^{-4} \, (\bar{M}_n)^{0.73}$$

and therefore

$$\bar{M}_n = 4.98 \times 10^4 [\eta]^{1.37} \qquad (6)$$

The Berkowitz equation[11] relates the intrinsic viscosity $[\eta]$ of PET to its $\bar{M}_w$:

$$[\eta] = 7.44 \times 10^{-4} \, \bar{M}_w^{0.648} \qquad (7)$$

For PET: $\bar{M}_w = 2 \, \bar{M}_n$, so

$$[\eta] = 11.66 \times 10^{-4} \, \bar{M}_n^{0.648}$$

and

$$\bar{M}_n = 3.29 \times 10^4 \, [\eta]^{1.54}$$

The Uglea equation[12] relates the intrinsic viscosity with $\bar{M}_n$

Table II Literature Mark–Houwink Constants for PET Solutions in Phenol/Tetrachloroethane 60/40% w/w at 25°C

Molecular Weight	$\bar{M} \times 10^{-3}$ (Range)	$k \times 10^4$ (dL/g)	a	Method	Reference
$\bar{M}_w$	10–147	4.68	0.680	Light Scattering	10
$\bar{M}_v$	45–185	2.37	0.730	Osmometry, GPC	6
$\bar{M}_w$	2–200	7.44	0.648	SEC, LALLS[a]	11
$\bar{M}_n$	4.7–25	2.52	0.800	Titration	12

[a] SEC = Size Exclusion Chromatography; LALLS = Low Angle Laser Light Scattering.

Table III Number Average Molecular Weight of a PET Sample (Blank, $\bar{M}_n = 19{,}800$), Calculated by Differing Proposed Mark–Houwink Equations

Moore	Hergenrother	Berkowitz	Uglea
24,700	32,400	20,300	21,300

$$[\eta] = 2.52 \times 10^{-4}\, \bar{M}_n^{0.80} \tag{9}$$

and

$$\bar{M}_n = 3.15 \times 10^4\, [\eta]^{1.25} \tag{10}$$

All the above equations were applied for the non-solid-state polycondensated sample (blank), which showed an intrinsic viscosity $[\eta] = 0.73$ and a number–average molecular weight, $\bar{M}_n = 19{,}800$, calculated from the end-group content (Table III).

The Moore equation shows a good approximation, but this equation involves the inherent viscosity at a concentration 0.25% and not the intrinsic viscosity as the Mark–Houwink equation requires. The Hergenrother equation yields molecular weights that are about 50% higher. The Uglea equation shows good agreement, but the use of titration for molecular weight determination rapidly loses sensitivity as the end-group content decreases and, thus, yields high values for the constant $a^{6,13-16}$ in the Mark–Houwink equation; in addition, all these end-group analyses were run on PET samples, prepared by ester interchange, assuming that all of the end groups are hydroxyl or carboxyl, but this is not true.[6,17] So, use of the Berkowitz equation was found to be better.[8]

Solid-State Polycondensation

PET samples, after solid-state polycondensation, were characterized by determination of intrinsic

Table IV Solid-State Polycondensation of Bottle PET, at 230°C

Sample	Time (h)	$[\eta]$ (dL/g)	$\bar{M}_n{}^a$	(COOH) $\times 10^6$ (mol/g)	(OH) $\times 10^6$ (mol/g)	$\bar{M}_n{}^b$
Blank	—	0.73	20,300	43	58	19,800
As Received	1	0.87	26,500	34	44	25,600
	2	1.00	32,900	29	38	29,900
	4	1.15	40,800	27	31	34,500
	6	1.16	41,300	23	29	38,500
	8	1.22	44,700	22	28	40,000
Blank	—	0.60	15,000	40	84	16,100
From BA	1	0.83	24,700	32	76	18,500
	2	0.91	28,500	30	70	20,000
	4	1.04	35,000	27	66	21,500
	6	1.12	39,200	25	50	26,700
	8	1.19	43,000	22	49	28,200
Blank	—	0.70	19,000	40	57	20,600
From PTCE	1	0.86	26,100	32	48	25,000
	2	0.93	29,400	28	42	28,600
	4	1.05	35,500	25	36	32,800
	6	1.14	40,300	23	37	33,300
	8	1.24	45,200	22	28	40,000
Blank	—	0.73	20,300	41	56	20,600
From OCP	1	1.03	34,400	27	40	29,900
	2	1.19	43,000	24	36	33,000
	4	1.31	49,900	22	30	38,500
	6	1.41	55,800	20	25	44,400
	8	1.48	60,200	18	20	52,600

a $\bar{M}_n$ was calculated from the $[\eta]$ value.
b $\bar{M}_n$ was calculated from the end-group content.

viscosity and the carboxyl and hydroxyl group content. The results obtained for PET, used as received from postconsumer soft-drink bottles at 230°C, are presented in Table IV.

The $\bar{M}_n$, calculated from the end-group content, was found to be in good agreement with that calculated from intrinsic viscosity. The dependence of $\bar{M}_n$, calculated by both methods on the square root of reaction time, was found to be approximately linear. This is an indication that the main reaction, during the studied solid-state polycondensation, was the esterification. This is considered to be a third-order reaction, in which the degree of polymerization is increased linearly with the square root of time (Fig. 1).[18]

However, by examining the differences,

$$\Delta(COOH) = (COOH)_0 - (COOH)_t$$

and
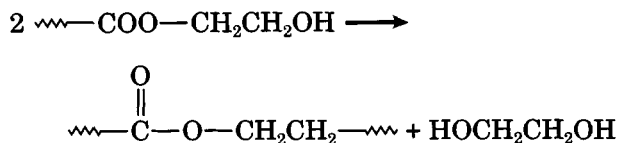
$$\Delta(OH) = (OH)_0 - (OH)_t$$

which express the mol/g of the carboxyl and hydroxyl groups, reacted in time t. It is shown that $\Delta(COOH) < \Delta(OH)$, which indicates that the transesterification reaction takes place at the same time as the esterification.

Esterification

$$\text{ww—COOH} + \text{HOCH}_2\text{CH}_2\text{—ww} \longrightarrow$$

$$\text{ww—}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{—O—CH}_2\text{CH}_2\text{—ww} + H_2O$$

Transesterification

$$2 \text{ ww—COO—CH}_2\text{CH}_2\text{OH} \longrightarrow$$

$$\text{ww—}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}\text{—O—CH}_2\text{CH}_2\text{—ww} + \text{HOCH}_2\text{CH}_2\text{OH}$$
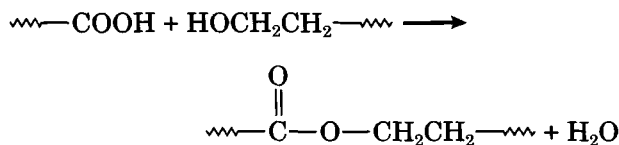
The PET sample, which was received after dissolution in BA and precipitation in methanol, showed a fibrous appearance, as did the sample observed for PET dissolved in trifluoroacetic acid/methylene chloride and precipitated in methanol, which was found to have a porous network with a high surface area.[2] This fibrous form was expected to increase the rate of the transesterification reaction during the solid-state polycondensation, because of the easier diffusion of ethylene glycol produced from transesterification. Esterification is not a diffusion-effected reaction, because water, produced from this reaction, is a small molecule with a high diffusion coefficient.

The PET sample, which was treated with BA and methanol, showed a higher hydroxyl content (84 mol/g) than the untreated PET (58 mol/g), because an alcoholysis reaction probably occurred during dissolution:
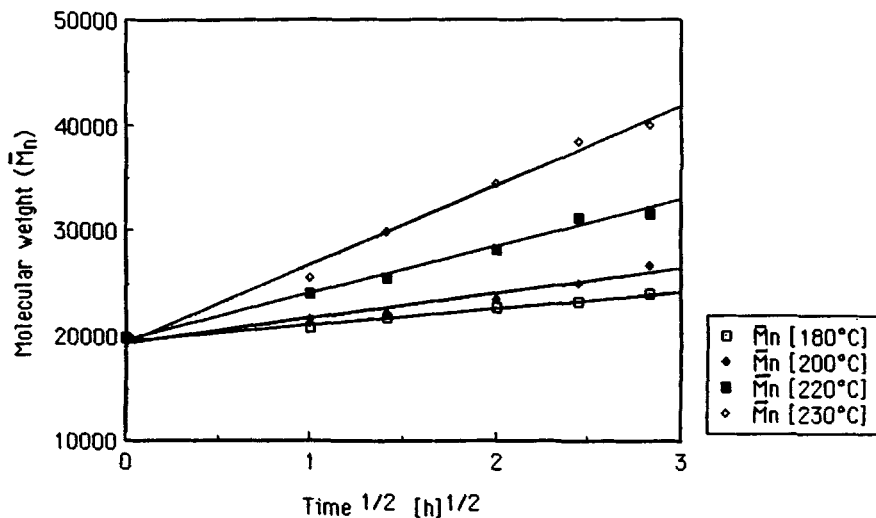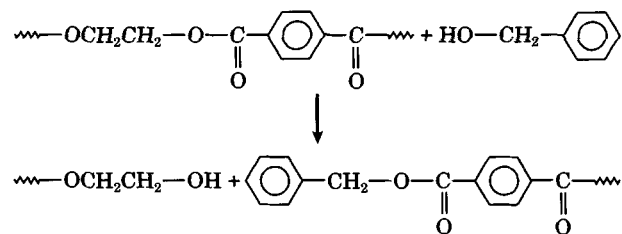

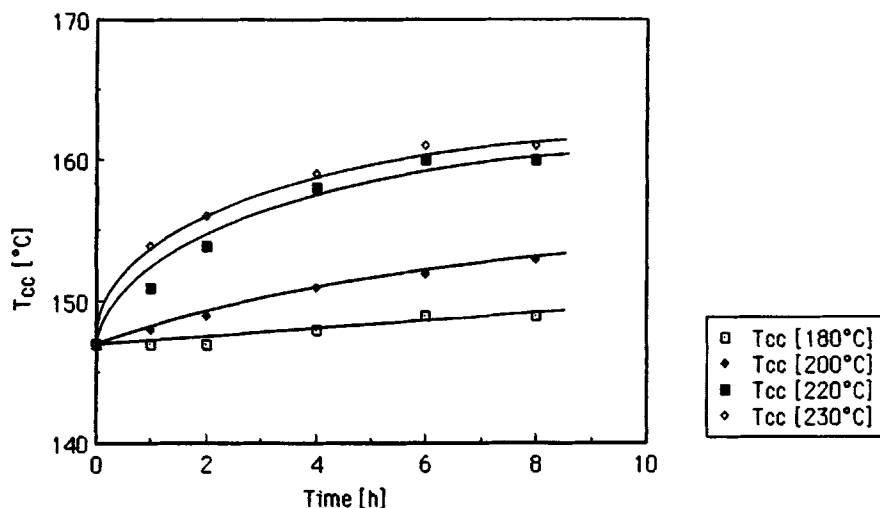Figure 1   Dependence of $\bar{M}_n$ on the square root of reaction time.

Figure 2 Cold crystallization temperatures against time for various solid-state polycondensation temperatures of PET samples derived from OCP.

This high hydroxyl content was also expected to increase the transesterification rate during solid-state polycondensation. The $\bar{M}_n$ values of solid-stated samples, calculated from the intrinsic viscosity, were not in agreement with those obtained from end-group content. However, the $\bar{M}_n$, calculated by both methods, increases linearly with the square root of time, indicating that in this case also, the esterification is the predominant reaction. After examining the decrease of (COOH) and (OH) with the time at various solid-state temperatures, it was found that $\Delta(\text{COOH})_t = \Delta(\text{OH})_t$ for 180°, 200°, and 220°, and only at 230°C was $\Delta(\text{COOH})_t < (\text{OH})_t$ (Table IV);

this indicates that, in this case, transesterification takes place only above 230°C. Such a finding was also reported by Droscher and Schmidt.[19] The fact that, in the solid-state polycondensation of the untreated PET, the transesterification was observed at lower temperature (180°C), must be attributed to the presence of the transesterification catalyst used for the PET preparation. This catalyst was probably extracted by the solvents during the dissolution of PET in BA and precipitation in methanol. However, the PET sample, obtained after this treatment after solid-state polycondensation at 230°C for 8 h, showed a higher increase in $\bar{M}_n$ (from
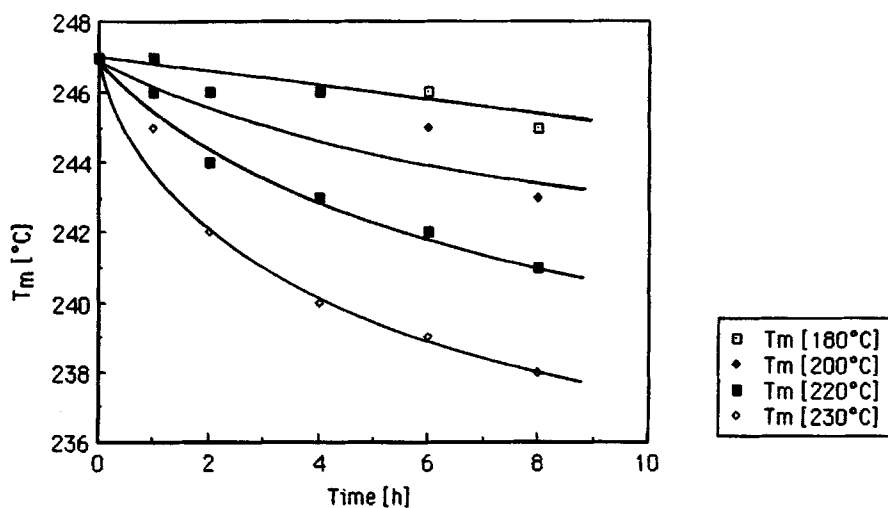

Figure 3 Melting temperatures against time for various solid-state polycondensation temperatures of PET samples derived from OCP.
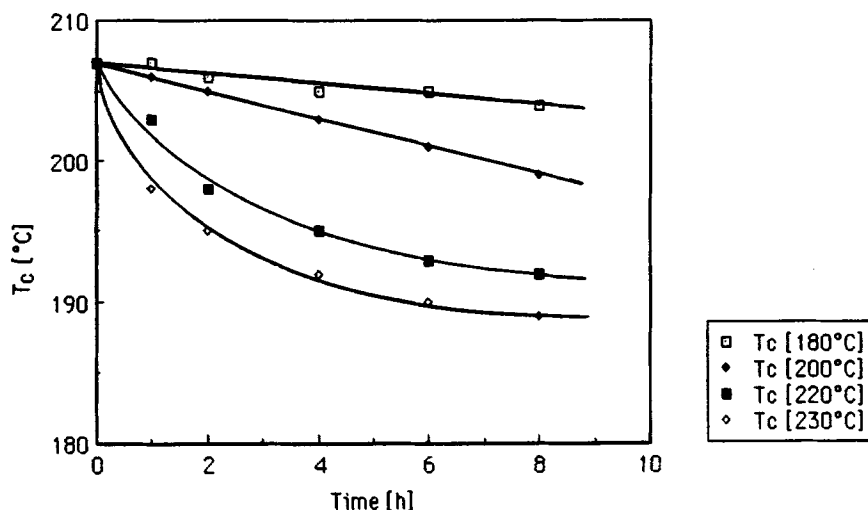
Figure 4 Crystallization temperatures against time for various solid-state polycondensation temperatures of PET samples derived from OCP.

15,000 to 43,000) than the untreated PET (from 20,300 to 44,700), solid-stated under similar conditions. This better result must be due to the fibrous form and the high hydroxyl content of the former, which enhanced the transesterification reaction.

In solid-state polycondensation of PET, received after dissolution in PTCE, the transesterification reaction was also observed at only 230°C (Table IV). At 230°C, where both esterification and transesterification take place, both samples showed the same results. The fibrous form of the sample dissolved in PTCE seems not to have enhanced the rate of the solid-state polycondensation.

Solid-state polycondensation of PET, obtained after dissolution in OCP, yielded the results. It is interesting to note that the highest number average molecular weight, $\bar{M}_n$ = 60,200, was obtained from PET with initial $\bar{M}_n$ = 20,300, after solid-state polycondensation at 230°C for 8 h.

Melting Behavior

Differential scanning calorimetric (DCS) measurements showed that solid-state polycondensations strongly affect the thermal behavior of the PET samples. Clear, double melting endotherms were obtained for all solid-state polycondensated samples at 180 and 200°C; when higher temperatures were used (200-230°C), this double peak appeared as a single one. According to the literature,[20-22] the first endotherm must be attributed to the melting of the crystalline material formed during solid-state polycondensation and the second to the original crys-

talline material, reorganized into more perfect and larger crystals during DSC scan. According to Yagpharov,[23] two types of crystal formation are found, and the presence of a premelting peak in the DSC curve is attributed to the melting of secondary crystals of the "fringed micelle" type.

After the first melting of the solid-state polycondensated samples, they were quenched and were reheated. During the second heating, all the amorphous samples produced about the same glass transition temperature (T_g = 80-81°C), but different cold-crystallization temperatures (T_{cc}) (Fig. 2); so, as the molecular weight increases, T_{cc} increases, that is, the crystallization during heating becomes more difficult.

As far as the melting temperature of the quenched samples is concerned, these are lower than those of the postpolycondensated samples and they decrease as the molecular weight increases (Fig. 3).

When the melts of the samples in the DSC were cooled with a cooling rate of 2.5°C/min, a significant decrease of crystallization temperature was observed (Fig. 4). This change of crystallization temperature, with increasing molecular weight, is probably caused by the increase of viscosity and the decrease in chain mobility of macromolecules.

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