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On specific factors affecting the crystallization of PET: the role of carboxyl terminal groups and residual catalysts on the crystallization rate

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The non-isothermal crystallization rate of poly(ethylene terephthalate) (PET) has been studied in differential scanning calorimetry experiments, by cooling from the molten state of samples of various molecular weights, prepared using various catalysts (mainly $Ti(O\text{-}n\text{-}Bu)_4$). The crystallization temperature, T_{cc}, was obviously influenced by the molecular weight, but also by the carboxyl group content, by the type of residual catalyst, by dissolution–reprecipitation treatments and by re-melting phenomena. The observed effects were interpreted assuming that interactions of terminal groups of the PET chains (mutual or with residual catalyst) led to an apparent increase in molecular weight, which in turn determined a decrease in the chain mobility and was responsible for a decrease in the rate of crystallization. Thus, a higher concentration of carboxyl terminal groups as well as interactions of PET terminal groups with the catalyst decreased T_{cc}. Any factor which was able to destroy these interactions (treatments of dissolution–reprecipitation, phosphorous derivatives, aging) led to an increase of the overall crystallization rate. © 1997 Elsevier Science Ltd.

(Keywords: poly(ethylene terephthalate); crystallization; catalyst)

INTRODUCTION

Poly(ethylene terephthalate) (PET) was first prepared in 1946 and was commercially introduced in 1953 as textile fibre, and soon thereafter as film. More recently a dramatic development in PET production has resulted from the application of the blow-moulding technology to the production of beverage bottles. The wide applications of PET for the production of fibres, films and bottles derive from the good balance of thermal and mechanical properties of PET in the semicrystalline form, combined with a relatively low cost with the possibility of easy recycling.

Despite these outstanding properties, PET has not still gained noticeable applications in the field of injection moulding, because of its low rate of crystallization under the usual mould temperatures (≤90–110°C) and the absence of a field of forces, which induces orientation of macromolecules and increases the crystallization rate in the case of fibres, films and bottles.

Due to the relevance of this argument, many studies on the crystallization rate of PET have been carried out, resulting in a large number of patents and articles. These studies have shown that many factors can affect the crystallization rate of PET: molecular weight[1-8]; residual catalysts[1,4,7-10]; comonomers[1,3,6,11]; various additives[1,4-8,12-22] and ionic terminal groups[18-22] have been recognized as the most important.

Despite the number of patents and papers appearing on this subject, the need for systematic studies of the factors that influence the crystallization rate of PET still exists, and the present paper is intended as a further contribution to the understanding of the effect of some factors that have been previously neglected, or whose role is not completely understood. In particular, the effects and the role of carboxyl terminal-groups and of

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residual catalysts on the overall crystallization rate will be discussed.

An overview of the role of polymerization

Most of the factors that affect the crystallization rate of PET are originated during the preparation of PET, and therefore it is useful to summarize the more important features of the polymerization.

PET is usually obtained either from the polymerization of terephthalic acid (TA) with ethylene glycol (EG) or from dimethyl terephthalate (DMT) and EG. In both cases, catalysts are needed to achieve high-molecular-weight PET. A large number of catalysts can be used either for the transesterification of DMT and EG (derivatives of Ca, Mn, Mg, Zn, Ti, Sn, etc.) or for the polycondensation stage (derivatives of Sb, Ti, Ge, etc.)[23]. Frequently a mixture of several catalysts is employed. Because PET is usually prepared by bulk polymerization, the used catalysts remain in the PET after polymerization. As will be discussed below, this is an important point because the residual catalysts can influence the crystallization rate.

A further aspect to be considered is that side reactions take place during polymerization[23], leading to changes in the chemical structure, e.g. the formation of diethylene glycol (DEG) moieties in the backbone chains and of carboxyl terminal-groups. The relative extent of these reactions depends on the reaction conditions. The content of DEG units is usually relatively small (0.5–2 mol%), whereas the nature and relative amount of terminal groups may be quite different, depending on the nature of the starting monomers, the extent of the reaction, the thermal history and the catalyst employed. Although most of the terminal groups are usually primary hydroxyl groups (–OH), a relatively large amount of aromatic carboxyl groups (–COOH) can be present when the polymerization is carried out for a long time at high temperature, or in the presence of catalysts such as Ca, Zn, Mn and Ti derivatives[24], or when PET undergoes hydrolysis after polymerization. Vinyl–ester terminal groups, deriving from thermal degradation and disappearing by other side reactions, and carbomethoxide terminal-groups, deriving from an incomplete transesterification of DMT, can also be present in small percentages; the evaluation of these groups is difficult and their presence is usually neglected.

Finally, it has to be remembered that to reduce the extent of side reactions (such as thermal degradation, hydrolysis, etc.) derivatives of phosphorous are frequently added as catalyst-deactivators during the polymerization of PET. These compounds are believed to interact with catalysts[25,26], so that their presence may affect (directly or indirectly) the crystallization rate.

From this short summary it is clear that PET samples may differ from each other due to a series of factors, which can affect the overall crystallization rate. A correct interpretation of the data of crystallization rate should consider all these factors. However, a complete characterization of PET samples would require a lot of data which are time consuming and sometimes difficult to achieve, in particular when samples are commercial ones. For this reason, most of these factors are often not considered and, as a consequence, the interpretation of the experimental data may suffer from this approximation.

In the present paper all PET samples used were prepared and characterized in our laboratories in order to know the type and amount of catalyst, to be sure that no phosphorous derivatives were added and that the methods used for characterization were the same for all the samples.

Crystallization rate of PET, a literature survey

As stated above, the crystallization of PET is probably one of the most studied subjects in macromolecular science. Due to the industrial relevance of this argument, most of the literature is patent literature, where a large number of substances have been claimed to be effective nucleating additives for PET[15]. Usually, the aim of these references is just to claim an improvement in the overall crystallization rate from the melt, without any purpose of understanding the role of the additive on the increase of the crystallization rate.

In many cases these substances are inert solids, and it was assumed that they act as nucleating agents according to the nucleation growth theory of crystallization. However, this type of approach for the improvement of the crystallization rate of PET has not been very successful. Rarely, solid additives are very effective in the nucleation of PET, and when it happens it has been suggested that the role of the solid additive is different from the conventional role of nucleating agent[5,14,18–22].

Among the patent literature one of the most interesting pieces of work[27] reports the effect of oligomers, obtained by NaOH hydrolysis of PET, on the crystallization rate of PET. The increase of the crystallization temperature, T_{cc}, is probably the highest reported, so far, for PET samples cooled from the melt. The results of ref. 27 were explained in subsequent papers[18–22] as a consequence of an improved nucleation deriving by the clustering of the sodium carboxylated terminal groups ($\sim$PET–COO$^-$/Na$^+$) of the PET oligomers. The same mechanism is presumably the basis of the effects of many additives claimed as nucleants, as demonstrated for sodium benzoate[19–22]. In most of these cases the improvement of the crystallization rate of PET derives from a mechanism of chemical nucleation, according to which the salt initially added is able to react (by acidolysis reaction) with the PET chains leading to ($\sim$PET–COO$^-$/Na$^+$) terminal groups which subsequently aggregate to form the crystallization nuclei.

A partial local hydrolysis (which decreases the average molecular weight of PET) was assumed to explain the increase of the crystallization rate in the presence of $Al(OH)_3$[5].

The effects of molecular weight on the crystallization rate of PET have been studied by several authors[1–8]. The decrease of the spherulite growth-rate[2] and of the overall crystallization rate with increasing molecular weight was ascribed to a lower chain mobility for higher molecular weights. Unfortunately, it is difficult to compare the results from different authors, because of the different test conditions used and/or the poor characterization of the samples (e.g.: molecular weight measured by intrinsic viscosity with different solvents/temperature conditions; crystallization performed under different cooling rates; unknown type and amount of residual catalysts; different OH/COOH terminal-group ratio, etc.).

Effects of the residual catalyst on the crystallization rate have been reported in several papers[3,4,6–10]. It has been suggested that the effect of the residual catalyst is on the nucleation rate, and derives from the solid nature of the catalysts which are not soluble in the reaction medium[1,4,9].

According to these conclusions, soluble catalysts should not have any effect on the crystallization rate[1]. In another paper it has been reported that titanium derivatives give the lowest crystallization rate among various catalysts[8]. Sometimes the reported results are conflicting; contrary to what had been previously reported[6], it was shown that an appreciable nucleating effect of Sb_2O_3, a typical catalyst for PET, can be observed only at concentrations much higher than the usual[10]. From all these studies it is clear that the residual catalysts can influence the crystallization rate, but the results reported until now are not able to explain unambiguously their role.

Far less studied are other factors which could also affect the crystallization rate. As a consequence, their influence is not clearly defined and usually neglected. In particular, the effect of –COOH groups has never been studied extensively. Some data are instead reported on the effect of various comonomers[1,3]; an increase of the rate of crystallization is observed for some comonomers, while other comonomers, and DEG in particular, do not have any effect at the usual low concentration[1].

EXPERIMENTAL

Products

DMT and EG were polymerization grade products purchased from EniChem. $Ti(O\text{-}n\text{-}Bu)_4$ (from Aldrich) was distilled under vacuum before polymerization. The catalysts ($Mn(CH_3COO)_2 + Sb_2O_3$ and $Sm(CH_3COO)_3 \cdot xH_2O$ ($x = 4$–6) were commercial products (from Aldrich) and were used as supplied. The catalysts $Eu(acac)_3 \cdot diPy$ and $Tb(acac)_3 \cdot diPy$ (lanthanides acetyl acetonate with 2,2′-dipyridyl) were prepared as previously described[28].

Solvents

The solvents, methylene chloride (CH_2Cl_2), methanol (MeOH), hexafluoroisopropanol (HFIP), 1,1,2-trichloro-1,2,2-trifluoroethane (TCTFE), and 1,1,2,2-tetrachloroethane (TCE), were distilled before use. Benzyl alcohol was distilled on NaOH before use.

Synthesis of PET

The synthesis of PET samples was performed using different catalysts by the usual two-stage process in a 1.8 l stainless-steel batch reactor equipped with a paddle agitator (driven at 30 rpm) with a strain-gauge bridge mounted on the drive shaft to indicate the extent of polymerization. A typical procedure of polymerization is as follows: on starting the first stage, EG, DMT and catalyst (EG/DMT molar ratio 2.2/1, catalyst 0.063 mol% with respect to DMT) were stirred at atmospheric pressure while the temperature was raised from 160 to 200°C and maintained at this value until more than 95% of the theoretical amount of methanol was distilled off. Then, during the second stage, the pressure was reduced to 0.3 mbar and the temperature was raised to, and maintained at, 270°C until the end of the run. In order to obtain samples having different molecular weights, draughts from the batch reactor at different reaction times were carried out.

PET samples

PET samples contained no additives other than the residual catalyst. They were mainly used as recovered from the polymerization reactor, but several samples were also prepared as follows:

(i) The original PET samples were dissolved (≈1% wt/vol) either in HFIP/CH_2Cl_2 (30/70 vol/vol) at room temperature, or in boiling TCE (147°C). PET was then recovered by reprecipitation either in cold MeOH or TCTFE. Reprecipitation was performed by pouring the PET solutions into the non-solvent or vice-versa, and by fast or slow addition of/to the non-solvents. A few samples were also submitted to repeated solution/reprecipitation treatments.

(ii) The original PET samples (≈0.6 g) were stirred at high temperature (≈270°C) in a mini-mixer apparatus[29] for a short time (1 min) and then extruded and cooled at room temperature.

Intrinsic viscosity measurements

The intrinsic viscosity of all samples studied was measured at 25°C in internal dilution Ubbelohde viscometers in a 40/60 (wt/wt) phenol/TCE solvent mixture. At least four concentrations for each sample were used to obtain the intrinsic viscosity $[\eta]$. Whenever desired, the number-average molecular weight, M_n, was obtained from $[\eta]$ using the following relationship[30]

$$[\eta] = 1.4 \times 10^{-3} \cdot M_n^{0.64}$$

Carboxyl groups titration

Carboxyl terminal groups were determined by titration using alcoholic KOH (0.01 N) and phenol-red as the indicator. Samples of PET (≈0.5 g) were dissolved in 10 ml of refluxing benzyl alcohol; the titrations were carried out at a temperature higher than 100°C in order to avoid the reprecipitation of the polymer.

Differential scanning calorimetry measurements

A Perkin-Elmer DSC-7 instrument was used to obtain the non-isothermal crystallization data. PET samples (≈10 mg), dried under vacuum at 100°C overnight, were heated in a crimped aluminium pan at 300°C followed by 1 min hold, and then cooled at $-10°C\ min^{-1}$. The differential scanning calorimetry (d.s.c.) response was unchanged upon repeated cycling of this treatment. The temperature corresponding to the maximum of the exothermic peak in the d.s.c. cooling-curve, T_{cc}, was taken as a measure of the crystallization rate. At least three tests for each sample were performed. The instrument was calibrated using indium and tin metal standards.

RESULTS AND DISCUSSION

Usually it has been found that factors which increase the crystallization rate do so indifferently in experiments carried out by cooling from the molten state or by heating from the glassy state. In addition, it has been reported that the half-time of primary crystallization in isothermal experiments correlates with the temperature corresponding to the maximum of the crystallization peaks in non-isothermal experiments (T_{cc})[20]. T_{cc} is more quickly achieved, and sometimes more reliable, than the half-time of primary crystallization[31], and therefore we decided to study the effects of various parameters on the crystallization of PET, with non-isothermal experiments carried out by cooling PET from the melt in the d.s.c. apparatus.

It is well known that the thermal history may affect dramatically the crystallization rate if the nuclei previously formed are not completely erased[32]. For this reason heating at high temperature for a suitable time is usually carried out. But a too-long heating time at high temperature can influence the crystallization rate by reducing significantly the molecular weight of PET as a consequence of thermal degradation reactions[23,24]. Therefore, in preliminary experiments we studied the effect of temperature (280–320°C) and time (0.5–20 min) of heating before starting the d.s.c. cooling runs for crystallization. For the same sample, the heating in d.s.c. at 300°C for 1 min gave the lowest values of T_{cc} and the best reproducibility (better than ± 1°C) in repeated d.s.c. runs. These conditions were assumed to be able to destroy the previous thermal history, leaving the molecular weight almost unchanged, and were used for all the experiments except when expressly reported in the following.

In all PET samples the DEG content is $\leqslant 2\%$ mol and therefore, according to ref. 1, the effect of DEG units on the crystallization rate of PET was neglected.

Molecular weight and carboxyl terminal-groups effects

The increase of the crystallization rate of PET, when the molecular weight decreases, has been confirmed by many authors with various techniques and with isothermal[1,2,4,12,33–35] or non-isothermal[6,18 22,31,33 36] experiments.

The values of T_{cc} for PET samples prepared in our laboratories using Ti(O-*n*Bu)$_4$ as catalyst and cooled at -10°C min^{-1} are reported in *Figure 1* and *Table 1*. It is apparent that, for the molecular weight range considered there is a decrease of the overall crystallization rate with increasing molecular weight, which can be described by a linear dependence of T_{cc} on $[\eta]$, as previously found by other authors[3–5]. Some values of T_{cc} are very similar to those reported in refs 3 and 5, but the comparison is impossible for all the data because the equation used to derive M_n from $[\eta]$ is not reported in the above-cited papers.

The equation which best fits the data of *Figure 1* in the range of M_n considered, obtained by a linear regression, is:

$$T_{cc} = 228.8 - 62.35\,[\eta] \qquad (1)$$

with T_{cc} in °C and $[\eta]$ in dl g^{-1} (coefficient of correlation 0.980).

In *Figure 1*, we can observe that some samples with high and very similar $[\eta]$ have different T_{cc}s, the discordance being significantly higher than the standard deviation.

The most relevant difference between these samples that may account for the differences in T_{cc} is the amount of carboxyl terminal groups. It is well known that in a low-polarity medium two carboxyl groups may associate by hydrogen bonding, and it was also reported that they can "interact" with titanium catalyst (more strongly than hydroxyl groups)[37]. These associations bring about an "apparent" increase of molecular weight, which in turn reduces the chain mobility, and therefore can influence the value of T_{cc}.

The effect of the concentration of carboxyl terminal groups has been relatively neglected in the study of the crystallization rate of PET. The little data spread in the literature[6–8] has never described this effect quantitatively.

We separated the effects of $[\eta]$ from that of carboxyl terminal groups by a multiple linear regression that resulted in the equation.

$$T_{cc} = 233.8 - 52.3\,[\eta] - 0.51[\text{-COOH}] \qquad (2)$$

which can describe the dependence of T_{cc} from both $[\eta]$ and [–COOH] (with [–COOH] in meq kg^{-1}).

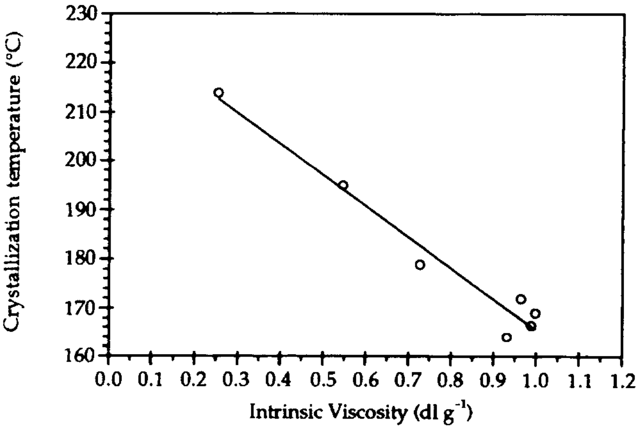

Figure 1 Cooling crystallization temperature against intrinsic viscosity for PET samples prepared with Ti(O-*n*-Bu)$_4$ catalyst

Table 1 Intrinsic viscosity data, concentration of terminal-groups and cooling crystallization temperature of PET obtained with various catalysts

	Catalyst	$[\eta]$ (dl g^{-1})	M_n	[COOH] (meq kg^{-1})	[OH] (meq kg^{-1})	T_{cc} (°C)
PET-Ti/A	Ti(O-*n*-C$_4$H$_9$)$_4$	0.252	3300	12	594	213.9
PET-Ti/B	Ti(O-*n*-C$_4$H$_9$)$_4$	0.545	11000	24	154	195.0
PET-Ti/C	Ti(O-*n*-C$_4$H$_9$)$_4$	0.726	17500	29	85	179.0
PET-Ti/D	Ti(O-*n*-C$_4$H$_9$)$_4$	0.931	25700	40	38	164.1
PET-Ti/E	Ti(O-*n*-C$_4$H$_9$)$_4$	0.962	27100	25	49	172.0
PET-Ti/F	Ti(O-*n*-C$_4$H$_9$)$_4$	0.988	28200	32	39	166.5
PET-Ti/G	Ti(O-*n*-C$_4$H$_9$)$_4$	0.997	28700	22	48	169.0
PET-Sm	Sm(CH$_3$COO)$_3$ · xH$_2$O	0.626	13800	–	–	195.0
PET-Eu	Eu(acac)$_3$ · diPy	0.665	15200	–		195.3
PET-Tb	Tb(acac)$_3$ · diPy	0.685	16000		–	177.6
PET-Mn,Sb/A	Mn(CH$_3$COO)$_2$ + Sb$_2$O$_3$	0.859	22700	–		195.2
PET-Mn,Sb/B	Mn(CH$_3$COO)$_2$ + Sb$_2$O$_3$	0.962	27100	37	37	182.2

By equation (2), it was possible to correct the experimental values of T_{cc} ($T_{cc,exp}$) for the contribution of –COOH terminal groups, and derive equations which gave the dependence of T_{cc} on $[\eta]$, at $[-COOH] = 0$, and of T_{cc} on [–COOH] at constant $[\eta]$, equations (3) and (4), respectively:

$$\begin{aligned} T_{cc,[-COOH]=0} &= T_{cc,exp} + 0.51\ [-COOH] \\ &= 233.8 - 52.3\ [\eta] \end{aligned} \tag{3}$$

and, for $[\eta] = 1\ \mathrm{dl\ g^{-1}}$:

$$\begin{aligned} T_{cc,[\eta]=1} &= T_{cc,exp} + ([\eta] - 1)\ 52.3 \\ &= 181.5 - 0.51\ [-COOH] \end{aligned} \tag{4}$$

Equations (3) and (4) are plotted in *Figures 2a* and *2b*. It is noteworthy that by subtracting the contribution of carboxyl terminal groups we obtained a much better linear correlation between T_{cc} and $[\eta]$, in particular for the high molecular weight samples (the coefficients of correlation are 0.980 and 0.995 for *Figures 1* and *2a*, respectively).

For linear chains, and assuming that the terminal groups are –OH and –COOH only, the value of [–COOH] is related to the number-average molecular weight, M_n, by the equation:

$$[-OH] + [-COOH] = \frac{2 \times 10^6}{M_n} \tag{5}$$

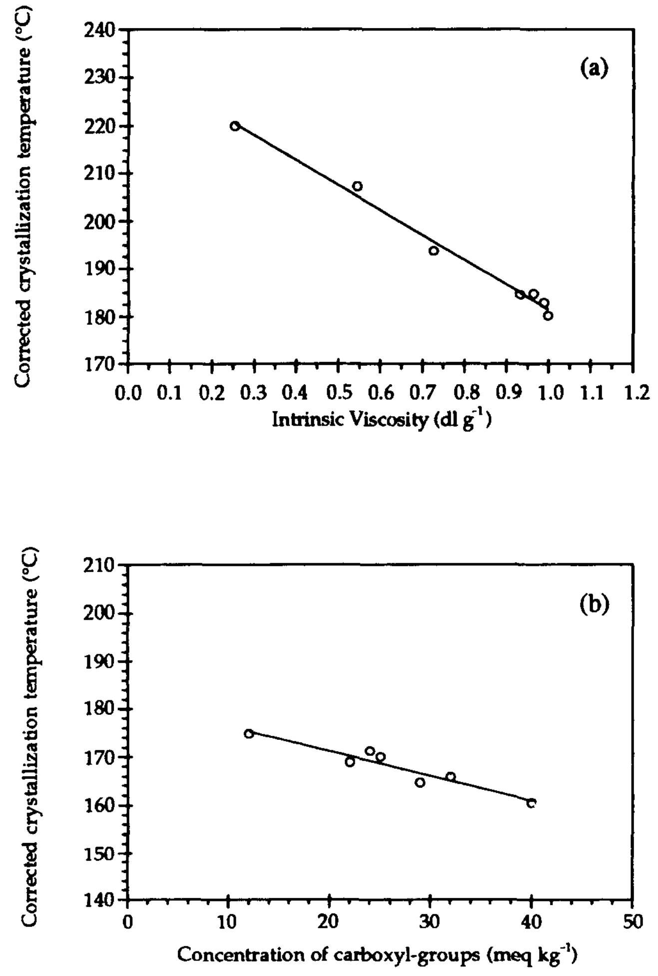

Figure 2 Corrected crystallization temperature against: (a) intrinsic viscosity for $[-COOH] = 0$; (b) carboxyl terminal groups for $[\eta] = 1\ \mathrm{dl\ g^{-1}}$

For a given M_n, the concentration of carboxyl terminal groups in PET is usually low ($[-OH]/[-COOH] \gg 1$), typically $\leqslant 20\ \mathrm{meq\ kg^{-1}}$ for a commercial PET, and its contribution to T_{cc} is relatively small. However in some cases, the concentration can be as high as 40–50 meq kg^{-1} or higher and the contribution to T_{cc} can become very important.

Of course equation (2) (and the related equations (3) and (4)) is an empirical equation that is expected to work for PETs with similar concentrations of Ti residual catalyst and at relatively high values of $[\eta]$. When the molecular weight decreases the specific concentration of very polar terminal groups (–OH, mainly) increases, leading to an increase of the overall polarity of the medium which in turn reduces the relative importance of the mutual association of –COOH groups or the interaction with titanium residual catalyst. So the effects of –COOH groups is expected to be more significant for PETs of high molecular weight, as was indeed observed. In equations (2)–(4) the concentration of hydroxyl terminal groups does not appear. This does not mean that interactions between –OH terminal groups and the catalyst do not exist, but that they give a constant contribution to the increase of the apparent molecular weight because their concentration is nearly constant.

Incidentally, it has recently been demonstrated that the interactions between terminal groups are responsible for significant changes in the glass transition temperature of polyesters[38], and also in that case the effects observed were ascribed to the influence of the interactions of terminal groups on the chain mobility.

Effects of the residual catalyst

The catalyst used to prepare PET is still present in the polymer after bulk polymerization and may influence the crystallization rate by different mechanisms. At present, the role of the residual catalyst is not clearly defined. Sometimes, the effects have been explained assuming that it is not soluble in the polymer and separates as a solid phase whose surface acts as a conventional nucleating agent[1,4]. In other cases, catalysts are believed to be soluble in PET, and their effects cannot be explained in this way.

We performed experiments with PET samples prepared with various catalysts, and the relative data are reported (as open circles) in *Figure 3* together with the line corresponding in equation (1) derived for PET samples prepared using $Ti(O\text{-}n\text{-}Bu)_4$ as catalyst at the same molar concentration (0.063 mol% with respect to DMT). As it is apparent, most of the new data do not fit equation (1) and, even though a small contribution from COOH terminal groups may play a role, we can conclude that the residual catalyst influences the crystallization rate, even at the relatively low concentration used.

Most of our PET samples were prepared using $Ti(O\text{-}n\text{-}Bu)_4$; in general it is assumed that the catalyst is soluble in the reaction medium, and that its catalytic activity requires, at first, an exchange of some O-*n*-Bu ligands with the terminal groups of the polymer chains[23]. For instance, the catalytic activity of organo-titanates is strongly reduced when O-*n*-Bu ligands are replaced with ligands which are able to form stronger linkages with titanium[37,39–41]. It is not clear what is the average number of polymer chains that can be bonded at the same time to a given titanium atom, however some evidence suggests that this number is two or more. For example, the melt viscosity of PETs of the same $[\eta]$ was found to be higher when $Ti(O\text{-}n\text{-}Bu)_4$ is used as catalyst instead of $Ca(CH_3COO)_2 + Sb_2O_3$ (unpublished results).

An interaction between the catalyst and the terminal groups of PET can be expected also for the other catalysts used for the preparation of PET, and can explain the change in catalytic activity observed in media with a different polarity[41,42].

If more than one chain is linked at one given catalyst atom, the catalyst behaves like a chain extender leading to an "apparent" increase of molecular weight. Of course, the possibility that more than one chain is bonded to a given catalyst atom depends on the nature and relative amount of catalyst atoms and terminal groups. For high molecular weight PET, the moles of terminal groups are of the same order of magnitude of the moles of catalyst, and the chain-catalyst interactions may result in a "quasinetwork" leading to a significant increase of the apparent molecular weight, which in turn influences chain mobility and the overall crystallization rate.

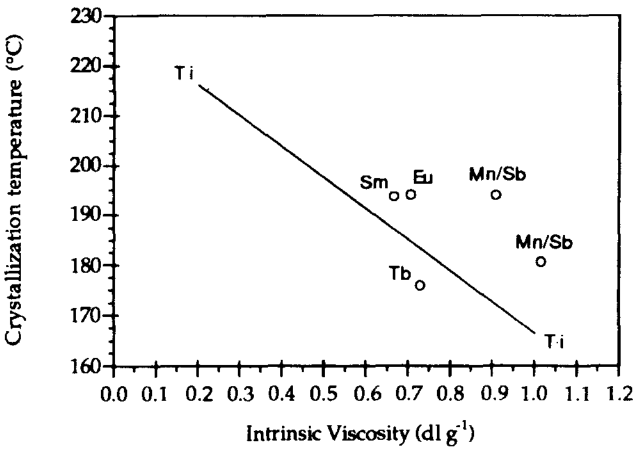

Figure 3 Crystallization temperature for PET samples prepared with various catalysts; the solid line is for $Ti(O\text{-}n\text{-}Bu)_4$ catalyst (equation (1))

Similar arguments were used to explain an increase of order of magnitudes of the viscosity of molten polyesters in the presence of metal oxides[43] and the reduced crystallizability of aliphatic polyesters, in the presence of Mg(II) derivatives[44], of nylon 6, in the presence of lithium and calcium inorganic salts[45,46].

Analogous effects were observed for PET and it-polystyrene in the presence of silica derivatives; the results were explained assuming a "quasicrosslinked" structure, originated in the molten state by interaction between polymer and filler[47,48].

Of course, it is expected that the extent of the apparent increase of the molecular weight depends on the coordinative ability of the catalyst and on the nature of the polymer and of the terminal groups. This can explain the different crystallization rate observed for different catalysts at the same concentration (see *Figure 3*), and the lower crystallization rate observed for Ti catalyst[8], if we assume that the terminal groups of the PET chains can coordinate more extensively with Ti derivatives than with other catalysts.

This hypothesis can also explain the strong increase of crystallization rate observed when phosphorous derivatives were added to PET[4]. In fact, according to literature references[25,26,49–55], the phosphorous derivatives act as catalyst inhibitors by removing the chain ends from the

Table 2 Effect of dissolution–reprecipitation treatments

	Solvent[a]	Non solvent	Number of dissolution–reprecipitation treatments	T_{cc} (°C)
PET-Ti/C	$HFIP/CH_2Cl_2$	TCTFE	1	199.4
PET-Ti/E	$HFIP/CH_2Cl_2$	MeOH	1	197.0
	$HFIP/CH_2Cl_2$	TCTFE	1	191.4
	HFIP	MeOH	1	191.4
	TCE	TCTFE	1	192.4
PET-Ti/G	$HFIP/CH_2Cl_2$	MeOH	1	187.3
	$HFIP/CH_2Cl_2$	TCTFE	1	190.8
	$HFIP/CH_2Cl_2$	TCTFE	2	193.7
	$HFIP/CH_2Cl_2$	TCTFE	3	197.0
	$HFIP/CH_2Cl_2$	TCTFE	4	195.3
	$HFIP/CH_2Cl_2$	TCTFE	5	197.0
	$HFIP/CH_2Cl_2$	TCTFE	6	199.0
	TCE	TCTFE	1	188.1
	TCE	TCTFE	2	193.3
	TCE	TCTFE	3	197.0
	TCE	TCTFE	4	195.3
	TCE	TCTFE	5	201.6
PET-Mn,Sb/A	$HFIP/CH_2Cl_2$	MeOH	1	198.1
	$HFIP/CH_2Cl_2$	TCTFE	1	198.4
PET-Mn,Sb/B	$HFIP/CH_2Cl_2$	MeOH	1	197.1
	$HFIP/CH_2Cl_2$	MeOH	2	201.2
	$HFIP/CH_2Cl_2$	TCTFE	1	194.7
	TCE	TCTFE	1	197.5
	TCE	TCTFE	2	204.7

[a] TCE at about 150°C; HFIP and $HFIP/CH_2Cl_2$ at room temperature

catalyst with which they form a stronger coordinative linkage or a non-reversible chelation of titanium.

This mechanism seems to be further supported by the results for crystallization rate obtained in this study on PET samples after dissolution and reprecipitation. In fact, when PET is dissolved, the solvent, which has to be able to interact strongly with the PET backbone to give favourable thermodynamics, can destroy the linkages between catalyst and terminal groups, and it is commonly assumed that the catalyst/chain-end interactions are not re-formed during reprecipitation and that the catalyst remains in solution. Therefore, the PET recovered after dissolution and reprecipitation has a molecular weight that is lower than the "apparent" molecular weight in the molten state in the presence of catalyst (the molecular weight measured in solution is the "true" molecular weight) and, accordingly, it is expected that the overall crystallization rate increases with respect to that observed for the original samples. This is actually what we found for all the PET samples submitted to such a type of treatment, as it appears from the data reported in *Table 2*.

In order to exclude that the observed increase was due to side effects of the solvent, we dissolved the same samples in different solvents (HFIP only, or HFIP/CH_2Cl_2, 30/70 vol/vol, at room temperature; or TCE at ≈150°C) and reprecipitated PET in different ways (slow or fast addition of the PET solution to the non-solvent and vice-versa) with various non-solvents (MeOH or TCTFE). In addition, we dried the recovered PET in various ways: for one night in vacuum at various temperature from 80 to 160°C, and for short times (1–5 min) at high temperature (300–320°C) in d.s.c. before starting the cooling run. A few samples were also dissolved and reprecipitated up to six times consecutively. The values of T_{cc} obtained for one given sample after several of these different treatments were identical, in the range of the experimental error (see *Figure 4*). The results reported in *Table 2* seem to exclude the possibilities that the increase of the overall crystallization rate is due to a residual amount of solvent, and that very stable PET-nuclei are formed during the solution reprecipitation treatment.

On the other hand, because most of the catalyst is usually removed during the dissolution–reprecipitation treatment[10,56], the increase of the overall crystallization rate cannot be ascribed to an effect of the residual catalyst.

An increase of T_{cc} after dissolution–reprecipitation treatments was observed previously for both PET and nylon 6, and explained assuming that memory-effects of the previous processing were erased by this treatment[57–59]

All these data seem to support the hypotheses that the effect of catalyst on the crystallization rate is indeed due to an apparent increase of molecular weight deriving from interactions between the catalyst and the terminal groups of the polymer chains. When PET is dissolved, these linkages are destroyed and the next crystallization step reflects the behaviour of the real molecular weight.

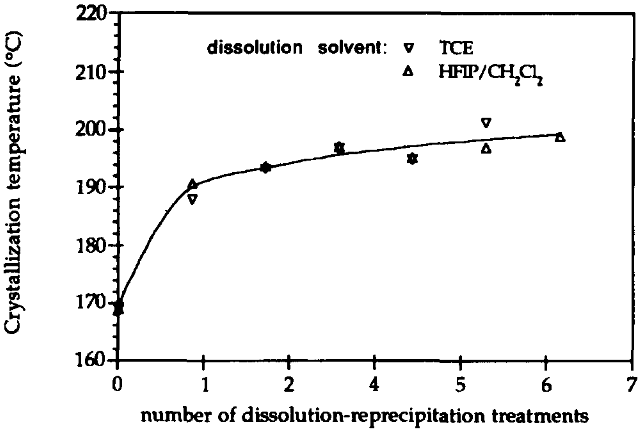

Figure 4 Crystallization of the same PET sample submitted to repeated dissolution–reprecipitation treatments

Table 3 Crystallization temperature of some PET samples stirred for 1 min in the molten state in contact with air

	[η] (dl g^{-1})	T_{cc} (°C) experimental	T_{cc} (°C) calculated from equation (1)
PET-Ti/B	0.470	212.1	199.5
PET-Ti/C	0.650	204.7	188.3
PET-Ti/D	0.772	200.0	180.7
PET-Ti/F	0.840	201.0	176.4

Further support for this hypotheses derives from experiments performed on samples stirred for a short time (1 min) in the molten state, in contact with air, before extrusion. After this treatment, the samples showed an increase of the crystallization rate (see *Table 3*). One can be tempted to ascribe this increase to the thermal and hydrolytic degradation of the ester groups of PET occurring at high temperature in the presence of humidity. However, the small decrease of [η] measured after extrusion cannot explain the increase of the crystallization rate observed—much higher than expected from equation (1). Another effect that could be thought responsible for the increase in T_{cc} is the orientation memory (orientation, and therefore nuclei formed under stress, could be frozen in the PET samples as a consequence of the extrusion step). However, in our case the orientation is little, if any, and this effect can be ruled out, as it was recently reported that much higher orientation (up to 200–300%) did not have significant effects on the crystallization rate of PET[57].

We believe instead that these results can be explained assuming again that during stirring of PET at high temperature the humidity present in the air is able to promote a fast hydrolysis reaction of part of the terminal groups/catalyst linkages. This results in a decrease of the "apparent" molecular weight, and hence in an increase of mobility of the PET chains, which in turn leads to an increase of the overall crystallization rate.

Similar conclusions were reported very recently in a paper by Jacques *et al.*[60] where the effects of phosphorous-based additives on the thermal behaviour of PET–poly(butylene terephthalate) blends were discussed. As we did, they concluded that the crystallization behaviour of PET is mainly affected by the chain extension originated by the linkages between terminal groups of PET and phosphorous derivatives. Similarly to us, they observed that the phosphorous–polyester linkages are labile and lead to unexpected modification in the thermal behaviour of PET with aging time.

On summarizing, the effects of the residual catalysts on the crystallization rate can derive from different mechanisms; when the catalyst is $Ti(O\text{-}n\text{-}Bu)_4$, the most relevant is the interaction with terminal groups which determines an increase of the apparent molecular weight. In other cases, mechanisms such as the capability of a catalyst to separate as a solid phase (for instance after reaction with itself or with low molecular weight by-products and/or additives) or the formation of ionic clusters between the metal ions of the catalyst and carboxyl terminal groups of PET chains may also contribute to the overall crystallization rate. Finally, the catalyst can affect the crystallization rate indirectly, by increasing the rate of side reactions that occur at high temperature such as, for instance, the formation of $-COOH$ terminal groups[24].

CONCLUSIONS

Our experimental results, and in our opinion also some of the data spread in the literature for the crystallization rate of PET, can be interpreted assuming that interactions of terminal groups of the PET chains lead to an apparent increase of the molecular weight in the molten state. This determines a decrease of chain mobility and, as a consequence, a decrease in overall crystallization rate. Mutual interactions of carboxyl terminal groups and, still more, interactions of terminal groups with residual titanium catalysts, are able to explain the influence of several factors on the crystallization rate of PET. Of course, the extent of the interactions depends on the nature of the catalyst, on the competitive presence of other additives, on the polarity of the medium and on the temperature. This can explain discrepancies in the results reported by different authors for apparently similar PET samples.

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