Chemical nucleation, a new concept applied to the mechanism of action of organic acid salts on the crystallization of polyethylene terephthalate and bisphenol-A polycarbonate

R. Legras, C. Bailly*, M. Daumerie*, J. M. Dekoninck and J. P. Mercier
Laboratoire des Hauts Polymères, Université Catholique de Louvain, Louvain-la-Neuve, Belgium

and Mrs V. Zichy† and E. Nield
New Materials Group, ICI Petrochemicals and Plastics Division, Research and Technology Department, Wilton, UK
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Bisphenol-A polycarbonate (PC) and Polyethylene terephthalate (PETP) systems containing different concentrations of sodium *o*-chlorobenzoate (SOCB) as crystallization promoters have been studied by d.s.c., i.r. and g.p.c. It is shown that the time and temperature of mixing of the salt with the polymer considerably affects the crystallization rates. G.p.c. and i.r. show that a chemical reaction occurs during the mixing process between the salt and the ester links of the macromolecules. This reaction produces ionic end-groups which are responsible for the acceleration of the crystallization rate. This phenomenon is called 'chemical nucleation'. The same behaviour is observed also with other alkali metal salts derived from aromatic carboxylic acids.

INTRODUCTION

It is generally believed that crystallization of polymers is controlled by heterogeneous nucleation; however, this initial step remains poorly understood[1].

A general discussion of heterogeneous nucleation has been given by Binsbergen[2-4] for polyolefins. He suggests that the activity of a large number of nucleating agents is related to the oriented deposition of polymer chains on shallow ditches present at the surface of the particles. Recently, it was proposed that the epitaxy of the polymer may be an important physical process governing the nucleating capacity or organic substances[5,6].

However, although sodium benzoate and similar organic salts are efficient nucleating agents for polyethylene terephthalate[7] and bisphenol-A polycarbonate[8], epitaxy of these polymers on the salts has never been observed.

Recently, it has been discovered, conjointly in the Laboratoire des Hauts Polymères of the Université Catholique de Louvain (Belgium) and 'ICI Petrochemicals and Plastics Division Research Department' (Welwyn Garden City, UK) that significant differences appear in the kinetics of crystallization of polyethylene terephthalate (PETP) mixed with alkali metal salts of the family of aromatic carboxylic acids, as a function of different mixing conditions[9]. A similar behaviour has been reported previously for polycarbonate (PC) in the presence of similar organic salts as a function of type of salt used[8]. In both polymers it was also observed that the presence of the salts markedly decreased the melt viscosity and induced, at high temperature, a significant decrease of the molecular weight.

On the basis of these results it was decided to re-examine the crystallization of PC and PETP in the presence of organic salts to determine the existence of a possible reaction between the two components of the system.

EXPERIMENTAL

Materials

Polymer. Bisphenol-A polycarbonate (PC) used in this work was a commercial product manufactured by General Electric under the trade name Lexan 135. The low molecular weight fractions of PC were removed by extraction in boiling benzene over 24 h. The $\bar{M}_n$ value determined by g.p.c. was $21\,000 \pm 1000$ and the heterogeneity index $Z = 2.1$.

The polyethylene terephthalate (PETP) samples were supplied by ICI under the trade name B 90. As supplied, this polymer contains a very low level of cyclic oligomers as it is solid-phase polymerized. These oligomers can be

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removed by Soxhlet extraction with chloroform. The $\bar{M}_n$ and Z values, measured after the melting process, were equal to $15\,800 \pm 300$ and 3.3, respectively.

Before any experiments, both polymers were dried, respectively, for 1 h at 160°C for PC and at 120°C for PETP.

Salts. The crystallization promoter was sodium *o*-chlorobenzoate (SOCB). It was synthesized by neutralization of the corresponding acid supplied by Aldrich, with sodium hydroxide. The purity of SOCB was 99% measured by high-pressure liquid chromatography (reverse phase). The other salts used here were synthesized by the same method or were commercially available (Aldrich). Before any experiment the salts were dried for 1 h *in vacuo* at 160°C.

Preparation of the samples

The nucleating agent was mixed with the polymer in a Brabender plastograph. The pure polymer was mixed for 5 min before adding the salt. A reference sample was taken 1 min before addition of the salt. The mixing times (t_M) reported in this paper were counted after the introduction of the salt.

Samples were taken after different time intervals (from 30 s onwards) and subsequently analysed by d.s.c., i.r and g.p.c. All the PETP samples were quenched in cold water when taken.

Methods

The d.s.c. experiments were carried out under nitrogen using a Perkin–Elmer DSC-2 Thermal Analyzer coupled with a Thermal Analysis Data Station (TADS). The size of the samples varied between 5 and 10 mg. The d.s.c. instrument was calibrated with metal standards (indium–lead). A 580 B Perkin-Elmer Infrared Spectrophotometer coupled with an i.r. Data Station was used for the i.r. determinations. The spectrometer was continuously purged with dry air.

The g.p.c. experiments on PETP were carried out on a Waters High Temperature GPC 150 C equipped with Shodex columns (AD-80 M/S). The experiments were carried out at 110°C in *m*-cresol at 1 ml min⁻¹ flow rate. The IR detector was coupled with a Sigma 15 Chromatography Data Station of Perkin-Elmer. Calibration standards were supplied by Agfa-Gevaert. A dimer and a trimer of PETP synthesized in the laboratory were used as low molecular weight standards.

For polycarbonate, g.p.c. was carried out at room temperature on a modular instrument made of a Perkin-Elmer Series 2 Pump, a Waters U6K Universal Injector, a Hewlett-Packard 1036 A UV Detector and Waters Microstyragel Columns (10⁵, 10⁴, 10³, 500 Å). The mobile phase was methylene chloride and the flow rate set at 1 ml min⁻¹.

G.p.c. standards were Lexan and Makrolon samples, the $\bar{M}_w$ of which were determined by light scattering. (Centre de Recherches sur les Macromolécules, Strasbourg, France)*. Bisphenol-A diphenyl carbonate, synthesized in the laboratory,was used as a low molecular weight standard of PC. The g.p.c. data were analysed with a 3600 Data Station of Perkin-Elmer.

Optical microscopic observations were carried out with a Leitz Orthoplan-POL microscope equipped with a FP5 Mettler hot-stage.

RESULTS

Preliminary experiments

Figure 1 shows a plot from a d.s.c. experiment (2°C min⁻¹) of a PC/0.5% SOCB system previously mixed for 1.5 min at 270°C and quenched to ambient temperature. On heating, the T_g observed at 145°C as for pure polycarbonate, was followed by a crystallization exotherm $(T_{ch} = 212°C)$ and a melting endotherm $(T_m = 302°C)$.

A thin film of the same sample annealed for a few minutes at 220°C became opalescent and a strong birefringence was observed under the polarized-light microscope. These results clearly demonstrate the very high efficiency of SOCB as a nucleating agent of PC considering that even low molecular-weight samples of PC do not crystallize at all on heating at 2°C min⁻¹ in the d.s.c. Similar behaviour has been reported previously for PC nucleated by substituted benzoic acid salts[8] other than SOCB.

The observed value of T_m (302°C) was unusually high for semi-crystalline PC as well as the degree of crystallinity (50%) calculated on the basis of an enthalpy of fusion (ΔH_m) equal to 109.7 J g⁻¹ for entirely crystalline PC[10].

Once melted, the sample used in *Figure 1* could not be recrystallized and a second d.s.c. examination showed only a glass transition at 145°C.

Figure 2a shows a plot from a d.s.c. experiment (10°C min⁻¹ scan rate) of PETP/1% SOCB mixed for 2 min in the Brabender at 280°C and *Figure 2b* shows a similar plot of the reference sample of pure PETP taken from the melt just before the introduction of SOCB. In both Figures the same values of T_g (77°C) and T_m (258°C) are observed. However, the temperatures corresponding to the peaks of
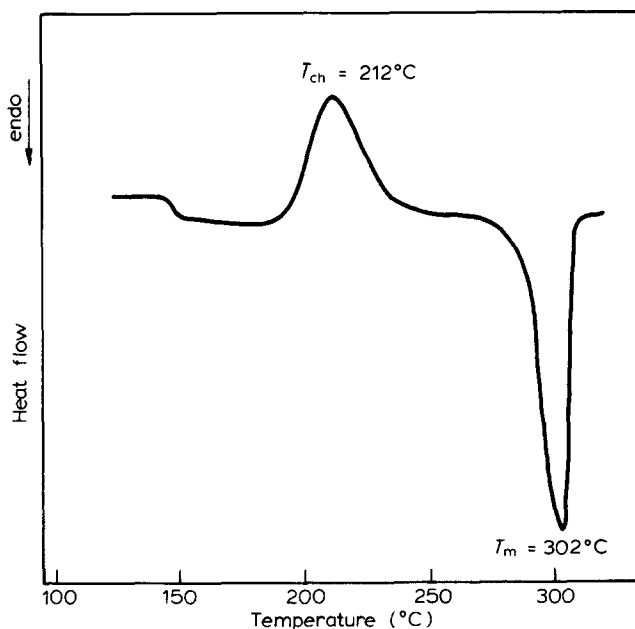

Figure 1 D.s.c. plot of a PC/0.5% SOCB system, previously mixed for 1.5 min at 270°C and quenched to ambient temperature (scan rate: 2°C min⁻¹)

the crystallization exotherms (T_{ch}) on heating, or on cooling (T_{cc}) are very different.

These temperatures, T_{ch} and T_{cc}, constitute an indirect measure of the rate of the crystallization process. Indeed, T_{ch} corresponds to the temperature at which approximately 50% of the primary crystallization was attained: the higher T_{ch}, the lower the crystallization rate. T_{cc} can be defined in the same manner if crystallization on cooling from the melt is considered; low T_{cc} values corresponding to low rate of crystallization.

T_{ch} and T_{cc} which are both dependent on the scan rate can be related to the half crystallization time $\tau_{1/2}$ measured at an arbitrary constant temperature. So, in *Figure 3*, the relation between T_{ch} and the half crystallization time measured at 110°C was established for a series of PETP samples which showed different kinetics of crystallization. Nucleated and unnucleated samples of various molecular weights were included in the series. *Figure 3* shows that for the nucleated sample of *Figure 2a*, $\tau_{1/2}$ at 110°C is equal to 40 s ($T_{ch} = 110$°C) whereas for pure PETP (*Figure 2*) it is longer than 500 s ($T_{ch} = 131$°C).

For samples exhibiting a very high rate of crystallization such as those studied in this work, T_{ch} and T_{cc} are parameters much easier to determine with precision than $\tau_{1/2}$ due to the thermal inertia of the experimental device (d.s.c.).
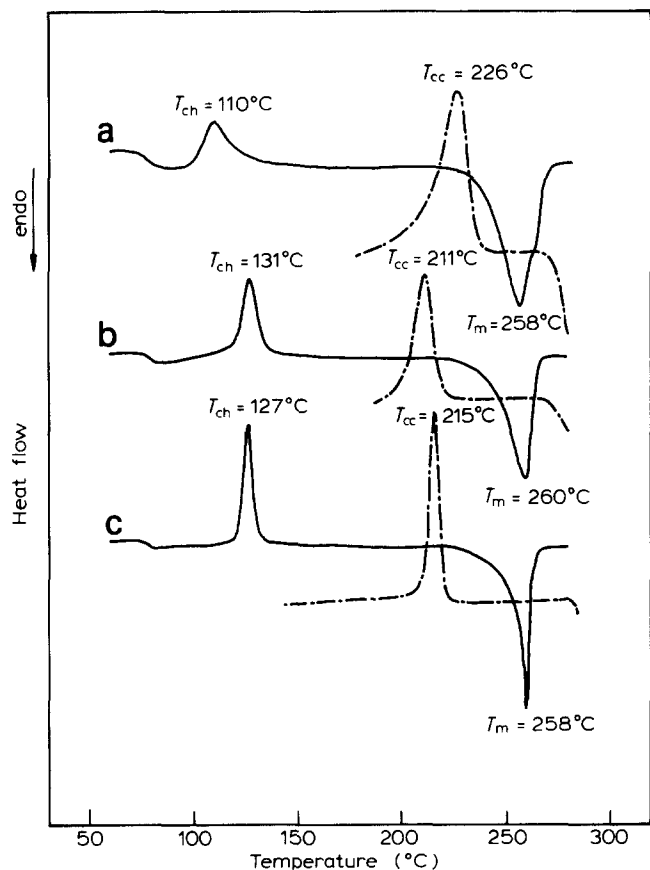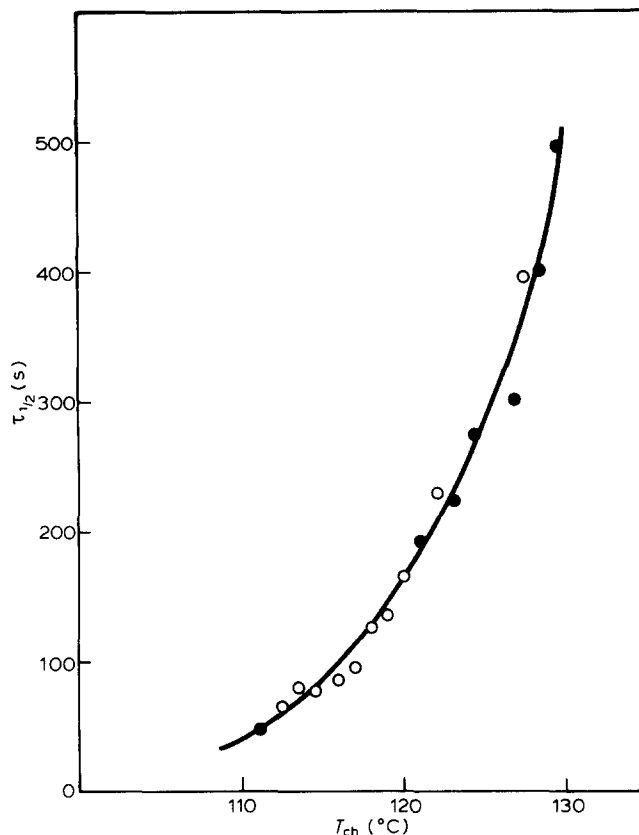
Figure 3 Experimental relation between T_{ch} (scan rate: 10°C min⁻¹) and $\tau_{1/2}$ at 110°C for various PETP samples. O, plain PETP (various M_n); ●, nucleated PETP
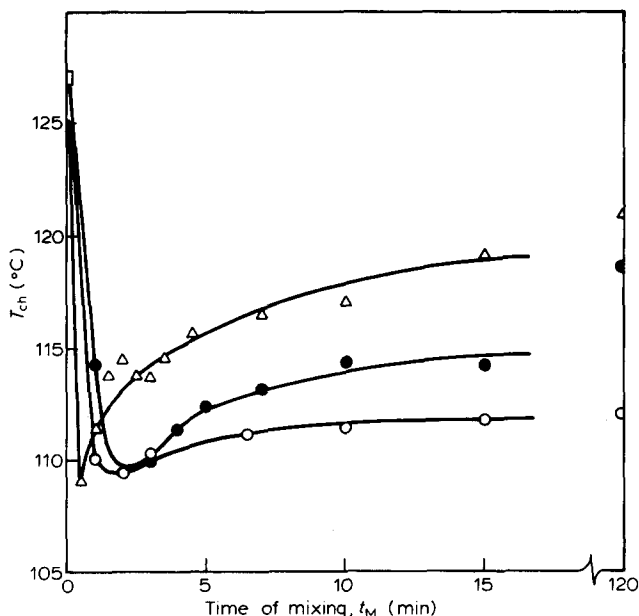
The relation between T_{ch} and $\tau_{1/2}$ at 110°C was obtained for $\tau_{1/2}$ situated between 40 and 500 s. Higher and lower values of $\tau_{1/2}$ are no longer measurable by d.s.c. A similar relation can be obtained for T_{cc}, if necessary. In the following, all the kinetics of crystallization characterizing different systems were assessed by the measure of T_{ch}.

*Influence of mixing conditions on the crystallization rates*

The variations of T_{ch} as a function of t_M (time of mixing) and T_M (temperature of mixing) are shown in *Figure 4* for the PETP/1% SOCB system. The T_{ch} versus t_M curves pass through a minimum which corresponds to the highest rate of crystallization of the system. The minimum value of T_{ch}, which is practically independent of T_M, slightly varies with t_M.

At high values of t_M, T_{ch} increases gradually for $T_M = 280$ and 300°C whereas for $T_M = 260$°C, T_{ch} practically remains constant ($T_{ch} \approx 110$°C). Therefore, after 2 h of mixing at 280°C or at 300°C, the crystallization rates are considerably reduced (from $\tau_{1/2} < 40$ s to $\tau_{1/2} = 160$ or 200 s, respectively, at 110°C). In contrast, for $T_M = 260$°C, the efficiency of SOCB as nucleating agent is practically unaffected by the time of mixing. For this series of experiments $\tau_{1/2}$ at 110°C remains very close to 40 s.

For PC, a marked dependence of the crystallizability on the time of mixing was observed. This behaviour is evident in *Figure 5* which shows the enthalpy of fusion of samples crystallized for 1 h at 225°C. It was separately verified that this annealing time is sufficient to ensure complete crystallization of all the samples. PC samples taken from the melt just after the introduction of the SOCB develop a very high crystallinity, up to 60%. With increasing t_M values, the enthalpy of fusion ΔH_∞ continuously

Figure 2 D.s.c. plots of various PETP samples (scan rate: 10°C min⁻¹).
(a) PETP + 1% SOCB mixed for 2 min at 280°C and quenched in cold water;
(b) pure PETP ($M_n = 16\,400$);
(c) pure PETP ($M_n = 9800$).
————, on heating; — · — · —, on cooling

Figure 4 Influence of the mixing temperature and of the mixing time on the crystallization kinetics of the PETP/1% SOCB system (T_{ch} measured at 10°C min^{-1}). $\bigcirc$, 260; $\bullet$, 280; $\triangle$, 300°C
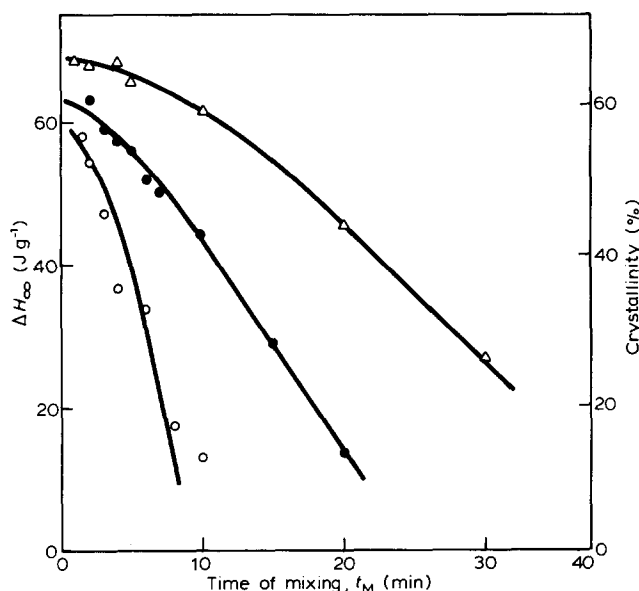
Figure 5 Variation of the enthalpy of fusion (ΔH_{∞}) of PC/SOCB systems crystallized 1 h at 225°C as a function of the mixing time at 270°C and of the salt concentration. $\bigcirc$, 1; $\bullet$, 0.5; $\triangle$, 0.1% SOCB

decreases and after 30 min of mixing at 270°C a sample containing 1% of SOCB no longer crystallizes. The t_M value corresponding to the occurrence of non-crystallizable sample increases as the salt content is reduced.

For T_M values <270°C, the crystallization rate is so high that the PC/1% SOCB system crystallizes in the Brabender mixer. On the contrary, at 300°C no crystallinity can be obtained even after short t_M values. At 300°C the torque of mixing increases markedly up to the gelation of the polymer.

These results obtained here show that SOCB is an efficient crystallization promoter for both PC and PETP. However, the maximum efficiency of this agent is only attained under very precise experimental conditions

(short t_M, low T_M). If these conditions are not respected, SOCB loses its nucleation efficiency.

Such behaviour is completely unexpected on the basis of the classical crystal nucleation theory[2] which considers substituted benzoic acid salts as insoluble, unreactive substrates.

Microscopic observations of polymer/salt systems

Polymer films of PETP and PC were prepared by hot melting or solvent casting on cover glasses and heated up to 250 and 230°C, respectively. At these temperatures both polymers were in the molten state and no birefringence was detected.

SOCB particles were then put onto the molten films, the temperature being kept constant. For PC as well as for PETP, the birefringence which was initially observed after addition of the salt was replaced by a new crystalline structure, the area of which increased as a function of the annealing time (*Figure 6*).

For PC, this rapid expansion of the crystalline fraction cannot be explained, as in the classical theory, by a crystal growth from the surface of the nucleating salt if it is considered that, in this temperature range, the growth rate is extremely slow[11,12].

These microscopic observations clearly show that crystallization promoters such as SOCB do not behave as classical heterogeneous nucleating agents. On the contrary, it is shown later that they dissolve in the polymer melt and react as true chemical reagents with the molten macromolecules to form the true nucleating species.

The experimental background leading to this new mechanism is readily illustrated by reference to the study of the behaviour of SOCB in the presence of PETP and PC model compounds.

*Chemical reaction of the crystallization promoters*

Full elucidation of the chemistry involved in the action of the nucleation promoters has been achieved by the study of the reaction of SOCB with model compounds. These results, which will be fully described in future papers[13,14], are only briefly summarized here. The model compounds used to represent the behaviour of PETP and PC are dimethylterephthalate (DMTP) and diphenyl-carbonate (DPC), respectively:
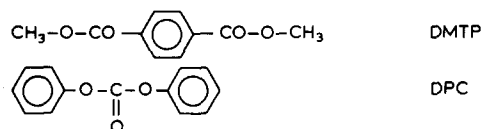

At >200°C, SOCB ($T_m = 267$°C) rapidly dissolved in the molten DMTP ($T_m = 140$°C) and as in PETP a new birefringence developed after complete dissolution of the SOCB.

This new birefringence corresponds to the formation of a new product resulting from a chemical reaction between SOCB and DMTP. The reaction path shown was determined by h.p.l.c. analysis of the reaction products:
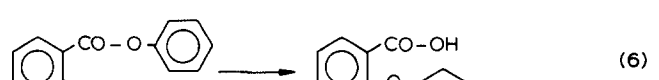
0 min

0.5 min

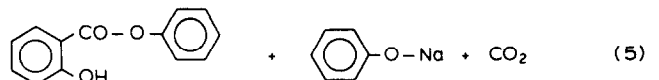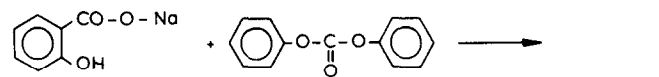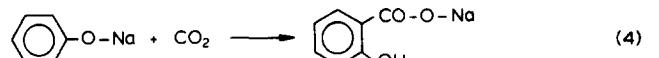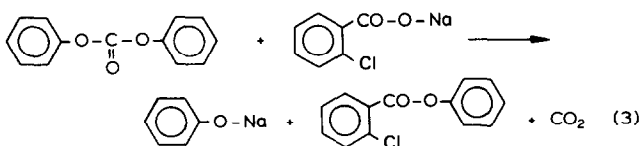1 min

15 min

a

├────── 200 µm ──────┤
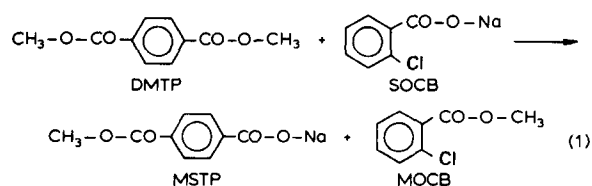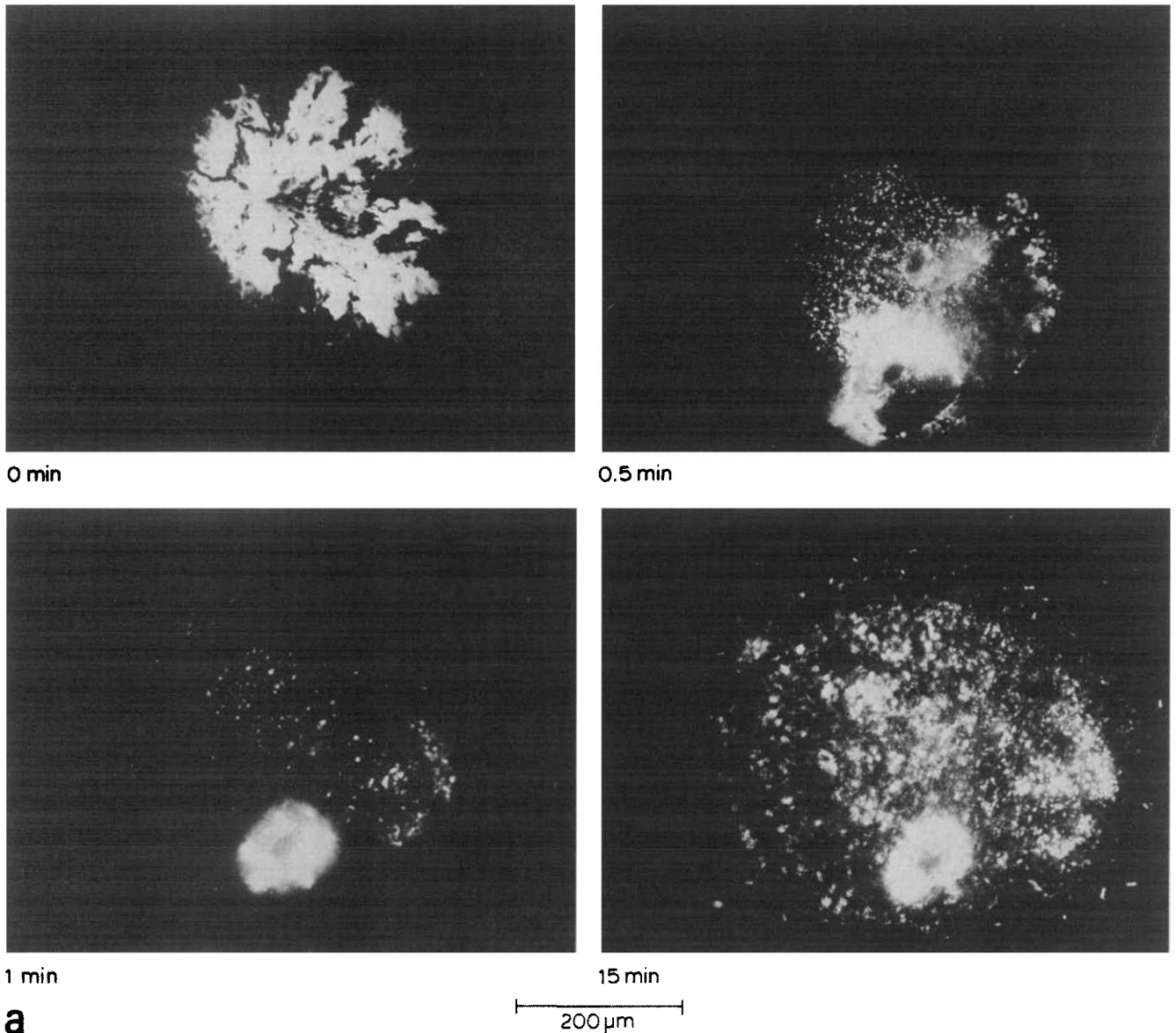
Figure 6 Polarized light microphotographs of PETP and PC films crystallized in the presence of SOCB particles. The photographs were taken on samples heated for different periods of time. (a) PETP at 250°C; (b) PC at 230°C
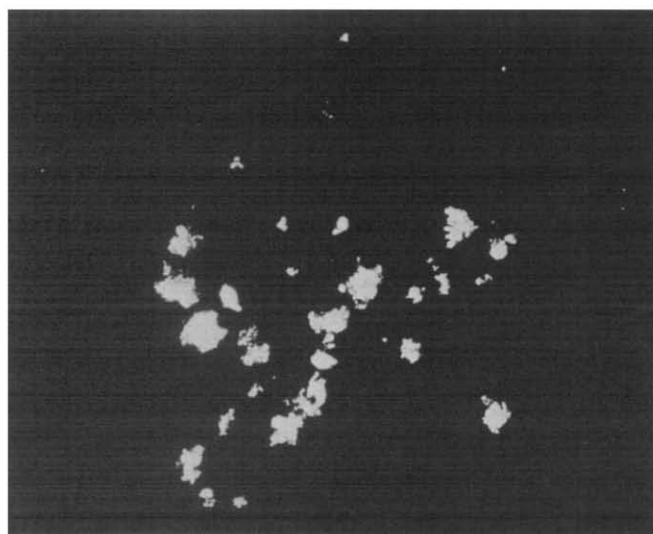
2 CH_3-O-CO-⟨⟩-$CO-O-Na$ → CH_3-O-CO-⟨⟩-$CO-O-CH_3$ +

MSTP   DMTP

$Na-O-CO$-⟨⟩-$CO-O-Na$ (2)
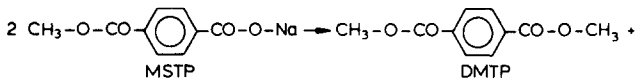
MSTP : Methyl sodium terephthalate   DSTP
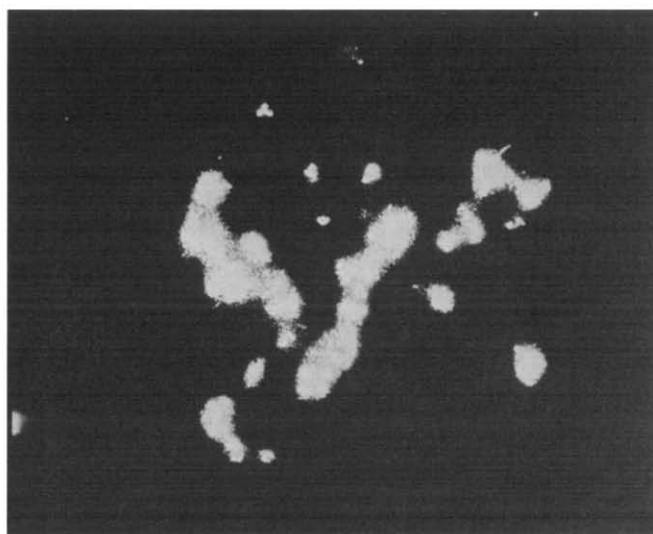DSTP : Disodium terephthalate
MOCB: Methyl o-chlorobenzoate

The birefringence appearing after reaction of SOCB with DMTP corresponds to the precipitation of MSTP which is solid and insoluble in DMTP at the temperature of reaction. After longer periods, formation of DSTP occurred in the precipitated MSTP phase.

A similar study was carried out on DPC-SOCB systems[14]. SOCB reacted rapidly at high temperature (225°C) with DPC (equation (3)). The complete reaction path was also elucidated by high-pressure liquid chromatography:

⟨⟩-$O-C-O$-⟨⟩ + ⟨⟩$^{CO-O-Na}_{Cl}$ ⟶
       O

⟨⟩-$O-Na$ + ⟨⟩$^{CO-O}_{Cl}$-⟨⟩ + CO_2 (3)

⟨⟩-$O-Na$ + CO_2 ⟶ ⟨⟩$^{CO-O-Na}_{OH}$ (4)

⟨⟩$^{CO-O-Na}_{OH}$ + ⟨⟩-$O-C-O$-⟨⟩ ⟶
                O

⟨⟩$^{CO-O}_{OH}$-⟨⟩ + ⟨⟩-$O-Na$ + CO_2 (5)

⟨⟩$^{CO-O}_{OH}$-⟨⟩ ⟶ ⟨⟩$^{CO-OH}_{O}$-⟨⟩   (6)

⟨⟩$^{CO-OH}_{O}$-⟨⟩ + ⟨⟩-$O-C-O$-⟨⟩ ⟶
                              O

⟨⟩$^{CO-O}_{O}$-⟨⟩ + ⟨⟩-OH + CO_2 (7)

0 min

10 min

30 min

40 min

b

$\vdash\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\dashv$ 200 µm
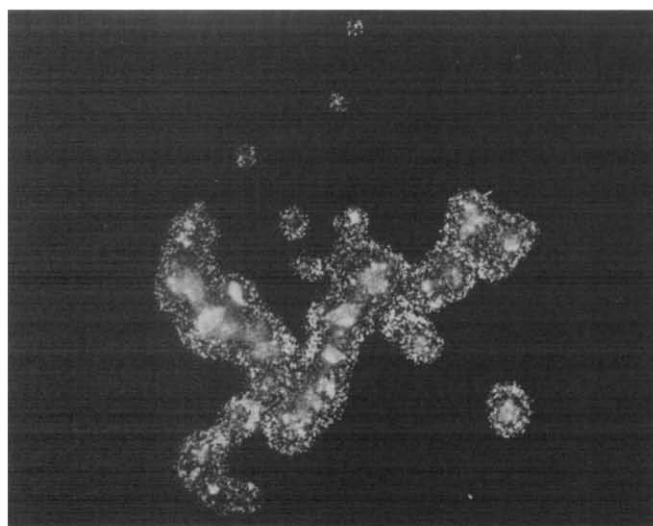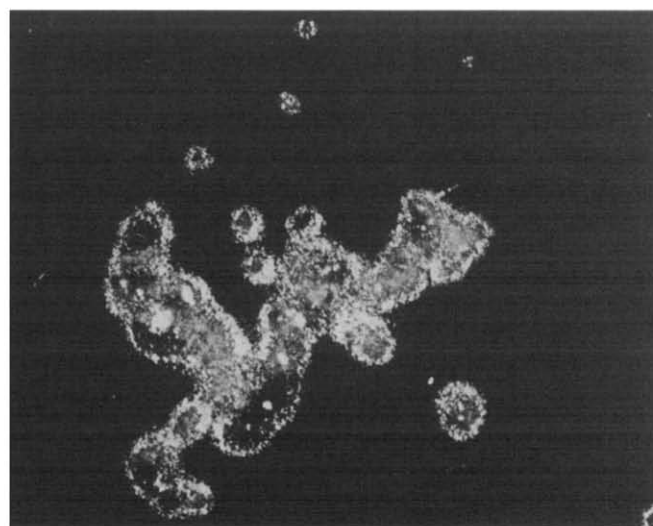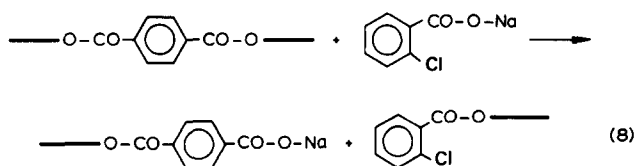
Reaction (3) results in the formation of sodium phenoxide, carbon dioxide and phenyl-*o*-chlorobenzoate. It is easily recognized that sodium phenoxide and carbon dioxide consumed in reaction (4) (Kolbe–Schmitt reaction[15]) are regenerated by reaction (5). Thus, phenylsalicylate accumulates at the expense of DPC. The reorganization of phenyl salicylate into *o*-phenoxybenzoic acid and the subsequent reaction of the latter with DPC leads to the formation of phenyl *o*-phenoxygenzoate (reactions (6) and (7). Reactions (4) and (6) are slow with regard to reactions (5) and (7), respectively. For this reason, the concentrations of sodium salicylate and *o*-phenoxybenzoic acid remain very low.
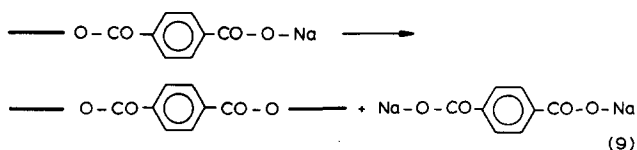
Application to the polymer: melt rheology, molecular weight and infra-red spectroscopy studies

The study of the model compounds shows that crystallization promoters such as SOCB do not behave as inert heterogeneous substrates but dissolve into the polymer melt and react as true chemical reagents with the ester and carbonate linkages of PETP or PC, respectively. This reaction is accompanied by chain scission of the polymer.

In the case of PETP, this mechanism is reported in equation (8):

$$—O-CO-\langle\bigcirc\rangle-CO-O— \quad + \quad \bigcirc\!\!<^{CO-O-Na}_{Cl} \quad \longrightarrow$$

$$—O-CO-\langle\bigcirc\rangle-CO-O-Na \quad + \quad \bigcirc\!\!<^{CO-O—}_{Cl} \qquad (8)$$

This chain scission mechanism is followed by precipitation of the ionic chain-ends. Then, as in MSTP, at longer reaction time, the precipitated chain-ends react with one another to form DSTP with subsequent chain rebuilding:

$$— O-CO-\langle\bigcirc\rangle-CO-O-Na \quad \longrightarrow$$

$$— O-CO-\langle\bigcirc\rangle-CO-O— \quad + \quad Na-O-CO-\langle\bigcirc\rangle-CO-O-Na \qquad (9)$$

On the basis of this mechanism, a quantitative expression can be devised for the number-average molecular weight. Taking into consideration that the fraction of cleft
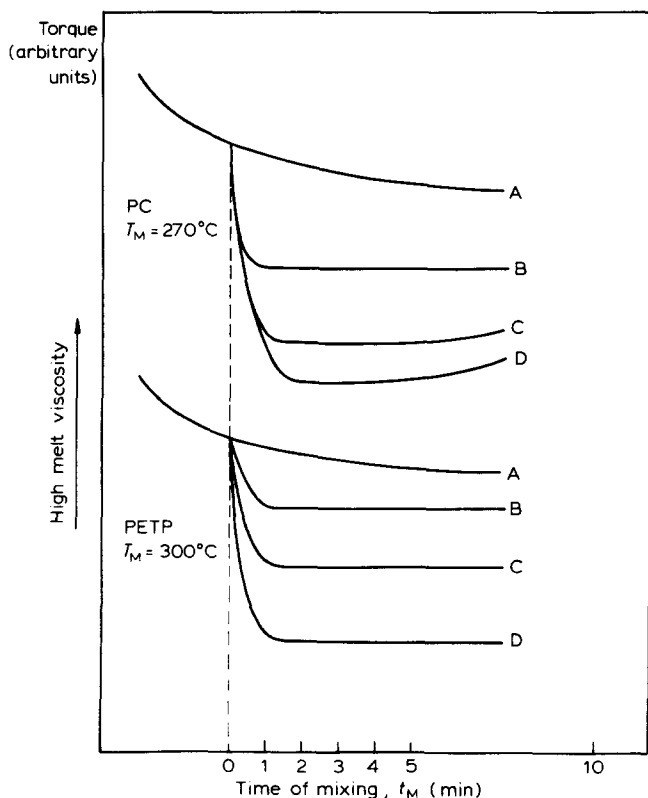
Figure 7 Brabender plastograms recorded during the mixing process of PC or PETP with various SOCB concentrations. A, 0; B, 0.1; C, 0.5; D, 1% SOCB

linkages should be equal to the fraction of salt molecules (expressed as a function of the number of linkages) less the fraction of DSTP formed by dismutation (also expressed as a function of chain linkages), the following expression can be deduced for the number of average molecular weight:

$$\frac{1}{\overline{M}_n} - \frac{1}{\overline{M}_n^0} = \frac{C_{salt}}{M_{salt}} - \frac{C_{DSTP}}{M_{DSTP}} \tag{10}$$

where C_{salt} and C_{DSTP} represent the weight concentration of salt and DSTP, respectively.

In the case of PC, modification of the number-average molecular weight only results from the initial attack of the salt on the carbonate linkages:
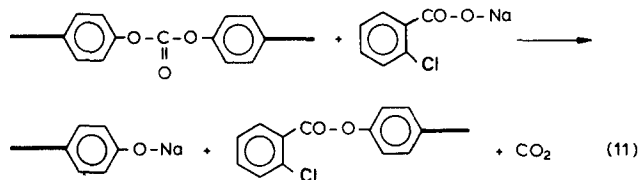
For this polymer the number-average molecular weight is given by:

$$\frac{1}{\overline{M}_n} - \frac{1}{\overline{M}_n^0} = \frac{C_{salt}}{M_{salt}} \tag{12}$$

The transposition of PC to reaction (4)–(7) of the model compound leads to the formation of phenoxy benzoate crosslinks. In these conditions, the number of macromolecules is not modified and $\overline{M}_n$ will remain unchanged after the initial decrease but $\overline{M}_w$ and, therefore, the heterogeneity index Z, will increase with the reaction time.

When SOCB was added to molten PC or PETP in a Brabender Plastograph significant changes in the torque were observed (*Figure 7*). This variation in melt viscosity was not observed when conventional inorganic nucleating agents, such as talc, were added to the polymer melts.

These results confirm that scission of the polymer chains occurs on addition of the organic salt. This was verified by molecular weight measurements on samples taken from the melt during the mixing process at high temperature and for different SOCB concentrations.

Figures 8 and *9* show a very rapid decrease of $\overline{M}_n$ after SOCB introduction. For both polymers, the $\overline{M}_n$ values almost exactly attained the values calculated (broken lines) on the basis of the scission mechanism postulated in equations (8) and (11).

For PETP, the chain rebuilding mechanism assumed in equation (9) was found to occur. Indeed, after a long period of mixing, the $\overline{M}_n$ values asymptotically tend toward the calculated figures indicated on the right of *Figure 9*.

For PC, $\overline{M}_n$ remained constant and practically equal to the values calculated on the basis of direct attack of the carbonate linkates by SOCB (*Figure 8a*).

In agreement with the mechanism deduced from the model compound study, the polydispersity increased on mixing from a value of 2.1 up to 4 (*Figure 8b*). After a long period of mixing, a gel was finally obtained.

The reaction path deduced from model compound and molecular weight studies has been fully confirmed in the PETP/SOCB system by infra-red spectroscopy from samples taken from the melt during the mixing in a
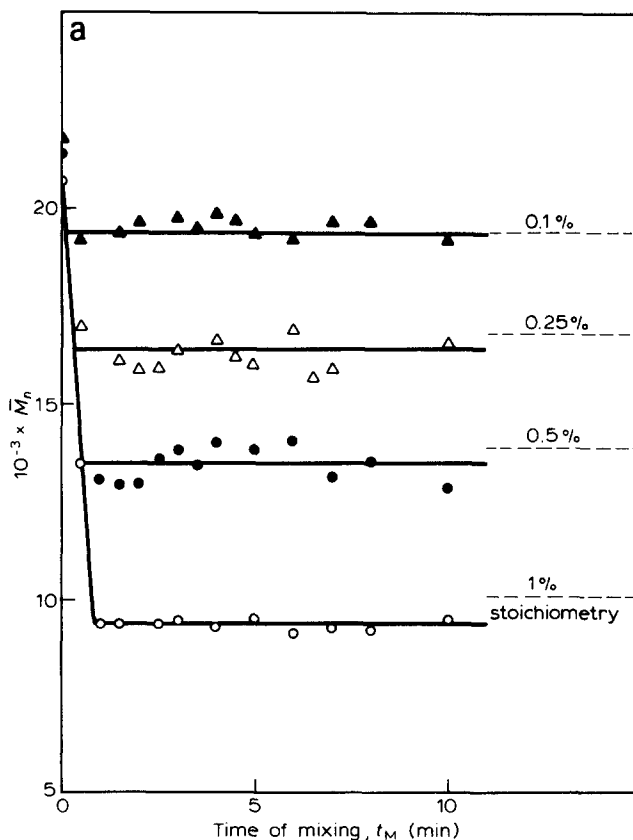

Figure 8a Variation of $\overline{M}_n$ for PC/SOCB systems mixed at 270°C, as a function of the mixing time and of the salt concentration. ○, 1; ●, 0.5; △, 0.25; ▲, 0.1% SOCB

Brabender Plastograph. These results, which will be fully described in a future paper[16], are only briefly summarized here.

The spectra of the samples taken at short mixing times ($t_M = 1$–3 min at $T_M = 260$–300°C) showed two new bands

Figure 8b Variation of the polydispersity for PC/SOCB systems mixed at 270°C, as a function of the mixing time and of the salt concentration. ○, 1; ●, 0.5; △, 0.25; ▲, 0.1; □, 0% SOCB

Figure 9 Variation of the number-average molecular weight for PETP/SOCB systems mixed at 280°C, as a function of the mixing time and of the salt concentration. ○, 0.5; ●, 1; △, 3% SOCB

at 1548 cm^{-1} (carboxylate C=O asymetric stretch) and 1594 cm^{-1} (aromatic C=C stretch), respectively, identical to that observed in *solid* MSTP. This result suggested that these bands are due to *precipitated carboxylate end groups.*

At longer reaction times ($t_M \approx 25$ min at $T_M \approx 300$°C) further changes were observed that showed that the exchange reaction between sodium carboxylate end groups had occurred with concomitant formation of DSTP in the molten polymer. This reaction is similar to that which produces DSTP from MSTP (equation (2)).

From i.r. results, it is concluded that the ionic end groups, produced by reaction between PETP and the organic salt, aggregate in a similar manner as in crystalline MSTP.

DISCUSSION

It is clearly demonstrated in this work that substituted benzoic acid salts do not behave as classical, inert, nucleating agents in polyester crystallization as it was very often assumed in other publications[3,7]. On introduction into the polymer melt, these salts dissolve and react with the molten macromolecules.

When the reaction between polymer and salt is completed, two new types of chain-ends are created, one carrying the sodium ion and the other being an ester group. As shown by molecular weight measurements (*Figures 8* and *9*) this chain scission very rapidly occurs and after a few minutes of reaction at high temperature (240–300°C), the value of $\bar{M}_n$, stoichiometrically calculated on the basis of a quantitative reaction between SOCB and the ester or carbonate linkages is attained.

In PETP, the sodium ion is associated with a carboxylate group. Comparison of the i.r. spectra of reacted PETP and of MSTP shows that ionic end-groups are aggregated in a separated phase as in solid MSTP. It appears that these 'solid' aggregates precipitated in the polymer melt are the true nucleating species of the crystallization.

The real nucleation efficiency of the crystallization promoters can only be assessed by comparison of polymer of equal molecular weight. In *Table 1*, the T_{ch} values corresponding to PETP systems of equal molecular weight are compared. From this data, the specific effect of the ionic species on the crystallization rate can be determined. The comparison of column 5 and 7 shows that 1% SOCB reduces the half-crystallization time at 110°C by a factor of at least 10.

For PC, the same type of reaction occurs between the salt and the polymer. Although it was impossible to detect directly the sodium phenoxy end-groups by i.r., there is very little doubt about their existence[14,17]. As in PETP, these ionic end-groups are essential in PC nucleation. In particular, if sodium phenoxy-ends are re-
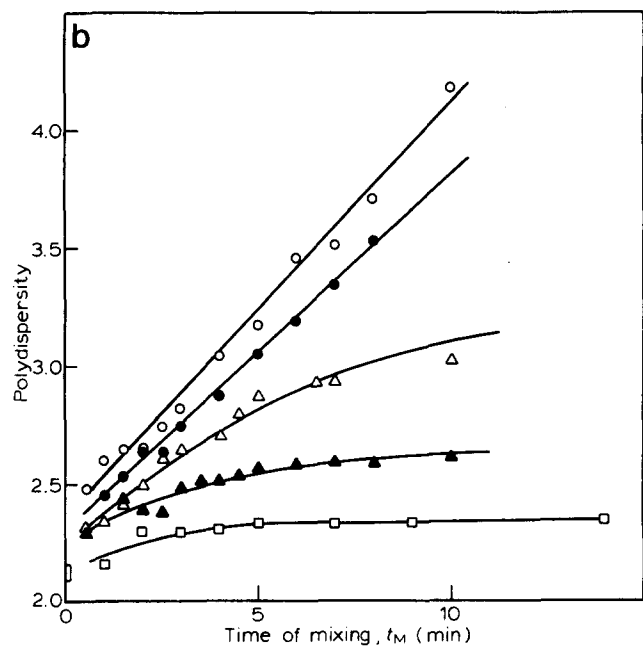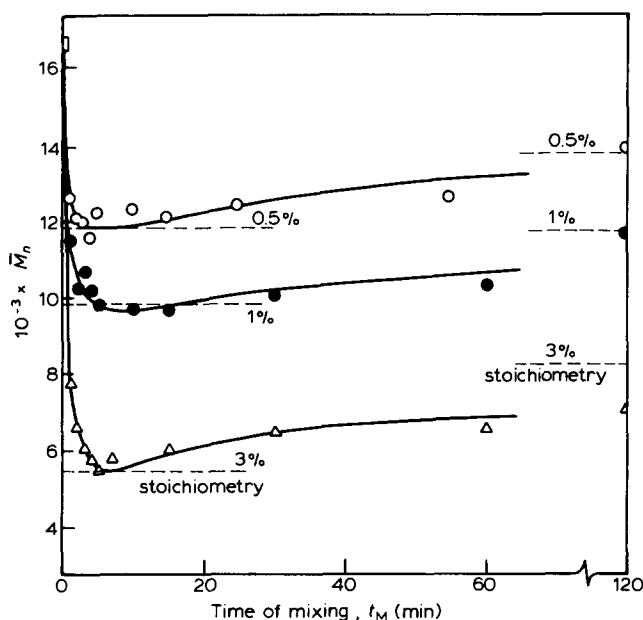
Table 1 Comparison between T_{ch} values and $\tau_{1/2}$ at 110°C of pure and nucleated PETP systems with equal $\bar{M}_n$

SOCB conc. (%)	$\bar{M}_n$ mes.	$\bar{M}_n$ calc.[a]	T_{ch} (°C)[b]	$\tau_{1/2}$ (110°C)[b] (s)	T_{ch} (°C)[c]	$\tau_{1/2}$ (110°C)[c] (s)
0.5	11400	12000	114	60	129	420
1	9200	9700	110	<40	128	340
3	5600	5500	101	<40	116	90

[a] On the basis of $\bar{M}_n$ of pure PETP before mixing equals 15800
[b] Sample mixed 2 min at 280°C
[c] Pure PETP sample with $\bar{M}_n$ equal to those of column (2)

Table 2 Efficiency of different organic salts as nucleating agents of PETP

Salt 1%	T_{ch} (°C)	$\tau_{1/2}$ (110°C) (s)	% soluble[b] in DMTP at 220°C
SOCB	110	<40	15
SPCB	115	80	4
SB	117	100	0.5
SPHB	123	216	Insoluble
DSTP	137[a]	>500[a]	Insoluble

All samples mixed 1 min at 300°C
[a] Same results as for pure PETP
[b] From solubility curve of the salts in DMTP (light microscopy)
SOCB Sodium o-chlorobenzoate
SPCB Sodium p-chlorobenzoate
SB Sodium benzoate
SPHB Sodium p hydroxy-benzoate
DSTP Disodium terephthalate

verted to the phenol form by the introduction of an acid, the PC completely loses its ability to crystallize at a high rate[14,17].

Considering recently published data on the nucleation of PETP by organic salts[9], it is noteworthy that the efficiency of the organic salts as crystallizing promoters varies considerably.

In *Table 2*, the T_{ch} values measured on a series of PETP samples containing 1% of different salts and mixed for 1 min at 300°C are summarized. Here, the degree of solubility of the various salts in DMTP is also reported[13]. SOCB, which is the most soluble salt in the PETP model compounds, is also the most efficient nucleating agent whereas sodium benzoate (SB), which is only partially soluble in DMTP, exhibits a nucleation efficiency which is considerably lower. In fact, under the mixing condition (1 min, 300°C) the reaction between SB and PETP remains incomplete. Almost insoluble salts such as sodium parahydroxybenzoate (SPHB) or completely insoluble ones such as DSTP are unable to react with PETP and have no nucleation efficiency.

A thorough study of the solubility and the reactivity of different salts in DMTP, related to their nucleation efficiency on PETP will be reported[13,16] later.

The decrease of nucleation observed after long periods of mixing can also be explained on the same basis. At increasing mixing times, the formation of DSTP occurs by reaction of COO-Na chain-ends. As DSTP is not an efficient nucleating agent, the formation of DSTP in the system goes together with an increase of T_{ch} and of the half-crystallization time of the system. However, the exchange reaction (equation (2)) is characterized by a high activation energy[13] ($E_a = 250$ kJ mole^{-1}) and at $T_M = 260$°C, the reactivity of ionic chain-ends is sufficiently reduced to avoid DSTP formation and the nucleation efficiency remains practically unchanged with increasing t_M.

Future work intends to establish the relation between the COO-Na concentration (i.r.) and the number of seeds. This study is needed to evaluate the influence of ionic chain-ends on the growth rate of PETP spherulites. The examination of various reactive alkali metal salts will be carried out to define the various parameters governing the solubility and the reactivity of different salts in PETP. This study should lead to a better understanding of the characteristics of the ionic chain-ends in view of reducing

their reactivity and thus avoiding the loss of nucleation efficiency at high mixing temperatures.

For PC, the crystallization rate and the maximum degree of crystallinity also decrease with increasing reaction time. This behaviour is explained by the reticulation of the polymer melt which reduces the chain mobility. At long time or even for short time at 300°C, complete gelation occurs and PC is no longer crystallizable.

For the PC/Salt system, it remains to be explained why this combination leads to very high degree of crystallinity (60%) while in normal PC, the degree of crystallinity hardly exceeds 25%[18]. In fact, the very fast rate of crystallization ($\tau \approx 10$ min at 225°C as compared with 12 days at 190°C for pure PC)[8] cannot solely be explained on the simple basis of an increase of the primary nucleation rate but a substantial enhancement of the crystal growth rate due to the presence of sodium phenoxide end-group[14,17] has to be taken in account to explain the overall rate of crystallization observed.

This point is certainly one of the most interesting to be explored in the future considering that the crystals formed by this 'chemical' mechanism are lamellar monocrystals[14,17].

CONCLUSIONS

It has been clearly shown in this paper that polyesters such as polyethylene terephthalate and bisphenol-A polycarbonate are readily nucleated by alkali metal salts of organic acids e.g. carboxylic acid. Contrary to previous claims[3,7], it has been shown conclusively that in these cases the nucleation proceeds via a chemical reaction rather than via a physical effect.

These polymers undergo chain scission on reaction with the alkali metal salts to form polymeric species with ionic end-groups. This chemical attack has been confirmed by infra-red spectroscopy and it has been shown, in particular, that for PETP the ionic chain-ends are aggregated in the solid state into the molten polymer. For this reason, it is believed that, at least for PETP, the aggregated ionic chain-ends, form the true nucleating species of the crystallization.

For the PC–salt system, the chemical attack of the carbonate linkage is complicated by other reactions, leading to reticulation and loss of the crystallizability of the polymer.

Detailed studies on these and other polymers are continuing with the aim to further establishing the principles of the 'chemical nucleation' and broadening its application. Of particular interest is the determination of the structure of the real nucleating species to understand their mechanisms of action. These studies will be reported later.

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