

# Nucleation of poly(ethylene terephthalate) by sodium compounds: a unique mechanism

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The high nucleation efficiency of sodium salts in PET is not due to additives but to reaction products. Ester linkages of PET are broken and sodium carboxylate chain ends are created. The ionic chain ends are the effective nucleating species.

(Keywords: PET; crystallization kinetics; nucleation; sodium compounds)

## INTRODUCTION

Although poly(ethylene terephthalate) (PET) is already a widely used polymer (for example as fibre or film in its semi-crystalline oriented state, or in plastic bottles in its amorphous state) its use in injection moulding compounds has so far been restricted because its crystallization rate is too slow. As a result of this low crystallization rate the published literature reports many examples of nucleating agents for PET<sup>1-13</sup>.

In 1981, it was discovered, jointly in the Laboratoire des Hauts Polymères of the Université Catholique de Louvain (Belgium) and I.C.I. Ltd (UK) that the sodium salts of aromatic carboxylic acids are very efficient nucleating agents for PET<sup>8,14</sup>.

We have observed that these compounds were not acting in the PET as classical nucleating agents, this is to say they were not inert, heterogeneous additives promoting polymer crystallization either by epitaxy or specific interaction. We have shown in two previous papers<sup>15,16</sup> that the salts of aromatic carboxylic acids react with PET. We have also postulated that sodium terephthalate chain ends, which are created by this reaction, are the real nucleating species.

In this paper, we use i.r. spectroscopy to give further confirmation of the chemical reactions observed when PET is mixed in the melt with sodium *o*-chlorobenzoate (SOCB). SOCB has been shown to be a particularly good representative of the salts of aromatic carboxylic acids<sup>15</sup>. It is also our purpose to broaden the discussion to a large class of sodium compounds used for nucleating PET. The patent literature reports the high efficiency of sodium nitrite<sup>12</sup>, sodium phenate and Surlyn<sup>13</sup> which is a sodium ionomer of copolyethylene/methacrylic acid, as nucleating agents. Is there a unique mechanism responsible for the nucleation ability of all these additives and what is this mechanism?

## MATERIALS

### Polymer

Polyethyleneterephthalate (PET) was supplied by I.C.I., batch number B90L. Before any experiment, the

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polymer was dried at 120°C under vacuum for at least 1 hour.

### Nucleating agents and model compounds

Sodium *ortho*chlorobenzoate (SOCB) is synthesized by neutralization of the corresponding acid supplied by Aldrich. Sodium nitrite (NaNO<sub>2</sub>) was an Aldrich product. Surlyn 1555 was obtained from Du Pont. Sodium phenate is synthesized by neutralization of phenol with sodium hydroxide. Disodium terephthalate (DST) was obtained by neutralization of terephthalic acid with sodium hydroxide. Methyl sodium terephthalate (MST) was prepared by the neutralization of methyl terephthalic acid as reported elsewhere<sup>16</sup>.

## PREPARATION OF SAMPLES

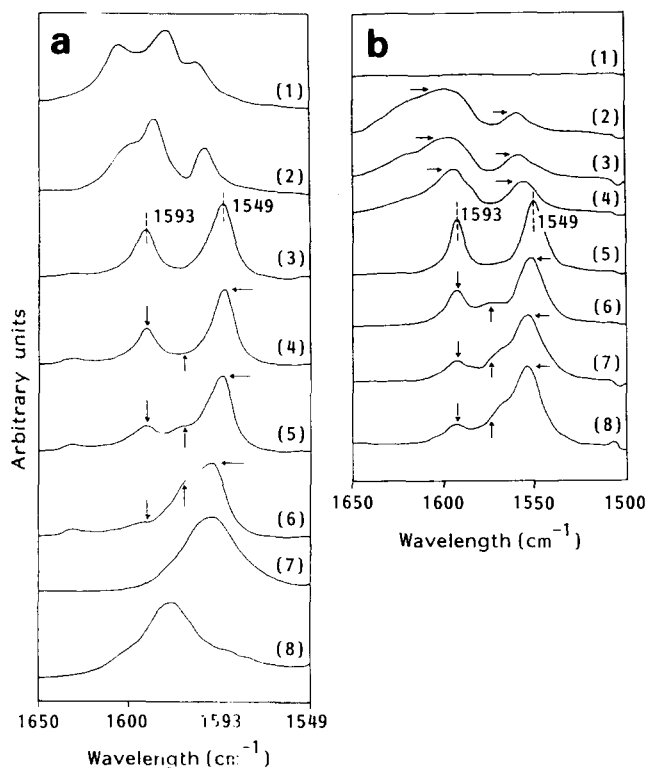
The additives were mixed with the PET in a Brabender plastograph. The pure polymer was mixed for 5 min before adding the nucleating agents. A reference sample was taken 1 min before addition of the salt. The mixing times ( $t_m$ ) reported here were counted from the introduction of salt. Samples were taken after different time intervals and subsequently analysed by d.s.c. and i.r. All the PET samples were quenched in cold water and dried under vacuum at 60°C.

## EQUIPMENT

The d.s.c. experiments were carried out under nitrogen using a Perkin-Elmer DSC-2 Thermal Analyser 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 and lead). A 580 B Perkin-Elmer Infrared Spectrophotometer coupled to an i.r. data station was used for the i.r. spectrophotometric determinations. The spectrometer was continuously purged with dry air.

## SAMPLE ANALYSIS

The samples quenched from the Brabender were directly used for d.s.c. analysis. During a heating run at 10°/min, we record the peak of the crystallization exotherm (labelled  $T_{ch}$ ). We have shown<sup>15</sup> that  $T_{ch}$  is directly linked to the isothermal half-crystallization time at low tempera-



**Figure 1** (a), I.r. spectra of model compounds: (1) solid SOCB; (2) dissolved SOCB; (3) solid MST; (4) MST after 5 min at 260°C; (5) MST after 15 min at 260°C; (6) MST after 30 min at 260°C; (7) Solid DST; (8) Dissolved DST. (b) I.r. spectra of PET/SOCB system (225 moles SOCB/m<sup>3</sup>) mixed at 260°C during (1) 0 min; (2) 0.5 min; (3) 1 min; (4) 1.5 min; (5) 7 min; (6) 45 min; (7) 120 min; (8) 240 min

ture, and is therefore a correct measure of the nucleation efficiency. The lower the  $T_{ch}$  of a sample, the higher is the nucleation density.

## I.R. SPECTROSCOPY

### Polymer

Thin films (~30 microns) were obtained by pressing samples under 10 tons for 10 s at 260°C and quenching in cold water. The spectra presented in this paper were obtained by electronically subtracting the spectrum of the neat PET, taking as reference the absorption band at 1948 cm<sup>-1</sup>.

### Other compounds

The spectra were obtained after dispersion of the compounds in KBr.

## RESULTS

In *Figure 1a*, we present the i.r. spectra of the main products of the reaction of SOCB with DMT, the model compound of PET.

SOCB has three characteristic absorptions at  $\approx 1605$ , 1580 and 1560 cm<sup>-1</sup> when dried and at  $\approx 1600$ , 1585, 1555 cm<sup>-1</sup> when dissolved in methanol (*Figure 1a*, curves 1 and 2). The methyl sodium terephthalate (MST) has two narrow absorptions at 1594 and 1548 cm<sup>-1</sup> (*Figure 1a*, curve 3). When heated alone at high temperature, we have previously shown<sup>16</sup> that MST gives DMT (which is volatile) and DST. The i.r. spectra (*Figure 1a*, curves 3–6)

of heated MST is consistent with this reaction. The decrease of the 1594 cm<sup>-1</sup> absorption is due to the loss of MST. The shift of the 1548 cm<sup>-1</sup> band to  $\approx 1555$  cm<sup>-1</sup> results from the combination of the loss of MST and the appearance of DST whose spectrum is shown in *Figure 1a*, curve 7. We have also attributed the new absorption at  $\approx 1565$  cm<sup>-1</sup> to DST initially dissolved in MST.

*Figure 1* shows the spectra resulting from the subtraction between the spectrum of neat PET and PET–SOCB samples mixed at high temperature. They therefore represent either pure SOCB or its reaction products with PET.

At short mixing times (*Figure 1b*, curves 1, 2 and 3), the spectra are broad and do not correspond to any of the model compounds. Nevertheless, we can attribute these spectra to dissolved SOCB. After 7 min of mixing, we obtained a spectrum (*Figure 1b*, curve 4) which is identical in both position and in relative intensity to MST. We can assume that it is characteristic of the sodium terephthalate chain ends of the polymer created by the reaction SOCB/PET.

At longer mixing times, the i.r. spectra evolve further in a way similar to MST heated alone. The second reaction that we postulated also occurs: disproportion of two ionic chain ends in DST. The contributions to the i.r. absorption corresponding to the model compounds and the PET/SOCB system are given in *Table 1*.

*Table 2* presents the i.r. absorption positions for a few sodium salts of aromatic carboxylic acid before mixing with PET and after 3 min at 280°C. Although the spectra of the various salts are all different, the absorption positions after mixing with PET are exactly the same and identical to MST. Two exceptions are DST and SPHB which do not change during mixing. It is interesting to note here that except for these two all the salts are good nucleating agents for PET.

*Figures 2a* and *b* show the i.r. spectra of NaNO<sub>2</sub>, Surlyn 1555, and sodium phenate before and after mixing with PET. Here again, the spectra after mixing are similar to the MST spectrum.

Most of the samples have been analysed by i.r. and d.s.c. In *Figure 3*, it can be seen that a good correlation exists between the nucleation efficiency (measured by  $T_{ch}$  from a d.s.c. run) and the absorbance of the 1594 cm<sup>-1</sup> i.r. absorption. In *Figure 3*, results obtained for PET/SOCB

**Table 1** Contributions of the model compounds and the PET/SOCB system to the i.r. absorption

Compound	Position	Attribution
SOCB dry	~1605 ~1580	Aromatic C=C stretch
	~1563	Carboxylate asymmetric stretch
SOCB dissolved in MeOH	~1600 ~1585	Id.
	~1557	
MST	1594	Id.
	1548	
DST dry	1555	Carboxylate asymmetric stretch
DST dissolved in water	~1577	Id.
PET/SOCB 0.5 min	~1600	?
	~1560	
PET/SOCB 7 min	1594	Id.
	1548	
PET/SOCB 240 min	1594	Id.
	1555	

Table 2 I.r. vibrations attributed to the presence of Na compounds in PET

Na compounds	Before blending		After blending (1 min, 280°C)	
	Aromatic C=C stretch	Carboxylate asymmetric stretch	Aromatic C=C stretch	Carboxylate asymmetric stretch
Na benzoate	1622, 1597	1553	1593	1550
Na 2-chlorobenzoate	1618, 1600, 1557	1588	1593	1550
Na 2-6-dichlorobenzoate	1612, 1586, 1570, 1560	1601	1593	1550
Na 2-chloro-4 nitro-benzoate	1616, 1606	1591	1593	1550
Na salicylate	1593, 1589, 1570, 1561	1550, 1532	1593	1550
Na 2-biphenyl carboxylate	1635, 1597, 1584, 1573	1559	1593	1550
Na 2-triphenyl carboxylate	—	1593, 1549	1593	1550
Na 2-naphthoate	1663, 1631, 1599, 1584	1551	1593	1550
Na mono methyl terephthalate	1593	1550	1593	1550
Surlyn 1555	—	1555 (very broad)	1593	1550
Na nitrite	—	—	1593	1550
Na phenate	1593	—	1593	1550
Di Na terephthalate	1510	1565 (very broad)	—	1562 (broad)

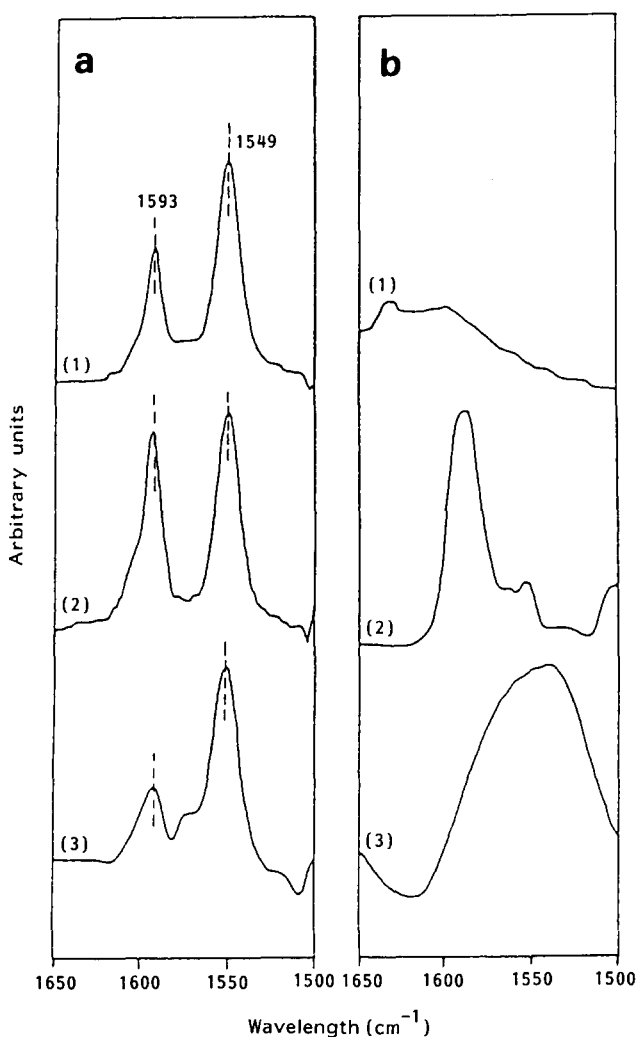


Figure 2 I.r. spectra of PET mixed with different Na compounds (75 equivalent g/m<sup>2</sup> of sodium ions). (a), (1) PET+NaNO<sub>2</sub> (5 min-300°C); (2) PET+sodium phenate (10 min-280°C); (3) PET+Surlyn 1555 (10 min-280°C). (b), (1) NaNO<sub>2</sub>; (2) sodium phenate; (3) Surlyn 1555

systems are represented with different salt concentrations (from 0.5 to 5, 10%), mixing temperatures (260 to 300°C) and mixing times (0 to 120 min). The results for PET/NaNO<sub>2</sub>, PET/sodium benzoate and PET/Surlyn 1555 are also indicated (1 w %, 280°C, 0 to 120 min). The significance of these results will be discussed later.

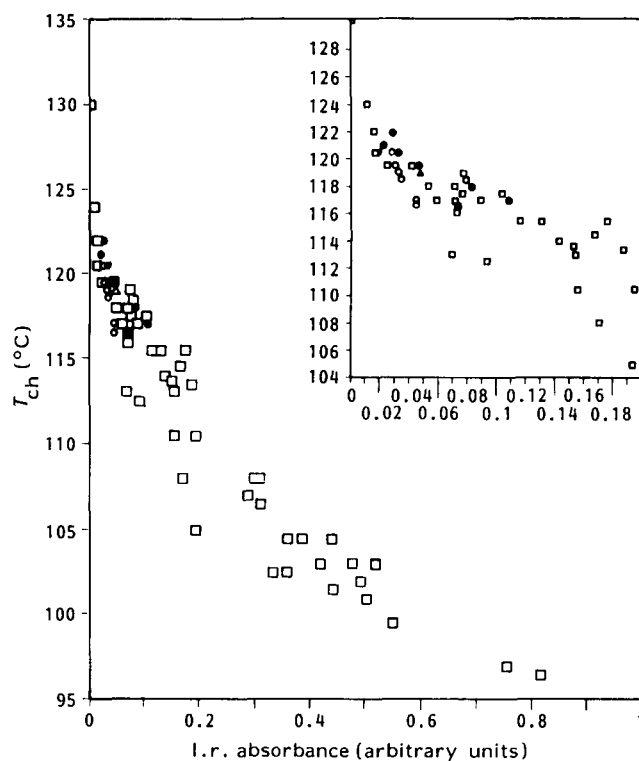


Figure 3 Relation between  $T_{ch}$  and the i.r. absorbance at  $1593\text{ cm}^{-1}$  for different PET/Na compounds systems  $\square$ , sodium orthochlorobenzoate;  $\bullet$ , sodium nitrite;  $\circ$ , sodium benzoate;  $\Delta$ , Surlyn 1555

DISCUSSION

In two previous papers<sup>15,16</sup> a chemical reaction between PET and sodium orthochlorobenzoate has been postulated. Model compound studies and g.p.c. measurements of modified PET have been reported. Figure 1a and b compares the i.r. spectra of model compounds and PET when mixed with SOCB. It is clear that after short mixing times the polymer i.r. spectrum is identical both in position and relative intensity to pure MST. For longer mixing times, subsequent modifications are similar in both systems.

In Table 2 and Figure 3 we show that the reaction path described in a previous paper can be extended to other compounds carrying a sodium atom. We now propose the following:



**Table 3** EXAFS preliminary results

	<i>N</i>	<i>R</i> (Å)
MC <sub>s</sub> T	5	3.11
PET-C <sub>s</sub>	4	3.03



where R can be nitric acid, aromatic carboxylic acid, phenol, and aliphatic carboxylic acid (Surlyn).

We have observed that reactions (1) and (2) do not occur with both DST and SPHB salts. In a previous paper<sup>16</sup>, we demonstrated that these compounds are insoluble in a model compound of the polymer. Therefore, solubility as well as reactivity are important parameters that control these PET-salt mixtures.

Although the reaction between the sodium compounds and PET is clearly proven, we have not so far shown what the real nucleating species is. We have indirect evidence that the reaction between the additive and the PET is necessary because both DST and SPHB which do not react, are not nucleating agents. On the other hand, *Figure 3* shows that a correlation exists between nucleation efficiency (as measured by  $T_{\text{ch}}$ ) and the i.r. absorbance at  $1593\text{ cm}^{-1}$  for the systems PET/SOCB, PET/ $\text{NaNO}_2$ , PET/SB and PET/Surlyn. The higher the  $1593\text{ cm}^{-1}$  absorbance, the higher is the nucleation efficiency (and thus the lower is the  $T_{\text{ch}}$ ). By examining the i.r. spectra, it is clear that when SOCB,  $\text{NaNO}_2$ , SB and Surlyn have reacted with PET, the  $1593\text{ cm}^{-1}$  absorption is due only to the sodium terephthalate (COONa) chain ends, whatever the concentration of DST formed by reaction (2), and the remaining additive.

This suggests that the COONa chain ends are the real nucleating species in these systems. This result brings two obvious conclusions. Firstly, all the nucleating agents studied here nucleate by the same mechanism. Secondly, the nucleation efficiency is unstable because during long mixing times, the COONa chain end concentrations decrease with the production of DST.

Based on the i.r. spectroscopic measurements of the concentration of the COONa chain ends, we can suggest that these COONa chain ends are in a crystalline form in the polymer. Indeed, the i.r. absorption of a carboxylate is very sensitive to its environment (solid or dissolved).

The actual mechanism we postulate for the nucleation efficiency of ionic chain ends in PET is as follows. After formation, the ionic chain ends precipitate in the polymer melt as ionic aggregates which act as seeds for the subsequent crystallization of the polymer. Preliminary results (*Table 3*) obtained by EXAFS (Synchrotron, Darresbury, UK) show an identical environment for a similar species, i.e. caesium methyl terephthalate (MC<sub>s</sub>T) and COOC<sub>s</sub> chain ends. The coordination number *N* and the first shell oxygen bond distance, *R*, for these are shown in *Table 3*.

## CONCLUSIONS

In this paper, we have presented extensive i.r. evidence for the reaction occurring between PET and certain sodium salts which have been used as nucleating agents for the polymer.

We have observed that the high nucleation efficiency of these salts is not due to the additive itself, but to products created by this reaction. Therefore, the name chemical nucleation has been given to these systems.

The details of the chemical reaction have been clearly identified by i.r. The salts react with the ester linkages of the PET, creating sodium carboxylate chain ends. These have been shown to be the effective nucleating species.

We have also observed that the nucleating efficiency is not stable and decreases significantly with mixing time. This instability is due to a disproportion reaction. The sodium chain ends react to give disodium terephthalate. The subsequent decrease of the ionic chain end concentration is directly linked to the loss in nucleation efficiency.

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