Crystallization of poly(ethylene terephthalate) induced by organic salts: Model compound study of the mechanism of action of the nucleating agent

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Dimethyl terephthalate (DMTP), a model compound of poly(ethylene terephthalate) (PETP), is used to simulate the behaviour of PETP in the presence of an organic acid salt, sodium *o*-chlorobenzoate (SOCB). On heating SOCB/DMTP systems, it is shown that the salt first dissolves in liquid DMTP. At higher temperatures, a reaction takes place between SOCB and DMTP, methyl sodium terephthalate (MSTP) being formed. MSTP is insoluble in the reaction medium and precipitates. A second reaction occurs when solid MSTP thermally decomposes to form disodium terephthalate (DSTP) and dimethyl terephthalate. The kinetic constants governing these reactions are determined and the influence of temperature and concentration are described.

(Keywords: crystallization; nucleation; polyester; model compounds)

INTRODUCTION

For many years, sodium benzoate (SB) has been recognized as an efficient nucleating agent for a large variety of polymers[1-3]. It was generally admitted that the nucleation process was due to specific interactions between the solid substrate (SB) and the polymer chains[3]. However, for polyesters[4] it was also observed that the salt brought about a marked degradation of the polyester under processing conditions. No clear relationship between this degradation process and nucleation was established.

In previous papers[5,6] concerning the crystallization of poly(ethylene terephthalate) (PETP) in the presence of organic salts, we have already shown that the high rates of crystallization of PETP depend strongly on the processing conditions, temperature, times and salt concentration. It is our purpose now to examine in detail the mechanism of the reaction, at high temperature, between the polymer chain and the salt. For this study we have used a model compound of PETP, dimethyl terephthalate (DMTP) and the organic acid salt, sodium *o*-chlorobenzoate (SOCB). This salt has been found to be one of the most efficient nucleating agents of PETP[7]. These two reactants and their reaction products can be quantitatively analysed by high-pressure liquid chromatography.

In a future publication[8] we intend to report the results obtained with other salts derived from benzoic acid. Other papers[9,10] have already been published on the behaviour of model compounds of polycarbonate in the presence of organic salts.

EXPERIMENTAL

Materials

The purity of the chemical used in this work was controlled by i.r. spectroscopy and high-pressure liquid chromatography (h.p.l.c.).

Dimethyl terephthalate. DMTP was a commerical product supplied by Aldrich. The melting point measured by d.s.c. is 140°C.

Disodium terephthalate. DSTP was synthesized by neutralization of terephthalic acid (Aldrich) with sodium hydroxide.

Sodium salt of o*-chlorobenzoic acid (SOCB).* The corresponding acid (Aldrich) was neutralized with sodium hydroxide.

Methyl ester of o*-chlorobenzoic acid (MOCB).* This ester was prepared as described by Vogel[11] in the synthesis of the methyl ester of benzoic acid.

Sodium salt of the monomethyl terephthalic acid ester (MSTP). Methyl sodium terephthalate was synthesized by neutralization of the monoacid monomethyl ester, which itself was prepared in two steps. A first reaction between DMTP and a stoichiometric quantity of potassium hydroxide gave methyl potassium terephthalate; the second reaction was the acidification of the potassium salt by HCl.

Preparation of the samples

Prior to any experiments, DMTP and SOCB were

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dried under appropriate conditions. The mixtures were obtained by grinding the products in a marble mortar.

Techniques

Melting temperatures and heats of fusion reported here were measured using a Du Pont 990 thermal analyser.

The chemical reactions were performed in hermetic cups (50–100 mg). The oven of the thermal analyser was used as a thermostat.

Optical microscopic observations were carried out with a Leitz Orthoplan-pol microscope equipped with a Mettler FP5 hot stage. H.p.l.c. experiments were performed on a Hewlett–Packard 1084 liquid chromatograph equipped with a Waters U6K universal injector, a Perkin–Elmer LC55 u.v. detector (240 nm) and a Waters Microbondapack C18 column.

The mobile phase was a gradient of solvents A and B corresponding respectively to a 80/20 methanol/water mixture and pure methanol. Both solvents A and B contained 0.005 mol of tetrabutyl ammonium phosphate. The flow rate was set at 1 ml min^{-1} at 30°C. Samples were dissolved in solvent A containing 0.5×10^{-3} mol of acetophenone (internal standard). The surface calibration was performed using solutions of different concentrations.

RESULTS

Preliminary experiments

Figure 1a shows a photomicrograph of a DMTP/SOCB mixture (0.15 molar fraction of salt) observed under polarized light at room temperature. One can see the simultaneous presence of large DMTP needles and fine SOCB crystals.

On heating, at 140°C, the birefringence due to DMTP vanishes (*Figure 1b*). Above 140°C, the SOCB crystals begin to disappear, completely vanishing at around 217°C (*Figure 1c*). At higher temperature, a new birefringence arises from the liquid medium as will be noticed in *Figure 1d*. In *Figures 2* and *3* the endotherms of fusion of DMTP and SOCB are shown to peak respectively at 140°C and 267°C. The d.s.c. results agree with the melting points as determined by optical microscopy (o.m.).

The d.s.c. runs of the DMTP/SOCB mixture (0.15) are reported at two different sensitivities (*Figure 4*). The run at the highest sensitivity shows an endotherm of fusion peaking at 139°C. It is followed by an endotherm of lower amplitude lying between 180 and 215°C. Above 220°C an important exotherm is recorded which ends at above 300°C. The fusion of SOCB at 267°C is not observed (*Figure 3*).

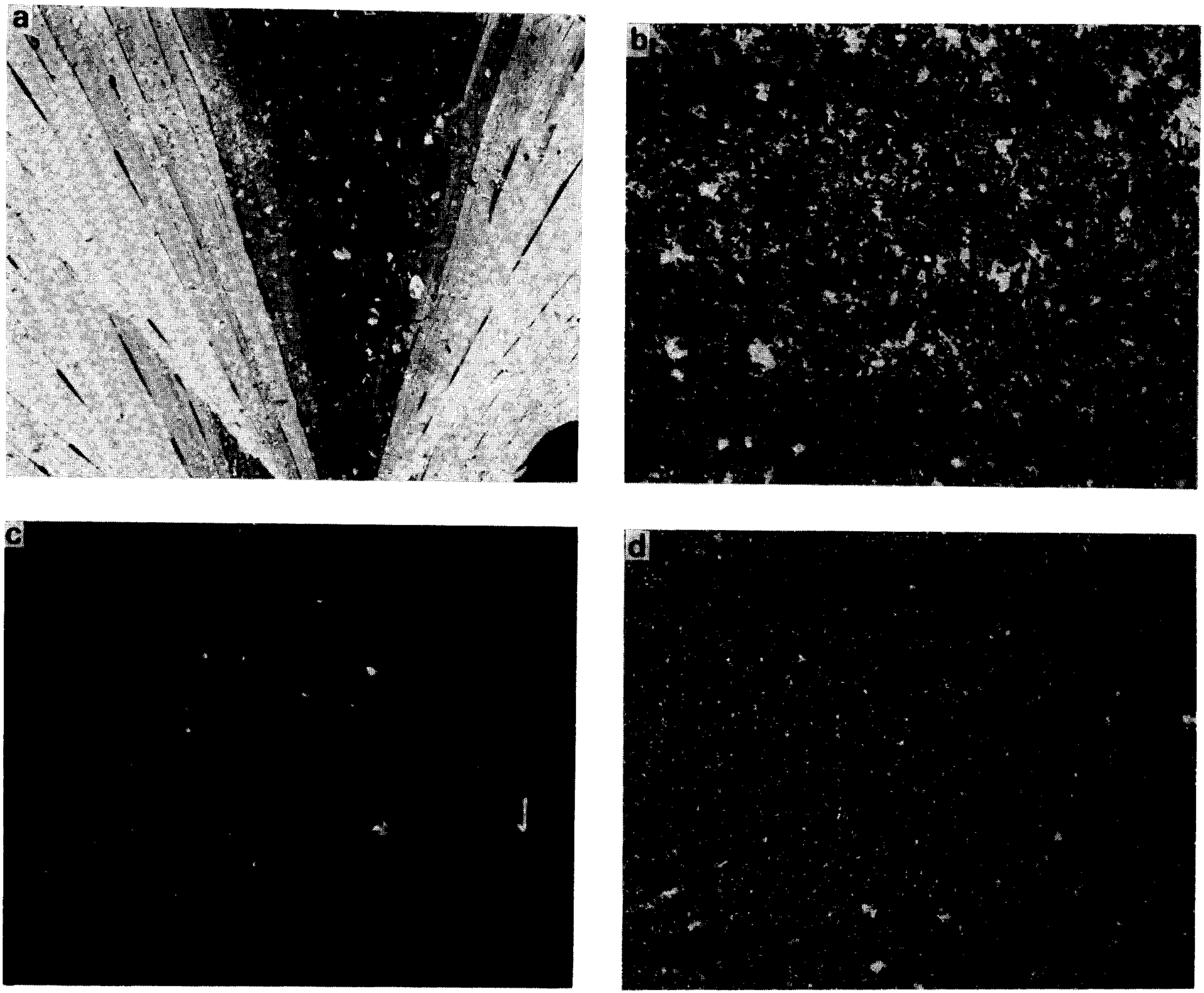


Figure 1 Photomicrographs of DMTP/SOCB mixture ($x_s = 0.15$) at different temperatures (polarized light): (a) room temperature; (b) 150°C; (c) 220°C; (d) 240°C

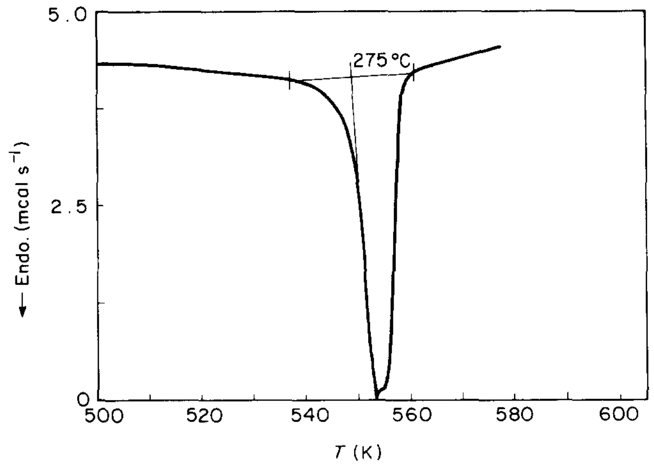


Figure 2 D.s.c. analysis of SOCB: 6.97 mg, 10.00°C min^{-1}

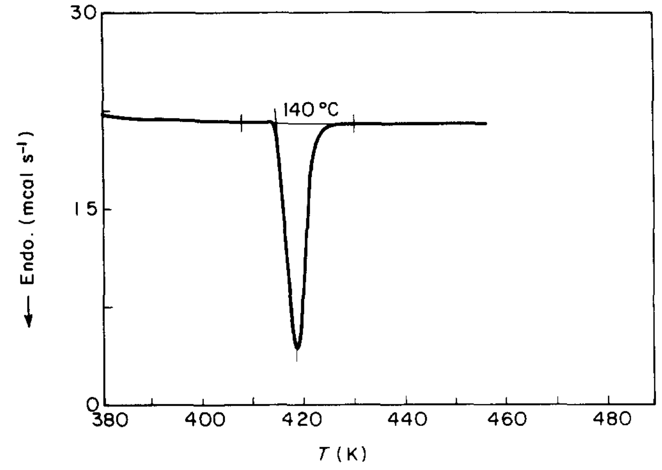


Figure 3 D.s.c. anslysis of DMTP: 11.32 mg, 10.00°C min^{-1}

The d.s.c. and o.m. results lead us to assume that SOCB dissolves in liquid DMTP at a temperature below its own melting point.

The disappearance of the SOCB birefringence occurs over the same temperature range corresponding to the endotherm detected by d.s.c. We conclude also that the large exotherm observed above 220°C and the simultaneous appearance of a new birefringence must be attributed to chemical reaction between DMTP and SOCB. This reaction forms a new solid component which can be observed under polarized light.

Solubility of SOCB in DMTP

Dry blends containing different molar fractions of SOCB, ranging between 1 and 20%, in DMTP were studied by d.s.c. and o.m. (heating rate 10°C min^{-1}). The homogeneity of these blends was improved by an initial thermal treatment at 150°C for 15 min. During this treatment, DMTP melts and its diffusion into the solid SOCB particles improves the homogeneity of the blend.

In the d.s.c. experiments we note the temperature T_s corresponding to the end of the endotherm of mixing (in *Figure 4*) and in o.m. we note the temperature corresponding to the disappearance of the last trace of birefringence of the SOCB crystals.

For molar fractions below 5%, no thermal effect can be detected by d.s.c. and we only report the values determined by o.m. The results are shown in *Figure 5*. One can see that the dissolution temperature of SOCB in DMTP gradually increases with the molar fraction of the salt. At 220°C a concentration of 15% SOCB is soluble in DMTP.

For molar fractions above 20%, the dissolution temperature becomes higher than 220°C and the chemical reaction between the components starts before SOCB is completely dissolved in DMTP.

For the sake of comparison we note that, at 220°C, DMTP dissolves less than 0.5% of sodium benzoate and that disodium terephthalate is completely insoluble. These observations must be related to the efficiency of these salts as nucleating agents of PETP. As reported previously[6], DSTP is not a nucleating agent of PETP, while SB is much less efficient than SOCB.

If one considers that the polarity of DMTP is the main factor governing the solubility of organic salts in the liquid, one can assume that the behaviour of those salts in PETP, at the same temperature, will be similar.

STUDY OF THE CHEMICAL REACTIONS BETWEEN DMTP AND SOCB

Mechanism

A system containing 0.529 molar fraction of SOCB in DMTP was annealed at 285°C for 60 s in an hermetic cup.

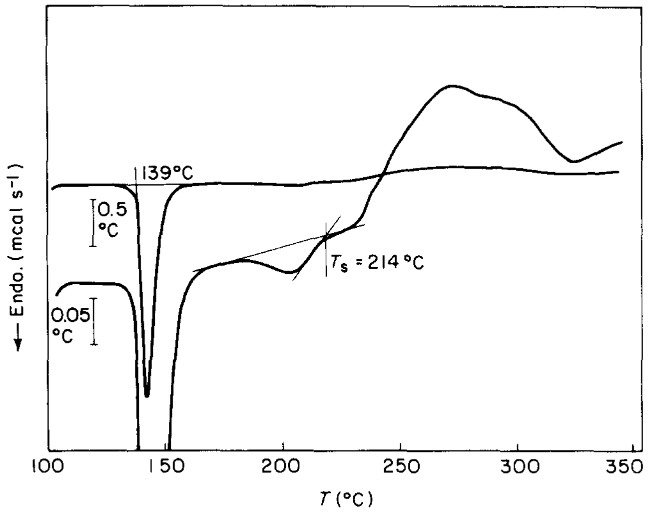


Figure 4 D.s.c. analysis of DMTP/SOCB mixture (x_s = 0.15)

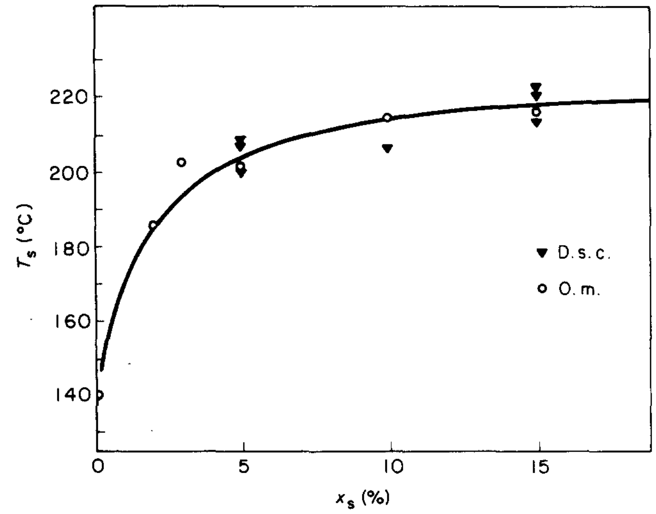
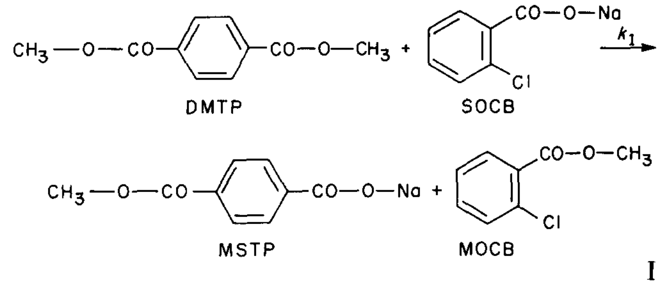


Figure 5 Temperature of dissolution of SOCB in DMTP (o.m. observations) as a function of the molar fraction of salt

Three reaction products were detected by h.p.l.c. (*Figure 6*): methyl *o*-chlorobenzoate (MOCB), methyl sodium terephthalate (MSTP) and disodium terephthalate (DSTP). Some dimethyl terephthalate and sodium *o*-chlorobenzoate remained after that time. This result suggests that the salt cleaves the ester bonds, producing MSTP and MOCB. Subsequently, a second attack of SOCB on the ester link of MSTP can lead to the production of DSTP. We propose the following reaction steps:



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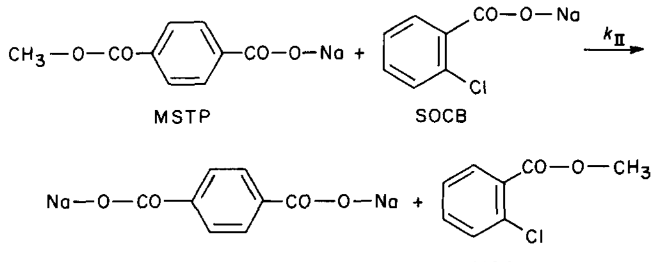
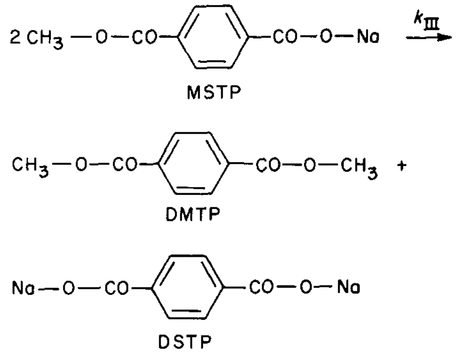


II

We further examined the thermal stability of the reaction products MSTP, MOCB and DSTP. MOCB and DSTP are stable over the temperature range studied (220°C–300°C). On the other hand, after 180 s at 280°C MSTP transforms into DMTP and DSTP. We conclude that the following reaction also occurred during the reaction between DMTP and SOCB:



III

This set of reactions indicates that DSTP can be produced in two different ways: MSTP could first decompose to form DSTP and DMTP, or SOCB could attack MSTP forming DSTP and MOCB. Only a kinetic study can demonstrate which of these two ways is predominant in the proposed mechanism.

Finally we verified that the systems DSTP/MOCB and DSTP/DMTP are stable over the temperature range studied (220°C–300°C). The system MSTP/MOCB produces DSTP and DMTP but no SOCB. These results permit the assumption that the three reactions involved in the mechanism are irreversible.

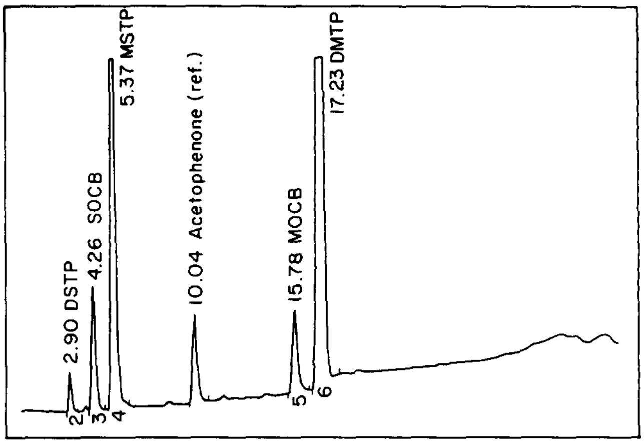
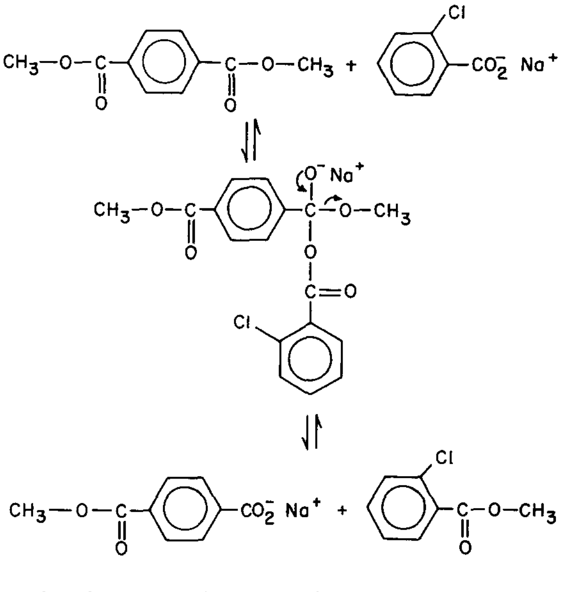


Figure 6 H.p.l.c. analysis of DMTP/SOCB mixture ($x_s = 0.529$) after 60 s at 285°C

We have also verified, by o.m., that MSTP remains in the solid state during its thermal decomposition. The birefringence corresponding to MSTP progressively disappears and is replaced by the gradual increase in the birefringence due to DSTP. These observations show that the thermal decomposition of MSTP is a solid-state reaction producing solid DSTP and DMTP, which immediately escapes from the system.

The reaction between DMTP and SOCB is likely to occur by acyl oxygen fission of the ester and formation of an intermediate anhydride:



IV

It is the precipitation of MSTP that ensures the irreversibility of the reaction. The solid-state decomposition of MSTP to form DMTP and DSTP is likely to proceed by a similar mechanism.

Kinetic studies

Thermal decomposition of MSTP. The reaction mechanism between DMTP and SOCB has been shown to involve three successive steps. Reaction III, corresponding to the thermal decomposition of MSTP, is the only one that can be studied individually:

$$2\mathrm{MSTP} \xrightarrow{k_{III}} \mathrm{DMTP} + \mathrm{DSTP}$$

This reaction is irreversible: MSTP and DSTP are in the solid state in the temperature range studied, whereas DMTP is vaporized. Reaction III is a heterogeneous reaction.

For this kind of reaction, the degree of conversion, corresponding to the ratio between the number of moles of MSTP reacted at time t, $(N_0 - N_t)$, and the total number of moles of MSTP involved in the reaction, N_0, is expressed by an Avrami equation[12]

$$\ln\left(\frac{1}{1-\alpha_t}\right)=k_{\text{III}}t^n \tag{1}$$

where

$$\alpha_t=(N_0-N_t)/N_0 \tag{2}$$

and n is the Avrami coefficient depending on the mechanism governing the formation of the products. If $n>1$, an induction period is observed when α_t is recorded as a function of t. (For convenience, we drop the subscript t and now write α only.)

The thermal modification of MSTP has been studied at six different temperatures ranging between 220 and 280°C. The results are reported in *Figure 7*, where α_r is shown as a function of t_r, each being the reduced variables:

$$\alpha_r=\alpha/0.3 \tag{3}$$

$$t_r=t/t_{0.3} \tag{4}$$

In *Figure 7* no induction period is observed, which means that n must be equal to 1. This value of n can be confirmed if equation (1) is linearized. If

$$F(\alpha)=\ln\left(\frac{1}{1-\alpha}\right) \tag{5}$$

and

$$F(0.3)=\ln\left(\frac{1}{1-0.3}\right) \tag{6}$$

$$t_r=t/t_{0.3} \tag{7}$$

$$F_r(\alpha)=F(\alpha)/F(0.3) \tag{8}$$

one obtains:

$$\ln F_r(\alpha)=n\ln t_r \tag{9}$$

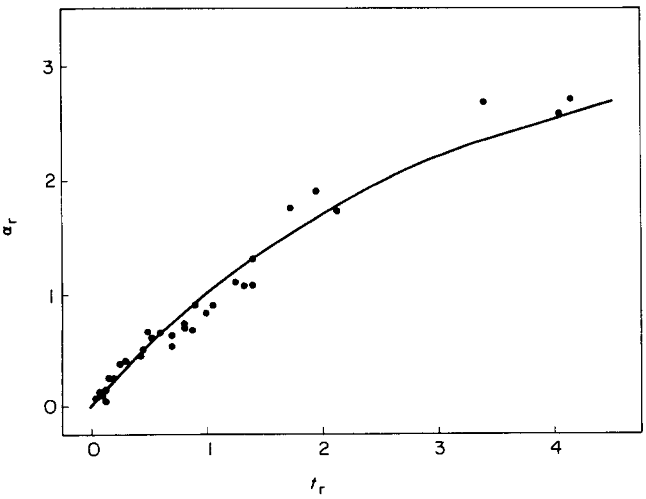


Figure 7 Thermal decomposition of MSTP: α_r as a function of t_r

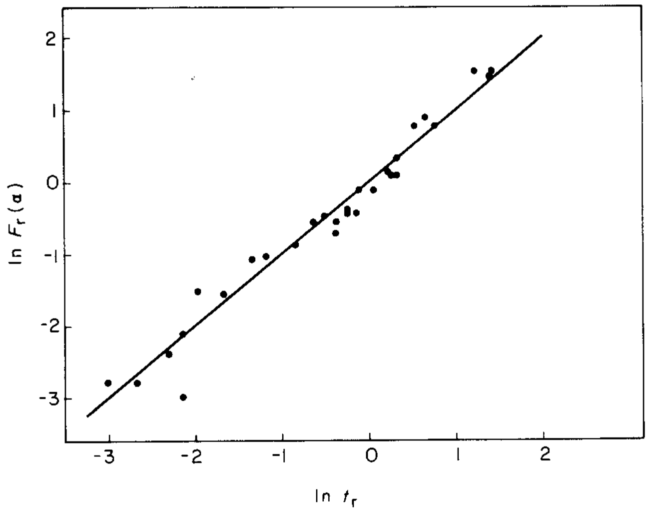


Figure 8 Thermal decomposition of MSTP: $\ln F_r(\alpha)$ as a function of $\ln t_r$

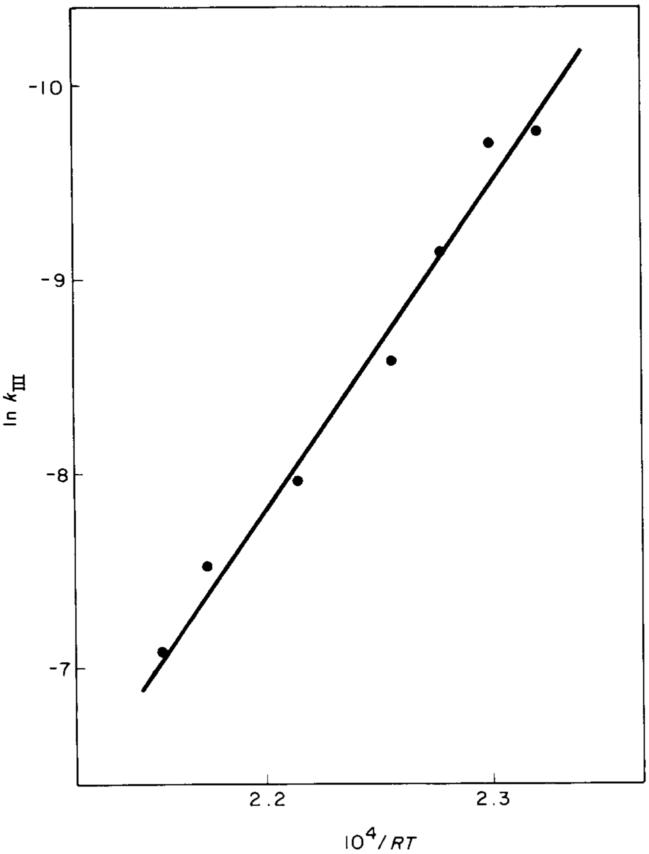


Figure 9 Arrhenius diagram for the thermal decomposition of MSTP

The plot corresponding to equation (9) is reported in *Figure 8*. The slope corresponding to the Avrami exponent is unity. On the basis of these results, the kinetic constants corresponding to the different temperatures of reaction can be calculated.

The activation energy of the reaction is calculated from an Arrhenius plot (*Figure 9*). One obtains for E_{III} a value equal to 167 kJ mol^{-1}.

Reaction between SOCB and DMPT. Reactions II and III were shown to be consecutive to reaction I. This last reaction can be analysed separately in initial kinetics, in such time intervals when reactions II and III can be considered as negligible.

We have shown that SOCB is soluble in DMTP at least for low salt concentrations. Under such conditions, reaction I occurs in a homogeneous phase. For the systems containing salt concentrations as high as 0.288 or 0.529 (molar fraction), it was not possible to determine the temperature of dissolution of the salt. However, in these kinetic studies we will consider these systems as homogeneous and apply the rules of homogeneous reaction kinetics. The results obtained with high salt concentrations will be compared to those obtained for low salt concentrations and a conclusive comparison will be carried out.

The study of the solubility of SOCB in DMTP has also shown that one of the reaction products (MSTP) precipitates in the system immediately after its formation and renders the reaction irreversible. This precipitation removes MSTP from the reaction system and thus modifies the reaction volume.

If one considers that, at time $t=0$, N_a moles of SOCB are mixed with N_b moles of DMTP, at time t the number of moles of both MSTP and MOCB produced is N_x and the remaining numbers of moles of SOCB and DMTP are respectively (N_a-N_x) and (N_b-N_x).

The general kinetic equation of a homogeneous reaction is:

$$\frac{1}{v}\frac{\mathrm{d}N_x}{\mathrm{d}t}=k_I\left(\frac{N_a-N_x}{v}\right)^p\left(\frac{N_b-N_x}{v}\right)^q \qquad (10)$$

where v is the reaction volume and p and q the orders of the reaction. The reaction volume can be calculated on the basis of the number of moles present in the reaction system. If v_m is the mean molar volume of the different reactants and products, one obtains:

$$v=v_m[(N_a-N_x)+(N_b-N_x)+N_x] \qquad (11)$$

It must be remembered that MSTP precipitates and does not contribute to the reaction volume. The general kinetic equation becomes:

$$\frac{(1-x)^{p+q-1}}{(a-x)^p(b-x)^q}\mathrm{d}x=k_1\,\mathrm{d}t \qquad (12)$$

where

$$a=\frac{N_a}{N_a+N_b},\qquad b=\frac{N_b}{N_a+N_b},\qquad x=\frac{N_x}{N_a+N_x} \qquad (13)$$

If we admit that the rate-determining step of the reaction between DMTP and SOCB is anhydride formation (IV), the orders p and q should be equal to 1. One obtains:

$$\frac{a}{b-a}\ln\left(\frac{b-x}{b}\right)-\frac{b}{b-a}\ln\left(\frac{a-x}{a}\right)=k_I(t-t_0) \qquad (14)$$

We notice

$$F(a,b,x)=k_I(t-t_0) \qquad (15)$$

The experimental results were obtained for molar fractions of 0.103, 0.288 and 0.529 and for reaction temperatures ranging between 220 and 285°C. In *Figure 10* we report $F(a,b,x)$ as a function of t for the different temperatures and for the different molar fractions of salt. The rate constants k_I are reported in *Table 1*.

In *Figure 11*, we show the Arrhenius plot corresponding to the three salt concentrations studied. One can see that the three systems can be fitted fairly well to a unique linear relation. From this plot, one calculates the value of the activation energy of the reaction between SOCB and DMTP, $E_I=88\ \mathrm{kJ\ mol^{-1}}$. These results correlate well with the previous assumptions, i.e. reaction I is a homogeneous reaction, and the order of the reaction is 1 for DMTP and SOCB.

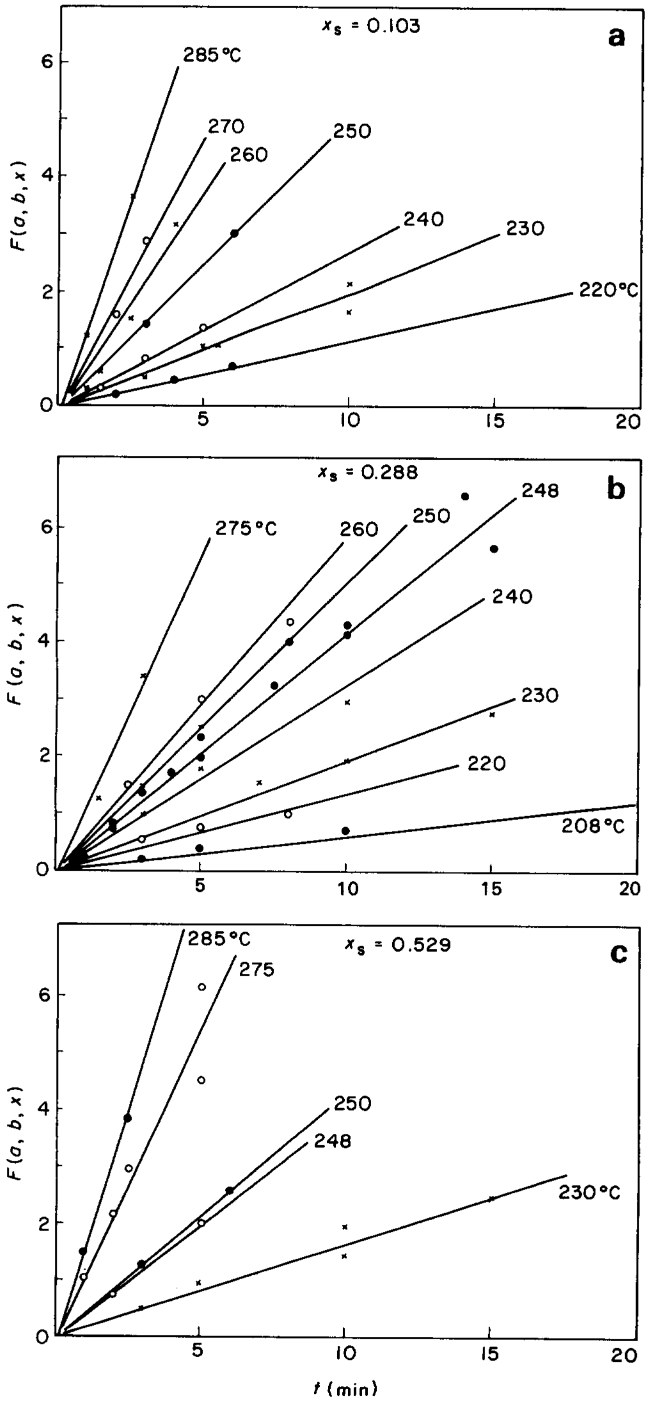


Figure 10 $F(a,b,x)$ as a function of t for the initial reaction between DMTP and SOCB ($x_s=0.103$ (a), 0.288 (b) and 0.529 (c))

Table 1 Rate constants of the reaction DMTP + SOCB (first attack) for molar fractions of salt of 0.103, 0.288 and 0.529

Reaction temperature (°C)	$k_I \times 10^3$ (s^{-1})		
	0.103	0.288	0.529
220	1.90	2.08	–
230	3.71	2.67	3
240	4.35	–	–
250	8.80	6.88	7.69
260	9.93	9.05	–
270	12.97	–	–
285	–	18.65	18.54
285	25.21	21.30	28.25

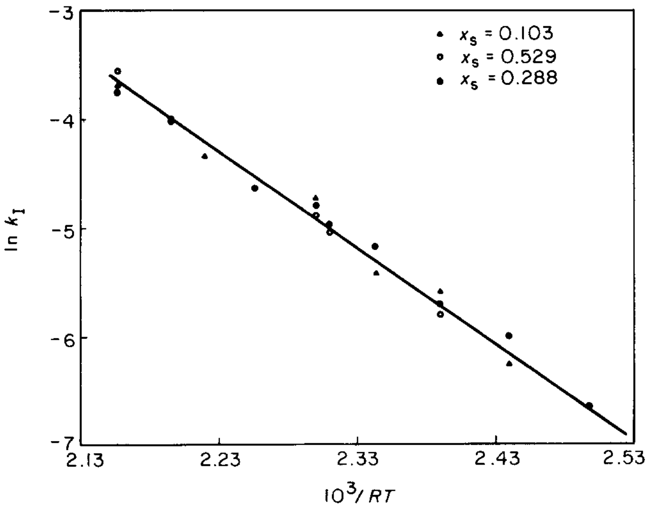


Figure 11 Arrhenius diagram for the initial reaction between DMTP and SOCB

Overall kinetics. A complete study has been carried out by h.p.l.c. with a system containing 0.288 molar fraction of SOCB at 255°C. The results are reported in *Figure 12*. For this system, we have shown that reaction I occurs in the liquid phase and that the order relative to the reagents is equal to 1. One also knows that MSTP precipitates in the system and decomposes into DMTP and DSTP. Thus reaction III is heterogeneous with an Avrami exponent of 1.

We suggest the following theoretical kinetics: a is the initial molar fraction of DMTP, b is the initial molar fraction of SOCB, and m, n, p, q and r are the molar fractions of DMTP, SOCB, MOCB, MSTP and DSTP respectively during the course of the reaction. One assumes that DMTP, SOCB and MOCB form the liquid phase and that MSTP and DSTP compose the solid phase.

During an increment of time dt, all the five chemicals vary in concentration. Each variation of one component is the result of the contribution of the three reactions as:

$$dm = dm_1 + dm_2 + dm_3$$

etc., where 1, 2 or 3 refer to reactions I, II or III.

For reaction I:

$$\underset{m}{\mathrm{DMTP}} + \underset{n}{\mathrm{SOCB}} \xrightarrow{k_I} \underset{p}{\mathrm{MOCB}} + \underset{q}{\mathrm{MSTP}}$$

$$-dm_1 = -dn_1 = dp_1 = dq_1 \tag{16}$$

and

$$-\frac{dm_1}{dt} = k_I \frac{mn}{(m+n+p)} \tag{17}$$

For reaction II:

$$\underset{q}{\mathrm{MSTP}} + \underset{r}{\mathrm{SOCB}} \xrightarrow{k_{II}} \underset{p}{\mathrm{MOCB}} + \underset{r}{\mathrm{DSTP}}$$

$$-dq_2 = -dr_2 = dp_2 = dr_2 \tag{18}$$

One assumes that this reaction occurs at the interface between solid MSTP and liquid SOCB. SOCB is in the liquid phase in a molar fraction equal to $n/(m+n+p)$ and MSTP is in the solid phase with DSTP in the molar fraction $q/(q+r)$. Such an interfacial reaction obeys the equation[12]:

$$\frac{d\alpha}{dt} = k'_{II}(1-\alpha)^{2/3} \tag{19}$$

where

$$\alpha = r/(q+r) \tag{20}$$

The apparent kinetic constant k'_{II} is related to k_{II} by:

$$k'_{II} = k_{II} \frac{n}{m+n+p} \tag{21}$$

One obtains:

$$\frac{dr_2}{dt} = k_{II} \frac{nq^{2/3}(q+r)^{1/3}}{m+n+p} \tag{22}$$

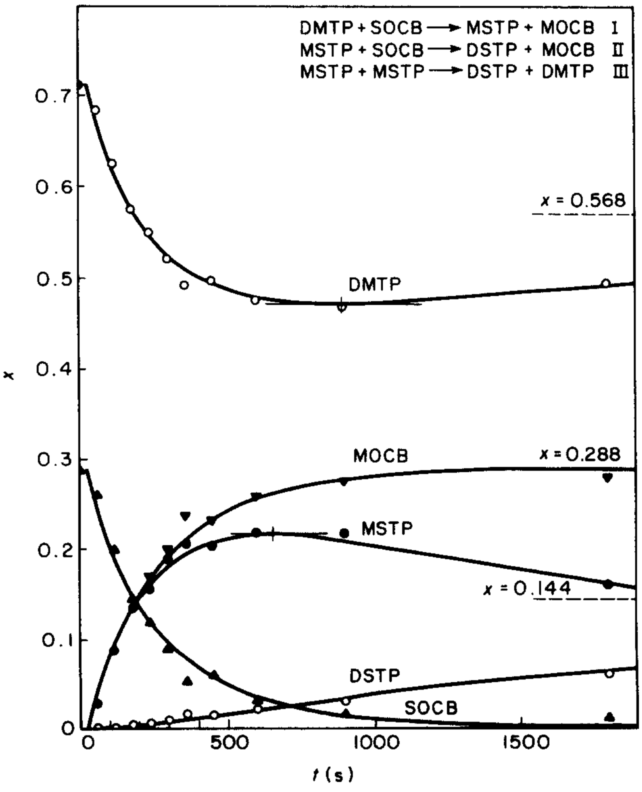


Figure 12 Overall reaction kinetics of the DMTP + SOCB reaction at 256.2°C (x_s = 0.288)

For reaction III:

$$\underset{q}{2\mathrm{MSTP}} \xrightarrow{k_{\mathrm{III}}} \underset{r}{\mathrm{DSTP}} + \underset{m}{\mathrm{DMTP}}$$

$$-\mathrm{d}q_3 = 2\mathrm{d}m_3 = 2\mathrm{d}r_3 \tag{23}$$

and

$$\frac{\mathrm{d}r_3}{\mathrm{d}t} = \tfrac{1}{2}k_{\mathrm{III}}q \tag{24}$$

Finally:

$$\mathrm{d}m = (A_1 + A_3)\ \mathrm{d}t \tag{25}$$

$$\mathrm{d}n = (-A_1 - A_2)\ \mathrm{d}t \tag{26}$$

$$\mathrm{d}p = (A_1 + A_2)\ \mathrm{d}t \tag{27}$$

$$\mathrm{d}q = (A_1 - A_2 - 2A_3)\ \mathrm{d}t \tag{28}$$

$$\mathrm{d}r = (A_2 + A_3)\ \mathrm{d}t \tag{29}$$

where

$$A_1 = k_{\mathrm{I}}\frac{mn}{m+n+p} \tag{30}$$

$$A_2 = k_{\mathrm{II}}\frac{nq^{2/3}(q+r)^{1/3}}{m+n+p} \tag{31}$$

$$A_3 = \tfrac{1}{2}k_{\mathrm{III}}q \tag{32}$$

This set of equations can be resolved in order to obtain the best agreement between the experimental results and the calculations. The theoretical curves are reported as full curves in *Figure 12*. The three kinetic constants determined by this calculation are compared to the values obtained from the studies of the isolated systems in *Table 2*. From *Table 2*, one can calculate that the rate constant of reaction II at 255°C is one order of magnitude lower than k_{I}. This means that SOCB preferentially attacks DMTP and that the reaction between MSTP and SOCB barely occurs. As a consequence, reaction II plays no role in the production of DSTP.

GENERAL DISCUSSION AND CONCLUSIONS

On heating DMTP in the presence of SOCB, one first observes the dissolution of the salt in the model compound. DMTP can dissolve up to 20% of SOCB at 220°C. On the other hand, DSTP was found to be insoluble in DMTP and the solubility of a salt like sodium benzoate is lower than 0.5% at 220°C. The high solubility of SOCB in DMTP was unexpected since it is generally thought that organic salts are soluble only in very polar solvents. Once solubilized, SOCB has been shown to react with an ester linkage of DMTP and produces a monosodium ester (MSTP). This product precipitates and decomposes to give DMTP and DSTP. The precipitation of MSTP hinders the second attack of SOCB on the ester linkage of MSTP.

Table 2 Global rate constants at 255°C for reactions I, II and III

	Overall kinetics	Isolated kinetics
k_{I} (s^{-1})	7×10^{-3}	8.4×10^{-3}
k_{II} (s^{-1})	3×10^{-4}	–
k_{III} (s^{-1})	2×10^{-4}	1×10^{-4}

The kinetic constants of the reaction between SOCB and DMTP were determined. For the decomposition of MSTP, an activation energy of 167 kJ mol^{-1} was obtained. The direct attack of SOCB on DMTP has been studied during the first steps of the reaction; E_{I} has been calculated and is equal to 88 kJ mol^{-1}. As mentioned above, the rate-determining step of reactions I and III is very likely to be intermediate anhydride formation. The higher energy of activation observed for the MSTP decomposition should be related to the fact that the reaction takes place in the solid state. It was also observed that the rate of dissolution of SOCB in DMTP was not the rate-determining step of the reaction. Finally, the study of the global reaction has confirmed that the second attack of SOCB on the ester linkage of MSTP is negligible.

The transposition of these results to the polymeric system leads us to assume that SOCB will first dissolve in PETP and attack an ester linkage of the chain. This attack will lead to a stoichiometric lowering of the molecular weight. The chain scission will be accompanied by the formation of sodium carboxylate end groups on the chain. MSTP precipitates in the liquid DMTP. This result allows us to predict that the ionic chain ends will also precipitate into the polymer melt. It is to this ionic phase, finely dispersed in the melt, that we attribute the enhancement of the crystallization rate of PETP/SOCB systems. We have also shown that MSTP decomposes, and produces DSTP and DMTP. We can thus predict that the ionic chain ends in the polymer will also react together at around 280°C. This reaction will lead to a chain rebuilding process and to the production of DSTP. These predictions have already received a clear confirmation in the polymer[5,6].

In the near future we intend to publish results concerning the kinetics of reaction between SOCB and PETP, and data concerning the crystallization of PETP induced by these reacting salts. We also intend to publish results concerning salts other than SOCB in the presence of DMTP.

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REFERENCES

1 Binsbergen, F. L. *Polymer* 1970, **11**, 253

2 Binsbergen, F. L. in 'Progress in solid state chemistry', (Eds. J. O. McCaldin and G. Somorjai), Pergamon Press, Oxford, 1973, Vol. 8

3 Binsbergen, F. L. *Polym. Sci. Polym. Symp.* 1977, **59**, 11

4 Van Antwerpen, F. and Van Krevelen, D. W. *J. Polym. Sci.* 1972, **10**, 2423

5 Legras, R., Mercier, J. P. and Nield, E. *Nature* 1983, **304**, 432 432

6 Legras, R., Bailly, Ch., Daumerie, M., Dekoninck, J. M., Mercier, J. P., Nield, E. and Zichy, V. *Polymer* 1984, **25**, 835

7 European Patent Application, 0021648, 1980

8 Leblanc, D., Dekoninck, J. M., Legras, R., Mercier, J. P. and Nield, E., to be published

9 Bailly, Ch., Daumerie, M., Legras, R. and Mercier, J. P. *J. Polym. Sci.* 1985, **23**, 493

10 Bailly, Ch., Legras, R. and Mercier, J. P. *J. Polym. Sci.* 1985, **23**, 343

11 Vogel, A. I. 'Practical Organic Chemistry', Longmans, Green and Co., London, 1956

12 Delmon, B., 'Introduction à la Cinétique Hétérogène', Technic, Paris, 1969

13 Patai, S., 'The Chemistry of Carboxylic Acids and Esters', Interscience, New York, 1969, p. 127