

# Liquid-induced crystallization of poly(2,6-dimethyl-1,4-phenylene ether)

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The liquid-induced crystallization process of poly(2,6-dimethyl-1,4-phenylene ether) (PPO) films in the presence of decalin as a swelling agent was investigated by means of a BMR differential microcalorimeter. Results of microcalorimeter measurements were used to obtain thermokinetic curves and to determine heat effects of the liquid-induced crystallization process. The degree of crystallinity and thermal properties of PPO films crystallized in decalin were determined by differential scanning calorimetry (d.s.c.).

## INTRODUCTION

Numerous studies of the properties of unsubstituted poly(phenylene oxide), poly(2,6-dimethylphenylene oxide) and poly(2,6-diphenylphenylene oxide) have been published. The regular structure of these aromatic polyethers would suggest their ability to crystallize readily. In practice it has been found, however, that a high degree of crystallinity can be achieved easily only in the case of the first of these three homologues subjected to thermal crystallization under various conditions<sup>1</sup>. Poly(2,6-diphenylphenylene oxide) crystallizes in the solid state, but it decomposes on melting<sup>2</sup>. Poly(2,6-dimethylphenylene oxide) was found to undergo thermal crystallization only with great difficulty<sup>1</sup>. Karasz attributes this to steric hindrance effects due to methyl groups<sup>3</sup>. There have also been some reports concerning the crystallization of poly(2,6-dimethyl-phenylene oxide) during the precipitation from solutions<sup>4</sup> and on exposure to vapours of different solvents<sup>5</sup>. It has been postulated that in these cases the solvent molecules form a part of the crystalline structure<sup>6</sup>. Evidence has been presented by Magre and Boon for a helical conformation of poly(2,6-dimethylphenylene oxide) in its decalin and  $\alpha$ -pinene complexes<sup>7</sup>.

It was the aim of this work to examine the liquid-induced crystallization of the poly(2,6-dimethyl-1,4-phenylene oxide), (PPO)–decalin system in the swollen state.

To obtain more detailed information about the mechanism of liquid-induced crystallization and the crystalline structure of PPO we have decided to study this process by different methods. Results obtained using a non-isothermal non-adiabatic differential microcalorimeter BMR<sup>8</sup> and scanning calorimeter will be presented in this paper. The use of microcalorimetric methods for investigating the process of liquid-induced crystallization has been rather limited. Liquid-induced crystallization studies reported in the literature do not make any reference to the above mentioned technique<sup>9,10</sup>. The works of Balcerzyk<sup>9–11</sup> are connected only indirectly with this technique.

In our opinion, the method involving the measurement of liquid-induced crystallization exotherms by means of a differential microcalorimeter should prove very useful in characterizing the course of this process.

## EXPERIMENTAL

### Materials

Poly(oxyphenylene) films 20 and 10  $\mu\text{m}$  thick were used throughout the present study. The polymer films were prepared by solvent casting of the solution of poly(2,6-dimethyl-1,4-phenylene ether) in chloroform on a glass plate at room temperature and then films were dried under vacuum at 373K for two weeks. Samples of films of PPO did not show any crystallinity by d.s.c. measurements, X-ray diffraction and polarizing microscope observations. The poly(2,6-dimethyl-1,4-phenylene ether) had a number-average molecular weight,  $M_n$ , of 25 000 and a viscosity-average molecular weight,  $M_v$ , of 36 700. The glass transition temperature,  $T_g$ , was 491K. Decalin made by Veb Jenapharm–Apolda was used as a swelling agent without any prior purification.

### Differential microcalorimeter measurements

Thermokinetic parameters of the liquid-induced crystallization process were determined using a non-isothermal non-adiabatic calorimeter of Zielenkiewicz<sup>8</sup>. Measurements were started on breaking a sealed glass phial containing a known amount of the PPO film, placed in a calorimetric cell containing decalin. The PPO samples had a mass between 0.5–0.1 g and the volume of decalin used was 16 ml. The differential BMR-type calorimeter of Zielenkiewicz and its properties have been described in literature<sup>8</sup>. Changes of the thermoelectric force (TEF) detected by the thermopile of the calorimeter were recorded on a EZ–10 type recorder (Laboratorni Pstroje, Prague). These changes represent temperature differences in the measuring calorimetric cell due to thermal effects produced in the process studied. The amount of heat evolved in the calorimeter was calculated from the following formula<sup>8,12,13</sup>:

$$Q(t) \Big|_{t_0}^{t_1} = K \theta(t) \Big|_{t_0}^{t_1} + \alpha \int_{t_0}^{t_1} \theta(t) dt \quad (1)$$

where  $\alpha = 0.4072$  cal/mV min, the coefficient of heat loss;  $K = 7.22$  cal/mV, the heat capacity of calorimeter;

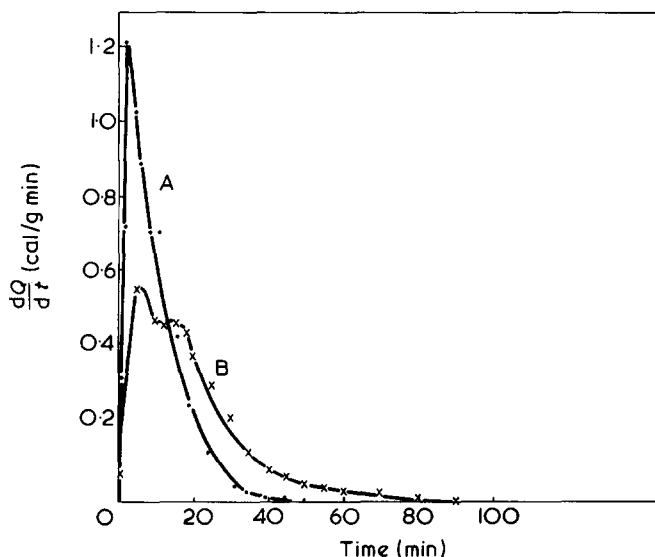


Figure 1 Thermokinetic curves of swelling and crystallization of poly(2,6-dimethyl-1,4-phenylene oxide)-decalin system at 50°C (A) and 40°C (B). Foil thickness 20  $\mu\text{m}$

$Q(t)|_{t_0}^{t_1}$  is the amount of heat developed during the interval  $(t_0, t_1)$ ;  $\theta(t)|_{t_0}^{t_1}$  are changes of TEF during the interval  $(t_0, t_1)$ ;  $\theta(t)$  describes the time variation of TEF and  $t$  is time.

The coefficient of heat loss  $\alpha$  was determined during the calibration of the instrument; the following formula was used:

$$\alpha = \frac{14.34 i^2 R}{\theta_t} \text{ cal/V min} \quad (2)$$

where:  $i$  is the current flowing through the heater in the calorimetric cell during calibration (after reaching constant  $\theta_t$ ) and  $R$  is the resistance of the heating coil in the calorimetric cell. The thermal capacity of the calorimeter was calculated from equation (3) and found to be  $K = 7.22 \text{ cal/mV}$ :

$$K = \frac{\alpha}{\beta} \quad (3)$$

where Newton's cooling constant,  $\beta$ , was calculated from equation (4) by a least squares procedure using the values of  $\theta(t)$  from the cooling curve obtained during calibration of the calorimeter.

$$\beta = \frac{n \sum_{i=1}^n t_i \log \theta_i - \sum_{i=1}^n t_i \sum_{i=1}^n \log \theta_i}{n \sum_{i=1}^n t_i^2 - \sum_{i=1}^n t_i} \quad (4)$$

$\beta$  was found to be equal to  $0.0564 \text{ min}^{-1}$ .

It was found that heat effects produced in the system investigated could be calculated from equation (1), the calorimeter being treated as a single body system<sup>12</sup>.

Thermokinetic curves  $\Delta Q/\Delta t = f(t)$  and the integral curves  $Q = f(t)$  were plotted using the TEF changes and applying

equation (1). Heat effects were expressed in terms of 1 g of the polymer investigated.

#### D.s.c. measurements

Amorphous samples of the PPO films were subjected to liquid-induced crystallization by immersing them in decalin maintained at the following constant temperatures: 295, 308 and 321K.

The temperatures were kept constant to within  $\pm 0.2\text{K}$ . After a predetermined period of time the film samples were taken out of the decalin and dried, some samples being dried thoroughly for a few days. A Perkin-Elmer differential scanning calorimeter model DSC-2 was used to obtain the thermograms of the PPO samples and PPO films crystallized in decalin. Heating rates employed were 10 K/min. Numerical values of the heat of fusion were obtained by determining the surface area under the peak corresponding to the endothermic fusion point. The differential scanning calorimeter was calibrated using indium as a standard. The heat of fusion of indium,  $\Delta H_{\text{ind}} = 6.80 \text{ cal/g}$ .

## RESULTS

Heat effects due to the decalin-induced swelling of the PPO samples were subsequently determined by BMR differential calorimeter at temperatures of 293, 303, 313 and 321K for films 10 and 20  $\mu\text{m}$  thick.

Results of measurements were used to obtain working curves,  $U = f(t)$ , where  $U$  stands for readings of the recording millivoltmeter. The working curves were then transformed into thermokinetic curves by differentiation (Figures 1 and 2) and also into integral curves (Figure 3).

The separation of the thermokinetic curves into two characteristic parts may be observed at various temperatures of liquid-induced crystallization. Better separation of the thermokinetic curve into the two characteristic parts was

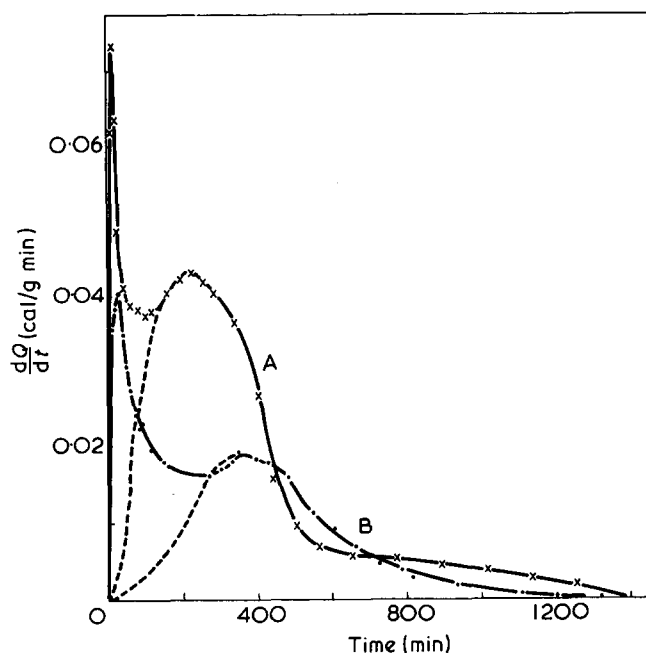


Figure 2 Thermokinetic curves of swelling and crystallization of poly(2,6-dimethyl-1,4-phenylene oxide)-decalin system at 25°C (A) and 21°C (B). Foil thickness 10  $\mu\text{m}$ . ---, Thermokinetic curves determined by calculation

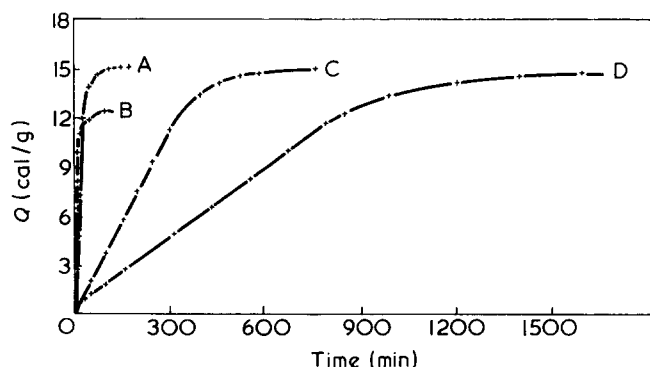


Figure 3 Integral curves of heat effects of swelling and crystallization of poly(2,6-dimethyl-1,4-phenylene oxide)-decalin system at various temperatures. Foil thickness 20  $\mu\text{m}$ . A, 40°C; B, 50°C; C, 30°C; D, 25°C

Table 1 Heats of fusion of PPO crystallized at different crystallization times in decalin at 321K and 308K

Crystallization time	$\Delta H$ (cal/g)	Crystallinity (%)	$T_{m\text{max}}$ (K)
<b>321K</b>			
3 min	0.34	3	394
11 min	0.57	5	395
1 h	3.97	35	422
3 h	3.87	34	423
10 h	4.40	39	423
<b>308K</b>			
10 min	0.25	2	394
14 min	0.30	3	392
7 h	4.56	40	421

found to occur using thinner films. By considering the magnitude of the heat effect accompanying the process studied for the 20  $\mu\text{m}$  thick films at various temperatures, it was found that the amount of heat produced is the same for different experimental temperatures, but the process lasts longer at lower temperatures. A slight decrease of the amount of heat produced was observed at 321K. It was noticed that the temperature of 323K was the limiting temperature of dissolution of the sample.

During heating at a rate of 10K/min in the DSC-2 calorimeter, the sample of PPO was found to exhibit an endotherm having its maximum at about 521K and responsible for the fusion of the crystalline phase. The sample was then rapidly cooled to 350K and subsequently heated again at a rate of 10K/min and a glass transition  $T_g$  was observed at 491K. No changes were found to have taken place in the sample heated at a rate of 10K/min, and that particular heating rate was accordingly used in all further investigations.

The heat of crystallization of PPO in decalin was then determined at various temperatures. The heats of crystallization  $\Delta H$  and melting (fusion) points of PPO are listed in Table 1.

The degree of crystallinity was calculated by taking the heat of fusion  $\Delta H_m^0$  of pure, crystalline PPO equal to 11.4 cal/g<sup>14</sup>.

Decalin was carefully removed from the samples by drying. The samples were then subjected to thermal analysis. Two endothermic peaks were found to appear upon heating, that effect being particularly characteristic of samples crystallized in decalin at 321 and 308K for longer periods of time (7 h *viz.* Figure 4).

Two endothermic peaks corresponding to the fusion of the crystalline phase can be observed on the thermograms. The maximum of the higher main peak is situated close to 381–385K, while that of the lower one is near 395–399K.

## DISCUSSION

It was found that the degree of crystallinity of PPO, determined by means of the differential scanning calorimeter, is equal to about 4%, after a period of time (approx. 6 min) corresponding to total primary crystallization according to microscopic investigations<sup>15,16</sup>. The degree of crystallinity, determined after 10 h, was equal to ~40%.

Let us now make a rather arbitrary assumption that at the time corresponding to the second maximum on the thermokinetic curve all other processes, i.e. diffusion, swelling etc., come to an end. Results of our unpublished optical data<sup>15</sup> would seem to make such an assumption plausible. Based on this assumption we can go further and assume that the part of the thermokinetic curve decreasing monotonically in the direction of the abscissa characterizes the actual course of the crystallization process investigated. It was decided to describe that part of the thermokinetic curve by an equation which, in our opinion, should also be valid after a suitable modification for the ascending portion of the thermokinetic curve.

In this way the approximate positions of the initial points of the crystallization curve were determined. It can be seen from Figure 2 that these points on the whole agree well with values (times) obtained using other experimental techniques. From polarizing microscopy observations<sup>15</sup> crystallization began after approximately 10 min (at 25°C). The d.s.c. measurements showed negligible crystallinity after this time. This fact would confirm our initial assumption that only a very small amount of the crystalline phase is formed at the conclusion of the first peak on the thermokinetic curve.

If we now assume the above to be a working hypothesis, the results obtained make it possible to state that: (a) the

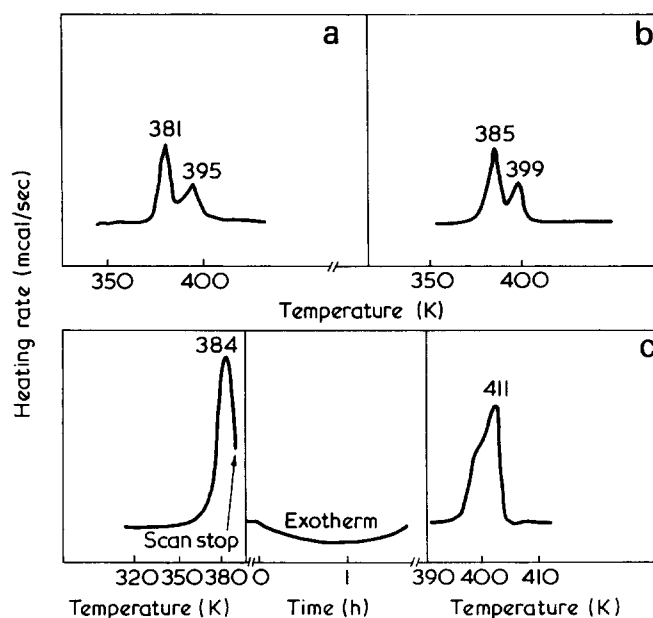


Figure 4 D.s.c. curves of poly(2,6-dimethyl-1,4-phenylene ether) previously crystallized in decalin (a) 308K for 7 h; (b), (c) 321K for 7 h

first part of the thermokinetic curve characterizes the processes of sorption, swelling and diffusion and the second part characterizes the course of the liquid-induced crystallization process; (b) crystallization temperature and film thickness are the two parameters influencing the course of the crystallization process (*viz.* Figures 1 and 2).

The process is faster if the temperature of the liquid-induced crystallization is increased, the two peak maxima then being superimposed on each other to a much greater extent, while even a single peak may be obtained in the limiting case.

The appearance at both crystallization temperatures of two peaks by d.s.c. measurements corresponding to the fusion of samples (Figure 4, 308K, 321K) requires a separate interpretation.

There are several possible explanations of the observed phenomenon which is thought to indicate the presence of two distinct crystalline forms of PPO exhibiting different melting points.

(1) The simplest explanation of this phenomenon would be to assume the existence of polymorphic structures, but that seems to be rather improbable in this particular case.

(2) The second possible interpretation is concerned with postulating the formation of crystals consisting of macromolecules of PPO and other crystals in whose lattice decalin molecules are also built in. This explanation is perhaps more plausible since the possibility of such crystals being formed has already been reported in the literature<sup>7,17</sup>. Our unpublished X-ray analysis data<sup>18</sup> would seem to confirm the above proposed interpretation.

(3) The third possible explanation may be provided by assuming the formation of crystals exhibiting a varying degree of structural defects. Crystals formed in the primary crystallization stage have many structural flaws and consequently, the more perfect crystals formed in the secondary crystallization stage can have a different melting point<sup>19</sup>.

There is also another possibility for explaining the presence of two peaks. According to Bell *et al.*<sup>20</sup> these two peaks may be caused by the presence of folded chain and extended chain lamellae. A number of conclusions in this paper are contradictory to another author's<sup>21,22</sup>. In our case the presence of extended chain lamellae under the condition of liquid-induced crystallization seems to be unlikely.

It is therefore probable that as a result of a superposition of these phenomena, two melting point peaks are observed in the thermograms.

In order to ascertain which of the proposed explanations

best describes the observed phenomena we did a separate experiment shown in Figure 4c. It can be seen that at a temperature below the melting point of the secondary crystalline form and above the melting point of the primary crystalline form there exists a distinctly increased amount of the secondary form. Thus, after heating the sample for 1 h and switching the scanning on, a peak appears and the secondary area under this peak is greater than that found before heating. An exothermic peak responsible for crystallization is observed for 1 h during heating the sample at 387.2K. These findings prove conclusively the existence of two different crystalline forms but do not enable us to say at this stage which of the proposed explanations is correct.

Elucidation of the above phenomenon necessitates further studies of the structure of the product.

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