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# DSC STUDY OF TRANSFORMATION KINETICS OF LIQUID-CRYSTALLINES BASED ON 1,4-PHENYLENE 4-*n*-METHOXYBENZOATE-4-ALLYLOXYBENZOATE

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## Abstract

The transformation kinetics of liquid-crystalline 1,4-phenylene 4-*n*-methoxybenzoate-4-allyloxybenzoate (PMOBAOB) and a liquid-crystalline poly(mesogen/methyl) siloxane (PMMS) was studied by means of a non-isothermal method using differential scanning calorimetry. This determination led to an apparent activation energy of transformation of 639.0 and 306.5 kJ $mol^{-1}$, respectively. The values of the Avrami exponent $n$ were 1.8 and 1.1. The results show that the process of transformation of PMOBAOB involves a constant number of nuclei growing in two dimensions at a constant rate, while the process of transformation of PMMS-PMOBAOB involves a constant number of nuclei growing in one dimension at a constant rate.

**Keywords:** DSC, liquid-crystalline, PMMS-PMOBAOB, PMOBAOB, transformation kinetics

## Introduction

The synthesis of liquid-crystallines poly(mesogen/methyl) siloxane (PMMS) exhibiting a high column efficiency and a low bleed, yet providing high selectivity over a wide temperature span, was undertaken several years ago. The study of transformation kinetics is one of the important subjects in the field of liquid-crystallines. However, a detailed study of the transformation kinetics for liquid-crystallines PMOBAOB and PMMS-PMOBAOB has not been reported, and hence such work was carried out by differential scanning calorimetry (DSC) in the present investigation.

## Experimental

### *Synthesis of 1,4-phenylene 4-n-methoxybenzoate-4-allyloxybenzoate (PMOBAOB)*

0.015 mol of 4-hydroxyphenyl 4-methoxybenzoate and 18 ml of dry pyridine were placed in a 100 ml three-necked round-bottomed flask equipped with an additional funnel, a reflux condenser and a mechanical stirrer. 4-(Allyloxy)benzoyl

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chloride was added through the funnel, and the mixture was then refluxed at 85°C for 5 h. After cooling to room temperature, 200 ml of distilled water was added and the mixture was acidified with 20% aqueous hydrochloric acid. The resulting precipitate was filtered off and washed with 200 ml of saturated aqueous sodium bicarbonate, and then with 100 ml of distilled water.

### *Synthesis of PMMS-PMOBAOB*

5.0 mmol of PMOBAOB in 15 ml of toluene and 0.37 mmol of poly[oxy(methylsilylene)] were placed in a 50 ml three-necked round-bottomed flask equipped with a reflux condenser, a drying tube and a mechanical stirrer. 0.2 ml (0.1 *M*) chloroplatinic acid in 2-propanol was added, and the solution was heated at 85°C for 20 h. The polymer was obtained by precipitation with 20 ml of methanol. The product was purified by dissolving it in 15 ml of methylene chloride, followed by precipitation with 20 ml of methanol.

### *Differential scanning calorimetry*

DSC scans were carried out with a CDR-1A Thermal Analyzer (SBIF, Shanghai) with an accuracy of ±0.1°C. Liquid-crystalline samples were heated from 323 to 473 K at a heating rate varying from 6 to 14 K $min^{-1}$. The resulting transformation curves were traced on a chart recorder. Data for all the dynamic runs were collected directly from the DSC by an interfaced computer system. A typical complete DSC trace for PMOBAOB at a heating rate of 10 K $min^{-1}$ is shown in Fig. 1. The DSC curves were normalized by using appropriate computer programs.

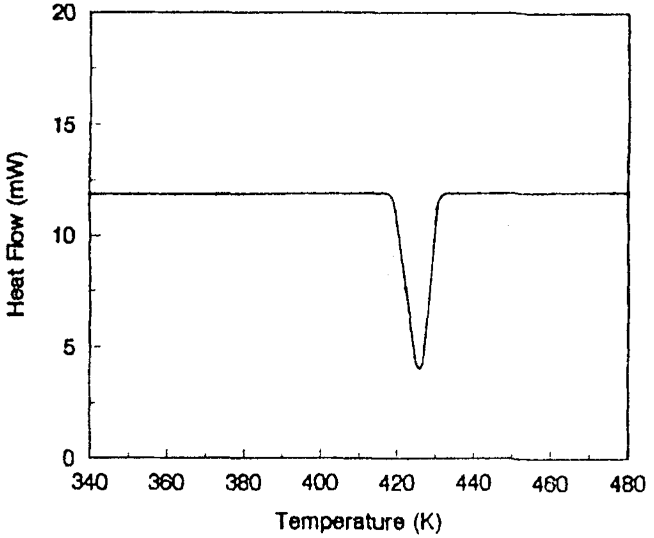

**Fig. 1** DSC curve of PMOBAOB at a heating rate of 10 K $min^{-1}$

## Results and discussion

The characteristic values of the peak temperatures, $T_p$, and the widths of the transformation peaks at half-maximum, $\Delta T_{HM}$, for various heating rates, obtained from the DSC curves, are given in Table 1. In order to obtain the values of the apparent activation energy of transformation for PMOBAOB and PMMS-PMOBAOB, a multiple heating method [1] (Kissinger's method) was applied.

$$\ln(T_p^2/\alpha) = \ln(E/R) - \ln v + E/RT_p \tag{1}$$

As shown in Fig. 2, the relationship $\ln(T_p^2/\alpha)$ *vs.* $1/T_p$, where $\alpha$ is the heating rate and $T_p$ is the maximum peak temperature of the phase transformation in the DSC curves, is linear. From the original data in Table 1, the apparent activation energy was determined to be 639.0 kJ mol$^{-1}$ for PMOBAOB and 306.5 kJ mol$^{-1}$ for PMMS-PMOBAOB. The linear correlation coefficient was 0.994 for PMOBAOB and 0.998 for PMMS-PMOBAOB.

The values of the Avrami exponent ($n$) for PMOBAOB and PMMS-PMOBAOB were determined via the equation of Augis and Bennett [2]:

$$n = \frac{2.5}{\Delta T_{HM}} \frac{T_p^2}{E/R} \tag{2}$$

where $\Delta T_{HM}$ is the width of the transformation peak at half-maximum. The values of the Avrami exponent, $n$, computed from Eq. (2) are also listed in Table 1.

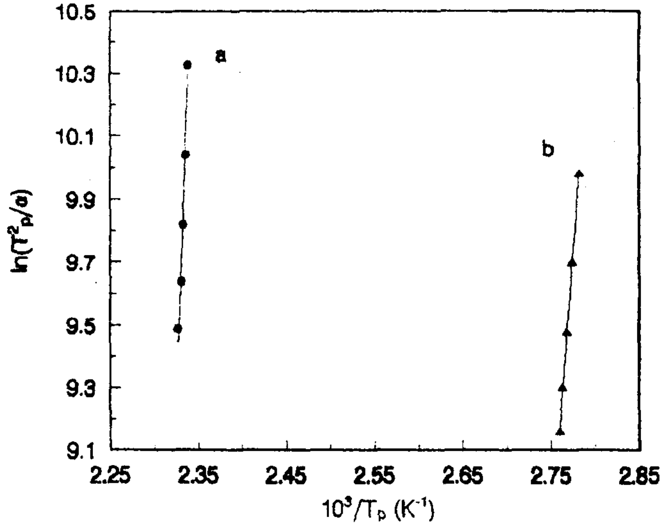

Fig. 2 Kissinger's plot of the transformation activation energy obtained by plotting $\ln(T_p^2/\alpha)$ *vs.* $1/T_p$ for a) PMOBAOB, b) PMMS-PMOBAOB

**Table 1** Values of parameters derived from non-isothermal DSC

| PMOBAOB | | | | PMMS/PMOBAOB | | | |
|---|---|---|---|---|---|---|---|
| $\alpha$/K min$^{-1}$ | $T_p$/K | $\Delta T_{HM}$ | $n$ | $\alpha$/K min$^{-1}$ | $T_p$/K | $\Delta T_{HM}$ | $n$ |
| 6 | 427.7 | 3.1 | 1.9 | 6 | 359.5 | 7.3 | 1.2 |
| 8 | 428.2 | 3.3 | 1.8 | 8 | 360.5 | 7.8 | 1.1 |
| 10 | 428.8 | 3.6 | 1.7 | 10 | 361.2 | 7.2 | 1.2 |
| 12 | 429.1 | 3.6 | 1.7 | 12 | 361.9 | 8.1 | 1.1 |
| 14 | 429.7 | 3.6 | 1.7 | 14 | 362.3 | 8.2 | 1.1 |
| | | Mean $n$ =1.8 | | | | Mean n =1.1 | |

The method of Ozawa [3] is quite simple and straightforward, and does not involve any assumptions. It is used to derive the value of $n$ via the following equation:

$$\ln[-\ln(1-x)] = n\ln k(T-T_0) - n\ln\alpha \tag{3}$$

According to Eq. (3), a plot of $\ln[-\ln(1-x)]$ *vs.* $\ln\alpha$ yields a straight line with slope equal to $n$, where $x$ is the volume fraction transformed after some time. It should be measured at the same temperature from a number of transformation endotherms obtained at different heating rates. Table 2 lists values of $\ln[-\ln(1-x)]$ at different heating rates for PMOBAOB and PMMS-PMOBAOB.

The problem with the Ozawa method is that it is not possible to obtain more than two or three values of $x$ at the same temperature for different heating rates, because the position of the transformation peak shifts to higher temperature with increasing heating rate.

It is well established that the Avrami exponent may be correlated to the transformation mechanism. Possible values of $n$ for different mechanisms based on constant or zero nucleation rate were reported by Henderson [4]. The values of $n$ for PMOBAOB in the present work were computed to be 1.8 and 1.5 from the Augis and Ozawa methods, respectively. The values of $n$ for PMMS-PMOBAOB with these

**Table 2** Determination of the Avrami exponent by plotting $\ln[-\ln(1-x)]$ *vs.* $\ln\alpha$

| PMOBAOB | | | | PMMS/PMOBAOB | | | |
|---|---|---|---|---|---|---|---|
| $\alpha$/K min$^{-1}$ | $\ln\alpha$ | $x$ | $\ln[-\ln(1-x)]$ | $\alpha$/K min$^{-1}$ | $\ln\alpha$ | $x$ | $\ln[-\ln(1-x)]$ |
| 6 | 1.792 | 0.548 | –0.231 | 6 | 1.792 | 0.572 | –0.164 |
| 8 | 2.079 | 0.398 | –0.678 | 8 | 2.079 | 0.490 | –0.395 |
| 10 | 2.303 | 0.316 | –0.968 | 10 | 2.303 | 0.421 | –0.604 |
| 12 | 2.485 | 0.242 | –1.283 | 12 | 2.485 | 0.366 | –0.786 |
| 14 | 2.639 | 0.209 | –1.451 | 14 | 2.639 | 0.305 | –1.011 |
| $\ln[-\ln(1-x)]=2.363-1.454\ln\alpha$, $n=1.5$, $r=0.998$ | | | | $\ln[-\ln(1-x)]=1.622-0.980\ln\alpha$, $n=1.0$, $r=0.994$ | | | |

two methods were 1.1 and 1.0, respectively. The values of $n$ obtained with the Augis technique are more reliable.

The value of $n=1.8$ suggests that the transformation of PMOBAOB is a process involving a constant number of nuclei growing in two dimensions at a constant rate. The value of $n=1.1$ for PMMS-PMOBAOB suggests a process involving a constant number of nuclei growing in one dimension at a constant rate.

## Conclusions

A study of the transformation kinetics of the liquid-crystallines PMOBAOB and PMMS-PMOBAOB gave the values of the Avrami exponent (1.8 and 1.1) and the transformation activation energy (639.0 and 306.5 kJ mol$^{-1}$). The results show that the process of transformation of PMOBAOB involves a constant number of nuclei growing in two dimensions at a constant rate, and that of the transformation of PMMS-PMOBAOB involves a constant number of nuclei growing in one dimension at a constant rate.

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