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Changes of Liquid-Crystalline Polymer Structure with Temperature

4. Kinetics of Mesophase Formation from Isotropic Melt*

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SUMMARY

Thermal changes in the structural state of liquid crystalline polymers with mesogenic side groups and the kinetics of mesophase formation were studied by means of small-angle X-ray scattering.

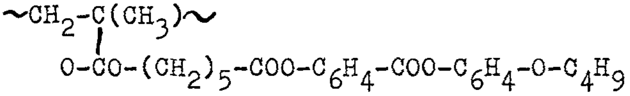
INTRODUCTION

Thermal changes in liquid-crystalline (LC) polymer structures and the kinetics of LC state formation while cooling isotropic melts have not yet been thoroughly studied. Only few refers consider the changes in LC ordering when heating polymers above glass transition temperature and above clearing temperature (1-4).

The aim of this work was to establish both the character and the kinetics of LC structural transformations in the region of isotropic state - smectic mesophase transition.

EXPERIMENTAL

The LC polymer with the methacrylate main chain and phenylbenzene side groups (molecular weight $M_n = 3.1 \times 10^4$, $M_w/M_n = 1.1$) has been investigated:



$$\begin{array}{l} \sim CH_2-C(CH_3)\sim \\ \qquad\;\; | \\ \qquad O-CO-(CH_2)_5-COO-C_6H_4-COO-C_6H_4-O-C_4H_9 \end{array}$$

According to calorimetric data and polarized-optical studies for this polymer the clearing temperature is $T_{cl}=421$ K (5).

Small-angle X-ray scattering (SAXS) curves were recorded on a Rigaku-Denki type diffractometer using step-by-step scanning. The temperature was maintained within ± 0.5 K.

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While studying the kinetics of mesomorphic structure formation after a rapid cooling of the isotropic melt, the detector was put at an angle corresponding to a maximum intensity; the recording has been taken each 30 s.

RESULTS AND DISCUCCION

The model of layer packing for the investigated polymer was proposed earlier (6). The layer thickness is 4.33 nm at room temperature, as follows from the position of the SAXS maximum (Fig. 1).

Increasing temperature up to 418 K results in the growth of intensity and a shift to smaller angles; the intensity growth is almost linear. When the polymer is overheated by 2 K above T_{cl}, the thermal changes of intensity are restored with small hysteresis (Fig. 2). It is seen that the melting and reappearance of smectic structure take place in a narrow temperature interval (5 K).

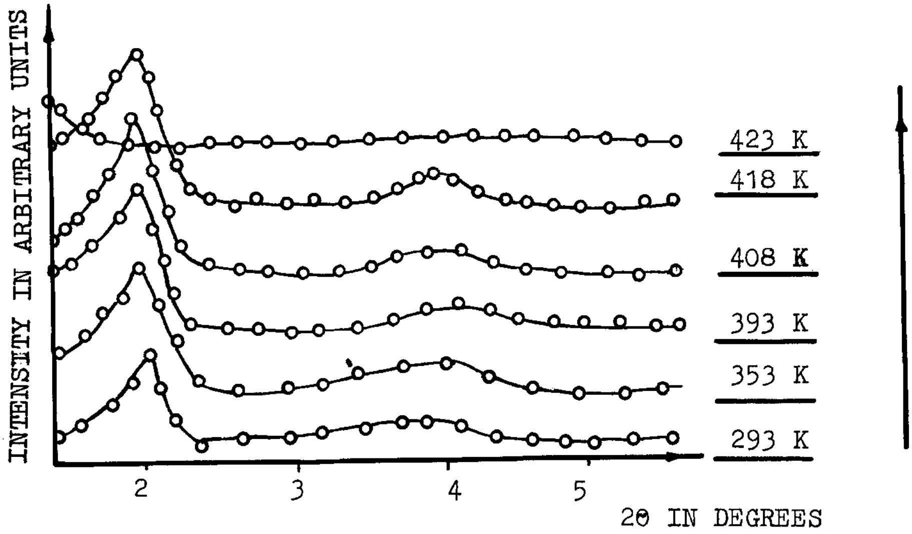

Fig. 1 SAXS curves for LC polymer during heating.

By rapid cooling of the isotropic melt below T_{cl}, a gradual increase of a SAXS maximum proceeds in few minutes (Fig. 3). By overheating above T_{cl}, a maximum disappears in less than 5 s.

Increasing intensity of a smectic maximum with temperature in the interval of 293-418 K is determined by the growth of the LC ordered region size size of layered packs (7). The shift of this maximum to smaller angles is associated with increase of thickness of a smectic layer due to thermal expansion (3,4).

The increase of the smectic maximum intensity with time during transition from the one-phase state of isotropic melt to the LC state testifies the prolonged perfection of LC ordering due to slow processes of structural transformation.

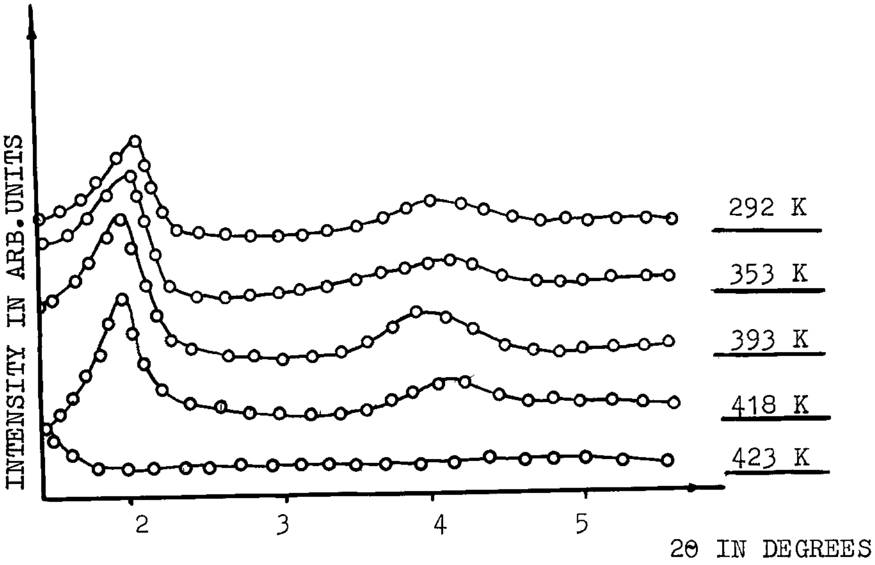

Fig.2. SAXS curves for LC polymer during cooling.

According to the method by Hashimoto (8),from dependence $I_{max}(t)$ the diffusion factor D of macromolecules has been calculated for the process of LC ordering.It happens to be equal to 0.7×10^{-16} cm^2/s,which is an order less as compared with flexible chain polymers (8).Such a difference in the diffusion factors is supposed to be connected with the branched structure of macromolecules and with the presence of mesogenic bulk groups in side chains.This factor should lead to the hindered transport of macromolecules in the melt.It is worth noting that the times of LC structure formation from the melt and the times of melting due to overheating differ by an order of 1.5.It is possible that the deceleration of ordered structure formation as compared with the process of its destruction is associated with the necessity to overcome the energetic barrier by nucleation.

Using the traditional approach to studying crystallization kinetics the $I_{max}(t) - I_0 / I_0$ curve (where I_0 is the SAXS maximum intensity in the LC state at $t \to \infty$) may be analysed in the coordinates of the Avrami equation (9). As it is seen from Fig.3b the experimental data obey the Avrami equation.From the straight line slope the exponent n in this equation may be estimated.In our case it is close to 1.This value coincides with the n-value obtained by dilatometric investigation of the mesophase formation in polymer nematic (4).It is known that such value of exponent are typical either for one-dimensional growth of ordered regions or for two-dimensional growth which is diffusion-controlled (in both cases at a constant number of nuclei) (9).

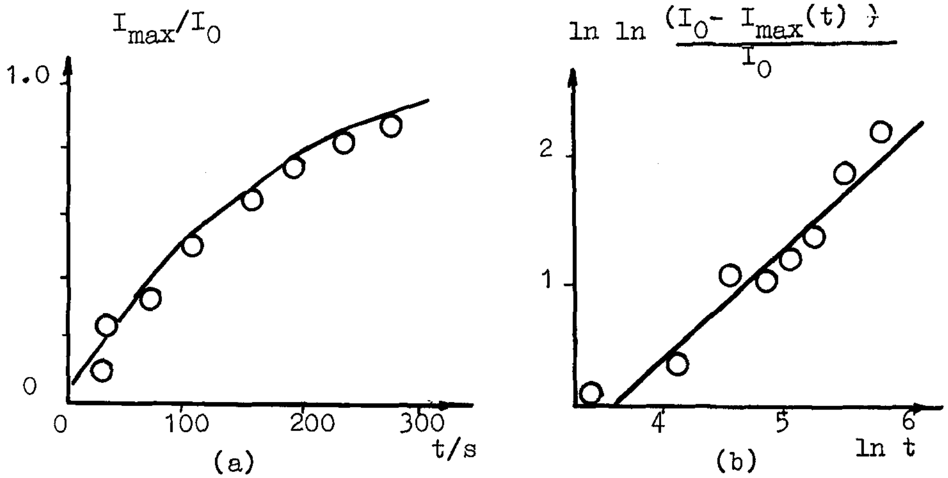

Fig.3. SAXS maximum intensity I_{max} vs time after rapid cooling of isotropic melt (a); the same in Avrami coordinates (b).

Taking into account a slow diffusion of comb-like macromolecules as compared with usual ones, a conclusion can be drawn that the formation of the LCphase from an isotropic melt proceeds with the one-dimensional growth of layered order at a constant number of nuclei.

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