# Equibiaxial extension of a thermotropic liquid-crystalline polymer

# Flow induced orientation, relaxation of orientation, and strain recovery

Y. G. LIN† and H. H. WINTER

University of Massachusetts, Department of Chemical Engineering, Amherst,
Massachusetts 01003, U.S.A.

and G. LIESER

Max Planck Institut für Polymerforschung, Mainz, F.R. Germany

The effects of equibiaxial extensional flow on the structural state of a thermo-tropic liquid crystal aromatic copolyester are studied through wide-angle X-ray scattering (WAXS), strain recovery above the melting point, and differential scanning calorimetry (D.S.C.). For that purpose, samples were melted, stretched and cooled to room temperature. WAXS patterns and strain recovery show that equibiaxial extension (achieved through the lubricated squeezing experiment) results in a planarly-oriented state, i.e. preferred molecular orientation perpendicular to the compression direction accompanied by random molecular orientation within the plane of extension. This flow-induced oriented state may relax partially if not prevented by stretching in the super-cooled liquid state (10–30 K below the melting point). Quenching immediately after deformation at a high temperature can also result in the retention of a high degree of orientation, but it lowers the degree of crystallinity. D.S.C. data show that low cooling rates and large extensions lead to the highest crystallinity. Strain recovery upon reheating is remarkably high for samples with high orientation. This large recovery is attributed to the elasticity of the macrostructure which is formed by the LCP molecules (structural elasticity) and not to the elasticity of the molecules.

## 1. Introduction

One of the most interesting characteristics of liquid-crystalline polymers is that flow induces a high degree of molecular orientation which can be retained by cooling to the solid state [1–13]. Exceptional mechanical properties are found in their as-spun fibres [1, 2], and in their as-injection molded plaques [3, 11]. For films, uniaxial processing enhances material properties in the machine direction, but biaxial and multiaxial processing may lead to overall enhancement [4–6, 12, 13]. All these effects can be related to flow-induced molecular orientation.

The purpose of this study is to investigate extensional flow-induced structural changes in a liquid-crystalline polymer. The equibiaxial extensional flow technique was developed earlier, using the lubricated squeezing method [14–16]. The state of orientation of the squeezed samples is characterized by wide-angle X-ray scattering (WAXS) and by the magnitude of strain recovery above the melting temperature. The effect of processing conditions on crystallinity was studied by differential scanning calorimetry (D.S.C.).

† Permanent address: Department of Chemical Engineering, University of Zhejiang, Hangzhou, China.

## 2. Experimental

### 2.1. *Materials*

The liquid-crystalline polymer studied, VECTRA A900 of Celanese, is a copolyester of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6 naphthoic acid (HNA), with a molar ratio HBA/HNA of about 73/27. The nominal D.S.C. melting temperature is 280°C and the clearing temperature is well above thermal decomposition. Silicone oil (General Electric, Viscasil 5000) was used as lubricant for the extensional flow.

### 2.2. *Sample preparation*

The polymer pellets were ground into powder and then dried under vacuum at 120°C for 20 hours. The samples for lubricated squeezing were 6 mm in diameter and 1·6 mm in thickness and molded under vacuum at 320°C.

### 2.3. *Flow experiment*

A linear rheometer (Rheometrics RDS-LA) was used to generate equibiaxial extensional flow by lubricated squeezing. This technique has the advantage that stretched film samples can be prepared under well-defined thermo-mechanical history. A moulded sample was placed between two preheated parallel disks which were coated with lubricant as shown in figure 1 (*a*). The sample was heated quickly to 303°C and held there for 2 min under nitrogen. The heater was then turned off and a cooling rate of about − 20 K/min was achieved by adjusting the nitrogen flow. While cooling, the sample was rapidly compressed (step strain [16]) to the final thickness $H_1$. Strains of 50 per cent, $(H_0 - H_1)/H_0 = 0.5$, and 90 per cent, $(H_0 - H_1)/H_0 = 0.9$, were chosen for the present study. After the temperature had dropped to 180°C, the squeezed samples were taken out from between the lubricated disks and cooled in air.

### 2.4. *Wide angle X-ray scattering analysis*

This was performed on strips which were cut from the squeezed samples. The X-ray beam was passed through these strips both along and perpendicular to the compression direction. These experiments were carried out in a flat film camera using Ni-filtered Cu-K$\alpha$ radiation. Scattering patterns were recorded photographically of a sample to film distance of 40 mm.



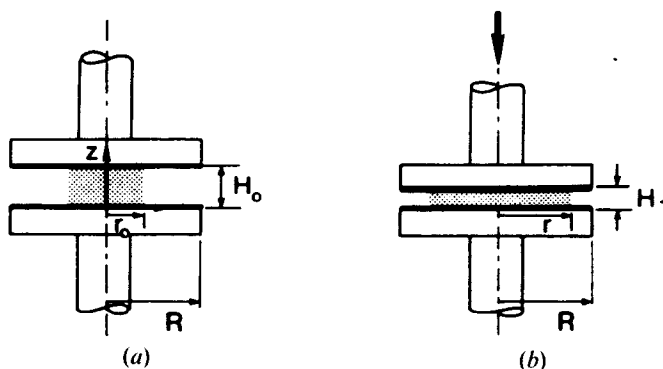$(a)$                                              $(b)$

Figure 1.   Sketch of lubricated squeezing geometry with compression direction $z$ and sample radius $r$. ($a$) Initial state; ($b$) after squeezing.

Several WAXS studies on biaxially-deformed liquid-crystalline polymer films have been reported [4–6, 7, 10, 12]. However, the measurements made only with the beam along the thickness direction could not bring into evidence the degree of molecular orientation of these biaxially-deformed samples. The present work using the beam perpendicular to the thickness direction can demonstrate molecular orientation and completes these studies.

### 2.5. *Strain recovery experiments*

Disks of 5 mm diameter were cut from the squeezed samples, heated on a lubricated plate to 300°C for 1 min, and then cooled to ambient temperature. The use of the lubricant was to ensure free strain recovery of the samples which is characterized by an increase in thickness and a reduction in diameter. The thicknesses of the disks before and after this process, $H_1$ and $H_2$, were measured with a micrometer at room temperature. A recovery ratio defined as $(H_2 - H_1)/H_1$ was calculated to compare the degree of orientation of the squeezed samples prepared under different conditions.

### 2.6. *Differential scanning calorimetry*

A PERKIN ELMER calorimeter was used to investigate the crystallinity of the various samples. The scanning rate was 20 K/min and the sample weights were about 10 mg for the sample of 90 per cent strain and about 20 mg for those of 50 per cent strain.

## 3. Results and discussion

### 3.1. *Flow induced structure*

Figure 2 displays WAXS patterns recorded at room temperature for a sample which was rapidly squeezed at 240°C to a strain ratio of 90 per cent. The two patterns differ in the direction of incoming X-ray beam with respect to the direction of compression. The texture which gives rise to the diffraction pattern of figure 2 is sketched in figure 3. All the crystallites are oriented predominantly with their chain axes in a plane perpendicular to the direction of compression. Two distinct orientations for the chain bundles which are isotropically distributed around $P$ are drawn. All orientations are allowed to deviate from perpendicularity to $P$ in the limit of drawn cones. Within the bundles, a quasiperiodic arrangement of the chain holds. Therefore we use the expression 'crystallite' for the bundles. In addition, any orientation of the crystallites around the chain axes is allowed.

The diffraction pattern A (as in figure 2 (*a*)) is a superposition of a fibre diagram and some continuous rings. The fibre diagram is due to reflections of crystallites which are oriented as in chain bundle 1. The $d$ values of the 002, 004 and 006 meridional reflections have the values 6·8 Å, 3·1 Å (barely visible in figure 2 (*a*)) and 2·1 Å. Comparison with data from the literature [17–20] confirms that these results are typical for a copolymer of 4-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphtoic acid (HNA) which is rich on HBA residues. In addition to the meridional reflections, two strong rings at $d = 4·6$ Å and $d = 3·3$ Å are seen together with a weak ring at 5·7 Å. The latter can only be seen in the direction of the meridian and is not resolved in the print.

The weak ring and the innermost strong ring are $hk0$ reflections due to crystallites which are oriented as shown in 2 of figure 3. The ring with $d = 3·3$ Å belongs to an $hk1$ reflection as can be seen in the better resolved fibre diagrams [17] of HBA/HNA
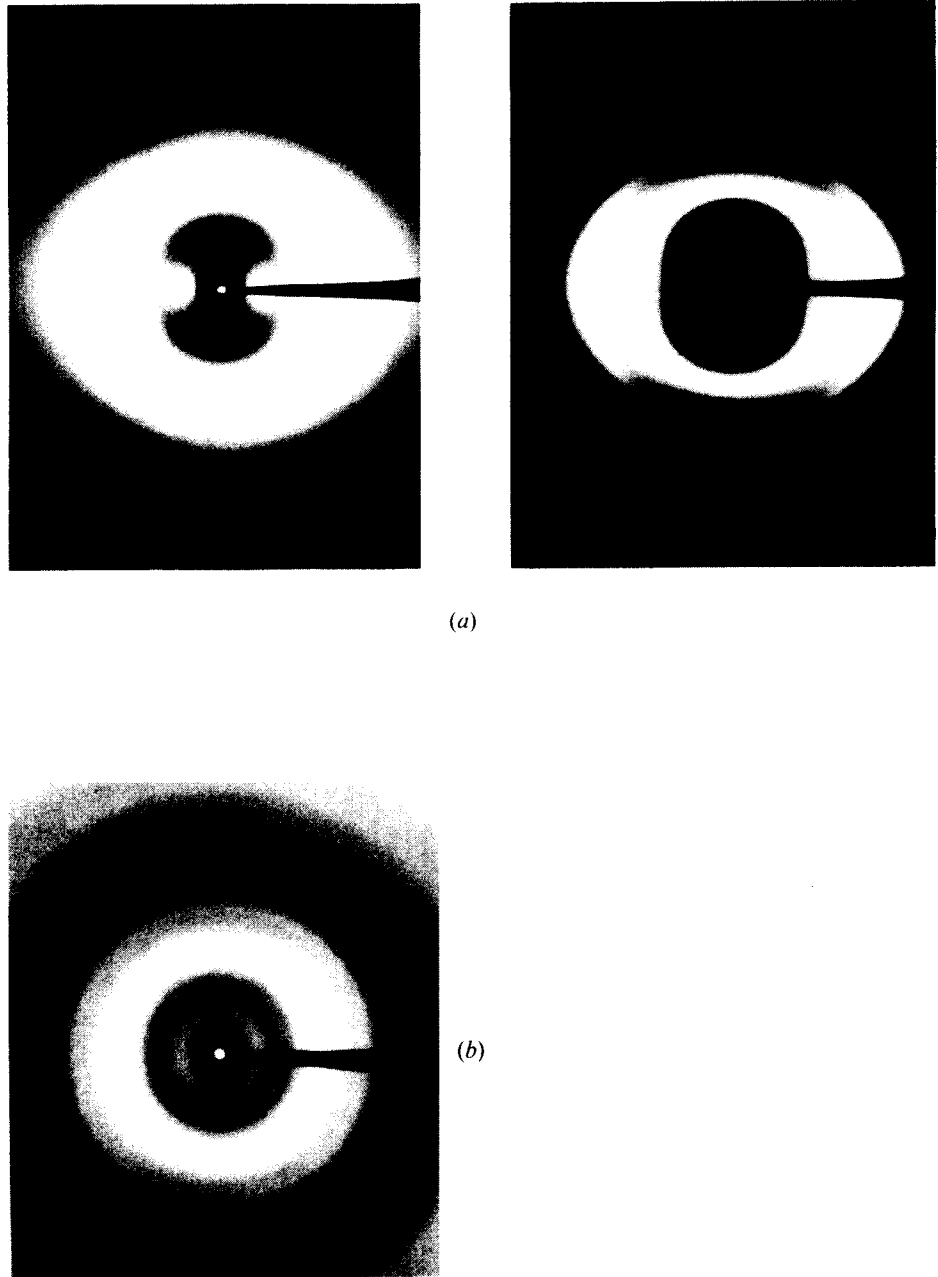
Figure 2. WAXS patterns made with the beam (*a*) perpendicular to, or (*h*) along the compression direction. The samples were squeezed with 90 per cent strain ratio at 240°C. Two exposure times were used in (*a*): short exposure time for showing the centre part and long exposure time for showing the outer part of the pattern.
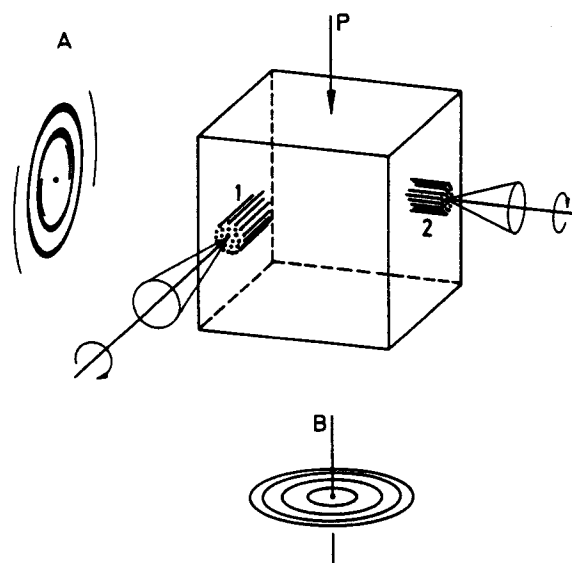
Figure 3.  Sketch of WAXS analysis on equibiaxially stretched sample. P indicates the direction of compression.

copolymers and in electron diffraction patterns of homo poly(HBA) at high temperatures [21]. The orientation of crystallites which fulfil the Bragg condition for $hkl$ reflections is not shown in figure 3. The rings show strong sampling near the equator because there the intensities of crystallites oriented as in 2 are superimposed upon the reflections of the fibre diagram originating from crystallites with orientation as in 1.

All the mentioned reflections can also be seen on the diffraction pattern of figure 2 (b). In contrast to figure 2 (a), the direction of beam incidence is here parallel to the compression direction. The intensity is distributed homogeneously over the rings thus proving the equibiaxial extension. Figure 2 (b) corresponds to B in figure 3.

It is clear from the diffraction data that the most chemical residues are HBA (by comparison with [17]). Although the sample was held at 303°C only for 2 min, we cannot totally exclude the formation of some blockiness due to transesterification. However, this would not influence the orientation. The packing of the chains is similar as in the homo poly(HBA) of phase III [22]. Due to the presence of HNA comonomers, this phase can obviously be frozen at room temperature. A small part of the sample, however, is able to crystallize into form II, as may be concluded from the observed reflection of 5·7 Å. In contrast to the homopolymer, we found form II was also more stable in a copolymer of 4-hydroxybenzoate with 3-hydroxybenzoate [23].

Figure 4 displays WAXS patterns for the samples which were squeezed at different temperatures. The strain ratio was also 90 per cent, as in figure 2, and the X-ray beam was perpendicular to the compression direction. As a function of the increasing squeezing temperature, the degree of orientation becomes lower (figure 4 (a)–(c)). This means that relaxation of the flow-induced molecular orientation is taking place during cooling, even with a rather fast cooling rate of 20 K/min. The WAXS pattern in figure 4 (d) was taken from a sample which was squeezed at 300°C and then immediately quenched in air. It shows a relatively high degree of orientation. On the other hand, the less sharp reflection rings, compared with those exhibited by the 20 K/min cooled samples, indicate a decrease in crystallinity in the quenched sample.

(a)                                                              (b)



(c)                                                              (d)
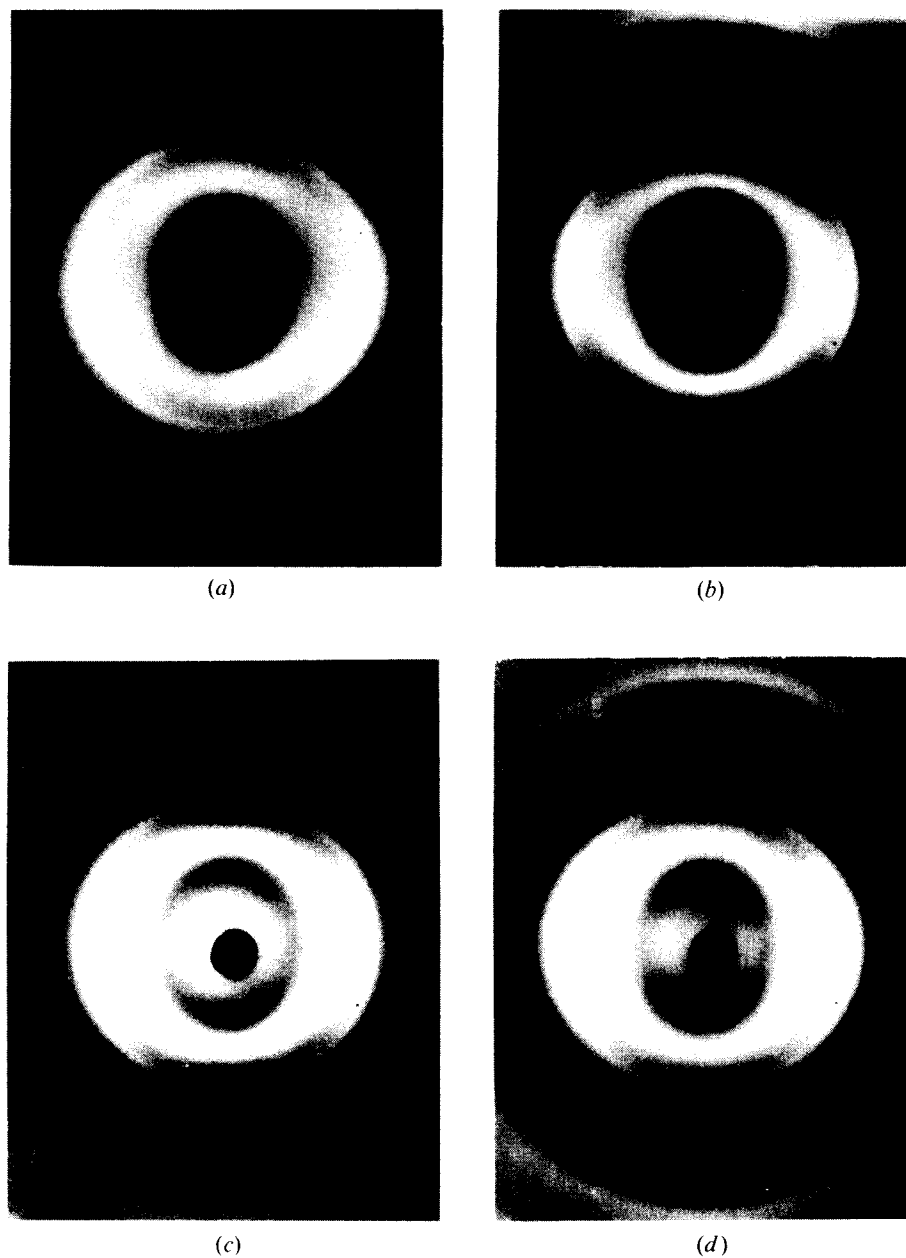
Figure 4.   WAXS patterns made with the beam perpendicular to the compression direction.
The samples were squeezed with 90 per cent strain ratio at (a) 250°C, (b) 270°C, (c) 300°C,
during cooling with a rate $-20\,\mathrm{K/min}$, or (d) squeezed at 300°C then immediately
quenched in air.

For comparison, the WAXS patterns made on the squeezed samples of 50 per cent
strain ratio do not show obvious molecular orientation due to the rather low strain ratio.

The dependence of the degree of orientation on the squeezing temperature can be
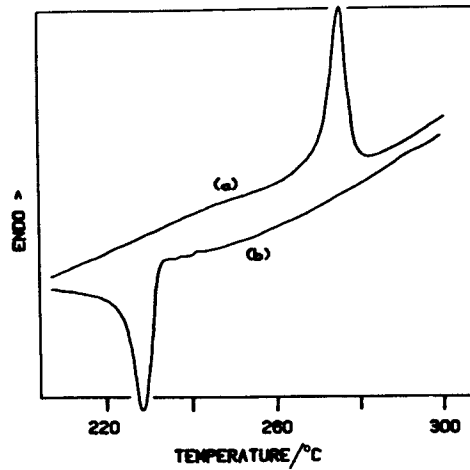explained by using D.S.C. and stress relaxation data. Figure 5 shows the D.S.C. curves.

Figure 5. D.S.C. curves recorded (*a*) during heating 20 K/min and (*b*) during cooling
− 20 K/min.

The endothermic peak in the heating scan and the exothermic peak in the cooling scan indicate the phase transformation temperature ranges under the present conditions. The observed crystallization temperature is about 50 K below the melting temperature. This means that during cooling the polymer passes through a supercooled liquid state, the polymer still possesses a certain degree of molecular mobility which allows a relaxation of flow-induced molecular orientation for approaching a thermodynamic equilibrium. However, the molecular mobility will reduce gradually with decreasing temperature. Figure 6 displays the stress relaxation curves recorded in the sample preparation process. It can be seen that while cooling, the samples compressed at lower temperatures exhibit lower relaxation rates. Obviously, a sample squeezed at lower temperatures has a lower relaxation rate and needs a shorter time to solidify. As a result, the equibiaxial flow-induced oriented state is found to be retained to a greater extent.
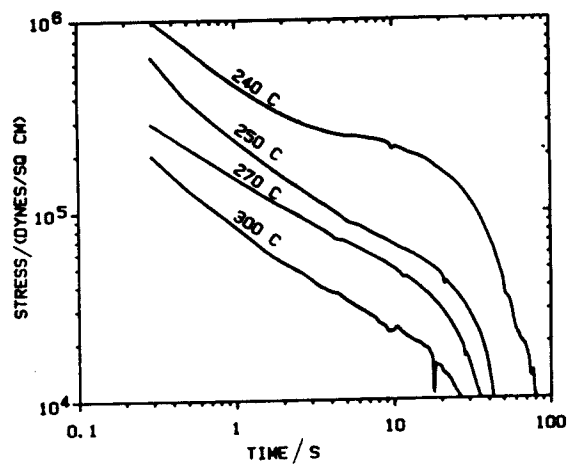


Figure 6. Stress relaxation curves recorded after a step strain, with 90 per cent strain ratio, at the indicated temperatures during cooling.
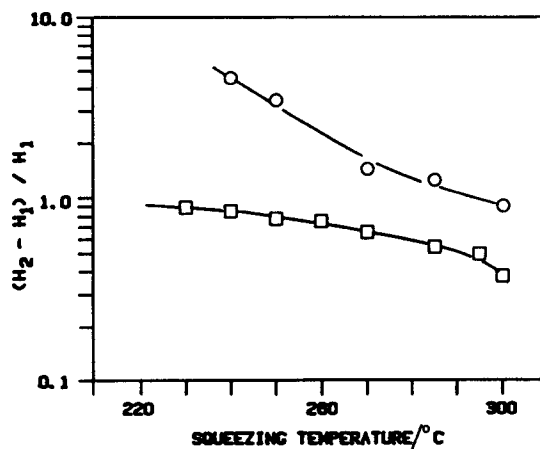
Figure 7.   Strain recovery ratios of the samples squeezed with 90 per cent strain ratio —O—, or 50 per cent strain ratio —□— at different temperatures.

## 3.2. *Recoverable strain*

As shown in the WAXS studies, the squeezed samples are in a biaxially-oriented state. Thermodynamically, this oriented state is not at equilibrium and there exists a molecular driving force which wants the molecular structure to return to an equilibrium state with less orientation. This can be achieved by two mechanisms: relaxation due to molecular motion (which we tried to suppress) and strain recovery. For measuring the strain recovery, the samples were heated to 300°C, free of external forces, and then quenched again. The recovery ratio is a measure of the degree of orientation. It was found to be surprisingly high, much higher than we expected for a liquid-crystalline polymer. The results in figure 7 show quantitatively the influences of squeezing temperature and of strain ratio on the degree of orientation. The recovery increases with the imposed strain. The samples squeezed at lower temperatures also exhibit higher recovery ratios.

This should be compared to relaxation due to molecular motion: in a recent paper, Baird [10] reported from the results of WAXS that all types of deformations (shear flow and uniaxial and equibiaxial extensional flows) carried out isothermally above the melting point result in quite low degrees of orientation, and that a much higher degree of orientation can be achieved if liquid-crystalline polymers are cooled and deformed simultaneously. These results agree with our study for the following reasons. The samples which were deformed above the melting point will relax during cooling. But if the polymers are cooled and deformed simultaneously while passing through the supercooled liquid state, the molecularly oriented state can be retained or even developed further.

The relaxation behaviour of liquid-crystalline polymers in the super-cooled liquid state is of great practical interest. Our studies aimed at this phenomenon will be reported in detail in a later paper [24].

## 3.3. *Crystallinity*

We also looked at the effect of extensional flow on the crystallinity of the liquid-crystalline polymer. The term crystallinity is used here in spite of the fact that no
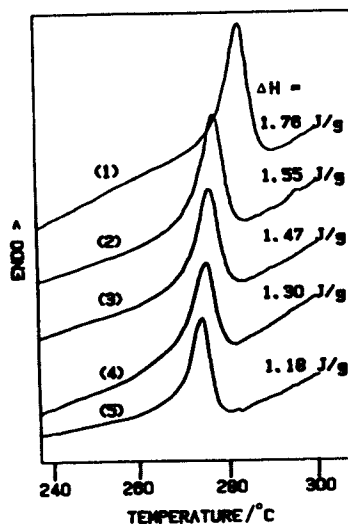
Figure 8. Influence of cooling rate on crystallinity. The different samples had been cooled with various cooling rates, (1) 1·25 K/min, (2) 2·5 K/min, (3) 5 K/min, (4) 20 K/min, (5) 80 K/min, from 310°C before the D.S.C. scan.
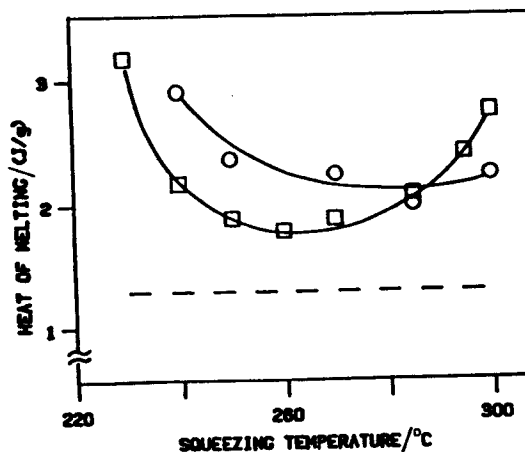


Figure 9. The effect of lubricated squeezing on crystallinity. —O—, 90 per cent strain ratio; —□—, 50 per cent strain ratio; ------, unstrained (value of 1·3 J/g taken from curve (4) of figure 8); the error from the instrument manufacturer is estimated to be ± 5 per cent of the indicated values.

two-phase morphology (fully crystalline/amorphous) is present. In general, the crystallinity of the polymer varies with cooling rate. As shown in figure 8, higher cooling rates lead to lower degrees of crystallinity. This may explain why quenched samples have less crystallinity. Therefore, the study of the flow effect on the crystallinity should be carried out with the same cooling rate ($-20$ K/min). The results in figure 9 shows that the squeezed samples have significantly higher degrees of crystallinity than the quiescently cooled sample. This is due to the fact that molecular orientation leads to an accelerated rate of crystallization [25]. It is noted that below 260°C, a decrease in the squeezing temperature results in an increase in crystallinity for the squeezed samples with both strain ratios, 50 and 90 per cent.

## 4. Conclusions

A lubricated squeezing technique has been applied to produce equibiaxial extensional flow in a liquid-crystalline polymer. This process leads to a planarly-oriented state in the sample, which is characterized by a random orientation within the plane of extension and a preferred orientation perpendicular to the compression direction. This has been proved by WAXS patterns recorded with the beam both along and perpendicular to the compression direction.

For thermodynamic reasons, a step-strain-induced molecular orientation can relax in the melted state. This has been demonstrated by WAXS and strain recovery experiments on the squeezed samples. However, the molecular mobility of the polymer reduces gradually with decreasing temperature in the supercooled liquid state. Therefore, the samples squeezed at a lower temperature can retain a higher degree of orientation than those squeezed at a higher temperature. A sample squeezed at a higher temperature and quenched immediately after squeezing can also retain a relatively high degree of orientation, but its crystallinity is reduced.

D.S.C. results show that lubricated squeezing results in a significant increase in the crystallinity of the polymer. An accelerated rate of crystallization due to molecular orientation is a reasonable explanation for this observation.

The strain recovery is surprisingly large for a polymer with 'stiff' molecules. It suggests that the molecules form an elastic structure in the melted state. The elasticity might be called 'structural elasticity' to distinguish it from the entropy elasticity of coiled macromolecules.

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