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Structural relaxation behaviour of a thermotropic liquid crystal aromatic copolyester in the super-cooled liquid state

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The thermotropic liquid crystalline polymer VECTRA A900 (Celanese Corp.) shows a super-cooled liquid state in which it undergoes gradual crystallization and in which it maintains, when sheared, a high degree of molecular orientation. Both phenomena were studied by annealing the polymer 40 K above its melting temperature, T_m, and then cooling it quickly to the desired experimental temperature level, T. For $T > T_m$, the sample is stable over a long time not showing significant changes. For $T < T_m$, the polymer is in a super-cooled liquid state and undergoes gradual crystallization which can be observed as an increase in the complex modulus by several orders of magnitude. The rate of crystallization increases significantly with the interval $T_m - T$. Samples could be sheared in the initial stage of crystallization. The sheared samples showed a high degree of orientation in wide angle X-ray scattering patterns and large constrained recovery. Recovery was studied in two stages: the first recovery occurred at the shearing temperature and finished soon after the suspension of the shearing stress; the second recovery took place after the sample was completely remelted. The recoverable strains of both stages are severely temperature dependent and moderately time dependent. These observations are discussed with respect to the crystallization rate and the crystallinity of the super-cooled melt.

1. Introduction

It is generally believed that the achievement of morphologies with a high degree of orientation is the key to using the potential of liquid-crystalline polymers for high strength. Usually, for thermotropic liquid-crystalline polymers, these morphologies are made by liquid-state processing [1–14], rather than by solid-state deformation. However for thermodynamic reasons, liquid-state processing involves the problem of structural relaxation before solidification of the polymer [1]. Baird [2] reported that the main types of deformation (shear flow and uniaxial and equibiaxial extensional flows) carried out isothermally in the liquid state result in low degrees of orientation, and a much higher degree of orientation can be achieved if liquid-crystalline polymers are cooled and deformed simultaneously while in the super-cooled liquid state. This also applies to VECTRA A900 when stretched equibiaxially [1]: a high degree of orientation can be retained in the case of carrying out a step strain in the super-cooled liquid state while cooling. Quenching immediately after the step strain conserves the flow-induced orientation, although it leads to a decrease in crystallinity. All these observations suggest strongly that for liquid-crystalline polymers, the achievement of desired morphologies depends not only on the structural changes

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induced by flow processing, but also on structural relaxation of the polymer melt before solidification.

The present studies are aimed at the structural relaxation behaviour of a liquid-crystalline polymer in the super-cooled liquid state.

2. Experiments

The liquid-crystalline polymer studied, VECTRA A900 (Celanese Corp.), is a random copolymer containing 73 mol per cent 4-hydroxybenzonic acid and 27 mol per cent 6-hydroxy-2 naphthoic acid. The nominal D.S.C. melting temperature (T_m) is about 280°C, above which the polymer is in a nematic state. The clearing temperature is well above the thermal decomposition temperature.

The polymer was received as pellets which were ground into powder and then dried under vacuum at 120°C for 20 hours. The samples for the experiments were 25 mm in diameter and 1·2 mm thick and were molded under vacuum at 320°C.

The crystallization and the structural relaxation of the super-cooled melt of the polymer were investigated on a Rheometrics Dynamic Spectrometer (RDS) and a Rheometrics Stress Rheometer (RSR) respectively.

For these experiments, a molded sample was placed between two concentric parallel disks. Upon relative rotation of one of the disks, the sample is sheared with a strain

$$\gamma(r) = \gamma_R r/R, \tag{1}$$

which increases linearly with distance r from the axis and having its maximum value γ_R at the outer edge of the sample (at $r = R$). This inhomogeneity of strain makes it impossible to analyse the large strain experiments described below in terms of non-linear material functions. The measured 'complex modulus' is calculated as if the data were taken in the linear viscoelastic range, i.e. one should call it an apparent complex modulus. On the other hand, the measured recovery is constrained by two mechanisms. The first constraint comes from the constant thickness of the sample during recovery (no swelling in normal direction). The second constraint is described in equation (1). The recovery of individual material elements is hindered by the recovery of neighbouring material elements in the rigidly rotating shear planes. The recovery experiments will therefore be discussed in terms of recovery at the outer edge of the sample, $\gamma_{R,\mathrm{rec.}}$.

In these studies, the temperature control is important. It proceeded as follows. Under a flowing nitrogen stream, the sample placed between two parallel plates was heated to 320°C, held there for 1 min, then quickly cooled to a desired temperature and held isothermally for the experiments. The cooling from 320°C to the desired temperatures took about 2 min. Because the behaviour of the super-cooled melt is time dependent, we define $t = 0$ as the time at which the sample reached the desired temperature and t_i as the time at which the shear experiment started.

On RDS, the time sweep started as soon as the sample was cooled to the desired temperature ($t_i = 0$). The measurement lasted 60 min, at a frequency of 1 rad/s and a strain amplitude of $\gamma_R = 0{\cdot}005$. A low strain amplitude was chosen to avoid strain-induced changes in the polymer.

On RSR, the experiment consisted of three steps: (i) for times $t \geqslant t_i$, the sample was sheared under a constant torque of 0·003 N m for 3 min; (ii) the first step of recovery was measured for 5 min at the same temperature at which the sample was sheared; (iii) the sample was heated to 300°C and the second step of recovery was measured for 5 min. Cogswell [15] had used a constant stress cone and plate rheometer to measure the recoverable shear strain of a liquid crystal polyester after steady flow had been reached. The sample exhibited an elastic response at low stress level. However, at a shear stress of about $10^3\,\mathrm{N\,m^{-2}}$, the high elasticity of the liquid crystal polyester collapsed. For the present experiment, VECTRA A900 demonstrates similar behaviour and the constant torque of 0·003 N m (corresponding to $\tau_R = 1000\,\mathrm{N\,m^{-2}}$) is close to the maximum of elastic response.

Wide angle X-ray scattering was performed on a strip which was cut from the outer edge of a sheared sample. The X-ray beam was passed through the strip both parallel and perpendicular to the shearing surfaces of the sample. This experiment was carried out using Cu-Kα radiation and a Nickel-filtered Statton camera. Scattering patterns were recorded using a sample to film distance of 53 mm.

3. Results and discussion

Figure 1 displays the results of time sweep at a constant frequency of 1 rad/s. At 285°C, the polymer melt showed constant storage modulus G' and less modulus G'' throughout 60 min. This means that the polymer was in a stable liquid state. This stability is due to the absence of high-melting crystallites, which had been melted by the preceding annealing at 320°C [16]. The liquid state was maintained for a short time, even when the polymer melt was quickly cooled to a temperature below the melting point. However, at lower temperatures, both storage and loss moduli increased with time until new stable levels were reached. Thermodynamically, the polymer is in an unstable super-cooled liquid state. Therefore, the increase in the moduli observed at these temperatures can be attributed to a gradual crystallization. It is noted that for the super-cooled melt, G' was lower than G'' at the beginning of time sweep, but became higher than G'' at later times. This could be regarded as an indication of the phase transformation from the liquid state to the solid state. The time which is needed to reach the cross point of G' and G'' curves, t_c, increased significantly as the temperature approached the melting point (figure 2). However, the plot of log G' and log G'' vs t/t_c give common curves (figure 3), indicating that the crystallization of the super-cooled melt may follow the same mechanism in the experimental temperature range.

The common curves of log G' and log G'' vs t/t_c show three regions, i.e. slow modulus growth ($t/t_c < 0{\cdot}5$), rapid modulus growth ($0{\cdot}5 < t/t_c < 3$) and final plateau ($t/t_c > 3$). This suggests that the crystallization of the super-cooled melt could have a slow nucleation stage before the relatively rapid crystal growing, if the residual crystallites has been melted by a prior heating to high temperature (e.g. 320°C) [16].

In the super-cooled polymer melt, crystallization reduces molecular mobility by intermolecular association. Therefore, it can be expected that structural relaxation behaviour varies with both temperature and time; this has been examined by experiments on the RSR.

The samples were sheared in the RSR at a constant torque of 0·003 N m, starting immediately after having reached the desired temperature level ($t_i = 0$). The resulting strain $\gamma_R(t)$ is shown in figure 4(*a*), for $T = 285°\mathrm{C} > T_m$, the sample reaches steady flow as indicated by a constant slope. For lower temperatures, $T < T_m$, the rate of strain does not reach a constant value and the total strain in 3 min of shearing decreases markedly with the degree of super cooling, $T_m - T$.

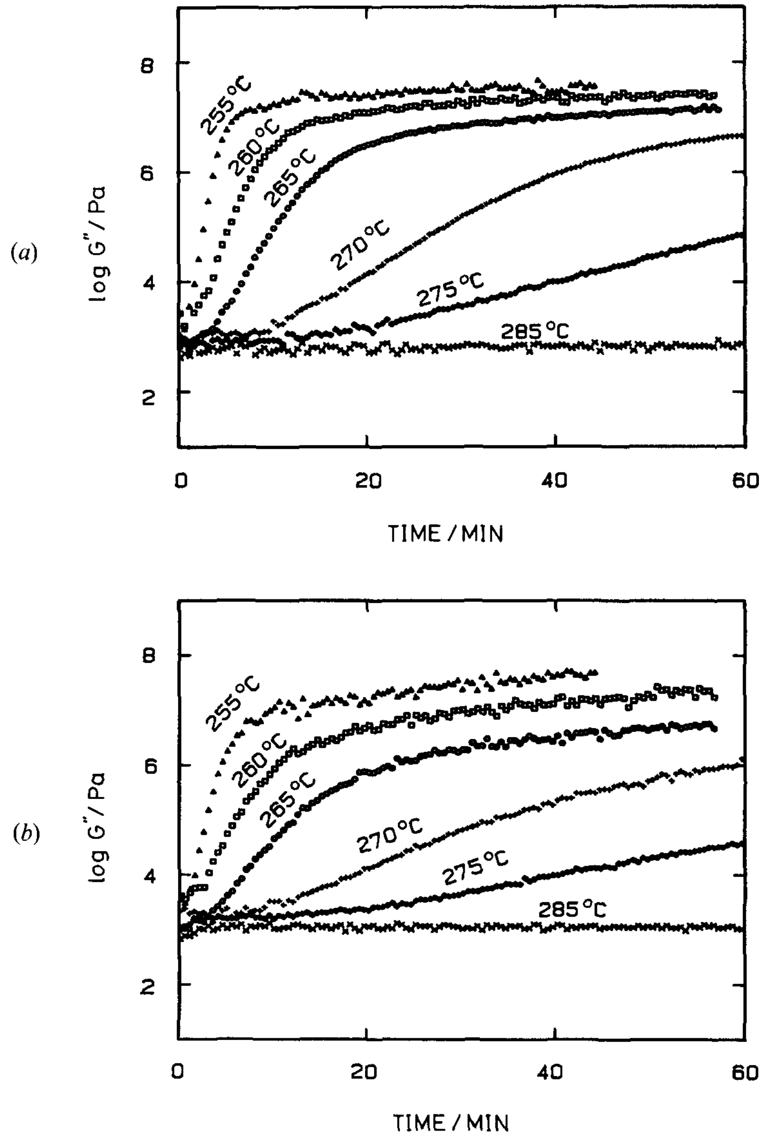


Figure 1. Evolution of (*a*) apparatus storage modulus, G', and (*b*) apparent loss modulus, G'', as a function of time. The time sweep started as soon as the melt was cooled to the desired temperature, at a frequency of 1 rad/s and a strain amplitude γ_R = 0·005.

After 3 min of creep, the applied torque of 0·003 N m was suspended, and the samples exhibited two stages of recovery (figure 4 (*b*)). The first recovery took place when releasing the torque at the same temperatures at which the samples were sheared. The second recovery occurred after the samples were heated above 290°C. In the present work, the second step of recovery was examined by heating the samples to 300°C. It can be clearly seen that a sample sheared at a lower temperature exhibits smaller recovery in the first step and larger recovery in the second step.

The macroscopic recovery is, in some unknown way, connected to the strained polydomain structure of the liquid crystal. It is associated with a reduction of

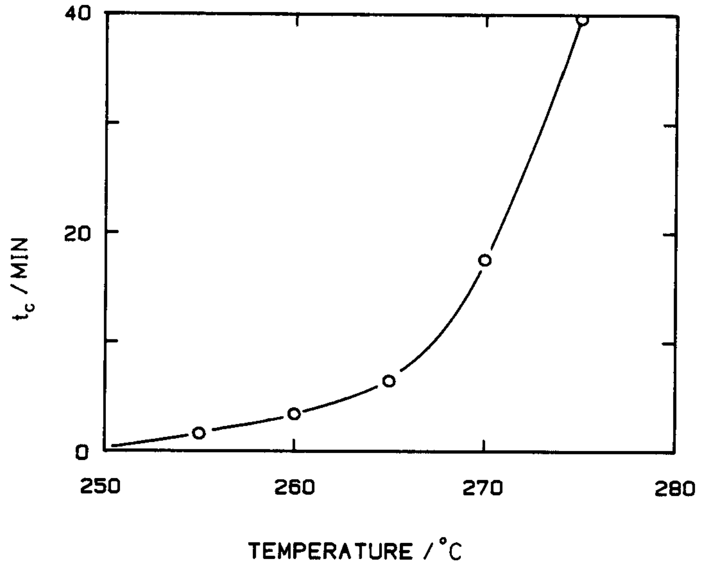


Figure 2. Temperature effect on t_c, the time which is needed for the super-cooled melt to reach the crosspoint of G' and G''.

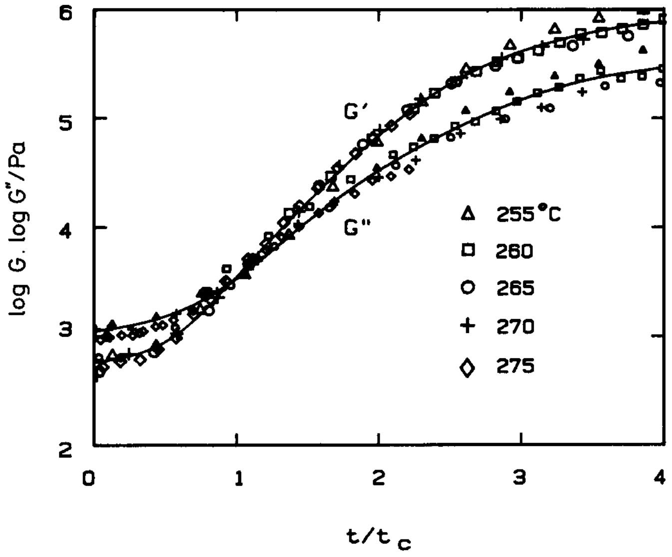


Figure 3. Common curves of modulus growth of the super-cooled melt. The data are taken from figure 1.

flow-induced molecular orientation as can be seen with wide angle X-ray scattering. A strip was cut from the outer edge of the sample sheared at 255°C. With the X-ray beam perpendicular to the shearing surfaces, the scattering pattern (figure 5(*a*)) shows that the molecular chains are moderately oriented in a direction which is projected in the flow direction. It should be noted that the orientation direction is tri-dimensional; the top view of the sheared sample cannot determine the real orientation direction. With the X-ray beam parallel to the shearing surfaces, the

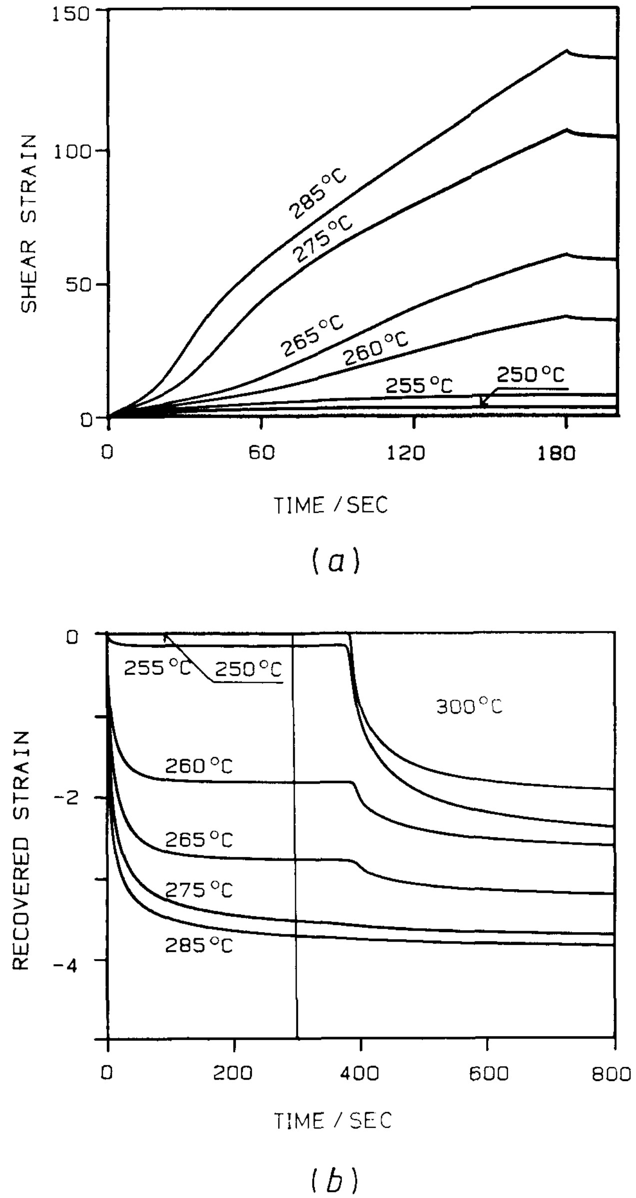
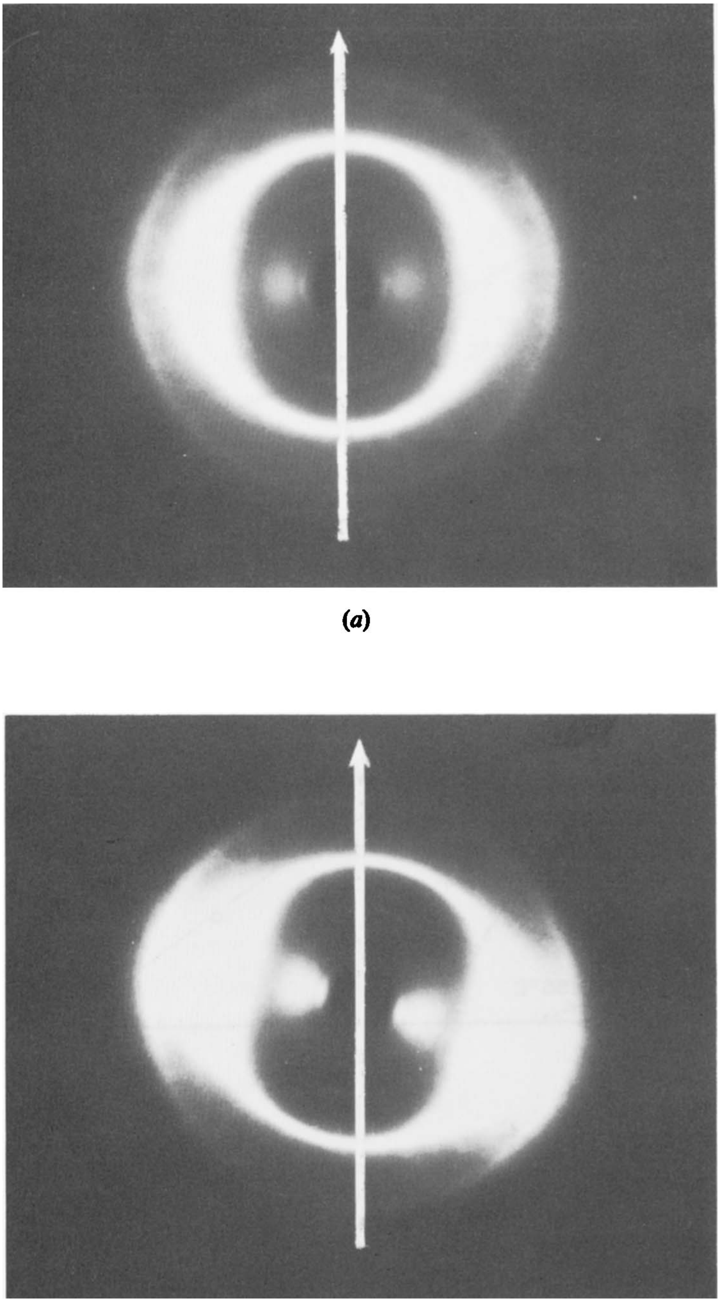


Figure 4. Characterization of the super-cooled melt with $t_i = 0$. (*a*) Shearing under a constant torque of 0·003 N m for 3 min; (*b*) two stages of recovery after the suspension of shear stress.

scattering pattern (figure 5 (*b*)) shows that the molecular chains are strongly oriented in the direction which makes an angle of 16° to the flow direction. These observations indicate that during shearing, mainly the molecular chains crossing shearing surfaces are oriented. Thermodynamically, such a morphology is not at equilibrium. Therefore there exists an internal force inducing the system to come back to an equilibrium state by reducing the degree of orientation. In the solid state, an equilibrium state is difficult to achieve because all molecular motions are restricted. When the sample is in the



(*a*)

(*b*)

Figure 5. Wide angle X-ray scattering patterns made on a strip which was cut from the outer edge of the sample sheared at 255°C, with the X-ray beam direction (*a*) perpendicular, (*b*) parallel to the shearing surfaces. The arrows indicate the flow direction.

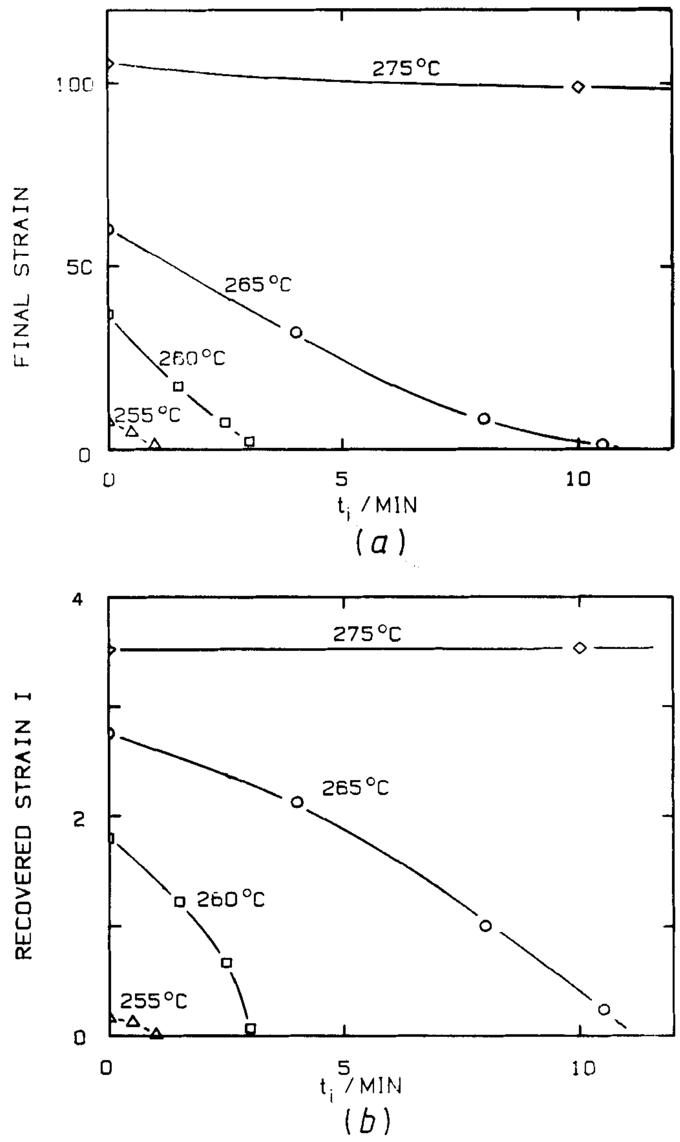


Figure 6. Effect of crystallization prior to shearing of the super-cooled melt. (*a*) Final strain, (*b*) recovered strain achieved in the end of the first recovery and (*c*) recovered strain in the end of second recovery are plotted as a function of t_i.

liquid state and free of the external forces, however, thermodynamical equilibrium can be approached by recovery. It should be noted that recovery is one of the ways of structural relaxation.

At temperatures near the melting point of the liquid-crystalline polymer, the sheared samples exhibit an important recovery strain in the first recovery and little recovered strain in the second recovery. This means that most flow-induced molecular orientation relaxed soon after the applied force was suspended. Reducing the processing temperature led to a decreased recovered strain in the first recovery and an increased recovered strain in the second recovery. This indicates that at lower temperatures, a

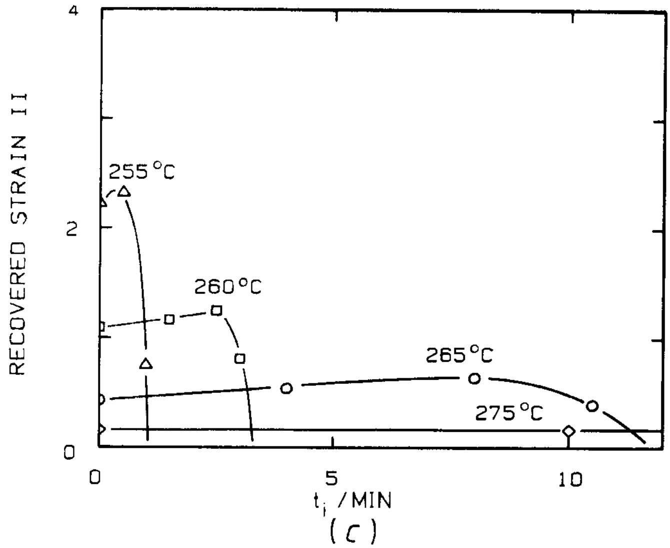


Figure 6. Continued.

relatively rapid crystallization can ‘freeze’ the flow-induced structure. Thus a higher degree of flow-induced molecular orientation can be maintained, unless the samples are remelted to allow the second recovery. However, with a constant torque, a further decrease in the processing temperature will result in reduced molecular orientation, because of too small deformation. As shown in figure 4, the sample sheared at 250°C had smaller recovered strain in the second recovery than that sheared at 255°C. At 245°C, neither shearing deformation nor recovery can be observed.

For the super-cooled melt, only a limited time period of low viscosity can be used for processing. The structural relaxation slows down as the molecules are immobilized in a macrostructure. This effect of time is studied by deforming the samples after some finite time t_i in the super-cooled state $T < T_m$ (for comparison, all preceeding experiments were performed at $t_i = 0$). Figure 6 (*a*) shows the final strain γ_R attained by 3 min of shearing under the torque of 0·003 N m. The strain decreases as the waiting time t_i increases, as expected for a crystallizing sample. The recovered strain of the first recovery also decreased as a function of t_i (figure 6 (*b*)). This is the result of two facts: (i) increased viscosity makes the sample less sheared, and (ii) the increase in the crystallinity restricts the structural relaxation. However, the recovered strain of the second recovery increased slightly with t_i, until insufficient shearing became a dominant factor (figure 6 (*c*)). As previously stated, the second recovery can be regarded as a measure of the degree of molecular orientation which is maintained in the sample after the suspension of the shearing stress. Therefore, the results in figure 6 (*c*) suggest that the initial increase in the crystallinity is favourable to maintaining the flow-induced molecular orientation.

With regard to achieving a higher degree of molecular orientation, the time dependence is much less pronounced than the temperature dependence. It is important to point out that the degree of molecular orientation retained in a sheared sample depends on the competition between the ability to induce molecular orientation and the rate of structural relaxation. Both competing phenomena are restricted by the crystallization of the super-cooled melt.

The effect of time t_i (waiting time prior to shearing) and of temperature can be analysed in a simple model. The experiments for the super-cooled melt were performed in the initial stage of crystallization, where the crystallization rate is mainly temperature dependent, rather than time dependent [16]. For this reason, we assume a constant rate of crystallization $\dot{c}(T)$ throughout the short experimental time and a zero initial degree of crystallinity. Then the degree of crystallinity at the imposition of shearing

$$C_s = \dot{c}(T)t_i, \tag{2}$$

and at the beginning of recovery

$$C_r = \dot{c}(T)(t_i + t_s) \tag{3}$$

can be estimated. Where t_s indicates the shear duration, 3 min in the present studies. The increase in the crystallinity during the shear experiment is estimated as

$$\Delta C = \dot{c}(T)t_s. \tag{4}$$

With the lapse of time at a constant temperature (i.e. t_i increases), both C_s and C_r increase, but ΔC does not significantly change. This implies that the ability to induce molecular orientation and the rate of relaxation are decreasing in a similar manner. Therefore, the degree of molecular orientation maintained increases only slightly. However, when the temperature decreases, an increase in $\dot{c}(T)$ enlarges ΔC (approximately, $\dot{c}(T) = k/t_c(T)$, k is a constant independent of temperature, $t_c(T)$ was plotted in figure 2), and thus the structural relaxation is more restricted. Consequently, a higher degree of molecular orientation can be retained. This explains why the temperature dependence is more pronounced than the time dependence.

In the case where there is no shearing stress, the structural relaxation of a sheared sample mainly takes the way of recovery. However, if the recovery is restricted by

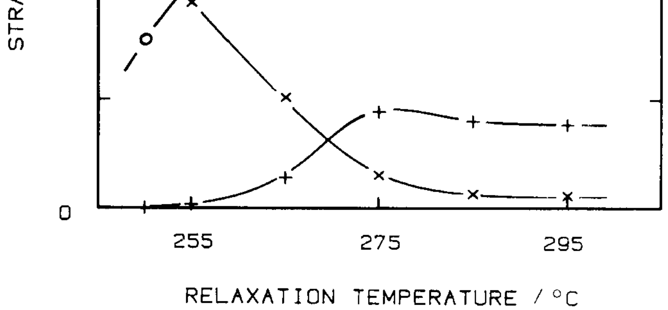


Figure 7. Temperature dependent structural relaxation under constant strain. The samples were deformed, with $t_i = 0$, up to four shear units, held there for 5 min at the indicated temperatures, then the two stages of recovery were measured. — + —, recovered strain of the first recovery; — × —, recovered strain of the second recovery; — o — irreversible strain are plotted as a function of relaxation temperature.

external forces, the structural relaxation will be realized by the intra- and intermolecular motions. This can be shown by another experiment.

When a sheared sample is held at a constant strain for some time before it is allowed to recover, the relaxation of the strained molecular structure increases the irreversible strain. The magnitude of the irreversible strain depends on the rate of relaxation. The experiment started with the annealed and super-cooled samples at $t_i = 0$ and was executed in 4 steps:

(1) the samples were rapidly sheared for four shear units ($\gamma_R = 4$), irrespective of the required stress;
(2) the strain was held constant for 5 min to allow relaxation of the strained molecular structure;
(3) the stress was set to zero and the first recovery is measured for 5 min;
(4) the samples were heated to 300°C for the second recovery in the completely melted state.

The irreversible strain was calculated as the difference between imposed strain (four shear units) and the total recovered strain (recovered strain I plus recoverec strain II). As shown in figure 7, the irreversible strain increases with the relaxation temperature. This indicates that the structural relaxation rate can be reduced by a decrease in processing temperature.

4. Conclusions

A stable structure in the melted state of VECTRA A900 can be achieved by annealing the sample at about 40 K above its melting temperature and then cooling it to a temperature just above T_m ($T_m + 5$ K). This stable state is used as a reference state for our experiments. The strong dependence of TLCP morphology on thermo- and mechanical history [17] did not make it obvious that such a stable state would exist in the melt.

The super-cooled melt of VECTRA A900, at $T < T_m$, undergoes a gradual crystallization, which can be shown by significant increase in the complex modulus. The crystallization rate increases with the degree of super-cooling $T_m - T$. In the initial stage of the crystallization, the super-cooled melt can be sheared under a constant torque. The crystallization tends to maintain the flow-induced molecular orientation.

The recoverable strain in a sheared sample is surprisingly high. Even if the result is in agreement with the large recovery found in stretched samples [1] and with the high elasticity in capillary flow [17], such recovery seems to be too large for a polymer with 'rigid rod' molecules. The high persistance length does not facilitate significant conformational changes (which presumably is the origin of the elasticity of flexible polymers). We believe that the LCP molecules form a super structure which behaves elastically. The structure has a high degree of local molecular order and random macroscopic orientation. Strain perturbs the structure and results in a macroscopic molecular orientation which can be detected by X-ray. In the liquid state, the strained sample attempts to gain its equilibrium structure by relaxation, i.e. by strain recovery and/or rearrangement of molecules.

The degree of molecular orientation retained in a sheared sample depends on the competition between the ability to introduce molecular orientation and the rate of structural relaxation. At temperatures above or slightly below T_m, the sample deforms readily, but the strain-induced orientation can relax quickly. As the degree of super-cooling $T_m - T$ increases, the sample can only deform during the initial time period;

however, a higher degree of molecular orientation can be maintained due to the fact that a rapid crystallization hinders the structural relaxation.

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