

STRESS RELAXATION AFTER OSCILLATORY SHEAR IN A THERMOTROPIC LIQUID CRYSTALLINE POLYMER

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(Received May 23, 1983)

Summary

We report investigations of the rheology of a thermotropic liquid crystalline polymer subjected to oscillatory shear. In particular, we have studied its stress relaxation behaviour and found it to be well-represented by the linear viscoelastic model. In our studies, we observed a strong dependence of the relaxation rate on the position in the strain cycle at which the shear is stopped, a result which we show to be a general phenomenon of viscoelastic fluids and not unique to liquid crystalline polymers.

Introduction

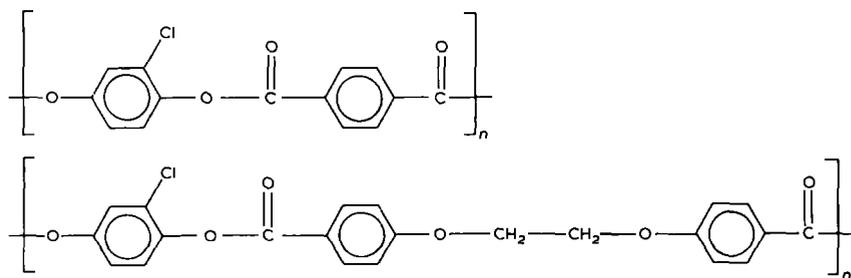
We have recently reported [1] on work performed in our laboratories which led to the recognition of several shear-induced optical textures which are common to a wide range of thermotropic liquid crystalline polymers (LCP's). These textures are unique to LCP's and have not been observed in conventional polymer systems or any other known class of materials. In an attempt to correlate the microscopic behaviours of these systems with their predicted macroscopic properties, the rheology of one thermotropic LCP was investigated.

We report herein measurements of dynamic properties of the LCP subjected to oscillatory shear of different frequencies. We also present results from an investigation of the stress relaxation behaviour of the polymer after the cessation of oscillatory shear. In these studies, we observed initial dependences on the stoppage position in the strain cycle which we show to

be predicted qualitatively by the linear viscoelastic model. To our knowledge, similar experiments with any type of material have not previously been reported in the literature, but we believe they offer a clear demonstration of the importance of strain history on the relaxation processes of the test material.

Experimental technique

The experiments were performed on a thermotropic LCP which was kindly supplied to us by I C I Petrochemicals and Plastics Division, Welwyn Garden City. The polymer, which we have labelled "A5", is believed to consist of a random arrangement of the following repeat units



A Rheometrics Mechanical Spectrometer at Celanese Research Company in Summit, New Jersey, was available for the experimentation. The instrument was operated with parallel plate geometry, with plates 25 mm in diameter. A sinusoidal input strain was generated in the sample by rotation of the top plate in an oscillatory mode. A force transducer measured the total torque on the bottom plate resulting from the strain input. Software in the spectrometer computer system converted the transducer measurements to values of the dynamic viscosity (η^*), the storage modulus (G') and the loss modulus (G'').

The dynamic parameters were measured in the frequency range between 0.1 and 100 rad/s with a strain angle amplitude of 0.01 radians on samples with thickness 1.4 mm. Experiments at the four test temperatures (220, 240, 260 and 280°C) were performed on different samples in order to subject them to the same shear and thermal histories. The polymer samples were moulded to the desired thickness in situ between the two parallel plates at 260°C. The sample was then brought to the test temperature and allowed to equilibrate for 5 minutes before beginning the measurements.

Stress relaxation after cessation of shear was followed by recording the torque measurements on chart paper progressing at a speed of 25 mm/s. Facilities were available to stop the strain input at 0 and $\pi/2$ radians into its

cycle. The samples were subjected to 5 strain cycles before the shear was stopped and stresses recorded against time. Stress relaxation experiments were conducted after oscillatory shear at higher strain amplitudes than those used for measurements of the dynamic properties because the sensitivity of the recorder was not adequate to yield accurate stress relaxation traces at low stresses.

Results

Standard dynamic testing and time-temperature superposition

Values of η^* , G' and G'' of polymer A5 measured in the frequency range 0.1–100 rad/s appear in Figs 1, 2 and 3, respectively. Experimental curves at four temperatures are presented for each of the three parameters. The curves at different temperatures of any one parameter are seen to be of similar shapes, which suggests the suitability of a time-temperature superposition as described by Ferry [2]. Figures 4, 5 and 6 give the results of the shifts to master curves of η^*/a_T , G' and G'' versus shifted frequency (ωa_T), respectively, where a_T is the shift factor at temperature T . The shift factors employed are plotted against the reciprocal absolute temperature in Fig. 7. The shift factor appears to vary linearly with $1/T$, and an activation energy of 300 kJ/mole describes the dependence.

Nothing unusual appears in the dependences on frequency and temperature of the dynamic properties of polymer A5 (as presented in Figs 1–6) which would distinguish this LCP from conventional polymer melts. Some shear and thermal history effects and strain amplitude and sample thickness dependences of the rheological properties were noted, however, which if investigated more thoroughly could lead to recognition of behaviours unique to LCP's.

Stress relaxation after oscillatory shear

Figures 8 and 9 illustrate the effects of shear stoppage position, frequency and temperature on the relaxation of the stresses after the cessation of oscillatory shear. In the curves of these figures, the stresses, normalised by dividing them by the stress at the time of shear cessation, are plotted against time for various runs conducted under different experimental conditions as detailed in the figure captions.

From a comparison of curves appearing in Fig. 8, parts (a) and (b), the rate of stress relaxation is seen to depend strongly on the shear stoppage position in the input strain cycle. The stress relaxes much more rapidly when the strain is stopped at 0 radians than at $\pi/2$ radians into the cycle. Curves

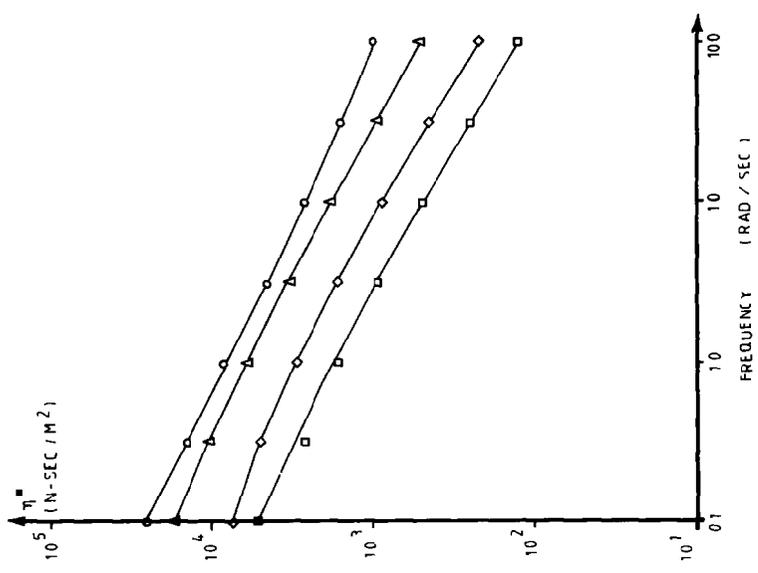
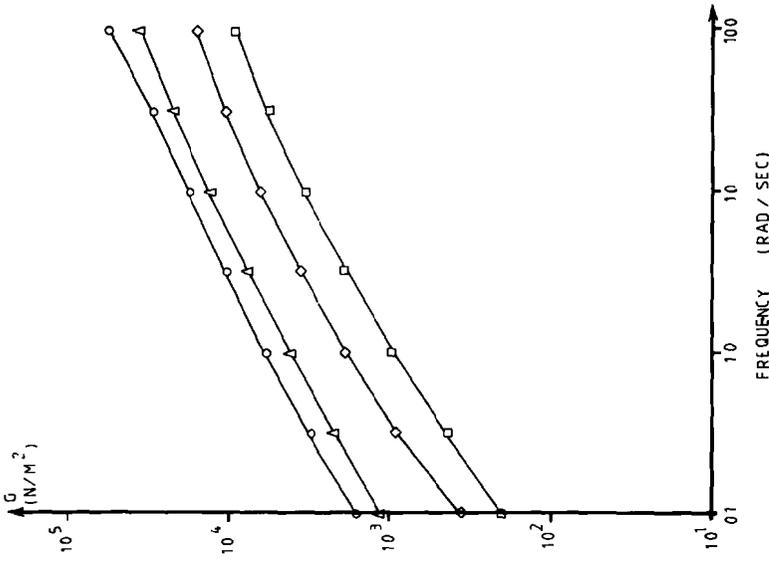


Fig 1 Dynamic viscosity versus frequency of polymer A5 ○ = 220°C, △ = 240°C ◇ = 260°C, □ = 280°C

Fig 2 Storage modulus versus frequency of polymer A5 ○ = 220°C, △ = 240°C, ◇ = 260°C, □ = 280°C

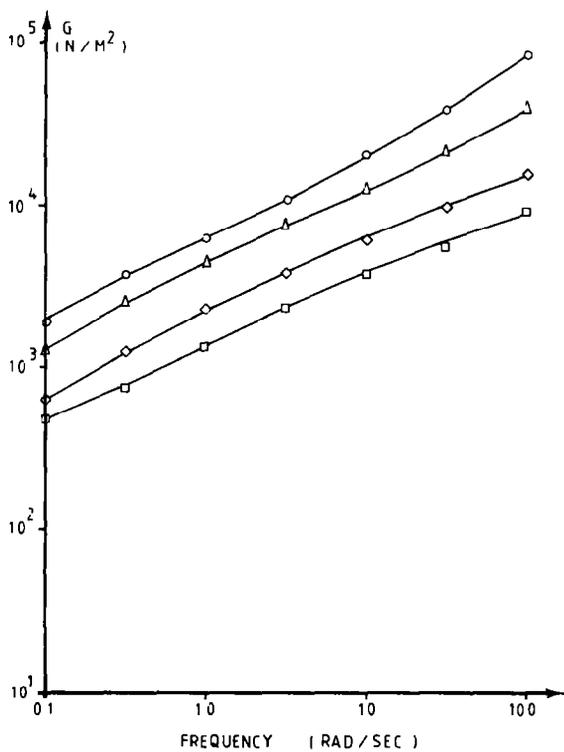


Fig 3 Loss modulus versus frequency of polymer A5 $\circ = 220^{\circ}\text{C}$, $\Delta = 240^{\circ}\text{C}$, $\diamond = 260^{\circ}\text{C}$, $\square = 280^{\circ}\text{C}$

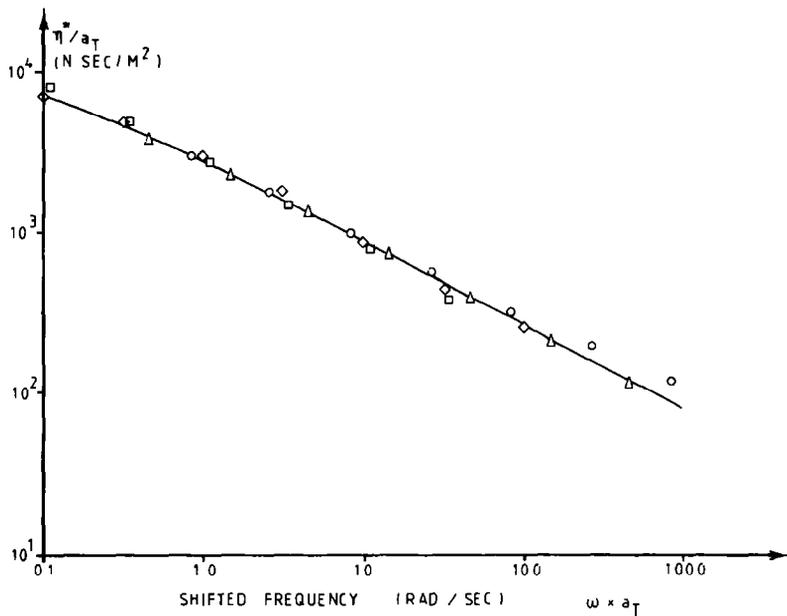


Fig 4 Master curve of dynamic viscosity versus frequency shifted to 260°C , polymer A5 $\circ = 220^{\circ}\text{C}$, $\Delta = 240^{\circ}\text{C}$, $\diamond = 260^{\circ}\text{C}$, $\square = 280^{\circ}\text{C}$

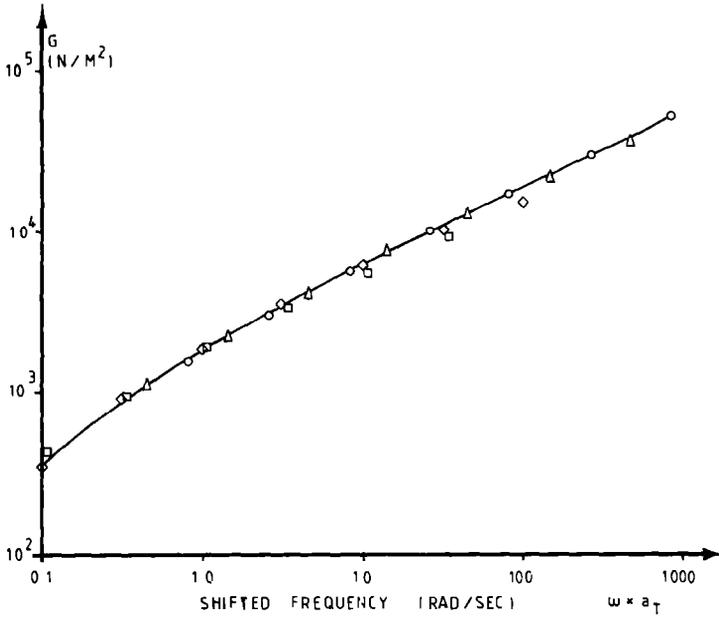


Fig 5 Master curve of storage modulus versus frequency shifted to 260°C, polymer A5
 ○ = 220°C, Δ = 240°C, ◇ = 260°C □ = 280°C

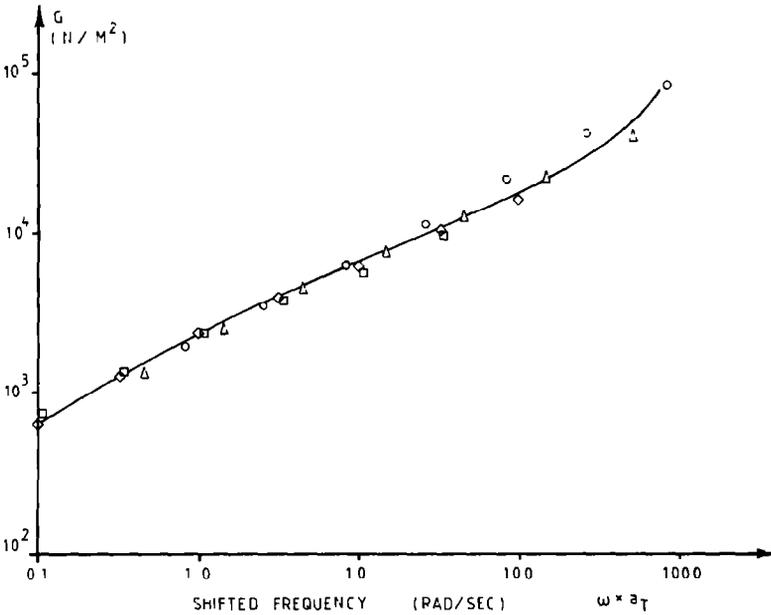


Fig 6 Master curve of loss modulus versus frequency shifted to 260°C, polymer A5
 ○ = 220°C, Δ = 240°C, ◇ = 260°C, □ = 280°C

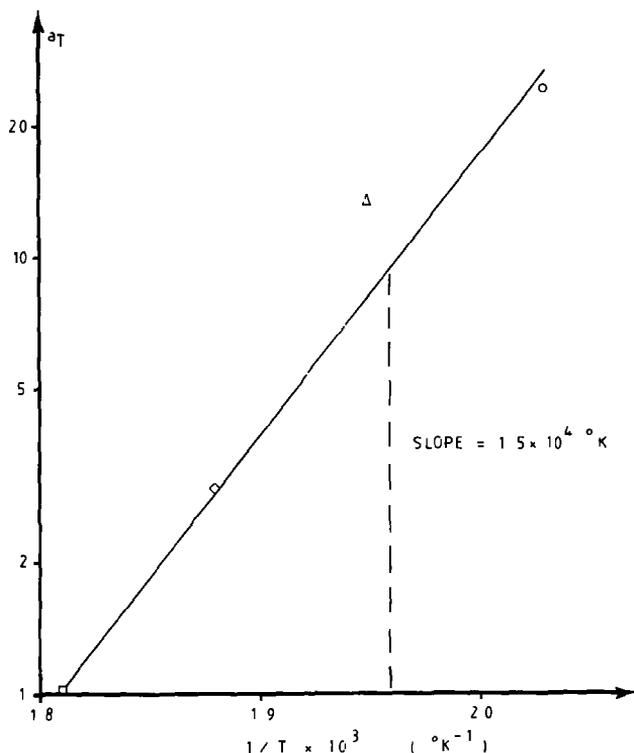


Fig 7 Shift factor versus reciprocal absolute temperature for polymer A5 ○ = 220°C, Δ = 240°C ◇ = 260°C □ = 280°C

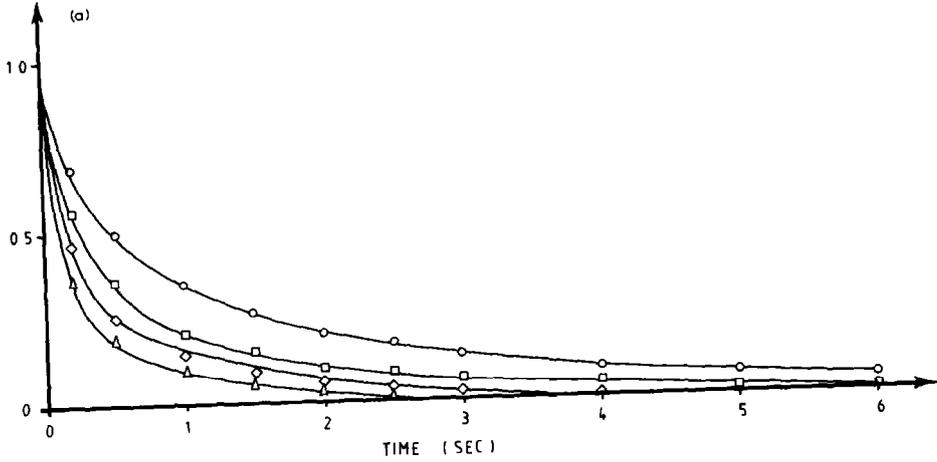
of Fig 8 also show the effect of the frequency of prior strain oscillations on the relaxation of the stresses. The rate of stress relaxation increases as the frequency increases.

The experimental results presented in Figure 9 suggest that within the range of temperatures studied, temperature has very little effect on the rate of relaxation of the stresses. A cumulative analysis of all the experimental results showed that the rate of stress relaxation increases slightly with increasing temperature, with this effect more pronounced at shear stoppage of $\pi/2$ than 0 radians into the strain cycle.

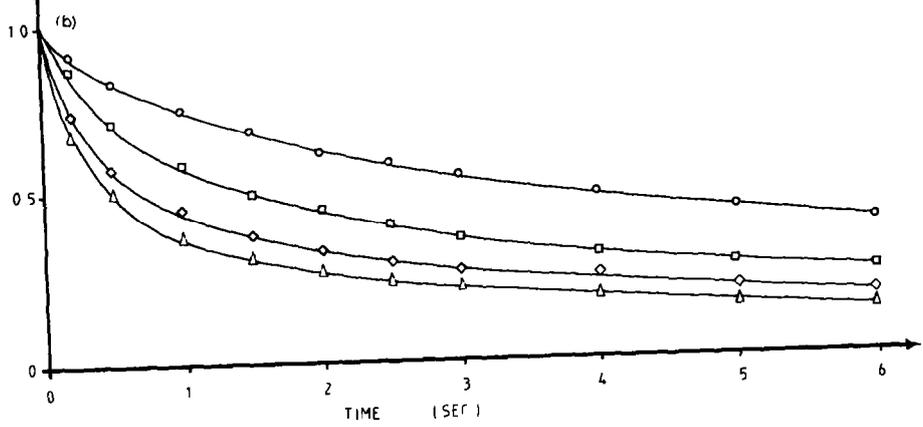
Application of linear viscoelastic model to stress relaxation problem

The success of the time-temperature superposition of the dynamic test results suggested that the polymer A5 is a well behaved viscoelastic fluid in the range of conditions studied. Therefore, the linear viscoelastic model was adapted to evaluate its predictions of stress relaxation behaviour after

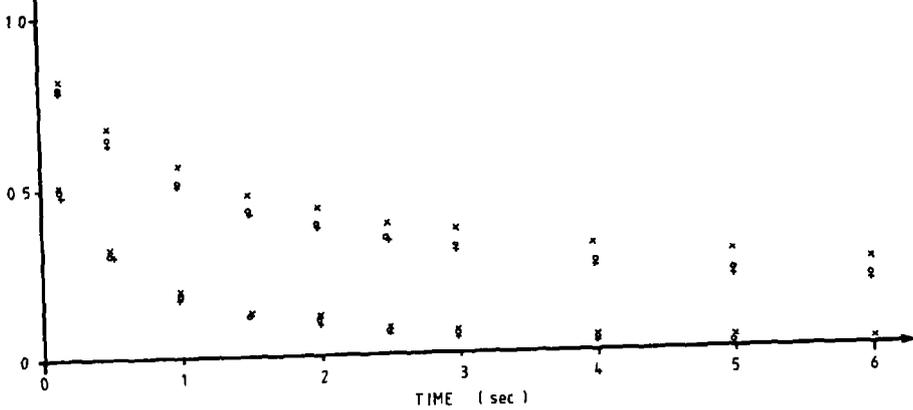
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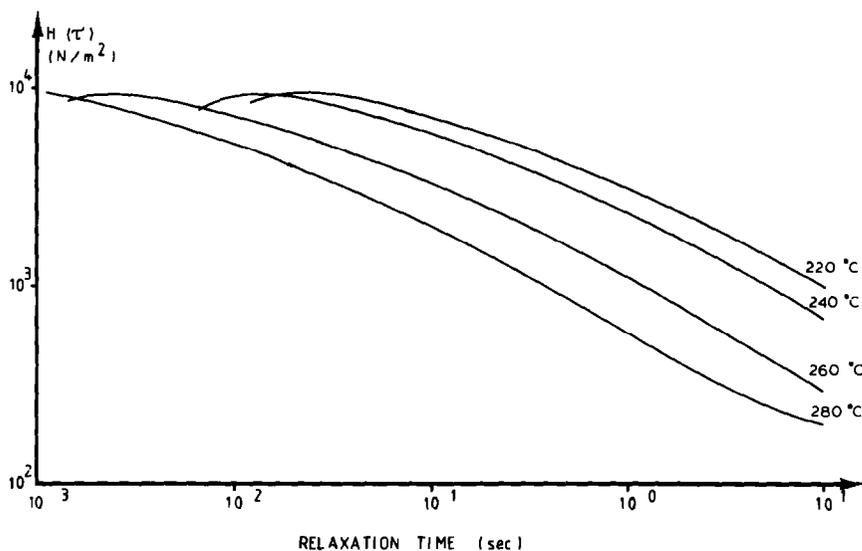


Fig 10 Relaxation spectrum of polymer A5 at four temperatures as determined from Schwarzl-Staverman approximation

oscillatory shear to see if the dependence on shear stoppage position was consistent with this simple model. The relevant equations, which are derived in the appendix, are as follows. For shear stoppage at 0 radians into the strain cycle

$$\sigma(t)/\gamma_0 = \int_{-\infty}^{\infty} H(\tau) \frac{\omega\tau}{1 + \omega^2\tau^2} e^{-t/\tau} d \ln \tau \quad (1)$$

For shear stoppage at $\pi/2$ radians into the strain cycle

$$\sigma(t)/\gamma_0 = \int_{-\infty}^{\infty} H(\tau) \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} e^{-t/\tau} d \ln \tau, \quad (2)$$

where $\sigma(t)$ = stress at time t , γ_0 = amplitude of strain oscillations, ω = frequency of strain oscillations, and $H(\tau)$ = relaxation spectrum value at time τ .

The relaxation spectrum, $H(\tau)$, of polymer A5 was evaluated in the range

Fig 8 Stress relaxation after oscillatory shear in polymer A5 at 240°C (a) Effect of frequency at shear stoppage 0 radians into strain cycle, (b) Effect of frequency at shear stoppage $\pi/2$ radians into strain cycle. Frequency of prior oscillatory strain: $\circ = 0.4$ rad/s, $\square = 1.0$ rad/s, $\diamond = 1.6$ rad/s, $\blacktriangle = 2.5$ rad/s

Fig 9 Effect of temperature on stress relaxation after cessation of oscillatory shear at frequency 1.0 rad/s in polymer A5: $+$ = 280°C, \circ = 260°C, \times = 240°C

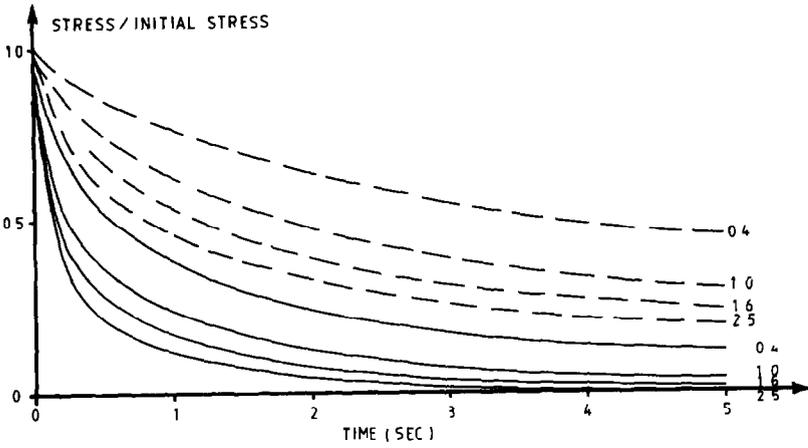


Fig 11 Linear viscoelastic model predictions for stress relaxation after oscillatory shear at four frequencies of polymer A5 at 240°C Solid line = shear stoppage at 0 radians into strain cycle Dashed line = shear stoppage at $\pi/2$ radians into strain cycle

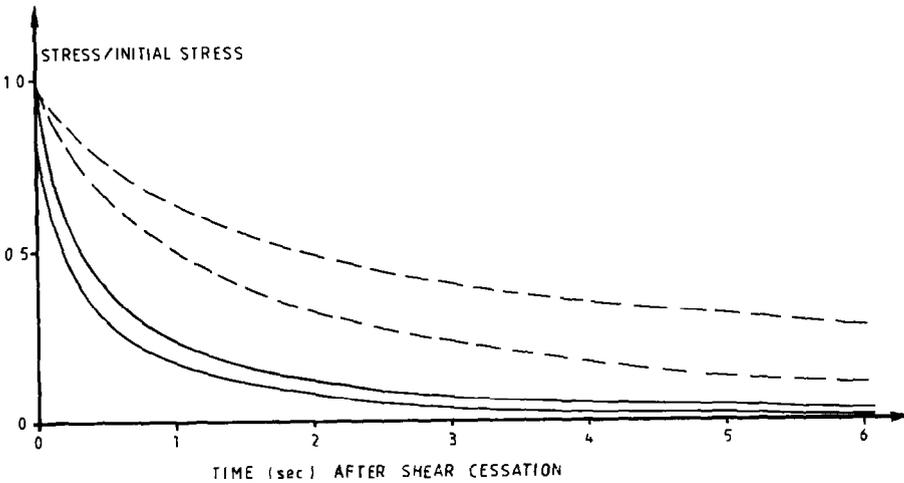


Fig 12 Linear viscoelastic model prediction for the effect of temperature on the stress relaxation of polymer A5 after oscillatory shear with frequency 1.0 rad/s Solid-line = shear stoppage at 0 radians into strain cycle Dashed line = shear stoppage at $\pi/2$ radians into strain cycle

$10^{-3} < \tau < 10^1$ from experimental data of G'' versus ωa_T (Fig 6) by means of the Schwarzl–Staverman approximation [2],

$$H(\tau) = \frac{2}{\pi} \left[G'' - \frac{d^2 G''}{d(\ln \omega)^2} \right] \Bigg|_{1/\omega = \tau} \quad (3)$$

This approximation technique was chosen because it is relatively simple to perform and not because it is thought to be the most rigorous or accurate one available Fig 10 presents plots of the relaxation spectrum at the four test temperatures determined from this approximation

Some of the model predictions (calculated from Eqns 1 and 2) of normalised stress versus time during relaxation after oscillatory shear appears in Figs 11 and 12 Figure 11 illustrates the predicted effect of frequency for shear stoppages at 0 and $\pi/2$ radians into the cycle Figure 12 details the predicted effect of temperature on the stress relaxation process

Discussion

Qualitatively, the linear viscoelastic model predicts identical stress relaxation behaviour to that observed experimentally

(1) Relaxation occurs more rapidly when the shear is stopped at 0 than at $\pi/2$ radians into the strain cycle

(2) The rate of relaxation increases with increasing frequency of prior strain oscillations

(3) The rate of relaxation increases with increasing temperature, but the effect of temperature is less than that of shear stoppage point and frequency in the ranges studied The effect of temperature is more pronounced in stress relaxations after stoppage at $\pi/2$ radians than at 0 radians into the strain cycle

Quantitatively, agreement between model and experiment was fair, although non-linear effects of strain amplitude and time dependences in the experimental results led to discrepancies Essentially, the experiments show that the LCP behaves as a linear viscoelastic fluid at low strains which is neither an unreasonable nor a surprising effect

The experiments reported in this paper illuminate a prediction of the linear viscoelastic model which is not initially obvious from the generalised model equations (i.e. eqns (A 1) and (A 2) of the Appendix). The model predicts and the experiments confirmed a strong dependence of the rate of stress relaxation on the frequency of prior strain oscillations and on the shear stoppage position in the strain cycle Such dependences have no counterpart in steady shear as can be seen from the model equation for

prediction of stress relaxation after steady shear [2]

$$\sigma^{ss}(t)/\gamma = \int_{-\infty}^{\infty} H\tau e^{-t/\tau} d \ln \tau \quad (4)$$

Thus, the rate of stress relaxation after steady shear as predicted by the linear viscoelastic model should be independent of prior shear rate and shear stoppage point. The difference between steady shear and oscillatory shear which causes the stress relaxation dependences to differ is that in oscillatory shear, the shear rate is not constant with time as it is in steady shear. In essence, the model predicts a strong dependence of the stress relaxation on the rate of change of the shear immediately prior to its cessation.

Finally, we make a tentative comparison between the rheological results reported in this paper and our optical observations of polymer A5 which appear in a separate publication [1]. The shear and thermal conditions under which the two types of experiments were conducted are generally similar with the exception of sample thickness. The high optical opacity of the polymer A5 dictated that optical observations be made on samples of 50 microns or less. The rheological work was performed on samples that were 1.4 mm thick.

The optical texture of a quiescent sample of polymer A5 melt is characterised by a large number of light scattering entities in a bright background with no detectable preferred direction to its principal optic axis. If a slow oscillatory shear is induced in the sample, the density of these light scattering entities increases, dependent on the exact shear and thermal conditions. At relatively low shears, an optical texture transition occurs in which the light scattering entities vanish and are replaced by a homogeneous texture with its principal optic axis aligned parallel to the flow direction. Upon the cessation of shear, light scattering entities redevelop in the sample, though their form is dependent on the temperature and prior shear history of the sample.

The smooth variation as a function of frequency and temperature of the rheological data gives no indication that major textural changes occur in the fluid. We conclude that either sample thickness effects account for the differences or, and in our opinion more plausibly, that the rheological measurements which we have made are unaffected by the occurrence of shear induced textural changes.

Evidence for the decoupling of rheological and optical behaviours in LCP's is not unprecedented in the literature. Onogi, White and Fellers [3] found that birefringences measured during steady shear and relaxation of anisotropic solutions of poly (phenylene terephthalamide) and of hydroxypropyl cellulose ester did not correlate with stresses measured simultaneously. Isotropic solutions of both polymers, on the other hand, obeyed the

stress-optical laws KISS and PORTER [4] have observed a correlation between the onset and outset of negative normal stresses with specific textural transitions in anisotropic solutions of poly(γ -benzyl-L-glutamate) They found, however, that the steady shear viscosity behaviour of these solutions was unrelated to the presence of the optical textures Therefore, the findings suggest that some rheological properties are insensitive to local structural changes in LCP's whereas others may be capable of defecting certain types of structural changes

Acknowledgements

We wish to acknowledge ICI Petrochemicals and Plastics Division, Welwyn Garden City, for their financial support of this research and their gifts of materials We thank K Noland for his assistance in obtaining the reported data

Appendix

Derivation of linear viscoelastic model predictions for stress relaxation after oscillatory shear

The basic linear viscoelastic model equations as stated by Ferry [2] are the starting point for the derivations of eqns (1) and (2) in the text

$$\sigma(t) = \int_{-\infty}^t G(t-t')\gamma(t')dt', \quad (\text{A } 1)$$

where

$$G(t-t') = \int_{-\infty}^{\infty} H(\tau)e^{-t'/\tau}d \ln \tau \quad (\text{A } 2)$$

In order to solve for the stress ($\sigma(t)$) as defined by eqn (A 1), an expression for the strain rate ($\gamma(t)$) at all past times t' is required A convenient mathematical description of the strain input to the relaxation process is

$$\begin{aligned} \gamma &= \gamma_0 \sin(\omega t' + \Phi); & \gamma &= \gamma_0 \omega \cos(\omega t' + \Phi) & \text{for } -\infty < t' < 0, \\ \gamma &= 0 = \dot{\gamma} & & & \text{for } 0 < t' < \infty \end{aligned} \quad (\text{A } 3)$$

The problem is stated in this way for two reasons (1) the definition sets time $t' = 0$ as the time of shear cessation, and (2) the insertion of a phase lag Φ introduces the dependence of shear stoppage position into the derivation in a general manner (If predictions after shear stoppage at 0 radians are desired, Φ is set to zero, and γ at shear cessation is correctly set to $\gamma_0\omega$ For

predictions after shear stoppage at $\pi/2$ radians, Φ is set at $\pi/2$, and γ at shear cessation is 0 as it should be)

Substituting the expressions for strain rate (γ) from eqn (A 3) into the linear viscoelastic model eqn (A 1) and simplifying leads to

$$\sigma(t) = \int_{-\infty}^0 G(t-t') \omega \gamma_0 \cos(\omega t' + \Phi) dt' \quad (\text{A } 4)$$

Equation (A 4) can be rewritten by employing the cosine summation formula

$$\frac{\sigma}{\gamma_0 \omega} = \int_{-\infty}^0 G(t-t') \cos \omega t' \cos \phi dt' - \int_{-\infty}^0 G(t-t') \sin \omega t' \sin \phi dt' \quad (\text{A } 5)$$

By letting $s = t - t'$ (and hence, $s = t$ when $t' = 0$ and $s = \infty$ when $t' = -\infty$), eqn (A 5) can be restated as

$$\frac{\sigma}{\gamma_0 \omega} = \int_t^{\infty} G(s) \cos \omega(t-s) \cos \phi ds - \int_t^{\infty} G(s) \sin \omega(t-s) \sin \phi ds \quad (\text{A } 6)$$

Substituting the trigonometric addition formulas for $\cos(\omega t - \omega s)$ and $\sin(\omega t - \omega s)$ into this equation and rearranging yields

$$\frac{\sigma}{\omega \gamma_0} = \cos(\omega t + \phi) \int_t^{\infty} G(s) \cos \omega s ds + \sin(\omega t + \phi) \int_t^{\infty} G(s) \sin \omega s ds \quad (\text{A } 7)$$

Into this equation, the expression for $G(s)$ (from eqn (a 2)) can be substituted which results in the following

$$\begin{aligned} \frac{\sigma}{\omega \gamma_0} = \cos(\omega t + \phi) & \left[\int_t^{\infty} \left(\int_{-\infty}^{\infty} H(\tau) e^{-s/\tau} d \ln \tau \right) \cos \omega s ds \right] \\ & + \sin(\omega t + \phi) \left[\int_t^{\infty} \left(\int_{-\infty}^{\infty} H(\tau) e^{-s/\tau} d \ln \tau \right) \sin \omega s ds \right] \end{aligned} \quad (\text{A } 8)$$

This equation can be simplified by observing the following

$$\int_t^{\infty} \left(\int_{-\infty}^{\infty} H(\tau) e^{-s/\tau} d \ln \tau \right) \cos \omega s ds = \int_{-\infty}^{\infty} \left(\int_t^{\infty} \cos \omega s e^{-s/\tau} ds \right) H(\tau) d \ln \tau \quad (\text{A } 9)$$

After rearranging the two double integrals of eqn (A 8) in a manner indicated by eqn (A 9), the resulting expression for the stress can be integrated by parts and simplified yielding the final form of the equation

$$\frac{\sigma}{\omega \gamma_0} = \int_{-\infty}^{\infty} H(\tau) \left[\frac{\tau}{1 + \omega^2 \tau^2} \right] e^{-t/\tau} (\tau \omega \sin \phi + \cos \phi) d \ln \tau \quad (\text{A } 10)$$

The stress relaxation equations (1 and 2 in the text) result by substituting $\phi = 0$ and $\phi = \pi/2$, respectively, into eqn (A 10)

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