polymer communications

Orientational changes induced by axial stress in a highly aligned liquid crystalline copolyester

D. I. Green*, G. R. Davies and I. M. Ward†
IRC in Polymer Science and Technology, University of Leeds, Leeds LS2 9JT, UK
(Received 9 February 1993)

The non-linear mechanical behaviour exhibited by oriented thermotropic liquid crystalline polymers has been attributed to an increase in molecular orientation caused by the applied tensile stress. In this work we have detected the postulated change in orientation by polarized infra-red spectroscopy. It is shown that there is reasonable quantitative agreement between the infra-red measurement of change in molecular orientation and the change predicted by modelling the change in tensile modulus with stress.

(Keywords: liquid crystalline polymers; orientation; stress)

Introduction

One of the more intriguing features of highly oriented liquid crystalline polymers (LCPs) is their non-linear mechanical behaviour[1–9] since, even at very low strains, the tensile compliance is highly stress dependent. Various theories have been advanced to account for this and, although they differ in detail, a common feature of many is the proposition that a stress-induced reorientation of a mechanical subunit is the physical basis of the effect[2,5,6]. This reorientation phenomenon, although widely postulated, has not been directly observed experimentally in highly oriented systems because of the difficulty in detecting the very small changes in orientation involved.

In this paper we compare stress-induced changes in orientation measured directly from changes in infra-red dichroism, with the predictions of non-linear mechanical modelling. The model of Allen and Roche[5] as modified by Zhang *et al.*[2] is used to predict changes in orientation, since recent research in our laboratory[1] has shown that this provides the best quantitative description of the non-linear behaviour.

Experimental

Samples. The thermotropic liquid crystalline copolyester was produced from 73% *p*-hydroxybenzoic acid and 27% 2,6-hydroxynaphthoic acid. It was supplied by Hoechst-Celanese (Summit, NJ, USA) under the trade name Vectra A950 (in some previous publications the name CO73:27 is used[7,10–12]). Highly oriented and annealed films, 9 μm in thickness, were studied. This thickness was sufficient to provide the necessary structural integrity for the mechanical studies yet was thin enough to avoid saturation of some of the absorption peaks in the infra-red spectrum.

Infra-red absorption spectroscopy. Experiments were carried out using a Nicolet 740 series Fourier transform infra-red spectrometer. A film 5 mm wide and 60 mm long was clamped in a temperature-controlled extensometer which was designed so that a sample could be rotated with respect to the polarized infra-red beam and the stress and temperature could be changed[8]. The sample orientation direction and polarizer could be aligned parallel or perpendicular to an accuracy of about 0.5°.

Measurements were made at 150°C and data collection was at 1 cm^{-1} resolution requiring about 15 min scanning time to produce an acceptable signal-to-noise ratio. An initial 10 min period was needed to purge the chamber of excess water vapour.

The loading cycle was about 0.5 h under load, during which an appropriately polarized spectrum was collected, followed by a similar period of recovery after which a similar spectrum was also collected. This corresponds to an equivalent frequency of about 10^{-4} Hz. The spectra were recorded at a nominal stress sufficient to keep the sample taut in the grips and at four equally spaced static stress values up to about 150 MPa. Final results were the average calculated from three sets of data.

Dynamic mechanical analysis. The non-linear stress–strain behaviour was examined by measuring the 1 Hz dynamic mechanical compliance as a function of static stress on a non-resonance dynamic mechanical modulus apparatus. The apparatus and technique of measurement are described in detail elsewhere[1].

Analysis

Infra-red absorption spectroscopy. Vectra A950 has a complex absorption spectrum. Between 400 and 2000 cm^{-1} there are more than 30 absorptions, many of which overlap to such an extent as to be of no value in quantitative work. To be of use, an absorption should be modelled well by a single peak function, highly dichroic, free from surrounding interferences, and should not exceed 2.5 absorbance units in intensity. Applying these criteria to the Vectra A950 spectra, the most satisfactory feature is a well resolved absorption at 1475 cm^{-1}. This band has been assigned to a skeletal vibration of the naphthalene moiety[13]. The infra-red

---

* Present address: Manchester Museum, The University, Manchester M13 9PL, UK

† To whom correspondence should be addressed

0032-3861/93/163526-03

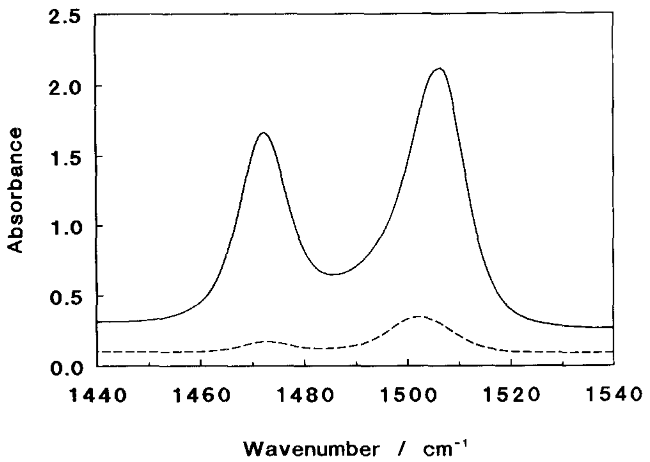

Figure 1 Infra-red spectra of Vectra A950 near 1500 cm^{-1} with polarizers set parallel (——) and perpendicular (– – –) to the orientation direction

spectrum in this region, recorded with the polarizer set parallel and perpendicular to the sample orientation direction, is shown in *Figure 1*. A high dichroic ratio is observed, suggesting that the transition dipole moment is in a direction close to the chain axis.

The transmission spectra were corrected for the effects of imperfect polarizers[14] (which results in highly absorbing peaks appearing flat topped because of a small amount of radiation leaking through the polarizers in the wrong direction). They were then converted to absorbance units, decomposed into a series of Lorentzian peaks plus a background[15] and corrected for anisotropic reflectance and internal fields[16] using measured refractive index values of $n_{\mathrm{perp}} = 1.63$ and $n_{\mathrm{par}} = 1.91$.

For a highly dichroic absorption, by far the largest contribution to the change in dichroic ratio under stress results from changes in intensity in the perpendicular spectrum. For this reason, only the changes in the perpendicular band at 1475 cm^{-1} are considered in the analysis that follows.

Peak heights, rather than areas, were used in quantifying the dichroism because the interference of an overlapping double peak on the high wavenumber side of the 1475 cm^{-1} peak (see *Figure 1*) rendered the area measurements less accurate and reproducible.

Once the dichroic ratio, R, had been determined, the orientation average, $\langle P_2(\cos\alpha)\rangle$, where α is the angle between the transition moment and the sample draw direction, was calculated from the relation:

$$\langle P_2(\cos\alpha)\rangle = \frac{R-1}{R+2} \qquad (1)$$

Dynamic mechanical measurements. Analysis of the dynamic mechanical data involves fitting the experimental data to an exponential functional form. Following our earlier work[1], this is written:

$$J = A + B\exp(-C\sigma) \qquad (2)$$

where J is the compliance, A, B and C are adjustable parameters and σ is the stress. Fitting is accomplished by standard least-squares techniques.

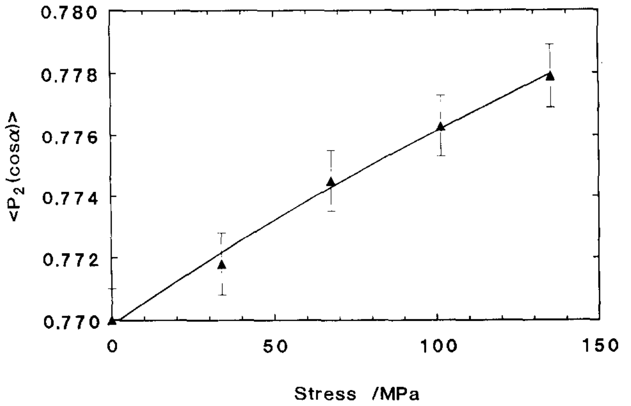

Figure 2 Orientation average, $\langle P_2(\cos\alpha)\rangle$, calculated from the dichroic ratio of the 1475 cm^{-1} skeletal naphthalene vibration at 150°C plotted as a function of applied tensile stress

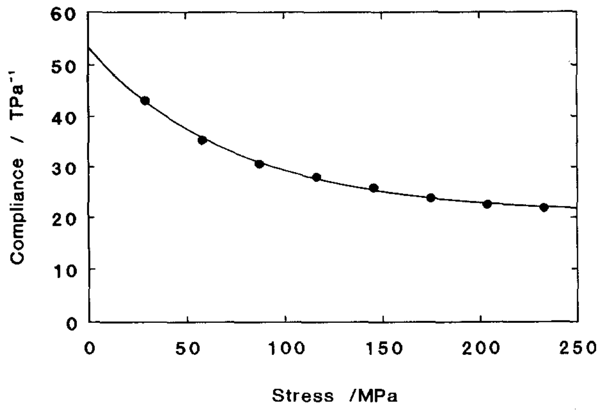

Figure 3 Change in dynamic compliance with stress for highly oriented Vectra tape at 150°C (●) and the best fit to the data using the exponential functional form (——)

Results

Lorentzian decomposition of the infra-red spectra following the procedure outlined above gives $\langle P_2(\cos\alpha)\rangle = 0.77$, corresponding to $\langle \sin^2\alpha\rangle = 0.15$ and a notional value of $\alpha \approx 23°$, with the sample held just taut in the clamps. The change in the orientation average with stress calculated from the change in the dichroic ratio is plotted in *Figure 2*.

The 150°C, 1 Hz dynamic compliance is plotted as a function of static stress in *Figure 3*. Also shown is the best fit of the exponential functional form (equation (1)). Best fit parameters are $A = 20.5\,\mathrm{TPa}^{-1}$, $B = 32.9\,\mathrm{TPa}^{-1}$ and $C = 13.1\,\mathrm{GPa}^{-1}$.

Discussion

Two exponential models have been proposed to explain the non-linear mechanical behaviour of Kevlar. These are due to Allen and Roche[5] and Northolt and van der Hout[6]. The Allen–Roche model is developed from tensor transformation arguments, although we have shown that essentially the same equation can be generated from a simple physical model[2]. We have adopted this model since our recent research on highly oriented thermotropic liquid crystalline copolyesters shows that at high temperatures, testable parameters of the model are in very good agreement with the same parameters determined by experiment[1,2].

According to Allen and Roche[5] the non-linear behaviour is described by:

$$J = J_\infty + \frac{\langle \tan^2\theta \rangle_0}{G}\exp(-2\sigma/G) \tag{3}$$

where J is the measured compliance, J_∞ is the compliance as the stress tends towards infinity, $\langle \tan^2\theta \rangle_0$ is the orientation at zero stress, G is the shear modulus and σ is the static stress. We modify this slightly[1], replacing $\langle \tan^2\theta \rangle$ by $\langle \sin^2\theta \rangle$ and explicitly including the frequency dependence of the shear modulus, to obtain:

$$J = J_\infty + \frac{\langle \sin^2\theta \rangle_0}{G_{\mathrm{dyn}}}\exp(-2\sigma/G_{\mathrm{stat}}) \tag{4}$$

The parameter B of our exponential fit is related to $\langle \sin^2\theta \rangle_0$ since $B = \langle \sin^2\theta \rangle_0 / G_{\mathrm{dyn}}$. The dynamic shear modulus at 150°C and 1 Hz is 190(20) MPa, implying $\langle \sin^2\theta \rangle_0 = 0.0062(7)$.

The change in orientation under stress is calculated from[2]:

$$\langle \sin^2\theta \rangle = \langle \sin^2\theta \rangle_0 \exp(-2\sigma/G_{\mathrm{stat}}) \tag{5}$$

We can thus calculate the expected dependence of $\langle P_2(\cos\theta) \rangle$ on the applied stress using equation (5) with $2/G_{\mathrm{stat}}$ replaced by the value of the fitting parameter C. This is strictly appropriate only if the infra-red measurements are taken on the same time-scale as the dynamic measurements. In fact, the dynamic measurements were taken in a short time 10 min after a change in the applied stress, whereas the infra-red measurements required data to be collected for about 30 min. Since the dynamic modulus changed little over the extended time-scale, we have assumed that little error is introduced by the above procedure.

As discussed above, the value of $\langle P_2(\cos\alpha) \rangle$ obtained from infra-red measurements is a measure of orientation which corresponds closely to the orientation of the chain axis. The transition dipole moment need not be perfectly aligned with the chain axis, however. We therefore assume that the oriented polymer is transversely isotropic and can be regarded as an aggregate of structural units for which there is no preferred orientation around the principal axis. The implications of these assumptions have been discussed in detail previously[1,7]. On this basis we may use the Legendre addition theorem:

$$\langle P_2(\cos\theta) \rangle = \frac{\langle P_2(\cos\alpha) \rangle}{\langle P_2(\cos\beta) \rangle} \tag{6}$$

where α is the angle between the transition dipole moment and the orientation direction of the sample, θ is the angle between the unique axis of a transversely isotropic aggregate unit associated with mechanical modelling and the orientation direction, and β is the angle between the transition dipole moment and the unique axis of the aggregate unit. This allows us to calculate $\langle P_2(\cos\theta) \rangle$ from $\langle P_2(\cos\alpha) \rangle$ by assuming a value for $\langle P_2(\cos\beta) \rangle$.

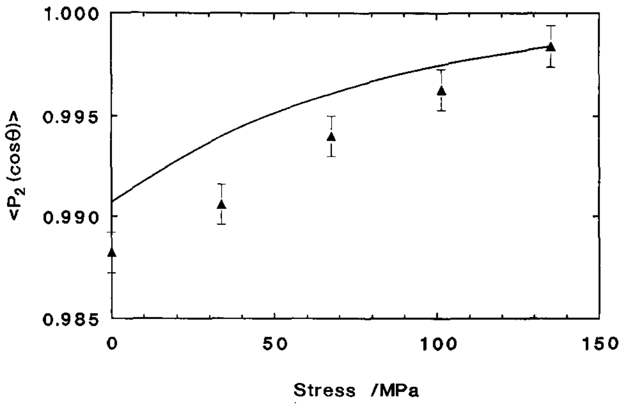

Figure 4 Comparison of the orientation average calculated from mechanical modelling (——) with that measured experimentally by infra-red absorption spectroscopy (▲) calculated by assuming $\langle P_2(\cos\beta) \rangle = 0.7792$ (chosen to match the most highly oriented datapoint)

It is now of interest to compare chain axis orientation changes determined by infra-red absorption spectroscopy with similar changes predicted by mechanical modelling, by choosing an appropriate value of $\langle P_2(\cos\beta) \rangle$. This comparison is made in *Figure 4* by choosing a value for $\langle P_2(\cos\beta) \rangle$ of 0.7792 ($\beta = 22.6°$) which makes $\langle P_2(\cos\theta) \rangle$ calculated from mechanical modelling equal to $\langle P_2(\cos\theta) \rangle$ from infra-red measurements at the highest stress.

It can be seen that the change predicted by the mechanical modelling is similar in magnitude to that measured by infra-red experiments. This provides direct evidence in favour of the hypothesis that the change in axial modulus under stress is due to the rotation of subunits rotating towards the axis of the applied stress.

Conclusions

In highly oriented Vectra tapes, the measured compliance is very stress dependent at low strains. This behaviour can be modelled by a simple exponential function. Non-linear mechanical modelling suggests that the physical basis for this behaviour at high temperatures is a stress-induced reorientation of mechanical subunits. Changes in orientation measured directly by infra-red spectroscopy or inferred from mechanical modelling are very similar. This provides direct evidence for reorientation as the mechanism of changing modulus in highly oriented LCP systems and once again reinforces the central role played by orientation in determining the physical properties of these materials.

References

1 Green, D. I., Zhang, H., Davies, G. R. and Ward, I. M. *Polymer* in press
2 Zhang, H., Davies, G. R. and Ward, I. M. *Polymer* 1992, **33**, 2651
3 Northolt, M. G. and de Vries, H. *Angwandte Makromol. Chem.* 1985, **133**, 183
4 Northolt, M. G., Kampschreur, J. H. and van der Zwaag, S. in 'Integration of Fundamental Polymer Science and Technology' (Eds P. J. Lemstra and L. A. Kleintjens), Elsevier Applied Science, London, 1989, Vol. 3
5 Allen, S. R. and Roche, E. J. *Polymer* 1989, **30**, 996
6 Northolt, M. G. and van der Hout, R. *Polymer* 1985, **26**, 310
7 Green, D.I. PhD thesis, University of Leeds, 1989
8 Zhang, H. PhD thesis, University of Leeds, 1992
9 Ii, T., Tashiro, K., Kobayashi, M. and Tadokoro, H. *Macromolecules* 1987, **20**, 552
10 Troughton, M. J., Davies, G. R. and Ward, I. M. *Polymer* 1989, **30**, 58
11 Troughton, M. J., Davies, G. R., Unwin, A. P. and Ward, I. M. *Polymer* 1990, **31**, 579
12 Troughton, M. J. PhD thesis, University of Leeds, 1988
13 Kaito, A., Kyotani, M. and Nakayama, K. *Macromolecules* 1991, **24**, 3244
14 Green, D. I. and Bower, D. I. *Spectrochim. Acta A* in press
15 Spiby, P. PhD thesis, University of Leeds, 1987
16 Cunninghan, A., Davies, G. R. and Ward, I. M. *Polymer* 1974, **15**, 743
17 McBrierty, V. J. and Ward, I. M. *Br. J. Appl. Phys.* (*J. Phys. D*) 1968, **1**, 1529