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Orientation kinetics of thermotropic main-chain liquid-crystalline polymers in a magnetic field*

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This work presents a quantitative analysis of the kinetics of orientation of main-chain thermotropic liquid-crystalline copolyesters in a magnetic field. Preferred chain orientation has been induced in samples with weight-average molecular weight up to 14400. The kinetics of the orientation process have been explored as a function of the time in the field, sample temperature and field strength (up to 1.12 T), and in particular the influence of molecular weight has also been determined. It has proved possible to achieve a degree of preferred orientation up to $\langle P_2 \rangle = 0.90$. Curve fitting the data leads to the determination of maximum $\langle P_2 \rangle$ values and characteristic time constants.

(Keywords: liquid-crystalline polymer; thermotropic; magnetic fields; orientation)

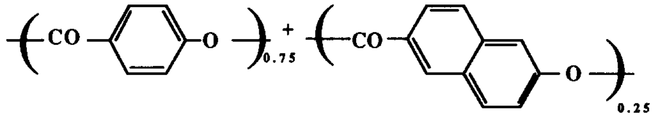
INTRODUCTION

It is well known that liquid-crystalline polymers (LCPs) can be oriented by electric and magnetic fields, and there have been many reports of such phenomena in the literature[1–5]. However, studies of orientation kinetics, especially with respect to main-chain mesogenic polymers, have been less widely discussed, with probably the most detailed work involving magnetic fields being that of Denn and of Stupp and coworkers[6,7]. One particular advantage of working with copolymers is that the level of crystallization is limited and the global orientation of the mesophase melt is not affected by the solidification process. It is thus possible to quench the polymer from the melt in the field and preserve its orientation. Furthermore, the crystals that do form are very small and accurately reproduce the orientation of the melt[8], and they can therefore be used as indicators of the overall quality of orientation and simplify the X-ray diffraction method of measuring orientation parameters. The degree of preferred orientation introduced by a field depends not only on its strength and period of application, but also on the composition and molecular weight of the polymer. In the case of magnetic fields and aromatic mesogenic polyesters, the molecular chains align in the direction of the field. As the mechanical properties depend critically on the orientation, in terms of both the orientation of the molecular director and the perfection of the orientation with respect to the director, it is possible to envisage magnetic orientation as an additional processing route, especially if it could be induced within a sufficiently short timescale.

EXPERIMENTAL

Materials

The work reported here focuses on a series of random copolyesters based on repeat units of 1,4-oxybenzoate (HBA) and 2,6-oxynaphthoate (HNA):



The polymers were synthesized by Hoechst Celanese Corporation. They were of constant composition with a mole ratio of 75/25 (HBA/HNA) but of different molecular weights. The weight-average molecular weights M_w were determined by inherent viscosity measurements in pentafluorophenol/hexafluoroisopropanol (PFP/HFIP) and are listed in *Table 1* along with the melting points of the polymers as determined by d.s.c.

Field orientation

The copolymer sample was finely ground and placed in a boat made from high-purity copper foil. The sample was held at 30°C (±1°C) above its melting point in a nitrogen atmosphere and positioned between the poles of a water-cooled electromagnet. The field was then applied and maintained for a fixed time before the sample was quenched by a nitrogen jet and removed. The field strengths ranged up to 1.12 T and were calibrated using a Hall probe flux meter. The field was uniform over the volume of the sample and was not affected appreciably

Table 1 Copolyesters of 3:1 HBA/HNA with varying molecular weights

M_w	M. pt (°C)
4600	271
5000	272
8600	274
14400	288

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by either the glass furnace tube or the non-ferromagnetic windings.

Measurement of orientation

The preferred orientation within the samples, which had dimensions 10 mm × 10 mm × 1 mm with the field orientation direction normal to the thin axis, was checked for uniaxial symmetry by transmission X-ray diffraction along the field axis. The symmetry was confirmed. The degree of preferred orientation or order parameter was measured by recording the fibre pattern using a transmission diffractometer with symmetrical geometry and monochromatic (Ni-filtered) Cu K_α radiation. The plate-like sample was rotated in its own plane within a Eulerian cradle. The main equatorial diffraction maximum ($2\theta = 19.9°$) was scanned azimuthally and corrected for background before being analysed to give the second order spherical harmonic coefficient, $\langle P_2 \rangle$, using procedures outlined in refs. 9 and 10. $\langle P_2 \rangle$ is defined as:

$$\langle P_2 \rangle = (3\langle \cos^2 \alpha \rangle - 1)/2 \qquad (1)$$

where α is the angle between the axis of the structural unit and the director. The background intensity for the azimuthal scan was obtained by subtracting the intensity value at $\alpha = 0°$ for the best oriented sample. This background was determined by averaging over 10 measurements.

In determining orientation functions from wide-angle diffraction data, there is the problem of correcting for the intrinsic azimuthal width of the reflection being used. For the purposes of this work, the assumption was made that, in a perfectly oriented sample, the equatorial peak would be equiaxial.The validity of this assumption has recently been underlined by diffraction patterns obtained from samples oriented in very high magnetic fields created by a superconducting magnet. In these cases the equatorial reflections are indeed close to equiaxial. The intrinsic azimuthal width of the equatorial reflection was thus assumed to be equal to its radial width. The value of $\langle P_2 \rangle$ corresponding to this intrinsic width was 0.97, and the measured $\langle P_2 \rangle$ values were thus corrected by dividing by this value.

RESULTS AND DISCUSSION

Magnetic orientation

Figure 1a shows a diffraction pattern of a control sample of $M_w = 14400$ annealed at 320°C for 30 min in the absence of any field. *Figures 1b* and *1c* show the alignment induced by the application of a magnetic field of 1.12 T for 10 min and 40 min respectively. The molecular alignment axis is vertical and parallel to the field. The continued improvement in the quality of the alignment is apparent between 10 and 40 min, although no further change was seen after 3 h.

Kinetic data

Figure 2 shows the development of orientation with time for four different field strengths applied to the lowest-molecular-weight sample ($M_w = 4600$) at 300°C. It is apparent that the initial response to the field is comparatively rapid, with the orientation tending slowly

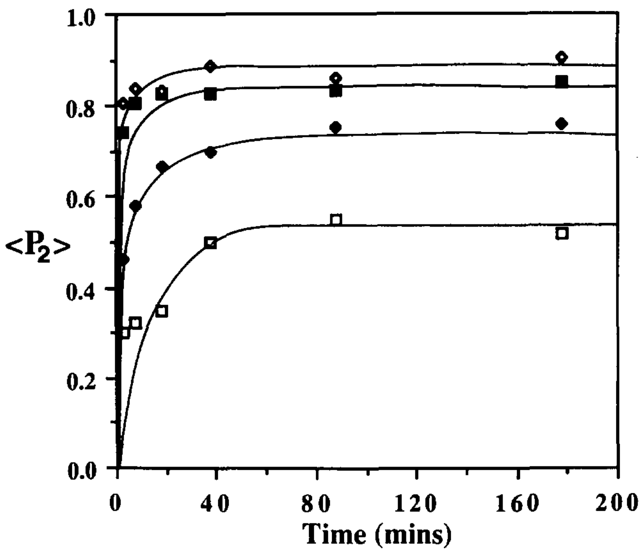

Figure 2 Plots of $\langle P_2 \rangle$ against time in the field for the polymer of molecular weight 4600, at different field strengths of 0.3 T (□), 0.55 T (◆), 0.92 T (■) and 1.12 T (◇)

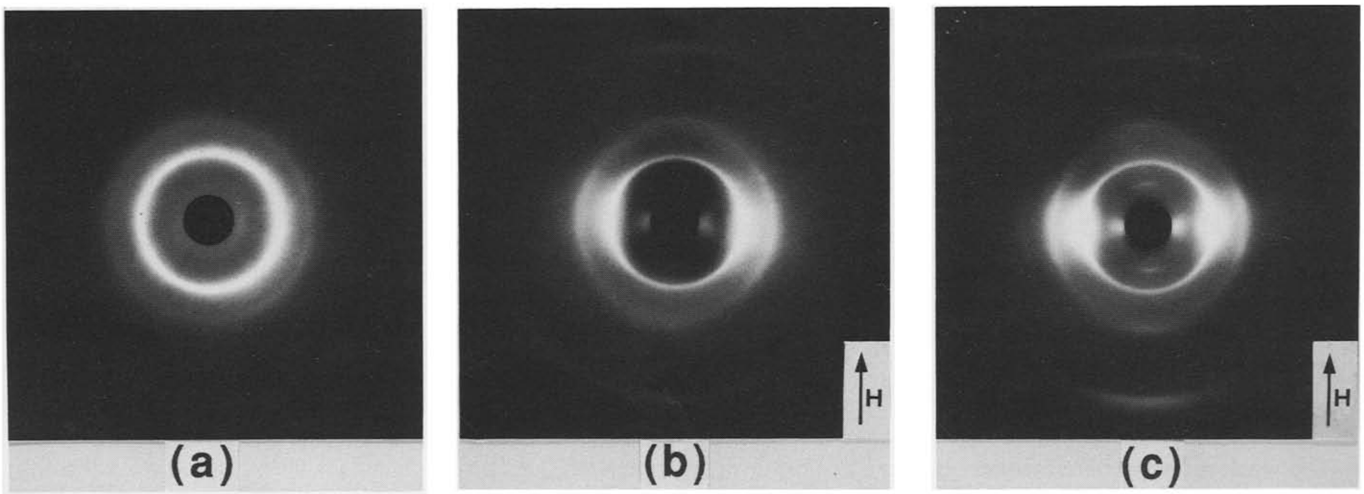

Figure 1 X-ray transmission photographs showing the development of orientation for increasing time in the field for the molecular weight of 14400, 320°C and 1.12 T: (a) control sample annealed for 30 min in the absence of a field, and samples subjected to a field for (b) 10 min and (c) 40 min

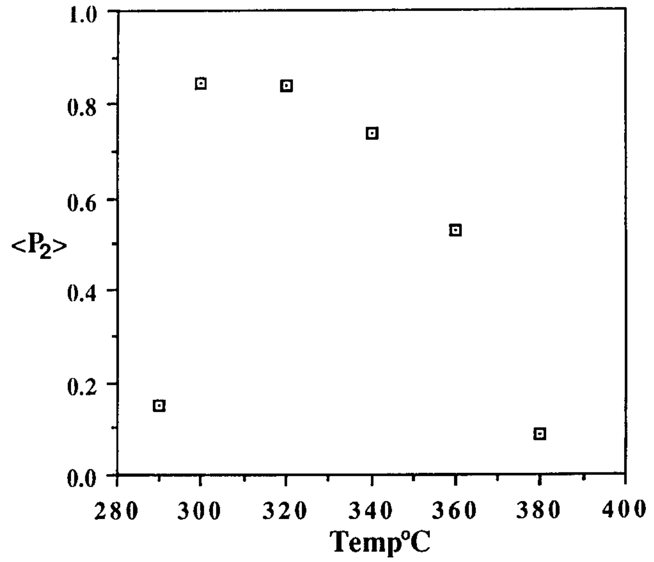

Figure 3 Relationship between $\langle P_2\rangle$ and the temperature at which the sample was held for 15 min in a field of 1.12 T. The polymer molecular weight was 5000

to an equilibrium value. Both the initial rate and the equilibrium value of orientation reached at long times increase with increasing field strength. Similar behaviour has been observed by Moore and Denn[6] for random copolyesters, and by Kozak *et al.*[11] for side-chain liquid-crystalline polymers oriented in an electric field.

The effect of sample temperature in the field orientation kinetics is illustrated in *Figure 3*. These particular data are for the $M_w = 5000$ sample held in a field of 1.12 T for 15 min. A very low $\langle P_2\rangle$ is observed at 290°C because the sample is not properly molten at this temperature. Above 340°C the orientation falls off. This was identified with an increasing concentration of bubbles in the sample, resulting from the onset of degradation, which disrupted the sample orientation. Detailed examination of orientation around bubbles has shown that the local disruption of the general alignment in the sample stems from the tendency of the molecules to lie tangentially to the internal surfaces of the bubbles. A second possibility, that the fall-off in orientation with increasing temperature was a consequence of an approach to the nematic–isotropic transition temperature, was discounted when examination in the polarizing microscope showed no evidence for such a transition, even at the highest temperatures possible.

Analysis of data

Figures 4a–d show the development of orientation in samples of four different molecular weights, for four different field strengths. In each case the orientation temperature was fixed at 30°C above the melting point listed in *Table 1*. The $\langle P_2\rangle$ *versus* time curves show that the orientation tends towards some maximum value. The general form of these curves suggests a relationship in which the rate of the process decreases in proportion to the difference between the actual orientation at any time and the maximum equilibrium value. That is:

$$\partial\langle P_2\rangle/\partial t = K(\langle P_2\rangle_{\max} - \langle P_2\rangle) \qquad (2)$$

Integration of this equation gives the familiar exponential-type relation:

$$\langle P_2\rangle/\langle P_2\rangle_{\max} = 1 - \exp(-t/\tau) \qquad (3)$$

where τ is the characteristic time of the process, which describes its rate for a given set of conditions. This is similar to the expression used to describe the orientation kinetics of side-chain liquid-crystalline polymers in an electric field[12]. The full curves in *Figure 4* are the best fit of equation (3) to the data points using a standard routine (F04FDF from NAG library). Each fit yields τ and $\langle P_2\rangle_{\max}$ as parameters describing the process, and these values are listed in *Table 2*.

Errors

An assessment of the reproducibility of the $\langle P_2\rangle$ measurement method was made by making a successive series of diffraction scans on one sample, which was remounted between runs. It was found that the measured values of $\langle P_2\rangle$ were reproducible to within limits of ± 0.025 for values greater than 0.5, and to within ± 0.035 at lower orientations. The r.m.s. error calculated from the numerical curve-fitting routine was of the order of 0.04. The fact that the parameters τ and $\langle P_2\rangle_{\max}$ are available for each curve means that all the data can be reduced onto a single plot of $\langle P_2\rangle/\langle P_2\rangle_{\max}$ against t/τ. Such a plot is shown in *Figure 5* for values of t/τ up to 35. It is clear that, within the experimental scatter, the exponential relation provides a very adequate description of the process; it also has the advantage of being based on a particularly simple premise.

Rate of orientation

The rate of orientation will be a function of the torque applied to the molecule by the applied magnetic field, and elastic and viscous terms which limit both the rate and the extent of the orientation achievable[13,14]. The characteristic time τ determined from the measurements of the development of orientation with time is taken as the description of the rate of the orientation process in relation to the final level of preferred orientation, irrespective of how much that level is limited by elastic constraints. Hence:

$$\text{rate} \propto 1/\tau \propto \Delta\chi H^2 \eta^{-1} \qquad (4)$$

where $\Delta\chi$ is the anisotropy diamagnetic susceptibility, H the applied field and η an effective rotational viscosity.

The prediction of this relationship, that $1/\tau$ is linear with H^2, is confirmed by the data for the polymers of different molecular weights as plotted in *Figure 6a*. The slopes of the lines are proportional to χ/η, and the dependence of the reciprocal of this term on molecular weight is shown in *Figure 6b*. If one is to assume that the curve should go through the origin[15], which would imply that the rotational viscosity would tend to zero at zero molecular weight, then the relationship is clearly non-linear. *Figure 7* shows these data plotted against the square of the molecular weight. The relationship is sufficiently linear to suggest a dependence on (molecular weight)^2, at least over the range of molecular weight investigated.

Maximum orientation

The orientation–time plots (*Figures 4a–d*) all show that the orientation tends towards a maximum value, which is a function of both the applied field and the molecular weight of the polymer. We identify the limiting value of $\langle P_2\rangle$ with elastic resistance to orientation

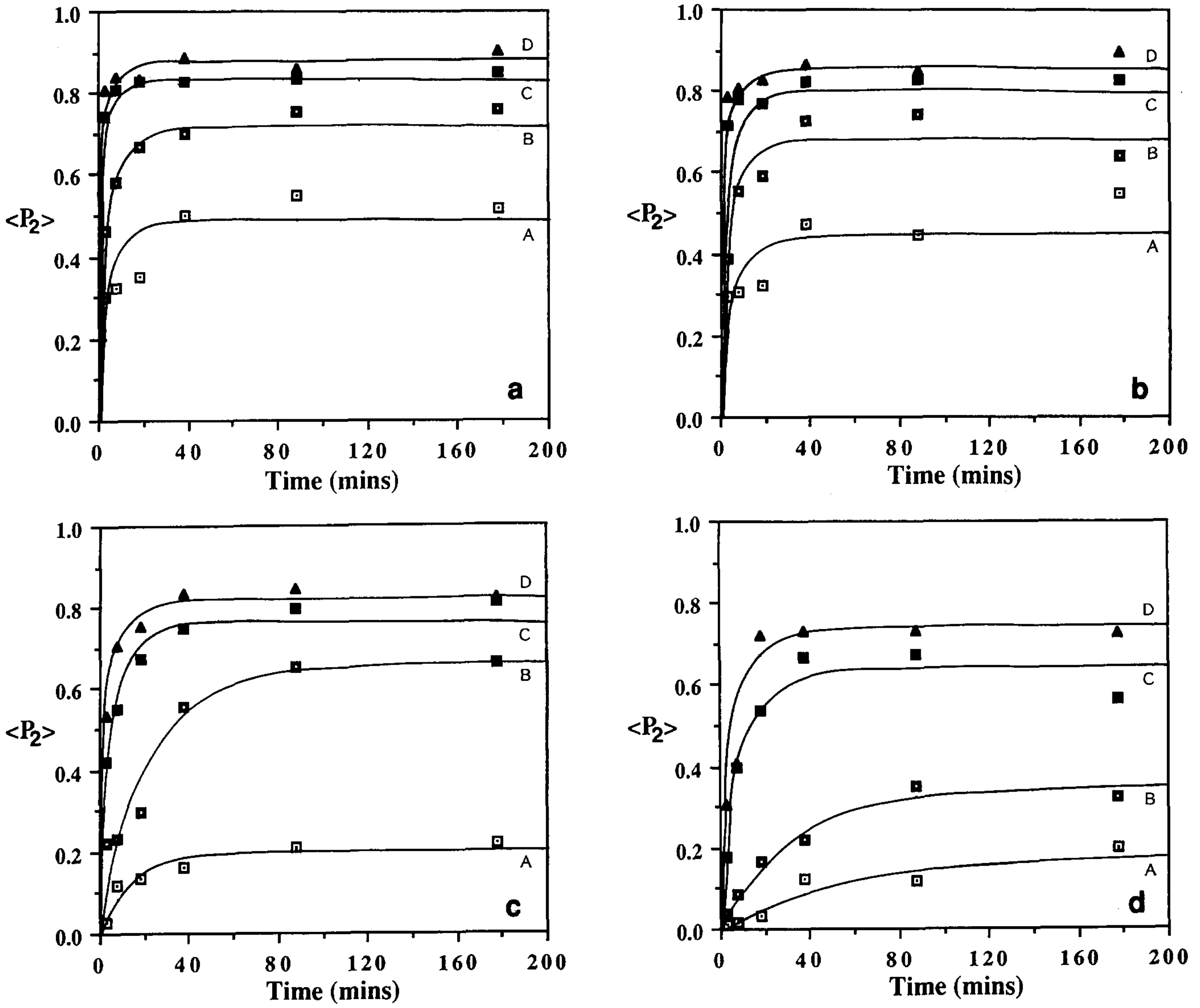

Figure 4 Curves of the form $\langle P_2\rangle/\langle P_2\rangle_{max} = 1 - \exp(-t/\tau)$ fitted to experimental measurements of $\langle P_2\rangle$ against time for the different field strengths of 0.3 T (A), 0.55 T (B), 0.92 T (C) and 1.12 T (D). The individual plots are each compared to a different molecular weight: (a) 4600, (b) 5000, (c) 8600 and (d) 14400

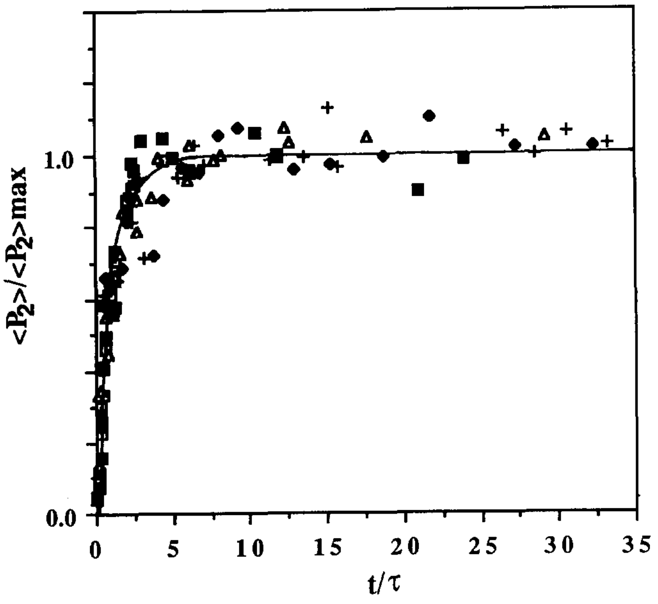

Figure 5 Data fitted to equation (3) and normalized with respect to $\langle P_2\rangle_{max}$ and τ, for different molecular weights of 4600 (+), 5000 (◆), 8600 (Δ) and 14400 (■)

Table 2 $\langle P_2\rangle_{max}$ and τ derived from best fit of expression (3) to data

Mol. wt.	$\mu_0 H$ (T)	$\langle P_2\rangle_{max}$	τ
4600	0.3	0.489	5.833
	0.55	0.709	3.330
	0.92	0.830	1.334
	1.22	0.866	1.140
5000	0.3	0.448	4.704
	0.55	0.676	4.054
	0.92	0.806	1.393
	1.12	0.851	1.174
8600	0.3	0.205	14.46
	0.55	0.659	21.87
	0.92	0.759	4.966
	1.12	0.806	3.015
14400	0.3	0.209	71.82
	0.55	0.337	28.89
	0.92	0.633	8.505
	1.12	0.735	7.488

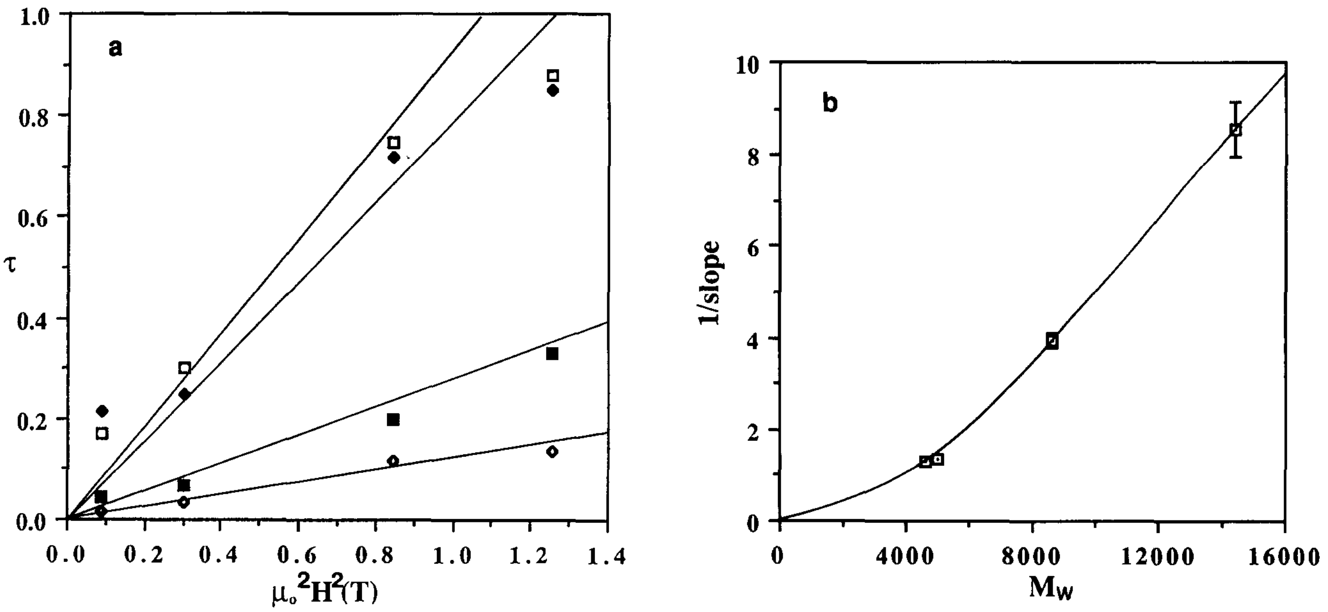

Figure 6 (a) Plot of the reciprocal of the time constant τ against the square of the field strength for the molecular weights 4600 (□), 5000 (♦), 8600 (■) and 14400 (◇). (b) Plot of the reciprocal of the slopes (from (a)) against molecular weight

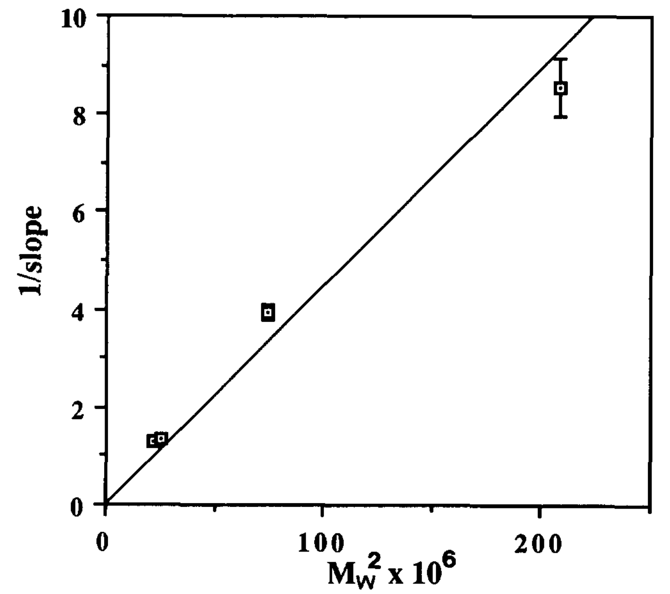

Figure 7 Plot of the reciprocal of the slopes (from *Figure 6a*) against the square of the molecular weight

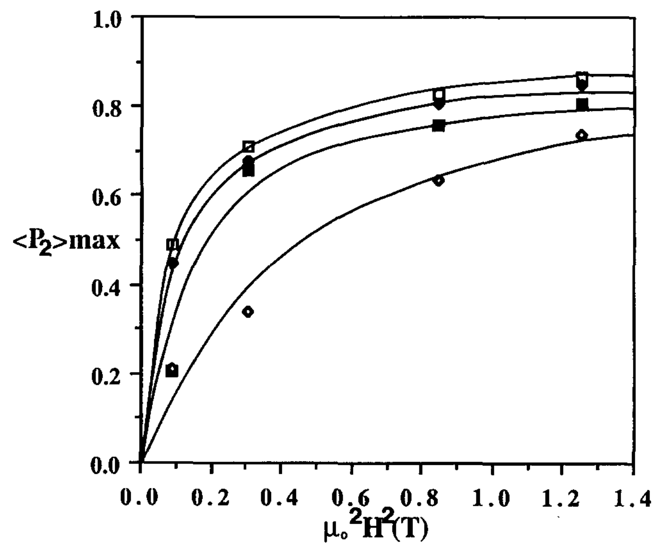

Figure 8 $\langle P_2\rangle_{\max}$ plotted against the square of field strength for the different molecular weights of 4600 (□), 5000 (♦), 8600 (■) and 14400 (◇)

possibly associated with defects and boundaries[16,17], which are observable in the polymer. The plot of $\langle P_2\rangle_{\max}$ values derived from the parameterization routine against H^2 is shown in *Figure 8*. It is clear that at fields of 1 T or more the maximum level of preferred orientation tends towards $\langle P_2\rangle$ values in the range of 0.8 to 0.9, and that given sufficiently high fields the maximum value is not very dependent on molecular weight. It is at lower fields that the influence of molecular weight becomes more marked. For the molecular weights 4600, 5000 and 8600, the value of $\langle P_2\rangle_{\max}$ increases rapidly with field to reach a value up to 0.75 at 0.55 T. For the high-molecular-weight sample, 14400, the increase in $\langle P_2\rangle_{\max}$ with field is more gradual, a value of only about 0.50 being reached at 0.55 T.

If we relate the increasing value of $\langle P_2\rangle_{\max}$ with increasing field to the rotation of the molecules against the internal elastic field associated with distortions in the polymer, then the data of *Figure 8* suggest an additional type of distortion, which resists perfect orientation, but is significant only in the higher-molecular-weight materials, although it can still be overcome at higher field strengths.

Predictions for higher molecular weights and higher fields

Commercial liquid-crystalline polymers of this type, which are designed for structural applications, typically have molecular weights about twice the maximum considered here, i.e. around 30000. In view of the possible application of magnetically induced orientation to the processing of these polymers, it is interesting to predict whether fields generated by conventional (i.e. non-superconducting) fields and limited to about 1.5 T could generate sufficient orientation sufficiently quickly to be useful.

Extrapolation of the plots of $\langle P_2\rangle_{\max}$ against field strength would indicate that conventional fields between 1.0 and 1.5 T should be sufficient to give values of $\langle P_2\rangle_{\max}=0.7$ or above in higher-molecular-weight material. On the other hand, the dependence of the rate of orientation on the square of the molecular weight would suggest that, for a given value of H^2, the rate achievable at a molecular weight of 30000 would only be about one-quarter of that we have seen in the polymer of molecular weight 14400. In other words it would take about 30 min to obtain an orientation of 90% of $\langle P_2\rangle_{\max}$. This timescale is likely to be too long in a processing context. On the other hand, the H^2 relationship for the rate means that very considerable benefits could be obtained by using superconducting magnets, which would give fields in the range of 6–12 T.

CONCLUSIONS

The conclusion is that, for polymers of molecular weight sufficient to give good mechanical properties, a useful degree of magnetic orientation can be induced by conventional fields in the 1–1.5 T range. However, if it is required to introduce the orientation on timescales of a few minutes or less, then only field strengths obtainable from superconducting magnets will suffice.

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REFERENCES

1 Talroze, R. U., Shibayev, V. P. and Plate, N. A. *Polym. Sci. USSR* 1983, **25**, 2863
2 Krigbaum, W. R. *Polym. Liq. Cryst.* 1982, 275
3 Maret, G. and Blumstein, A. *Mol. Cryst. Liq. Cryst.* 1982, **88**, 295
4 Herlach, F., 'Strong and Ultrastrong Magnetic Fields and Their Applications', Topics in Applied Physics, Vol. 57, Springer-Verlag, Berlin, 1985
5 Hardouin, F., Achard, M. F., Gasparoux, H., Liebert, L. and Strzelecki, L. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 975
6 Moore, R. C. and Denn, M. M., 'High Modulus Polymers, Approaches to Design and Development' (Eds. A. E. Zachariades and R. S. Porter), Marcel Dekker, New York, 1988
7 Moore, J. S. and Stupp, S. *Macromol.* 1987, **20**(2), 282
8 Spontak, R. J. and Windle, A. H. *J. Mater. Sci.* in press
9 Windle, A. H. 'Developments in Oriented Polymers', Vol. 1 (Ed. I. M. Ward), Applied Science, London, 1982
10 Mitchell, G. R. and Windle, A. H. 'Developments in Crystalline Polymers' (Ed. D. C. Bassett), Elsevier Applied Science, London, 1988, p. 115
11 Kozak, A., Simon, G. P. and Williams, G. *Polym. Commun.* 1989, **30**, 102
12 Plate, N. A., Talroze, R. U. and Shibaev, V. P. *Pure Appl. Chem.* 1984, **56**, 403
13 de Gennes, P. G., 'The Physics of Liquid Crystals', Clarendon Press, Oxford, 1974
14 Martins, A. F., Esnault, P. and Volino, F. *Phys. Rev. Lett.* 1986, **57** (14), 1745
15 Tai-Shung Chung *Polym. Eng. Sci.* 1986, **26** (13), 901
16 Lemmon, T. J., PhD Thesis, University of Cambridge, 1989
17 Anwer, A., Spontak, R. J. and Windle, A. H. *J. Mater. Sci. Lett.* 1990, **9**(8), 935