In situ X-ray scattering study of anisotropic solutions of hydroxypropylcellulose subjected to shear flow

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Molecular orientation parameter values measured by laboratory-based X-ray scattering techniques are reported for liquid crystalline solutions of hydroxypropylcellulose in water subjected to a range of steady shear rates. The global orientation exhibits a marked transition from a low orientation at low shear rates to high values ~0.5 at higher shear rates. This transition occurs at shear rates in the range of 0.3–1 s^{-1} and correlates quantitatively with similar transitions observed using small-angle light scattering. This behaviour is attributed to an out-of-shearing plane to an in-shearing plane transition which has been predicted theoretically by Larson and Ottinger.

(Keywords: hydroxypropylcellulose solution; shear flow; X-ray scattering)

Introduction

The effects of flow upon the molecular organization of polymer systems are of fundamental interest in both scientific and technological terms. In general, liquid crystal polymer flow has been studied using mechanical rheology and through rheo-optics (see ref. 1 for a recent review). Little work has been performed using probes which examine molecular level information[2–4]. Here we report the preliminary results of an *in situ* X-ray diffraction study of aqueous solutions of hydroxypropylcellulose (HPC) subjected to shear flow. At the concentrations and the temperature considered in this study, such aqueous solutions of HPC exhibit liquid crystal phases. These experiments provide quantitative measurements of structural correlations at a molecular level, i.e. 1–100 Å, which can be correlated with larger scale data obtained using optical techniques.

Experimental

The liquid crystalline solutions studied were prepared using HPC from Aqualon (Klucel E) with a given molecular weight[5] of 60 000. The HPC powder, which was dried *in vacuo* at 50°C for 12 h prior to use, was mixed thoroughly with distilled water to yield solutions of concentrations of 55 and 60% (w/v) HPC. These solutions were left to stand for 24 h before they were centrifuged at 4000 rev min^{-1} for 4 h to remove air bubbles. The liquid crystalline state of the solution was verified using optical microscopy.

X-ray diffraction measurements were performed using AXIS, an electronic area detector system developed at the University of Reading[6,7]. This provides the capability of recording in parallel the scattered intensities over a significant part of reciprocal space. The X-ray detector, supplied by Photonic Science Ltd, uses at its heart a charge-coupled device which produces standard video output. Individual video frames are co-added to provide an enhanced signal-to-noise ratio in the final image. For the solutions studied here, between 10^3 and 10^4 frames were co-added, providing data accumulation times of between 60 and 300 s. The system provides access to quantitative intensity values across the range of reciprocal space measured and hence the evaluation of peak positions, peak breadths, integrated intensities and orientation parameters is straightforward. The system uses a conventional sealed X-ray tube operating at 40 kV and 40 mA coupled with an incident beam graphite monochromator and pinhole collimation as the source of CuKα X-radiation. The area of the beam on the sample is ~1 mm^2. Full details of the AXIS system are provided elsewhere[6,7].

The shear cell used for these experiments was specifically designed for X-ray scattering studies[8]. It consists of two parallel plates, one fixed with a small aperture for the diffracted beam and one rotating with slotted windows allowing transmission during 90% of each rotation. The plates were spaced ~2 mm apart using a Teflon spacer which also acted as a seal to prevent water loss during the experiments. The plates were fitted with thin mica windows. The shear cell could be driven at a range of constant speeds from 3×10^{-2} to 100 rev min^{-1} which provides, with this sample thickness, a range of shear rates of 0.04–120 s^{-1}. The shear cell was maintained at a constant temperature of 18°C using a recirculating temperature-controlled water bath. The shear cell–detector distance for these experiments was 84 mm, which provided a scattering vector range $|s|$* of 0–1.0 Å^{-1} with an azimuthal angular range of 360°, although some part was obscured by the beam stop and its mount.

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* $|s| = 4\pi \sin\theta/\lambda$, where 2θ is the scattered angle and λ is the wavelength of the incident X-ray beam

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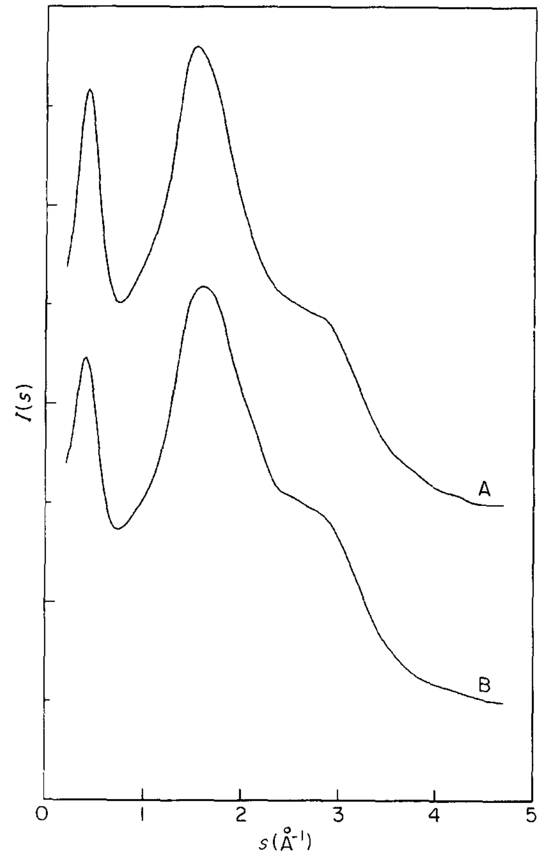

Figure 1 The X-ray scattering function $I(s)$ recorded under static conditions using a diffractometer[12] for anisotropic aqueous HPC solutions. HPC concentrations: A, 60% and B, 55%

Diffraction data were recorded at a number of fixed shear rates using data accumulation times of 280 s. At each shear rate, the shear cell was run for a time equivalent to at least 100 shear units before the diffraction data recording was initiated, to ensure that the solution was in a steady state[9]. Each set of diffraction data was corrected for air scattering and absorption by the windows. The orientation parameter values were evaluated using the azimuthal variation in the scattering intensity at $s \sim 0.4\,\mathrm{Å}^{-1}$. Standard procedures[10,11] were employed to calculate the orientation parameter $\langle P_2(\cos\alpha)\rangle$ from this azimuthal variation $I(\alpha)$, where α is the angle to the velocity axis of the shear cell. Since the angle of diffraction (2θ) is small, $\sim 10°$, no corrections were made for the fact that a flat-faced detector was used which does not fully access the data at $\alpha = 0°$. The orientation parameter derived is a measure of the global orientation ($\langle P_2(\cos\alpha)\rangle_G$) in the sample and takes account of both the orientation distribution of the liquid crystal directors ($\langle P_2(\cos\alpha)\rangle_D$) and the liquid crystal order parameter ($\langle P_2(\cos\alpha)\rangle_L$), i.e.

$$\langle P_2(\cos\alpha)\rangle_G = \langle P_2(\cos\alpha)\rangle_D . \langle P_2(\cos\alpha)\rangle_L \qquad (1)$$

Results

Figure 1 shows the scattered intensity function $I(s)$ for the two samples of HPC solutions under static conditions recorded using a diffractometer system[12]. As can be seen, the scattering function displays only diffuse peaks commensurate with a liquid crystalline structure. Of particular interest is the first diffuse maximum at $\sim 0.4\,\mathrm{Å}^{-1}$, which is only observed in anisotropic solutions. The position of this peak varies with the concentration of HPC and may be related to spatial correlations between neighbouring HPC chain segments[12]. The width of this diffuse maximum indicates spatial correlations over 20–30 Å. We shall utilize the anisotropy in the scattering of this maximum to evaluate the orientation parameter of the HPC solutions as a function of shear rate.

Figure 2 shows four diffraction patterns recorded for the 60% HPC solution subjected to shear rates of 0.0, 0.2, 1.0 and 116.0 s^{-1} using the AXIS system. In all cases the shear direction is parallel to the vertical axis of the page. The diffuse scattering at $\sim 0.4\,\mathrm{Å}^{-1}$ may be clearly seen as an almost continuous ring at low shear rates. The other features in the diffraction pattern are crystalline reflections from the mica windows. As the shear rate increases the scattering becomes noticeably anisotropic. There is a sharp intensification onto the equatorial section of the scattering pattern, i.e. normal to the shear direction. This indicates a preferential alignment of the HPC chain segments parallel to the shear direction.

Figure 3 shows a plot of the orientation parameters obtained for the two solutions as a function of the shear rate. Note that the shear rate axis is plotted on a logarithmic scale. At low shear rates, i.e. $< 1\,\mathrm{s}^{-1}$, the orientation parameter is positive but low. As the shear rate is increased, there is an increasing level of preferred orientation, and at around $\sim 1\,\mathrm{s}^{-1}$, there is a transition to a substantially higher level of orientation. At even higher shear rates there is a much more gradual increase up to the maximum possible of $116\,\mathrm{s}^{-1}$ in these experiments.

Discussion

The results presented in *Figure 3* show that the orientation parameter exhibits a sudden increase from ~ 0.1 to 0.4–0.6 at a critical shear rate. This result differs from that reported by Picken *et al.*[3] who performed similar experiments with an aramid solution using a parallel plate shear device and a synchrotron radiation X-ray source. They measured an order parameter of 0.6–0.7 in steady shear, independent of the applied shear rate. The origin of these very different behaviours may lie in the differences in chain rigidity between the HPC and aramid systems, but clarification clearly requires further investigations.

A comparison of these current data with rheo-optical data obtained for HPC–water solutions shows a good agreement for both the 55 and 60% HPC solutions. Depolarized small-angle light scattering (SALS) patterns are circular at low shear rates with an intensity maximum at zero scattering angle, while above a shear rate of $\sim 0.3\,\mathrm{s}^{-1}$, four lobe patterns with a long streak are observed[13]. The change in the SALS patterns with shear rate appears to correlate with the transition in orientation parameter observed using X-ray scattering. This quantitative agreement between the optical and X-ray results was not found for the aramid solutions, which nevertheless show a similar transition in the SALS patterns[3].

For the shear cell used in this study, the X-ray scattering experiments probe the anisotropy in a plane containing the velocity direction and a neutral direction. An order parameter close to zero means that a substantial fraction of the irradiated volume has a liquid crystal director which is aligned out of the shearing plane containing

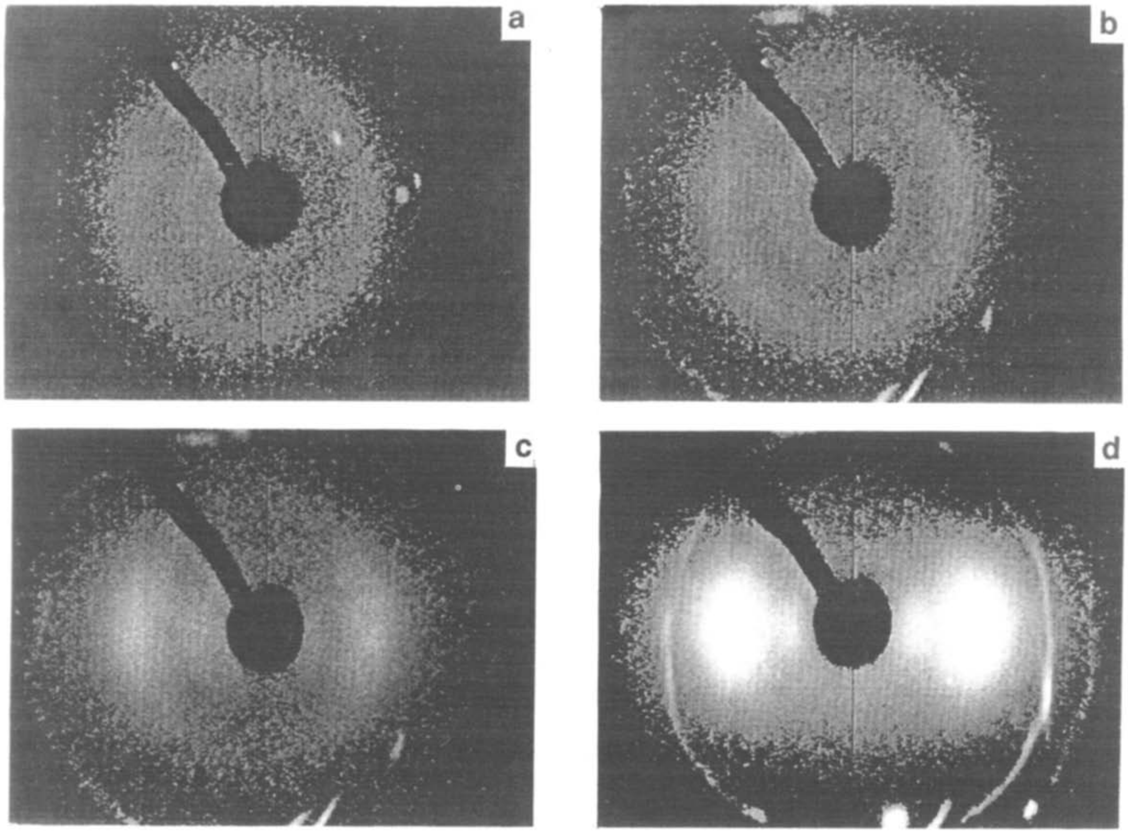

Figure 2 X-ray diffraction patterns recorded using the AXIS system for 60% HPC aqueous solutions at 18°C subjected to shear rates of (a) 0.0 s^{-1}, (b) 0.2 s^{-1}, (c) 1.0 s^{-1} and (d) 116.0 s^{-1}. The shear direction is parallel to the vertical axis of the page and the high intensity areas are white. The central portion is masked by the beam stop. The diffraction pattern is recorded over a range of $|s| = 0.0$–1.0 Å^{-1}

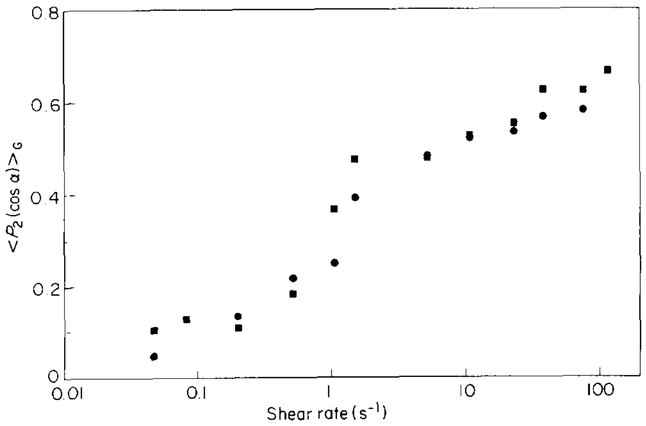

Figure 3 The measured global orientation parameter $\langle P_2(\cos\alpha)\rangle_G$ for liquid crystalline solutions of HPC in water subjected to a steady shear flow, plotted against the shear rate for solution concentrations of 55% (●) and 60% HPC (■). The uncertainty associated with each orientation parameter value is ±0.02

both the velocity direction and the shear gradient. The observed transition is then an out-of-shearing plane to an in-shearing plane transition. A similar transition has been predicted theoretically by Larson and Ottinger[13]. They show that at low shear rates, if the director is not in the shearing plane before starting the shear, which is the case in our experiments, the director is attracted by either a time-periodic tumbling in the shearing plane or an orbit that lies out of the shearing plane. Upon increasing the shear rate, the tumbling in the shearing plane is the only attractor. These predictions are in full agreement with the X-ray scattering measurements reported here. They are also in agreement with the fact that above this critical shear rate, the anisotropic fluid is still in a tumbling state. The cessation of tumbling at high shear rates is thought to relate to the occurrence of a negative first normal stress difference[14,15]. For the 50% HPC solution, a negative first normal stress difference has been observed at ~50 s^{-1} and for the 60% HPC solution[9] at 150 s^{-1}, well above the critical shear rate of ~0.3–1 s^{-1} observed by SALS and X-ray scattering.

The picture for the flow mechanisms of anisotropic solutions of HPC may be envisaged as an out-of-shearing plane tumbling at low shear rates, with a transition to an in-shearing plane tumbling at moderate shear rates and an additional transition from tumbling to flow alignment at high shear rates. The occurrence of this out-of-shearing plane tumbling might also be the origin of the shear-thinning behaviour of the viscosity at low shear rates; the transition between this first shear-thinning region to the Newtonian plateau occurs at the same shear rate as the out-of-plane to in-shearing-plane transition[13].

At the highest shear rates studied, the director distribution, in terms of time, is mostly parallel to the flow direction and in the shearing plane. The situation is very close to that of a monodomain and the orientation parameter which is obtained from the anisotropy in the X-ray scattering reflects the degree of ordering of the nematic phase, ~0.65 for the 60% HPC solution.

We have shown that reliable X-ray based rheological data may be obtained in the laboratory, using conventional X-ray sources. This has been achieved using a novel electronic area X-ray detector which enables quantitative scattering data to be obtained in parallel over a useful scattering vector range. The data accumulation time is dependent upon the nature and thickness of the sample. In this study, a cycle time of 60–300 s was possible. The system is ideally suited to both the measurement of time-dependent phenomena (such data for these HPC solutions will be reported in the future[8]) and to the study of systems with limited optical transmission, including polymer blends and colloidal systems.

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