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In situ X-ray scattering investigations of solutions of cellulose in *N*-methylmorpholine-*N*-oxide during shear flow

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There are conflicting reports that concentrated solutions of cellulose in *N*-methylmorpholine-*N*-oxide (MMNO) exhibit liquid crystal structures as is the case for many cellulose derivatives. We have prepared cellulose/MMNO solutions using two different approaches with compositions in the range 9 to 34% w/w. We have subjected these solutions to *in situ* X-ray scattering studies during shear flow. Such solutions do not develop any significant level of preferred orientation during shear flow. Such zero macroscopic orientation contrasts with the behaviour of related lyotropic liquid crystal polymers based on cellulose derivatives and with other liquid crystal polymer systems, for which, in all cases, a substantial level of preferred orientation develops during shear flow. We conclude that the range of cellulose/MMNO solutions studied here do not exhibit liquid crystal phases. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: cellulose; liquid crystal polymers; shear flow)

Introduction

Many derivatives of cellulose form both thermotropic and lyotropic liquid crystal phases[1]. Over the past 10 years or so there have been various conflicting reports that the parent cellulose also forms a liquid crystal phase in solutions of *N*-methylmorpholine-*N*-oxide (MMNO)[2–7]. In the original studies, the critical criteria appear to be a concentration greater than 20% and at temperatures less than 90°C, although more recent studies indicate the thermal stability to be much higher ~120°C[6]. This material is of particular interest since the same system in dilute form is utilized in the production of TENCEL fibres[8] and the solutions have been subjected to many varied studies[9–14]. Cellulose and the majority of its derivatives are formed from saturated hydrocarbon groups and hence the dielectric polarizability is rather small. As a consequence, for those systems which do exhibit liquid crystal phases, the polarizing optical microscope reveals low birefringent textures, and there is the potential for confusion of such birefringence patterns with other optical phenomena induced through stress, strain and density inhomogeneities including crystallization and the associated light scattering[15]. Unoriented wide-angle X-ray scattering (WAXS) patterns of isotropic and liquid crystal phases are often rather similar[16]. However, due to the intrinsic long-range orientational ordering, the imposition of an external field leads to characteristic patterns for the liquid crystal state, with distinctive anisotropic features. Electric and magnetic fields have very weak interactions with cellulose, as indicated above, and so we have explored the effects of shear flow of a number of cellulose derivatives which exhibit liquid crystal phases[17–21]. For all such materials, the imposition of shear flow leads to the development of a macroscopic preferred orientation, even for quite modest shear rates. Similar results have been reported by others for a variety of liquid crystal polymers including both lyotropic and thermotropic systems[22–25].

Such behaviour contrasts strongly with the very low levels of macroscopic orientation which are generated during shear flow on simple polymer melts[26]. In this report we utilize *in situ* WAXS studies of cellulose/MMNO solutions subjected to shear flow to unambiguously determine whether such solutions exhibit liquid crystalline properties.

Experimental

Materials. The monohydrate of MMNO (97%) was obtained from Fluka Chemie AG, Buchs (Switzerland). Pure MMNO (97%) was obtained from Aldrich Ltd., Gillingham, UK. Both were used without any further treatment. The cellulose (fibrous, long, Sigma Chemical Co.) was dried at 70°C under vacuum before use. Propyl gallate (98%, BDH Laboratory Supplies, Poole, UK) and isopropanol (99%, Merck Ltd., Poole, UK) were used without further purification.

The samples were prepared according to two methods.

Method A:. A mixture of 30 g of MMNO monohydrate and 7 ml distilled water was stirred at 50°C until dissolved. Then the desired amount of dried cellulose was added, together with 0.05 wt% of propyl gallate solution (10 wt% in isopropanol) as a stabilizer[27]. The mixture was stirred at ~100°C until clear and about 8 ml of water was removed under vacuum. The dark honey coloured solution was poured into an aluminium template covered with Kapton to obtain films of ~1 mm thickness. After cooling, the samples were stored in a refrigerator. With this method concentrations between 9 and 23 wt% were obtained; because of the high viscosity of the solution, no higher concentrations could be achieved.

Method B. A mixture of 26 g of pure MMNO, 4 ml of distilled water and 32 ml of dry *N,N*-dimethylformamide (DMF) were stirred at 50°C until dissolved. Then the desired amount of dried cellulose was added, together with 0.05 wt% of propyl gallate solution (10 wt% in isopropanol)

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as a stabilizer. The mixture was stirred at ~100°C until clear and about 16 ml of DMF was removed under vacuum. The honey-coloured solution was poured into an aluminium template covered with Kapton to obtain films of ~0.5 mm thickness. After cooling, the samples were stored in a refrigerator. With this method concentrations between 20 and 34 wt% were obtained.

The *in situ* X-ray scattering measurements used a specially designed shear cell based around a parallel plate assembly with apertures covered with mica windows. A complete description of the shear cell has been given elsewhere[28]. The temperature of the shear cell was regulated using a circulating fluid system. The X-ray scattering patterns were recorded using an electronic area detector which was one component within an integrated 2-d X-ray detection, control and analysis system (AXIS) developed at Reading that allows the synchronous collection of X-ray data and control of the sample environment, including temperature and shear rate[29]. A copper target tube together with a graphite monochromator and pinhole collimation was used as the X-ray source. The incident X-ray beam is parallel to the velocity gradient vector of the shear flow and hence it is the structure in the flow axis–vorticity vector plane which is probed in these experiments.

The rheometer was filled at room temperature and then heated to 85–90°C. The solutions were investigated both in the SAXS (0.05 to 0.2 Å^{-1}) and in the WAXS range (0.2 to 1.6 Å^{-1}). The X-ray scattering data were recorded for shear rates between 0.1 and 50 s^{-1}. In order to obtain steady state conditions each shear rate was applied for at least 200 shear units. The integration time for each X-ray scattering pattern was 50 s.

Results and discussion

A series of solutions of cellulose/MMNO (9–23 % w/w) prepared by Method A was considered. The X-ray scattering patterns were dominated by the scattering from the solvent and identification of cellulose specific features was difficult. Over the complete range of shear rates and temperatures considered, no anisotropic scattering features were observed; that is the solutions were macroscopically isotropic. Since the upper end of the concentration range considered only just overlapped with the critical concentration of 20 to 24% indicated by the initial work of Navard *et al.*[11], we also studied the higher concentration solutions prepared using Method B.

A second series of samples with higher cellulose concentrations in the range 20 to 34% w/w prepared by Method B were considered over the temperature range 84 to 90°C corresponding to the conditions initially reported[11]. From the report of Taeger *et al.*[6], these measurements would be deep in the liquid crystal phase for concentrations >27% w/w. In these measurements, a diffuse peak at $|Q| \approx 1.4$ Å^{-1} ($|Q| = 4\pi \sin \theta/\lambda$, 2θ is the scattering angle and λ the incident X-ray wavelength) was observed. The position of this peak varied slightly with concentration and temperature. We monitored the azimuthal dependence of the intensity at a fixed value of $|Q|$ corresponding to this feature. The intensity function $I(\alpha)$, where α is the angle between the flow axis and the projection of the scattering vector on to the detector face, was used to derive values for the orientational parameters $\langle P_2 \rangle$, $\langle P_4 \rangle$ using standard procedures[30]. $\langle P_2 \rangle = 0$ indicates that there is no global preferred orientation. *Figure 1* shows one example of the data obtained for $\langle P_2 \rangle$ as a function of shear rate for a solution containing 33.4 wt% cellulose at 87°C. It is clear that the level of global anisotropy in this solution under shear flow is essentially zero. There is a small variation with shear rate which is of the same order as that observed in simple polymer melts such as poly(ethylene)[26]. Similar data were recorded for each of the solutions in this series. In all such measurements, the solutions were globally isotropic. These results contrast most strongly with all other measurements reported in the literature on both lyotropic[17–23] and thermotropic[20–25] liquid crystal polymers during shear flow. We have shown, for comparison purposes, the high level of global anisotropy induced through shear for a solution of hydroxypropyl cellulose in water (50% w/v) at room temperature. Such data are typical of both lyotropic and thermotropic liquid crystal phases formed from cellulose derivatives and from other rigid rod systems. The response of liquid crystal polymers to shear flow is complex and some such materials can exhibit the so-called regime I in which the level of global orientation remains relatively low[31]. However, such behaviour is only observed at low shear rates, that is $\gamma < 1$ s^{-1}[18,23] and here we have evaluated the level of anisotropy up to shear rates which are two orders of magnitude greater. Moreover, even within this regime, small but significantly non-zero levels of anisotropy are observed[23], which are easily differentiated from the essentially zero values shown in *Figure 1* for the cellulose/MMNO system. It is clear that the series of samples prepared here do not exhibit the global anisotropy
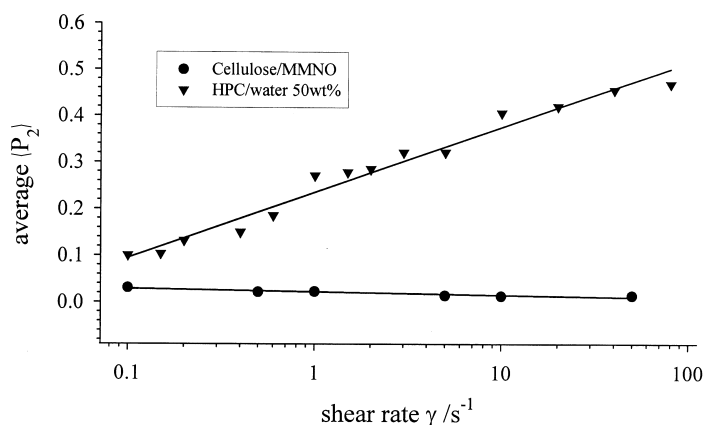

Figure 1 A plot of the global orientation parameter $< P_2 >$ measured for (•) a cellulose/MMNO solution (33.4 wt%) prepared using method B (see text) at a temperature of 87°C and (▼) an aqueous solution of hydroxypropylcellulose (50% w/v) at room temperature as a function of shear rate

expected for liquid crystal structures and we conclude on that basis, that these materials are no liquid crystalline. These results confirm the revised report of Navard *et al.*[15], in that cellulose does not form liquid crystal structures in MMNO solutions. The X-ray rheological approach offers a useful route to the study of materials which have limited or no optical transparency and to those in which stress or form birefringence may be a dominating factor in optical procedures.

Summary

Relatively high concentration solutions of cellulose in MMNO have been prepared and subjected to *in situ* X-ray scattering studies. In contrast to lyotropic and thermotropic cellulose derivatives studied using similar procedures, no global preferred orientation was induced by the shear flow and we deduce that such solutions are not liquid crystalline even for concentrations of 34% cellulose in MMNO.

Acknowledgements

References

1. Gray, D. G. and Harkness, B. R., in *Liquid Crystalline and Mesomorphic Polymers*. Springer, New York, 1994, Chapter 9.
2. Navard, P. and Haudin, J.-M., *Br. Polym. J.*, 1980, **12**, 174.
3. Chanzy, H., Peguy, A., Chaunis, P. and Monzie, P., *J. Polym. Sci., Polym. Phys. Ed.*, 1980, **18**, 1137.
4. Chanzy, H., Paillet, M. and Peguy, A., *Polym. Commun.*, 1986, **27**, 171.
5. Navard, P. and Haudin, J.-M., *Polym. Process Eng.*, 1985, **3**, 291.
6. Taeger, E., Michels, Ch. and Nechwatal, A., *Das Papier*, 1991, **45**, 784.
7. Gray, D.G., *Carbohydrate Polym.*, 1994, **25**, 277.
8. Woodings, C.R., *Int. J. Biol. Macromol.*, 1995, **17**, 305.
9. Lang, H., Laskowski, I., Lukanoff, B., Schleicher, H., Mertel, H., Franz, H. and Taeger, E., *Cellulose Chem. Technol.*, 1986, **20**, 289.
10. Chanzy, H., Nawrot, S., Peguy, A., Smith, P. and Chevalier, J., *J. Polym. Sci., Polym. Phys. Ed.*, 1982, **20**, 1909.
11. Navard, P., Haudin, J.-M., Quenin, I. and Peguy, A., *J. Appl. Polym. Sci.*, 1986, **32**, 5829.
12. Bochek, A. M., Kalyuzhnaya, L. M., Petropavloaskii, G. A. and Frenkel, S. Ya, *J. Appl. Chem. USSR*, 1992, **65**, 2300.
13. Bochek, A. M., Petropavlovsky, G. A. and Kallistov, O., *Cellulose Chem. Technol.*, 1993, **27**, 137.
14. Bochek, A. M., Petropavlovskii, G. A. and Shek, V. M., *J. Appl. Chem. USSR*, 1987, **60**, 634.
15. Arvieu, C. and Navard, P., *J Polym. Sci. Polym. Phys.*, 1989, **27**, 2157.
16. Mitchell, G. R., in *Comprehensive Polymer Science*, Vol. 2, ed. C. Booth and C. Price. Pergamon, Oxford, 1989, Chapter 31.
17. Keates, P., Mitchell, G. R., Peuvrel-Disdier, E. and Navard, P., *Polym. Communcations*, 1993, **34**, 1316–1319.
18. Keates, P., Mitchell, G. R., Peuvrel-Disdier, E. and Navard, P., *Polymer*, 1996, **37**, 893–901.
19. Keates, P., Mitchell, G. R., Peuvrel-Disdier, E., Riti, J. B. and Navard, P., *J. Non-Newtonian Fluid Mechanics*, 1994, **52**, 197.
20. Andresen, E. M. and Mitchell, G. R., *Europhys. Lett.,* in press.
21. Andresen, E. M. and Mitchell, G. R., *Macromolecules*, submitted.
22. Hongladsrom, K., Ugaz, V. M., Cinader, D. K., Burghardt, W. R., Quintana, J. P., Hsiao, B. S., Dadmun, M. D., Hamilton, W. A. and Butler, P. D., *Macromolecules*, 1996, **29**, 5346.
23. Ugaz, V. M., Cinader, D. K. and Burghardt, W. R., *Macromolecules*, 1997, **30**, 1527.
24. Gervat, L., Mackley, M. R., Nicholson, T. M. and Windle, A. H., *Philos. Trans. R. Soc. London, Ser. A*, 1995, **350**, 1.
25. Romo-Uribe, A. and Windle, A. H., *Macromolecules*, 1996, **29**, 6246.
26. Pople, J. A., Mitchell, G. R. and Chai, C. K., *Polymer*, 1996, **37**, 4187–4191.
27. US patent no. 4246221, McCorsley, C.C., 1979.
28. Pople, J. A. and Mitchell, G. R., *Liquid Crystals*, 1997, **23**, 467–473.
29. Pople, J. A., Keates, P. A. and Mitchell, G. R., *J. Synchrotron Rad.*, 1997, **4**, 267–278.
30. Mitchell, G. R. and Windle, A. H., in *Developments in Crystalline Polymers-2*, ed. D. C. Bassett. Elsevier, London, 1988, Chapter 3.
31. Asada, T., Onogi, S. and Yanase, H., *Polym. Eng. Sci.*, 1984, **24**, 355.