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A novel orientation technique for semi-rigid polymers. 1. Preparation of cross-linked cellulose acetate and hydroxypropylcellulose films having permanent anisotropy in the swollen state

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Abstract: It has been predicted that unusually good mechanical properties can be obtained by drying swollen networks of semi-rigid chains while they are in the deformed state, as described in several theoretical investigations [*Macromolecules*, **23**: 5335, 5341 (1990), **24**: 901 (1991)]. The present investigation involves the preparation of networks of this type from cellulose acetate (CA) and hydroxypropylcellulose (HPC), in order to test these concepts. The cross-linking required to maintain anisotropy during the drying process was obtained using formaldehyde, while the polymers were in either the anisotropic or isotropic state. Control of the cross-linking was obtained by studying the effects of the concentration of formaldehyde, temperature, and reaction time.

The liquid-crystalline phase separations in CA and HPC, and in their networks, were studied with cross-polarized optical microscopy. CA and HPC showed anisotropic phases in trifluoroethanol and in methanol, respectively, and under shear the HPC systems exhibited the band textures associated with macroscopic orientation. In the case of the uncross-linked polymers, this band texture disappeared shortly after shearing was discontinued. The networks prepared by cross-linking the HPC in either liquid-crystalline solutions or in isotropic solutions also showed band textures, but these textures now persisted long after removal of the shearing stress. As shown in the following paper, the extensibility required in the proposed processing technique was highest for the networks prepared in the isotropic state, suggesting that these materials should have the greatest potential for dramatic improvements in mechanical properties.

Key words: Semi-rigid polymers – novel orientation technique – cellulose acetate – hydroxypropylcellulose – liquid-crystalline phase separation – polarizing microscopy – band textures – cross-linking

Introduction

Anisotropic materials are very important in many branches of industry, primarily because of their attractive mechanical properties in directions important in a given application [1]. Not surprisingly, there is growing interest in developing new materials, especially polymers, with controlled anisotropy. Several processing methods have generally been used to induce segmental orientation of polymer chains, ranging from drawing at elevated temperatures to spinning from liquid-crystalline solutions or gels [2–4]. One disadvantage of these methods is that the degree of segmental orientation is difficult to control. Also, the inevitable relaxation of the chains when the external field is removed results in losing some or all of the induced anisotropy [1]. There is

therefore an obvious need for new orientation techniques for processing polymers into highly-ordered, high-performance materials.

Liquid-crystalline polymers are ideal candidates for such processing techniques, and have been extensively studied for the last several decades [5, 6]. There is a natural tendency for the rigid segments in these polymers to self align into ordered domains, in melts or in solutions. This enables liquid-crystalline polymers to be processed into ordered materials having excellent high-performance properties [7, 8], and these properties would presumably be further improved if the domains themselves could be oriented along a common director. One type of semi-rigid polymer of particular interest is the cellulosics [9]. Because of the rigid sequences of hemi-acetal cyclic rings in their backbones, these chains are relatively stiff and are known to form chiral nematic mesophases in a variety of solvents [9–18]. These chains can form helicoidal structures, particularly in the undiluted state and in concentrated solutions, in a way that may not be covered in the theory cited below. However, there should be at least a semi-quantitative correspondence, particularly in the case of networks formed in dilute solutions.

The possibility that some cellulosics may have some partial biodegradability could also be an advantage in applications in which disposability is a problem [9, 19]. Another reason for studying the cellulosics in the proposed technique is the fact that these polymers do not have the tremendous thermal stability required in the conventional high-temperature methods frequently used to improve orientation in many polymer films [20].

Outline of the processing steps

The method is based on the fact that rigid or semi-rigid liquid-crystalline chains have exceptional orientability and exhibit an isotropic-to-anisotropic phase transition under a mechanical force [21–26]. Specifically, the novel orientation technique to be tested consists of the following steps [19]:

i) Identifying polymeric chains of sufficient stiffness to give liquid-crystalline, anisotropic phases.
ii) Cross-linking the chains in the presence of solvent. (The cross-links confer sufficient solidity for the polymer to remain in a deformed state for any length of time, and the solvent prevents the premature ordering of the stiff chains). The conditions must be such that the network structure does not interfere with the formation of the desired anisotropic phase.
iii) Deforming the swollen network uniaxially or biaxially to induce segmental orientation.
iv) Removing the solvent, at constant length or at constant force, causing a first-order transition, in the hope of obtaining a *single-phase*, homogeneous, and highly-ordered material.

The purpose of the first of the two studies reported here is to prepare networks from both cellulose acetate and hydroxypropylcellulose, in the liquid-crystalline state as well as in the isotropic state. Characterization of anisotropic phase separation in these materials will then permit their use in the subsequent deformation-drying steps designed to improve chain orientation and mechanical properties.

Experimental part

Materials

Cellulose acetate (CA) was purchased from the Eastman Kodak Company, and had a quoted weight-average molecular weight M_w of 61.0×10^3 g mol^{-1}. It had a degree of substitution of 2.54, which corresponds to 39.8% acetyl content by weight. Two samples of Klucel ("food grade") hydroxypropylcellulose (HPC) were generously provided by Hercules Inc., and had quoted values of M_w of 80.0×10^3 and 95.0×10^3 g mol^{-1}, respectively. Both HPC samples had a degree of substitution between 3.0 and 4.4. Also obtained was an additional sample of HPC having the very high molecular weight of 370×10^3 g mol^{-1}. Formaldehyde [HCHO] was used as a 37 wt% aqueous solution obtained from the Fisher Scientific Company. All solvents, including acetone, methanol, tetrahydrofuran, and trifluoroethanol, were chemical grades. They were obtained from the Aldrich Chemical Company, and were used as received.

Table 1. Conditions for cross-linking cellulose acetate (CA) and hydroxypropylcellulose (HPC) in the liquid-crystalline state

Polymer	Polymer/Solvent (wt/wt)	M_w (g mol^{-1})	Solvent	[HCHO] (wt%)	[HCl] (mol l^{-1})	Temp (°C)	Reaction time (h)
CA	1/1	61 000	Acetone	1	0.01	45	8
HPC	1/1	80 000	MeOH	1	0.01	60	12

Cross-linking in the liquid-crystalline state

Guidance was provided by several attempts to cross-link cellulosics, mostly in the liquid-crystalline state or in high-shear fields [27–33]. In the present case, the cross-linking in the liquid-crystalline state was carried out at a relatively high concentration, well above the isotropic-to-anisotropic transition concentration c* [34]. Dissolution of these polymers generally requires a long time, and often results in the production of a large number of air bubbles in the samples [27–29]. In order to reduce these difficulties, powdered forms of the polymers were first cast into films (thickness $\approx$ 1 mm) by dissolution in acetone, followed by drying under a hood. The films were then dried under vacuum at 60 °C for several hours to remove any remaining traces of solvent and moisture. The dried films were then placed into a methanol solution containing formaldehyde (the cross-linking reagent) and hydrochloric acid (a catalyst). The composition of the solution is listed in Table 1, and the polymer/solvent ratio employed was 1/1 by weight. The glass dish holding the polymer film and methanol solution was then sealed. After a week or more at room temperature, a bubble-free polymer solution exhibiting iridescent colors was formed. Cross-linking was achieved by heating the solution in an oven, at 45 °C for 8 h in the case of CA, and at 60 °C for 12 h in the case of HPC. The resulting gels were then dried, and extracted with methanol to remove soluble polymer, excess formaldehyde, and hydrochloric acid. Table 1 summarizes the reaction conditions for these cross-linking procedures in the anisotropic state.

Cross-linking in the isotropic state

The cross-linking of CA and HPC in the isotropic state was carried out using relatively dilute solutions, well below the critical concentrations c*. Six grams of CA was added to 60 ml of acetone, and dissolved in it by stirring for 2 days. To this solution was added 0.20 ml of 37 wt% formaldehyde aqueous solution and a sufficient amount of hydrochloric acid to make its concentration 0.01 M. After it was stirred for another few hours, the solution was heated in an oil bath controlled at 56 $\pm$ 1 °C for the cross-linking process. After 2 h, the stirring was stopped and the resulting, partially-gelled solution was poured into a glass dish for drying at room temperature. Four days later, the dried, cross-linked film was extracted with methanol to remove the remaining formaldehyde and hydrochloric acid. It was then dried at room temperature for a few days under a hood, and then at 60 °C for 10 h under vacuum.

HPC was cross-linked in the same way. Six grams of polymer (M_w = 80 000 g mol^{-1}) was dissolved in 40 ml of acetone, with the help of stirring, for about 2 days. An additional 5 ml of acetone containing 0.023 ml 37 wt% aqueous formaldehyde was added to the solution, with continuous stirring until completely mixed. Hydrochloric acid was added in an amount making its concentration 0.01 M, and the reaction was carried out at 56 $\pm$ 1 °C for 1 h, with light stirring. The rest of the procedure was essentially the same as that used for the CA [34].

The reaction conditions for cross-linking CA and HPC in the isotropic state are listed in Table 2.

In the case of the CA, some additional cross-linking experiments were carried out to characterize the effects of formaldehyde concentration, reaction temperature, and reaction time. The specific conditions chosen are given in Table 3.

Characterization using cross-polarized optical microscopy

In these experiments, solutions of CA and HPC were prepared with trifluoroethanol and

Table 2. Conditions for cross-linking CA and HPC in the isotropic state[1])

Polymer	Weight polymer (g)	Vol acetone (ml)	Vol formaldehyde[2]) (ml)	Reaction temp (° C)	Reaction time (h)
CA	6	60	0.200	56	2
HPC	6	40	0.023	56	1

[1]) CA: $M_w = 61\,000\ g\,mol^{-1}$; HPC: $M_w = 80\,000\ g\,mol^{-1}$
[2]) 37 wt% aqueous solution

Table 3. Effects of formaldehyde concentration, temperature, and reaction time on cross-linking of CA, as judged by its insolubility

Formaldehyde (wt%)	Temp (°C)	Reaction time	Observation of insolubility
2	20	2 hrs	Dissolves in acetone
2	20	5 days	Partially dissolves in acetone (50 wt% sol fraction)
0.3	56	30 min	Swells in acetone, partially dissolves (20 wt% sol fraction)
0.5	56	30 min	Swells in acetone to 50 wt% polymer (5 days later to 28%)
2	56	30 min	Does not swell in acetone

methanol, respectively. At least 2 weeks were required to allow the solvents to diffuse uniformly throughout the samples. The samples were placed between two cover glasses. To generate the desired band textures, a shearing force was applied by moving the two cover glasses in opposite directions, at a rate of shear estimated to be $10\ s^{-1}$. A Nikon polarizing optical microscope equipped with an Olympus camera was used to study the phase separations, both in polymer solutions and in swollen networks. The magnification of the lens used was $40\times$, and the camera lens provided an additional magnification of $2.5\times$.

Results and discussion

The effects of reaction variables on cross-linking

The cross-link density achieved has a strong (inverse) effect on the maximum extension to which the swollen networks can be stretched, in the orientation step of the procedure. The dependencies of the cross-linking of CA in relatively dilute solutions on formaldehyde concentration, temperature, and reaction time were determined by examining the swelling properties of the resulting networks. Insolubility and low degrees of swelling are, of course, the hallmarks of high degrees of cross-linking. The results are summarized in Table 3. The density of cross-linking is seen to increase with increase in reaction time and with increase in formaldehyde concentration, as expected. At room temperature, the cross-linking reaction is extremely slow, and days or even weeks are required for gelation. The reaction becomes much faster as the temperature is increased, with a practical upper limit around 56 °C (the boiling point of the acetone used as solvent). It was also found that the reverse reaction (de-cross-linking) could occur in the presence of hydrochloric acid, because of the equilibrium nature of the process. Therefore, both excess hydrochloric and formaldehyde have to be removed in order to control the degree of cross-linking.

The above results generally agree well with those on the formaldehyde cross-linking of cellulose [35, 36], except for much lower formaldehyde concentrations and shorter reaction times being successful in the case of CA. This is presumably due to the CA solutions being much more homogeneous than cellulose dispersed in water.

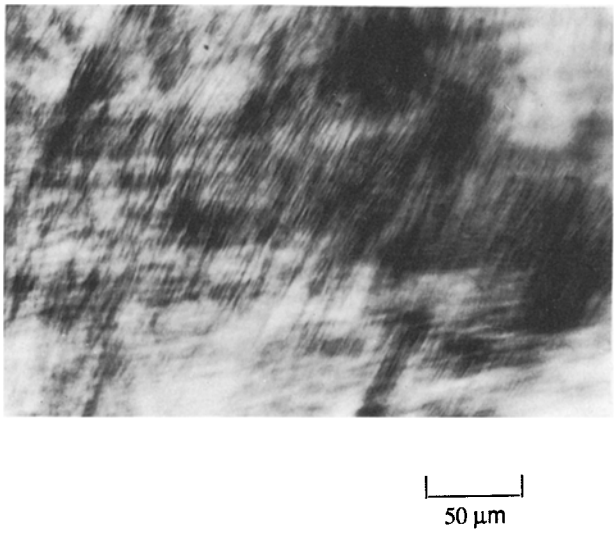

Fig 1. Cross-polarized optical micrograph of 40 wt% cellulose acetate solution in trifluoroethanol. The bar in the figure indicates a scale of 50 μm.

Liquid-crystalline phase separations

Figure 1 shows a micrograph of a 40 wt% CA/trifluoroethanol solution obtained using cross-polarized optical microscopy. The solution appears to be birefringent, suggesting anisotropic phase separation. This was to be expected since the critical concentration c* for the isotropic-to-anisotropic phase transition for CA in trifluoroethanol is slightly above 30 wt% [10]. This anisotropic phase is believed to be cholesteric [37].

A solution of HPC in methanol at 30 wt% was transparent and displayed no birefringence in cross-polarized optical microscopy [34]. Solutions above 40 wt%, however, showed iridescent colors (due to the selective reflections of white light by the layers of the twisted-nematic (cholesteric) mesophase). Under the cross-polarized microscope, this mesophase exhibited brilliant birefringence, as shown in Fig. 2(a). The microphotograph shows a mesophase with anisotropic domains of dimensions around 10–30 μm. One of the characteristics of liquid-crystalline polymer solutions or melts is the formation of a band texture during shearing or shear relaxation [38]. The band texture consists of alternating dark and bright bands under a cross-polarized microscope, and these dark and bright bands are aligned perpendicular to the shear direction. Figure 2(b) shows the band texture of a solution of HPC ($M_w = 80\,000\ g\,mol^{-1}$) in methanol. The photograph was taken right after the cessation of shear, which had been imposed at a rate estimated to be $10\ s^{-1}$.

It was reported that the band textures of HPC decay after cessation of shear as a result of chain relaxation, which restores the globular texture [27, 31, 39, 40]. The time required for the band texture to totally decay ranges from a few seconds to several days, depending on the mobility of polymer chains. It was therefore of special interest to study the relaxation of chain segments, particularly when they are subject to an external mechanical force. The band texture observed for the HPC solution shown in Fig. 2(b) is highly mobile, having disappeared only a few seconds after the cessation of shear. The system had quickly returned to its original structure, as shown in Fig. 2(c). HPC with a higher molecular weight ($M_w = 95\,000\ g\,mol^{-1}$) in methanol displays a similar anisotropic phase at 50 wt% [34]. This increase in molecular weight made the chains less mobile and the band texture persisted for around 15 min after the shearing. Chains of very high molecular weight should have very long relaxation times and long-lived band textures. Band textures in network structures would be expected to be maintained indefinitely.

The decay rate of the band texture of HPC was found to depend on solvent type, as well as on molecular weight [34]. The band texture of the $80\,000\ g\,mol^{-1}$ polymer in tetrahydrofuran (THF) remained for several hours after the cessation of shear, probably due to a strong interaction of HPC with THF.

Effects of cross-linking agents and network structure

As already mentioned, the basic goal of this part of the work is to cross-link CA and HPC chains so that their orientation in the swollen state is preserved under deformation. It is therefore important to test whether the presence of the cross-linking reactant or the subsequent network structure interferes in any way with the formation of an anisotropic phase [28–32].

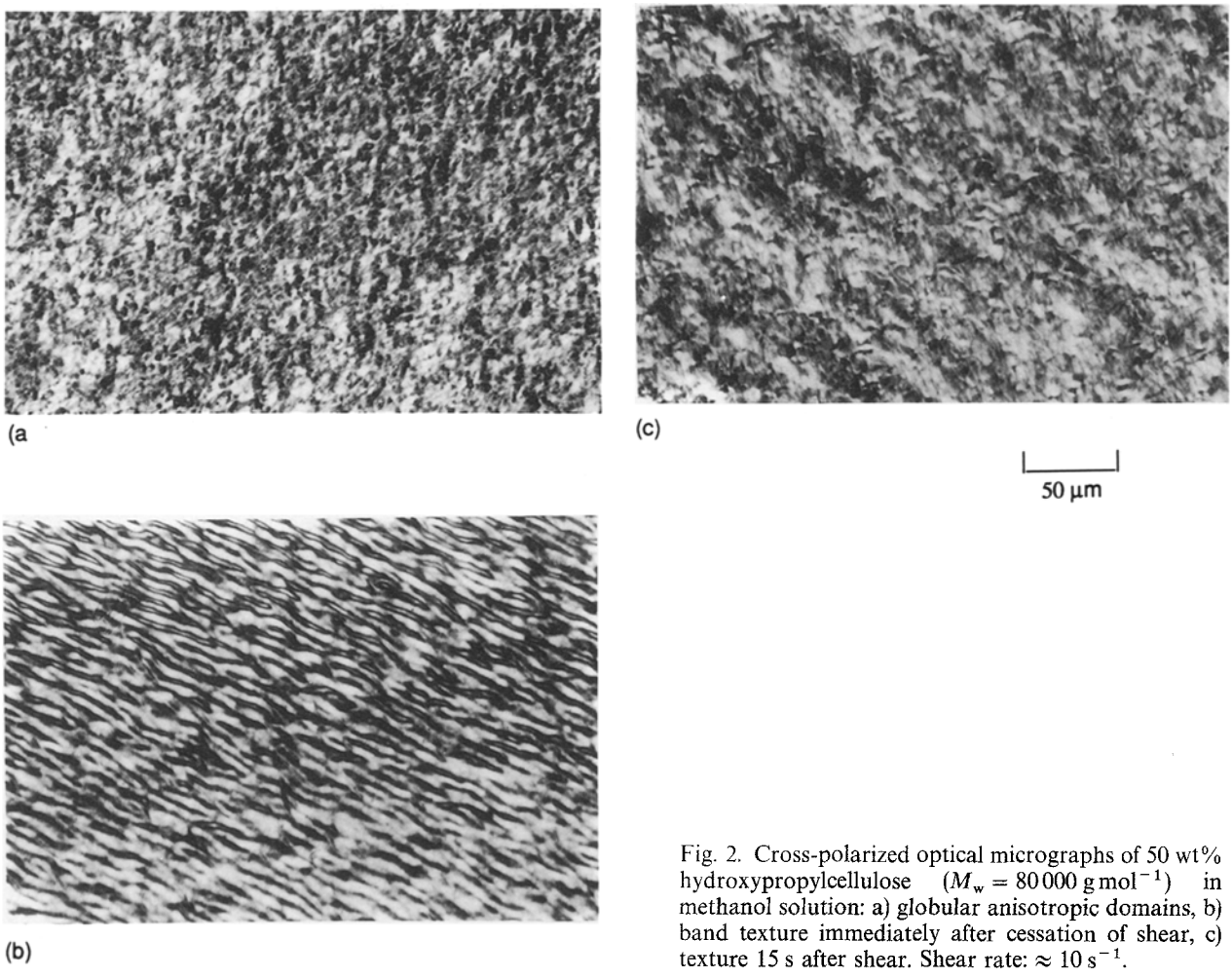

Fig. 2. Cross-polarized optical micrographs of 50 wt% hydroxypropylcellulose ($M_w = 80000\,g\,mol^{-1}$) in methanol solution: a) globular anisotropic domains, b) band texture immediately after cessation of shear, c) texture 15 s after shear. Shear rate: $\approx 10\,s^{-1}$.

Figure 3 is a photograph obtained using cross-polarized optical microscopy on HPC ($M_w = 80000\,g\,mol^{-1}$) in a methanol solution containing 0.01M HCl and about 1.0 wt% formaldehyde. The latter two ingredients are those required for the cross-linking of the HPC, and are seen to have little effect on the formation of the mesophase and texture of the polymer. There were no discernible changes in the system even after 2 weeks, indicating the cross-linking reaction is extremely slow at room temperature. In any case, the band texture induced by shear shown in Fig. 3(a) is similar to that in Fig. 2(b) for a HPC/methanol solution without any formaldehyde and hydrochloric acid. Also, the decay rate of the band texture did not appear to be significantly different and resulted in the usual type of globular structure shown in Fig. 3(b).

Results on a typical gel obtained from this cross-linking approach are given in Fig. 4 [34]. Part (a) shows the band texture of a HPC gel at a concentration of 50 wt% in methanol immediately after shearing. It demonstrates that the texture of the mesophase was essentially the same as that of uncross-linked HPC, in spite of the network structure. Part (b) is a micrograph taken 4 h after the cessation of shear. The desired stability of this texture over a considerable period of time has obviously been attained.

CA and HPC were also cross-linked in acetone at sufficiently high dilutions ($\approx 10\%$) for the

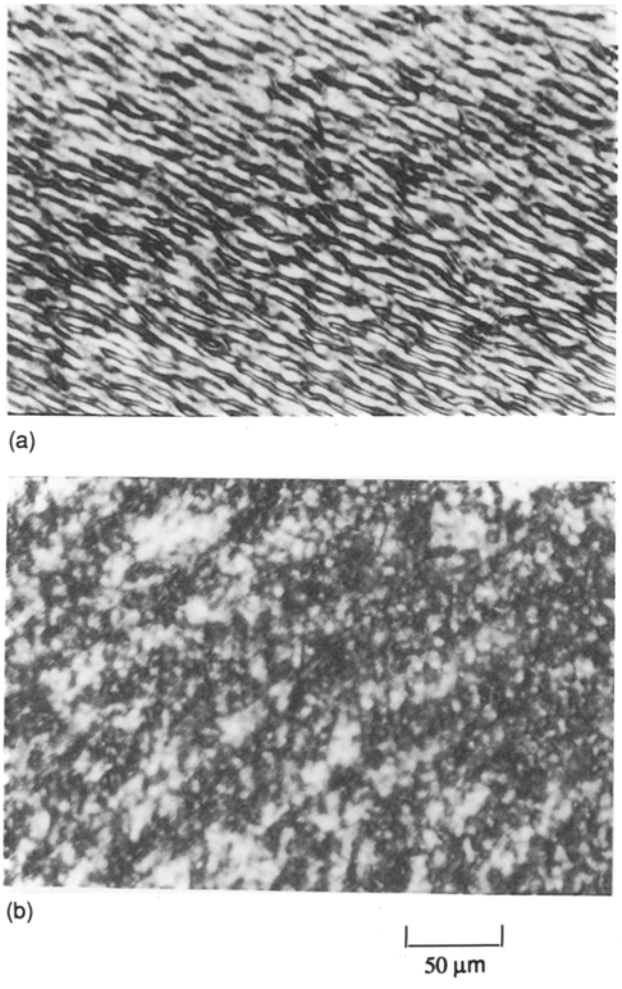

Fig. 3. Cross-polarized optical micrographs of 50 wt% HPC ($M_w = 80\,000\ g\,mol^{-1}$) methanol solution also containing the cross-linking reactants 0.01M HCl and 1.0 wt% formaldehyde: a) band texture immediately after shear, b) globular phase regenerated after cessation of shear. Shear rate: $\approx 10\ s^{-1}$.

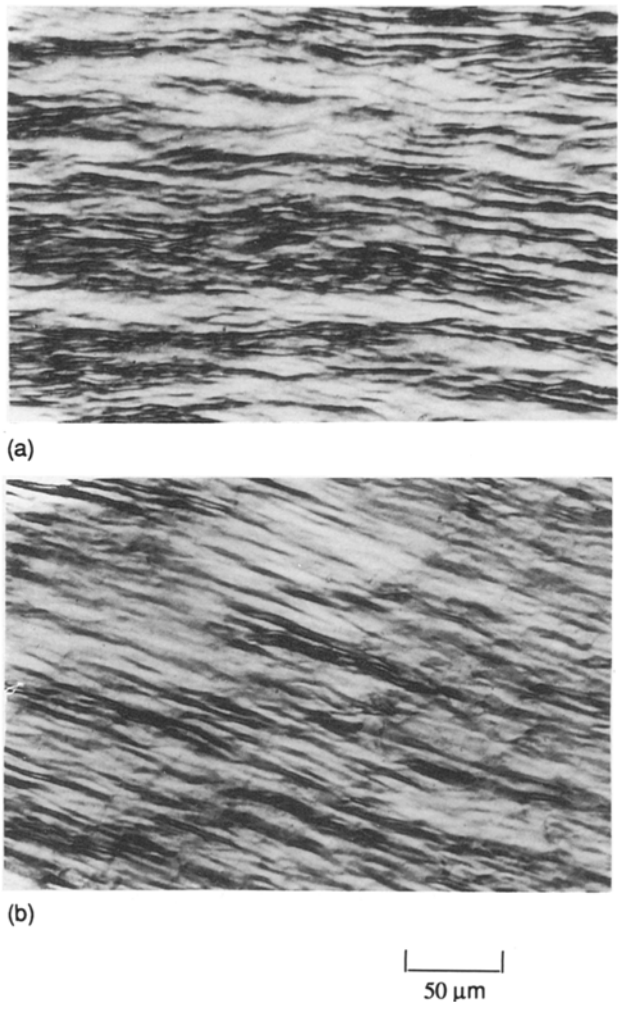

Fig. 4. Cross-polarized optical micrographs of *cross-linked* HPC swollen in methanol (50 wt%) a) band texture right after shear, b) band texture retained 4 h after shear. Shear rate: $\approx 10\ s^{-1}$.

solutions to be isotropic [34]. The resulting gels were then dried and reswelled (the CA in trifluoroethanol and the HPC in methanol), to a concentration of 50 wt%. Both displayed strong birefringence in cross-polarized optical microscopy. For example, the HPC gel in methanol was opaque and exhibited the same iridescent colors as uncross-inked HPC. It also showed a band texture after shearing, as shown in Fig. 5, which persisted for at least 4 h after cessation of shearing.

Since the cross-links in the networks have been shown to have little or no effect on the mesophases, it becomes of interest to obtain an estimate of their concentration, i.e., the cross-link density. Equilibrium swelling measurements of HPC gels in water gave volume increases of 5 to more than 10, which are much higher than those reported in an earlier study [34]. More quantitatively, the degree of cross-linking can be estimated using the standard Flory equation [41]:

$$M_c = \frac{-V_1\rho_2(v_{2m}^{1/3} - v_{2m}/2)}{\ln(1 - v_{2m}) + v_{2m} + \chi v_{2m}^2}, \quad (1)$$

where M_c is the average molecular weight between junctions (and thus an inverse measure of cross-link density), V_1 the molar volume of the

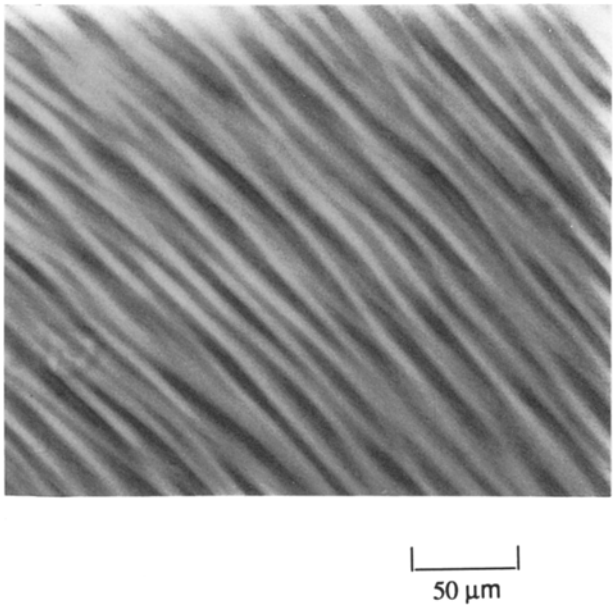

Fig. 5. Band texture generated upon shearing *networks* formed from HPC ($M_w = 80\,000\ g\,mol^{-1}$) in dilute, isotropic solution. The texture shown remained 4 h or more after cessation of shear. The concentration of polymer after drying and reswelling was 50 wt% (in MeOH).

solvent, ρ_2 the density of the polymer network, and v_{2m} the volume fraction of polymer in the network at equilibrium swelling. The Flory-Huggins interaction parameter χ was taken to be 0.47 for HPC in water at 25 °C [42]. Values of M_c thus estimated are in the vicinity of $20\,000\ g\,mol^{-1}$, suggesting a low degree of cross-linking. Additional values of M_c are presented elsewhere [34, 43].

The networks prepared as described above seem well suited for the processing steps to be applied in the second part of this investigation [43].

Conclusions

Anisotropic liquid-crystalline phase separations were observed in cellulose acetate and hydroxypropylcellulose in solutions of trifluoroethanol and methanol, respectively. Band textures were formed in these solutions upon applying a shearing force, and relaxed quickly to a globular texture.

Networks prepared from these polymers in the anisotropic state preserved their band structures after shearing, and should be well suited for the studies described in the following paper.

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References

1. Ward IM (1975) (ed) Structure and properties of oriented polymers. John Wiley & Sons, New York
2. Schuur G, Van Der Vegt AK (1975) In: Ward IM (ed) Structure and properties of oriented polymers. John Wiley & Sons, New York
3. Mark HF, Altas SM, Cernia E (1967) Man-made fibers, science and technology. Vol I, Wiley, New York
4. Carter CB, Schenk VTJ (1975) In: Ward IM (ed) Structure and properties of oriented polymers. John Wiley & Sons, New York
5. Gordon M, Platé NA (1984) (eds) Adv Polym Sci. Vol 59, Springer-Verlag Pub, Berlin
6. Ciferri A (1991) (ed) Liquid crystallinity in polymers. VCH Pub, New York
7. Welsh WJ, Bhaumik D, Jaffe HH, Mark JE (1984) Polym Eng Sci 24:218, and relevant references cited therein
8. Ciferri A (1975) Polym Eng Sci 15:191, and relevant references cited therein
9. Young RA, Rowell RM (1984) (eds) Cellulose. Structure, modification and hydrolysis. John Wiley & Sons, New York
10. Aharoni SC (1980) Mol Cryst Liq Cryst Lett 56:237
11. Kennedy JF, Phillips GO, Williams PA (1989) (eds) Cellulose. Structure and functional aspects. Ellis Horwood Limited, West Sussex
12. Shimamura K (1983) Makromol Chem Rapid Commun 4:107
13. Conio G, Bianchi E, Ciferri A, Tealdi A, Aden MA (1983) Macromolecules 16:264
14. Werbowyj RS, Gray DG (1976) Mol Cryst Liq Cryst Lett 34:97
15. Werbowyj RS, Gray DG (1980) Macromolecules 13:69; (1984) Macromolecules 17:1512
16. Bheda J, Fellers JF, White JL (1980) Colloid Polym Sci 258:1335
17. Asada T, Toda K, Onogi S (1981) Mol Cryst Liq Cryst 68:231
18. Nishio Y, Yamane T, Takahashi T (1985) J Polym Sci, Polym Phys Ed 23:1043
19. Erman B, Bahar I, Yang Y, Kloczkowski A, Mark JE (1992) In: Noda I, Rubingh DN (eds) Polymer solutions, blends, and interfaces. Elsevier Sci Pub, Amsterdam
20. Suto S, Kudo M, Karasawa M (1986) J Appl Polym Sci 31:1327
21. Warner M, Wang XJ (1991) Macromolecules 24:4923

22. Warner M, Wang XJ (1992) In: Mark JE, Erman B (eds) Elastomeric polymer networks. Prentice Hall, Englewood Cliffs, New Jersey
23. Erman B, Bahar I, Kloczkowski A, Mark JE (1991) Macromolecules 23:5335
24. Bahar I, Erman B, Kloczkowski A, Mark JE (1991) Macromolecules 23:5347
25. Erman B, Bahar I, Kloczkowski A, Mark JE (1992) In: Mark JE, Erman B (eds) Elastomeric polymer networks. Prentice Hall, Englewood Cliffs, New Jersey
26. Mark JE, Erman B (1988) Rubberlike elasticity. A molecular primer. Wiley-Interscience, New York
27. Suto S, Tashiro H (1989) Polymer 30:2063
28. Suto S (1989) J Appl Polym Sci 37:2781
29. Suto S, Tashiro H, Karasawa M (1992) J Appl Polym Sci 45:1569
30. Giasson J, Revol J-F, Gray DG, St.-Pierre J (1991) Macromolecules 24:1694
31. Song CQ, Litt MH, M-Zloczower I (1991) J Appl Polym Sci 42:2517
32. Song CQ, Litt MH, M-Zloczower I (1992) Macromolecules 25:2166
33. Mitchell GR, Gao W, Davis FJ (1992) Polymer 33:68
34. Yang Y (1993) Ph. D. Thesis in Chemistry, University of Cincinnati
35. Willard JJ, Schwenker Jr RF (1967) Text Res J 37:316
36. Lewin M, Weinstein S (1967) Text Res J 37:751
37. Gilbert RD, Patton PA (1983) Prog Polym Sci 9:115
38. Qian R, Chen S (1992) Makromol Chem Makromol Symp 53:345
39. Navard PJ (1986) J Polym Sci, Polym Phys Ed 24:435
40. Horio M, Ishikama S, Oda K (1985) J Appl Polym Sci, Appl Polym Symp 41:209
41. Flory PJ (1953) Principles of polymer chemistry. Cornell Univ Press, Ithaca, New York
42. Barton AFM (1991) Handbook of solubility parameters and other cohesion parameters. 2nd Ed, CRC Press, Boca Raton, Florida
43. Mark JE, Yang Y, Kloczkowski A, Erman B, Bahar I (1994) Colloid Polym Sci 272:391–397

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