Experimental Studies of Elastomeric and Optical Properties, and Strain-Induced Liquid-Crystalline Phase Transitions, in Deformed (Hydroxypropyl)cellulose Networks in the Swollen State

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ABSTRACT: Experimentally-determined stress–strain and strain–birefringence isotherms were used to characterize orientation, optical birefringence, and strain-induced liquid-crystalline phase transitions in (hydroxypropyl)cellulose networks. These networks were prepared by cross-linking the polymer in the isotropic state in dimethyl sulfoxide, with the network structure preserving the liquid-crystalline order exhibited by these semirigid chains. Measurements were carried out on the swollen networks, in both the anisotropic and the isotropic states. Discontinuities in the stress–strain and strain–birefringence isotherms were observed, suggesting a strain-induced isotropic-to-nematic phase transformation. The experimental results are in at least qulitative agreement with recent theoretical results based on a lattice model.

Introduction

There has been growing interest in polymer networks prepared from semirigid chains.[1–6] Chains of this type typically acquire their stiffness from aromatic or other ring structures having large rotational energy barriers, and their segments tend to be self-aligning, forming liquid-crystalline mesophases in melt or in solutions. Networks composed of these chains usually show exceptionally high degrees of segmental orientation and an isotropic-to-nematic phase transformation under macroscopic deformation. They thus have properties that are quite different from those of the idealized rubbery networks described by the classic theories of elasticity and photoelasticity.[7,8] Not surprisingly, their stress–strain and strain–birefringence isotherms show significant deviations from the predictions of these classical theories.[1]

In the last few years, several theoretical models for elastic properties of nematic networks have been proposed. For example, a lattice model was recently used to study the stress–strain and strain–birefringence properties of such materials.[6] Numerical analysis of the model showed not only nonlinear relationships between the strain, stress, and optical birefringence but also discontinuities in the stress–strain and stress–birefringence isotherms. This extraordinary behavior is associated with strain-induced isotropic-to-nematic phase transformation of the semirigid chains upon deformation. However, little experimental work has been done on such networks, particularly when they are in the swollen state.

The isotropic-to-nematic phase transformation in a deformed network of semi-rigid chains is of special interest when the networks are swollen because the liquid-crystalline phase transition may then be driven either by an applied force or by changes in the degree of swelling. These two parameters are coupled in that the anisotropic phase can occur only at polymer concentrations exceeding a critical value.

(Hydroxypropyl)cellulose (HPC) is a good candidate for studies of this type since it shows liquid-crystalline phase separation in a variety of solvents,[9–14] and cross-linking it is known to make quite permanent the desired anisotropic ordering of the chains.[15–19] In fact, if the cross-link density is properly controlled, networks of this polymer can have extension ratios larger than 10. They are thus eminently suitable for experimental studies of stress–strain and strain–birefringence properties of semirigid chains. Experimental measurements of stress–strain and strain–birefringence isotherms in the present work were therefore carried out on HPC networks swollen to different extents, with the networks occurring in various types of phases. Of particular interest was strain-induced orientational ordering (as measured by the orientation function and by optical birefringence) and isotropic–nematic phase transitions driven by the force or by changes in the degree of swelling. The experimental results thus obtained were compared with theoretical predictions of a lattice model of the system.[6]

Experimental Details

The sample of HPC employed was obtained from Hercules Inc. and had a weight-average molecular weight $M_w = 370\,000$. It was cross-linked using formaldehyde (Aldrich Co.) in a solution of acetone at a concentration of about 5%. Hydrochloric acid was used as the catalyst, the solution had a pH of 2, and the reaction was carried out at 56 °C for 1 h. The resulting gel was dried under ambient conditions, so as to form a film which was then extracted with distilled water to remove any soluble polymer as well as unreacted formaldehyde and hydrochloric acid. The HPC network thus prepared had a cross-link density corresponding to a molecular weight M_c between cross-links of approximately 20×10^3 as determined from equilibrium swelling measurements[20] (using 0.47 for the Flory–Huggins interaction parameter).[21]

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The stress–strain and strain–birefringence measurements were carried out at room temperature (22 °C) by uniaxial extension of the cross-linked HPC in the form of strips ($40 \times 4 \times 0.5$ mm^3) swollen in dimethyl sulfoxide (DMSO). Each measurement was taken 2 h after the force had relaxed to a steady value to assure a close approach to equilibrium.

The results of the stress–strain measurements were conventionally analyzed, in terms of the reduced modulus

$$[f^*] \equiv f^* v_2^{1/3}/(\alpha - \alpha^{-2}) \qquad (1)$$

where f^* is the force applied over the cross-sectional area of the undeformed sample, v_2 is the volume fraction of polymer, and α is the extension ratio. Values were analyzed in the usual way, as a function of the reciprocal elongation.

The birefringence was measured as a function of strain using the compensation method.[22] The results of the strain–birefringence measurements were analyzed by plotting the reduced birefringence

$$[\Delta n] \equiv \Delta n v_2^{1/3}/(\alpha - \alpha^{-2}) \qquad (2)$$

against reciprocal elongation. The stress-optical coefficient was then calculated from

$$C \equiv \Delta n/\sigma \qquad (3)$$

where σ is the true stress (force per unit deformed area of the sample).

Results and Discussion

HPC networks which had been prepared in an isotropic solution (~5% g/mL in acetone) retained liquid-crystalline order in DMSO, as observed under a cross-polarized optical microscope. This anisotropic phase was further evidenced by the appearance of a band texture upon applying a sheer force. The cross-linking did not seem to alter the texture of the liquid-crystalline phase and permitted attainment of the liquid-crystalline order in the network even when it was cross-linked in the isotropic state. The critical concentration for the phase transition for a HPC network in DMSO remained about the same as that of un-cross-linked HPC, specifically with a value of v_{2c} slightly above 0.40.[23] The networks swollen to different volume fractions exhibited states ranging from isotropic to biphasic and to cholesteric (twisted nematic) phases. Stress-strain and strain–birefringence isotherms were obtained for networks in all these phases.

Figure 1a shows the stress–strain isotherms of the HPC network swollen in dimethyl sulfoxide. The network with a volume fraction v_2 of 0.70 is anisotropic, forming a cholesteric phase. Phases of this type have previously been reported for this polymer under similar conditions.[15–19,23] The stress–strain curve shown in Figure 1a reveals a continuous increase of stress with elongation. The stress–strain behaviour does not indicate a "polydomain-to-monodomain" transformation, as reportedly observed for side-chain liquid-crystalline elastomers[1] (in which the stress–strain curve exhibits a "flat horizontal region", suggesting a reorientation of directors when the applied force reaches a threshold value).

This absence of a polydomain-to-monodomain transformation for the HPC network is probably due to the effect of swelling, which reduces the threshold value for an external field, such as the mechanical force, to reorient the directors of the nematic mesophases. Such a critical value could be reduced to zero. Therefore, rather than a sudden initiation of reorientation of the directors at a critical value of the external mechanical force, the directors of the anisotropic phases in the swollen network may be orienting continuously with stress. In this case, the polydomain-to-monodomain transformation would be a gradual and continuous process.

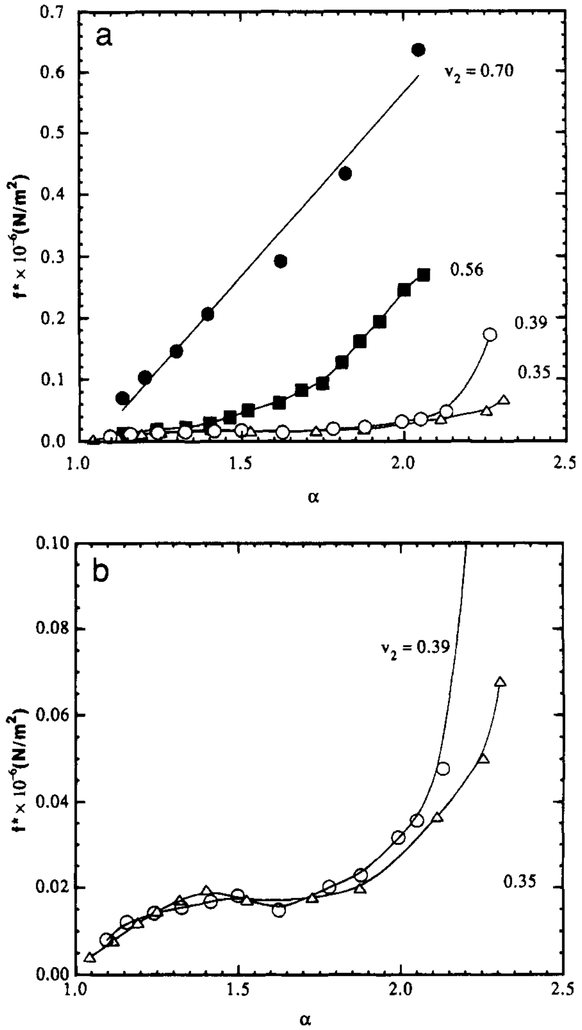

Figure 1. Stress–strain isotherms for (hydroxypropyl)cellulose (HPC) networks swollen in DMSO, with volume fractions of polymer present as indicated: (a) $v_2 = 0.70$, 0.56, 0.39, and 0.35; (b) a detailed and expanded plot for $v_2 = 0.39$ and 0.35.

For the network with v_2 equal to 0.56, the stress–strain isotherm has two distinct regions. At low elongations, the stress increases slowly with an increase in elongation. This part of the curve is flat and has a much smaller slope in comparison to that for v_2 at 0.70. When the elongation exceeds approximately 1.5, the stress–strain curve shows an upturn, with the stress increasing rapidly with elongation, which is similar to the case $v_2 = 0.70$. The flat region at low elongations is most probably associated with the stress–strain behavior of a HPC network in a biphasic state, which was observed for samples of this un-cross-linked polymer in a number of other solvents.[10] With further increase in elongation, the network reaches a single anisotropic phase. The stress–strain behavior is then represented by the second part of the curve, which is very similar to that for a network with v_2 equal to 0.70.

The stress-strain curves for networks with v_2 smaller than the critical isotropic-to-nematic phase transition concentration are shown in more detail in Figure 1b. They consist of three parts. In the region with elongation below 1.4, the stress is continuously and smoothly

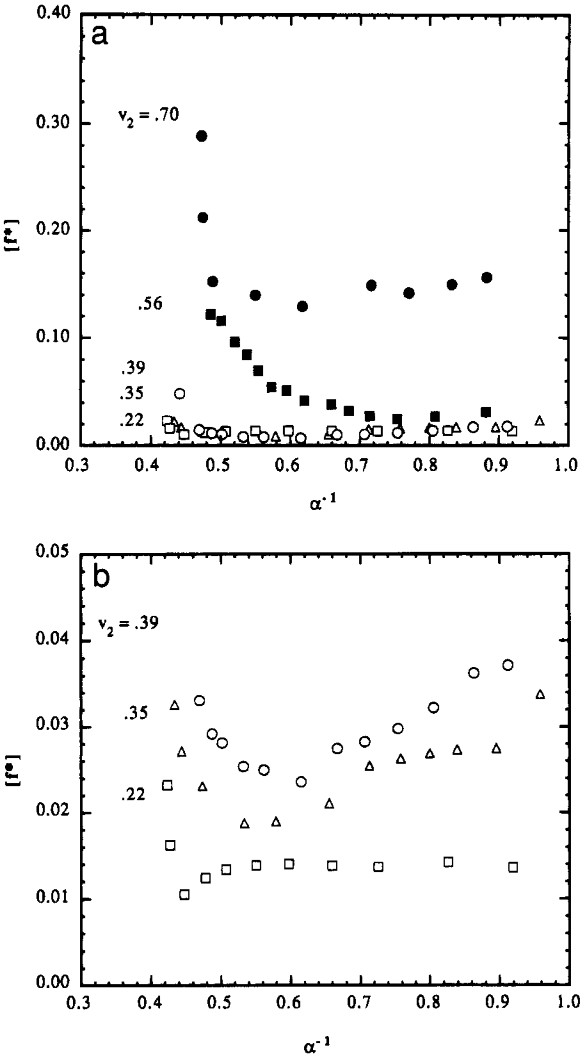

Figure 2. Reduced modulus versus reciprocal elongation for HPC networks swollen in DMSO, with volume fractions of polymer as indicated: (a) $v_2 = 0.70$, 0.56, 0.39, 0.35, and 0.22; (b) a detailed and expanded plot for $v_2 = 0.39$ and 0.35.

increasing with extension. In the second region, with elongations between 1.4 and 1.8, the force remains almost constant, regardless of the elongation. As the elongation is increased to 1.8, the stress–strain isotherm reaches the third region, where the stress increases rapidly with elongation.

These experimental results are in good qualitative agreement with the theoretical predictions of the lattice model.[6] The experimental stress–strain isotherms obtained for networks with v_2 of 0.39 and 0.35 in Figure 1b are similar to that calculated from the lattice model (for v_2 of 0.60 and 0.62) shown in Figure 2 of ref 6. The experimental results, however, also show higher forces for lower volume fractions of the polymer, the opposite of the theoretical predictions. This is probably due to the strong hydrogen bonding of (hydroxypropyl)cellulose, which increases drastically with an increase in the polymer concentration.

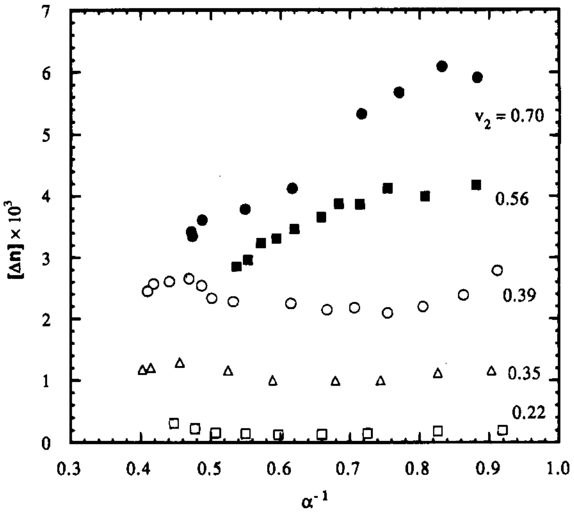

Figure 3. Reduced birefringence versus reciprocal elongation for HPC networks swollen in DMSO, with volume fractions of the polymer as indicated.

The reduced modulus is plotted in parts a and b of Figure 2 a function of reciprocal elongation for HPC networks having the swelling values indicated on the curves. These figures also show an increase in the reduced modulus with an increase in the polymer concentration, due to the strong hydrogen bonding. The reduced modulus [f^*] remains almost constant or decreases slightly at small elongations for networks in the anisotropic state (with v_2 of 0.56 and 0.70). This is possibly due to the reorientation of liquid-crystalline mesophases (the polydomain-to-monodomain transition). The response of the chiral nematic phase to the elongation could be a combination of reorientation of the directors and an untwisting of the chain segments. Higher elongations could then make the anisotropic phase nematic. At such higher elongations, an increase in [f^*] with elongation is observed, which may be attributed to anisotropic phase separation. The liquid-crystalline domains probably act as fillers as well as additional junctions. Films with values of v_2 below 0.4 are isotropic in the undeformed state. Their stress–strain isotherms display a continuous decrease of the modulus [f^*] with α^{-1} at small elongations, which is typical behavior of nonorganizing networks. Further increase in the elongation then results in a strain-induced isotropic-to-anisotropic phase transition, at which the reduced modulus first drops and then increases rapidly in a sharp upturn. Results recently obtained from the lattice model are at least qualitatively in agreement with this.[6]

A plot of reduced birefringence against reciprocal elongation is shown in Figure 3. For the anisotropic network with a volume fraction of HPC equal to 0.70 there is an approximately monotonic decrease of the reduced birefringence with increasing elongation. At $v_2 = 0.56$, the curve displays a flat region at low elongations followed by a similar decrease in reduced birefringence with increasing α. This observation may have the same interpretation as that for the stress–strain isotherms. Undeformed networks with v_2 at 0.56 are in the biphasic state, and the mechanical deformation induces a single anisotropic phase. Gels with smaller volume fractions of polymer (v_2 equal to 0.39 or 0.35) are isotropic in the undeformed state. The strain-induced isotropic–nematic phase transition in these networks is revealed by the zigzag-type of dependence of the reduced birefringence [Δn] on α^{-1}.

It may be expected that, for gels with very small v_2, the anisotropic phase may never be obtained upon deformation or that one will see only a biphasic state. The reduced birefringence of cross-linked HPC with v_2 equal to 0.22 in Figure 3 shows almost a constant value with increasing elongation and only a small upturn at large extensions. This suggests that for low and moder-

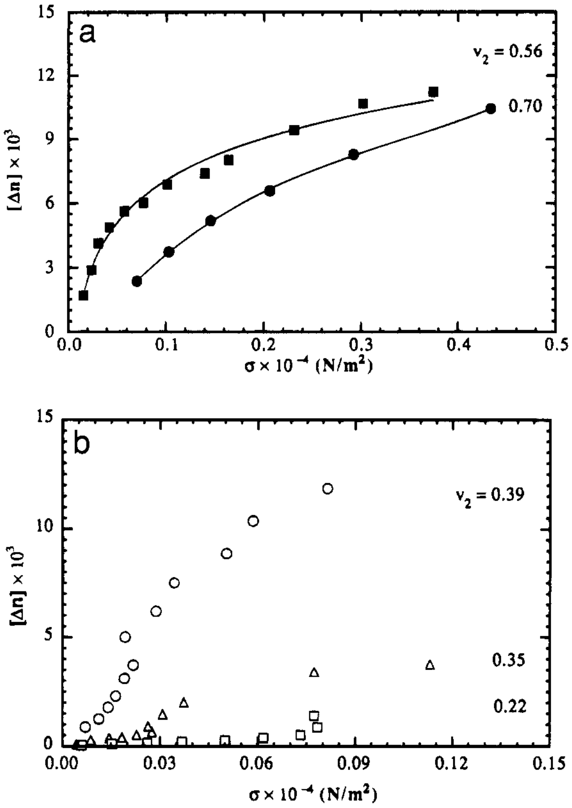

Figure 4. Birefringence as a function of true force for HPC networks swollen in DMSO, with volume fractions of the polymer as indicated: (a) v_2 = 0.70 and 0.56; (b) v_2 = 0.39, 0.35, and 0.22.

ate extensions the network is in the isotropic state and at large elongations is in the biphasic state.

The similarities between the experimental results and those obtained from numerical analysis of the lattice model[6] support the conclusion that the observed anomalies in the isotherms are associated with strain-induced phase transitions in these swollen, deformed networks. It is also worth noting that the experimentally-observed isotropic-to-nematic phase transition may be associated with much broader regions of extensions and much milder downturns in the modulus than in the theoretical predictions, most probably due to the biphasic state of the network during the phase transition.[24-26]

Parts a and b of Figure 4 show the birefringence Δn as function of the true force σ. The S-shaped birefringence–force relation in Figure 4b for HPC networks with v_2 = 0.35 and 0.39 suggests a strain-induced phase transformation from isotropic to biphasic and finally to a single anisotropic state.[27] The changes are gradual, as is shown for the elongation dependence of the properties of such networks over some composition ranges.[6,28] For the network with v_2 equal to 0.22, the upturn in the $\Delta n-\sigma$ relation at large elongations suggests a phase transition from the isotropic phase to the biphasic state. Figure 4a shows the birefringence–stress relations for the networks with v_2 = 0.70 and 0.56, which correspond to the anisotropic state (v_2 = 0.70) and the biphasic state (v_2 = 0.56) of the undeformed network. The birefringence of the network with v_2 = 0.56 shows a rapid increase at small stresses, suggesting an induced biphasic-to-nematic phase transformation. The increase levels off with a further increase in the stress, displaying a linear relation similar to that for the network in a single anisotropic state (v_2 = 0.70). The birefringence (at the same stress) of the gel with v_2 = 0.56 is larger than that for 0.70. This is probably due to strong hydrogen bonding, which requires much larger stresses to deform the network with higher volume fractions of polymer.

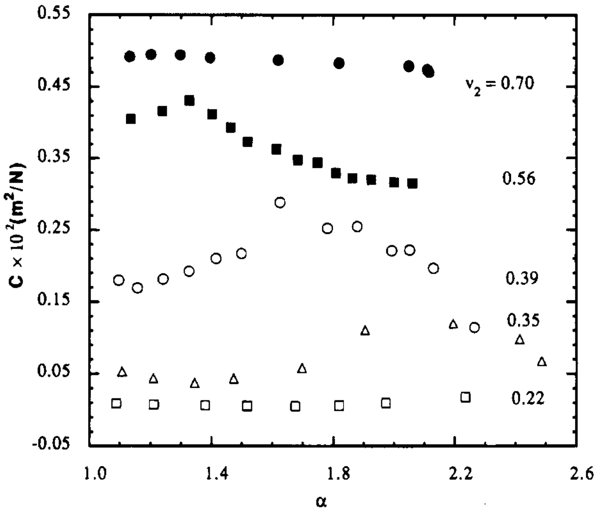

Figure 5. Stress-optical coefficient C plotted against elongation α for HPC networks swollen with DMSO, with volume fractions of the polymer as indicated.

The stress-optical coefficient C for networks having different degrees of swelling is shown as a function of the elongation in Figure 5. The absolute values of C do not show any regularity and require no discussion. The curves are shifted vertically in order to compare the individual behavior for the networks with different volume fractions of polymer. The strong dependence of C on α for the HPC networks is another indication of isotropic-to-nematic phase transitions induced by the macroscopic deformation. The network which had stretched in the isotropic state and had ruptured in the anisotropic state exhibited two interesting features in the $C-\alpha$ plot. The first corresponds to a isotropic-to-biphasic phase transformation and the second to a biphasic-to-anisotropic transformation, respectively. These transformations were observed in swollen networks with v_2 = 0.35 and 0.39. The stress-optical coefficient C remains almost constant for v_2 = 0.22, indicating that chains are more flexibile in a dilute system until much larger elongations, where a small increase in C suggests a phase transition. The downturn in the $C-\alpha$ relation for a network with v_2 at 0.56 reflects a transformation of the biphasic-to-anisotropic type. At v_2 equal to 0.70, the gel is anisotropic, and an almost linear dependence of C on elongation α is observed. A very similar dependence of the stress-optical coefficient on elongation and the degree of swelling in networks of semirigid chains undergoing stress-induced liquid-crystalline phase transitions was recently predicted theoretically by the lattice model.[6]

The experimental results presented in this paper show that cross-linked (hydroxypropyl)cellulose networks swollen in DMSO show induced nematic–isotropic phase transitions, which may be driven both by mechanical deformation and by the degree of swelling. There is at least qualitative agreement between the experimental data and theoretical predictions for networks of semirigid chains.

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