Enhanced anisotropic ordering and phase separation in lyotropic polysaccharide blends

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^2H n.m.r. spectroscopy is employed to characterize the mesomorphic behaviour of hydroxypropyl cellulose (HPC) in D_2O. This analysis is further extended to ternary solutions containing HPC and xanthan gum (XG). A compositional range over which addition of XG to HPC enhances single-phase anisotropic ordering is reported. Convoluted spectra representative of HPC-rich and XG-rich components are observed at some blend and solution concentrations, suggesting that phase separation occurs between these two lyotropic polysaccharides.

(Keywords: hydroxypropyl cellulose; xanthan gum; lyotropic polysaccharide; liquid crystalline polymers; nuclear magnetic resonance)

Several derivatives of native cellulose are known to exhibit liquid crystalline behaviour due to retention of a semiflexible backbone composed of β-D-glucose monomers. One of the most extensively studied synthetic polymers in this vein is hydroxypropyl cellulose (HPC), which becomes lyotropic over broad concentration ranges in a variety of common solvents[1,2], including water[3–6], and thermotropic at temperatures just above 200°C[7]. Another common cellulosic derivative is xanthan gum (XG), a natural polysaccharide produced from the bacterium *Xanthomonas campestris* and used in numerous applications as a thickener[8]. Due to the β-(1 → 4) linkages connecting its glucose monomers along the backbone, XG also behaves as a relatively rigid molecule, even in dilute solution[9]. Three-dimensional order is, however, frustrated by the bulky side group composed of two mannose units and one glucuronic unit. Rinaudo *et al.*[10–12] have demonstrated that XG, like HPC, exhibits a mesophase in water.

Most cellulose derivatives, including HPC and XG, assume helical conformations[13–15] and consequently exhibit cholesteric mesophases. A variety of analytical techniques (such as polarized light microscopy, X-ray diffractometry and circular dichroism) have been employed to characterize these textures and to identify the conditions responsible for such supramolecular ordering. A technique introduced by Werbowyj and Gray[4] for studying mesomorphic HPC in an aqueous medium is ^2H n.m.r. spectroscopy. Due to alignment of the HPC molecules, D_2O becomes preferentially oriented in the imposed magnetic field, and resulting spectra exhibit quadrupolar peak splitting. More recent efforts[16,17] using this technique have shown that the extent of peak splitting (and molecular anisotropy) decreases with temperature and increases with HPC concentration (ϕ_{HPC}). ^2H n.m.r. has also been applied to aqueous solutions containing XG and reveals that the resultant single D_2O peak broadens and flattens with an increase in XG concentration (ϕ_{XG})[17]. The objectives of the present work are to (1) employ ^2H n.m.r. to correlate the anisotropic order arising in mesomorphic HPC solutions with ϕ_{HPC} and (2) extend the analysis to blends of HPC/XG in D_2O when $\phi_{XG} \leqslant 0.2$.

The HPC used throughout this study was Klucel-E purchased in powder form from Aqualon (Wilmington, DE, USA). According to the manufacturer, this material possessed a nominal molecular weight of ~80 000 g mol^{-1}. Unfractionated XG powder was supplied as Keltrol-F by Kelco (San Diego, CA, USA). The molecular weight was not determined here but can range from 2×10^6 to 15×10^6 g mol^{-1}, depending on bacterial strain[8]. Solutions of as-received HPC and HPC/XG were prepared in 99.9% pure D deuterium oxide from Cambridge Isotope Laboratories (Woburn, MA, USA). Since HPC and XG are known to be hydrophilic, powders of each were dried for at least 12 h at 100°C prior to dissolution. After heating, the polymers possessed ~2.5 wt% water from moisture uptake, which was taken into account in determining the final solution concentrations. Solutions containing HPC and XG were prepared by first mixing the dried powders.

Upon equilibration for 10 days at ambient temperature, each resulting solution was inserted into a 10 mm n.m.r. tube and analysed at 46.12 MHz in a General Electric GN-300 spectrometer. All of the spectra shown here were acquired at 25°C using a single pulse with a 1 s delay. Since some of the concentrated solutions showed signs of shear thinning during insertion into the glass tubes, spectra were collected at several different times to guarantee spectra representative of the initial relaxed solutions[17].

^2H n.m.r. spectra obtained from pure HPC at various concentrations in D_2O are shown in *Figure 1*. Below the critical concentration of mesophase formation ($\phi^*_{HPC} \approx 0.41$)[2–4], the spectra consist of a single isotropic peak. Above ϕ^*_{HPC}, though, the peak develops base wings, followed by peak splitting as ϕ_{HPC} increases. Quadrupolar peak splitting reflects the preferential orientation of the D_2O molecules in an anisotropic HPC mesophase. For axially symmetric systems, the magnitude of the main

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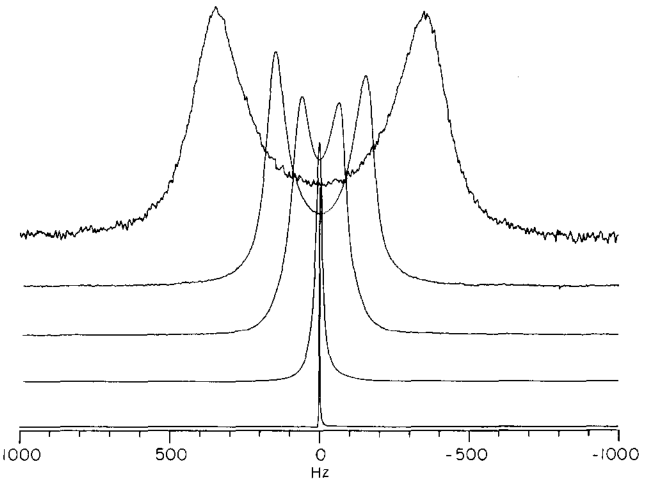

Figure 1 ^2H n.m.r. spectra obtained from solutions of HPC in D_2O. The concentrations of HPC are (from bottom to top) 0.00, 0.40, 0.50, 0.60 and 0.70. Note that the quadrupolar peak splitting increases with ϕ_{HPC} in mesomorphic solutions above the critical concentration (ϕ^*_{HPC}) of 0.41 (refs 2–4). All of the data presented here have been acquired at 25°C

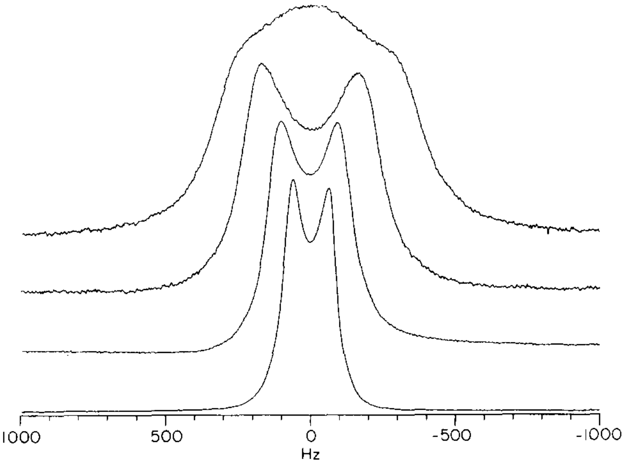

Figure 2 Representative ^2H n.m.r. spectra from mesomorphic solutions containing both HPC and XG. Here, $\phi_{HPC} = 0.50$ and ϕ_{XG} is increased from 0.00 to 0.15 (in increments of 0.05) from bottom to top. The peak splitting seen in the lower three spectra reflects single-phase behaviour, increasing in magnitude with ϕ_{XG}. The spectrum shown at the top ($\phi_{XG} = 0.15$ and $\phi_P = 0.65$) possesses convoluted components from both HPC (split peaks) and XG (middle peak)

splitting ($\Delta\nu_q$) is given by:

$$\Delta\nu_q = \frac{3}{4}\frac{e^2|q|Q}{h}\langle 3\cos^2\theta - 1\rangle \qquad (1)$$

where $e^2|q|Q/h$ is the quadrupole coupling constant[16,18], equal to ~220 kHz for D_2O[19], and θ is the angle between the applied magnetic field and the O-D bond vector. The angled brackets in equation (1) denote a time average. As seen in *Figure 1* and discussed again later, $\Delta\nu_q$ is found to be a monotonically increasing function of ϕ_{HPC}. No spectra are provided here for pure XG in D_2O. Suffice it to say that D_2O (and H_2O) molecules lose their mobility in the presence of XG[17,20].

Spectra representative of blends composed of HPC and up to 20% XG are presented in *Figure 2*, in which ϕ_{HPC} is held constant at 0.50 and ϕ_{XG} is increased from 0.00 to 0.15 in increments of 0.05. The total polysaccharide concentration is denoted here by ϕ_P and is equal to $\phi_{HPC} + \phi_{XG}$ on a wt/v basis. As in *Figure 1*, $\Delta\nu_q$ increases with ϕ_P. Note that the spectra appear to reflect single-phase behaviour when $\phi_{XG} \leqslant 0.10$. Similar results are observed up to $\phi_P = 0.55$ in blends containing 40% HPC. When $\phi_{XG} > 0.15$ or $\phi_P \geqslant 0.65$, however, three peaks develop in the frequency spectra, as seen for $\phi_{XG} = 0.15$ in *Figure 2*. Deconvolution of the peaks reveals two sets of spectra, one from an XG-rich component possessing a broad middle peak and the other from an HPC-rich component exhibiting a pair of split peaks. The value of $\Delta\nu_q$ obtained from the split peaks is sensitive to the shear thinning induced prior to analysis. Upon relaxation, however, $\Delta\nu_q$ reaches a constant value nearly equal in magnitude to that of pure HPC at $\phi_{HPC} = \phi_P$. This observed behaviour is discussed further below.

Values of $\Delta\nu_q$ are plotted as a function of ϕ_P on double-logarithmic coordinates in *Figure 3*. When $\phi_{XG} = 0$ and $\phi_P = \phi_{HPC}$, $\Delta\nu_q$ is correlated with ϕ_P to yield:

$$\Delta\nu_q = \Delta\nu_q^\circ \phi_P^\alpha \qquad (2)$$

where $\Delta\nu_q^\circ = 4434$ Hz, $\alpha = 5.18$ and the correlation coefficient is 0.9993. The prefactor $\Delta\nu_q^\circ$ corresponds to the peak split in the hypothetical limit of zero solvent (i.e. $\phi_P \rightarrow 1$). Similar scaling behaviour has been reported[2,21] for another parameter characteristic of the anisotropic ordering in HPC/H_2O solutions, namely, the cholesteric pitch (p). This physical property is a direct measure of the supramolecular organization and is also found to scale as ϕ_{HPC}^β, where β is a function of the solvent employed. For an aqueous medium, $\beta \approx -3.20$.

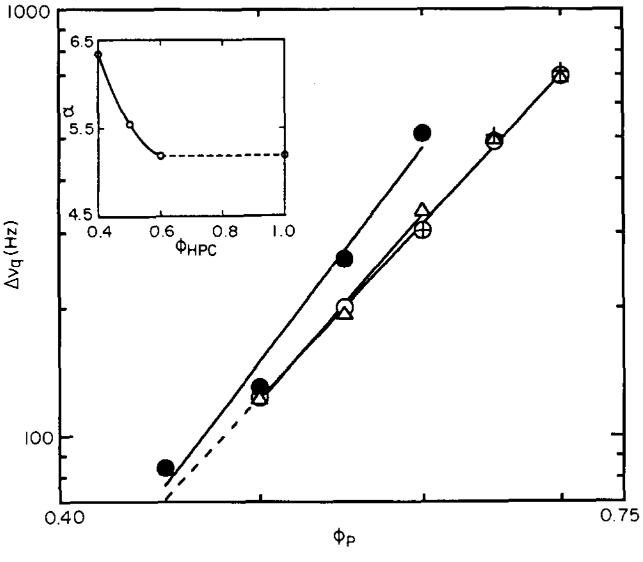

Figure 3 Graphical representation of $\Delta\nu_q$ as a function of polysaccharide concentration ϕ_P for blends with ϕ_{HPC} equal to 0.40 (●), 0.50 (△), 0.60 (+) and 1.00 (○). Note that small increases of XG ($\leqslant$0.20) can promote a significant increase in the extent of anisotropic ordering in mesomorphic HPC. The broken line extending from the $\phi_{HPC} = 1.00$ curve has been extrapolated to 0.45 using equation (2); further extrapolation to $\phi^*_{HPC} = 0.41$ yields 38 Hz (which compares favourably with 36 Hz from the extrapolated $\phi_{HPC} = 0.40$ curve). Above $\phi_P = 0.65$, the observed peak splitting for HPC/XG solution blends coincides with that of pure HPC at $\phi_{HPC} = \phi_P$, suggesting that partial phase separation occurs between the two polysaccharides. The inset shows the dependence of the scaling exponent α (in $\Delta\nu_q \sim \phi_P^\alpha$) on ϕ_{HPC}

Combination of these relationships suggests that, for aqueous mesophases containing HPC only, $\Delta\nu_q$ can be estimated from p.

When ϕ_{XG} is increased from zero in *Figure 3*, $\Delta\nu_q$ is nearly proportional to ϕ_P^α, where α assumes values of 6.34 ($\phi_{HPC} = 0.40$) and 5.55 ($\phi_{HPC} = 0.50$). (Note that the curve corresponding to $\phi_{HPC} = 0.40$ appears to possess some upward curvature on this double-logarithmic representation.) If $\phi_P > 0.65$ and ϕ_{HPC} is equal to 0.50 or 0.60, $\Delta\nu_q(\phi_P) \approx \Delta\nu_q(\phi_{HPC} = \phi_P)$, which suggests that some of the added XG mimics HPC and is incorporated into the HPC mesophase. The deconvoluted split peaks in the top of *Figure 2* consequently reflect HPC/XG and not HPC alone. As the HPC texture becomes tighter at these levels of ϕ_{HPC}, not all of the XG present is accommodated within the HPC-rich mesophase and partial phase separation between HPC and XG results. In this regime, $\alpha(\phi_{HPC} < 1.0)$ reduces to $\alpha(\phi_{HPC} = 1.0)$. The functional relationship of $\alpha(\phi_{HPC})$ determined here is presented in the inset of *Figure 3*. The magnitude of $\alpha(\phi_{HPC} = 1.0)$ may vary[16,17], depending on processing. Under identical preparation conditions, though, addition of XG to HPC consistently produces an increase in α at low ϕ_{HPC} or no change in α at high ϕ_{HPC}.

This work has demonstrated that the addition of small quantities ($\leqslant 20\%$) of XG to mesomorphic HPC influences the anisotropic ordering of the resulting HPC/XG mesophases. Since XG by itself enters into a lyotropic mesophase at relatively low concentrations (~ 3.5 wt%) in water, it is presumed to assist HPC in co-operatively developing a single cholesteric texture insofar as it can be accommodated within the HPC mesophase. At relatively low ϕ_{XG}, the disruptive influence of the bulky side chains on XG is expected to be minimal and single-phase behaviour is observed when ϕ_{HPC} is low. At specific blend and solution concentrations (ϕ_{XG} and ϕ_P, respectively), phase separation becomes favoured and the single peak corresponding to XG emerges in ^{2}H n.m.r. spectra. Under these conditions, XG may be excluded from the more tightly packed HPC texture (recall that p decreases as ϕ_{HPC} increases) due to its bulky side groups or it may undergo self-association or a conformational change[20,22]. A fraction of the added XG is, however, believed to remain incorporated in the HPC mesophase, assisting in supramolecular organization, as demonstrated by the observed shift in $\Delta\nu_q$ from $\Delta\nu_q(\phi_{HPC})$. It is of interest to note here that blends of HPC and ethyl cellulose have been observed[23] to phase-separate and produce coexisting mesophases in acrylic acid.

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