

# Quick Way to Prepare Anisotropic Solutions of Hydroxypropylcellulose in Water

## INTRODUCTION

The hydroxypropylcellulose (HPC)–water system is one of the first systems where liquid crystallinity in solutions of polymers has been recognized.<sup>1</sup> An idealized structure of HPC is shown in Figure 1.

This system is known to exhibit a complex phase behavior including the formation of an isotropic and a mesomorphic phase, but also a reversible phase transition upon heating.<sup>1–4</sup> However, it is quite difficult and time consuming to obtain homogenous solutions with a concentration of 50–80%. Therefore an alternative way to obtain anisotropic and isotropic solutions of HPC in water will be described.

## EXPERIMENTAL

The different mixtures investigated were prepared by the following procedure. Air dry HPC (Aldrich,  $M_w = 100,000$ ) was mixed with the calculated amount of distilled water in a Teflon-sealed sample vial. The vial was heated to about 70°C until a white precipitate was formed. After cooling to 25°C, the solution became transparent. Using several cycles, the solution was homogenized and was ready for the investigations. A gas phase chromatograph (GPC) with two aquagels [Polymer Laboratories (OH60 and OH40)] was used to check the molecular weight distribution before and after the dissolving process. Liquid crystalline behavior was determined visually with a Linkam THM 600 hot stage mounted on a Zeiss Ultraphot optical microscope.

## RESULTS AND DISCUSSION

A modified phase diagram of the HPC–water system is shown in Figure 2.<sup>4</sup> The different regions are marked in the phase diagrams. The similarity of the phase diagrams of different systems of stiff main-chain polymers in solution is obvious.<sup>4,5</sup> Moreover, all systems display a peritectic line connected with the formation of a crystal solvate at high temperatures. These crystal solvate phases have very similar constitutions, specifically the systems PBZT–

PPA/H<sub>2</sub>O<sup>5</sup> and HPC–H<sub>2</sub>O<sup>4</sup> form a crystal solvate where two solvent molecules are aggregated to an H-bond active site (NH— group and OH group). The association of solvent molecules is also present in all systems in the homogeneous phases, in the isotropic phase, and in the anisotropic phase.<sup>1,4–6</sup> The isotropic phase at high temperatures was described as an infinitely diluted solution<sup>3</sup> which has been proved by <sup>1</sup>H-NMR spectroscopy.<sup>4</sup> With a change in temperature there is a change in the degree of associated water per monomeric unit, which includes either the formation of crystal solvates or a precipitation of the polymer. Therefore, the isotropic phase at high temperatures is formed by the split off water, which is not associated to the crystal solvate.

The knowledge of the phase diagram and the composition of the phases has led to a novel technique for preparation of highly concentrated solutions by an easy and quick way. As described in the experimental part, the solutions were prepared by heating a mixture of water and dry HPC until the crystal solvate was formed. This happened in a short time due to the high vapor pressure of water at high temperatures and the shortening of swelling time of HPC. Once the crystal solvate is formed, one can prepare any concentration by simple “dilution” of the crystal solvate with the amount of water requested and cooling down to the homogeneous region. No change in the molecular weight distribution has been recorded (Fig. 3).

This procedure is only applicable up to a final concentration of about 76% HPC (composition of the crystal solvate).<sup>6</sup> So the maximum concentration of HPC in the system HPC–water is approximately 76% before the lyotropic system becomes a thermotropic system. A similar value has been reported by Fortin and Charlet.<sup>3</sup> They observed no discontinuity in the reflection wavelength for solutions with a weight fraction above 75% HPC with increasing temperature. Also only a small amount of separated isotropic phase and only a minor change in turbidity has been reported by these authors<sup>3</sup> for solutions around 80% during heating. Mixtures with higher concentration can be achieved by application of a controlled vacuum to the crystal solvate.

Optical microscopy studies with polarized light were used to examine the isotropic and the anisotropic phase. A 65% solution shows an anisotropic texture at room temperature between crossed polarizers typical for nematic/cholesteric mesophases (Fig. 4).

The question now arises, what is the nature of the homogeneous phases? We think that there is no clear distinction between the so-called lyotropic liquid crystalline polymers formed from “solutions” of stiff main-chain

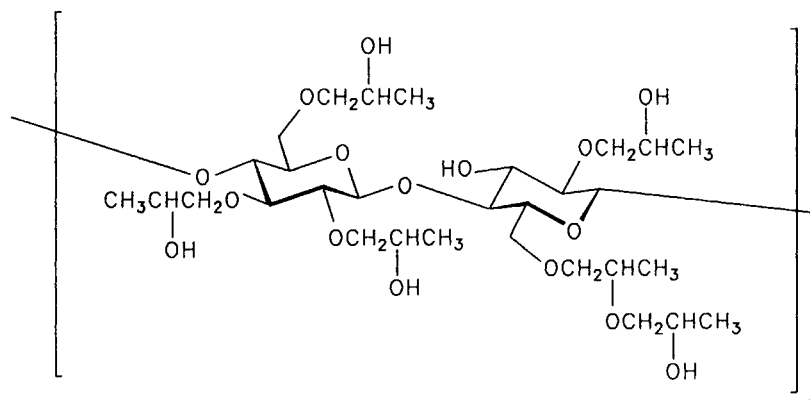


Figure 1 Idealized structure of HPC.

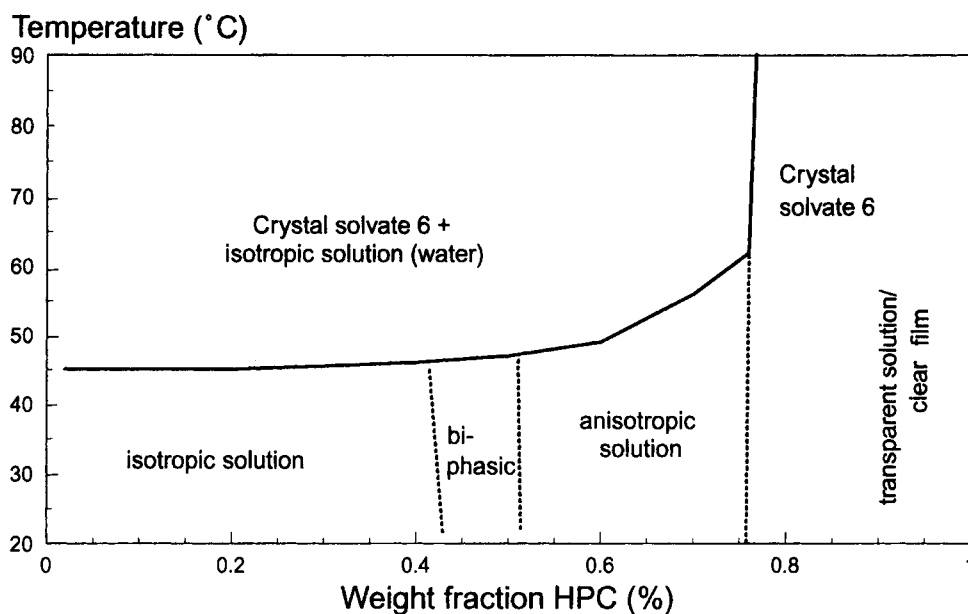


Figure 2 Modified phase diagram of the HPC-water system.

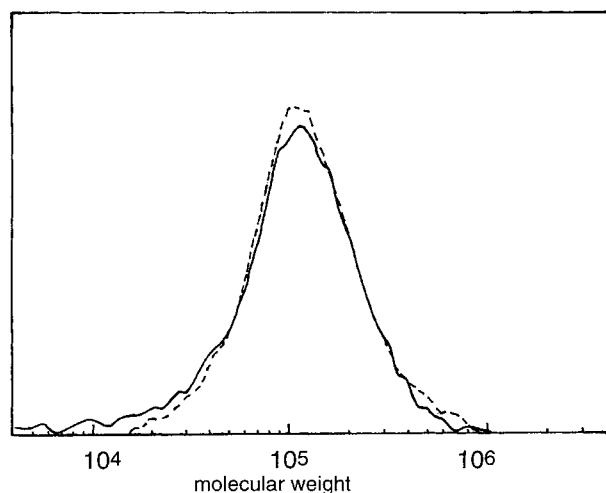
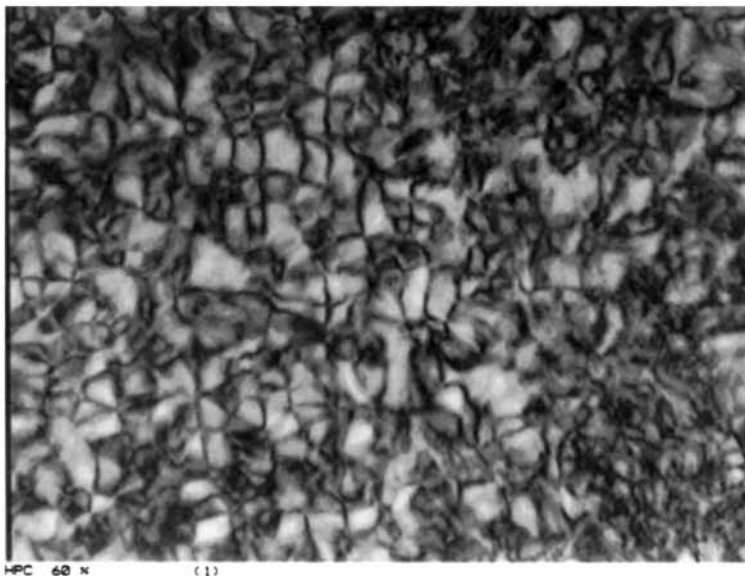


Figure 3 GPC traces of the HPC: solid line: as supplied; dashed line: after the dissolving process.

polymers and thermotropic polymers. The association of solvent molecules is very strong in the case of the lyotropic polymers and very little “free” solvent is left. So the main action of the solvent is the lowering of the melting temperature of the stiff chain polymers by formation of a “new” substance, the solvate aggregate. This is clearly the case for the HPC-water system where the pure, single-phase anisotropic area starts at a concentration, which corresponds to about 18 molecules of water per monomeric unit. A monomeric unit contains nine oxygen atoms, so that almost all the water could be well fixed to the whole monomeric unit with little or no “free” water left.

### CONCLUSIONS

A novel preparation technique has been introduced that enables a quick and easy preparation of highly concentrated solutions of stiff chain polymers. The technique of



**Figure 4** Micrograph of a 60% solution of HPC, 25°C, crossed polars.

solution preparation may have general applicability to lyotropic systems.

#### References

1. R. S. Werbowyj and D. G. Gray, *Macromolecules*, **13**, 69 (1980).
2. G. Conio, E. Bianchi, A. Ciferri, A. Tealdi, and M. A. Aden, *Macromolecules*, **16**, 1264 (1983).
3. S. Fortin and G. Charlet, *Macromolecules*, **22**, 2286 (1989).
4. H. Fischer, M. Murray, A. Keller, and J. A. Odell, *J. Mat. Sci.*, to appear.
5. H. Fischer, J. A. Odell, A. Keller, and M. Murray, *J. Mat. Sci.*, **29**, 1025 (1994).
6. P. Keates, G. R. Mitchell, and E. Peuvrel, *Polymer*, **33**, 3298 (1992).

H. FISCHER  
A. KELLER  
J. A. ODELL

H. H. Wills Physics Laboratory  
University of Bristol  
Tyndall Avenue  
Royal Fort  
Bristol, BS 8-1 TL, United Kingdom

*Received June 21, 1994*  
*Accepted July 12, 1994*