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On the phase diagram of the system hydroxypropylcellulose–water

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The phase diagram of the system hydroxypropylcellulose (HPC)–H_2O has been investigated using differential scanning calorimetry (DSC), X-ray diffraction, optical microscopy and ^1H (NMR) nuclear magnetic resonance spectroscopy. A peritectic line at higher temperatures has been found similar to the lytropic systems described before. This phase transition, from a solution consisting of solvate aggregates and free solvent, into a crystal solvate–isotropic phase system is completely reversible. The formation of crystal solvate phases is independent of the water content of the system until the system transforms into a thermotropic system. The solvent molecules are strongly associated with the macromolecules.

1. Introduction

The system HPC–H_2O is one of the first systems where liquid crystallinity in solutions of polymers has been recognized [1]. An idealized structure of HPC is shown in Fig. 1. This system is known to exhibit a complex phase behaviour including the formation of an isotropic and a mesomorphic phase, but also a reversible phase transition upon heating [1–5]. However, the nature of the phases at equilibrium at high temperatures is still not known. The occurrence of a "white gel" is often mentioned, and the phase behaviour is described as a LCST behaviour [1, 2]. Other authors describe this phase as a mesophase with cholesteric order [4]. The other phase present at high temperatures is described as infinitely diluted solution [2, 4]. However, not even the structures of the homogenous phases at lower temperatures are clear. Some authors understand the anisotropic phase as a solution consisting of discrete clusters of HPC chains [6], most are convinced that structuring of water through H bonds plays an important role in the structure of the different phases [1, 2, 4, 5, 7]. There are some investigations by means of light scattering [1] and X-ray diffraction [7] which suggest a strong association of water molecules with each HPC chain.

Previous investigations on the system poly-*p*-phenylene-benzbisthiazol (PBZT)–Polyphosphoric acid (PPA)–H_2O, which is similar to the system HPC–H_2O, have shown that solutions exhibit a more or less complex behaviour, including the formation of different kinds of crystal solvates depending upon solvent content and temperature [8]. Orientation and relaxation of the dissolved macromolecules and the solvent molecules in this system have been observed during shear experiments [9]. There are some hints that there are two different kinds of solvent molecules present in the solution, molecules which are somehow adsorbed or bonded to the dissolved macromolecules and free solvent molecules in between them.

The investigations described in this paper have been carried out in order to understand the nature of the solid phase at high temperatures and to understand the principal features of phase diagrams of lyotropic polymeric systems.

2. Experimental procedure

The different mixtures investigated were prepared by the following procedure. Air dry HPC 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 homogenized and was ready for the investigations. A GPC with two aquagel polymer laboratories (OH60 and OH 40) columns was used to check the molecular weight distribution before and after the dissolving process. Liquid crystalline behaviour was determined visually with a Linkam THM 600 hot stage mounted on a Zeiss Ultraphot optical microscope. A Sony video recorder was used to record crystal solvate formation and phase transitions from the nematic or the isotropic phase to the mixed phase. Thermal analysis was carried out using a Perkin–Elmer DSC 7 with heating and cooling rates of 10 ° K min^{-1} to a temperature limit of 200 °C. Samples were prepared in stainless steel high pressure pans from Perkin– Elmer. The ^1H NMR spectra were obtained using a Jeol Alpha 500 spectrometer. X-ray experiments were carried out on a GX 21 rotating anode generator with copper target, equipped with a graphite crystal monochromator and a two-dimensional X-1000

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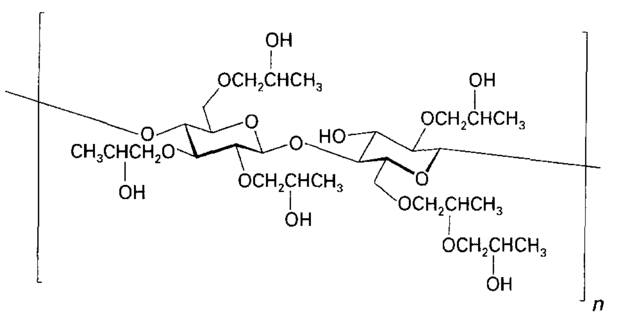

Figure 1 Idealized structure of HPC.

GADDS detector from Siemens. The usual time for collection of data for one frame was 180 s.

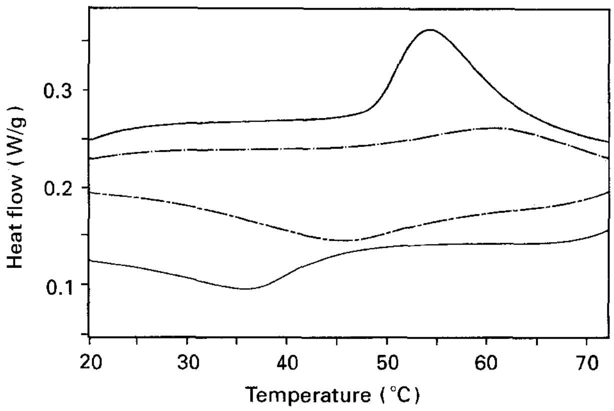

Figure 2 DSC heating and cooling trace of an (a) 35% isotropic solution of HPC in water (solid lines), and (b) 65% anisotropic solution of HPC in water (dashed lines).

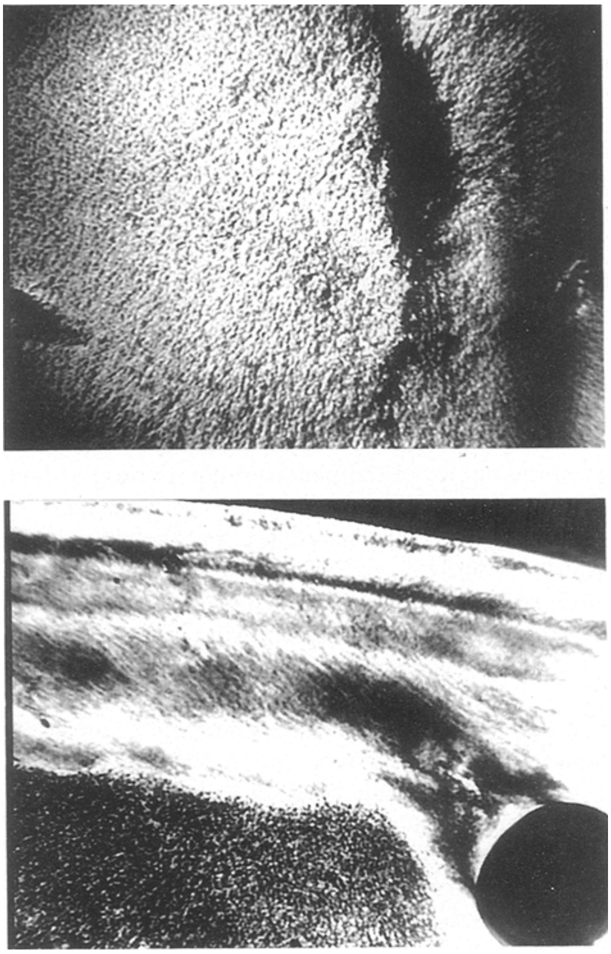

Figure 3 Photomicrograph of the formation of the white crystal solvate out of an (a) 35% isotropic solution of HPC in water at 65 °C; and (b) 65% anisotropic solution of HPC in water at 65 °C.

3. Results and discussion

The thermal behaviour of the system HPC–H_2O was studied by DSC using a sample with an isotropic phase (35% HPC) and a sample with a mesophase (65% HPC). The traces obtained from both solutions show a phase transition in the heating and cooling mode, see Fig. 2. This phase transition at 46–61 °C corresponds to the formation of the "white gel" as reported by several authors before [1–5]. On cooling, the transition from the white gel–isotropic phase to the anisotropic or to the isotropic solution is supercoolable by 15 K. Similar results have been obtained in the system PBZT–PPA–H_2O [8]. There the phase transition was attributed to the formation of a mixed phase crystal solvate–solvent out of a homogeneous phase. Therefore it is believed that the behaviour in HPC–H_2O is essentially similar.

Optical microscopy studies with polarized light were used to examine the isotropic and the anisotropic phase, and especially the formation of the "white gel" at higher temperatures. A 65% solution shows an anisotropic texture at room temperature between crossed polarizers, which is a typical texture known for nematic–cholesteric mesophases. By heating up to 65 °C a phase separation connected with the formation of a crystal solvate and a very low viscosity isotropic phase could be observed. The formation of the crystal solvates is associated with a change in transparency; also crystallization of a different structure could be detected under the polarizing microscope.

Fig. 3a, b shows the development of a crystal solvate out of an anisotropic and of an isotropic solution. The crystal solvate exhibits very small crystal sizes. It no longer shows the properties of a solution: no flow under shear conditions can be observed. The crystal solvate behaves like a network of macroscopic crystals. Together with the crystal solvate the presence of some isotropic liquid is observable. The formation of the crystal solvates is reversible. By cooling to 25 °C a single phase solution is present again.

The composition of the crystal solvate could be calculated by separation of the isotropic liquid phase from the solid crystal solvate at 70 °C and subtracting the weight of the isotropic phase (water) from the original amount of water in the solution used. The crystal solvate was found to consist of approximately six water molecules per monomeric unit of HPC and hence will be described as crystal solvate six (CS 6). This value corresponds to an association of approximately two water molecules per functional group (OH group). Again a similar result has been found in the system PBZT–PPA–H_2O [8], where a crystal solvate consisting of four phosphoric acid groups per monomeric unit was estimated. Hence, the maximum concentration of HPC in the system HPC–H_2O is

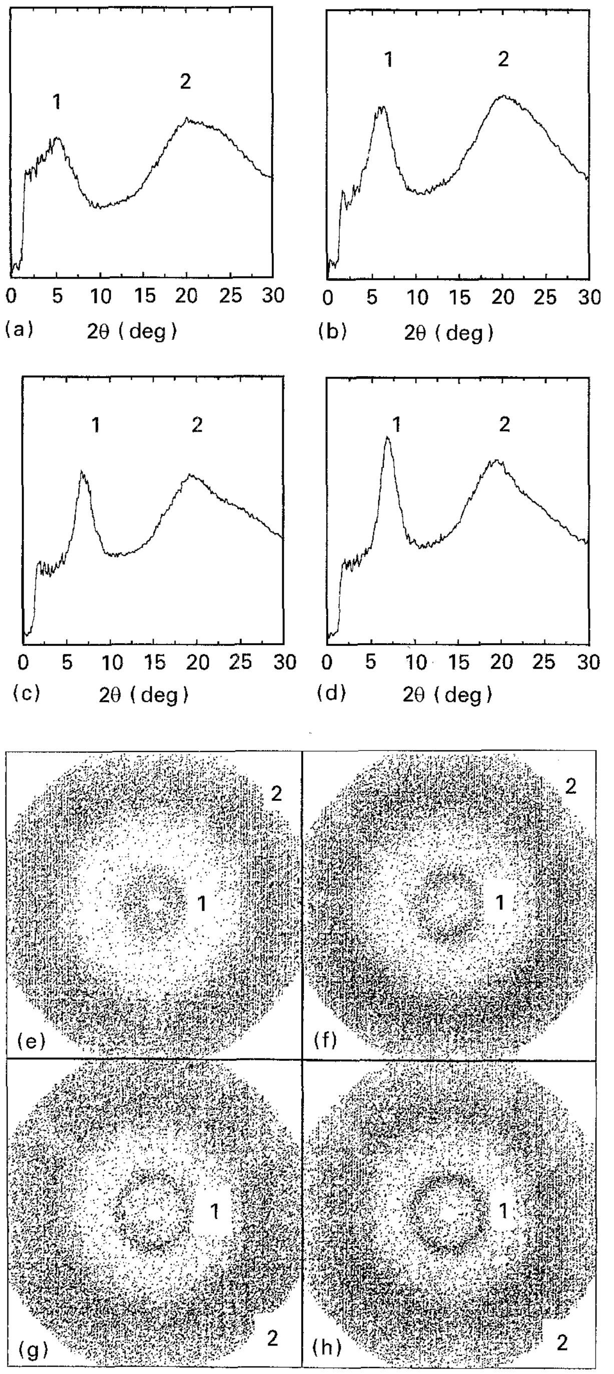

Figure 4 X-ray diffraction patterns and diffractograms from the (a, e) isotropic phase at room temperature, (b, f) at room temperature, (c, g) isotropic phase at 65 °C, and (d, h) anisotropic phase at 65 °C.

approximately 76% before the lyotropic system becomes a thermotropic system. A similar value has been reported by Fortin and Charlet [4]. 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 [4] for solutions around 80% during heating.

Interestingly enough, it was estimated by Fortin and Charlet that the concentration where the pure anisotropic phase is stable (50–55%) corresponds to about 18 molecules of water per monomer or six molecules of water per hydroxyl group.

The isotropic phase was described by Fortin and Charlet [4] as an infinitely diluted solution. This has now been proved by ^{1}H NMR spectroscopy. The NMR spectra showed only a very small concentration of monomeric and oligomeric HPC. The existence of monomers in the isotropic solution could be concluded from the appearance of a signal corresponding to aldehyde groups, which can only be explained through the existence of the ring opened monomer of HPC. 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 is formed by the splitoff water, which is not associated with the crystal solvate.

X-ray diffraction patterns were taken from the isotropic phase and the anisotropic phase at room temperature and at 65 °C, see Fig. 4. The diffractograms and the pattern show a clear difference between the isotropic and the anisotropic phase; the low angle reflection of the anisotropic phase is much more resolved and clear [7]. However, the patterns at 65 °C are very similar for both samples. Both display a very sharp small angle reflection and a more or less sharp wide angle reflection indicating the existence of some crystallinity. The small angle reflection is slightly shifted to larger angles compared with the pattern obtained from the anisotropic solution. This indicates closer packing of the chains in the crystal solvate phase due to the split-off water molecules and the formation of a coexisting isotropic solution at higher temperatures.

X-ray diffraction patterns were also recorded while shearing the anisotropic solution, Fig. 5. There is clear evidence that not only the main chains are orientated due to the shear (reflection 1), but also some orientation of the wide angle reflection associated with the water could be recorded (reflection 2). This observation is very similar to that reported by Feijo *et al.* [9] for sheared PBZT–PPA–H_2O samples. An association of water molecules with the main chain in the system HPC–H_2O is very likely and has been found before from Keates *et al.* [7] by means of X-ray diffraction and by Werbowij and Gray by light scatting methods [1]. Time resolved X-ray studies show a quick decay in the Hermans orientation parameter of reflection 1 and 2 after cessation of shear, Fig. 6. Since the decay rate is very similar for both water and HPC this also suggests a strong association of water with the HPC.

One of the most informative methods for the investigation of the structure of the different liquid and solid phases in the system HPC–H_2O should be ^{1}H NMR spectroscopy. The isotropic sample, a solution with a concentration of 35% HPC did not show a clear splitting of the H_2O line at 4.75 p.p.m. at room temperature, Fig. 7a.

Spectra at room temperature from solutions with higher concentrations of HPC (65%) show a line broadening effect and a solid state like spectrum of the HPC part. ^{1}H NMR spectra were also recorded at higher temperatures. Fig. 7b shows a spectrum of the 35% solution at 65 °C in the mixed phase crystal solvate–isotropic solution. There are two different

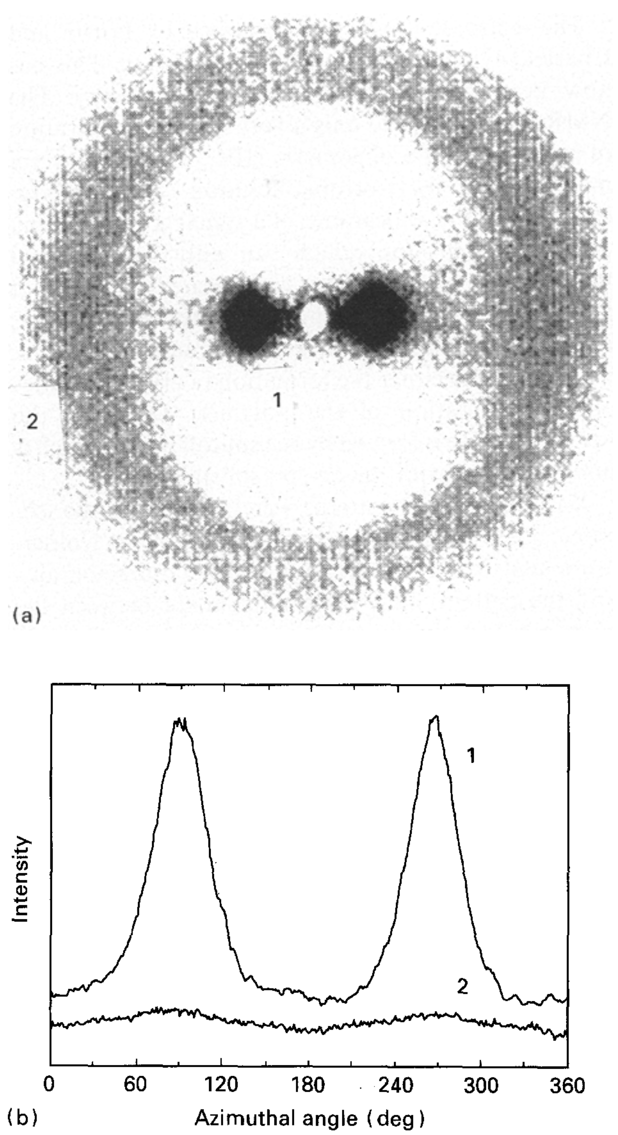

Figure 5 (a) X-ray diffraction pattern recorded while shearing the anisotropic solution, and (b) plot of the azimuthal intensity of the reflections 1 and 2.

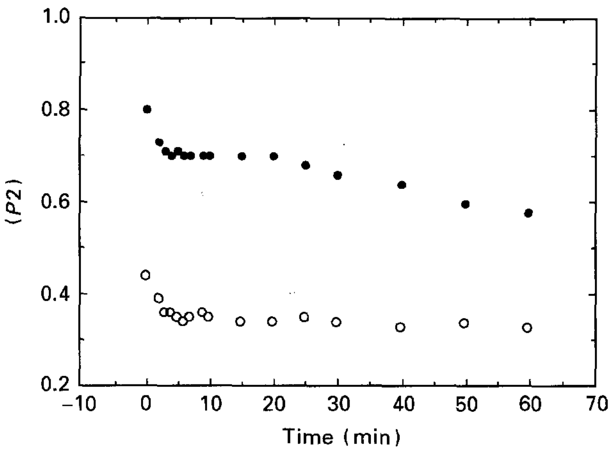

Figure 6 Herman's orientation parameter of the reflection 1 (●) and 2 (○) after cessation of shear, determined by X-ray diffraction.

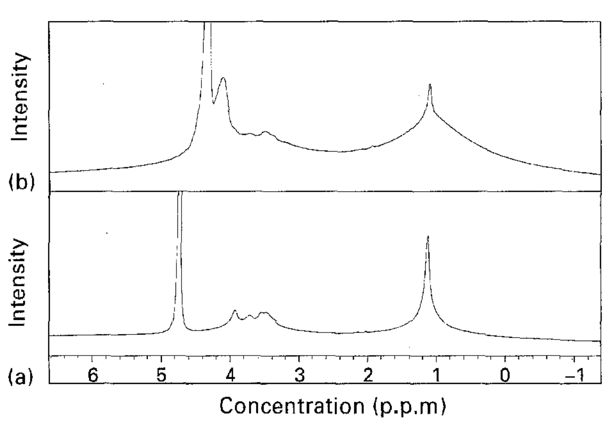

Figure 7 ^{1}H NMR spectra of a 35% solution of HPC in H_2O, 500 MHz: (a) 25 °C, and (b) 65 °C.

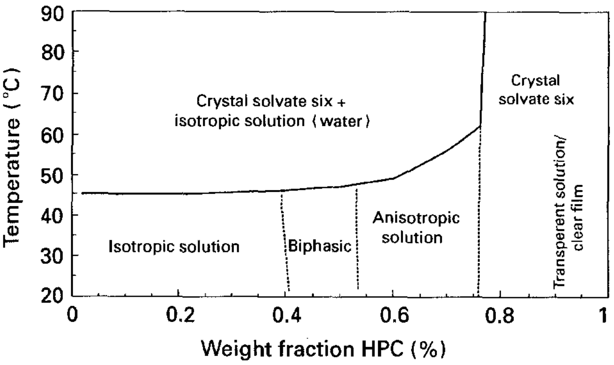

Figure 8 Modified phase diagram of the system HPC–H_2O.

lines observable at the range of the water resonance. It is assumed that there is free water present (small line at 4.4 p.p.m.) as well as aggregated water on HPC chains (broader line shifted to higher field). An investigation of the differences between the interaction of the solvent with the polymer in the cholesteric solution and the crystal solvate phase was not possible. The spectrum shows broader lines than the spectrum at room temperature and is now comparable with the spectrum discussed by Werbowyj and Gray [1]. They also noticed the splitting of the water signal into two lines, a narrow line associated with the free water in the solvent and a broad line corresponding to the HPC associated protons. There are two different lines observable in the region of the water resonance.

4. Conclusions

It is possible to modify the existing phase diagram, see Fig. 8, [1, 3, 4]. 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 [8, 10]. All show the main features of the theoretically described phase diagram of stiff rods in solution [11]. 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_2O [8] and HPC–H_2O forming a crystal solvate where two solvent molecules are aggregated to one 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 [8].

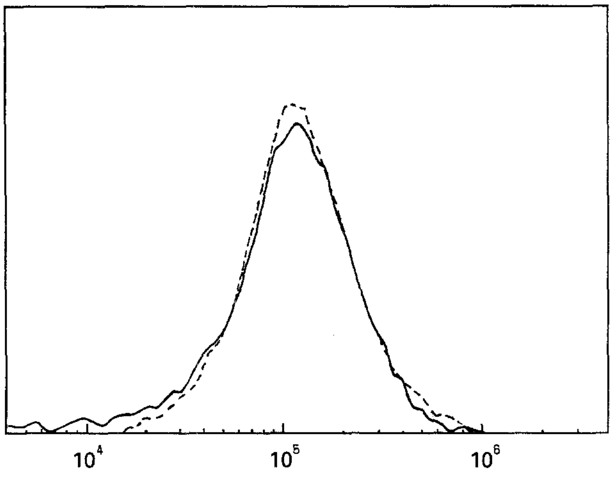

Figure 9 GPC traces of the HPC: (——) as supplied, (– – –) after the dissolving process.

The question now arises, what is the nature of the homogeneous phases? The authors think that there is no clear distinction between the so called lyotropic liquid crystalline polymers formed from "solutions" of stiff main chain polymers and thermotropic polymers. The association of solvent molecules is very strong in the case of the lyotropic polymers and in some cases 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–H_2O 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.

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 [12]. 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 vapour pressure of water at high temperatures and the shortening of the 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 required and cooling down to the homogeneous region. No change in the molecular weight distribution has been recorded, Fig. 9.

This procedure is only applicable up to a final concentration of about 76% HPC (composition of the crystal solvate). Mixtures with higher concentration can be achieved by application of a controlled vacuum to the crystal solvate. The technique of solution preparation may have general applicability to lyotropic systems.

Thus, at high temperatures a precipitation of a crystal solvate phase of HPC is forced due to an increase in the condensation degree of the solvent and the elimination of water as a non-solvent. Optics, X-ray shear experiments and NMR experiments point to the existence of closely associated water with approximately two water molecules per functional group (OH) of HPC. A novel preparation technique has been introduced which enables a quick and easy preparation of highly concentrated solutions of stiff chain polymers.

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