DOI: 10.1002/masy.201051058

Phase Behaviour of Hydroxypropyl Cellulose/ Polyacrylamide Gels

Carlos Castro,[1] *Ana Morales,**[1] *Andreas Koschella,*[2] *Thomas Heinze*[2]

Summary: Polysaccharide-based materials have gained nowadays a great importance in many fields of industry, e.g., in the pharmaceutical industry. Some characteristics of such compounds are their non-toxicity and the presence of a lower critical solution temperature (LCST) and/or an upper critical solution temperature (UCST). This work presents results on the synthesis and characterization of composites from hydroxypropyl cellulose (HPC) and polyacrylamide (PAAm). The ratio of HPC/PAAm was varied as well as the concentration of the crosslinker and the pH value of the reaction mixture. The compounds prepared were characterized by means of Fourier Transform Infrared spectroscopy (FTIR) and turbidity measurements. FTIR spectroscopy showed the presence of the main structural features of the precursors in the gels. The turbidity measurements of the gels in water showed the presence of a LCST in all samples. The LCST decreased when the quantity of HPC was increased in the gel and diminished also with increasing quantities of crosslinker and pH. The turbidity measurement showed the presence of an UCST when the concentration of the polymer was higher than 1% (w/w). This phenomenon is caused by the presence of the PAAm, which acted as precipitant and influenced over the entropy of the system and provoked phase separation.

Keywords: miscibility; phase behaviour; polysaccharides; polyamides; solution properties

Introduction

Polymers are macromolecules obtained from monomers by different types of polymerization reactions.[1] Many polymers are soluble, but their solubility depends not only on their polarity, but also on the change of entropy in the solution. When a polymer is dissolved in a poor solvent, it will be soluble only in a narrow range of temperature.[2] Some polymers become insoluble when temperature is raised, yielding a two phase system: the temperature is known as lower critical solution temperature (LCST).[3] Other polymers become insoluble when temperature is lowered. This temperature is known as upper critical solution temperature (UCST).[3] Moreover, some polymer systems present both phenomena, giving a small "solubility window".[3] A polymer showing these properties is hydroxypropyl cellulose (HPC), which is a material that is soluble in water below its LCST at 45°C.[4] This temperature depends on the concentration of the solution.[5] HPC is an interesting material because is biodegradable, non toxic and therefore used for pharmaceutics.[6] Polyacrylamide (PAAm) is a well known water soluble polymer without any solubility limits[3] and is widely used due to its high absorbing properties, PAAm is used in pharmaceutics, medicine and agriculture. Recently, smart gels were prepared that contain a polymer having a LCST/UCST in a matrix of a polymer without any solubility limits.[7]

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[1] Departamento de Estudios de Posgrado e Investigación, Instituto Tecnológico de Ciudad Madero, Juventino Rosas y Jesús Urueta s/n, 89440, Ciudad Madero, México
E-mail: abmoralesc@prodigy.net.mx
[2] Kompetenzzentrum Polysaccharidforschung, Friedrich-Schiller-Universität Jena, Humboldtstrasse 10, D-07743 Jena, Germany

Methodology

A given quantity of (see Table 1) HPC (Aldrich $M_n = 10000\,g\,mol^{-1}$, MS= 3.6) was dissolved in 20 mL of distilled and deionized water (DI) for 15 h, then acrylamide (AAm, Aldrich, 97%) was added and the solution was stirred until complete dissolution.

At the beginning of the reaction 8 mL of water containing 0.1% wt of methylene bisacrylamide (MBAm, Aldrich, 99%) and 0.2% wt of ammonium persulfate (APS, Sigma-Aldrich, 98%) were added followed by 0.2% wt of tetramethyl ethylenediamine (TEMED, Sigma-Aldrich, 99%) dissolved in 8 mL of water. Vinyl sulfone (DVS, Aldrich, 97%, see Table 2) was injected and the mixture was allowed to stir for 3 h at 40°C in an inert atmosphere. The pH was adjusted at 7 and 12 by the addition of 1.0 M NaOH. After the desired reaction time the solution was poured in a badge of silicon and was allowed to dry at 40°C under vacuum, rinsed with DI water and let to dry again[8] under vacuum.

The samples were characterized with Fourier Transform Infrared Spectroscopy (FTIR) with a Spectrum One spectrophotometer (Perkin-Elmer) equipped with an ATR accessory in the range from 4000 to 500 cm^{-1} with 32 scans and a spectral resolution of 2 cm^{-1}. The phase behavior was evaluated by means of turbidity measurements using a temperature controlled turbidimeter TP1 (E. Tepper) operating at a wavelength of 670 nm with heating and cooling rates of 1°C/min in a temperature range from 5°C to 95°C. The samples were cut in small pieces, dissolved in DI water and filtered. The samples were characterized with Dynamic Mechanical Analysis (DMA) with a TA Instruments model 2980 in the multifrequency mode using a cantilever in the film mode of 35 mm. The heating rate was of 5°C/min with a frequency of 1 Hz in the range from –20°C to 150°C.

Table 1.
Quantities of HPC/PAAm.

Formulation	% wt of HPC	% wt of PAAm
E	50	50
F	75	25
G	75	25

Table 2.
Quantities of DVS.

Concentration	g DVS/g HPC
1	0.18
2	0.36
3	0.09

Results

FTIR

The FTIR spectrum of a sample with the specification HPC/PAAm 50/50, 0.18 g DVS/g HPC prepared at pH 7 showed the presence of the main functional groups of the reactants (Figure 1).

The characteristic stretching absorption of the NH group of acrylamide appeared at 3348 cm^{-1}, while at 3196 cm^{-1} the stretching vibration of the OH group of HPC was observed. Further bands corresponding to CH vibrations were detected at 2970 cm^{-1} (asymmetric stretching of the CH_3 groups of the HPC), as well as at 2921 cm^{-1} and 2876 cm^{-1} (asymmetric and symmetric vibrations of the C-H of the methylene groups of the modified anhydroglucose unit). The absorption of the symmetric stretching vibration of the C = O bond appeared at 1657 cm^{-1} (symmetric stretching), while the bending of the NH group led to a signal at 1608 cm^{-1}. Absorption bands were observed at 1451 cm^{-1} (CH_2 deformation of the PAAm and the HPC) and at 1421 cm^{-1} (CH_2 wagging vibration of PAAm and HPC). The absorption band at 1278 cm^{-1} was assigned the CN stretching vibration. Also a strong band corresponding to the asymmetric stretching of the C–O–C bond of the HPC and the networks formed during crosslinking could be observed. The CH_2 rocking band appeared at 776 cm^{-1}.

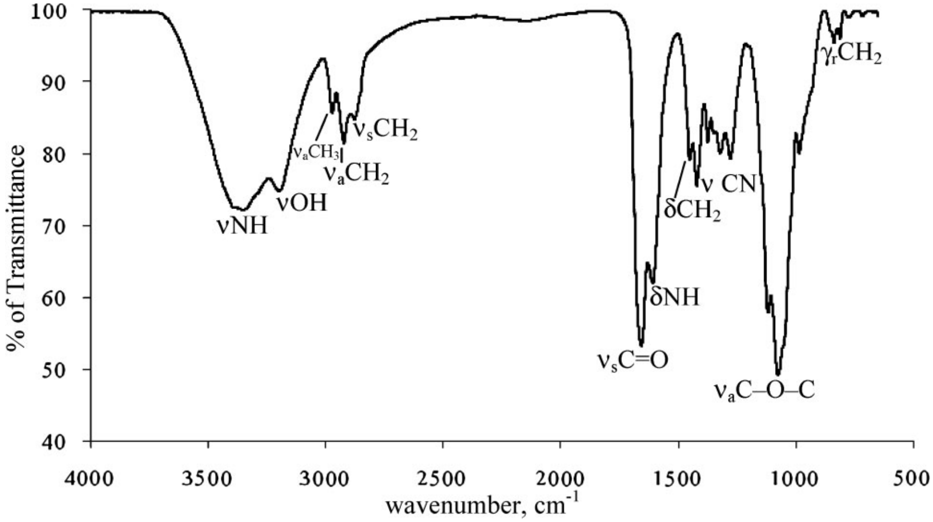


Figure 1.
IR spectrum of the sample HPC/PAAm 50/50 prepared with 0.18 g DVS/g HPC at pH 7.

Solution Behavior

The samples synthesized at pH 7 were soluble in water but did not dissolve neither in polar solvents, nor in non-polar solvents. The samples synthesized at pH 12 were water insoluble. They swelled without dissolving and were not soluble in polar and non-polar solvents. The turbidimetry showed the presence of an LCST in all the samples at any concentration. Figure 2 shows the effect of the content of the DVS on the LCST. In both cases the LCST diminished when the content of DVS is increased on the polymer. This is because the system becomes more crosslinked and hence the polymer is more hydrophobic. A sample with 75%(w/w) of HPC exhibited a more pronounced behavior than the sample with 50% HPC, which contained a larger content of DVS.

Figure 3 shows the effect of the HPC content on the LCST of the samples. In both cases the LCST diminished when the content of HPC was increased. This

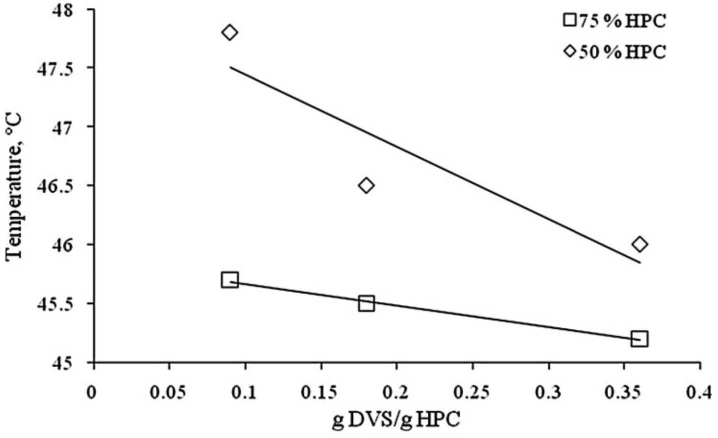


Figure 2.
Effect of the content of DVS on the LCST of the polymers.

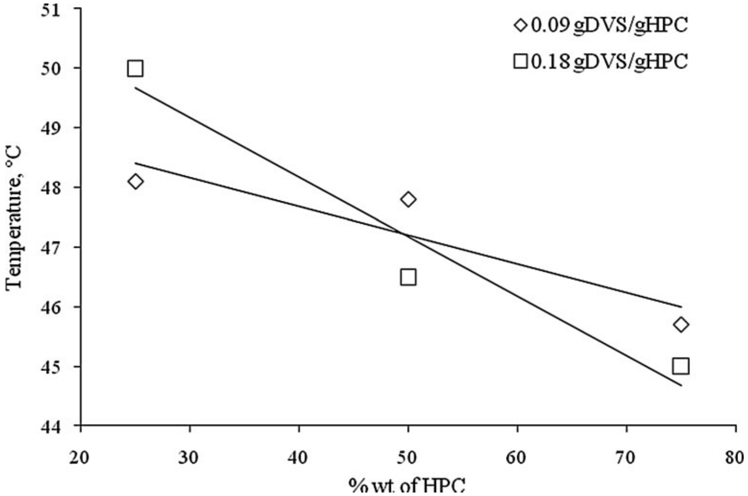


Figure 3.
Effect of the content of HPC on the LCST of the polymers.

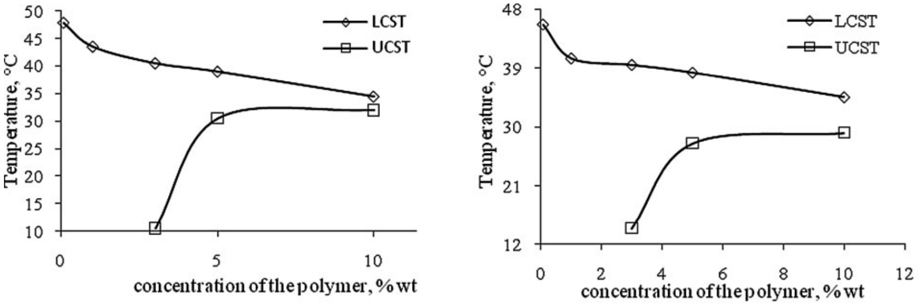
phenomenon is caused by the HPC, which demonstrates a change in its polarity in water upon heating, becoming insoluble.[9] A higher HPC content will lead to a lower LCST because the polymer will become more hydrophobic.

When the concentration of the polymer was increased, an UCST was observed, thus giving a polymer with both LCST and UCST. Figure 4 shows the phase behavior for some samples. All samples exhibited both LCST and UCST, the latter one arising at concentrations above 3%wt. LCST tended to decrease when the polymer concentration was increased. This is because the polymer content in the solution is bigger and it will lead to more hydrophobic samples. UCST tended to increase when the polymer content is increased. This is because the polymer content makes that the entropy of solution diminishes and the solubility of the polymer is not possible, according to the polymer solubility theory of Flory.[2] The presence of an UCST is not reported in the literature.[3] However, an UCST could be found, which is due to the unique structure of the network and the presence of secondary hydrogen-bonding complexes between the HPC and PAAm networks. At lower temperatures hydrogen bonding forces dominate and maintain the particles in a collapsed state; however, as temperature is increased these bonds are weakened and a hydrophilic front is established within the polymer. These two effects work synergistically together to rapidly swell the particles resulting in the UCST-like behavior that is seen in these materials.[7,10] In Figure 4, the Θ conditions were calculated by linear regression according to the method described by Brandrup,[11] with the experimental data of the LCST at different polymer concentrations and composition. The characteristics shown by the turbidity measurements make this material very interesting for use in pharmaceutics as a smart delivery drug material.

Table 3 summarizes the cloud points of all the samples. As discussed above, the LCST was found in all samples, and the UCST arose in high concentrations.

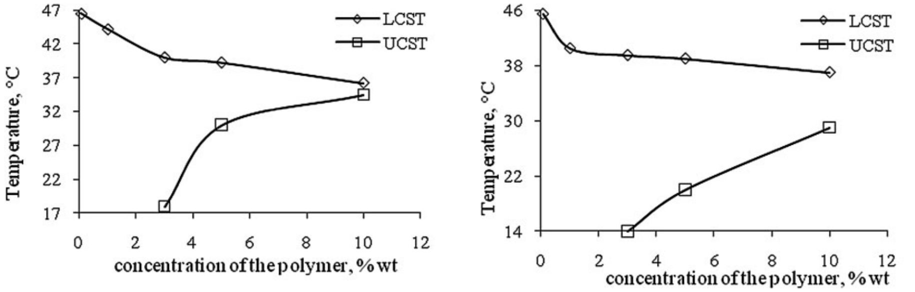
Dynamic Mechanical Behavior (DMA)

Figure 5 shows the DMA curves of the sample HPC/PAAm 25/75 with 0.09 g DVS/g HPC prepared at pH 12. The storage modulus was 8350 MPa. The polymer began to soft at -49°C and is totally relaxed at



a) HPC/PAAm 50/50 with 0.09 gDVS/gHPC at pH 7, Θ = 30.2°C

b) HPC/PAAm 75/25 with 0.09 gDVS/gHPC at pH 7, Θ = 30.73°C



c) HPC/PAAm 50/50 with 0.18 gDVS/gHPC at pH 7, Θ = 32.67°C

d) HPC/PAAm 75/25 with 0.18 gDVS/gHPC at pH 7, Θ = 33.52°C

Figure 4.
Phase behavior of some samples.

Table 3.
Cloud points of some samples.

Sample	Concentration (%wt)	% HPC/ % PAAm	g DVS/ g HPC	pH	LCST,°C	UCST, °C
HPC/PAAm	0.1	50/50	0.09	7	47.8	—
HPC/PAAm	1	50/50	0.09	7	43.5	—
HPC/PAAm	3	50/50	0.09	7	40.5	10.5
HPC/PAAm	5	50/50	0.09	7	39	31
HPC/PAAm	10	50/50	0.09	7	34.5	32
HPC/PAAm	0.1	75/25	0.09	7	45.7	—
HPC/PAAm	1	75/25	0.09	7	40.5	—
HPC/PAAm	3	75/25	0.09	7	39.5	14.5
HPC/PAAm	5	75/25	0.09	7	38.3	27.5
HPC/PAAm	10	75/25	0.09	7	34.5	29.1
HPC/PAAm	0.1	50/50	0.18	7	46.5	—
HPC/PAAm	1	50/50	0.18	7	44.2	—
HPC/PAAm	3	50/50	0.18	7	40	18
HPC/PAAm	5	50/50	0.18	7	39.25	30
HPC/PAAm	10	50/50	0.18	7	36.2	34.5
HPC/PAAm	0.1	75/25	0.18	7	45.5	—
HPC/PAAm	1	75/25	0.18	7	40.5	14
HPC/PAAm	5	75/25	0.18	7	39	18
HPC/PAAm	10	75/25	0.18	7	37	29

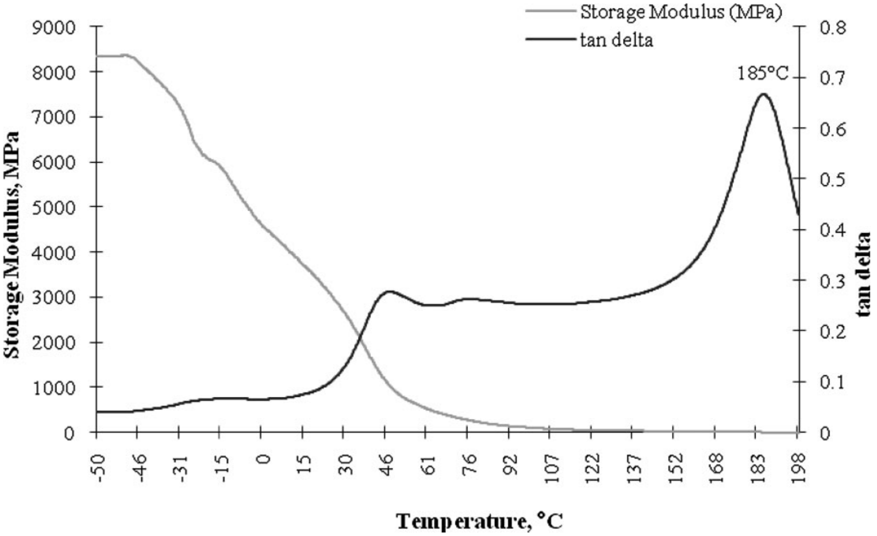


Figure 5.
Dynamic Mechanical Analysis curves of the sample HPC/PAAm 25/75 with 0.09 g DVS/g HPC prepared at pH 12.

120°C. The tan delta curve showed a shoulder at 45°C corresponding to a glass transition temperature (T_g), mainly caused by secondary relaxations of the polymer side chains in the glassy region. A peak at 185°C was assigned to the T_g of the polyacrylate. Figure 6 shows the loss modulus curve of the same sample, it shows a T_g of 36°C, which is the same shown at 45°C in the tan delta curve. This T_g was attributed to the movements of the side chains of the HPC.[12,13] As there are two T_g's, there is a phase separation in the sample.

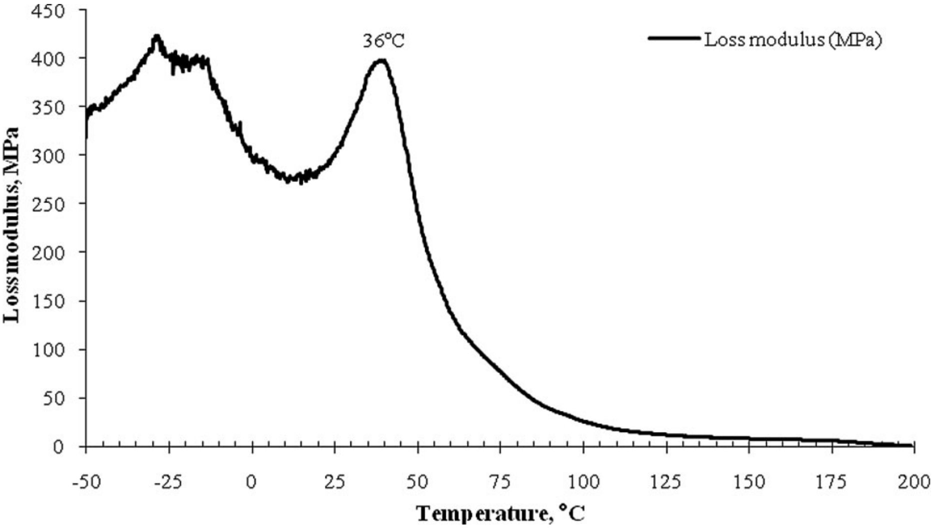


Figure 6.
Loss modulus curve of the sample HPC/PAA 25/75 with 0.09 g DVS/g HPC prepared at pH 12.

Conclusions

Samples show LCST at any concentration and UCST at higher concentrations. The LCST is owed to the change in the dipole moment of the hydroxypropyl substituents of the HPC[13] with the change of temperature. It decreased with increasing HPC content in the composite polymer due to the higher content of HPC and decreases with increasing content of DVS, because the crosslinker increases the stiffness of the network and limits the solubility of the substance. LCST decreases with the change of pH at synthesis, this is thought to be caused by the effect of pH on crosslinking, an alkaline pH will lead to a more effective crosslinking of the HPC and DVS. UCST arose due to the presence of secondary hydrogen-bonding complexes that develop between the HPC and PAAm networks. UCST increased when the polymer content in solution is increased, because the chains have less space to interact with the solvent. The Θ temperature for many samples is in the range of 30 – 35°C. FTIR showed the presence of the main functional groups of HPC and PAAm in the composite polymer. DMA showed two T_g's, indicating a phase separation in the system. One T_g is due to the movements of the side chains of the HPC and another is due to the transition of the acrylate.

Acknowledgements: To CONACyT for their grant 181581, to the SEP for their economical support for an academic stay at the Friedrich Schiller University of Jena with key 082007011EST. To the División de Estudios de Posgrado e Investigación of the Instituto Tecnológico de Ciudad Madero and to the Institute for Organic Chemistry and Macromolecular Chemistry (Center Excellence for Polysaccharide Research) of the Friedrich Schiller University of Jena for allowing us the use of their facilities and equipment. To Dr. Dominik Fenn for his support in the use of the turbidimeter and in the interpretation of the data.

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