58 | Macromol. Symp. **2010**, 294-II, 58–63 DOI: 10.1002/masy.200900173

Mesophases in a Gel from Hydroxypropyl Cellulose/Polyacrylamide

Carlos Castro-Guerrero,[1] *Ana Morales-Cepeda,*[*1] *Oxana Kharissova,*[2]
Andreas Koschella,[3] *Thomas Heinze*[3]

Summary: The objective of the present work is to analyze the different mesophases observed in a gel synthesized from hydroxypropyl cellulose (HPC) and polyacrylamide (PAAm) and its phase behavior in water. Hydroxypropyl cellulose is a material derived from cellulose it is non toxic and degradable. HPC is widely used in pharmaceutics, food additives, stabilizer, thickener, etc., HPC is approved by the FDA for use in the food industry. HPC has the characteristic that it forms liquid crystals, depending on the solvent and on the concentration of the polymer. In this work a lower critical solution temperature (LCST) and an upper critical solution temperature (UCST) were observed, the resulting gel showed anisotropic, nematic and cholesteric phases in water, the phase formed depended on the concentration of the polymer.

Keywords: cellulose derivatives; LCST; liquid crystals; mesophases; UCST

Introduction

Hydroxypropyl cellulose (HPC) is a material derived from cellulose which has interesting properties.[1] In concentrated solutions it forms liquid crystals which exhibit different mesophases.[2] Among the phases found in HPC solutions are nematic, cholesteric, anisotropic[3], the phase type depends on the solvent and on the concentration of the polymer; the cholesteric mesophase is found at about 60% wt of the polymer and shows birefringence. Polymers with the ability of forming liquid crystals have achieved many applications nowadays. HPC possesses phase transitions in solvents. The lower critical solution temperature (LCST) in water is observed at 45°C and decreases with increasing concentration of HPC and/or decreasing molar substitution (MS) degree. This property is interesting because it makes HPC an intelligent gel that releases a drug when the LCST is reached. This property is being used in some gels.[4] HPC is also an interesting material because it is non-toxic and is allowed for use in pharmaceutical products and food derivatives.[5] HPC can also form mesophases when subjected to a mechanical shear stress.[6] Polyacrylamide is a polymer that has good solvent-absorbing properties[4] and is non-toxic. Polyacrylamide is widely used as a matrix for controlled drug delivery.[7] It has been shown that polyacrylamide-based polymers provide an alternative for modifying the hydrophobicity of drugs.[8,9,10]

Methodology

2 g of HPC (Aldrich $M_n = 10000\,g\,mol^{-1}$, MS= 3.6) were dissolved in 20 mL of distilled and deionized water (DI) for 15 hours. 2 g of acrylamide (AAm, Aldrich, 97%) were added and the solution was stirred until complete dissolution. At the beginning of the reaction 8 mL of water

---

[1] División de Estudios de Posgrado e Investigación, Instituto Tecnológico de Ciudad Madero, J. Urueta y J. Rosas s/n, Col. Los Mangos, 89440, Cd. Madero, Tamaulipas, Mexico
E-mail: abmoralesc@prodigy.net.mx

[2] Facultad de Ciencias Físico-Matemáticas, Universidad Autónoma de Nuevo León, Av. Universidad s/n. Ciudad Universitaria, 66451, San Nicolás de los Garza, Nuevo León, Mexico

[3] Friedrich-Schiller-Universität Jena, Institut für Organische Chemie und Makromolekulare Chemie, Kompetenzzentrum Polysaccharidforschung, Humboldtstrasse 10, 07743, Jena, Germany

containing 2 mg of methylene bisacrylamide (MBAm, Aldrich, 99%) and 40 mg of ammonium persulfate (APS, Sigma-Aldrich, 98%) were added followed by 40 mg of tetramethyl ethylenediamine (TEMED, Sigma-Aldrich, 99%) dissolved in 8 mL of water and 0.36 g of vinyl sulfone (DVS, Aldrich, 97%) are injected and the mixture was allowed to react for 3 hours at 40°C in an inert atmosphere with constant stirring. 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[11] under vacuum. The sample was named BE111.

The amount of absorbed water was measured with the gravimetrical method, a sample of the gel was cut, it measured 1.0 cm × 1.3 cm, it was weighed continuously and water was added until total saturation was achieved, the swelling percentage was quantified with the following equation 1 [4]:

$$W = \frac{m_s - m_d}{m_d} \cdot 100\% \qquad (1)$$

W = swelling percentage,
s = weight when wet
d = weight when dry.

The sample was characterized with Fourier Transform Infrared Spectroscopy (FTIR) with a Spectrum One spectrophotometer (Perkin-Elmer) equipped with an ATR accessory in the range of 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 sample was cut in small pieces, dissolved in DI water and filtered. Microscopic studies of the gel were carried out at room temperature with a Carl Zeiss optical microscope with crossed polarizers (magnification of 2.5x, 10x, and 40x), the sample was cut, weighed, dried and let to absorb the desired amount of water. Atomic force microscope (AFM) was carried out in a VEECO di CPII operated with the software WSXM[12] in the tapping mode.

Results and Discussion

FTIR Characterization

Sample BE111 was able to absorb up to 312% wt of water. Figure 1 shows the FTIR spectrum of BE111.

The characteristic stretching absorption of the NH group of acrylamide appears at 3348 cm^{-1}, while at 3196 cm^{-1} the stretching vibration of the OH group of HPC is

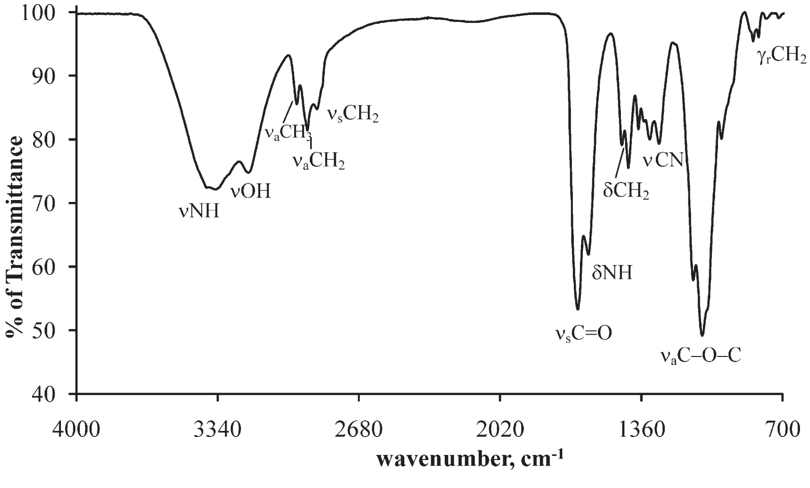

Figure 1.
IR spectrum of the sample BE111.

observed. Further bands corresponding to CH vibrations are detected at 2970 cm^{-1} (asymmetric stretching of the CH_3 groups of the HP), 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 cellulose chair). The absorption of the symmetric stretching vibration of the C = O bond appears at 1657 cm^{-1} (symmetric stretching), while the bending of the NH group leads to a signal at 1608 cm^{-1}. Absorption bands are 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 of the CN stretching is present at 1278 cm^{-1}. At 1076 cm^{-1} there is a strong band corresponding to the asymmetric stretching of the C–O–C bond of the HPC and the networks formed during crosslinking. The CH_2 rocking band is observed at 776 cm^{-1}.

Turbidity Measurements

The temperature dependent turbidity measurements in water showed the presence of a LCST in all the solutions prepared, an upper critical solution temperature (UCST) arose when the concentration of BE111 exceeded 3% wt in the solvent (Figure 2).

HPC is known to have a LCST.[3] The LCST of the HPC/PAAm gel decreases as the polymer content increases (Figure 2). Thus, a higher polymer weight fraction will lead to a higher content of HPC and the LCST will be lowered in this way because there is more polymer content that will become hydrophobic when temperature is raised. Above 3% wt an UCST occurs when the temperature is increased. This phenomenon is very common in other polymers[13], but it has neither been observed in pure HPC, nor in pure PAAm, however, an UCST arises by combining PAAm with other OH-containing polymers.[14] The presence of this phenomenon may be due to the PAAm in the network, which works as a precipitant in high concentrations. In this case the interaction of the PAAm- and HPC networks causes a positive heat of mixing and then an UCST occurs.

Optical Microscopy

The gel was observed with an optical microscope with crossed polarizers, many dilutions were done of the gel in DI water were done. At 10% wt the sample is no longer transparent and becomes whitish, which indicates the presence of an anisotropic phase. At 50% wt the water-solubility of the polymer disappears and it formed a white swollen gel instead. Figures 3 and 4 show the optical micrographs of the gel at 30% wt and 80% wt in water. In Figure 3 birefringence is visible. This is caused by the presence of the HPC in the network. The birefringence is due to a liquid crystalline phase in the gel, which is a nematic one. Figure 4 shows the optical micrograph of the gel at 80% wt in water.

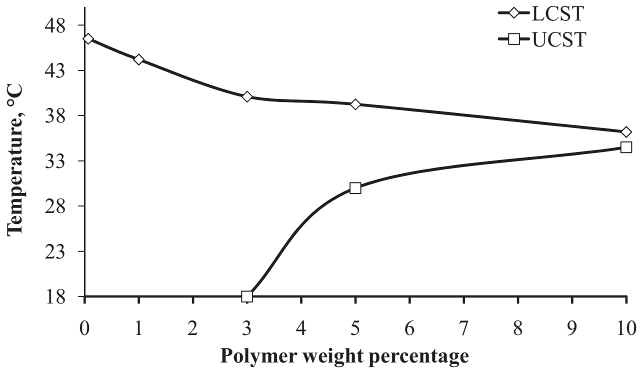

Figure 2.
Phase transition temperatures of the gel BE111 at different concentrations in water.

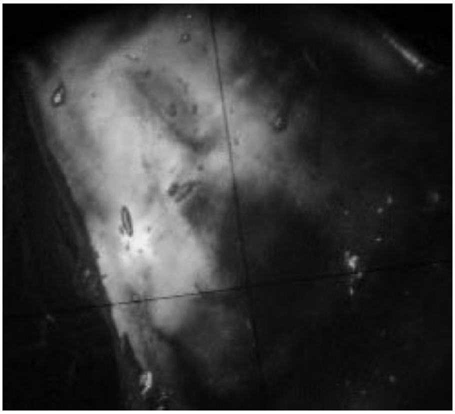

Figure 3.
Optical micrograph of the gel BE111 at 30% wt in water, magnification 10x.

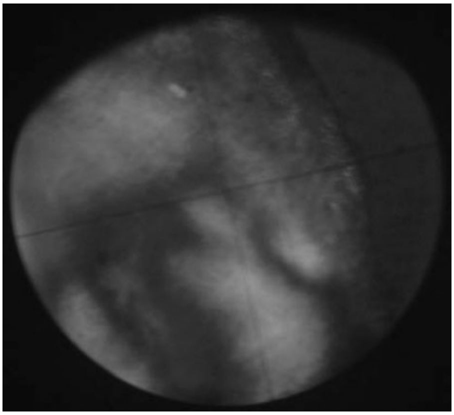

Figure 5.
Optical micrograph of the gel BE111 at 90% wt in water, magnification 10x.

Birefringence is still visible and some lines are clearly seen in the micrograph. The lines arose at 34° of the crossed polarizers. Those lines are characteristic in the cholesteric mesophase, which are a result of the presence chain of asymmetric carbons in the anhydroglucose that are imparting optical activity to cellulose and cellulose derivatives.

Figures 5 and 6 show the gel BE111 in 90% wt in water with different augments. Both images show iridescent colors in the sample, this phenomenon is again due to the presence of the cellulose derivative. Fringed patterns are visible in Figure 5, but they are not very clear. This pattern arose at every 6° of the polarizers, the fringed patterns are characteristic of cholesteric phases. Figure 6 shows the optical micrograph of the same gel, but with a lesser augment. The sample shows iridescent colors when observed with crossed polarizers.

The sample showed the presence of a violet region that was visible to the naked eye in the formulations of 0.8 and 0.9 polymer weight fraction. This was formed by the cholesteric phase of the liquid crystal. The violet region was localized in

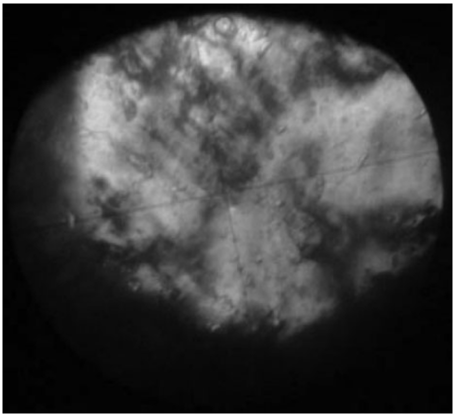

Figure 4.
Optical micrograph of the gel BE111 at 80% wt in water, magnification 10x.

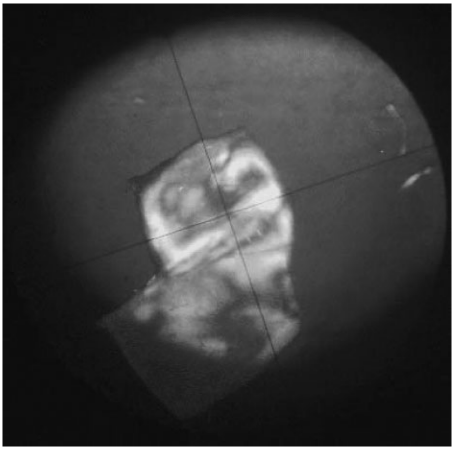

Figure 6.
Optical micrograph of the gel BE111 at 90% wt in water, magnification 2.5x.

Table 1.
Mesophases found on the sample HPC/PAAm 50/50 with 0.18 gDVS/ gHPC.

Polymer weight fraction	Mesophase	Polymer weight fraction	Mesophase
0.01–0.1	Isotropic	0.5	Nematic
0.1	Anisotropic	0.6	Nematic
0.2	Anisotropic	0.7	Nematic, cholesteric,
0.3	Anisotropic, nematic	0.8	Cholesteric
0.4	Nematic	0.9	Cholesteric

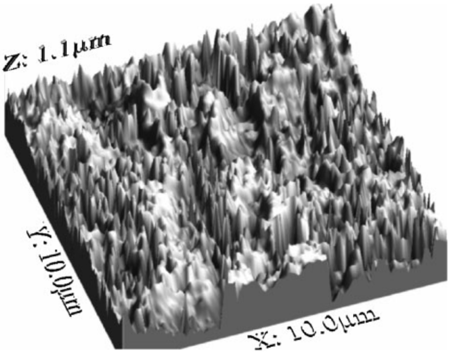

Figure 7.
AFM micrograph of the gel BE111.

half of the sample, indicating that the distribution of the HPC is inhomogeneous inside the gel. The Table 1 summarizes the mesophases found on the diluted sample.

Atomic Force Microscopy (AFM)

The AFM showed the presence of lamellae in the surface of the gel, Figure 7 shows a region of the gel.

The gel in Figure 7 is smooth and homogenous, showing a single phase, the surface is not smooth, but uneven and irregular. Lamellae are seen on the surface. These lamellae are formed during drying of the sample and suggest a liquid crystal during the reaction and during the process of drying when the solvent was being evaporated. Some authors have observed similar features.[15,16]

Conclusion

A gel which can form liquid crystals was synthesized. It showed both LCST and UCST, the first one is owed to the HPC and decreases as the polymer content in water increases. The UCST is due to the structure of the HPC/PAAm network and the presence of secondary hydrogen-bonding complexes that develop between the two 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. Those two effects work together to rapidly swell the gel forming an UCST.[13,17] The FTIR showed the presence of the main functional groups of the precursors. The orientation of these groups and their interaction leads to a LCST/UCST behavior. The FTIR confirmed the presence of the groups of HPC and the ‘‘cellulose chair’’ that acts as a mesogenic group. The optical microscopy showed the presence of anisotropic, nematic, and cholesteric phases, caused by the mesogenic group and starting from 10% wt (anisotropic) and 30% (nematic). This behavior is due to the stiffness added by the substituents of PAAm. AFM showed lamellae in the surface and it depicts structural features of the cholesteric liquid crystals.

Acknowledgements: To CONACyT for their grant 181581, to the SEP for their economical support for an academical 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, to the Institute for Organic Chemistry and Macromolecular Chemistry (Center Excellence for Polysaccharide Research) at the Friedrich Schiller University of Jena and to the Facultad de

Ciencias Físico-Matemáticas of the Universidad Autónoma de Nuevo León for allowing us the use of their facilities and equipment.

[1] D. Klemm, B. Philipp, Th. Heinze, U. Heinze, W. Wagenknecht, "*Comprehensive Cellulose Chemistry*", Ed. Wiley-VCH **2001**, Vol 2, p. 234.

[2] R. S. Werbowyj, D. G. Gray, *Mol. Cryst. Liq. Cryst.* **1976**, *34*(4), 97.

[3] R. S. Werbowyj, D. G. Gray, *Macromolecules* **1980**, *13*, 69.

[4] I. Katime, O. Katime, D. Katime, "*Los Materiales Inteligentes de este Milenio. Los Hidrogeles Macromoleculares: Síntesis, Propiedades y Aplicaciones.*", Bilbao Universidad del País Vasco, Bilbao **2004**, pp. 336.

[5] U.S. Food and Drug Administration. "*Code of Federal Regulations*" **1981**, Title 21, part 21CFR172.870, Rockville, MD.

[6] M. H. Godinho, J. G. Fonseca, A. C. Ribeiro, L. V. Melo, P. Brogueira, *Macromolecules* **2002**, *35*, 5932.

[7] D. Gao, H. Xu, M. A. Philbert, R. Kopelman, *Nano Lett.* **2008**, *8*, 3320.

[8] R. Duncan, L. C. W. Seymour, L. Scarlett, J. B. Lloyd, P. Rejmanova, J. Kopecek, *Biochim. Biophys. Acta* **1986**, *880*, 62.

[9] R. Duncan, *Nat. Rev. Drug Discovery* **2003**, *2*, 347.

[10] R. Duncan, *Nat. Rev. Cancer* **2006**, *6*, 688.

[11] R. F. Estrada, C. Álvarez-Gayosso, V. M. Castaño, *e-Polymers* **2002**, *54*, 1.

[12] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, *Rev. Sci. Instrum.* **2007**, *73*, 013705.

[13] J. I. Kroschwitz, "*Concise Encyclopedia of Polymer Science and Engineering*", Ed. Wiley **1990**, pp. 715.

[14] D. E. Owens, Y. Jian, J. E. Fang, B. V. Slaughter, Y. Chen, N. A. Peppas, *Macromolecules* **2007**, *40*, 7306.

[15] V. Arrighi, J. M. G. Cowie, P. Vaqueiro, *Macromolecules* **2002**, *35*, 7354.

[16] Y. Huang, J. Loos, Y. Q. Yang, J. Petermann, *J. Polym. Sci., Part B: Polym. Phys.* **1998**, *36*, 439.

[17] T. Okano, *Adv. Polym. Sci.* **1993**, *110*, 179.