Polymer Diffusion in Microgels with Upper Critical Solution Temperature as Studied by Incoherent Neutron Scattering

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Abstract. Poly(acrylic-acrylamide) interpenetrated microgels present continuous phase transition from collapsed to swollen state around 42 ºC. The upper critical solution temperature (UCST) of this polymeric system has prompted scientists to consider them candidates for its use in biological applications such as smart drug delivery devices since the swelling of the polymer matrix would permit the release of the drug previously entrapped within the microgels. In these systems the increment of the temperature can break inter-chain interactions, mainly hydrogen bonds, which reduce the elastic tension that stabilizes the microgel, favoring the polymer swelling. The microgel molecular dynamics at the UCST can be investigated using Incoherent Elastic (IENS) and Quasielastic Neutron Scattering (IQNS). From the analysis of the IQNS data we obtained that the diffusion coefficient of the polymer segments depends on the composition of the interpenetrated matrix. Thus, at room temperature, microgels with a polymer composition of 50% of each component present a diffusion coefficient $1 \cdot 10^{-12}$ m^2/s, while for the microgels formed by only one component the diffusion coefficient is 5.10^{-10} m^2/s. This huge difference in the diffusion coefficient is conspicuously reduced when temperature increases, and we attribute this effect to the breaking of the inter-chain interaction. By means of FTIR-ATR analysis we have identified the groups that are involved in this phenomenon and we associate the breaking of the polyacrylic-polyacrylamide interactions with the swelling of the microgels.

1. Introduction

Microgels based on PNIPAM have been extensively studied due to their ability to swell at low temperature and to collapse when temperature increases above 33 ºC[1-4]. It has been speculated using thermoresponsive microgels as drug delivery systems [5]. This would require an opposite behavior to that of PNIPAM, that is, the microgel has to remain collapsed at room temperature to trap the drug, and when increasing temperature, the microgel should swell and thus release the drug. This behaviour was found in poly(acrylic acid-acrylamide) interpenetrated microgels (PAAc/PAA) which present continuous phase transition from collapsed to swollen state around 42 ºC. The UCST of this polymeric system has prompted scientists to consider them candidates for its use as smart drug delivery devices since the swelling of the polymer matrix would permit the release of the drug entrapped within the microgels. However, unlike PNIPAM where the volume phase transition spans a range of only 2-3 degrees, the transition in PAA elapses at an interval of about 30 ° C.

2. Experimental

2.1. Materials and methods

The UCST microgels were prepared using the concentrated emulsion polymerization method. The concentrated emulsion was prepared with a low fraction of the oil phase, which

constitutes the continuous phase [6]. We have also prepared microgels with 100% poly(acrylic acid) (PAAc) and 100% poly(acrylamide) (PAA). In order to obtain PAA microgels, 5 mL of an aqueous solution consisting of acrylamide (17mmol), 12.5 mg of bisacrylamide (BIS), and ammonium persulfate (25 mg) was added with a syringe to the continuous oil phase (750 μL of dodecane and 250 μL of Span 80). To obtain, PAAc microgels we added sodium acrylate (17 mmol) keeping the same amount of BIS and ammonium persulfate used for PAA microgels. The emulsion was homogenized by magnetic stirring and purged with nitrogen to remove residual oxygen. The polymerization was started by adding TEMED (63 μL) and after 1 h of reaction, the polymer was precipitated and washed with acetone several times. Microparticles were isolated by centrifugation (10,000 rpm) for 10 min at 10 °C. In order to produce interpenetrated microgels (IPNs), part of the monomers were substituted by a defined amount of linear poly(sodium acrylate) or polyacrylamide (giving as mmol of repeated units). The resulting solution together with the initiator and cross-linking agent were used as internal aqueous phase of the concentrated emulsion and polymerized as described above. The Table 1 shows the microgels composition.

Table 1. Concentration of each component in the dispersed aqueous phase (5 ml water) used in the production of the microgels. The continuous oil phase consists of 750 μL of dodecane and 250 μL of Span 80.

AA(mmol)	AAc (mmol)	Linear PAA (mmol)	Linear PAAc (mmol)	Sample name
17	0	0	0	PAA
12	0	0	5	PAA/PAAc (70/30)
10	0	0	7	PAA/PAAc (60/40)
8.5	0	0	8.5	PAA/PAAc (50/50)
0	10	7	0	PAA/PAAc (40/60)
17	0	0	0	PAAc

Methods. The microgel particles were studied using transmission electron microscopy (SEM) at an acceleration voltage of 20 kV in a JEOL JSM-6400. The ATR-FTIR spectra were taken with a Nicolet IR200 FTIR spectrometer equipped with a Peltier (Linkam Scientific). Background spectra were taken before sample spectra and subsequently subtracted. Specifically, for each sample containing 20% The neutron scattering experiments were performed at the Institut Laue Langevin in Grenoble using the high energy resolution (1 μeV) neutron backscattering spectrometer IN10.

2.2. The incoherent scattering function

The IQNS data were analyzed considering the molecular motion consist in a combination of a faster vibrational component with a mean square displacement $\langle u^2 \rangle^{1/2}$ and a translational diffusion motion with diffusion constant D [7-8]. For Fickian diffusion the dynamic structure factor is a Lorentzian function, with a half-width at half-maximum $D.Q^2$. Thus, the scattering function can be written as,

$$S(Q,\omega) = \exp(-\frac{1}{3}\langle u^2 \rangle Q^2)\delta(\omega) \otimes \frac{1}{\pi}\frac{DQ^2}{(DQ^2)^2 + \omega^2} \quad (1)$$

where $\delta(\omega)$ is a delta function, and $\otimes$ is the convolution product in ω. The mean square displacement $\langle u^2 \rangle^{1/2}$ can be derived from the Q^2 dependence of $S(Q,0)$ at fixed temperature, and D is obtained from the fitting of the quasielastic component with a Lorentzian function [7-8].

3. Results

Figure 1 shows a SEM image of the PAA/PAAc (70/30) microgels. As is shown in Figure 1 the polymerization of the concentrated emulsion produces microgel particles with diameters between 0.3 and 3 μm, which is approximately the size of the precursor emulsion polyhedral cells. The particles are spherical and the dispersity is low. With the aim of evaluating the UCST behavior of the microgels with different polymer composition, we study the increment of their volume as a function of the temperature and the results are depicted in Figure 2. This measurement was performed in water at pH 3 since at this pH the UCST present its maximum.

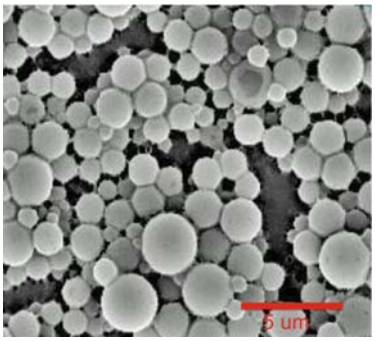

Figure 1. SEM micrograph of microgel particles.

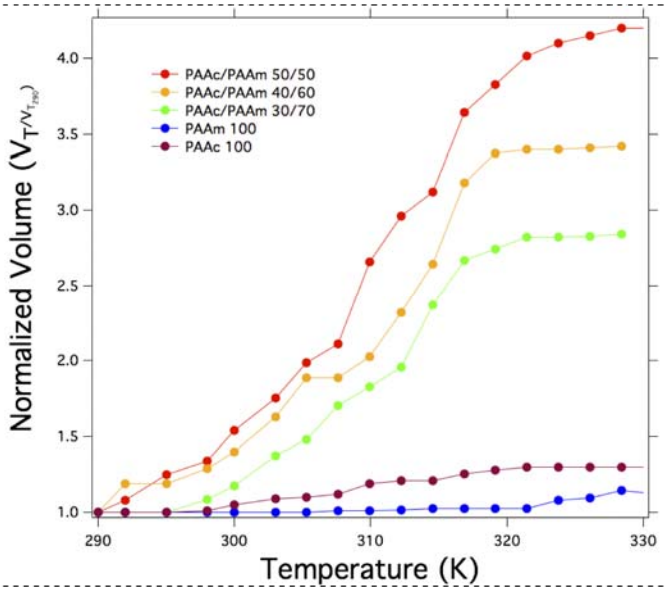

Figure 2. Volume increment of microgels with different polymer composition as a function of the temperature.

Diffusion motions of polymer chain segments can be investigated using inelastic neutron scattering since they are prominent in the quasielastic region. Furthermore, by dispersing the microgels in D_2O is possible to obtain enough contrast between the polymer network and the solvent. The elastic neutron-scattering function $S(Q, \omega=0)$ normalized to its value at 190 K, $S(Q, 0)_{190K}$ was measured as a function of the temperature with IN10 using the so-called "fixed elastic window" method. The measured incoherent elastic neutron scattering function as a function of temperature is shown in Figure 3. From this function, the apparent mean square displacement $\langle u^2 \rangle^{1/2}$ of the polymer chains can be obtained analyzing the Q dependence of $S(Q,0)$ at fixed temperature

$$\ln [S(Q,0)_T / S(Q,0)_{190K}] = -1/3 [\langle u^2(T) \rangle - \langle u^2(190\ K) \rangle] \cdot Q^2 \qquad (2)$$

From the analysis of the IQNS data (see Figure 4) we obtained that the diffusion coefficient of the polymer segments depends on the composition of the interpenetrated matrix. Thus, at room temperature, PAA/PAAc (50/50) microgels present a diffusion coefficient $1 \cdot 10^{-12}$ m^2/s, while for microgels formed by only one component the diffusion coefficient is 5.10^{-10} m^2/s in both cases, PAA and PAAc.

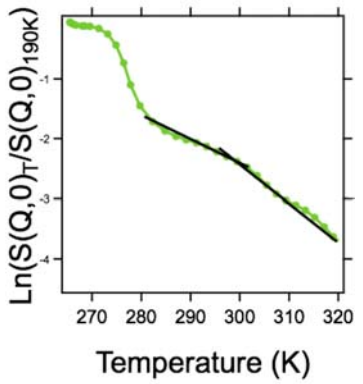

Figure 3. Normalized elastic scattering function during the heating of PAA/PAAc (50/50) microgels taken at Q = 0.5 Å^{-1}.

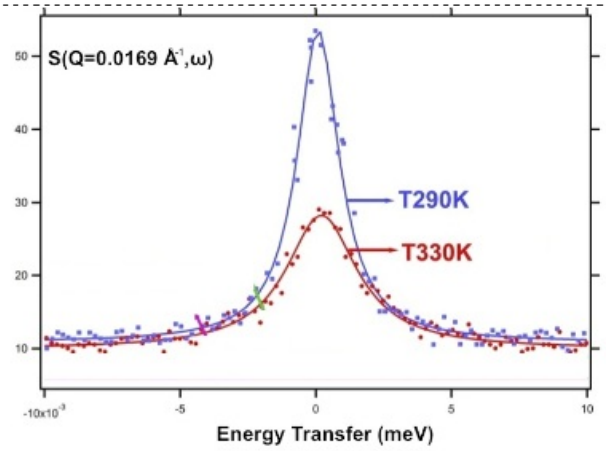

Figure 4. The *S(Q,ω)* function shows the different dynamics of the microgel networks in the swollen (330 K) and collapsed (290 K) states.

We have used IR spectroscopy to determine the interactions of the polymer matrix with the local environment. Specifically, we look for the change in the vibration bands of the amide and acrylic acid groups during the swelling process of the microgels. First, we collected the IR-ATR spectra of microgels dispersion of neat PAAc and neat PAA at 290 and 330 K. The PAA spectra present the following bands: 1607 cm^{-1} corresponding to the bending vibration amide II (C-NH2), 1635 cm^{-1} associated with the stretching vibration of the C=O···H-O-H , and 1670 cm^{-1} corresponding to the stretching vibration of the C=O. The PAAc presents a band at 1714 cm^{-1} corresponding to the stretching of the carbonyl group of the carboxyl acid. Thus, the peaks of the spectrum of the PAA/PAAc samples can be identified (see Figure 5). At 290 K, due to the formation of H-bonds, the band at 1730 cm^{-1}, corresponding to the stretching of the carbonyl group, shifts to 1714 and the band at 1635 shifts to 1610 cm^{-1}. When the temperature increases at 330 K, the intensity of the bands at 1607 and 1714 cm^{-1} decrease due to the H-bonds rupture**.** Thus, the swelling of the microgels seems to be governed by the breaking of hydrogen bonds above 300 K.

4. Conclusions

We have synthesized IPN microgels with different compositions using the concentrated emulsion polymerization method. These microgels present the greatest UCST when the matrix composition was PAA/PAAc (50/50). IQNS experiments permit determining the mean square displacement of polymer segments and their diffusion coefficient for the different microgel compositions. The FTIR spectrum seems to indicate that the swelling of the microgels is governed by hydrogen-bonds, which are broken above 300 K resulting in a reduction of the elastic tension of the polymer matrix

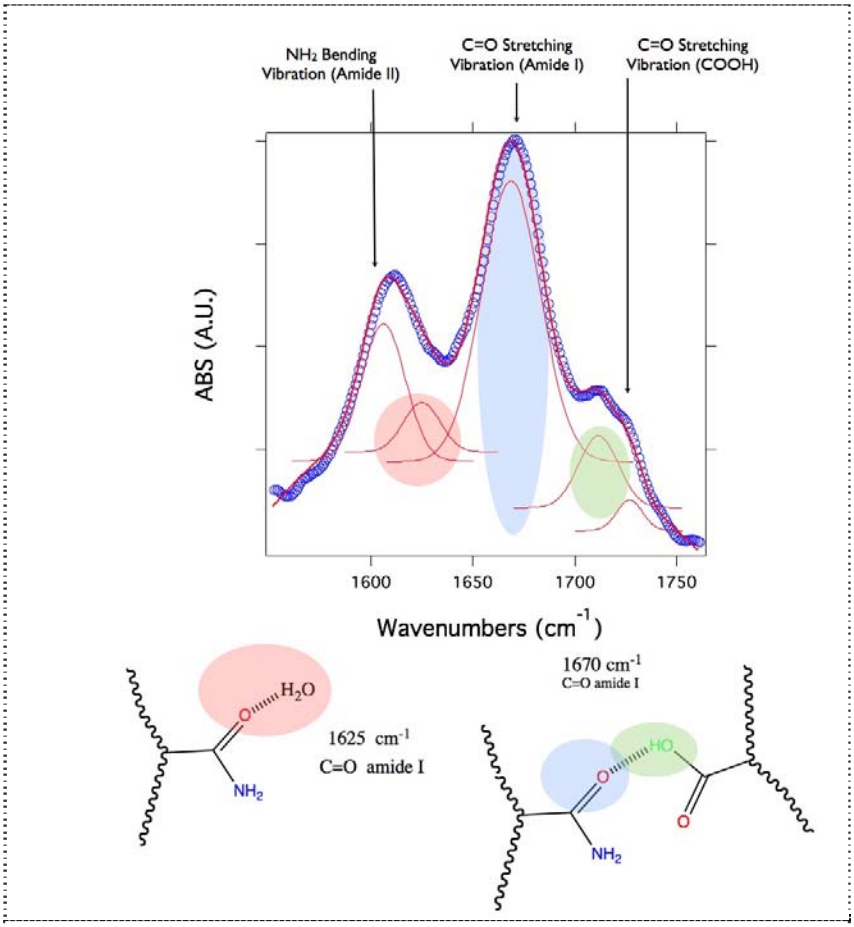

Figure 5. FTIR absorption spectra of the amide I, amide II and C=O stretching bands for PAA/PAAc microgels in the collapsed state (temperature = 25ºC)

Acknowledgements
The authors acknowledge financial support from the Spanish Science and Innovation Ministry (grant MAT2010-15349), and from the COST Action CM1101.

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