

Effect of SDS on the rheological behavior in aqueous solution of new thermosensible copolymers synthesized by micellar polymerization

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1. Abstract

Polymers based of Poly(acrylamide-*co*-N-isopropylacrylamide-*co*-hydrophobe) with low amounts of dihexylacrylamide (DHAM) and dioctylacrylamide (DOAM) were prepared by micellar polymerization. The presence of SDS at different milimolar concentrations (3 to 35mM) showed the effect of shift the LCST to higher temperatures with the increase of SDS amounts and inclusive to avoiding the macroscopic phase separation of the aqueous system at 5% in weight. Steady-state experiments showed that the presence of SDS increased the viscosity of the solutions (showing the higher viscosity value between 5-8 mM) and allowed at concentration of 3mM to keep the viscosity of the solution in an interval of temperature at 25-60°C. Relaxation times T_R and plateau modulus G_0 obtained in linear regime suggest strong interactions between hydrophobe groups induced by SDS chains at below temperatures of the LCST, while at temperatures above of the LCST these interactions were stronger between NIPAM units.

2. Introduction

Water-soluble polymers modified with a small amount of hydrophobic groups have become of great interest in the past years, and specifically the Hydrophobically Modified Polyacrylamides (HMPAM). Above a certain polymer concentration in aqueous solution, the hydrophobic groups in the hydrophilic backbone associate and build up a transitory three-dimensional network that induces a strong increase in viscosity (due to the formation of hydrophobic intermolecular associations). In order to improve the performance of these polymers, a small amount of surfactant may be used (mainly the SDS was used for this purpose). The surfactant self-assembles around the hydrophobes creating mixed micelles and generating new intermolecular associations between HMPAM chains. At constant polymer concentration, the viscosity of the aqueous solution first increases upon addition of surfactant, passes a maximum, and finally decreases [1]. The fact of use the NIPAM monomer in the terpolymers synthesized here, is due to PNIPAM exhibits a LCST at 32°C, which means that

below of 32°C the chains are hydrophilic, but above of this temperature are hydrophobic. In this way, the inherent hydrophobicity of PNIPAM above 32°C will permit the interaction with SDS, which allowed to maintain almost constant the viscosity of polymeric aqueous solutions.

3. Experimental section

3.1 Synthesis of associative polymers

The synthesis of associative polymers was carried out using a micellar polymerization technique. In this process, the hydrophobe (DHAM or DOAM, which were synthesized according to the procedure that we reported previously [2]) is solubilized within SDS micelles, whereas the water-soluble monomers [Acrylamide (AM) and N-isopropylacrylamide (NIPAM)] is dissolved in the aqueous medium. The initiator used was 4, 4'-azobis(4-cyanovaleric acid)(ACVA) and the N_H used during the synthesis was 3 (number of hydrophobes per micelle), which determined the length of the hydrophobic blocks in the hydrophilic backbone. The total polymerization time was 7 h at 50°C. The final polymer was recovered by three re-dissolution (in water) and precipitation (in acetonitrile) cycles. The weight-average molecular weight \overline{M}_w was determined by static light scattering (SLS) using formamide as solvent. The SEC (Size Exclusion Chromatography) technique was impossible to use due to aggregation phenomena.

3.2 Cloud point measurements(LCST)

The determination of the LCST of polymer aqueous solutions at 5% wt was done with an UV-Vis spectrophotometer Shimadzu 2401 at 500 nm. The measurements consisted in check the transmittance every 0.5°C. The cloud point was defined as the temperature at which exist a decrease of the 50% of initial transmittance.

3.3 Rheological measurements

The viscosity analyses of aqueous solutions at different temperatures (25-50°C) were carried out on a Paar-Physica UDS 200 controlled stress rheometer using a cone-plate geometry (2° and 50 mm). The measuring system was equipped with a solvent trap in order to prevent water evaporation during the scanning experiments. The zero-shear rate viscosity (η_0) was obtained by extrapolation of the apparent viscosity at very low shear rates carried out in steady-state experiments. Oscillatory experiments were carried out in linear regime.

4. Results and discussion

Table 1 shows the \overline{M}_w and A_2 (second virial coefficient) values obtained by SLS. The fact that $A_2 > 0$ is indicative of a good solvent quality of formamide [3].

Table 1. Static light scattering results of associative polymers in formamide.

SAMPLE	$z = 6$ DHAM		$z=8$ DOAM	
	\overline{M}_w (g/mol)	A_2 (cm ³ mol/g ²)	\overline{M}_w (g/mol)	A_2 (cm ³ mol/g ²)
PA50N50Di _z -3	425,600	0.001453	479,400	0.000929
PA55N45Di _z -3	387,200	0.001338	375,200	0.001055
PA60N40Di _z -3	383,900	0.001356	396,900	0.001141
PA65N35Di _z -3	359,900	0.001160	411,800	0.001234
PA70N30Di _z -3	408,300	0.001244	315,200	0.001147

Table 2 shows the LCST values obtained for different millimolar concentrations of SDS in aqueous solutions at 5% wt. The LCST values were shifted towards higher temperatures with the increase of SDS amount, due to interactions hydrophobe-SDS, which change the neutral polymer backbone in a polyelectrolyte and this affects the hydrophilic-hydrophobic balance.

Table 2. LCST of associative polymers at different SDS concentrations.

SAMPLE	LCST (°C)									
	0mM	2mM	3mM	4mM	5mM	6mM	8mM	10mM	15mM	35mM
PA50N50Di ₆ -3	43	46.8	53.6	59.5	64.5	68.2	70.4	84.7	NP ¹	NP ¹
PA55N45Di ₆ -3	45.1	47.7	54.3	59.8	65.2	69.4	71.3	NP ¹	NP ¹	NP ¹
PA50N50Di ₈ -3	52.4	53.8	58.5	60.6	62.4	68.5	70.5	NP ¹	NP ¹	NP ¹
PA55N45Di ₈ -3	55.2	57.3	59.6	61.2	63.7	69.7	71.2	NP ¹	NP ¹	NP ¹

¹ Not showed LCST in an interval of temperatures of 25-85°C.

Relaxation times T_R and plateau modulus G_0 obtained in linear regime for PA50N50Di₆-3 at different temperatures are showed in Figure 1 at SDS concentrations of: a) 0 mM and b) 3 mM. The increase of G_0 and the decrease of T_R from 25 to 30°C (Figure 1.a) is due that temperature affects the interaction time between hydrophobic groups (decrease of T_R) and at

the same time the intramolecular interactions are increased (increase of G_0). The decrease of G_0 and T_R up to 30°C is attributed at interactions time very short caused for temperature. In the case of 3mM of SDS (Figure 1.b) (3mM < cmc of SDS) the η_0 values showed good thermal stability up to 70°C. In the interval of 25 to 40°C, is observed a decrease of T_R caused for the increase of the temperature, while that few amounts of SDS cause the formation of new intermolecular interactions (increase of G_0), which result in constant viscosity values. At 50°C, a decrease of G_0 and increase of T_R is presented, probably due at this temperature exist links between SDS-DHAM y SDS-NIPAM units (for the large amount of PNIPAM in the polymer), the intermolecular interactions are affected for the temperature (decrease of G_0), but at the same time the presence of SDS improve the interaction time (increase of T_R). On another hand, at temperatures $\leq 40^\circ\text{C}$ the viscosity is maintained almost constant due to the formation of new interactions in the aqueous medium (SDS-DHAM and SDS-NIPAM interactions), but at temperatures $>50^\circ\text{C}$, the viscosity is maintained without variation due at the interactions between NIPAM chains are stronger than DHAM.

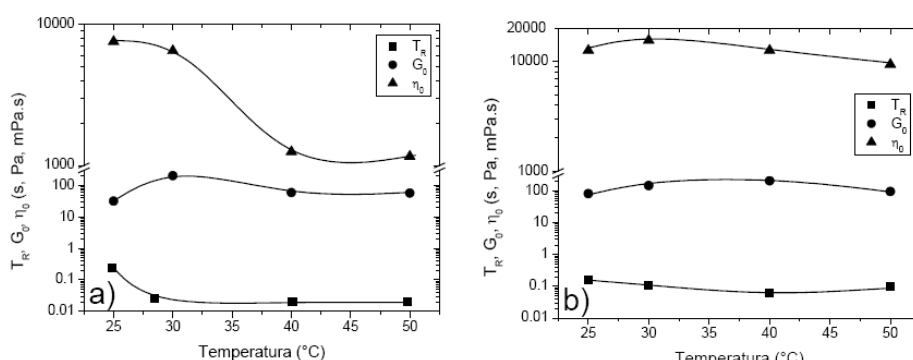


Figure 1. T_R y G_0 evolution as function of temperature of PA50N50Di6-3: a) without SDS and b) [SDS]=3 mM. Aqueous solutions at 5% in weight.

5. Conclusions

The presence of SDS at different milimolar concentrations (3 to 35mM) showed the effect of shift the LCST to higher temperatures with the increase of SDS amounts and inclusive to avoiding the macroscopic phase separation of the aqueous system at 5% wt.

Relaxation times T_R and plateau modulus G_0 obtained in linear regime suggest strong interactions between hydrophobe groups induced by SDS chains at below temperatures of the LCST, while at temperatures above of the LCST these interactions were stronger between NIPAM units, which allowed to maintain almost constant the viscosity of the solutions.

6. References

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