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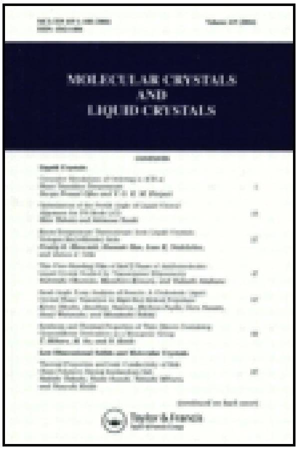

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Synthesis and Properties of Hydrophobically Modified Polyampholytes

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Synthesis and Properties of Hydrophobically Modified Polyampholytes

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Hydrophobically modified, low charge density polyampholytes were prepared by copolymerization of acrylamide, [2-methacryloyloxy)ethyl] trimethylammonium chloride, sodium 2-acrylamido-2-methylpropane sulfonate and a hydrophobic monomer (N,N-dihexylacrylamide) in a micellar aqueous medium. The resulting polymer is soluble in pure water and in sodium chloride aqueous solutions and exhibits improved thickening properties with respect to the unmodified polyampholyte due to intermolecular association. This behavior manifests itself particularly in high-salinity media.

Keywords: hydrophobically modified polymers; polyampholytes; associative thickeners; aqueous solution; viscosity

INTRODUCTION

In recent years, an increasing number of studies concerning water-soluble polymers have focused on their hydrophobic modification. The incorporation of a few hydrophobic moieties in a hydrophilic polymer chain results in materials with unique rheological properties in aqueous solution[1-4]. This makes these systems useful in a large number of applications including enhanced oil recovery, coatings or cosmetics. The choice method for the synthesis of these so-called "associative polymers" is copolymerization in micellar systems[4]. In this case, a water-soluble monomer, together with a micelle-forming compound (surfactant), are dissolved in water, while a hydrophobic comonomer is

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preferentially placed inside the micelles. Due to their high density in the micelles, the hydrophobic monomers are randomly distributed as small blocks in the hydrophilic backbone[4]. Although acrylamide is often used as the main water-soluble monomer, other ionic comonomers were also applied in order to synthesise hydrophobically modified polyelectrolytes[5-8]. In the present study, we extend this micellar polymerisation process to the synthesis of hydrophobically modified polyampholytes. These materials, bearing both positive and negative groups in the hydrophilic backbone, seem to be extremely interesting in all types of applications where thickeners are required in brine solution, as in flocculation[9]. To the best of our knowledge, this preliminary report is the first one, in which a micellar synthesis of modified polyampholytes is described. A few previous reports dealing with the synthesis of such type of materials describe solution polymerization of ionomer pairs, where one compound was modified with long hydrocarbon chain[10,11].

EXPERIMENTAL

Monomers, acrylamide (AM, Aldrich), [2-(Methacryloyloxy)ethyl]trimethyl ammonium chloride (M, Elf-Atochem) and 2-acrylamido-2-methyl propanesulfonic acid (AMPS, Lubrizol) were purified as described previously[12]. AMPS was neutralized by slow addition to an aqueous solution of NaOH at pH=9, resulting in sodium 2-acrylamido-2-methyl propanesulfonate (A). Water was purified by a Millipore Milli-RO / Milli-Q system. The surfactant, sodium dodecylsulfate (SDS, Acros) and the water-soluble initiator VA086 (Wako Chemicals) were used as received. The hydrophobic comonomer, N,N-dihexylacrylamide (DHAM)[13] was prepared according to Valint *et. al*[14]. A detailed description of the micellar copolymerization is given elsewhere[15]. Briefly, the initial concentration of hydrophilic monomers was kept constant at 3 wt% and the initiator concentration was set to 0.2 mol%

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relative to monomer feed. The polymerization was initiated by the injection of the stock solution of initiator under irradiation at 25°C with ultraviolet light (mercury lamp, Philips). The reaction was stopped after 3 h by precipitation of polymer in isopropanol. Subsequently, the polymer was washed in isopropanol and acetone, dried under reduced pressure, redissolved in water, reprecipitated in isopropanol and again washed and dried as described above. The polymer composition was determined by elemental analysis[12, 16]. The incorporation of the hydrophobic comonomer was measured by ^{1}H-NMR[13] in 1 wt% polymer solution in D_2O/methanol-d_4 9/1 (w/w) mixtures (Bruker AC 200). The molecular weight of the samples was determined in formamide solution containing 0.15 M NaCl by classical light scattering (multiangle spectrometer Brookhaven Instr., λ=514.5 nm). The rheological measurements[13] in dilute solution were performed on a Contraves LS 30 low-shear rheometer. The viscosity of semi-diluted solutions was measured using a Haake RS100 controlled-stress rheometer (cone-plate geometry – diameter 35 or 60 mm, angle 1°). The solubility measurements in pure water or sodium chloride solution were done by measuring the optical transmittance at 600 nm of the 1% polymer solution at 20°C (Schimadzu UV-2101PC).

RESULTS AND DISCUSSION

Polyampholytes with a relatively low charge density (15 %) were synthesised. The hydrophobe level in the polymerization mixture was 1 mol% with respect to the monomer feed. The SDS concentration was selected in order to achieve the blocky structure of the polymer i.e. the number of hydrophobes per micelle (N_h) was about 4. The length of the hydrophobic blocks in the copolymers is then assumed to correspond roughly to N_h. It was shown that this type of structure effectively enhances the association and the thickening efficiency[4,13,15]. The elemental analysis and NMR data for the modified polymer and its unmodified analogue are given in Table I. As can be seen, the synthesised polymers are characterised by a low positive net charge (<1 mol%). However, they are obtained at high conversion, and therefore can present a distribution of the net charge among individual chains that can considerably affects the solution properties[9,12]. As far as the ionic monomer units are concerned, the microstructure of these materials is the most probably not far from alternate, in contrast to the polymers obtained in microemulsion, where the fully charged polyampholytes of a random structure are synthesised[9,16].

TABLE I Compositional characteristics of the polyampholytes

Sample	Feed composition (mol%)[a]				Polymer composition (mol%)				
	[AM]	[DHAM]	[SDS][b]	N_h[c]	[AM]	[A]	[M]	[DHAM]	Conv.
NM	90	0	1.1	0	85.0	7.1	7.9	0	80%
M-4	89	1	1.8	4	85.2	6.7	6.9	1.2	80%

[a] ionic monomer concentration was constant and equal to [A]=7% mol and [M]=3% mol.
[b] SDS concentration is given in weight percent
[c] N_h was calculated taking a critical micelle concentration and an aggregation number equal to 0.003 M and 80, respectively[17].

The molecular weight of both samples is within the same range and equals *ca.* 9.3×10^5 Da. The unmodified sample (NM) is soluble in pure water and in a sodium chloride solution (concentration above 0.5 M), and gives an opaque solution at lower NaCl concentrations. In contrast, the modified polymer (M-4) is soluble in water and NaCl solutions over the entire range of salt concentrations investigated (up to 3.5 M). This different behavior can be due to the suppression of the intramolecular electrostatic attractions between the charged segments of the polymer in the case of M-4 sample. The hydrophobic groups, present in this polymer, tend to associate intermolecularly and can disrupt the electrostatic clusters, which are responsible for the insolubility of the unmodified polymer. At high NaCl concentration, the added salt screens the charges and the electrostatic interactions in the clusters weaken, which allows the chains to relax and, in the case of NM sample, also to dissolve. The changes

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of the reduced viscosity for both samples recorded in 0.5 and 3.5 M NaCl are depicted in Figure 1. The viscosity of M-4 sample increases with polymer concentration much faster than for NM polymer. Moreover, this behavior is more pronounced upon increasing the salt concentration, indicating more efficient associative properties[4,13]. The dependence of the reduced viscosity on polymer concentration for NM sample is linear. Calculated values of the intrinsic viscosity and Huggins constant increase and decrease respectively with NaCl concentration, indicating an improvement of the solvent quality. This behavior is often observed in polyampholyte solutions[9,12]. In the case of M-4 sample, the calculation of the above mentioned parameters was not possible because of a significant curvature of the measured dependence. Nevertheless, a simple comparison of the viscosity values measured in 0.5 M NaCl and 3.5 M NaCl solutions confirms that a combination of hydrophobic and polyampholytic effects are still operative in this case.

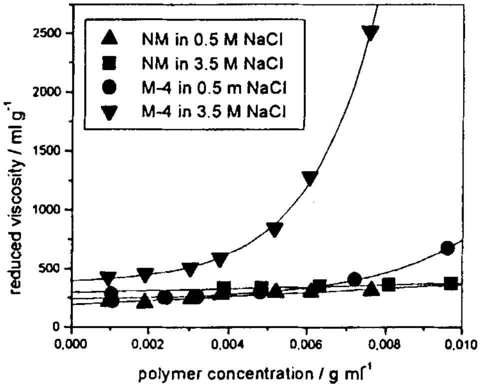

FIGURE 1. Reduced viscosity versus polymer concentration in dilute 0.5 M and 3.5 M NaCl solutions.

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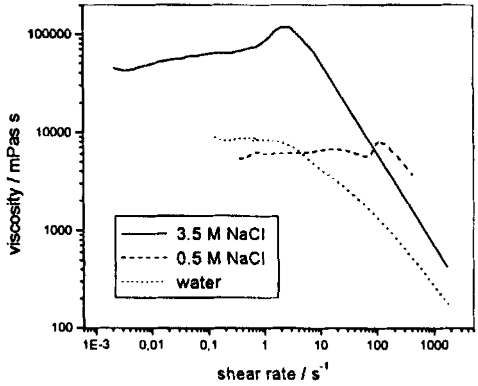

FIGURE 2. Viscosity of 4 wt% M-4 solutions as a function of shear rate.

Another evidence of these effects is the rheological behavior of M-4 solutions in the semi-dilute regime in the presence of salt (Figure 2). In 0.5 M NaCl solution, the value of the newtonian plateau is lower than in water, while in 3.5 M NaCl this value is much higher. Moreover, in the presence of salt, a shear-thickening effect (i.e. viscosity increases with shear rate in the intermediate region of shear rates) is observed. This effect is attributed to the changes in the conformation of the polymeric chains under shear[13]. At a certain shear rate, the intramolecular junctions in the polymer sample can be disrupted. Thus, the released hydrophobic groups can effectively form new intermolecular associations in the transient network, leading to an increase in viscosity. It should also be noted that the shear-thickening region is displaced towards lower values of the shear rate upon increasing the concentration of electrolyte. This indicates a slowing down of the relaxation process, when more salt is added to the sample. The flow curves of the NM sample in the same range of polymer and salt concentrations show a newtonian behavior with a few hundred times lower values of the viscosity (results not shown). All these observations confirm

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the polyampholytic (viscosity growth with salt concentration) and associative (high viscosity values compared to unmodified samples, shear-thickening and shear thinning effects) character of the polymer formed by this process.

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References

[1] M. A. Winnik and A. Yekta, *Curr. Opin. Colloid Interface Sci.,* **2,** 424 (1997).

[2] J. E. Glass, Ed., *Polymers in Aqueous Media: Performance Through Association,* Advances in Chemistry 223, American Chemical Society, Washington, DC, 1989.

[3] J. E. Glass, Ed., *Hydrophilic Polymers: Performance with Environmental Acceptability,* Advances in Chemistry 248, American Chemical Society, Washington, DC, 1996.

[4] F. Candau and J. Selb, *Adv. Colloid Interface Sci.,* **79,** 149 (1999) and references cited therein.

[5] C. L. McCormick, J. C. Middleton and D. F. Cummins, *Macromolecules,* **25,** 1201 (1992).

[6] C. L. McCormick, J. C. Middleton and C. E. Grady, *Polymer,* **33,** 4184 (1992).

[7] K. D. Branham, H. S. Snowden and C. L. McCormick, *Macromolecules,* **29,** 254 (1996).

[8] I. Lacik, J. Selb and F. Candau, *Polymer,* **36,** 3197 (1995).

[9] F. Candau and J. F. Joanny, in *Polymeric Materials Encyclopedia,* edited by J. C. Salamone (CRC Press, Boca Raton, 1996), Vol. 7, p. 5476.

[10] A. C. Watterson, C. R. Hunter, A. M. Thompson and J. C. Salamone, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.,* **32** (1), 126 (1991).

[11] A. C. Watterson, C. R. Hunter and J. C. Salamone, *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.,* **33** (1), 1160 (1992).

[12] A. Ohlemacher, F. Candau, J. P. Munch and S. J. Candau, *J. Polym. Sci., Part B,* **34,** 2747(1996).

[13] E. Volpert, J. Selb and F. Candau, *Macromolecules,* **29,** 1452 (1996).

[14] P. L. Valint, J. Bock and D. N. Schulz, in *Polymers in Aqueous Media: Performance Through Association,* edited by J. E. Glass (Advances in Chemistry 223, American Chemical Society, Washington, DC, 1989), Chap. 21, p. 399.

[15] A. Hill, F. Candau and J. Selb, *Macromolecules,* **26,** 4521 (1993).

[16] J.-M. Corpart, J. Selb and F. Candau, *Polymer,* **34,** 3873 (1993).

[17] Y. Croonen, E. Gelade, R. Van der Zegel, R. Van der Anweraer, H. Vandendriessche, F. C. De Schryrer and M. Almgren, *J. Phys. Chem.,* **87,**1426 (1983).