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Micellar copolymerisation of *N*,*N*-dimethylacrylamide and *t*-butylacrylamide

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Abstract

A copolymer of the water-soluble hydrophilic monomer *N*,*N*-dimethylacrylamide and of the practically water-insoluble hydrophobic *t*-butylacrylamide was synthesised in aqueous solution in the presence of sodium dodecylsulfate (SDS) micelles. Its behaviour in dilute aqueous solution was compared to the behaviour of its respective counterpart with practically the same composition, prepared under homogeneous conditions in tetrahydrofuran. The product synthesised under micellar conditions exhibits a pronounced hydrophobic character, as it phase separates in water by increasing temperature at about 46°C, i.e. 29°C lower than the copolymer prepared under homogeneous conditions and associates much stronger with SDS. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: *N*,*N*-dimethylacrylamide; *t*-Butylacrylamide; Micellar copolymerisation

1. Introduction

Radical copolymerisation of a hydrophilic and a hydrophobic, practically water-insoluble, monomer in an aqueous micellar environment has been proved well suited for the preparation of hydrophobically modified water-soluble polymers [1–12]. According to this method, the hydrophobic monomer, usually an alkylacrylamide, otherwise insoluble in water, is solubilised in the non-polar micellar microenvironment of a suitable surfactant, like sodium dodecylsulfate (SDS), while the hydrophilic monomer is dissolved in the continuous water medium. The confinement of more than one hydrophobic monomers in each micelle results in the formation of copolymers with a blocky structure, as it was revealed by photophysical studies [2,4–6,8,9]. Candau and co-workers [8,10,11] have shown that the associative properties of the hydrophobically modified products are more pronounced when the blockiness of their structure is higher, while it could be effectively controlled by varying the ratio of the SDS to the hydrophobic monomer molar concentration. In these works, the incorporation of hydrophobic monomers in the copolymers synthesised was limited to low molar ratios (less than 5 mol%), as the products with a higher hydrophobic content were insoluble in water.

In this communication, we report on the preparation of a water-soluble copolymer containing a considerable amount, about 30 mol%, of the hydrophobic monomer *t*-butylacrylamide (TBAM), via micellar copolymerisation. The solubility of TBAM in pure water has been reported to be very low, ~0.2 wt% [13]. *N*,*N*-dimethylacrylamide (DMAM) was chosen as the second monomer. Apart from its hydrophilic character and its high water solubility, this monomer, and the corresponding homopolymer, is soluble in common organic solvents [14]. This allowed us the easy preparation of the corresponding DMAM–TBAM statistical copolymer, with a similar monomer composition, under homogeneous conditions [15]. The solution properties of the two products in dilute aqueous solution are compared.

2. Experimental

2.1. Materials

Both monomers, DMAM and TBAM, were products of Aldrich and used as received. Analytical grade tetrahydrofuran (THF), SDS (Fluka), azobisisobutyronitrile (Fluka), ammonium persulfate (Serva) and sodium metabisulfite (Serva) were also used.

2.2. Copolymerisations

The micellar copolymerisation was conducted at 29°C in

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Table 1
Copolymerisation conditions and ^{1}H NMR characterisation of the copolymers synthesised

Entry	Notation	Solvent	Monomer feed concentration (M)		TBAM content in the copolymer (^{1}H NMR) (mol%)
			[DMAM]	[TBAM]	
1	DMAM–TBAM-H	THF	0.36	0.12	29
2	DMAM–TBAM-M	1 M SDS	0.24	0.08	28

an aqueous 1 M SDS solution. The redox couple ammonium persulfate/sodium metabisulfite was used as initiator. After 24 h, the reaction mixture was dialysed for several days against a solution of poly(diallyl dimethylammonium chloride) in order to remove SDS. Finally, the copolymer was obtained by freeze-drying. The conductivity of a 1 wt% copolymer solution in water was comparable to that of pure water.

The homogeneous copolymerisation was conducted at 65°C in THF for 24 h. Azobisisobutyronitrile was used as initiator. The product was recovered by precipitation in diethylether and dried under vacuum at 40°C for 24 h.

The yield of both copolymers was higher than 70%. Their composition was determined by ^{1}H NMR.

2.3. Cloud point measurements

The change in absorbance of the aqueous solutions of the polymers was monitored as a function of temperature at a fixed wavelength of 490 nm by means of a Hitachi spectrophotometer model U 2001, equipped with a circulating water bath.

2.4. Pyrene fluorescence probing

Steady-state fluorescence spectra were recorded on a Perkin Elmer LS50B luminescence spectrometer. Pyrene was used as a fluorescence probe at a concentration 6×10^{-7} mol/l. The excitation wavelength was 334 nm and the intensities at 373 and 384 nm were used to calculate the first over the third peak intensity ratio, I_1/I_3.

3. Results and discussion

Table 1 presents the copolymerisation conditions and the ^{1}H NMR characterisation of the two copolymer samples synthesised in this work. DMAM–TBAM-H has been synthesised under homogeneous conditions in THF and is considered to be statistical, as the reactivity ratios of the two monomers are not expected to be very different, given that both monomers are *N*-substituted acrylamides. On the contrary DMAM–TBAM-M, that has been synthesised in a 1 M SDS aqueous solution, is expected to have a blocky structure. As TBAM is sparingly soluble in water, it is practically distributed in the SDS micellar ‘phase’. Taking into account that the aggregation number of the SDS micelles is around 60 [14], we estimate that in the reaction conditions each micelle should contain about five TBAM molecules. Given that DMAM is water-soluble, a non-uniform distribution of the two monomers in the reaction medium should occur, reflected on a rather blocky structure of the copolymer prepared. Even if a direct verification of such a structure is not easily feasible, the phase behaviour of the two copolymers in dilute aqueous solution could provide evidence for this hypothesis. This is facilitated by the fact that the two copolymer samples prepared from solutions of the same feed composition present a quite similar monomer composition, 29 and 28%, respectively, as it was determined by ^{1}H NMR spectroscopy.

Fig. 1 presents the optical density of the aqueous solutions of the two copolymers as a function of the temperature. Both copolymers present lower critical solution temperature (LCST) behaviour in water and their solutions turn cloudy upon heating. Nevertheless, important qualitative differences are observed. The onset of turbidity for DMAM–TBAM-H, i.e. its cloud point, is observed at 75°C. This value is well comparable with the observations

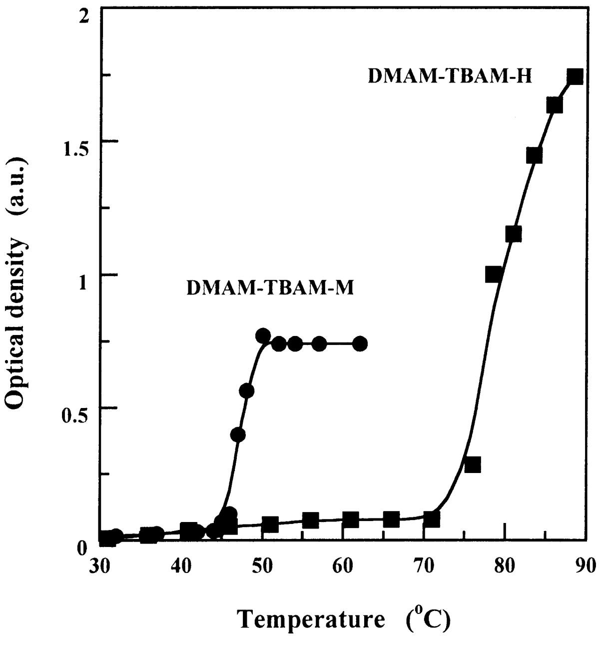

Fig. 1. Variation of the optical density of the aqueous solutions of the copolymers DMAM–TBAM-H and DMAM–TBAM-M as a function of the temperature. The polymer concentration is 2×10^{-3} g/ml.

of Liu et al. [15] for a series of DMAM–TBAM statistical copolymers prepared in methanol under homogeneous conditions. On the contrary, the cloud point of the copolymer DMAM–TBAM-M, prepared in the SDS micellar environment, is observed at 46°C, a much lower temperature. This behaviour could be explained by a difference in the structure of the two copolymers. DMAM–TBAM-M sample should contain an important number of sequences considerably rich in the hydrophobic TBAM units. Of course, the rest sequences are enriched in DMAM units. Such a copolymer structure of hydrophilic and hydrophobic sequences could explain the much lower cloud point temperature and the relatively low turbidity level observed at temperatures higher than the cloud point temperature of DMAM–TBAM-M. As temperature increases, water becomes a poor solvent for the TBAM-rich sequences, while it is still a good solvent for the DMAM-rich sequences. The hydrophilic sequences, exposed in the water environment, could stabilise the phase-separated hydrophobic sequences in the form of small colloidal particles. In contrast, for the copolymer DMAM–TBAM-H, where a rather random distribution of the monomers is expected, as temperature increases above the cloud point, which now is much higher, water becomes a poor solvent for the whole polymer chain and the phase-separated particles could not be stabilised in the colloidal form. Larger particles are formed and the turbidity increases continuously up to a very high level.

In Fig. 2, the cloud point of the two copolymers, as a function of the NaCl concentration, in dilute aqueous solution is shown. An important salting out effect, rather typical for LCST polymers, is observed for the two copolymers. For instance, in the presence of 1 M NaCl, the cloud point of DMAM–TBAM-H is 56°C and that of DMAM–TBAM-M is 32°C, i.e. 19 and 14°C lower than the cloud points of the respective copolymers in pure water. It is noteworthy that for poly(*N*-isopropylacrylamide) (PNIPAM), a typical LCST polymer, the corresponding change of the cloud point is similar, namely ~15°C [16].

Pyrene fluorescence probing measurements at 25°C have been conducted in order to investigate the interactions of DMAM–TBAM-H and DMAM–TBAM-M with SDS in water. As known, the ratio I_1/I_3 of the intensity of the first over the third vibronic peak of the fluorescence emission spectrum of pyrene is sensitive to the polarity of the microenvironment and it is successfully applied to detect in aqueous solution the formation of hydrophobic microdomains, where pyrene molecules are preferentially solubilised [17].

In Fig. 3, the ratio I_1/I_3 is plotted as a function of the SDS concentration for pure SDS solutions and for SDS solutions containing 2×10^{-3} g/ml DMAM–TBAM-H or DMAM–TBAM-M. In pure SDS solutions, the value of the I_1/I_3 ratio is about 1.7 for low SDS concentration, while for high SDS concentration it takes substantially lower values, namely ~1.2, indicative of a micellar hydrophobic microenvironment. In fact, the transition in the values of I_1/I_3 corresponds to the formation of the first SDS micelles and it is used to determine the critical micelle concentration (cmc) of SDS. From Fig. 3, cmc is determined to be ~8 mM, in good agreement with the values reported in literature [18]. In the presence of DMAM–TBAM-H, the I_1/I_3 ratio is displaced to lower values at low SDS

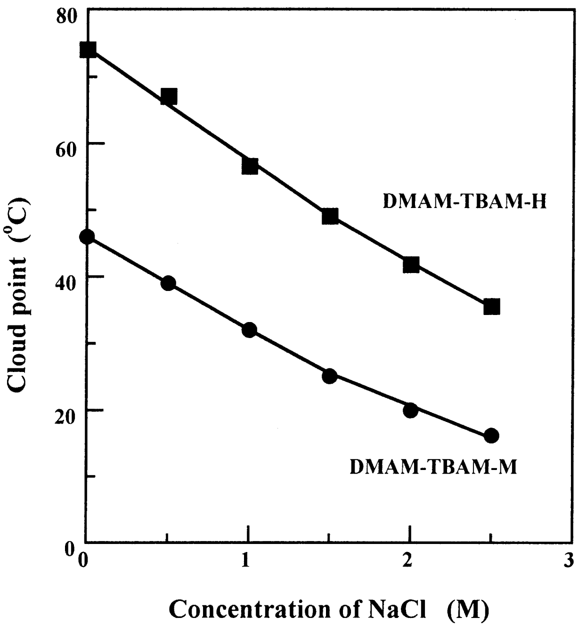

Fig. 2. Variation of the cloud point of aqueous solutions of the copolymers DMAM–TBAM-H and DMAM–TBAM-M as a function of the NaCl concentration. The polymer concentration is 2×10^{-3} g/ml.

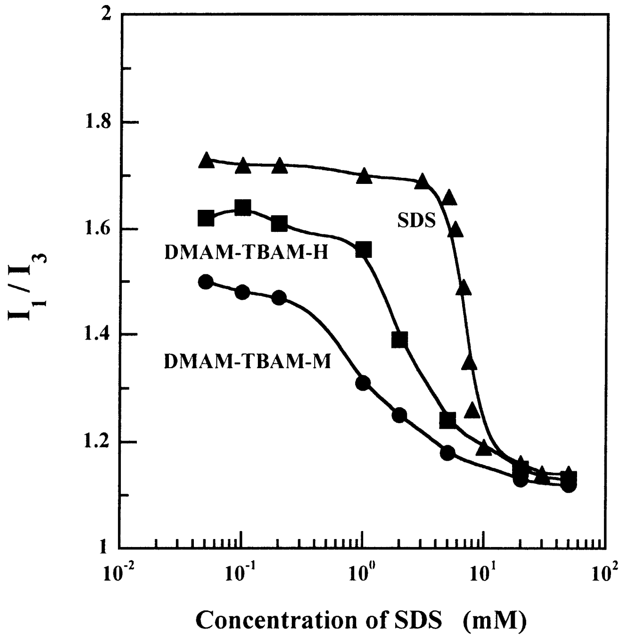

Fig. 3. Variation of the I_1/I_3 ratio of the pyrene spectrum as a function of the SDS concentration for pure SDS aqueous solutions (▲) and aqueous mixtures of SDS with DMAM–TBAM-H (■) or DMAM–TBAM-M (●). The polymer concentration is 2×10^{-3} g/ml; $T = 25$°C.

concentration, indicating the presence of a more hydrophobic environment, due to the presence of the polymer, while the transition point is displaced to a lower SDS concentration. This is also an evidence of the hydrophobicity of the polymer that is able to form mixed aggregates with SDS molecules. The critical aggregation concentration (cac) is determined from Fig. 3 to be about 2 mM for the system DMAM–TBAM-H/SDS, higher than that of the PNIPAM/SDS system (~0.8 mM) [18] and lower than that of the polyethyleneoxide/SDS system (~4 mM) [19]. This behaviour should be related with the intermediate value of the cloud point of DMAM–TBAM-H in aqueous solution, 75°C, as it compares with the higher value of PEO, 98°C [20], and the lower value of PNIPAM, 33°C [21]. In the case of the copolymer DMAM–TBAM-M, a more pronounced hydrophobic character is revealed. The I_1/I_3 values are lower than these of the DMAM–TBAM-H/SDS aqueous system, especially at low SDS concentration, lower than 0.2 mM. This could be attributed to an increased hydrophobicity of DMAM–TBAM-M. Moreover, a much more gradual decrease of the I_1/I_3 ratio with increasing SDS concentration is now observed. Therefore, the determination of a cac is very difficult. This could be attributed to the structural heterogeneity of DMAM–TBAM-M. The TBAM-richer sequences are more hydrophobic and their presence is indicated by the lower I_1/I_3 values at low SDS concentration. As the SDS concentration increases, a continuously increasing association of the copolymer with SDS is taking place. Aggregates of an increasing hydrophobic character are formed, until the final level of the pure SDS micelles is attained. However, the I_1/I_3 curve in the presence of DMAM–TBAM-M is always lower than the corresponding curve of DMAM–TBAM-H, showing its stronger association with SDS and higher hydrophobicity.

4. Conclusion

The radical copolymerisation in aqueous SDS micellar solution of a hydrophilic monomer, DMAM, with a hydrophobic, practically water-insoluble monomer, TBAM, leads to the synthesis of a copolymer with a blocky structure. This is revealed by the pronounced LCST character of this copolymer in aqueous solution and by its higher ability to form mixed aggregates with SDS, as it compares with its respective statistical product prepared homogeneously in THF. The results obtained show that copolymerisation of a hydrophobic and a hydrophilic monomer in a micellar environment could be a useful tool to control the distribution of the two monomers in the copolymer chain, i.e. of the blockiness of the copolymer, reflected in its physicochemical properties.

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