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Copolymers of sodium styrenesulphonate with *n*-butylvinylether and *n*-octadecylvinylether prepared by micellar copolymerization

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Abstract

Copolymers of *n*-butylvinylether (BVE) and *n*-octadecylvinylether (OVE) with styrenesulphonate (SS) were obtained by micellar copolymerization in the presence of the cationic detergent CTAB. The polymerization reaction proceeds mainly in the domain of the hydrophobe-containing cationic micelles, to which SS and the initiator are attracted electrostatically. The monomer distribution along the polymer chain was found to be dependent on the ratio between the concentrations of hydrophobic monomer and surfactant [H]/[S]. At high [H]/[S] ratios block structures are formed and at the lower [H]/[S] ratios random distributions of the monomers were obtained. The structures of the copolymers were characterized by their NMR and emission spectra. The fluorescence emission of the copolymers obtained at higher [H]/[S] ratios were similar to that of PSS, whereas for those obtained at lower [H]/[S] ratios the spectra were like that of SS. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Micellar copolymerization; Vinylether polymerization; Block polyelectrolytes

1. Introduction

Synthetic polymers containing non-polar groups that aggregate in polar media were first used as model compounds for studying the conformation of proteins [1]. Copolymers with surfactant-like properties were prepared chemically, for instance, by *n*-dodecylation of poly(2-vinylpyridine) or the hydrolysis of alternating copolymers of maleic anhydride and alkylvinylethers [2]. Macromolecules which behave this way are frequently called micelle-forming polymers or polysoaps [3]. Polysoaps with better defined chemical structures can be obtained by the polymerization of surfactants with appropriate vinyl groups [4–7]. Another strategy that may be used is the hydrophobization of pre-formed polyelectrolytes [8,9].

The copolymerization of hydrophobic and hydrophilic monomers yields well-defined hydrophobic fragments in the chain of the copolymer [10–14]. However, the copolymerization of monomers of very different polarities might be difficult because of the insolubility of the hydrophobic monomers in water. The use of aqueous surfactant solutions to ensure the solubilization of the hydrophobic monomers was proposed to overcome this problem. Many publications deal with copolymers synthesised by this technique [15–18]. In this process the hydrophobic monomer is solubilized in the micelles, whereas the hydrophilic monomer is placed in the intermicellar aqueous phase. When the polymerization of the monomer is performed in micellar solutions, the polymerization rate and the molecular weights of the polymer are strongly increased because of the aggregation. This one-step micellar copolymerization renders water soluble copolymers that can be adequately used in a number of applications including enhanced oil recovery, latex paints and aqueous viscosifiers [19]. Acrylamide based copolymers obtained by this technique are among those most studied [16–18].

The microstructure of the copolymer is influenced by the amount of surfactant micelles present during the synthesis. It has been shown that copolymers prepared under micellar conditions have properties that can be related directly to the ratio between the concentrations of hydrophobic monomer and surfactant ([H]/[S]) [16,17]. The high local concentration of the hydrophobic monomers in the micelles favours their incorporation in the copolymer as blocks rather than as isolated units. In contrast, random copolymer structures are obtained using low [H]/[S] ratios, typically less than one monomer per micelle. Evidence of the formation of block

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Table 1
Polymerization conditions and properties of the copolymers of SS/VE obtained by micellar copolymerization. [CTAB] = 0.0559 M, [KPS] = 0.3 wt%

	Copolymer	%mol[a] in the feed		%mol[a] in the Copolymer		[VE]/[CTAB]	M_w[b]	M_w/M_N	Yield %
		SS	VE	SS	VE				
1	co-BVE17-R	95	5	83(77)	17	0.14	172000	4.43	71
2	co-BVE25-R	90	10	75(82)	25	0.29	125000	3.25	95
3	co-BVE39-R	80	20	61	39	0.43	102000	3.62	60
4	co-BVE38-R	70	30	62(66)	38	0.74	107000	3.98	84
5	co-BVE10-R	60	40	90	10	1.15	87000	3.50	50
6	co-BVE41-B	50	50	59(57)	41	1.77	44000	3.14	40
7	co-BVE4-R	25	75	96	4	5.19	80000	3.63	29
8	co-OVE8-R	95	5	92(86)	8	0.09	92000	3.55	74
9	co-OVE11-B	90	10	89(95)	11	0.17	58000	3.29	73
10	co-OVE8-B	80	20	92(94)	8	0.43	68000	3.62	79
11	co-OVE15-B	75	25	85(88)	15	0.58	56000	3.26	69
12	co-OVE1-R	70	30	99	1	0.74	85000	3.25	40

[a] Determined from NMR spectra (± 3%). Values in parentheses refer to S elemental analysis (± 5%).
[b] Determined by GPC. The M_w determined for PSS was 76000 g mol^{-1}.

structures was provided by Dowling and Thomas [15] from photophysical studies on polyacrylamides containing styryl groups as the hydrophobic monomer. The length of the blocks can be regulated by adjusting the [H]/[S] ratio in the synthesis.

The copolymerization of alkylvinylethers was performed using both ionic and free radical initiations, although the formation of polymers of vinylethers has proved to be rather difficult. Nonetheless, free radical initiated copolymerization of alkylvinylethers with monomers bearing strong electron withdrawing substituents is used to manufacture commercially used products [20].

In this work, we report on the micellar copolymerization of *n*-butylvinylether (BVE) and *n*-octadecylvinylether (OVE) with sodium styrenesulphonate (SS). To our knowledge, no studies have been done on the copolymerization of these monomers with an anionic monomer by free radical initiation. It is known that the homopolymerization of alkylvinylethers is only possible using cationic initiators at low temperature [21,22]. However, the homopolymerization of BVE under micellar conditions by free radical initiation at 70°C, was found to be possible. These co-monomers yield copolymers containing strong hydrophobic segments. Depending on their composition and structure, these polymers may form micelle-like microdomains and be soluble in water.

2. Experimental

2.1. Chemicals

n-Butylvinylether (Polyscience, 99%), *n*-octadecylvinylether (Polyscience, 99%), styrene-4-sulphonate sodium salt (Aldrich), potassium persulphate (KPS, Merck) and cetyltrimethylammonium bromide (CTAB, Sigma), were used as received. Poly(styrene-4-sulphonate) sodium salt (Aldrich) was precipitated twice from acetone before use. Water was purified in a Milli-Q system.

2.2. Synthesis of copolymers

The BVE/SS (co-BVE) and OVE/SS (co-OVE) copolymers were prepared by aqueous micellar polymerization. The initial concentration of the monomers and the amount incorporated in the copolymers are shown in Table 1. The concentration of KPS was 0.3 wt%. The CTAB content was kept at 2 wt%, corresponding to about 100 times its critical micellar concentration (cmc) at 25°C.

The copolymerization reactions were carried out in a 50 mL reactor fitted with a reflux condenser, magnetic stirrer, rubber septum cap, thermometer, and nitrogen inlet/outlet. The reactor containing the solution of CTAB and alkylvinylether was flushed with nitrogen for 20 min. After complete solubilization of the hydrophobic monomer in the micellar solution the hydrophilic monomer was added. The mixture was heated to 70°C while stirring. When the mixture was homogeneous (within about 10–30 minutes, depending on the amount of the hydrophobic monomer), the KPS was added. The reaction was run for 7 h.

After cooling the reaction mixture, the polymer was precipitated by dropwise addition of a large excess of acetone. The polymer recovered by filtration was repeatedly washed with acetone to remove surfactant and residual monomers and dried for several days under vacuum and stored in a dissecator.

2.3. Gel permeation chromatography

Molecular weights and molecular weight distributions were determined by Gel Permeation Chromatography (GPC) on a Shimadzu HPLC Chromatograph with an RI detector using a combination of an ultrahydrogel precolumn and two ultrahydrogel linear columns (Waters).

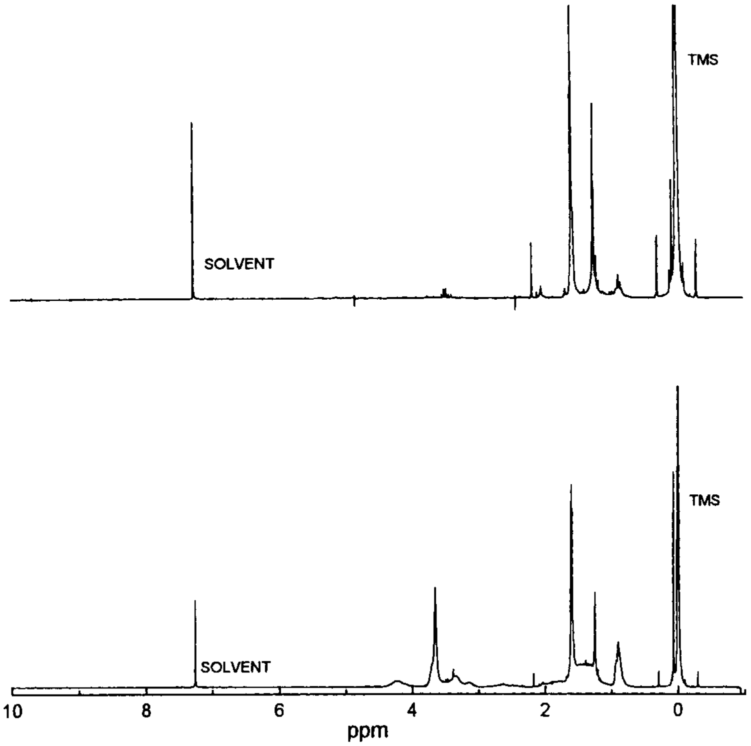

Fig. 1. ^{1}H-NMR spectra of polyBVE (below) and co-BVE41-B (above) in $CDCl_3$, using TMS as external standard.

Calibration was carried out using poly(styrene-4-sulphonate) sodium salt standards (Aldrich) ranging from 1600–354000 g mol^{-1}. The eluent was a solution of 0.1 M $NaNO_3$ in water:methanol (8:2), at a flow rate of 1.0 mL min^{-1} at 35°C. The molecular weight obtained for the commercial sample of PSS was 76000, which is in reasonable agreement with the value of 71000 given in the specifications.

2.4. Nuclear magnetic resonance spectroscopy

All NMR spectra were recorded on a Bruker AC200 MHz spectrometer, using 3 wt% solutions in D_2O or 1 wt% solutions in $CDCl_3$, at room temperature.

2.5. Fluorescence measurements

Steady-state fluorescence measurements were performed on air-equilibrate solutions at 25°C using a Hitachi F-4500 spectrofluorimeter. The emission spectra of phenyl moieties of the SS monomer, PSS homopolymer and copolymers were measurements in 0.01 g dL^{-1} solutions and excited at 255 nm. No time-dependent intermolecular associations, as reported by McCormick and Chang [12] for concentrated solutions, were observed here. All measurements were repeated after three days and no alteration was detected in the results.

2.6. Nomenclature

The sample names refer to the content in mol% of the vinylether incorporated in the copolymers. The B or R labels indicate block or random copolymers, respectively. By instance, co-BVE39-R refers to a random copolymer with 39 mol% of *n*-butylvinylether incorporated. co-OVE8-B indicates a block copolymer with 8 mol% of *n*-octadecylvinylether incorporated in the copolymer.

3. Results

3.1. Copolymer syntheses

Although the copolymerization of alkylvinylethers with monomers bearing electron withdrawing substituents by free radical polymerization has been reported in the literature [20,21], the experimental conditions needed for their copolymerization with ionic monomers are different because of the solubility in water of the co-monomers. In these cases it is convenient to dissolve the hydrophobic monomer in micelles with charge opposite to that of the co-monomer. Thus, the ionic monomer (anionic SS in our case) will be attracted towards the micelle surface, together with the initiator (KPS).

Homopolymerization of BVE and OVE was attempted under micellar conditions but only the formation of polyBVE was observed, although with a very low yield ($<$ 1%). Usually, the polymerization of alkylvinylethers is made by cationic polymerization [20]. However, copolymers of these same alkylvinylethers with styrenesulphonate could be obtained by the former method with yields between 29% – 95%. The copolymers, the experimental conditions for

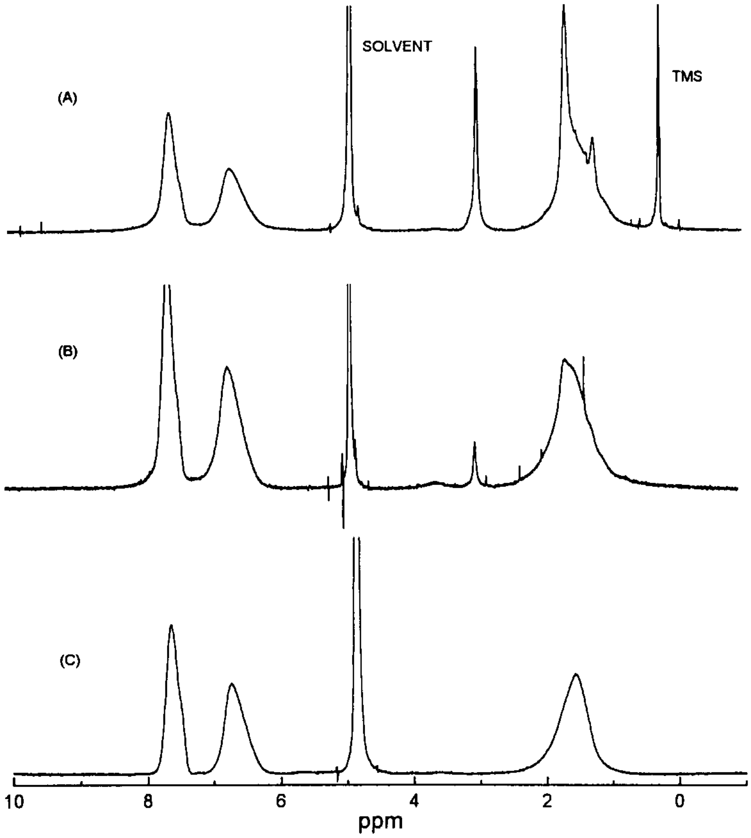

Fig. 2. ^{1}H-NMR spectra of co-OVE8-R, co-OVE1-R and PSS in D_2O (from top to bottom). TMS used as external standard.

their preparation and some properties are given in Table 1. The formation of significant amounts of insoluble material was observed at the higher hydrophobic monomer concentrations (entries 7 and 12 in Table 1). ^{1}H-NMR and FTIR analyses of these solids showed a large proportion of the hydrophobic monomer, whereas this proportion was lower in the copolymer recovered by precipitation. The molecular weights and compositions of these insoluble copolymers were not determined.

Random copolymers of the very hydrophobic octadecylvinylether monomer were only obtained at rather low [H]/[S] ratios because of its high tendency to solubilize in the micelles.

3.2. Copolymer characterization

The ^{1}H-NMR spectrum of polyBVE in $CDCl_3$ is shown in Fig. 1. The peaks between δ 3.0 and 3.7 correspond to methylene protons in the α-position of the ether group. The methine protons in the α-position of the ether group are observed at δ 4.0–4.5. The peaks around δ 0.9 are ascribed to the methyl end group of the *n*-butyl chain. Peaks due to methylene and methine protons in the backbone and methylene protons of the *n*-butyl chain are observed in the region of δ 1.1–2.3 [21,22]. The resonance signals of polymer solutions are usually split because of their sensitivity to composition, configurational sequence, conformation as well as molecular weight [23]. The broadening of signals is also an evidence of the presence of a polymeric structure.

The ^{1}H-NMR spectra of PSS and copolymers in D_2O are shown in Fig. 2. The spectra of co-OVE1-R and co-OVE8-R, show peaks in the 0.7–2.3; 2.9 and 6.0–7.5 regions. These peaks can be ascribed to the methylene and methine protons on the backbone of the chain (see Fig. 1), to methylene protons in the α position of the ether group of the side chain, and to the aromatic protons of the phenyl groups (Fig. 2c), respectively.

The composition of the copolymers was determined from the analysis of the ^{1}H-NMR spectra. The molar fraction of the vinylether monomers is given by

$$F_{\mathrm{VE}} = \frac{I_{\mathrm{VE}}/n_{\mathrm{VE}}}{I_{\mathrm{VE}}/n_{\mathrm{VE}} + I_{\mathrm{SS}}/n_{\mathrm{SS}}} \qquad (1)$$

where F_{VE} is the mole fraction of vinyl ether in the copolymer, I_{VE} and I_{SS} are the total integration of the signals of the vinylether and styrenesulphonate protons, respectively, and n_{VE} and n_{SS} are the total number of protons of each monomer. I_{SS} and I_{VE} were calculated from

$$I_{\mathrm{SS}} = I_{\mathrm{Ph}} + (I_{\mathrm{Ph}}/1.3637) \qquad (2)$$

and

$$I_{\mathrm{VE}} = I_{\alpha} + I^{*} - (I_{\mathrm{Ph}}/1.3637) \qquad (3)$$

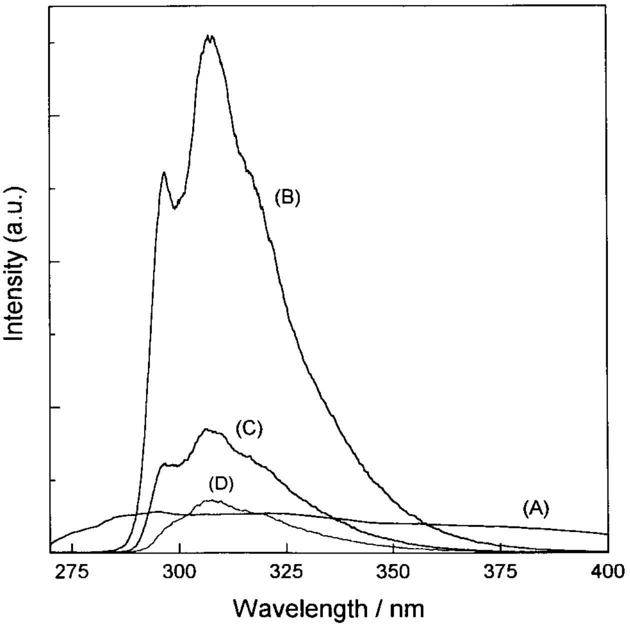

Fig. 3. Fluorescence spectra of PSS and SS: (A) [PSS] = 0.97 mequiv/L, SS; (B) 0.15; (C) 0.20; (D) 0.97 mmol/L, λ(exc) 255 nm.

where I_{Ph} is the integration of the signals from the phenyl protons (δ 6.0–7.5); I_α is the integration of the signals from the methylene protons in the α-position of ether function (δ 2.9); and I^* is the integration of the signal from the protons of the backbone and the hydrocarbon side chain of the copolymer (δ 0.7–2.3). To distinguish between the hydrogens of the aliphatic chains and those of the aromatic ring which appear at the same δ, the total integrations are corrected by the factor (I_{Ph}/1.3637). This factor was obtained from the relationship between the areas of the signals at δ 6.0–7.5 and 0.7–2.3 in the PSS spectrum. The composition of the copolymers calculated in this way are shown in Table 1, together with values obtained from elemental analysis of sulphur. Both sets of values are within the expected experimental error.

HPLC analysis of the resulting copolymers did not show any peaks due to free monomers. Also, no significant amounts of CTAB were detected by elemental analysis of nitrogen. GPC analysis showed a decrease in the molecular weights of the copolymers with the increase of the [H]/[S] ratio. An effect of this type can be related to the presence of micelles during the synthesis, and may be ascribed to an increase of the radical transfer reactions associated to the hydrophobic groups [24]. The molecular weight distributions of the copolymers were rather large, but seem to be an intrinsic effect of method as no adsorption of copolymers on the column was observed.

3.3. Solubilization behaviour

All copolymers are easily soluble in water, except co-OVE8-B, co-OVE11-B and co-OVE15-B, which present a slightly turbid solution at 1 g L^{-1}. They are insoluble in methanol and acetone. The copolymers with higher hydrophobic content (co-BVE41-B and co-OVE15-B), are slightly soluble in $CHCl_3$. The solubility behaviour gives additional qualitative indication of the effect of the polymerization procedure on the copolymer microstructure. Although co-OVE8-R (prepared at [H]/[S] = 0.09) and co-OVE8-B (at [H]/[S] = 0.43) have the same hydrophobic content, only the latter shows a turbid solution at 1 g L^{-1} whereas solutions of the other compound are limpid at this concentration.

The comparison of the solubilization behaviour of co-BVE41-B and co-OVE15-B in $CHCl_3$ shows that block structures are better solvated by less polar solvents than random structures. Interestingly, the ^{1}H-NMR spectrum of co-BVE41-B in $CDCl_3$ shown in Fig. 1, only presents signals caused by hydrophobic protons and the signals of the hydrophilic protons of the SS units seem to be quenched because of aggregation. Also the signals of the protons localised in the α-position of the ether group are quenched. These results point to a more restricted mobility of the hydrophobic segments of co-BVE41-B, compared to poly-BVE. This effect may be explained considering that co-BVE41-B has a strong surfactant activity forming micelles in water and reverse micelles in $CHCl_3$. Therefore, poly-BVE will present a more extended conformation in $CHCl_3$. Somehow, the behaviour observed for these compounds is similar to that reported for other types of copolymers [5,8,10,11,13,14].

3.4. Fluorescence analysis

Fig. 3 shows the fluorescence emission of the SS monomer at several concentrations. Under extreme dilution the band has a maximum at 308 nm with a peak at 292 nm. This spectrum is similar to that of styrene in apolar solvents, but less structured because of the presence of the sulphonate group in the *para* position. An overall decrease in the emission efficiency is observed at higher concentrations together with the onset of a small shoulder around 320 nm, which may be due to excimers or ground-state aggregates. The emission spectrum of the homopolymer PSS, differs from that of SS in the sense that a general broadening of the spectrum is obtained, which extends into a long wavelength tail. The peak at 292 nm is ascribed to the monomer and those at 325 and 380 nm correspond to dimers and higher aggregates formed by the isotatic sequence of phenyl units [9,21]. No modification of the shape of the PSS spectrum was observed in the range of 0.01 – 2.0 g L^{-1} except for a general broadening owing to specific local conformations and configurations of the polymer chain.

4. Discussion

In general, for micellar polymerizations systems involving neutral monomers, Hill et al. [17] suggested that the

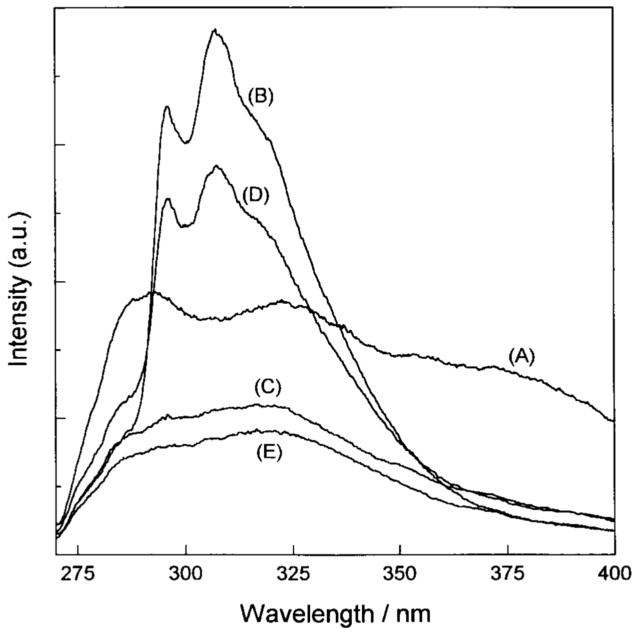

Fig. 4. Fluorescence emission of PSS and copolymers. (A) PSS; (B) co-BVE39-R; (C) co-BVE41-B; (D) co-OVE8-R; (E) co-OVE8-B. Concentrations 0.01g/dL, λ(exc) 255 nm.

reaction mechanism consisted of an initiation step in the intermicellar aqueous phase where the water-soluble monomer is placed. When the growing macroradical encounters a hydrophobe-containing micelle, several of these monomers will add to it, forming a short hydrophobic block. After leaving the micelle, the macroradical will add other hydrophilic units until another micelle is encountered to form a new hydrophobic block. According to this mechanism, the key parameter which regulates both length and the number of hydrophobic blocks is the number of hydrophobic molecules per micelle, i.e., the [H]/[S] ratio [17,18]. Random copolymers are obtained using sufficiently low [H]/[S] ratios, when each micelle is occupied, in average, by less than a single hydrophobic monomer.

Contrary to what happens in conventional micellar copolymerization involving non-charged hydrophilic monomers, when using charged co-monomers and surfactants with opposite charge, the co-monomers will be placed near the surface of the micelles because of electrostatic interactions. In this case, the initiation already happens in the microdomain of the micelle. This indicates that a significant amount of the growth of the polymer chain could easily alternate between both monomers, so that the length of the possible blocks will be determined mainly by their cross-polymerization rates. As known [20], homopolymerization of vinyl ethers in homogeneous solutions is quite difficult. Therefore, a great probability exists that the growing polymer will incorporate a SS monomer after each VE, leading to the PSS blocks observed experimentally from fluorescence measurements.

As seen from Table 1 the proportion of incorporation of the hydrophobic vinylether decreases with feed compositions above 30%. It seems that in these cases the [H]/[S] ratios, or rather, the number of hydrophobe molecules per micelle (about 50 for BVE and 10 for OVE) are too high, exceeding the actual capacity of the micelle. Therefore, it may reasonably be assumed that beyond a certain hydrophobe content, the detergent-hydrophobe micelles will become saturated, similar to what happens in detergent-alcohol micelles [25]. The rest of the hydrophobic monomers will remain associated in the bulk of the solution, or eventually in the microdomains formed by the copolymer chains in later stages of the polymerization. As a result of the electrostatic repulsion few SS monomers will be near these microdomains, leading to the formation of insoluble polymers with little SS content in feeding compositions with high VE content.

Copolymers with the same monomer composition present different emission spectra depending on the [H]/[S] ratio used in the synthesis (Fig. 4). Copolymers synthesised at low [H]/[S] ratios have an emission spectrum similar to highly diluted SS, whereas those synthesised at higher [H]/[S] ratios have an emission similar to PSS. This confirms that for the copolymers synthesised at low [H]/[S] ratios the hydrophobic monomers are incorporated more randomly, so that the phenyl groups are present mostly as isolated units or smaller blocks with emission similar to SS solutions. At higher concentrations of the hydrophobic monomers, the incorporation of the monomers occurs in larger blocks, resulting in larger sequences of phenyl groups, yielding emissions similar to that of PSS. The presence of either block or random structures for copolymers of styrene and acrylamide was also reported by Thomas [15]. McCormick [20] demonstrated that the length of the hydrophobic blocks is also a function of the [H]/[S] ratio used in the synthesis.

Also, for the OVE containing polymers, the stronger hydrophobic character of the alkyl chain induce larger and more hydrophobic sequences that will reduce significantly the solubility of the macromolecular chain in water. It is well established that di- or triblock hydrophilic/hydrophobic copolymers are very difficult to dissolve in water, even when the hydrophobic part is only a small fraction of the polymer chain. However, random copolymers of similar composition are fully water soluble [17]. This large difference between the solubility of co-OVE8-R and co-OVE8-B confirms that the formation of hydrophobic blocks in the polymer is associated with the number of hydrophobic monomers per micelle during the synthesis.

5. Conclusions

The synthesis of copolymers of BVE and OVE with SS by micellar copolymerization was successfully achieved using cationic CTAB micelles. The copolymers were easily identified by conventional techniques. Block structures are formed at higher [H]/[S] ratios and random structures are formed at the lower [H]/[S] ratios.

The effect of the [H]/[S] ratio used in the synthesis on the copolymer structures was characterised by their emission behaviour. The fluorescence spectra of the copolymers obtained at higher [H]/[S] ratios were similar to that of PSS, because of the presence of blocks of the phenyl groups. At lower [H]/[S] ratios the spectra were like that of SS, indicating that the SS moieties in the copolymer were sufficiently separated, not interacting between them. For very high [H]/[S] ratios the copolymers were practically insoluble in water. The residual copolymer remaining in the solution had a small amount of hydrophobic monomers, proving that almost all of the hydrophobic monomers were incorporated in the insoluble copolymer, forming block structures. The copolymers with higher content of the hydrophobic monomers showed a surfactant-like behaviour forming reversed micelles in low polarity solvents.

The polymerization processes initiated near the cationic micelles and the growth of the macroradical will be determined by the reactivity ratios and concentrations of the monomers, which are dissolved in the micelle (VE) or on its surface (SS).

Acknowledgements

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