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ORIGINAL CONTRIBUTION

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A photophysical study of the interactions in poly(styrene-4-sulphonate)–*n*-butylvinylether block and random copolymers

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Abstract Interactions between the moieties responsible for the conformations and hydrophobic microdomains in poly(styrene-4-sulphonate) (PSS) and its copolymers with *n*-butylvinylether (BVE) were studied by their emission spectra and the lifetimes of the phenyl groups and pyrene used as a photochemical probe. The emission spectra of PSS shows bands due to dimers and higher aggregates as well as the characteristic excimer band. At low concentrations, the random copolymers have spectra similar to that of the free monomer, whereas the block copolymers have spectra like that of PSS. At higher concentrations, the random copolymer also shows these excimer bands, due to interchain interactions. Results from the emission of pyrene prove that the behaviour of the copolymers with approximately 40% BVE seems to be relatively independent of having random or block configurations. Except at low concentrations (< 0.05 g/dl), where the block copolymer already has a conformation with "stable" hydrophobic microdomains, both types of copolymers behave similarly. There is an initial aggregate equilibrium between individual chains and aggregates, associated with a relocation of the probes. At higher concentrations, both copolymers suffer a severe change in conformation, due to the formation of "stable" hydrophobic microdomains, resulting from interchain interactions. In both cases the lifetimes of pyrene are of the order of 240 ± 10 ns.

Key words Polyelectrolytes – Poly(styrene sulphonate) – Hydrophobic microdomains

Introduction

Water-soluble polymers associating by hydrophobic interactions are called micelle-forming polymers or polysoaps. Usually, these polymers have hydrophobic groups linked to the main chain [1, 2]. In solution, above a certain concentration, these interactions lead to the formation of interchain associations. As a consequence, the copolymers exhibit properties equivalent to those observed for higher-molecular-weight-homopolymers [3].

The behaviour of polyelectrolytes in solution has frequently been studied using photophysical methods [4]. In particular, photophysical analysis has been used to determine the aggregation of hydrophobically modified polyelectrolytes in aqueous media [5] and their interaction with surfactants [6]. Experiments with hydrophobic monomers containing long alkyl chains, using fluorescent probes, proved the lack of an equivalent to the critical micelle concentration, (cmc) even at moderately high concentrations. Biwana-Limbelé and Zana [7] showed that alternate copolymers of alkylvinylethers and maleic anhydride with hydrocarbon chains of more than eight carbon atoms have stable hydrophobic microdomains over the whole concentration range. Therefore, the aggregation processes in these systems is assumed to occur intramolecularly. Copolymers with random distribution of monomers have a similar behaviour; however, the overall composition seems to be the determining factor [8–10]. Uemura et al. [9], studying the behaviour of a series of randomly hydrophobically modified poly(N,N-dimethylacrylamides) of different molecular weights and degrees of hydrophobic modification, showed that the extension of hydrophobic associations were only dependent on hydrophobic content and the polymer concentration. The pH-induced aggregation behaviour of these amphiphilic polymers was also investigated [8, 11–13].

At higher concentrations, the primary intramolecular aggregation of these polymers may be superposed by a secondary intermolecular aggregation [1]. In these conditions, a critical concentration for the associations (point for intermolecular aggregations), as well as cmc-like breaks in the surface tension curves, have been reported [2]. The latter processes seem to depend on the molecular weight [14] and on the length of the hydrophobic chains [15–17]. Intermolecular associations were reported by Kramer et al. [13] studying mixed solutions of naphthalene (donor) and pyrene (acceptor) labelled copolymers. The enhancement of the acceptor emission at low polymer concentrations implies that intermolecular associations occur even at polymer concentrations where association-driven viscosification is not observed.

Recent studies indicated that the distribution of the hydrophobic groups along the polymer chain also significantly affects these type of associations. In copolymers with block distributions, hydrophobic interactions promote intermolecular associations. On the other hand, polymers with similar compositions, but with random distribution of the units along the chain, exhibit predominantly intramolecular associative behaviour [18, 19].

This paper describes the properties of aqueous solutions of copolymers of *n*-butylvinylether (BVE) with sodium styrene sulphonate (SS) obtained by micellar copolymerization [20]. Copolymers of almost identical composition, but with random and block distributions were correlated and compared with poly(styrene-4-sulphonate) (PSS), to ascertain the effect of random versus block incorporation of the hydrophobic monomer. The behaviour of the solutions was investigated using the intrinsic fluorescence of the polymers, time-resolved and steady-state fluorescence of pyrene, reduced viscosity and spin-lattice relaxation times (T_1). The experimental data are interpreted in terms of inter- and intramolecular associations.

Experimental

Chemicals

BVE (Polyscience, 99%), SS (Aldrich), potassium persulphate (Merck) and cetyltrimethylammonium bromide (Sigma), used for the synthesis of the polymers, were used as received. PSS sodium salt (Aldrich) was precipitated twice from acetone before use. Pyrene (Aldrich) was recrystallized twice from ethanol before use. Milli-Q purified water was used throughout.

Copolymers

The copolymers were prepared by an aqueous micellar copolymerization technique and characterized as described in a previous paper [20]. The concentrations of the monomers incorporated in the copolymers, as well as other parameters related to the copolymers used in this work, are shown in Table 1.

Viscosity in dilute solutions

Measurements were carried out using an automatic capillary viscosimeter (Ubbelohde type) in aqueous solutions with polymer concentrations in the range 0.005–0.1 g/dl at 25 °C. The solutions were made up by diluting stock solutions.

Fluorescence measurements

Steady-state fluorescence measurements were performed on air-equilibrated solutions using a Hitachi F-4500 spectrofluorimeter. Fluorescence lifetimes were measured by the time-correlated single-photon counting method using an Edinburgh CD-900 instrument. The fluorescence decay profiles were obtained by exciting all samples at 337 nm and were analysed with a nonlinear least-squares iterative reconvolution method. The concentrations of pyrene, when used as the probe, were 1×10^{-6} and 5×10^{7} mol/l. All samples were examined at 25 °C.

The solutions containing the probe were prepared by transferring a sufficient amount of a methanolic stock solution of pyrene to a flask under a stream of nitrogen, after which the polymer solution was added. Solutions were allowed to equilibrate for at least 2 h prior to fluorescence measurements. The emission spectra were obtained at a scanning rate of 240 nm/min, and the excitation/emission slits were 10 and 1.0 nm, respectively. The excitation wavelength was 330 nm, and the intensities of the first and third peaks of the pyrene emission were measured at 373 and 384 nm, respectively.

The emission spectra due to the phenyl moieties of the SS monomer, the PSS homopolymer and the copolymers were measured at concentrations between 0.01–1.0 g/dl, exciting at 255 nm. No time-dependent intermolecular associations, as report-

Table 1 Properties of poly(styrene-4-sulphonate) (*PSS*) and PSS-*n*-butylvinylether (*BVE*) copolymers

Polymer	%mol in the copolymer[a]		M_w(g mol^{-1})[b]	M_w/M_{vn}
	SS	BVE		
PSS	100	–	76000	3.20
COP17R	83	17	17200	4.43
COP25R	75	25	125000	3.20
COP39R	61	39	102000	3.62
COP41B	59	41	44000	3.14

[a] Determined by NMR (±3%). Spectra were obtained using 3 wt% solutions in D_2O [20]

[b] Determined by GPC using PSS standards. The eluent was 0.1 M $NaNO_3$ in water:methanol (8:2) [20]

ed by McCormick and Chang [21] in concentrated solutions, were observed here. All measurements were repeated after 3 days with the same solutions, with identical results.

^1H spin-lattice relaxation time

^1H spin-lattice relaxation time (T_1) measurements were performed on a Bruker AC200 MHz instrument using the inversion recovery method (180°-τ-90° pulse sequence). The concentrations of the solutions were kept constant at 0.6 g/dl in D_2O.

Results

Fluorescence

The fluorescence spectra of the SS-BVE copolymers are shown in Fig. 1. The block or random sequence of the monomers in the copolymers can be deduced from the shape of these spectra. At low concentrations the block polymer shows spectra similar to that of PSS, with maxima at 292, 325, and a shoulder around 380 nm, which can be ascribed to monomers, dimers, and higher aggregates along the chain, respectively. On the other hand, the random copolymer shows spectra like that of the monomeric SS, with its characteristic splitting of the monomer peak at 292 and 310 nm.

The fluorescence emission of PSS at increasing concentrations is shown in Fig. 2a. The increase in the concentration has two effects. On one hand, the total fluorescence emission decreases, evidencing an efficient self-quenching process. On the other hand, a neat spectral change is observed at concentrations above about 0.4 g/dl, showing an increase in the dimer peak and a shoulder of higher aggregates, the latter eventually becoming the main peak at sufficiently high concentrations (>0.5 g/dl). These higher aggregates result mainly because of interchain interactions, which enhance the approach between phenyl groups. The effect of an increase in the ionic strength due to the Na^+ counterions cannot be ruled out, as it corresponds to about 0.05 M at the higher concentrations. In this case the approach between the negatively charged phenyl groups will also be favoured. This effect may also be responsible for the spectral changes at lower concentrations. Possible effects of the presence of oxygen in the solutions can be discarded as a possible site-dependent solubilization would quench preferentially the signals due to the more hydrophobic sites, therefore reinforcing the conclusions drawn from the emissions of the aggregates.

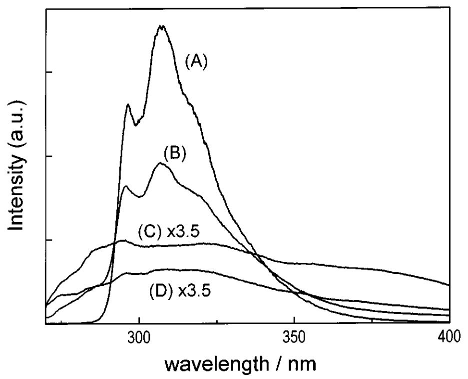


Fig. 1 Fluorescence emission of styrene sulphonate (*SS*) (0.03 g/dl), poly(styrene-4-sulphonate) (*PSS*) and copolymers (0.02 g/dl). *A* SS 1.5 mEq/l; *B* COP39R 0.74 mEq/l; *C* PSS 0.97 mEq/l; *D* COP41B 0.73 mEq/l (mEq refers to SS units)

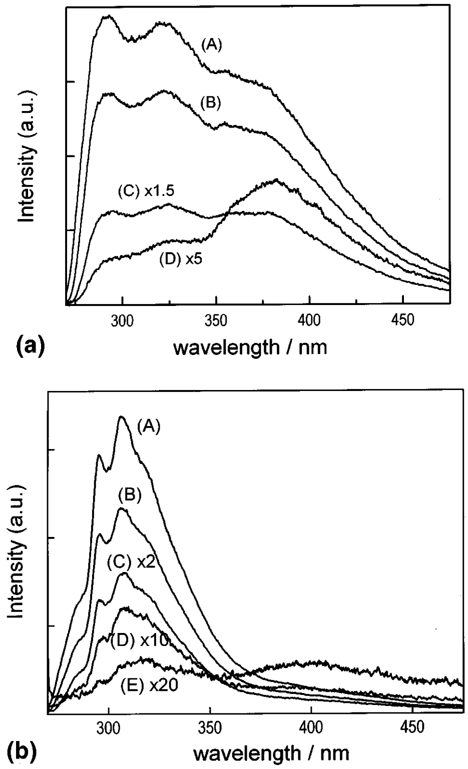


Fig. 2 a Fluorescence emission of PSS at various concentrations. *A* 0.04; *B* 0.2; *C* 0.4; *D* 0.8 g/dl. **b** Fluorescence emission of COP17R at various concentrations. *A* 0.06; *B* 0.12; *C* 0.25; *D* 0.5; *E* 1.0 g/dl

The spectral change of COP17R at various concentrations is shown in Fig. 2b. The behaviour is like that of PSS, but the excimer emission only becomes significant at 1.0 g/dl, showing the tendency of these copolymers to form intramolecular aggregates. On the other hand, the block copolymer COP41B only shows significant intermolecular association at 0.5 g/dl.

As can be seen from Fig. 3, at higher concentrations the random and block copolymers also have emissions at longer wavelengths due to higher aggregates (∼400 nm), similar to PSS. These peaks are not present at lower concentrations, especially in the case of the random polymers, evidencing interchain aggregation. Nevertheless, the interaction between chains in COP41B is larger

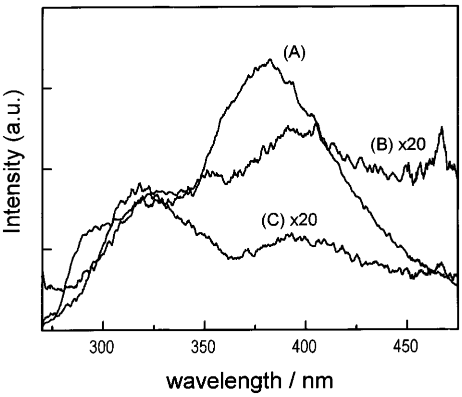


Fig. 3 Fluorescence emission of PSS and copolymers at higher concentrations. *A* PSS 0.8 g/dl; *B* COP41B 1.0 g/dl; *C* COP39R 0.7 g/dl

than in COP39R, the former presenting a larger emission around 400 nm, with little or no emission at lower wavelengths. At similar concentrations COP39R has its major emission at 320 nm (dimers or excimers), demonstrating smaller local concentrations of phenyl groups in the microdomains formed by the interchain interactions. This is in agreement with the conclusions drawn from viscosity measurements [21–23], proving that block copolymers form interchain aggregates more efficiently than random copolymers.

Pyrene emission

The use of pyrene as a probe for evaluating the polarity of different hydrophobic microdomains is well documented [2, 24]. The ratio between the intensities of the peaks in the fine structure emission spectrum, I_1/I_3, measures the polarity of the medium in which the probe is placed, i.e. large values (~1.8) are expected for polar media, such as aqueous solutions. Lower values are obtained for hydrophobic microdomains, as well as for organic solvents.

The I_1/I_3 ratio for solutions of PSS decreases steadily from 1.65 to 1.30 for concentrations up to 0.2 g/dl. At higher concentrations the ratio remains constant at approximately 1.3, which is similar to the value found for micelles. This suggests that at low polymer concentrations pyrene molecules will be partitioned between the aqueous environment and the more hydrophobic microdomains near the backbone of the polymer chain [25]. As the concentration of PSS is increased, more pyrene molecules migrate to the hydrophobic microenvironments until all of them are in these regions, after which no further decrease in the I_1/I_3 ratio should be observed.

The I_1/I_3 ratio for the copolymers shows a behaviour that seems to be independent of their block or random character. At very low concentrations the I_1/I_3 ratio has values lower than those for aqueous solutions, and is apparently influenced only by the hydrophobic monomer content. As can be observed in Fig. 4, COP39R and COP41B behave similarly. There is a steady decrease up to 0.2 g/dl, followed by a plateau extending to 0.5 g/dl. At this concentration some structural change must happen, as the I_1/I_3 value drops abruptly from 1.18 to 0.97 in the interval 0.5–0.7 g/dl, after which the pyrene emission remains constant with I_1/I_3 around 0.95. The copolymer COP17R shows a behaviour intermediate between those of PSS and COP39R, possibly due to the lower content of hydrophobic monomers.

Time-resolved fluorescence

Time-resolved fluorescence measurements were performed on aqueous solutions of the copolymers to which pyrene was added, and compared with those for PSS. The pyrene concentration was 10^{-6} M and the wavelength excitation used in all time-resolved experiments was 337 nm. The results shown in Table 2 were obtained by fitting the decay profiles with multiexponential functions, $\sum A_i \exp(-t/\tau)$. For PSS a triple exponential was used, considering two decay lifetimes for pure PSS [26–28] and one more for the probe. On the other hand, a double exponential seemed to be enough to fit the curves for the copolymers, as the addition of one more lifetime did not improve significantly the χ^2 values.

The emission decay of dilute solutions of PSS with no added probe could be adjusted with a double exponential function, yielding lifetimes of 2.1 and 10.9 ns. These values remained practically constant in more concentrated solutions, but with a significant increase in the value of χ^2, indicating the presence of various types of interactions in the solution. The lifetimes are coherent with those reported by Turro and Okubo [27] for very

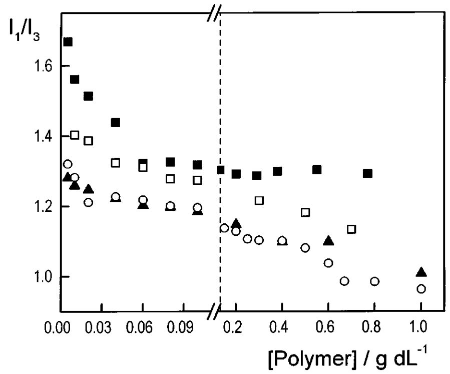


Fig. 4 Dependence of the I_1/I_3 ratio with polymer concentration. (■) PSS; (□) COP17R; (▲) COP39R; (○) COP41B. $\lambda_{exc.}$ = 330 nm, I_1 = 373 nm, I_3 = 384 nm

Table 2 Emission lifetimes of the polymers (τ_1, τ_2) and pyrene (τ_p). Pyrene concentration = 10^{-6}M, λ_{ex} = 337 nm

System	τ_p (ns)	A_1	τ_1 (ns)	A_2	τ_2 (ns)	A_3	χ^2
PSS 0.01 g/dl	141 ± 7.3	0.121	1.6 ± 0.20	0.685	6.8 ± 3.0	0.047	1.129
0.1	163 ± 1.7	0.017	1.8 ± 0.05	0.842	12.0 ± 1.7	0.014	1.203
0.4	164 ± 3.1	0.007	1.7 ± 0.06	0.951	7.1 ± 0.9	0.037	1.021
COP17R 0.01 g/dl	162 ± 0.6	0.391	1.9 ± 1.56	0.136			1.105
0.1	209 ± 0.8	0.183	3.0 ± 0.12	0.637			1.041
0.4	236 ± 1.6	0.062	2.6 ± 0.06	0.652			1.092
COP39R 0.01 g/dl	200 ± 0.7	0.327	3.2 ± 0.03	0.258			1.309
0.1	232 ± 1.2	0.174	2.0 ± 0.09	0.674			1.188
0.4	244 ± 2.0	0.068	2.1 ± 0.06	0.865			1.064
COP41B 0.01 g/dl	187 ± 0.7	0.220	3.0 ± 0.25	0.335			1.269
0.1	237 ± 2.2	0.045	2.3 ± 0.05	0.988			1.104
0.4	235 ± 3.4	0.018	2.2 ± 0.05	0.741			1.235
SDS 20 mM + DBS 0.05 mM	176 ± 0.6	0.281			15 ± 2.0	0.084	1.033
DBS 100 mM	170 ± 2.0	0.037	1.5 ± 2.9	0.081	5.9 ± 0.4	0.625	1.103
PSS no probe 0.1 g/dl			2.1 ± 0.02	0.027	10.8 ± 0.1	0.004	1.228
10.0			1.8 ± 0.00	0.113	11.9 ± 0.2	0.001	1.544

dilute solutions (2.5 and 5.2 ns) and by Philips et al. [28] (0.8–1.5 and 10–14 ns) for styrene copolymers. The latter authors assumed different species for the longer lifetime emission.

Analysis of the decays for the copolymers was done using a double exponential, taking into account the large difference between the lifetimes of the pyrene probe and the emission of the phenyl groups. The values found for the pyrene lifetime in dilute solutions of the copolymers were in the range 160–200 ns, which is higher than that for the probe in PSS or in aqueous solution, and is within the range of lifetimes found in air-saturated SDS and DBS micelles. This means that the copolymers offer a more hydrophobic medium for pyrene than PSS, and similar to that present in surfactant micelles.

For the random polymers the increase in the copolymer concentration results in a steady increase in the lifetime, indicating the formation of more hydrophobic microdomains in the system. On the other hand for PSS and the block copolymer, the lifetimes remain constant at concentrations above about 0.1 g/dl. These values, approximately 160 and 235 ns, respectively, also reflect the difference in hydrophobicity of the microdomains.

Viscosity

The reduced viscosity curves shown in Fig. 5 show the characteristic behaviour of polyelectrolytes, implying the change of an extended coil to a compact conformation [23]. Whereas for PSS and COP39R a continuous decrease of η_{red} is observed, for the block copolymer COP41B the viscosity remains constant in the range 0.01–0.1 g/dl. Possibly the hydrophobic sequences of the chain in the block produce compact conformations even before aggregation, or at reasonably low concentrations characterising typical polysoap behaviour. For the random polymer, the "original" hydrophobic regions will be farther away from each other. Therefore, the increase in concentration will decrease the dissociation of sulphonate groups, screening the charges and promoting increasing hydrophobic interactions, which give rise to larger aggregation and favour the compactness of the microdomains.

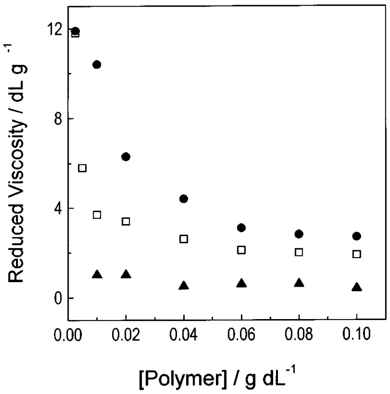


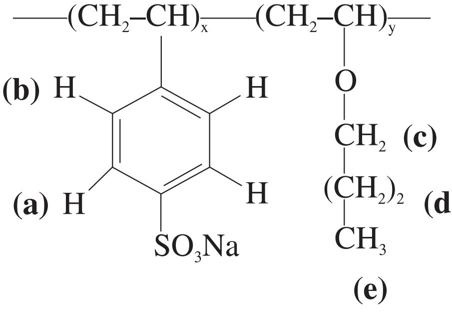
Fig. 5 Dependence of the reduced viscosity with polymer concentration in aqueous solutions. (□) PSS; (▲) COP41B; (●) COP39R

Spin–lattice relaxation times

Spin-lattice relaxation times of the copolymers may give additional information on the conformation of the copolymers in solution. The relaxation times can be related to the rigidity of the chain as a result of the distribution of the monomers along the polymer backbone. The relaxation times are shown in Table 3 and correspond to the protons shown in Structure 1. The different values of T_1 determined for the protons of the hydrocarbon chain of the vinylether group suggest the formation of a microphase, as in homogeneous system all the protons usually have similar T_1 values due to spin-transfer processes [29]. An increase in the relaxation times of the methyl group protons is observed for the copolymers. Increases in the relaxation times for polymers with molecular weights similar to those in this work indicate more rigid chains [30, 31]. For the random copolymers, the changes in T_1 with the hydrophobe content point to an increase in the rigidity according to the BVE content, 17R $<$ 25R $\sim$ 39R. When comparing the values of the copolymers with the same monomer composition, but different distribution, such as COP39R and COP41B, it can be noticed that the relaxation times for the methyl and the phenyl protons are larger for the COP41B copolymer, as expected for a more hydrophobic, i.e. rigid environment.

Discussion

Due to the fact that all the monomer units are charged in the homopolymer of SS, its conformation in dilute solutions will be rather rod-like, with little flexibility thus avoiding extensive interactions between segments of the same chain. Nevertheless, the same charges will preclude any regularity in the spatial distribution of the aromatic rings in the polymer, so that in different sections of the chain there will be different emitting entities, i.e., monomers, dimers, and higher aggregates, as can be seen from the fluorescence spectra, even at very low PSS concentrations.



Structure 1

Table 3 ^{1}H relaxation times (T_1) for the protons in structure 1

Polymer	y (mol%)	T_1 (s) ± 10%				
		a	b	c	d	e
PSS	–	0.77	0.44	–	–	–
COP17R	17	0.54	0.39	0.29	0.34	0.21
COP25R	25	0.55	0.40	0.29	0.35	0.30
COP39R	39	0.57	0.43	0.30	0.36	0.30
COP41B	41	0.72	0.46	0.31	0.37	0.37

At higher concentrations there will be aggregation of the chains, enhancing the existence of dimers and higher aggregates. These interchain interactions seem to be the result of an aggregation equilibrium rather than the formation of stable ‘‘micelle-like’’ structures. This point of view is supported by the evolution of the pyrene I_1/I_3 ratios and lifetimes with concentration. The former decreases from 1.65 to about 1.30 (at 0.1 g/dl), and then remains constant, whereas the lifetimes rise from 141 ns in dilute solution to around 160 ns at 0.1 g/dl, staying practically constant afterwards. At the same time, the viscosity shows a constant decrease in the region up to 0.1 g/dl. These results can be rationalized assuming the existence of two different sites where the probe can be placed on the PSS chain, e.g. one in a more hydrophobic region, probably somewhere near the backbone of the polymer, and a second more aqueous one, associated with the sulphonic group on the benzene ring. It seems unlikely that the interactions between the highly charged polymer chains will produce new hydrophobic microdomains when the concentration is increased. Still, a larger number of hydrophobic sites will be present and the probe will migrate preferentially to them, resulting in a decrease in the I_1/I_3 ratio and an increase in the lifetime. The effect on the viscosity can also be traced to this aggregation equilibrium.

The aggregation of the copolymers depends on their composition, as well as on the distribution of the monomers in the chain (block or random). Block polymers, even in dilute solutions, show broad emission peaks displaced towards the red, as also found for PSS. This indicates the existence of local sites with higher phenyl moiety concentration. The increase in concentration enlarges the peaks at longer wavelengths, as expected for higher aggregates. On the other hand, at low concentration the random copolymer shows an emission spectrum similar to monomeric SS, indicating that there is a little chance for the interaction between the phenyl moieties of the same chain. The emission around 400 nm is observed at higher concentrations and can be ascribed to the formation of phenyl group aggregates, or dimers, originating from interchain interactions.

The I_1/I_3 ratios of the pyrene emission have the same behaviour for the COP41B and COP39R copolymers. The initial value of around 1.3 is similar to that found for micelles and seems to indicate that there are always sets of hydrophobic monomers forming organic-like microdomains. The value decreases slowly with concentration, probably due to the redistribution of the probes to the additional hydrophobic domains, reaching a plateau at 1.1. At approximately 0.5 g/dl a discontinuity occurs with the I_1/I_3 value falling to around 0.95, then remaining constant again. It is noteworthy that the same behaviour is observed for both copolymers, indicating that the formation of more stable aggregates due to interchain interactions seems to be somehow independent of the form in which the monomers are sequenced, at least for this composition. The lifetime of the probe is also approximately the same in both copolymers at this concentration.

The only difference observed between the two copolymers is related to the reduced viscosity at low concentrations. Whereas the random copolymer shows a steep decrease before a plateau is reached at around 0.05 g/dl, the viscosity for the block copolymer is lower and is more or less constant in the range 0.01–0.10 g/dl. The more extended conformation of the random copolymer seems to give it a better opportunity to be influenced by the ionic strength. On the other hand, the conformation of the block copolymer will be more compact and less sensitive to the dissociation of the sulphonate groups. The same effect is observed from the ^{1}H relaxation times. The longer relaxation times for the phenyl ring and methyl protons indicate a more rigid conformation.

COP17R shows a behaviour intermediate between PSS and the COP41B and COP39R copolymers. The initial I_1/I_3 value is around 1.4 and falls steadily to nearly 1.15 at concentrations of 0.8 g/dl. Neither a plateau nor a discontinuity is found up to this concentration. For this copolymer, the amount of hydrophobe incorporated may be below the critical alkyl group content needed to show polysoap behaviour [2, 26]. For instance, copolymers of poly(sodium 2-acrylamido-2-methylpropane sulphonate) only show polysoap behaviour when the N-phenylacrylamide content is greater than 60% [3]. The conformation of the 17R copolymer will be closer, with a few hydrophobe monomers being surrounded by charged phenyl units. This may give rise to more or less hydrophobic domains. As in PSS, the increase in the concentration will promote interchain interactions which produce better protected hydrophobic microdomains, as can also be seen from the variations in the pyrene lifetimes, which are always larger than those for PSS at the same concentrations.

Conclusions

The block polymers have emission spectra similar to those of PSS. Bands due to phenyl dimers and higher aggregates as well as the characteristic excimer band are observed, even at low concentrations. On the other hand, the emission spectra of the random polymers at low concentrations are similar to that of monomeric SS. Only when increasing the concentration do dimer, aggregate and excimer bands start to appear.

The individual chains of PSS and the copolymers of PSS with BVE in aqueous solution do not change their conformation when the concentration is increased, except for small variations induced by the higher concentrations of counterions. At higher concentrations there is an aggregation process which gives rise to hydrophobic domains. The decrease in polarities found at low concentrations when probing the solutions with pyrene, seems to be due to a redistribution of the probes towards the increasing amount of hydrophobic domains of the polymer backbone when increasing its concentration.

The behaviour of the copolymers with around 40% BVE seems to be relatively independent of having random or block configurations. Except at low concentrations (<0.05 g/dl), where the block copolymer already has a conformation with “stable” hydrophobic microdomains, both types of copolymers behave similarly. There is an initial aggregate equilibrium between individual chains and aggregates, associated with a relocation of the probes, which leads to a plateau between 0.2 and 0.5 g/dl. At this concentration, both copolymers suffer a severe change in conformation, due to the formation of “stable” hydrophobic microdomains, resulting from interchain interactions. In both cases the lifetimes of pyrene are of the order of 240 ± 10 ns, with the only difference being the clusters formed by the block copolymer.

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