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The photoinitiated copolymerization of styrenesulfonate with methacrylate monomers in hydrotropic medium

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Abstract

Copolymers of styrenesulfonate (StyS) and methyl methacrylate, or hydroxyethyl methacrylate, were prepared by photoinitiated polymerization using the cationic dye Safranine. The reactions were be carried out at StyS concentrations higher than the MHC (0.10–0.15 M) where the monomer forms aggregates. The size of these aggregates depends on the amount of the methacrylic monomer present in the mixture prior to polymerization. The amount of the non-aromatic monomers incorporated in the polymers is mainly determined by the relative reactivity ratios. In the case of HEMA, the lower amount of methacrylate in the aggregates will reduce its proportion in the final polymer. The distribution of the monomers in the copolymers is random, as deduced from the behaviour of the emission spectra, especially the relation between the band corresponding to isolated phenyl rings and that of interacting aromatic systems.

Keywords: Photopolymerization; Copolymerization; Hydrotropes; Safranine

1. Introduction

Synthesizing copolymers from hydrophobic and hydrophilic monomers is possibly one of the most difficult problems to solve experimentally. In some cases, the use of two different phases, like micelles, emulsions or dispersions has been used to obtain some of these compounds. Nevertheless, the co-existence of two phases in the polymerizing formulation may pose some other problems, mainly the homogeneous distribution of the reactants.

An alternative to those procedures is the use of monomers that present hydrotropic properties, like styrenesulfonate and similar [1]. It has been found that these compounds, when in sufficiently high concentration will form domains in which hydrophobic species will dissolve [2]. Moreover, if the process is initiated photochemically, in some cases there is no need to add extra co-initiators or other compounds in the initial mixture [3–5].

We recently reported on the dye-initiated photopolymerization of styrenesulfonate, using cationic and anionic dyes [6]. It has been found that cationic dyes are incorporated in the hydrotropic domains initiating the polymerization process when excited [3]. On the other hand, the use of anionic dyes induces the photopolymerization outside the prototropic domain, due to the repulsion of the highly negatively charged monomer clusters [7].

We want to report here results obtained for the copolymerization of styrenesulfonate with methyl methacrylate, photoinitiated by the cationic dye Safranine.

2. Experimental details

2.1. Chemical

The dye Safranine T (Sf, Aldrich) and the monomers, sodium styrenesulfonate (StyS, Polyscience), were precipitated twice from methanol. The comonomers methyl methacrylate and hydroxyethyl methacrylate were washed thoroughly with a basic solution (NaOH 10%) to extract the stabilizers (mainly hydroquinones), dried, distilled and kept in the dark at low temperature until its use. Other chemicals used were of the highest available purity and used as received. All solutions were prepared in Milli-Q purified water.

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2.2. Polymerization

Polymerizations were performed in 5 mL tubes to which an appropriate volume of an aqueous stock solution of StyS 0.5 M was added (around 2.5 mL), together with 0.5 mL of an aqueous solution of Safranine T (1×10^{-5} M). Pure water, Milli-Q purified, was added to reach the desired monomer concentrations. Irradiations were performed for in a photoreactor using eight 6 W G 5 XELUX visible light lamps. The temperature was kept at 30 °C to assure a minimum contribution of the thermal process.

The polymers were precipitated with acetone and washed twice with the same solvent, after which they were dried in vacuum for 3 days. The solutions were dialysed for several days using cellulose membranes (14 000 Da), until no fluorescence in the range 290–450 nm (due to the StyS aromatic groups) was detected. Gel permeation chromatography performed on a Shimadzu system with RI detector and using Asahipak (Shodex) GS 520 7E e GS-320H columns. Analyses were performed at fixed ionic strength (0.1 M NH_4NO_3 in 20% of methanol), using poly(styrenesulfonate) standards (American Polymer).

^{1}H NMR spectra were determined on a 200 MHz Brucker AC instrument using 3% solutions in D_2O, at room temperature.

2.3. Photophysical determinations

Steady-state fluorescence measurements were recorded using a Hitachi F-4500 spectrofluorimeter at room temperature (25 ± 1 °C). About 1.0 cm path-length quartz cuvette were used throughout.

The size of the monomer aggregates was analysed by dynamic light scattering using a Brookhaven Instruments BI9000-AT autocorrelator with a Uniphase Nd:YAg laser light source operating at 532 nm (125 mW). All experiments were performed at a scattering angle of 90° at 25 °C. The autocorrelation function was analysed by the method of cumulants, the analysis of light scattering data was made using the CONTIN program as implemented by Brookhaven Instruments assuming spherical particles.

3. Results and discussion

3.1. Monomer aggregation

Similar to other hydrotropes, StyS forms aggregates at relatively high concentrations, typically above 0.1 M. As shown in Fig. 1, the increase of the concentrations is accompanied by changes in the fluorescence emission spectra. The main emission peak for StyS at low concentrations (~10^{-4} M) is found at 307 nm, and is displaced towards higher wavelengths (~317 nm) when increasing the concentration. This rather small shift can be assigned to the fluorescence of monomers placed in a different microenvironment. At even higher concentrations, that peak starts to decrease and an increasing broad absorption is observed at 405 nm. The latter should correspond to the emission of excimers and higher aggregates [8].

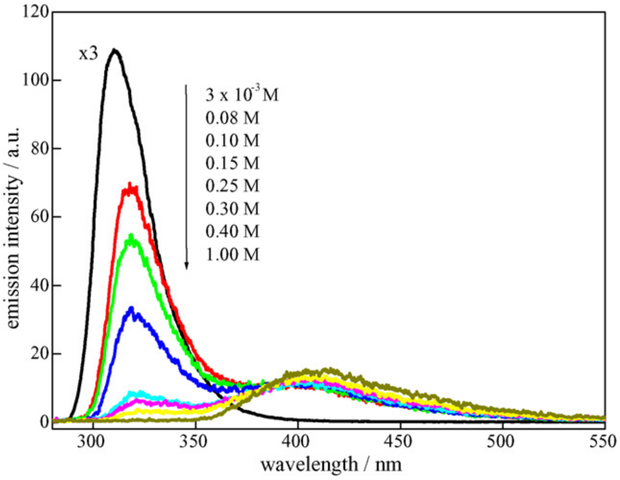

Fig. 1. Emission spectra of StyS at different concentrations. $\lambda_{exc} = 255$ nm.

The ratio between the aggregate and monomol emission intensities, I_{agg}/I_{mono}, measured at 410 and 307 nm, respectively, can be used to determine the *minimum hydrotrope concentration*, MHC [2], as shown in Fig. 2. A change in the slope of the aggregate/monomol emission ratio is observed around ~0.18 M. It can be considered that at this point the addition of further StyS will be incorporated to the hydrotropic aggregates.

Similarly, studies performed with dynamic scattering [9] showed that the size of the monomer aggregates increases quite rapidly up to 0.15 M StyS concentrations. Afterwards, the size increases much less, up to sizes around 260–270 nm, as showed in Fig. 3. The point corresponding to the change of behaviour can be estimated at ~0.11 M, in good agreement with what is found from the I_{agg}/I_{mono} determination [7].

3.2. Polymerization

In view of the results discussed above, it can be assumed that at sufficiently high StyS concentrations, hydrophobic domains will be formed in which non-polar monomers, like methyl methacrylate might dissolve [6]. In view of this feature, the pho-

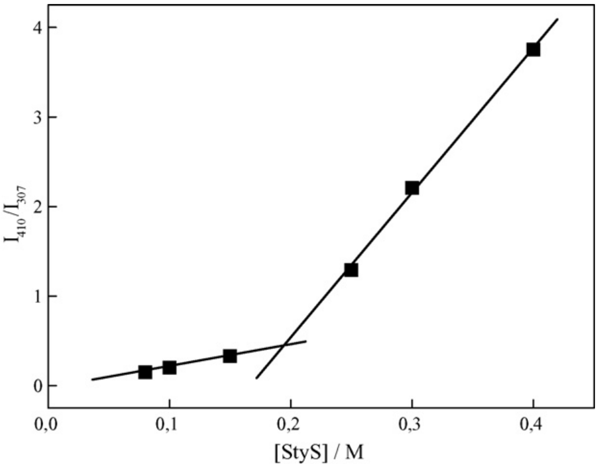

Fig. 2. Ratio of the aggregate to monomol emissions of StyS, measured at 410 and 307 nm, respectively.

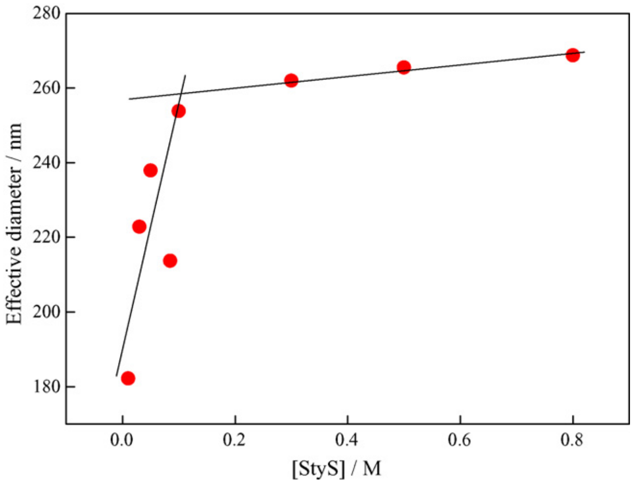

Fig. 3. Effective diameter of StyS aggregates measured by dynamic light scattering.

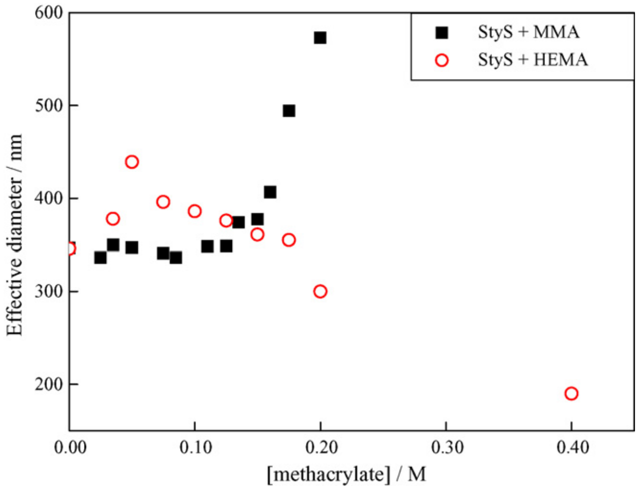

Fig. 4. Effective diameters of aggregates in StyS/MMA and StyS/HEMA solutions determined by dynamic light scattering. [StyS] = 0.5 M.

toinitiated chemically copolymerization of both monomers was attempted using the cationic dye Safranine, which is known to incorporate readily in the StyS aggregates [3].

It can be seen from Fig. 4 that there is practically no change in the size of the aggregates when up to 25% of MMA is added to the StyS solution. Therefore, this is region can be considered as a mere solubilization of the methacrylate monomer in the StyS aggregates. When the MMA concentration is larger than 25% a dramatic increase in the size may be observed, possibly due to a change in the aggregate structure. On the other hand, when hydroxyethyl methacrylate is added to the StyS solution, there is an initial growth of the aggregate size. But at higher concentrations of the HEMA, the aggregates start to decrease in size, suggesting a deaggregation effect similar to that observed when alcohols are added to aggregates [10], which is assigned to the change in the dielectric constant of the solution. The change of the growing to the deaggregation regime occurs at approximately 15% HEMA.

Tables 1 and 2 show the results of the polymerization experiments, in the conditions described in Section 2.

The incorporation rates of MMA in the copolymer were deduced from the ^{1}H NMR spectra. In the spectra, the peaks corresponding to the aromatic rings were found in the 6.5–8.0 ppm region and the MMA methyl hydrogens can be assigned to the absorption between 0.5 and 1.0 ppm. As these methyl groups and the aromatic rings can be assigned unequivocally to the MMA

Table 1
Photoinitiated copolymerization of MMA with StyS in the presence of Sf 1×10^{-5} M

[MMA] (M)	%MMA in feeding mixture	%MMA in copolymer[a]	M_w[b]	M_w/M_n	Yield (%)
0	0	–	77450	1.26	67
0.025	5	2	432090	1.29	63
0.05	10	3	553479	1.30	62
0.15	30	25	507280	1.30	47
0.25	50	35	702460	1.29	38

[StyS] = 0.5 M. Yields obtained after 3 h of irradiation.

[a] Determined from NMR spectra.

[b] Determined by GPC.

Table 2
Photoinitiated copolymerization of HEMA with StyS in the presence of Sf 1×10^{-5} M

[HEMA] (M)	%HEMA in feeding mixture	%HEMA in copolymer[a]	M_w[b]	M_w/M_n	Yield (%)
0	0	0	165000	1.26	95
0.025	5	10	189000	1.21	86
0.05	10	22	175000	1.80	69
0.10	20	26	158000	2.90	52
0.15	30	32	136000	3.60	48
0.25	50	45	99000	3.78	45

[StyS] = 0.5 M. Yields obtained after 3 h of irradiation.

[a] Determined from NMR spectra.

[b] Determined by GPC.

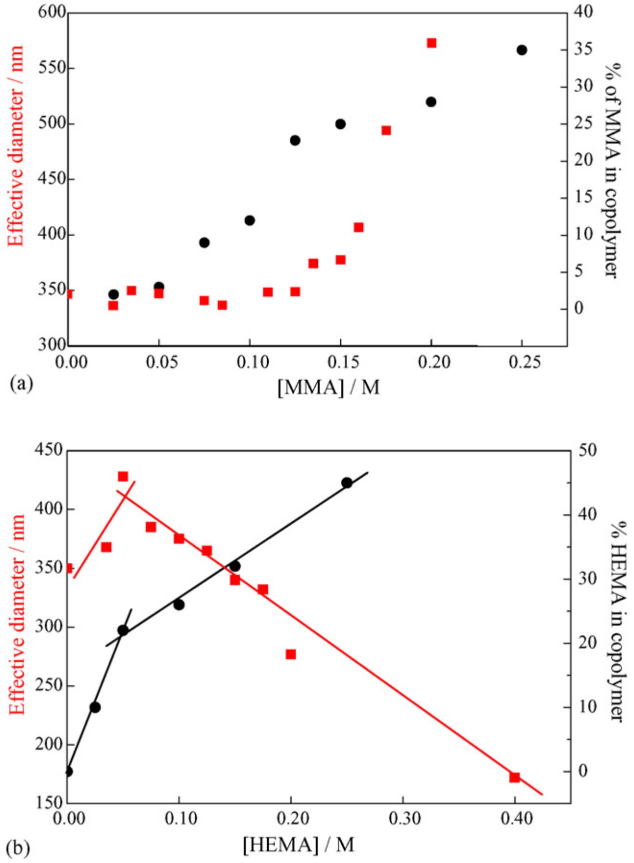

Fig. 5. Relation between monomer aggregate sizes and proportion of methacrylate monomer incorporated in the polymer: (a) StyS-MMA system and (b) StyS-HEMA system.

and StyS meres, their ratio can be correlated with the composition of the copolymer. Other peaks, like the backbone hydrogens around 2 ppm and the methoxy entities are of no major interest in this evaluation.

For the StyS-co-MMA copolymers, the gradual increase in the incorporation of the hydrophobic monomer can be associated to the larger availability of these monomers, although the size of the aggregates changes abruptly at 0.15 M of MMA. There seems to be dissolution of the MMA in the StyS aggregate domains. As the reactivity rates of both monomers are similar ($r_1 = 0.51$, $r_2 = 0.46$) [11,12] the expected trend should be maintained, even when the size of the aggregates increases.

For the StyS-co-HEMA systems, the proportion of HEMA incorporation increases at different rates when the size of the monomer aggregates increases with HEMA concentration, and when it decreases, as shown in Fig. 5. The reactivity ratio for HEMA in the StyS-HEMA system is larger than that for StyS ($r_1 = 0.33$, $r_2 = 0.86$) [11,12], so that under similar conditions one would expect a larger proportion of HEMA in the copolymer. This is found, although the proportionality changes when the StyS aggregates start to be destroyed (at [HEMA] ~0.05 M). In that region, the incorporation of the methacrylate monomer is lower, possibly because the smaller StyS domains in which the chains are initiated contain less HEMA than the analytical concentration.

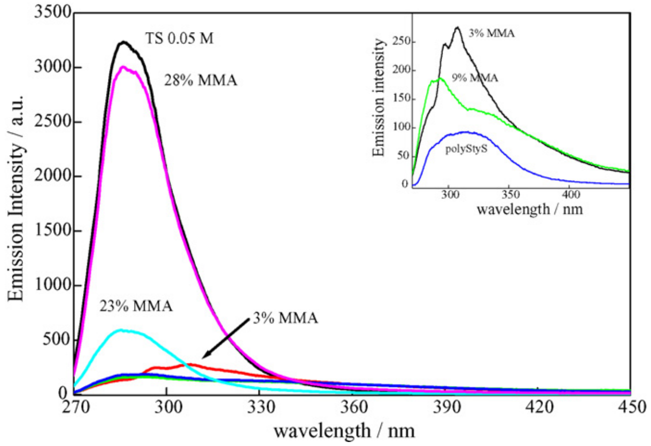

Fig. 6. Emission spectra of StyS-co-MMA copolymers at high and low (inset) MMA content 0.025 g/L. Concentrations correspond to equivalent phenyl moieties.

Fig. 6 shows the emission spectra of poly(StyS) and the copolymers, normalized for the same amount of StyS in them, as well as the emission spectrum of toluenesulfonate (TS). It can be assumed that at low concentrations, TS is a good model for polymers where the StyS meres are reasonably separated one form the other, reducing the possibility of excimer emission [13].

The emission spectrum of pure polyStyS presents a broad band in the 275–400 nm region, due to the emission of higher aggregates, corresponding to the interactions between contiguous phenyl rings (see inset in Fig. 6). As the amount of MMA in the copolymer increases, the emission band becomes narrower and more structured, with the gradual increase of the emission in the TS emission region (285 nm). This points to the fact that the incorporation of the non-aromatic monomer affects randomly the proximity between the aromatic rings, decreasing their interactions and the possibility of excimer or higher aggregate emission.

4. Conclusions

Copolymers of styrenesulfonate and methyl methacrylate, or hydroxyethyl methacrylate, can be readily obtained in aqueous solution photoinitiating the polymerization process by exciting a cationic dye like Safranine. The reactions should be carried out at StyS concentrations higher than the MHC, which in this case is in the 0.10–0.15 M interval.

Measurement of the effective size of the monomer aggregates, prior to polymerization, show the incorporation of MMA to the StyS aggregates, whereas HEMA is initially incorporated but at higher concentrations destroys the aggregates.

The amount of the non-aromatic monomers in the polymers is mainly determined by the relative reactivity ratios. In the case of HEMA, the lower amount of methacrylate in the aggregates will reduce in a certain degree its proportion in the final polymer.

The distribution of the monomers in the copolymers seems to be at random, as can be deduced from the behaviour of the emission spectra, especially the relation between the band corresponding to isolated phenyl rings and that of interacting aromatic systems.

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