

Visible light photopolymerization in BHDC reverse micelles. Laser flash photolysis study of the photoinitiating mechanism

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ARTICLE INFO

Article history:

Received 7 November 2012

Received in revised form 30 January 2013

Accepted 31 January 2013

Available online xxx

Keywords:

Visible photopolymerization

Safranine

Microemulsion polymerization

Reverse micelles

Triplet quenching

ABSTRACT

The photopolymerization of acrylamide (AA) in reverse micelles (RMs) of benzyl hexadecyl dimethylammonium chloride (BHDC) was investigated. The polymerization was performed by irradiation in the 500 nm region of the spectrum, employing as photoinitiating system the synthetic dye safranine-O and triethanolamine (TEOA) as co-initiator. The characterization of the nanoparticles of polyacrylamide was done by dynamic light scattering. Molecular weight determinations were carried out by viscosimetry. Small nanoparticles of polyacrylamide are formed with a low polydispersity and a molecular weight close to 10^6 . The results were compared with those in AOT (sodium bis(2-ethylhexyl) sulfosuccinate) RMs. Laser flash photolysis was used to investigate the photoinitiating mechanism. The maximum of the $T-T$ absorption spectra in RMs confirms that, in spite of its positive charge, the dyes remain at the interface co-micellizing with BHDC. The triplet lifetime is much longer in the RMs than in homogeneous organic solvents. The triplet quenching by TEOA was very much more effective in the RMs than in a homogeneous solvent. The quantum yield of formation of active radicals was evaluated from the transient absorption spectra. It was concluded that they are generated by an intermicellar electron transfer process followed by an intramicellar proton transfer reaction. The quantum yield was found to be 0.2 ± 0.02 . A similar radical yield in a homogeneous solvent requires an amine concentration near 50 times higher.

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1. Introduction

Microemulsion polymerization was developed as an alternative process for the production of monodisperse small polymeric nanoparticles. The size of the particles can be controlled by the size of the microdroplets in the w/o microemulsions [1]. In this way latexes with particle sizes below 100 nm could be prepared. This is a very important topic with many potential applications in drug delivery, microencapsulation, etc. For this reason, a considerable amount of activity has been conducted in this area [2,3].

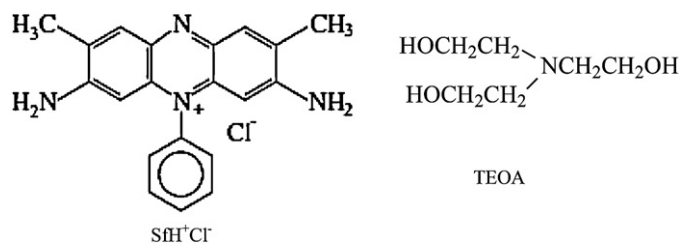
Previous studies of polymerization in microemulsions mostly employed AIBN or persulfate as a photochemical UV or thermal initiator. The use of radiation in the visible region presents several advantages compared to thermal or UV initiation of polymerization [4,5]. These advantages are, for example: (i) lower cost by making use of visible photons emitted by the Hg lamps which are lost when the light is only absorbed by a UV photoinitiator (PI), (ii) a better matching of the emission spectrum of the light source and the absorption spectrum of the PI when laser lights are used, (iii) higher penetration ability of the visible radiation, and (iv) the opportunity to use sunlight for the curing of outdoor coatings. The most

common photoinitiator systems for vinyl polymerization in the visible are composed by a dye and an amine as an electron donor. In our laboratory we have been interested for many years in the mechanistic aspects of PI systems operating in the visible [6–9]. Here we present results on the polymerization of acrylamide (AA) in reverse micelles of benzyl hexadecyl dimethylammonium chloride (BHDC). The polymerization was photoinitiated by irradiation in the 500 nm region of the spectrum, using as PI the synthetic dye safranine-O (SfH^+Cl^-) and triethanolamine (TEOA) as co-initiator (structures in Scheme 1).

The PI system SfH^+ -TEOA was employed successfully to initiate the polymerization of vinyl monomers in methanol [6] and in water [7,9]. Recently we have also published a study on the photophysics and photochemistry of the dye in reverse micelles (RMs) of BHDC and the reactivity of their excited states with TEOA [10]. It was found that a high efficiency of triplet quenching was achieved with an amine concentration much lower than that in homogeneous solution. Therefore, it was of interest to explore the potential use of the PI system safranine/TEOA in microemulsion polymerization. The BHDC based microemulsion system was chosen in order to study the influence of the cationic head group and of the chloride counterion present in the aqueous pseudophase on the polymerization process. Photopolymerization in AOT (sodium bis(2-ethylhexyl) sulfosuccinate) reverse micelles was also studied for comparison.

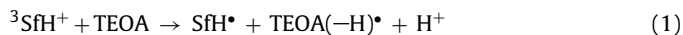
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Scheme 1. Structures of the initiator and co-initiator compounds.

The laser flash photolysis technique has been used to investigate the mechanistic aspects of the initiation process. In homogeneous solvent the initial step is an electron transfer quenching of the triplet state of the dye by the amine. It is assumed that active radicals derived from the amine (TEOA(-H)[•]) are formed with the same quantum yield that the semireduced dye, Eq. (1)



The quenching of the triplet state of the dye by TEOA was investigated in AOT [11] and BHDC [10]. In AOT semireduced dye in its diprotonated state is formed in the quenching process with a quantum yield comparable to that for the formation of the monoprotinated state in homogeneous solvents. However, the characterization of the quenching process in terms of the quantum yield of active radicals was not carried out in BHDC. In this paper we present a laser flash photolysis investigation of the SfH⁺ – TEOA PI system in BHDC RMs, and the characterization of the polyacrylamide nanoparticles produced in this way.

2. Experimental

2.1. Materials

Safranin-O from Aldrich ($\geq 85\%$) was recrystallized from ethanol. BHDC (Sigma) was two times recrystallized from ethyl acetate and dried under vacuum. Benzene and methanol were from Sintorgan (HPLC grade) and used as received. Triethanolamine (TEOA) was commercially available and purified by standard procedures. Water was purified through a Millipore Milli-Q system. Reverse micelles solutions were prepared by the addition of a small amount of the dye dissolved in water to BHDC/benzene solutions. The water content in the micelle, $w = [\text{H}_2\text{O}]/[\text{surfactant}]$ was varied by adding neutral water. The final analytical concentration of the dye was ca. $5 \times 10^{-6} \text{ M}$. Acrylamide (AA) from Aldrich was added to the reverse micelles solution to the required concentration.

2.2. Polymerization

Irradiation was carried out with a Rayonet photoreactor equipped with eight lamps with $\lambda_{\text{max}} = 575 \text{ nm}$. Solutions were deoxygenated by bubbling for 30 min with organic solvent-saturated high-purity argon. Nanoparticles of polyacrylamide remain disperse in the BHDC reverse micellar solution which was directly used for particle size determination by dynamic light scattering.

For molecular weight determination polyacrylamide was separated by precipitation with excess of methanol, filtered, and washed with organic solvent to remove traces of surfactant and vacuum dried. A set of solutions of different concentrations was prepared by dissolving the solid in water. The intrinsic viscosities η_{int} , of aqueous solutions of the polyacrylamide samples were determined by viscosimetry at $25 \pm 0.1 \text{ }^\circ\text{C}$. Molecular weights were obtained from Mark–Houwink–Sakurada [12,13] Eq. (2)

$$\eta_{\text{int}} = 0.0049M^{0.80} \quad (2)$$

2.3. Laser flash photolysis

Transient absorption measurements were carried out by excitation at 532 nm using laser flash photolysis equipment as previously described [14]. The samples were deoxygenated by continuous bubbling with solvent-saturated high-purity argon. All measurements were carried out at $30 \text{ }^\circ\text{C}$.

2.4. Dynamic light scattering (DLS)

The hydrodynamic diameter and size distribution of particles was measured by dynamic light scattering using a Malvern 4700 goniometer and 7132 correlator with an argon-ion laser operating at 488 nm. All measurements were made at a scattering angle of 90° at temperature of $25 \text{ }^\circ\text{C}$. The measurements were analyzed by triplicate and CONTIN analysis to obtain the size distribution of the particles.

3. Results and discussion

3.1. Polymerization

The effect of the water content, surfactant and monomer concentration on the polymerization was investigated. The results are summarized in Table 1. Since the aggregation number of BHDC in benzene at $w = 10$ is ca. 300 [15], at the surfactant concentration used the mean occupation number of the dye was less than 0.03. Therefore, the initiation of the polymer chain takes place in a small fraction of the reverse micelles. The chain growth is most likely governed by an exchange mechanism as previously proposed [16]. AA photopolymerization in AOT reverse micelles have been previously investigated by other groups [17,18]. We have also studied the photopolymerization in AOT with the same PI as in BHDC for the sake of comparison of the resulting nanoparticles. The size of nanoparticles and molecular weight obtained in AOT are similar to those in the literature using a different PI.

Representative plots of DLS experiments are shown in Fig. 1 for BHDC microemulsions. It can be seen that the RMs are very small (hydrodynamic diameter of $\sim 10 \text{ nm}$) and that the size distribution is very narrow. The presence of AA increases the particle size and the ulterior polymerization broadens the distribution while keeping the average size of the particles around 20 nm. A summary of the DLS results is presented in Table 2. The particle size and molecular weight are lower in BHDC than in AOT, although a lower monomer concentration was employed. From the first two rows in Table 1 and the results in Table 2, it can be concluded that the properties of the nanoparticles are practically independent of the water content and BHDC concentration.

Since the initial monomer units per micelle is 400–500 in the case of BHDC and 150 in the case of AOT the exchange of growing chains among water pools must take place several times before termination. This may explain that the molecular weight doubles when BHDC and AA concentrations are made twice higher. Doubling the surfactant concentration at the same w duplicates the number of RMs and the probability of recombination is greatly reduced.

3.2. Photochemical properties of the PI system

The T – T absorption spectrum of the dye in reverse micelles of BHDC is shown in Fig. 2.

In the RMs the spectrum is red shifted ($\lambda_{\text{max}} = 850 \text{ nm}$) with respect to that in water ($\lambda_{\text{max}} = 800 \text{ nm}$). It is the same independent of the water content in the range $w = 5$ to $w = 20$. This is interpreted as a localization of the dye in the interface of the RMs, co-micellizing with BHDC [10] and sensing a medium of lower polarity than water.

Table 1
Results of AA photopolymerization in BHDC and AOT reverse micelles.

	w	AA (M)	TEOA (mM)	% conversion	$M_w/10^6$
BHDC 0.05 M	6	0.075	0.75	~80–85	0.5
BHDC 0.05 M	12	0.075	0.75	~80–85	0.4
BHDC 0.1 M	5	0.15	0.75	85	1.0
AOT 0.38 M	5	0.5	2.0	95	2.2

Table 2
Peak diameter values and full width at half maxima (FWHM) of size distributions obtained by CONTIN analysis.

	AOT 0.38 M in heptane w = 5		BHDC 0.1 M in benzene w = 5		BHDC 0.05 M in benzene w = 12	
	d (nm)	FWHM (nm)	d (nm)	FWHM (nm)	d (nm)	FWHM (nm)
RM	3.6	1.9	9	4.6	9.6	3.5
RM + AA	7.0	7.5	22	12.5	20	9
Latex	49	70	30	28	23.7	27

It is interesting to note that the dye remains at the interface, at all water contents, in spite of the positive charges of the dye and the head groups of BHDC. The triplet lifetime is much longer in the RMs (106 μ s in BHDC [10], 103 μ s in AOT [11]) than in homogeneous organic solvents (18 μ s in MeOH [11]) or in water (60 μ s). In the homogeneous media the triplet decays with a first order

kinetics as a result of an electron transfer quenching by ground state molecules [19]. On the other hand, in RMs the decay is not strictly first order and the self quenching process is partially inhibited by the compartmentalization of the dye. Since the mean occupation number of the RMs by the dye is less than 0.03 it is most unlikely that an intramicellar self quenching process takes place.

The semireduced and semioxidized forms of the dye present a characteristic absorption in the region of 400–450 nm [20,21]. In the inset of Fig. 2 an increase in the absorption in the region of 400–450 nm relative to the T - T maximum at 850 nm can be observed at long times. The origin of this remaining absorption can be found in an intermicellar exchange mechanism leading to self-quenching reaction. This process would take place with a time constant of several tens of microseconds.

When SfH^+ is irradiated with $\lambda > 500$ nm in the presence of TEOA a bleaching of the dye is observed [9]. The effect of BHDC on the photobleaching rate is shown in Fig. 3. The bleaching rate was measured by the decrease of the absorption at the same wavelength as that of irradiation. The data were plotted according to Eq. (3) where A_0 and A are the absorbances at the irradiation wavelength when $t=0$ and after time t , respectively, ϵ_G is the extinction coefficient at the same wavelength, I_0 is the incident light intensity and Φ_R is the reaction quantum yield.

$$\ln \left(\frac{10^A - 1}{10^{A_0} - 1} \right) = (2.303 I_0 \epsilon_G \Phi_R) t \quad (3)$$

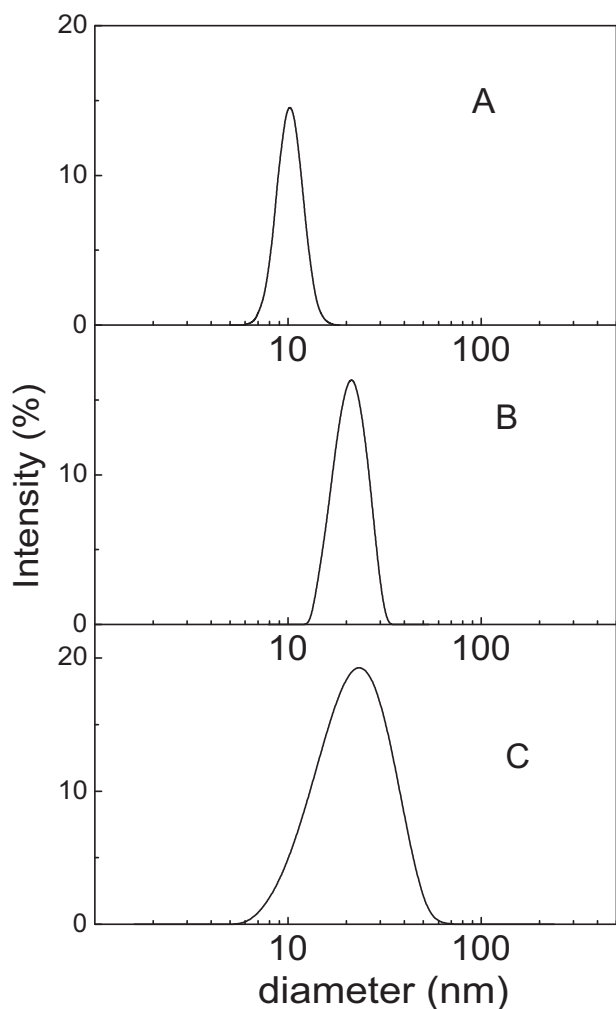


Fig. 1. Size distributions of (A) BHDC/benzene RMs (BHDC 0.05 M w=12), (B) BHDC/benzene 0.05 M + AA 0.075 M, w=12 RMs and (C) polyacrylamide nanoparticles.

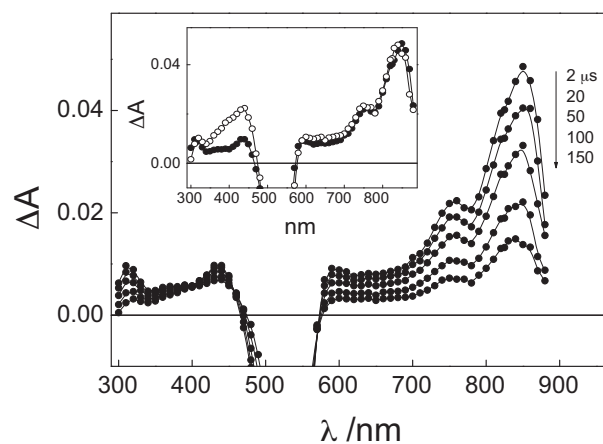


Fig. 2. Transient absorption spectrum of SfH^+ in BHDC 0.05 M, w=15. Inset: spectrum at 2 μ s (●) and 150 μ s (○) normalized at 850 nm.

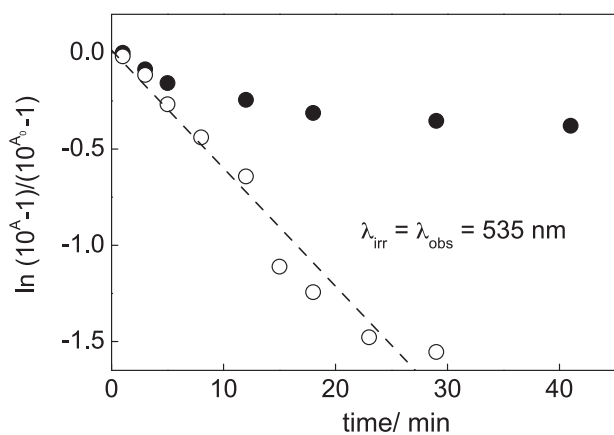


Fig. 3. Plot of the absorbance function, Eq. (3) vs. irradiation time of deaerated solutions of safranine 10^{-5} M – TEOA 0.04 M in EtOH–H₂O 50%, v/v (○), and TEOA 0.5 mM in BHDC 0.05 M , $w = 15$ (●). Irradiation at 535 nm .

A nearly linear plot is observed in the homogeneous solvent. In the RMs, after an initial fast bleaching, the reaction is inhibited. This is most likely due to the compartmentalization that inhibits the secondary reactions of the radicals formed in the quenching process. This photochemical stability renders the PI system more stable in RMs than in homogeneous systems. At the low concentration of TEOA used there is not interception of the excited singlet state of the dye (lifetime $< 2 \text{ ns}$). Therefore, the photoreaction must be initiated from the triplet state.

The triplet quenching by TEOA was investigated in homogeneous solvents and in the RMs. In both media the triplet decays with a first order kinetics in the presence of the amine. Apparent quenching rate constants (k_q) were obtained from the triplet lifetime (measured by the T – T absorption at 825 nm) as a function of the amine concentration according to

$$\tau^{-1} = k_o + k_q[Q]_T \quad (4)$$

where τ is the triplet lifetime, k_o is the first order rate constant for the triplet decay in the absence of the amine and $[Q]_T$ is the analytical concentration of the amine. A plot according to Eq. (4) is presented in Fig. 4 in MeOH and BHDC RMs.

From the slopes in Fig. 4 apparent rate constants $3.8 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ in MeOH and $4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in BHDC were obtained. The apparent rate constant in BHDC is one order of magnitude higher than in AOT, $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [11]. This fact may be related to the higher occupation number by TEOA of the RMs in the case of the cationic surfactant. TEOA is a hydrophilic molecule (the octanol–water partition coefficient is 0.1) [22] and it is expected to be totally incorporated into the micellar pseudophase partitioning between the water pool and the polar interface. The micellar concentration at 0.05 M BHDC and $w = 15$ is ca. $2 \times 10^{-4} \text{ M}$. Since, the TEOA concentration in the quenching experiments varies from 1×10^{-4} to $1 \times 10^{-3} \text{ M}$, the mean occupation number is ≥ 1 . Therefore, triplet quenching may take place by an initial fast intramicellar process, depending on the occupation number of TEOA, and a posterior intermicellar exchange of amine molecules [11].

In homogeneous media the triplet quenching reaction leads to the active radicals for the initiation of polymerization. The formation of radicals in BHDC RMs was investigated by laser flash photolysis. In Fig. 5, the transient absorption spectrum of SfH^+ in the presence of TEOA in BHDC RMs is shown.

At the concentration of TEOA employed in these experiments, $5 \times 10^{-4} \text{ M}$, at $10 \mu\text{s}$ after the laser flash, the triplet state is totally quenched as evidenced by the lack of absorption at 820 nm . The absorption in the region 400 – 430 nm is an indication of the

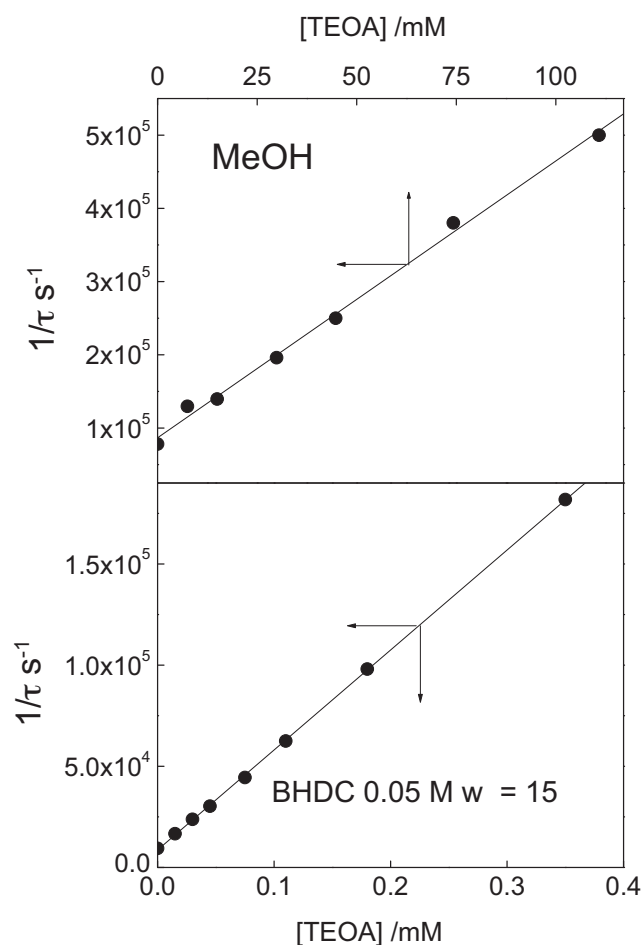


Fig. 4. Triplet quenching by TEOA in MeOH and in BHDC 0.05 M , $w = 15$.

presence of the semireduced form of the dye [20]. It can be seen in the inset that the radical grows at the same time that the triplet decays in a few microseconds after the laser pulse. The apparent rate constant is of the same order of magnitude that the one for the intermicellar exchange of material in BHDC [15]. At difference of the quenching in AOT the diprotonated semireduced dye, absorbing at 700 nm , is not observed. Therefore a fast process leading to the monoprotonated semireduced form, similar to that in

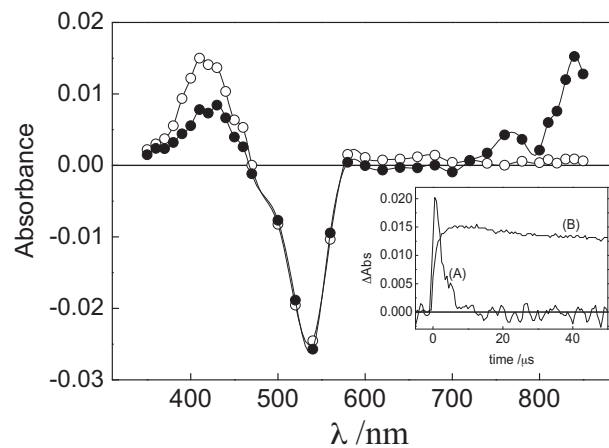


Fig. 5. Transient absorption spectrum of SfH^+ in BHDC 0.05 M , $w = 15$ at $1 \mu\text{s}$ (●) and $10 \mu\text{s}$ (○) after the laser pulse in the presence of TEOA 0.5 mM . Inset: time profile of the absorption at 840 nm (A) and 410 nm (B).

homogeneous solvent is probably occurring in BHDC. The mechanism involves an initial proton transfer process to an amine (A), yielding the unprotonated form of the triplet dye, which in turn undergoes a slower electron transfer reaction with a second amine molecule [19].



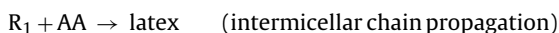
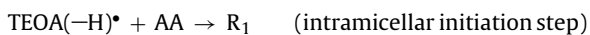
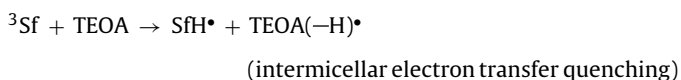
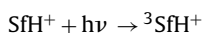
The last step involves a fast in-cage proton transfer from the amine radical cation to the unprotonated radical to give the semireduced form of the dye.

The active radicals from the amine are formed with the same yield than the reduced form of the dye in reaction (6). The semireduced dye quantum yield were estimated from the transient absorption as previously discussed for the case of AOT [11] according to Eq. (7)

$$\Phi_R = \frac{\Delta A_R \varepsilon_T}{\Delta A_T \varepsilon_R} \Phi_T \quad (7)$$

where ΔA_R is the long time absorption remaining after the triplet decay in the presence of TEOA measured at 410 nm, ΔA_T is the prompt T - T transient absorption measured at 850 nm immediately after the laser pulse, ε_R and ε_T are the respective absorption coefficients and Φ_T is the triplet quantum yield in the absence of the amine. The triplet state parameters are those given in ref [10] and ε_R was determined by the ground state depletion (GSD) method [23] using the long time negative absorbance at 540 nm. In this way a quantum yield of 0.22 ± 0.02 was obtained for a TEOA concentration of 0.5 mM. A similar radical yield in a homogeneous solvent requires an amine concentration near 50 times higher. Since the triplet yield in BHDC is 0.27 [10] the formation of radicals in the reverse micellar system is a highly efficient process.

Based on the laser flash photolysis and the characterization of the polymer particles the following detailed mechanism may be proposed for the photopolymerization of AA in BHDC RMs:



In comparison with the results in AOT the PI system presents a higher efficiency for generation of active radicals. The apparent quenching rate constant by TEOA is one order of magnitude higher in BHDC, $4.5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in BHDC and $2.9 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in AOT, and also the radical quantum yield is higher, 0.22 at TEOA 0.5 mM in BHDC and 0.14 at TEOA 10 mM in AOT [10]. The lower initiation efficiency in AOT explains the higher molecular weight and particle sized found in AOT (Tables 1 and 2).

In summary, AA can be polymerized in BHDC RMs by a mechanism photoinitiated by visible excitation of the dye in the presence of amine as co-initiator. Active radicals are generated by an intracellular proton transfer reaction followed by an intermicellar electron transfer process. Small nanoparticles of polyacrylamide are formed with a low polydispersity and a molecular weight close to 10^6 .

Acknowledgments

Financial support from the Agencia Nacional de Promoción Científica (PICT 2213/07) CONICET (PIP 2010-0284) and Universidad Nacional de Río Cuarto is gratefully acknowledged. G.V.P. and E.M.A. thank CONICET for a post-doctoral research fellowship.

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