Polymerization in Microemulsions with Polymerizable Cosurfactants: A Route to Highly Functionalized Nanoparticles

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ABSTRACT: The polymerization of styrene-in-water microemulsions prepared using polymerizable cosurfactants, such as hydroxyalkyl acrylates or methacrylates, gives rise to stable suspensions of well-defined highly functionalized nanoparticles in the 15−25 nm diameter range. Among the various associations of ionic surfactants with hydroxyalkyl (meth)acrylate cosurfactants tested, the surfactant/cosurfactant system (sodium dodecyl sulfate/2-hydroxypropyl methacrylate) is found to be the most effective and allows the preparation of oil in water microemulsions of styrene (up to 7 wt %) or mixture of monomers. Polymerization with 100% conversion is achieved at room temperature using either an oil-soluble photoinitiator (DMPA) or water-soluble redox systems (hydrogen peroxide/ascorbic acid or ammonium persulfate/diamine). GC monitoring of conversion for both monomers clearly demonstrates that the mechanism of copolymerization depends on the location of the reactive species (monomer, polymerizable cosurfactant, and radical initiator). The resulting polymers contain up to 40% of hydroxylated units.

I. Introduction

A great deal of research interest has been devoted to polymerization in microemulsion since the pioneer papers published fifteen years ago.[1−5] Polymerization of water-soluble monomers (e.g., acrylic acid or acrylamide) in water-in-oil (w/o) microemulsions, as well as hydrophobic monomers (e.g., styrene or methyl methacrylate) in oil-in-water (o/w) microemulsions, has been studied, and the main contributions have been recently reviewed by Candau[6] and Antonietti et al.[7] Stable latexes in the nanosize range (<50 nm) can be produced using the technique of polymerization in microemulsion. Such nanolatexes find numerous specific applications for example in drug delivery, microencapsulation, and biomedical diagnosis.[8−10] Most of these applications require highly functionalized polymer particles. As emphasized by Antonietti et al.,[7,11] the well-defined structure of the microemulsions and their very large interfacial area (in the order 10−100 m^2/mL) offer new opportunities to synthesize special polymer materials, such as copolymers with high surface functionality, which are not accessible using other techniques. The synthesis of such functionalized nanoparticles requires the incorporation of a second monomer (comonomer), bearing the desired functionality, which obviously modifies the structure of the starting microemulsion. Nevertheless, except in Antionietti's papers, the preparation of highly functionalized nanoparticles via polymerization in microemulsion has been scarcely described.[7,11−14]

In this paper, we describe a general pathway to highly functionalized, narrowly dispersed, nanoparticles via polymerization in microemulsion of styrene in water formulated with ionic surfactants using the comonomer, a hydroxyalkyl acrylate or methacrylate, as a polymerizable cosurfactant instead of the usual aliphatic alcohols. This approach allows a substantial molecular economy since a component of the stabilizing system for the starting microemulsion is incorporated in the final polymer giving rise to more concentrated polymer dispersions. Thus, in the first part, a general method to prepare microemulsions using polymerizable cosurfactants is described and the resulting functionalized polymers are characterized. In a second part, we study the conversion versus time for both monomers, styrene and polymerizable cosurfactant, in the presence of various initiating systems, either water or oil soluble. It is shown that the polymerization process, random or block copolymerization, depends on the location of the initiator.

II. Experimental Section

Materials and Methods. 3-Vinylbenzyl chloride (VBC; Aldrich, 97%), methacrylic acid (MA; Aldrich, 99%), 2-hydroxypropyl methacrylate (HPMA; Aldrich, 97%), 2-hydroxyethyl acrylate (HEA; Aldrich, 97%), 4-hydroxybutyl acrylate (HBA; Lancaster, 97%), pentan-1-ol (Aldrich, 99%), sodium dodecyl sulfate (SDS; Janssen, 99%), sodium dodecylbenzenesulfonate (DBS; Aldrich, 99%), cetyltrimethylammonium bromide (CTAB; Aldrich, 95%), hydrogen peroxide (Aldrich, 30 wt % solution in water), ascorbic acid (Aldrich, 99%), ammonium persulfate (Aldrich, 98%), tetramethyldiaminomethane (Aldrich, 99%), and 2,2-dimethoxy-2-phenylacetophenone (DMPA; Aldrich, 99%) were used as received. Styrene (Aldrich, 99%) was distilled before use.

Surface tension measurements were performed at 20 °C using the ring method with a Du Nouy tensiometer (Kruss K10T). Water was doubly distilled before use. The infrared spectra were recorded using a FTIR apparatus (Nicolet 250) on polymer films obtained by slow evaporation of dilute chloroformic solutions. The ^1H and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded on a Brucker AM300 spectrometer. Elemental analysis have been obtained from the Service Central d'Analyse (CNRS, Vernaison, France). Quasielastic light scattering (QELS) analysis was obtained with a 3 W Spectra Physics laser (Brookhaven BI 2030 correlator) from the Centre de Recherche d'Aubervilliers (Rhône-Poulenc, France). Some samples were analyzed by transmission electron microscopy (TEM, obtained from the Centre de Microscopie, University of Rennes I, Rennes, France). The photographs are in good agreement with the QELS results. Gas chromatography analysis were performed on a Carlo Erba FTV4000 equipped with a RSL 150 (25 m)

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capillary column; temperature program, isotherm plateau at 40 °C for 3 min, then increase of temperature at a rate of 10 °C/min to 180 °C, and isotherm plateau at 180 °C for 3 min; detector (FID) and injector temperatures, 210 and 180 °C; carrier gas N_2 (90 kPa).

Preparation of the Microemulsions. The microemulsions were prepared by the so-called titration method:[8] the desired amount of monomer (or mixture of monomers) is added to an aqueous solution of surfactant at the desired concentration and the mixture stirred until a milky emulsion is formed. The chosen cosurfactant (pentanol, HEA, HBA, or HPMA) is then added dropwise with a buret under gentle magnetic stirring until a clear, transparent, microemulsion is obtained. This procedure was used for SDS and DBS but was found unsuccessful with CTAB because of its very low solubility in water. In this case, the titration method was slightly modified as follows: the desired amount of CTAB and cosurfactant are mixed together and the resulting solution is added dropwise with a buret under gentle magnetic stirring to a biphasic mixture of water and monomer (desired amounts) until a clear, transparent, microemulsion is obtained.

Polymerization Reactions. (a) Water-Soluble Radical Initiators: H_2O_2/Ascorbic Acid[15] or Ammonium Persulfate/Tetramethyldiaminomethane.[16] The previously prepared microemulsion is transferred in a three-necked round-bottom flask and degased with nitrogen for 20 min. The two components of the desired redox couple are then successively introduced with a syringe. When the H_2O_2/ascorbic acid system is used, hydrogen peroxide (30% in water) and then ascorbic acid (aqueous solution 12.5 g/L) are added at room temperature and the reaction mixture is then heated under nitrogen to 30−35 °C with an oil bath. When the ammonium persulfate/tetramethyldiaminomethane system is used, ammonium persulfate in the minimum amount of water and then pure tetramethyldiaminomethane are added. The reaction is carried out at room temperature (20−25 °C) under nitrogen.

(b) Oil-Soluble Radical Initiator: DMPA.[17] The desired amount of DMPA is solubilized in the monomer (or mixture of monomers) before the preparation of the microemulsion. The freshly prepared microemulsion is transferred in a reactor equipped with a UV lamp and degassed with nitrogen for 20 min before the lamp is switched on. The reaction is carried out at room temperature (20−25 °C) under nitrogen.

Separation and Characterization of the Resulting Polymers. The polymer suspension (20 g) is transferred into a round-bottom flask containing 30 g of an aqueous saturated solution of sodium sulfate. The resulting mixture is heated at 80 °C for 2 h. The flocculated polymer is separated by filtration, the resulting white paste is dispersed in 100 mL of water, and the suspension is heated to reflux for 2 h. The crude polymer, isolated either by filtration or centrifugation, is dried at 50 °C until the sample weight remains constant. For spectroscopic and elemental analysis, the polymers are further purified as follows: 500 mg of the previously isolated polymer is dispersed in acetone (100 mL) and the suspension stirred for at least 2 h. The polymer, separated by filtration, is solubilized in chloroform and the resulting solution dried over magnesium sulfate. The pure polymer, isolated after removal of the solvent under reduced pressure, is then characterized by elemental analysis (Table 3) and spectroscopy (IR and NMR when soluble). Poly(styrene/HXA): IR (film, cm^{-1}) 3400 (m br, OH), 3050−3000 (s, CH arom), 2900−2850 (s, CH skeleton), 1740 (s, CO). Poly(styrene/HPMA): ^1H NMR ($CDCl_3$, ppm) 1−1.5 (skeleton and chain), 1.66 (CH_3, skeleton), 2.4 (CH_2 chain), 3.1−4 (CH_2O and CHO), 6.4−7.4 (ArH); ^{13}C NMR ({^1H} and DEPT, $CDCl_3$, ppm) 16.02 (CH_3, HPMA), 19.31(CH_3, HPMA), 38.76 (CH skeleton), 40.4 (CH_2 skeleton and chain), 44−47 (CH_2 skeleton), 48.5−52 (CH_2 skeleton), 65.4 and 65.6 (CHO, HPMA), 69.2−70.3 (CH_2O, HPMA), 72.4−73.9 (CHO, HPMA), 125.67, 126.69, and 128.06 (CH arom), 145−145.7 (C_{ipso} arom), 176.4−177.7 (CO, HPMA). Poly(styrene/HBA): ^1H NMR ($CDCl_3$, ppm) 1.3−2.6 (skeleton and chain), 3.4−4 (CH_2O), 6.3−7.3 (ArH); ^{13}C NMR ({^1H} and DEPT, $CDCl_3$, ppm) 25 (CH_2 chain, HBA), 29.04 (CH_2 chain, HBA), 40.41 (CH skeleton), 41−47 (CH_2 skeleton), 62.16 (CH_2O, HBA), 63.2−64.5 (CH_2O, HBA), 125.8, 127.7, and 128 (CH arom), 145.3 (C_{ipso} arom), 175.6−176.4 (CO, HBA). Poly(styrene/HPMA/VBC): IR (Nujol, cm^{-1}) 3400 (m br, OH), 3050−3000 (s, arom CH), 2900−2850 (s, CH skeleton), 1720 (s, CO), 1270 (m, CH_2Cl). Poly(styrene/HPMA/MA): IR (film, cm^{-1}) 3600−2800 (very br, OH), 3050−3000 (s, arom CH), 2900−2850 (s, CH skeleton), 1710−1730 (s, CO).

Studies of the Conversion versus Time. The conversion of the various monomers versus time has been studied by quantitative GC analysis of the amount of unreacted monomer(s) using an internal standard (ethylbenzene). The samples are prepared as follows: 0.5 mL of the reaction mixture is withdrawn with a syringue, diluted in 1 mL of an aqueous solution saturated with sodium nitrite (radical inhibitor), and added to 1 mL of a titrated solution of ethylbenzene (20 g/L) in ethyl acetate containing 200 ppm of di-*tert*-butylphenol (radical inhibitor). After vigorous stirring and decantation, an aliquot of the upper organic phase is taken for the GC analysis. It has been checked that the monomers are quantitatively extracted in the aqueous phase and that no further polymerization takes place during the preparation of the samples.

III. Results and Discussion

1. Microemulsion Formulation and Characterization of the Resulting Polymers. Microemulsions Based on Polymerizable Cosurfactants. The preparation of microemulsions of styrene in water were tested with various associations of hydroxyacrylic or methacrylic esters (HEA, HBA, HPMA) with ionic surfactants: two anionic surfactants (SDS, DBS) and a cationic surfactant (CTAB). For this purpose, the versatile so-called titration method proposed by Schulman and co-workers was used:[18−20] the potential cosurfactant is slowly added to an emulsion of styrene in water stabilized by the chosen ionic surfactant until a clear, transparent microemulsion is obtained.

Microemulsions are thus obtained with most of the associations of a hydroxy(meth)acrylic ester and an ionic surfactant (Table 1). Thus, HEA allows the preparation of microemulsions with both cationic (CTAB) and anionic (SDS, DBS) surfactants. On the other hand, with the more lipophilic hydroxyacrylic and methacrylic esters such as HBA and HPMA, microemulsions are only obtained in the presence of SDS. Thus, when SDS is used, microemulsions of styrene in water can be prepared using HEA, HBA, or HPMA. HPMA is the most effective cosurfactant and allows the preparation of microemulsions containing ~7 wt % of styrene for a molar ratio HPMA/SDS = 0.7:1.5 (Table 1: M41, M34, M37). Moreover, microemulsions of mixtures of styrene with other monomers like methacrylic acid (MA) or chloromethylstyrene (VBC) can also be prepared using SDS and hydroxy ester cosurfactants (Table 1: M60, M58, M61, M70, M67, M214).

The cosurfactant behavior of the hydroxy(meth)acrylic esters HEA, HBA, and HPMA is confirmed by the increase of the amount of styrene that can be incorporated, for a given SDS concentration, when the molar ratio hydroxy ester per SDS (z) is increased. The greatest solubilization enhancement is observed with HPMA in agreement with its highest effectiveness (Table 1: M179, M34). Furthermore, measurements of the surface tension of aqueous solutions of SDS (Figure 1) show a decrease of the critical micellar concentration (cmc) when hydroxy esters are added. In the presence of HEA or HBA, the superficial tension reaches a plateau at ~40 mN m^{-1}, like that for pure SDS, and the cmc value is slightly decreased from 5 mM for pure SDS to 4.5 and 3.5 mM, respectively, in the presence of HEA and HBA. The decrease of the cmc value demon-

Table 1. Microemulsions Prepared Using Ionic Surfactants and Polymerizable Cosurfactants

				composition, wt %				
no.	cosurfactant HXA[a]	surfactant[a]	monomer(s)	water	surfactant	HXA	monomer(s)	z[b]
M118	HEA	CTAB	styrene	87.62	2.50	7.60	2.28	9.53
M157	HEA	DBS	styrene	83.59	6.69	6.69	3.04	3
M155	HEA	DBS	styrene	80.41	6.43	9.65	3.51	4.5
M152	HEA	DBS	styrene	60.44	6.04	30.22	3.3	15
M147	HEA	SDS	styrene	86.39	9.5	0.65	3.46	0.17
M186	HBA	SDS	styrene	84.75	9.32	2.54	3.39	0.55
M179	HPMA	SDS	styrene	84.23	9.27	3.14	3.37	0.67
M41	HPMA	SDS	styrene	77.68	7.59	5.13	5.52	1.4
M34	HPMA	SDS	styrene	77.68	9.2	6.32	6.68	1.4
M37	HPMA	SDS	styrene	68.44	18.54	6.28	6.64	0.7
M61	HPMA	SDS	styrene + VBC (85/15)[c]	82.00	9.98	3.74	2.83 + 0.7[d]	0.7
M60	HPMA	SDS	styrene + VBC (85/15)[c]	84.39	9.08	2.99	2.9 + 0.64[d]	0.7
M58	HPMA	SDS	styrene + VBC (85/15)[c]	84.05	9.18	3.13	2.69 + 0.67[d]	0.7
M214	HPMA	SDS	styrene + MA (90/10)[c]	81.17	8.93	4.30	4.99 + 0.61[d]	1
M70	HPMA	SDS	styrene + MA (77/23)[c]	83.80	9.10	3.00	2.28 + 0.64[d]	0.7
M67	HPMA	SDS	styrene + MA (80/20)[c]	84.20	9.21	3.13	2.7 + 0.67[d]	0.7

[a] HEA, hydroxyethylacrylate; HBA, hydroxybutyl acrylate; HPMA, hydroxypropyl methacrylate; SDS, sodium dodecyl sulfate; DBS, sodium dodecylbenzenesulfonate; CTAB, cetyltrimethylammonium bromide. [b] Molar ratio hydroxy(meth)acrylate/surfactant. [c] Molar ratio styrene/comonomer. VBC, vinylbenzyl chloride; MA, methacrylic acid. [d] Weight percent styrene + weight percent comonomer.

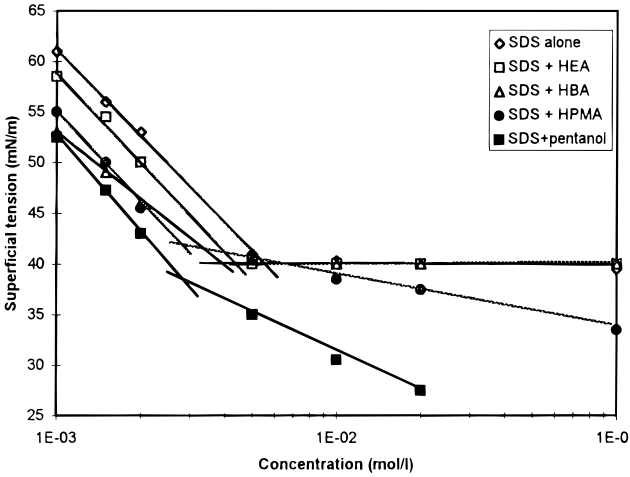

Figure 1. Surface tension of aqueous solutions of SDS alone or in the presence of cosurfactant. Molar ratio (z) cosurfactant/SDS = 20.

strates that comicellization occurs: HEA and HBA, partly located at the interface, decrease the ionic repulsions between SDS anionic head groups. Nevertheless, since the surface tension reaches the SDS plateau, the alcohol (HEA or HBA) molar excess at the interface is restricted. HEA and HBA are probably partitioned between the interface and the aqueous or oil phase. On the other hand, in the presence of HPMA, the superficial tension does not reach a plateau and decreases well below 40 mN m^{-1}: from the break of the slope, one can approximate a cmc value of 3 mM. It is noteworthy that the same behavior is observed in the presence of pentan-1-ol, a well-known SDS cosurfactant. Apart from the fact that comicellization takes place, these measurements demonstrate that HPMA is preferentially located at the interface and that the decrease of the surface energy is higher with HPMA than with HEA or HBA. HPMA is therefore the best polymerizable cosurfactant for SDS in agreement with the microemulsion compositions.

Polymerization. The polymerizations were performed under mild conditions below 35 °C in order to ensure the microemulsions remained stable during the whole reaction. Both water-soluble (redox systems: hydrogen peroxide/ascorbic acid,[15] ammonium persulfate/tetramethyldiaminomethane[16]) and oil-soluble (DPMA decomposed under UV irradiation[17]) radical initiators were used. Kinetic studies and comparison of these initiating systems are described below. Whatever the experimental conditions, polymerization of both monomers, styrene and the polymerizable cosurfactant, occurs with 100% conversion within 10 min to a few hours (GC analysis) depending on the initiating system and on the experimental conditions (*vide infra*).

After polymerization, the aspect of the medium depends on the starting composition (Table 2). When the cosurfactant is mainly located at the interface of the swollen micelles, stable translucent bluish suspensions of nanoparticules are obtained: this is the case for microemulsions prepared using SDS and HEA, HBA or HPMA (P147 to P67), CTAB and HEA (P118), or DBS and HEA (P157) for low molar ratio hydroxy ester/surfactant. On the other hand, when a significant amount of polymerizable hydroxy ester is located in water, gel or porous polymer is produced: for example, microemulsions based on DBS and hydrophilic HEA with high molar ratio HEA/DBS (P155, P152).

When clear suspensions are obtained, the size of the particles and the dispersity, determined by QELS and TEM, depend on the surfactant/cosurfactant pair. Associations of SDS with HEA (low molar ratio), HBA, or HPMA lead to monodisperse suspensions of nanoparticles of ~20 nm diameter (P147 to P58). On the other hand, associations of CTAB or DBS with HEA at high molar ratio hydroxy ester/surfactant give rise to broader size distributions (P118). With a poorly water-soluble surfactant like CTAB, the progressive precipitation of the surfactant during the polymerization, owing to the disappearance of the hydroxy ester, gives rise to polydisperse suspensions of larger particles.

Polymerization of microemulsions prepared using SDS and polymerizable cosurfactants HEA, HBA, or HPMA is thus the most effective pathway to monodisperse suspensions of nanoparticles of about 15−25 nm diameter range. It is noteworthy that this approach is suitable for styrene microemulsions and also for mixtures of styrene with other monomers such as MA or VBC (P61 to P67) giving rise to polyfunctionalized nanoparticles. Moreover, these suspensions are very stable since no sedimentation or flocculation was observed over a period of two years.

Characterization of the Polymers. The spectrocopic characterization of the polymers, isolated by flocculation, demonstrates that copolymerization of the

Table 2. Polymerization of Microemulsions Prepared Using Polymerizable Cosurfactants[a]

no.	surfactant[b]	cosurfactant[b] (% wt)	monomer(s)[b] (% wt)	size, nm	aspect
P118[c]	CTAB	HEA (7.6)	styrene (2.28)	50 ± 30 polydiperse	transparent, bluish
P157[c]	DBS	HEA (6.69)	styrene (3.04)	22 ± 10	transparent, bluish
P155[c]	DBS	HEA (9.65)	styrene (3.51)		gel
P152[c]	DBS	HEA (30.22)	styrene (3.3)		porous solid
P147[c]	SDS	HEA (0.65)	styrene (3.46)	27 ± 3	transparent, bluish
P186[c]	SDS	HBA (2.54)	styrene (3.39)	20 ± 3	transparent, bluish
P179[c]	SDS	HPMA (3.14)	styrene (3.37)	20 ± 4	transparent, bluish
P41[d]	SDS	HPMA (5.13)	styrene (5.52)	17 ± 2	transparent, bluish
P34[e]	SDS	HPMA (6.32)	styrene (6.68)	15 ± 3	transparent, bluish
P37[e]	SDS	HPMA (6.28)	styrene (6.64)	15 ± 3	transparent, bluish
P61[c]	SDS	HPMA (3.13)	styrene (2.83) VBC (0.7)	18 ± 3	transparent, bluish
P60[d]	SDS	HPMA (2.99)	styrene (2.9) VBC (0.64)	15 ± 2	transparent, bluish
P58[e]	SDS	HPMA (3.74)	styrene (2.69) VBC (0.67)	20 ± 4	transparent, bluish
P214[c]	SDS	HPMA (6.28)	styrene (4.99) MA (0.61)	22 ± 5	transparent, bluish
P70[d]	SDS	HPMA (3.00)	styrene (2.28) MA (0.64)	12 ± 1	transparent, bluish
P67[e]	SDS	HPMA (3.13)	styrene (2.7) MA (0.67)	20 ± 4	transparent, bluish

[a] Suspension P*x* results from polymerization of microemulsion M*x* (Table 1). [b] Components and weight percent in the starting microemulsion: HEA, hydroxyethyl acrylate; HBA, hydroxybutyl acrylate; HPMA, hydroxypropyl methacrylate; SDS, sodium dodecyl sulfate; DBS, sodium dodecylbenzenesulfonate; CTAB, cetyltrimethylammonium bromide; VBC, vinylbenzyl chloride; MA, methacrylic acid. [c] Initiator, $(NH_4)_2S_2O_8$/TMDAM. [d] Initiator, H_2O_2/ascorbic acid. [e] Initiator, DMPA/UV.

Table 3. Composition of Polymers Resulting from Polymerization of Microemulsions Prepared Using Polymerizable Cosurfactants[a]

	microemulsion		polymer				
			elemental analysis, %				
no.	components[b]	molar ratio HXA/monomer(s)	C	H	O	Cl	molar ratio HXA/monomer(s)
P179b[c,d]	HPMA/SDS styrene	40/60	75.76	8.10	15.85		40/60
P179c[d,e]	HPMA/SDS styrene	40/60	80.92	7.94	10.57		25/75
P41[f]	HPMA/SDS styrene	40/60	78.42	8.01	13.17		30/70
P60[b]	HPMA/SDS styrene/VBC	40/48/12	77.46	7.55	9.86	5.29	24/59/17
P58[f]	HPMA/SDS styrene/VBC	40/48/12	72.70	7.94	15.86	3.90	38/49.5/12.5
P214[c]	HPMA/SDS styrene/MA	35/57/8	76.76	7.90	14.22		25/65/10
P70[f]	HPMA/SDS styrene/MA	39/47/14	78.04	7.96	13.96		25/65/10
P147[c]	HEA/SDS styrene	15/85	84.25	7.43	3.23		8/92
P186[c]	HBA/SDS styrene	35/65	84.51	7.93	6.72		15/85
P126[c]	HBA/CTAB styrene	57/43	81.77		10.22		25/75

[a] Polymers P*x* isolated after polymerization of microemulsion M*x* (Table 1). [b] HEA, hydroxyethyl acrylate; HBA, hydroxybutyl acrylate; HPMA, hydroxypropyl methacrylate; SDS, sodium dodecyl sulfate; DBS, sodium dodecylbenzenesulfonate; CTAB, cetyltrimethylammonium bromide; VBC, vinylbenzyl chloride; MA, methacrylic acid. [c] Initiator, $(NH_4)_2S_2O_8$/TMDAM. [d] Same starting microemulsion, M179. [e] Initiator, DMPA/UV. [f] Initiator, H_2O_2/ascorbic acid.

polymerizable cosurfactants (HEA, HBA, or HPMA) with styrene has taken place. The IR spectra show the vibration bands of hydroxy(meth)acrylate units [ν_{OH} (3400 cm^{-1}) and ν_{CO} (1740 cm^{-1})] and the vibration bands of styrene (aromatic CH and overtones). NMR spectroscopy also demonstrates the incorporation of both monomers: the ^1H NMR spectra show the presence of deshielded aliphatic protons α to an oxygen atom between 3.5 and 4 ppm and the presence of aromatic protons (6.5−7.3 ppm). Moreover, the integration curves show that a high amount of hydroxy ester has been copolymerized. The ^{13}C NMR spectra also reveal the incorporation of both monomers: characteristic signals of hydroxy ester around 176 (CO ester), 69 (Csp^3 linked to the ester function), and 62 ppm (Csp^3 linked to the alcohol) and characteristic aromatic signals resulting from styrene between 125 and 145 ppm. For example, ^1H and ^{13}C NMR spectra of copolymers (HBA/styrene and HPMA/styrene) are given in Figure 2.

Furthermore, elemental analyses demonstrate that both monomers initially introduced have been incorporated in the copolymer (Table 3). For HPMA/SDS associations, it is noteworhty that the polymer composition is close to that of the monomer blend in the initial microemulsion (P179b, P41) even in the presence of a third monomer like MA or VBC (P58, P214). In the presence of HBA or HEA, the proportion of hydroxy ester incorporated in the polymer is slightly lower

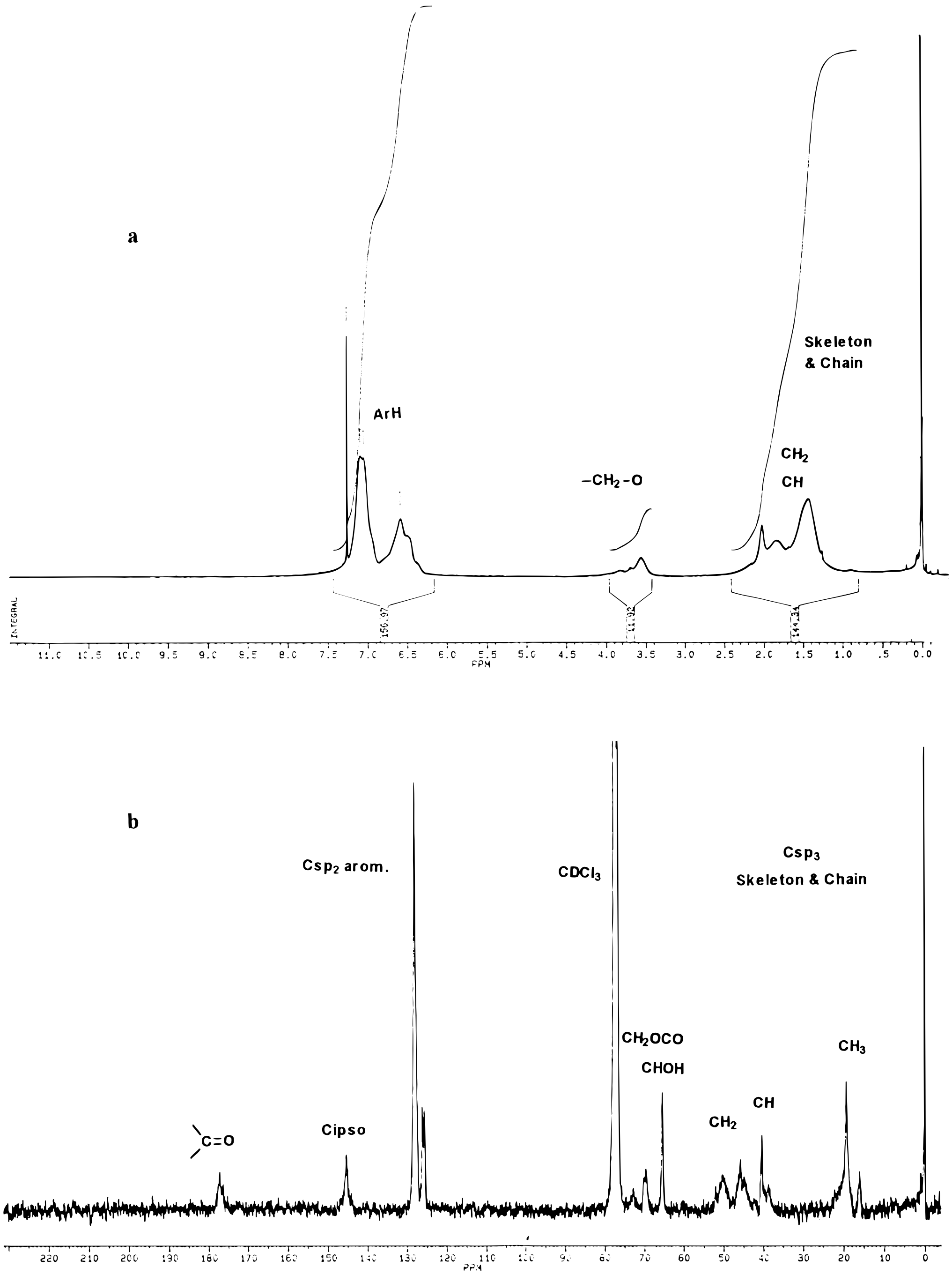

Figure 2. NMR spectra of copolymers: (a) ^1H NMR spectrum (300 MHz, $CDCl_3$) of HBA/styrene (P186). (b) ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of HPMA/styrene (P179b). Substitution of carbon nuclei determined using a DEPT sequence.

probably owing to acrylate homopolymerization in water, mainly for HEA (P147, P186). It is notewothy that, whatever the polymerizable cosurfactant, HEA, HBA, or HPMA, copolymers containing high molar amounts (15−40%) of hydroxy groups are obtained and that polyfunctionalized nanoparticles are produced in the presence of a third monomer.

Removal of the Surfactant. The use of polymerizable cosurfactants not only affords a substantial molecular economy but also makes the purification of the polymer suspensions easier. Indeed, pure ionic surfactants like SDS exhibit a much lower solubility in water below a critical temperature, the so-called "Krafft point" ($T_k = 16$ °C for SDS[21]). Accordingly, in suspensions produced by polymerization of microemulsions based on polymerizable cosurfactants, SDS behaves as in aqueous solution and is easily removed by precipitation upon cooling below the Krafft point (e.g., 10 °C). Two cyles of cooling and filtration allow the removal of ~85% of the surfactant initially introduced. A last step of dialysis leads to suspensions containing less than 1 wt % surfactant.

Discussion. The use of polymerizable cosurfactant as comonomer for styrene polymerization is thus a very successfull method to prepare (i) highly functionalized nanoparticles with up to 40% of hydroxylated units and (ii) polyfunctionalized nanoparticles when a third monomer is incorporated. Nanoparticles, among the smallest particles described in the literature until now, with diameters ranging from 15 to 25 nm and a narrow distribution, are obtained from globular microemulsions. It must be pointed out that the size of the particles also depends on the polymerization rate: the faster the polymerization, the smaller the particle size. Although further studies are required, it could be assumed that, as the cosurfactant polymerization takes place, the microemulsion becomes thermodynamically unstable and narrowly sized nanoparticles can only be produced when the polymerization is kinetically faster than the microemulsion breakdown.

Moreover, this approach allows a substantial molecular economy since a component of the starting microemulsion surfactant system is incorporated in the final polymer, giving rise to much more concentrated polymer dispersions (up to 13 wt %). Our method thus overcomes the main drawbacks of microemulsion polymerization (high amounts of surfactant and difficulty in obtaining a surfactant-free polymer dispersion), since the consumption of the cosurfactant makes the removal of the surfactant easier. Nearly surfactant-free nanoparticle suspensions, with potential biomedical applications, can thus be obtained.

2. Effect of the Nature of the Radical Initiator on the Conversion versus Time. Various kinds of initiating systems either water soluble or oil soluble have been tested. Kinetic studies have been performed to determine both (i) the effect of the polymerizable cosurfactant on the polymerization of styrene and (ii) the influence of the location of the radical initiator on the copolymerization of polymerizable cosurfactant with styrene. In order to compare polymerization of styrene alone and in the presence of polymerizable cosurfactant, experiments were performed first on styrene polymerization in microemulsions formulated by using a conventional, widely studied,[22−25] surfactant/aliphatic alcohol cosurfactant system (SDS/pentan-1-ol) and the results were then compared with microemulsions containing a polymerizable cosurfactant (mainly SDS/HPMA).

Water-Soluble Initiator (Redox Couple H_2O_2/Ascorbic Acid). Studies were performed with the redox system H_2O_2/ascorbic acid, which has been found successful to produce very small particles via polymerization of styrene in nonionic microemulsions.[15] This redox system, scarcely used, produces radicals upon heating at 30−35 °C.

(a) Polymerization of Styrene in SDS/Pentanol Microemulsions. The study of the conversion of styrene (monitored by GC analysis) versus time for various initiator concentrations and various molar ratios of H_2O_2/ascorbic acid using the same microemulsion (8.5 wt % styrene) shows that the rate and the conversion depend on the initiator concentration and mainly on the molar ratio H_2O_2/ascorbic acid (R) (P11, P18, P54, and P78, Figure 3). The highest rate with 100% conversion within 10 min is obtained when the molar ratio R is lowered to ∼1 (P78) or when the initiator concentration is increased to 1.5 mol of H_2O_2/mol of styrene (P18). For high molar ratios R and lower concentrations (P11), the yield of production of radicals is lower; the reaction rate is lowered and rapidly reaches a plateau: the polymerization appears to be limited by the diffusion within the growing particles and termination by transfer to the monomer. Accordingly, for a given initiator concentration and a given molar ratio R, the reaction rate and the final conversion increase when the amount of styrene in the microemulsion is increased (P18 8.5 wt %, P23 4.1 wt %, P24 1.5 wt %, Figure 4). Therefore, the redox system hydrogen peroxide/ascorbic acid does indeed allow the polymerization of styrene with 100% conversion in SDS/pentanol microemulsions in a very short period of time (5−10 min) provided that (i) the styrene concentration is high enough and (ii) the concentration of both components of the redox system is properly chosen.

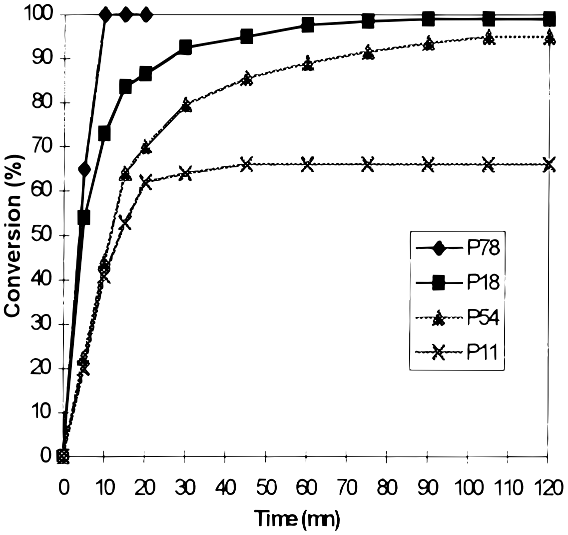

Figure 3. Polymerization of styrene in SDS/pentanol microemulsion initiated by H_2O_2/ascorbic acid. Influence of the concentration and the composition of the initiator redox system. Microemulsion composition (wt %): water 75.9, SDS 7.92, pentanol 6.78, and styrene 8.5. For P11 $[H_2O_2] = 0.128$ mol/kg; [ascorbic acid] $= 2.4 \times 10^{-3}$ mol/kg; $R = 53$; $[H_2O_2]$/[styrene] $= 0.156$. For P54 $[H_2O_2] = 0.127$ mol/kg; [ascorbic acid] $= 2.4 \times 10^{-2}$ mol/kg; $R = 5.3$; $[H_2O_2]$/[styrene] $= 0.156$. For P18 $[H_2O_2] = 1.09$ mol/kg; [ascorbic acid] $= 2.1 \times 10^{-2}$ mol/kg; $R = 53$; $[H_2O_2]$/[styrene] $= 1.56$. For P78 $[H_2O_2] = 0.127$ mol/kg; [ascorbic acid] $= 0.12$ mol/kg; $R = 1$; $[H_2O_2]$/[styrene] $= 0.156$.

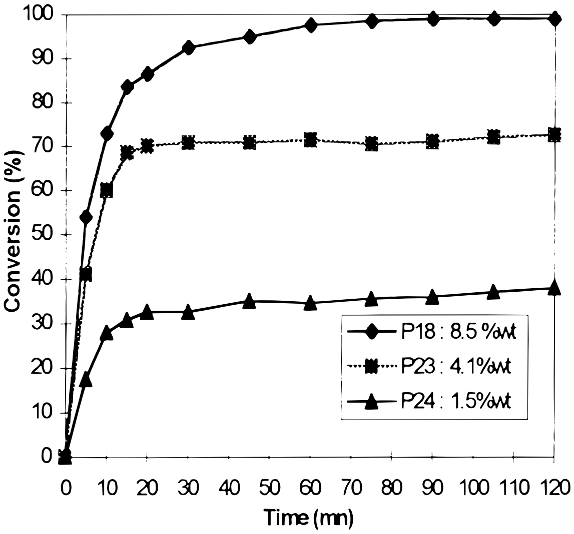

Figure 4. Polymerization of styrene in SDS/pentanol microemulsion initiated by H_2O_2/ascorbic acid. Influence of styrene concentration. $[H_2O_2] = 1.09$ mol/kg; [ascorbic acid] $= 2.1 \times 10^{-2}$ mol/kg. Microemulsion compositions (wt %): For P18 water 75.9, SDS 7.92, pentanol 6.78, and styrene 8.5. For P23 water 80.07, SDS 6.87, pentanol 5.88, and styrene 4.14. For P24 water 81.83, SDS 6.8, pentanol 5.82, and styrene 1.47.

(b) Polymerization of Styrene and Polymerizable Cosurfactant (HPMA) in SDS/HPMA Microemulsions. The study of the conversion of styrene and HPMA versus time (determined by GC analysis, at a given initiator concentration and composition) for various monomer concentrations shows that the polymerization rate and the conversion depend on the concentrations of both monomers (P41 and P30, Figure 5a). The polymerization rate and the conversion of both

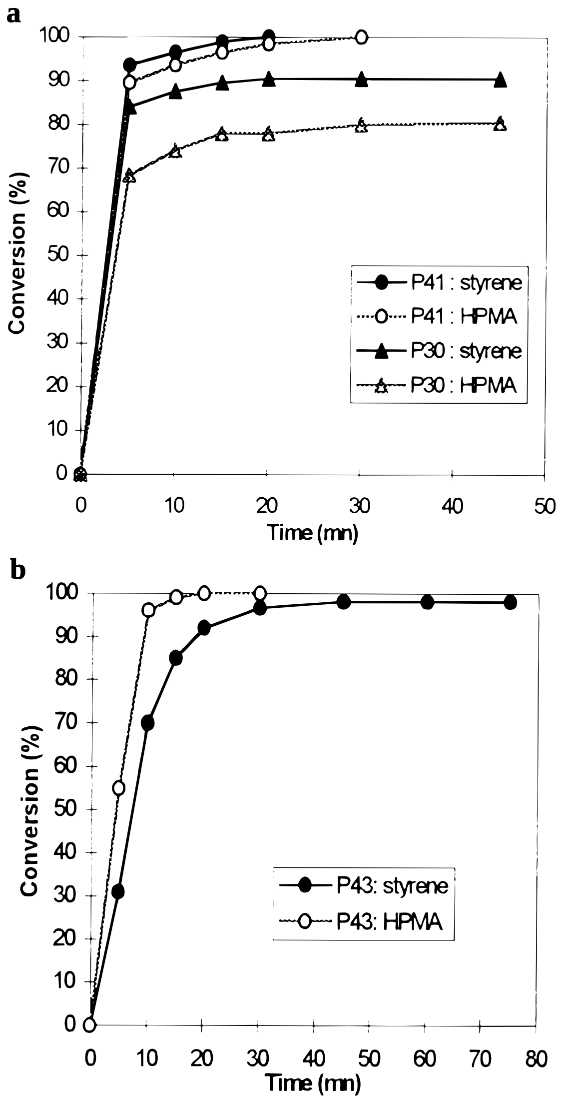

Figure 5. Copolymerization of styrene and HPMA in SDS/HPMA microemulsions initiated by H_2O_2/ascorbic acid. (a) Influence of styrene and HPMA concentrations. $[H_2O_2] = 1.1$ mol/kg; [ascorbic acid] $= 2.1 \times 10^{-2}$ mol/kg; molar ratio styrene/HPMA = 1.5. Microemulsion compositions (wt %): For P41 water 77.68, SDS 7.59, HPMA 5.13, styrene 5.52. For P30 water 85.28, SDS 7.79, HPMA 1.32, styrene 1.43. (b) Influence of styrene and HPMA concentrations. $[H_2O_2] = 1.1$ mol/kg; [ascorbic acid] $= 2.1 \times 10^{-2}$ mol/kg; molar ratio styrene/HPMA = 0.8. Microemulsion composition for P43 (wt %) water 84.7, SDS 9.3, HPMA 3.8, and styrene 2.2.

monomers depend on the molar ratio styrene/HPMA: when the concentration of styrene is higher than those of HPMA (molar ratio 1.5, P41 and P30), the polymerization of styrene is slightly faster and reaches a higher conversion. While the opposite is observed for a molar ratio of styrene/HPMA lower than 1 (P43, molar ratio 0.8, Figure 5b). In every case, both monomers polymerize simultaneously. It is noteworthy that, whatever the experimental conditions, true copolymerization of styrene and HPMA does occur with high yields, reaching 100% for adequate concentrations, in very short period of time (30 min to 1 h).

The conversion versus time curves for styrene alone (microemulsion formulated with pentanol, P18) and for styrene in the presence of HPMA (P45) are shown Figure 6: the comparison clearly demonstrates that the polymerization of styrene is greatly enhanced in the presence of the polymerizable cosurfactant and that the initial rate is much higher even for a lower monomer concentration. Moreover, the concentration of radical initiator required to obtain 100% conversion is much lower in the presence of HPMA. These results can be qualitatively interpreted by assuming that the initiation step occurs at the interface, where the local HPMA concentration is expected to be high, or in the aqueous phase, where HPMA is slightly soluble. The propagation then takes place within the oil droplets near the interface with either HPMA or styrene and leads to an almost random copolymerization.

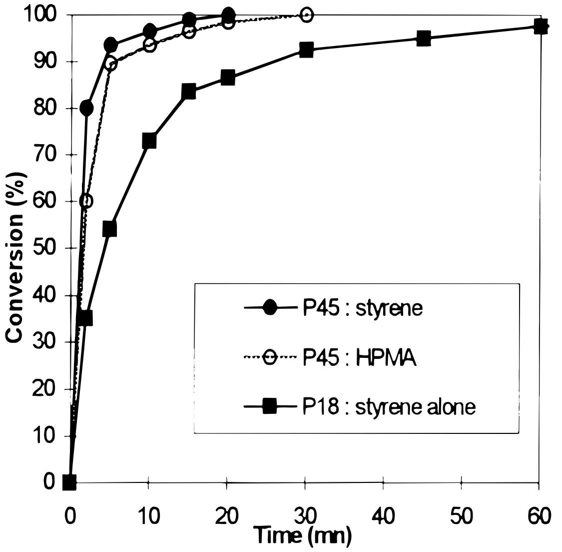

Figure 6. Copolymerization of styrene and HPMA in SDS/HPMA microemulsions initiated by H_2O_2/ascorbic acid: comparison with polymerization of styrene alone in SDS/pentanol microemulsion. P18: $[H_2O_2] = 1.09$ mol/kg; [ascorbic acid] $= 2.1 \times 10^{-2}$ mol/kg; $R = 53$; $[H_2O_2]/[\text{styrene}] = 1.56$. P45: $[H_2O_2] = 0.22$ mol/kg; [ascorbic acid] $= 4.2 \times 10^{-3}$ mol/kg; $R = 54$; $[H_2O_2]/[\text{styrene}] = 0.5$. Microemulsion compositions (wt %): For P18 water 75.9, SDS 7.92, pentanol 6.78, and styrene 8.5. For P45 water 86.28, SDS 7.59, HPMA 2.57, and styrene 2.76.

Other Water-Soluble Initiator (Redox Couple Ammonium Persulfate/Tetramethyldiaminomethane). Similar studies were performed with the persulfate/diamine redox couple widely used for polymerization at room temperature (25 °C).[16] In SDS/pentanol microemulsions, the conversion of styrene reaches 100% within 2 h, while hydrogen peroxide/ascorbic acid initiator, at the same initiator/monomer molar ratio, leads to a partial conversion (75%) (P51 and P23, Figure 7a). In microemulsions formulated with a polymerizable cosurfactant, HPMA, the conversion−time curve shows, as in the case of H_2O_2/ascorbic acid-initiated reactions, that both monomers polymerize simultaneously with 100% conversion within 1 h (P50, Figure 7b) and also that the polymerization of styrene is faster in the presence of the polymerizable cosurfactant.

Thus, with the water-soluble radical initiators studied in the present work, similar trends are observed, e.g., higher polymerization rates and conversions as well as simultaneous polymerization of both monomers, styrene and polymerizable cosurfactant, giving rise to random copolymers.

Oil-Soluble Initiator (DMPA). The studies were performed mainly with DMPA decomposed under UV irradiation. DMPA was preferred to the widely used AIBN because the rate of radical production under UV irradiation (366 nm) is much higher at room temperature.[17]

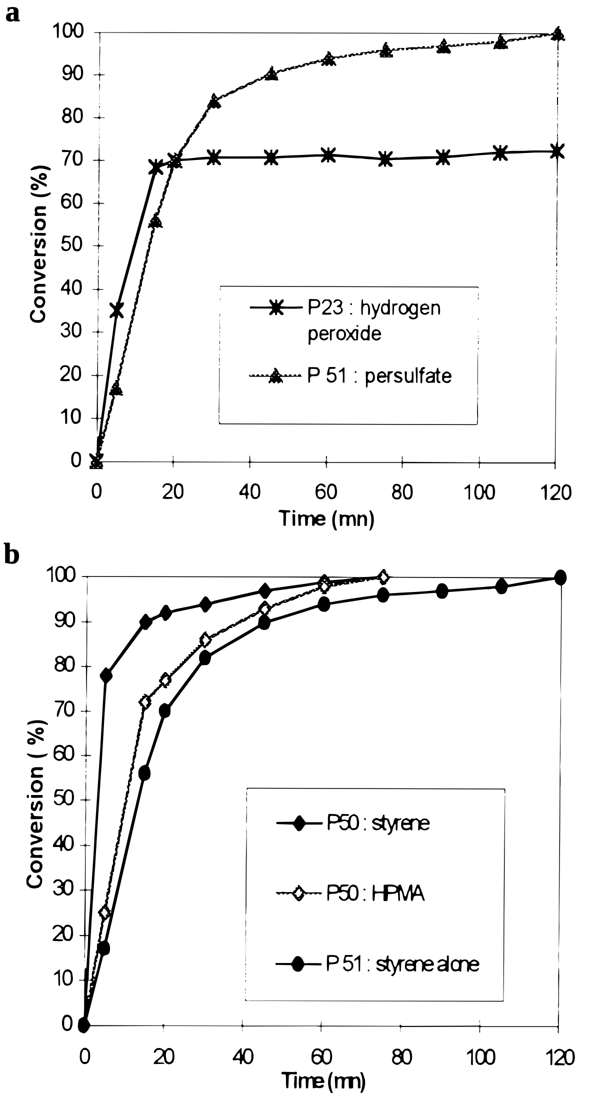

Figure 7. Polymerization initiated by ammonium persulfate/tetramethyldiaminomethane. (a) Polymerization of styrene in SDS/pentanol microemulsions. Comparison of the redox systems H_2O_2/ascorbic acid and persulfate/diamine. P23: (H_2O_2/ascorbic acid) $[H_2O_2] = 1.09$ mol/kg (2.77 mol/mol of styrene); [ascorbic acid] $= 2.1 \times 10^{-2}$ mol/kg (0.053 mol/mol of styrene). Microemulsion compositions (wt %): water 80.07, SDS 6.87, pentanol 5.88, and styrene 4.14. P51: (persulfate/diamine) $[(NH_4)_2S_2O_8] = 2.04 \times 10^{-2}$ mol/kg (0.07 mol/mol of styrene); [TMDAM] $= 2.85 \times 10^{-2}$ mol/kg (1 mol/mol of styrene). Microemulsion composition (wt %): water 85.0, SDS 8.35, pentanol 2.83, and styrene 3.04. (b) Copolymerization of styrene and HPMA in SDS/HPMA microemulsion. Comparison with polymerization of styrene alone in SDS/pentanol microemulsion. $[(NH_4)_2S_2O_8] = 2.04 \times 10^{-2}$ mol/kg; [TMDAM] $= 2.85 \times 10^{-2}$ mol/kg. Microemulsion compositions (wt %): For P51 water 85.0, SDS 8.35, pentanol 2.83, and styrene 3.04. For P50 water 84.11, SDS 8.86, HPMA 3.01, and styrene 3.22.

(a) Polymerization of Styrene in SDS/Pentanol Microemulsions. The conversion−time curves for various styrene concentrations show that the reaction rate and the final conversion increase when the amount of styrene in the microemulsion is increased (P2 8.8 wt %, P10 5.1 wt %, P8 3.7 wt %, and P7 1 wt %; Figure 8). When the monomer concentration is high enough (>5%), complete polymerization is achieved within a few hours (4−6 h). As already described by Feng and Ng,[26,27] it is noteworthy that water-soluble-initiated systems result in higher polymerization rates while "oil-soluble" DMPA-initiated reactions give rise to higher final conversion (for a given initiator/monomer ratio).

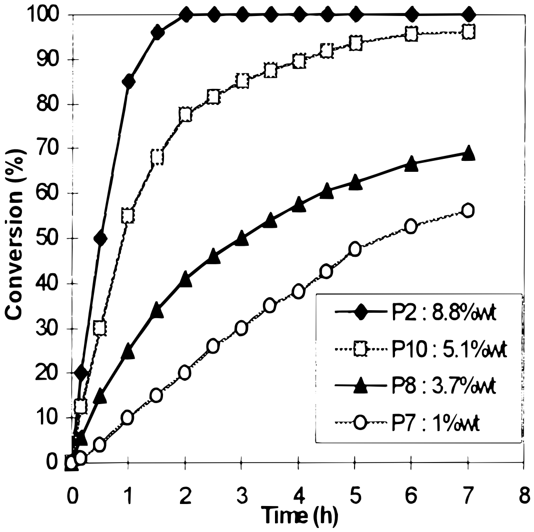

Figure 8. Polymerization of styrene in SDS/pentanol microemulsions initiated by DMPA. Influence of styrene concentration. [DMPA]/[styrene] $= 7 \times 10^{-3}$. Microemulsion compositions (wt %): For P2 water 75.7, SDS 8.3, pentanol 7.1, and styrene 8.8. For P7 water 82.3, SDS 9.02, pentanol 7.72, and styrene 0.97. For P8 water 79.97, SDS 8.77, pentanol 7.5, and styrene 3.7. For P10 water 78.8, SDS 8.64, pentanol 7.4, and styrene 5.13.

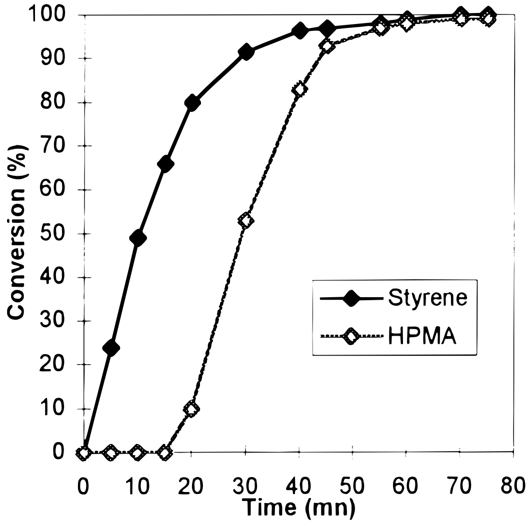

Figure 9. Copolymerization of styrene and HPMA in SDS/HPMA microemulsions initiated by DMPA. [DMPA]/[styrene] + [HPMA] $= 7 \times 10^{-3}$; molar ratio HPMA/styrene = 1.5. Microemulsion composition (wt %): For P56 water 84.2, SDS 9.21, HPMA 3.13, and styrene 3.37.

(b) Polymerization of Styrene and Polymerizable Cosurfactant (HPMA) in SDS/HPMA Microemulsions. The study of the conversion of styrene and HPMA demonstrates that, whatever the molar ratio of styrene to HPMA, a "two-step" polymerization process takes place: styrene polymerizes first, and polymerization of HPMA begins only when about 60−70% styrene has been converted [P56 (styrene/HPMA = 1.5), Figure 9]. The styrene polymerization rate and conversion are not significantly modified in the presence of the polymerizable cosurfactant HMPA. In this case, the initiation step is not controlled by diffusion of the free radicals from the aqueous phase to the oil droplets; the free radicals are produced within the styrene oil droplet core and react first with styrene.

Discussion. From these results, it can be concluded that the mechanism of copolymerization of styrene with a polymerizable cosurfactant like HPMA and the structure of the resulting copolymers depend on the location of the radical initiator: when the initiating system is located in the continuous aqueous phase, a simultaneous, random copolymerization takes place; the polymerization rate and the final conversion are enhanced in the presence of a polymerizable cosurfactant. On the contrary, when an oil-soluble initiator is used and introduced within the monomer dispersed phase, a two-step, block, copolymerization is observed: styrene polymerizes first (up to 60−70%) and then HPMA. These results demonstrate that the relative location (aqueous continuous phase/interface/droplet core) of the reactive species and the so-called compartmentalization effect play a major role. The mechanism obviously depends on the microenvironment and on the local monomer concentrations at the region where the free radicals are produced and where the initiation step takes place. If one refers to the component partitioning behavior previously described in o/w microemulsion consisting of styrene, water, SDS, and pentan-1-ol, more than 60% of the cosurfactant partitions into the interface with most of the styrene (∼90%) residing in the oil phase.[22,23] Thus, when the free radicals are produced within the oil droplets (oil-soluble initiating system), the local concentration of styrene at the reaction site is much higher than that of HPMA (from ref 23, the approximate weight ratio of cosurfactant to styrene in oil core phase is ∼0.1, e.g., molar ratio ∼0.12), so that the polymerization proceeds first with styrene until the concentration of polymerizable cosurfactant at the reaction locus reaches a significant value (about 60−70% styrene conversion, approximate molar ratio HPMA/styrene 1.5−2). When free radicals are produced in the aqueous phase (water-soluble initiating system), initiation occurs in the cosurfactant-rich interfacial region so that HPMA acts as a “phase transfer agent” for radicals. The very first oligomeric radicals produced from HPMA are more lipophilic than their monomer precursor, and they probably partition in between the oil droplet core and the interface. Therefore, a random polymerization is observed since the monomer proportions are not so different at the polymerization locus. However, according to Candau’s proposal, a mechanism based on interparticular collisions followed by complete mixing of the particle contents may account fairly well for our results.[6,28] Indeed, in this case, the monomer proportions at the reaction sites would be maintained throughout the polymerization at their initial values, thus generating a homogeneous microstructure.

IV. Conclusion

Hydroxyalkyl (meth)acrylates such as HEA, HBA, and HPMA have been proved to act as cosurfactants in o/w microemulsions of styrene or a mixture of monomers. The polymerization of microemulsions prepared using a polymerizable cosurfactant allows the synthesis of well-defined highly functionalized nanoparticles, in the 15−25 nm diameter range, and affords a substantial molecular economy since a component of the surfactant system is incorporated within the resulting polymer.

Polymerization with 100% conversion is achieved at room temperature with either oil-soluble photoinitiator (DMPA) or water-soluble redox systems (H_2O_2/ascorbic acid or ammonium persulfate/tetramethyldiaminomethane). GC monitoring of conversion of both monomers, styrene and polymerizable cosurfactant, sheds light on the tremendous influence of the location of the reactive species (monomer, polymerizable cosurfactant, radical initiator) on the mechanism of copolymerization. Further investigations are currently being developed to demonstrate that one can take advantage of such microenvironment effects to control the level of surface functionalization of well-defined nanoparticles.

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