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Use of a Lewis Acid Surfactant Combined Catalyst in Cationic Polymerization in Miniemulsion: Apparent and Hidden Initiators

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ABSTRACT: A Lewis acid surfactant combined catalyst (LASC) was tentatively used in a cationic polymerization in miniemulsion of *p*-methoxystyrene (*p*MOS). In a first part, the initiating potential of trisdodecyl sulfate ytterbium (Yb(DS)$_3$, 0.25H$_2$O) was evidenced in the solution polymerization of *p*MOS initiated by the corresponding chlorinated adduct *p*MOS−HCl. Miniemulsion polymerizations of *p*MOS performed using the same initiating system gave rise to oligomers, but experimental conditions chosen could not evidence the expected LASC-mediated cationic polymerization process. Further studies showed that LASC is located at the interface and acts only as a surfactant together with SDS. The polymerization occurred due to the hydrolysis of *p*MOS−HCl. The resulting acidification of the water phase leads to the transformation of SDS into its sulfuric acid form acting as an inisurf according to an interfacial cationic polymerization process. Latex particles of *p*MOS incorporating narrowly distributed low molar mass chains were obtained.

Introduction

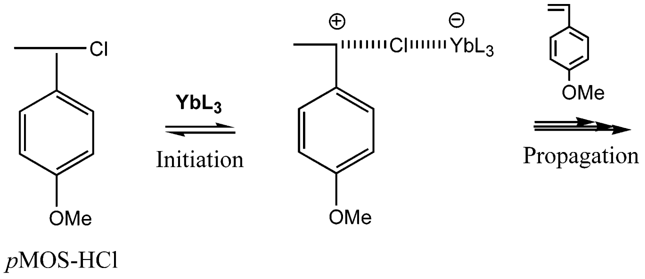
In 1994, Kobayashi et al.[1] reported a new type of Lewis acid based on triflate derivatives of rare earths, Ln(OSO$_2$CF$_3$)$_3$, otherwise abbreviated Ln(OTf)$_3$. While most Lewis acids are decomposed and/or deactivated in the presence of water, these compounds are stable and seem to keep the chemical activating properties of a Lewis acid in water solution. Their potentialities were first investigated in organic chemistry, and many reactions such as aldol reactions were successfully conducted in water.[2] With a view of improving the system, the same team also studied the effect of added surfactants such as SDS and Triton X in the reaction medium.[3] While reactions proceeded sluggishly in water, remarkable enhancement of the reactivity was observed in the presence of small amounts of surfactant due to a micellar organization. They eventually realized that SDS and rare earth chloride derivatives react together (Scheme 1) to give a new type of Lewis acid exhibiting surfactant properties: the Lewis acid surfactant combined catalysts (LASC).[4−6]

Scheme 1

$$\mathrm{LnCl_3 + 3\ C_{12}H_{25}\text{-}SO_3ONa \longrightarrow Ln(OSO_3C_{12}H_{25})_3 + 3NaCl}$$

Ln = Sc, Yb

Scheme 2



L = OTf (triflate) or DS (dodecylsulfate)

Polymerizations performed in dispersed media with water as continuous phase are among the most commonly used methods for polymer synthesis in industry. They indeed present many advantages[7] such as providing an excellent medium to remove the heat of reaction, a final product of low viscosity and easy to handle even for high polymer content recipes. However, these processes are so far limited to mostly radical polymerizations. Coordination or ionic polymerizations are often carried out in stringent conditions, and even traces of water are to be avoided. However, several attempts have successfully been conducted in emulsion or miniemulsion with water as continuous phase.[8−11] In the case of cationic polymerization, on the basis of Lewis acid properties in water of ytterbium triflate (Yb(OTf)$_3$), Sawamoto et al. reported a series of works related to the cationic polymerization of *p*-methoxystyrene (*p*MOS) in the presence of water under nonconventional emulsion polymerization conditions.[12−15] In a first study,[12] polymerization of *p*MOS with Yb(OTf)$_3$ as activator and with HCl or the hydrogen chloride monomer adduct (*p*MOS−HCl) or HCl (Scheme 2) as initiator was shown to be controlled while molar masses (MM) increased linearly with conversion up to 25% conversion. Initiation by sulfonic acids in the presence of Yb(OTf)$_3$ activator was also investigated.[14] In both cases, molar masses remained low (typically less than 3000 g mol^{-1}). The authors proposed that dormant ω-chlorinated chains were activated by the few Yb(OTf)$_3$ penetrating the monomer droplets to generate long-lived polymer chains. Some other studies were also performed in the same vein with phosphonic acids instead of sulfonic acids.[16]

Cauvin et al.[17,18] recently showed that, using dodecylbenzenesulfonic acid (DBSA) as inisurf in a miniemulsion process, polymerization of *p*MOS proceeded without the need for Yb(OTf)$_3$. Although poly(*p*MOS) average molar mass increases with conversion, a "controlled" active center generation could not be put forward. Rather, the authors proposed that an interfacial poly-

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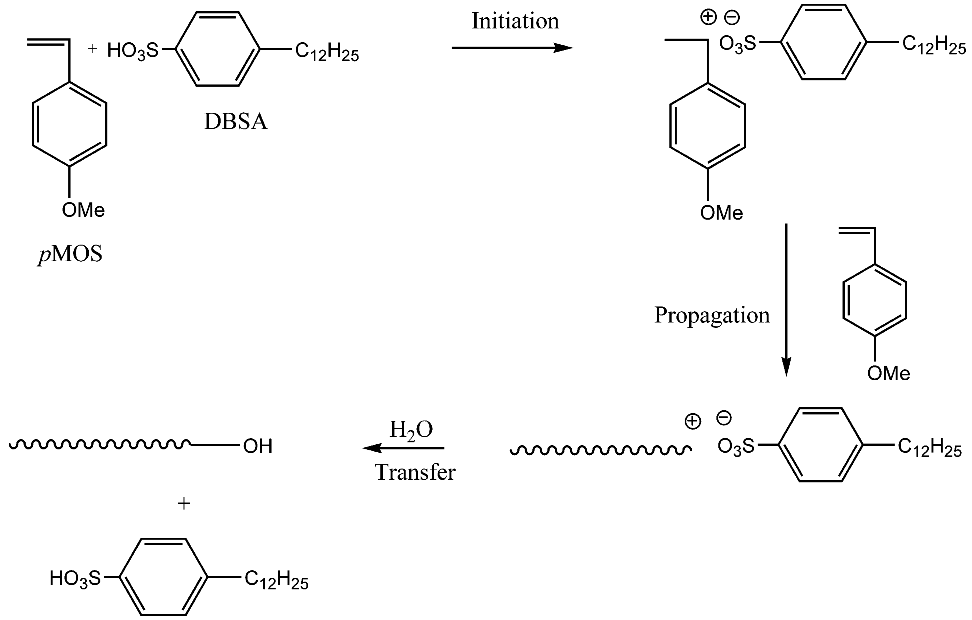
Scheme 3



merization[11] initiated by DBSA takes place at the surface of the monomer droplets according to Scheme 3. Transfer reactions with water decrease with conversion, decreasing the polarity of the interface, but molar masses of a plateau MW value (around 1000 g mol^{-1}) were finally formed. The result was a latex containing poly(*p*MOS) chains of narrowly distributed low molar masses. To produce longer polymer chains, the authors concluded on the importance to find conditions where polymerization locus could be displaced from the interface to the inside of the monomer droplets.

These results together with the discovery of LASC compounds prompted us to assess tris(dodecyl sulfate)-ytterbium (Yb(DS)$_3$) LASC as "activator-surf" in cationic polymerization in miniemulsion. Avoiding a diffusion step of Lewis acid molecules from the water phase to the monomer droplets, the use of LASC could favor the polymerization locus displacement recommended by Cauvin et al.[17,18] Polymerizations of *p*MOS were first investigated in organic solvent in the presence of Yb(DS)$_3$ and then transposed to a miniemulsion process. To our knowledge, this study is the first example on the use of such LASC in polymerization media whatsoever.

Experimental Section

In the following, LASC stands for Yb(DS)$_3$, 0.25H$_2$O.

Materials and Methods. Ytterbium nitrate (Yb(NO$_3$)$_3$) (2.62 M solution in water), ytterbium chloride (YbCl$_3$, 6H$_2$O), and ytterbium triflate (Yb(OTf)$_3$, 7.5H$_2$O) were provided by Rhodia and used as received. *p*-Methoxystyrene (*p*MOS) (Lancaster, 98%) was distilled from calcium hydride for polymerization in organic media and used as received for miniemulsion polymerization. 1-(4-Methoxyphenyl)ethanol (*p*MOS−H$_2$O) (Lancaster, 95%) was used as received. Dodecyl sulfate sodium salt (SDS) (Acros, 99%) and polyoxyethylene(40) octylphenyl ether (Triton-X 405) (Acros, 70% in water) were used as received. Thionyl chloride (SOCl$_2$) (Aldrich) was used as a 2 M solution in dichloromethane. Dichloromethane (LauryLab, 99.8%) was dried over calcium hydride and freshly distilled before used. Carbon tetrachloride (Aldrich, 99.9%) was distilled over phosphorus pentoxide (P$_2$O$_5$).

^{1}H NMR measurements were carried out on a Bruker DRX 400 spectrometer in CDCl$_3$, DMSO-d_6 or acetone-d_6 at room temperature. The chemical shift scale was calibrated relative to the TMS peak used as reference.

Particle size measurements were performed on a multiangle DLS Zetasizer 4800 from Malvern Instruments. Particle sizes are expressed as *z*-average diameters (d_z).

Size exclusion chromatography (SEC) measurements were carried out on a device composed of a 600 HPLC pump (Waters) and an autosampler 717Plus (Waters). Three columns (Waters Styragel HR4E, HR5E, and Eurogel HE145) thermostated at 40 °C were used with THF as eluent at a flow rate of 1 mL min^{-1}. Molar masses were calculated on the basis of polystyrene standards.

MALDI−TOF MS spectra were recorded on Applied Biosystems Voyager DE-STR equipment. All experiments were done using an accelerating potential of 20 kV and a 337 nm nitrogen laser. The samples were prepared by mixing a solution of polymer in THF (10 mg mL^{-1}), a solution of DHB matrix in THF (20 mg mL^{-1}), with a volumetric ratio in the ratio 1/10 ($V_{\text{sample}}/V_{\text{matrix}}$), and a solution of NaI (cationization agent Na$^+$) in acetone (10 mg mL^{-1}). 1 μL of the resulting mixture was placed onto the sample plate, and the solvent was evaporated at room temperature. Spectra were recorded in the reflectron mode. This last mode, modifying the ion trajectory through an ion mirror, provides a better resolution and more accurate structural information.

Syntheses of Yb(DS)$_3$. Whatever the ytterbium salt used the synthesis procedure is the following. Ytterbium salt (1 equiv) is dissolved in Milli-Q water and added to a SDS (3 equiv) solution in 100 mL of Milli-Q water. A white precipitate immediately appears, and the reaction medium is stirred for 30 min. The precipitate is then filtered, washed with water (three times with 50 mL), and dried in vacuo (30 mbar). The water content estimated by ^{1}H NMR analysis performed in dried DMSO-d_6 is then 7 molecules of water. A thorough drying (in vacuo (10^{-2} mbar)) for 10 h allows to reduce this water content to 0.25.

Characterizations of the obtained Yb(DS)$_3$, 0.25H$_2$O in the case of each ytterbium salt are given below.

Starting from YbCl$_3$. ^{1}H NMR (DMSO-d_6) δ: 0.87 (t, 9H, J = 6.6 Hz), 1.26 (m, 54H), 1.55 (m, 6H), 3.87 (t, 6H, J = 6.6 Hz). ^{13}C NMR (DMSO-d_6) δ: 14.04, 22.19, 25.64, 28.80, 28.89, 29.13, 29.21, 31.38, 65.71. Elemental analysis[19] Yb(OSO$_3$-C$_{12}$H$_{25}$)$_3$, 7H$_2$O: Calculated: C = 39.48%, H = 8.19%, S = 8.78%, Yb = 15.80%. Experimental: C = 39.50%, H = 8.00%, S = 8.60%, Yb = 15.4%.

Starting from Yb(OSO$_2$CF$_3$)$_3$. ^{1}H NMR (DMSO-d_6) δ: 0.86 (t, 9H, J = 6.6 Hz), 1.25 (m, 54H), 1.51 (m, 6H), 3.75 (t, 6H, J = 6.6 Hz). ^{13}C NMR (DMSO-d_6) δ: 14.43, 22.56, 26.04, 29.18, 29.27, 29.50, 29.61, 31.77, 66.02. IR (KBr): 1195, 1210, 1261

cm^{-1} . Elemental analysis[19] $Yb(OSO_3C_{12}H_{25})_3$, $7H_2O$: Calculated: C = 39.48%, H = 8.19%, S = 8.78%, Yb = 15.80%. Experimental: C = 39.60%, H = 8.40%, S = 8.10%, Yb = 14.2%.

Starting from $Yb(NO_3)_3$. ^1H NMR (DMSO-d_6) δ: 0.86 (t, 9H, J = 6.6 Hz), 1.25 (m, 54H), 1.51 (m, 6H), 3.75 (t, 6H, J = 6.6 Hz). ^{13}C NMR (DMSO-d_6) δ: 14.43, 22.56, 26.04, 29.18, 29.27, 29.50, 29.61, 31.77, 66.02. IR (KBr): 1190, 1240 cm^{-1}. Elemental analysis[19] $Yb(OSO_3C_{12}H_{25})_3$, $7H_2O$: Calculated: C = 39.48%, H = 8.19%, S = 8.78%, Yb = 15.80%. Experimental: C = 39.8%, H = 9.00%, S = 8.78%, Yb = 15.80%.

Synthesis of *p*MOS−HCl. 2.58 mL (35.45 mmol) of $SOCl_2$ is carefully added to a solution of 1-(4-methoxyphenyl)ethanol (*p*MOS−H_2O) (33.45 mmol) in CCl_4 (20 mL). All residual acid vapors were eliminated by argon bubbling. The CCl_4 solution is washed with water several times, and the resulting organic phase is dried with $MgSO_4$ and the solvent evaporated in vacuo. ^1H NMR (acetone-d_6) δ: 1.82 (d, 3H, J = 6.8 Hz), 3.81 (s, 3H), 5.24 (q, 1H, 7 Hz), 6.93 (d, 2H, J = 9 Hz); 7.41 (d, 2H, J = 9 Hz). ^{13}C NMR (acetone-d_6) δ: 25.90, 54.70, 58.84, 113.79, 127.86, 135.12, 159.66.

Polymerization in Organic Solution. Solution polymerizations were performed at 25 °C in dried and freshly distilled dichloromethane. A typical polymerization recipe is as follows. In a 50 mL flask, LASC (0.03 g, 3.1×10^{-5} mol suspended in 10 mL of dichloromethane) was added, followed by 10 mL of CH_2Cl_2. The monomer *p*MOS (2 mL, 6.71×10^{-3} mol) was then added to the suspension under stirring. The polymerization was started by adding the initiator (*p*MOS−HCl, 30 μL, 1.77×10^{-4} mol). For experiments performed in the presence of additional water, 1 μL (5.5×10^{-5} mol) was added with a microsyringe before the initiator. Polymerizations were stopped with addition of methanol. Samples were regularly withdrawn from the polymerization mixture for conversion determination. The conversion was obtained by ^1H NMR analysis of one drop of the sample dissolved in acetone-d_6. The obtained spectra showed the decrease of two vinyl monomer peaks at 5.64 and 5.72 ppm (integral I_1) compared to the third vinyl monomer peak and the aromatic broad peak from the monomer and the polymer around 7 ppm (integral I_2). Monomer conversion, C, was then calculated as follows:

$$I_1 = 2M; \quad I_2 = 4P + 5M; \quad C = 100P/(M + P) = 100(I_2 - 2.5I_1)/(I_2 - 0.5I_1)$$

where M and P are the integral values of one proton of the monomer and the polymer, respectively. The precipitated polymer was filtered and washed several times and dried in vacuo up to constant weight.

Miniemulsion Polymerization. Typically, two solutions, the organic one composed of 1.816 g of *p*MOS (13.5×10^{-3} mol, 20 wt %) mixed with hexadecane (0.09 g, 1.04×10^{-3} mol, 5 wt %/*p*MOS) and the aqueous one containing the surfactant solution (0.135 g of LASC, 1.35×10^{-4} mol, 0.052 g of SDS, 1.8×10^{-4} mol, in 7.2 g of water, 0.4 mol), were separately stirred for 30 min before being mixed together. The resulting mixture was stirred for an additional 30 min, placed in an ice bath, and ultrasound sonicated using a 600 Ultrasonic Processor sonifier (ampl 90%) for 2 min. An ^1H NMR analysis of the resulting miniemulsion confirmed the absence of polymerization or any degradation of the reagents during the sonication process. The obtained miniemulsion was then degassed under argon for 30 min. The polymerization was started by adding the initiator (*p*MOS−HCl, 11 μL, 6.5×10^{-5} mol). The polymerization proceeds under thermal regulation and magnetic stirring. Samples were regularly withdrawn from the polymerization mixture. Few drops were immediately used for conversion and size determination. For the rest of the sample the polymer was precipitated with methanol, washed, dried, and recovered for SEC analyses. The conversion was obtained by ^1H NMR analysis as in the case of organic solution polymerization. Methanol was added to the remaining sample to precipitate the polymer. The polymer was then separated and analyzed by SEC.

Table 1. LASC-Mediated Polymerization of *p*MOS in Dichloromethane at 40 °C for 40 h; [*p*MOS] = 1.25 mol L^{-1}

entry	*p*MOS−HCl/LASC/H_2O molar ratio	conv (%)[a]	M_n (g mol^{-1})[a]/ final conv (%)	I_p[b]
1	5.7/0/0	16	12200/33	1.9
2	5.7/0.6/0	30	8800/36	1.9
3	5.7/1/0	70	8200/74	1.9
4	5.7/1/1.8	9	15400/27	1.9
5	5.7/0/1.8	70	9900/100	2.2
6	0/1/0	0		

[a] After 40 h. [b] Obtained by SEC using polystyrene standards.

Results and Discussion

Syntheses of $Yb(DS)_3$. The hydrated form of LASC is easily obtained by reaction of the ytterbium chloride ($YbCl_3$), triflate ($Yb(OSO_2CF_3)_3$), or nitrate ($Yb(NO_3)_3$) with sodium dodecyl sulfate (SDS) in water. The various reagents perfectly soluble in water separately give upon mixture a fine white precipitate. The formed LASC is isolated by filtration and dried under vacuum. The analysis data are in perfect agreement with the expected ones and confirmed the LASC structure given in Scheme 1. In all cases, water molecules are complexed onto the metal (0.25 water molecule by metal). Syntheses were also successfully carried out with $Yb(OSO_2CF_3)_3$ and $Yb(NO_3)_3$, contrary to Kobayashi et al.'s claims in the case of scandium triflates.[4]

Polymerization of *p*MOS in Organic Solution in the Presence of LASC. Prior to any polymerization in water and in order to evaluate the potential of LASC for cationic polymerization of *p*MOS, solution polymerization experiments were first carried out in dichloromethane at 25 °C. The chlorinated adduct of the corresponding monomer (*p*MOS−HCl) was used in combination with LASC as the initiating system according to Scheme 2. Recipes were chosen so as to stress the influence of the *complexed* or *free* water on the polymerization process (chain-transfer reactions,[20] parasite initiation[21]) (Table 1). Several experiments were conducted with an additional amount of water. Blank experiments were carried out with LASC and *p*MOS−HCl adduct as lone initiator. As expected, no polymerization occurs with LASC alone (entry 6) whereas smooth polymerization occurs without LASC with 16% conversion reached in 40 h (entry 1). The origin of the initiation in the case of the experiment conducted with *p*MOS−HCl alone may originate from hydrolysis of *p*MOS−HCl by unavoidable water traces. When a combination of *p*MOS−HCl adduct and LASC is used, conversion is increased up to 70% (entries 2 and 3). This effect may arise from LASC (according to Scheme 2) or from the water introduced with LASC which could increase the hydrolysis of *p*MOS−HCl. However, an additional amount of *free* water used with *p*MOS−HCl increases the polymerization conversion (entry 5) whereas used in conjunction of *p*MOS−HCl and LASC (entry 4) drops the conversion from 70% to 9%. According to this last result, the added water seems to act as a poison of LASC by complexation. Besides, the kinetics profile obtained in this case is very similar to the one obtained when *p*MOS−HCl is used alone, a result which is in agreement with a complexation of the *free* water onto the LASC. LASC being deactivated by this complexation, polymerization occurs as if *p*MOS−HCl was used alone. As a conclusion, LASC has the ability to catalyze the initiation of the cationic polymerization of *p*MOS in organic media.

Table 2. Miniemulsion Polymerizations of *p*MOS at 40 °C for 40 h, [SDS] = 0.02 mol L^{-1}, [*p*MOS] = 1.5 mol L^{-1}, [*p*MOS−HCl] = 0.007 mol L^{-1}; Polymerization Data

entry	surfactant	inititator/activator	LASC (mM)	conv (%)	M_n (g mol^{-1})^a	I_p^{a}	particle diameter (nm)	PDI
6	SDS	*p*MOS−HCl/−		70	1400	1.2	150	1.002
7	SDS	*p*MOS−HCl/LASC	1.5	70	1200	1.2	122	1.002
8	SDS	*p*MOS−HCl/LASC	7.5	70	1100	1.2	125	1.002
9	SDS	*p*MOS−HCl/LASC	15	70	1100	1.3	96	1.023
10	SDS	HCl/−	0	100	1700	1.3	135	1.005
11	SDS	HCl/LASC	1.5	80	1400	1.2	135	1.002
12	SDS	HCl/LASC	15	90	1100	1.3	90	1.024
13	SDS (buffered)	*p*MOS−HCl/−		*b*				
14	Triton X (0.1 mol L^{-1})	HCl/−		*b*				

^{a} Obtained by SEC using polystyrene standards. ^{b} No polymerization.

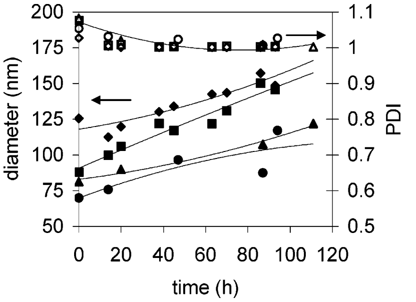


Figure 1. Particle diameter (plain symbols) and corresponding polydispersity indexes (PDI, empty symbols) data for the miniemulsion polymerization of *p*MOS (1.5 mol L^{-1}) with *p*MOS−HCl (7 × 10^{-3} mol L^{-1}) at 40 °C with [SDS] = 20 × 10^{-3} mol L^{-1} and LASC at (◆) 0, (■) 1.5 × 10^{-3}, (▲) 7.5 × 10^{-3}, and (●) 15 × 10^{-3} mol L^{-1}.

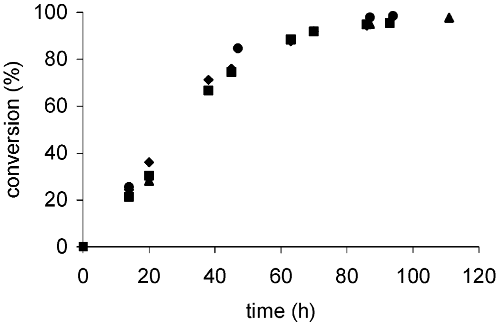


Figure 2. Time−conversion data for the miniemulsion polymerization of *p*MOS (1.5 mol L^{-1}) with *p*MOS−HCl (7 × 10^{-3} mol L^{-1}) at 40 °C with [SDS] = 20 × 10^{-3} mol L^{-1} and LASC at (◆) 0, (■) 1.5 × 10^{-3}, (▲) 7.5 × 10^{-3}, and (●) 15 × 10^{-3} mol L^{-1}.

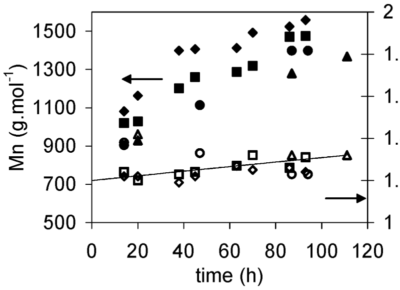


Figure 3. Molar masses (plain symbols) and corresponding polymolecularity indexes (I_p, empty symbols) data for the miniemulsion polymerization of *p*MOS (1.5 mol L^{-1}) with *p*MOS−HCl (7 × 10^{-3} mol L^{-1}) at 40 °C with [SDS] = 20 × 10^{-3} mol L^{-1} and LASC at (◆) 0, (■) 1.5 × 10^{-3}, (▲) 7.5 × 10^{-3}, and (●) 15 × 10^{-3} mol L^{-1}.

Preliminary Comments to the Miniemulsion Polymerizations. The initiating activity of LASC in polymerization of *p*MOS being demonstrated, and prior to any miniemulsion polymerizations, it was particularly interesting to get an insight into the behavior of this LASC as a surfactant in water. The idea behind that is that if the LASC exhibits some surfactant properties, in addition to its initiating activity, it should drive the polymerization inside the monomer droplets where the polymerization should ideally proceed. LASC is insoluble in water (as mentioned in the Experimental Section) and most surprisingly also in the monomer *p*MOS. This issue was solved by using surfactant aqueous solutions, typically SDS solutions, where LASC was found indeed dispersible, at a LASC/SDS ratio of 0.7 (see Supporting Information). LASC dispersibility increases with the SDS concentration. A rapid light scattering study of the obtained solutions after mixing showed that the addition of a small quantity of LASC to an aqueous solution of SDS (0.7cmc$_{SDS}$, where cmc$_{SDS}$ = 2.3 g L^{-1} or 8.2 mmol L^{-1} and stands for critical micellar concentration of SDS) gives rise to the formation of two object populations of 20 and 80 nm size. The further addition of LASC leads to a complete disappearance of the small size population. The same behavior is observed for SDS concentrations of 1.5cmc$_{SDS}$ and 2.9cmc$_{SDS}$. LASC, though insoluble in water, is an amphiphile and exhibits a structure similar to SDS. It thus may form combined micelles in the presence of SDS molecules (20 nm size). Larger structures could result from aggregates formation (80 nm size) by ligand exchange between formed micelles as represented in the Supporting Information (Scheme 4).

Considering a SDS stabilized miniemulsion of *p*MOS incorporating LASC, two possibilities could be put forward: (i) LASC is effectively directed in such a way that the metal is mainly “facing” the water phase. In that case, any improvement regarding the generation of large molar mass polymers according to Cauvin et al. results is hardly possible. (ii) The metal is buried inside the droplets, and the polymerization may be favored in the organic phase, giving rise to higher molar mass polymers. The rest of this study is devoted to give a try deciding between these two assumptions.

Miniemulsion Polymerizations. All the experiments were carried out on a 9 mL total volume with a targeted solid content of 20% (i.e., [*p*MOS] = 1.5 mol L^{-1}). Cauvin et al.[17] did not use any hydrophobic molecule to cancel particle ripening by increasing the inner particle osmotic pressure of small droplets. The authors explained this stability by the formation of small oligomers through rapid initiation by DBSA, as soon as the system is ultrasonicated, thus acting as hydrophobes and suppressing Ostwald ripening. In an other study, adding hexadecane enabled the same authors[18] to significantly decrease the particle diameter and thus favor a faster polymerization rate. In our case,

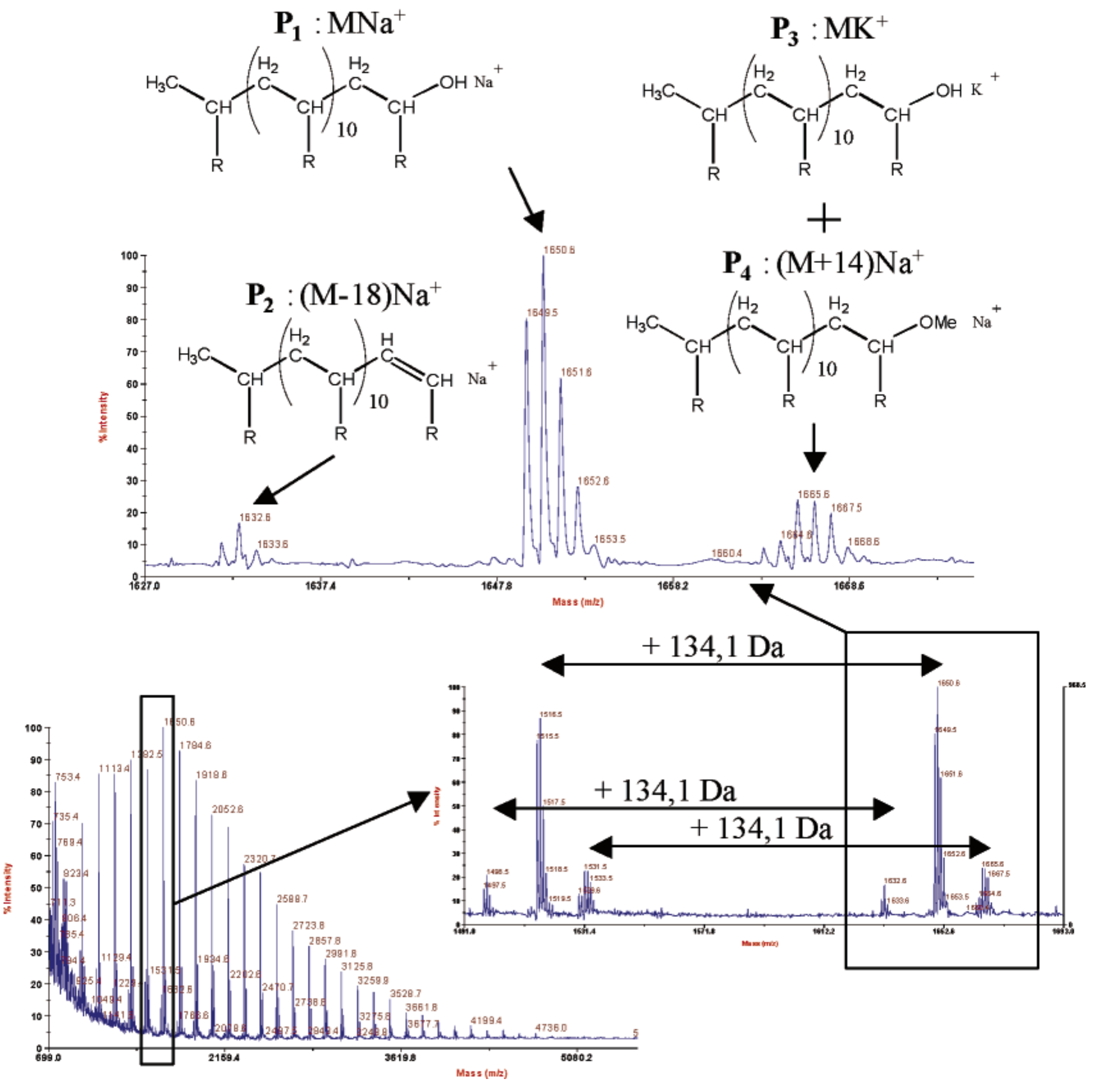


Figure 4. MALDI−TOF MS of poly(*p*MOS) obtained after deactivation with methanol of a LASC/0.5*p*MOS−HCl-mediated miniemulson polymerization.

the initiatior *p*MOS−HCl is post-added. ^{1}H NMR and SEC analyses of the obtained miniemulsions immediately after ultrasonication showed that no oligomer was formed. The use of an hydrophobic molecule (hexadecane) was thus required to cancel particle ripening and ensure droplet stability after ultrasonication. A stable miniemulsion of 130 nm diameter particles was obtained using a concentration of SDS of 0.02 mol L^{-1} and 5 wt % compared to monomer of hexadecane. However, a decrease of the droplet size was observed upon the addition of an increasing amount of LASC in the recipe (Figure 1). This result suggests a strong contribution of the LASC to the stabilization of the droplets through surfactant interactions and is a first clue that LASC may be located at the interface monomer droplet/water interface. Experimental conditions of the polymerizations presented in this part together with conversion, molar mass, and particle size data are summarized in Table 2.

LASC/*p*MOS−HCl Initiating System. Experiments carried out without and with increasing amounts of LASC (entries 6−9, Table 2) were first performed, and the corresponding conversion, particle size, and molar mass vs time curves are presented in Figures 2, 1, and 3, respectively. For all the experiments, kinetics are similar, and a quantitative conversion is observed after 100 h. As shown in Figure 1, final particle sizes ranged from 90 to 150 nm. Narrowly distributed molar masses leveled off at 1200 g mol^{-1}. Final latexes are stable over periods of time longer than months. According to these first results, cationic polymerization in miniemulsion of *p*MOS occurs. (It could not be a radical process considering the polymerization time and the polymerization temperature.) Surprisingly, although polymerization does proceed smoothly in all the cases, no major kinetic difference is noticeable, and LASC seems to have no influence on the polymerization rate. Our first thought was to incriminate a cationic process initiated by protons coming from HCl which could be generated by hydrolysis of *p*MOS−HCl. According to entry 10 (Table 2), polymerization takes place when HCl is used alone as the initiating system, and again molar masses are in the same range as the already obtained molar masses. When LASC is added (entry 11), no effect is observed although the particle size tends to slightly decrease probably due to the fact that LASC helps to the stabilization of the particles as a surfactant, as already mentioned above. In an attempt to favor a hypothetical polymerization process involving LASC against the observed one, several comparative experiments have also been performed at different temperatures (10, 25, and 40 °C), but kinetic profiles and the

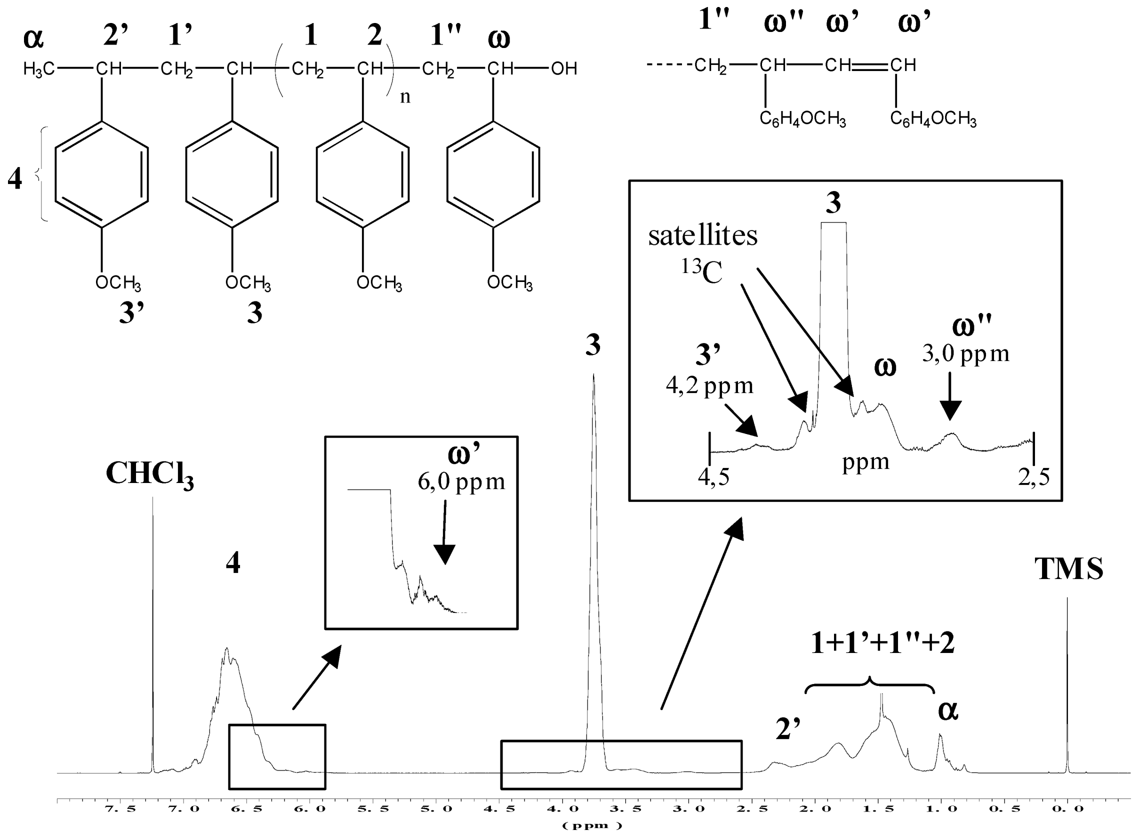


Figure 5. ^1H NMR spectrum (400 MHz, $CDCl_3$, room temperature, 1000 scans) of poly(*p*MOS) obtained after deactivation with methanol of a LASC/0.5*p*MOS−HCl-mediated miniemulson polymerization.

molar mass characteristics of the obtained polymers definitively remain identical with or without LASC. At this stage, unfortunately, LASC seems clearly to be not active in the required way for our system. Located at the interface, the Lewis acid properties of the LASC may be deactivated by the presence of polar species (H_2O, SDS) as already shown in the solution polymerization part. As a result, LASC only acts as a surfactant together with SDS.

Origin of the Initiating System. Since HCl as lone initiator gives rise to polymerization and since LASC initiation upon *p*MOS−HCl activation seemed too low, the stability of *p*MOS−HCl adduct in the presence of water can be discussed again. The stability of the *p*MOS−HCl adduct in the presence of a small amount of water has been evaluated to be high.[12] As a hydrophobic molecule, *p*MOS−HCl is therefore likely to be only weakly hydrolyzed to give hydrochloric acid and the corresponding alcohol. Then, its hydrolysis, if any, should generate HCl in the organic phase, and polymerization of *p*MOS should take place in the organic phase. However, a rapid decrease of the pH of the miniemulsion immediately after the introduction of *p*MOS−HCl is observed, in agreement with a strong hydrolysis and release of protons in the water phase. The obtained molar masses remained low and narrowly distributed (entry 6, Table 2).

True Polymerization Process. Interfacial Polymerization. Now considering that the polymerization media is acidic, one should take care of the chemical form of the surfactant used. In fact, SDS could then turn into its sulfuric acid form and initiate the polymerization at the interface as depicted by Cauvin et al. in the case of dodecylbenzenesulfonic acid-mediated miniemulsion polymerization of *p*MOS. The question now to be answered is whether the sulfuric acid molecules, derived from SDS, or the free protons coming from HCl are effectively initiating the polymerization at the interface droplet/water. To get a better understanding on the polymerization process and to elucidate whether the polymerization effectively takes place at the interface or elsewhere, we performed several experiments by substituting *p*MOS−HCl adduct by HCl (entries 10−12, Table 2). According to the last results, we may assume that protons alone, either generated by the hydrolysis of *p*MOS−HCl or coming from HCl, when used as initiator, are responsible for the initiation of the polymerization. This assumption is confirmed by experiment 13, where the miniemulsion is buffered to pH 6 with $NaHCO_3$. In that case no polymerization occurred even after 100 h. In the same vein, the use of Triton X in experiment 14 instead of SDS in a miniemulsion polymerization with HCl failed. These last results suggest that not only a low pH is required (source of protons) but also SDS must be used as surfactant. In that conditions, miniemulsion polymerization of *p*MOS occurs according to a cationic process and obtained polymers exhibited molar masses narrowly distributed. Under the conditions of a successful polymerization (acidic medium), dodecylsulfuric acid (acid form of SDS) is favored and could act as an inisurf meeting the work of Cauvin et al.[17] concerning the dodecylbenzenesulfonic acid (DBSA) inisurf in the polymerization *p*MOS in minemulsion via a cationic process. The low molar masses and the corresponding narrowly distributions obtained finally found an explanation here in an interfacial polymerization.[11,17,22−24]

Characterization of the Obtained Polymer Chains. MALDI−TOF mass spectrometry (MALDI−TOF MS) and ^1H NMR analyses of the obtained polymers have been performed in order to identify the chain ends and get further information on their formation mechanism.

MALDI−TOF MS. An example of a spectrum is presented in Figure 4. Four populations are visible, namely P_{1-4}. The molar mass (MM) difference between two peaks is in agreement the molar mass of the monomer unit (134.1 g mol^{-1}). The main population (P_1) corresponds to polymer chains cationized by a sodium and bearing an hydroxyl ω-end group (MM = 1649.5 g mol^{-1}). The hydroxyl function is generated after a transfer reaction with water (Scheme 5, Supporting Information). The same population cationized by potassium (P_3) is also present (MM = 1665.5 g mol^{-1}). Another population (P_4) overlaps P_3 and corresponds to polymer chains bearing a methoxy ω-end group (MM = 1663.5 g mol^{-1}), generated after the deactivation of the polymerization media with methanol. Eventually, the last population P_2 (MM = 1631.5 g mol^{-1}) is assigned to polymer chains cationized by sodium and bearing a double bond as a terminal group. The last chain population could be generated after β-H-elimination during the cationic process (possible side reaction well-known in cationic polymerization) or by dehydration of hydroxyl-terminated chains.

^{1}H NMR. The sample analyzed by MALDI−TOF MS was also analyzed by ^{1}H NMR, and the spectrum together with a full assignment of the different peaks[25] is given in Figure 5. The presence of the different populations observed in the MALDI−TOF MS analyses is confirmed.

As a conclusion, both MALDI−TOF and ^{1}H NMR analyses evidenced the formation of chains in agreement with a cationic process.

Conclusions

The main aim of this work was to tentatively use a Lewis acid surfactant combined catalyst in a cationic miniemulsion polymerization of *p*-methoxystyrene (*p*MOS) in order to favor a polymerization locus inside the monomer droplets rather than at the interface monomer droplets/water. The first step of the work assessed the efficiency of trisdodecyl sulfate ytterbium ($Yb(DS)_3$, $0.25H_2O$) as activator in the organic polymerization of *p*MOS initiated by the corresponding chlorinated adduct *p*MOS−HCl. This property was demonstrated, and to our knowledge, the activity of LASC compounds was shown in cationic polymerization for the first time. The miniemulsion polymerization of *p*MOS performed using the same initiating system was apparently successful but unfortunately not due to LASC. Neither the LASC amounts in the recipe nor the temperature could be adjusted to evidence the predicted LASC-mediated cationic polymerization process. Located at the interface, the Lewis acid properties of the LASC may be deactivated by the presence of polar species (H_2O, SDS). As a result, LASC only acts as a surfactant together with SDS. However, polymerization still occurred due to the hydrolysis of the *p*MOS−HCl initiator. The resulting acidification of the water phase leads to the transformation of SDS surfactant into its sulfuric acid form which could act as an inisurf according to an interfacial cationic polymerization process giving rise to latex particles of *p*MOS, incorporating narrowly distributed low molar mass chains. To overcome the problem of the localization of the LASC at the interface and to favor its displacement into the monomer droplets, our efforts are now directed to the synthesis, and their further use in a miniemulsion process, of new LASC inisurfs, based on a tris(amphiphilic block copolymer) ytterbium in which the hydrophobic part of the block copolymer will be bound to the metal.

This work has emphasized on the importance of the true initiators involved and wishes to show that a particular attention should be paid in the case of systems involving LASC or its derivatives and water.

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Supporting Information Available: Aggregates formation by ligand exchange between formed micelles (Scheme 4), hydroxyl function generated after a transfer reaction with water (Scheme 5), solubility of LASC in SDS solutions (Table 3), and variation of droplet size upon amount of LASC in the miniemulsion (Table 4). This material is available free of charge via the Internet at http://pubs.acs.org.

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