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Cationic Polymerization of *p*-Methoxystyrene in Water with Dodecylbenzenesulfonic Acid and Ytterbium Triflate: Evidence for an Inverse Emulsion Process

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ABSTRACT: The cationic polymerization of *p*-methoxystyrene in water using dodecylbenzenesulfonic acid as a surfactant and ytterbium triflate as a catalyst was studied in terms of kinetics and physicochemistry. Preliminary stability studies showed that stable inverse (water in monomer) emulsions were obtained using excess catalyst and cocatalyst. Rates of polymerization and molar masses were respectively found slower and larger than for direct emulsion processes, in accordance with previous results published by Sawamoto on similar systems. The presence of the catalyst did not affect the mechanism scheme of ionic polymerization in aqueous dispersion; i.e., the polymerization is interfacial, and physicochemical issues govern molar masses.

Introduction

The ionic polymerization in emulsion (IPE) is now a well-recognized process that is taking off in terms of released publications for about a decade. The most applied system deals specifically with cyclosiloxanes, whose patent and article survey grows exponentially since it has been discovered in the late 1950s.[1] Other monomers are known to be quite reactive in anionic polymerization, such as alkyl cyanoacrylates,[2] methylidene malonates,[3] or episulfides.[4] Recent studies also described the polymerization of less reactive monomers, such as glycidyl ethers,[5] *N*-carboxy-α-amino acids,[6] or *p*-alkoxystyrenes[7] (including *p*-methoxystyrene or *p*MOS).

Most of the processes described so far entailed a simple ionic polymerization process, i.e., the use of a sole molecule playing the role of both surfactant and initiator (INISURF). The (slow) initiation step is ensured by a proton (a hydroxide group) attached to the anionic surfactant, typically sulfate or sulfonate (a cationic surfactant, generally a quaternary ammonium salt). Once a chain is initiated, it grows rapidly at the interface before transfer/termination reactions with water occur. The rate of polymerization depends exclusively on the nature, e.g., bulkiness and hydrophobicity, of the surfactant head which plays the role of counterion during the propagation. For systems involving the first three monomers cited above, chains are terminated and reactivated to give “controlled” polymerization. However, only oligomers of definite chain lengths are systematically formed due to the decreasing surface activity of the hydroxylated-terminated dormant chains with increasing their molar masses; for a critical DP of about 10 monomer units, chains penetrate the particles and stop propagating.

An approach to facilitate polymerization against termination was proposed in early patents dealing with episulfide polymerization.[4a−c] The polymerization is catalyzed by $Cd(OH)_2$ or $Zn(OH)_2$, generated by cadmium or zinc oxide hydrolysis. Propagation is fast even in the presence of an excess of water, and molar masses of more than 10^4 g/mol were obtained. A coordination mechanism was proposed[4d] and confirmed by the head-to-tail microstructure of the polymer. Polymerization is believed to occur at the surface of the solid catalyst surrounded by the monomer (“pearl polymerization”).[4b] Since propagation occurs without involving ionic species and because water is so poorly soluble in the monomer, chains grow to a large extent before any transfer/termination reactions.[4e]

Sawamoto and co-workers described the polymerization of *p*-methoxystyrene initiated by the HCl adduct of the monomer (or directly HCl) and cocatalyzed by rare earth triflates, a water-resistant Lewis acid.[7a,b] The idea behind that is to control the polymerization by activating few chains in the row through their chloride moiety. Sawamoto’s team proposed a mechanism where both adduct and ytterbium triflate penetrate into the organic phase and associate to start a new chain. Polymerization is controlled at the beginning (up to 30% conversion) until transfer reactions with water stop the chains (final values of typically 3000 g/mol) and deviate the M_n/conversion curve from the theoretical slope. The fact that the molar mass distribution increases (final value of about 1.7) is explained from a slow initiation step. Sulfonic[7d] and phosphonic acids[7f] were also used as initiators, with apparently an increase of the rate of polymerization and also, in the latter case, of the average molar mass (typically of 10 000 g/mol).

Clearly, some questions remain on the role of ytterbium triflate in such process of polymerization in

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dispersion. Ytterbium triflate totally dissociates in water[7g] but does not turn into nonreactive hydroxides in a large range of pH ("water-resistant" Lewis acid).[8] Its Lewis acid activity is thus difficult to assess in aqueous medium. Furthermore, Storey et al.[7f] showed by varying the content of phosphonic acid initiators that there was no means of controlling the molar masses. Finally, there are no reports of colloidal parameters in these studies, such as particle size or surface tension measurements, although it seems clear that working in heterogeneous medium influences deeply the polymerization mechanism.[7e,h] For instance, we reported recently[7g] that at such high catalyst (a trivalent salt!) concentrations only electrosteric-type surfactants could generate stable latexes.

From the previous study dealing with *p*MOS cationic polymerization in the presence of excess ytterbium triflate in direct miniemulsions,[7g] a mechanism that differs sensibly from the one given by Sawamoto was proposed. Polymerization proceeds at the surface of the particles through initiation by triflic acid generated in situ and ytterbium triflate molecules that associate to the growing chain to generate a so-called Lewis-assisted Brönsted acid.[9] The generation of such a bulky counteranion, namely $YbOTf_4^-$, allows faster polymerization to proceed. Nevertheless, chain termination by transfer reactions from water is likely at the interface and limits the polymer chain length, independent of the content of acid introduced in the recipe. The fact that chains of growing sizes were generated at increasing conversion is understood from the decrease of surface polarity with conversion, thus allowing faster propagation among termination.

The aim of the present report is to understand the role of ytterbium triflate in the polymerization of *p*-methoxystyrene (*p*MOS) in emulsion, using a conventional ionic surfactant, namely dodecylbenzenesulfonic acid (DBSA). The discussion will be specifically oriented onto the nature of the colloidal objects generated here and its consequence on the mechanism of polymerization. This text will also provide evidence that controlling the polymerization may not be trivial using Lewis acids as those containing rare earth ions.

Experimental Part

Materials and Methods. All reagents were characterized at least by ^1H NMR before use. *p*-Methoxystyrene (*p*MOS) (Acros, purity 99%) and dodecyl benzenesulfonic acid or DBSA (98%, Janssen Chimica) were used as supplied. Ytterbium triflate or $Yb(OTf)_3$ (donated by Rhodia Terres Rares, La Rochelle, France) contains traces of ytterbium oxide, Yb_2O_3, which were discarded by filtration of an aqueous catalyst solution. pH's of ytterbium triflate solutions are unchanged compared to that of pure water, which is an indication that no triflic acid formed in the sample during storage. Ytterbium chloride hexahydrate or $YbCl_3{\cdot}6H_2O$ (Aldrich, 99,9%), Alum salt or aluminum potassium dodecahydrate (Aldrich, 98%), and sodium trifluoromethanesulfonate or sodium triflate (Aldrich, 98%) were used as received. Trifluoromethanesulfonic acid or triflic acid (Aldrich, 98%) was first dissolved in water before introduction in the emulsion.

All analytical methods, e.g. ^1H NMR, particle size measurements, and SEC, were described previously.[7e] TEM analysis was performed on a JEM100CXII UHR microscope from JEOL, with a 100 kV acceleration tension. One drop of the sample was diluted in toluene and was deposited on carbon-coated grid and allowed to evaporate before analysis. Negative electrospray analyses were performed on a Microssmass platform apparatus, with a capillary and cone tensions of 3 kV and −42 V, respectively, and a probe temperature set at 150 °C. Samples were dissolved in a 50% aqueous methanol solution containing 0.5 wt % of formic acid. ^{19}F NMR measurements were carried out on a Brüker DRX 300 spectrometer in DMSO-d_6 or at room temperature, without internal standard.

Polymerization Procedures. The surfactant was first solubilized in the water phase, and then ytterbium triflate was added. A brown precipitate spontaneously formed (LASC preparation,[10] see Results and Discussion). The monomer (and possibly the solvent, toluene) was (were) then mixed with the water phase and sonicated using a 450 Branson Ultrasonics Corp. sonifier at power 7 (25 W). Polymerization was carried out under thermal regulation (typically at 30 °C) and through mechanical stirring (350 rpm). At regular time intervals, 1 mL aliquots were withdrawn and neutralized with an excess of methanol solution in order to stop the reaction. An excess of water was also systematically added to decrease the solubility of monomer in the water/methanol phase. The organic phase was then separated from the aqueous one by centrifugation. CH_2Cl_2 was also systematically added to achieve a better phase separation and to ensure that no organic product remained in water.

Results and Discussion

Evidence for an Inverse Emulsion System. Despite the extensive use of ytterbium triflate as a catalyst, its behavior in various bulk or solution reactions has hardly been studied[9] and clearly never in water. Its role as a catalyst may not be that straightforward in water, since triflates dissociate from the rare earth atom to produce the 1:3 electrolytes.[7g,11]

The question that arises then is, how in such high ionic strength media (ytterbium is a trivalent salt) may an emulsion be produced? It was already noted in a former article that a small amount of ytterbium salt would crash a regular miniemulsion stabilized by DBSA.[7e] It turns out that, using large contents of salt, monomer, and DBSA and after sonication (run 1, Table 1), metastable *inverse* (i.e., water-in-oil) miniemulsions are produced (Figure 1a).

An easy way to demonstrate whether a direct or inverse emulsion is formed is to add a drop of it in water and see whether it spreads or not. Figure 1b clearly shows that the drop of dispersion felt down the assay tube. The conductance of the w/o emulsion (1 μS) compared to the actual salt aqueous solution (10.6 mS) also demonstrates that the continuous phase is the monomer and that salt is trapped into water droplets. A definitive proof is also given in Figure 1c, where TEM measurements were performed on the polymerized emulsion, diluted beforehand in toluene. One clearly sees the white water "pools" of typically 100−200 nm in size trapped into the monomer/polymer phase.

The DBSA may not be regarded as a powerful surfactant for preparing inverse emulsion, since its HLB (about 12) is too large compared to these required for inverse emulsion (between 3 and 6). However, the complexation of sulfonate groups with ytterbium generates a different type of surfactant, called by Kobayashi a Lewis acid surfactant complex or LASC (Chart 1),[10] which is not soluble in water or toluene. This surfactant satisfies the prerequisite to form the inverse emulsion observed here, aided with the saturation of the water phase with ytterbium and triflate ions.[12,13]

Colloidal "Stability" during a Typical Polymerization Experiment. The emulsion shown in Figure 1a has been obtained in optimized surfactant, monomer, and salt concentrations, a condition that was not met in many of the experiments performed here. In addition, polymerization severely modifies the physicochemistry

Table 1. Summary of the Different Inverse Emulsion Polymerization Experiments Carried out in This Study[a]

run	w_{H_2O} (g)	w_{pMOS} (g)	$w_{Yb(OTf)_3}$ (g)	w_{DBSA} (g)	M_n (g/mol)	M_w/M_n	R_p (% conv/day)	initial state of emulsion[c]
1	0.83	1.91	0.80	0.12	2270	1.69	30	C
2	1.60	3.80	1.60	0.13	2910	1.88	36	B
3	0.91	1.91	0.83	0.06	2490	1.79	12	C
4	1.61	1.02	1.61	0.12	1940	1.78	26	B
5	1.62	1.62	1.60	0.13	2020	1.77	25	B
6	1.97	1.67	0.81	0.13	1370	1.51	8	B
7	1.00	1.90	0.42	0.06	1540	1.53	6	B
8	1.63	1.03	0.81	0.13	1450	1.64	20	B
9[b]	1.66	1.05	0.81	0.13	1140	1.34	10	A
10[b]	1.74	1.07	1.61	0.12	1420	1.46	11	A
11[b]	1.65	1.04	0.80	0.12	1060	1.28	90	A

[a] All experiments were done at 30 °C, except for run 11 (60 °C); w_i = mass of solute i (water, monomer, catalyst, and surfactant) in the recipe; M_n and M_w/M_n = number-average molar mass and molar mass distribution; R_p = rate of polymerization obtained from initial kinetics data. [b] Toluene: 0.60 g. [c] Letters A, B, C correspond to photos given in Figure 2a. A = unstable inverse emulsion, water droplets sediment, and coalesce; B = unstable inverse emulsion, but sedimented water droplets do not coalesce; C = metastable inverse emulsion.

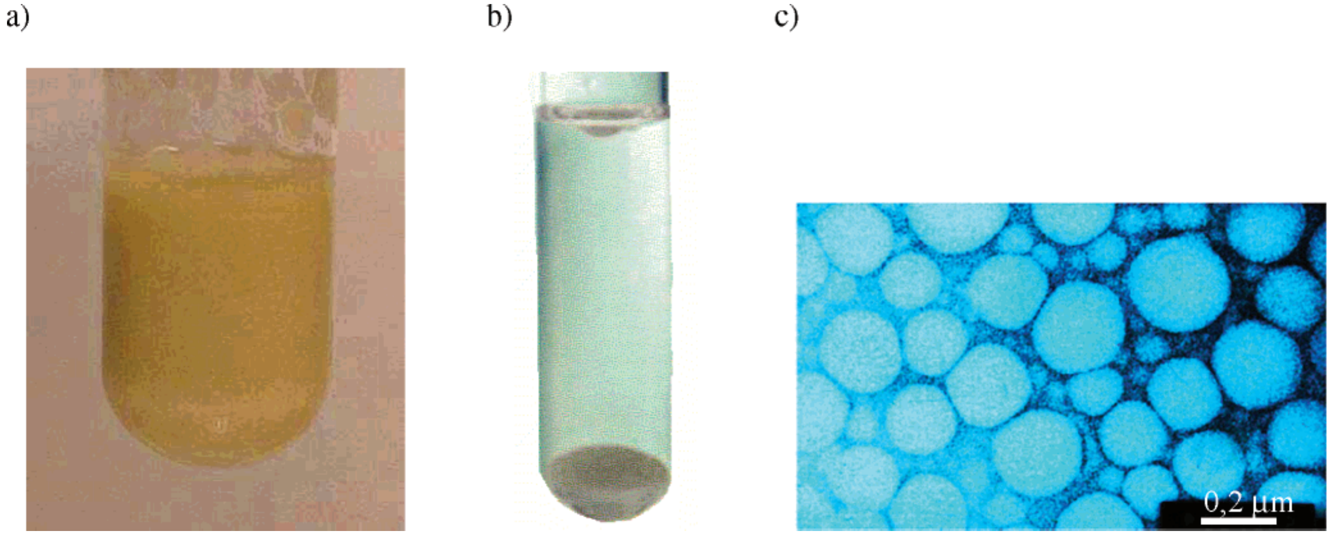
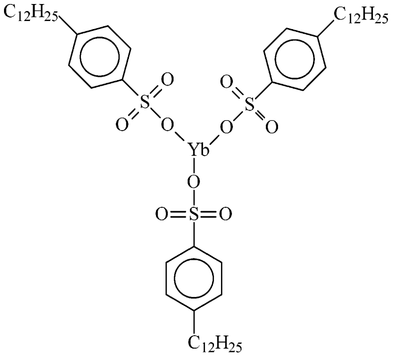


Figure 1. Evidence for the generation of a stable w/o miniemulsion (run 1, Table 1): (a) photograph of the stable emulsion; (b) drop test in water; (c) TEM micrograph on the sample polymerized and diluted in toluene prior to analysis.

Chart 1



of the system, as observed from the macroscopic aspect of the emulsion at various conversions (Figure 2a, run 2 in Table 1). The actual state of the emulsion is schematized in Figure 2b.

Basically, the water domains gradually decrease in size with conversion. At the beginning of the process, water droplets are too big to stay suspended in the organic medium and quickly sediment and coalesce when the agitation is stopped. The upper phase is mainly composed of monomer and surfactant, according to the brownish color typical of DBSA surfactant (state A). At 41% conversion, the inverse emulsion is already produced, but water droplets are still too large to remain suspended in the monomer/polymer medium. These however do not coalesce (state B). The inverse emulsion is perfectly stable at 70% conversion, presumably because the size of the droplets and the viscosity of the organic phase are optimal (state C). At the end of polymerization, water gets repelled from the thick and hydrophobic organic phase (state D).

Depending on the initial recipe, the emulsion may be stable in the first place (like in Figure 1, state C) or may go from these different stages. The state of emulsion influences significantly the rate of polymerization, as exemplified in Figure 3a for two polymerization sets performed at similar ratios of all components but different overall volumes (Table 1, runs 2 and 3). Polymerization is slow in both cases (200 h), but conversion/time curves vary from one set to another. On the other hand, the volume of the emulsion has no effect on the variation of molar masses with conversion (Figure 3b), which depends only on physicochemical parameters. Note that molar masses are typically tripled compared to conventional direct miniemulsions, with[7g] or without[7e,h] ytterbium triflate, just because less water is available at the interface for terminating the chains.

Kinetics and Molar Mass Variations for Various Parameters. Table 1 summarizes all the polymerization runs treated in this article, including the recipe, the initial rate of polymerization, the final molar mass and molar mass distribution, and the initial state of the emulsion (corresponding to stage A, B, or C in Figure

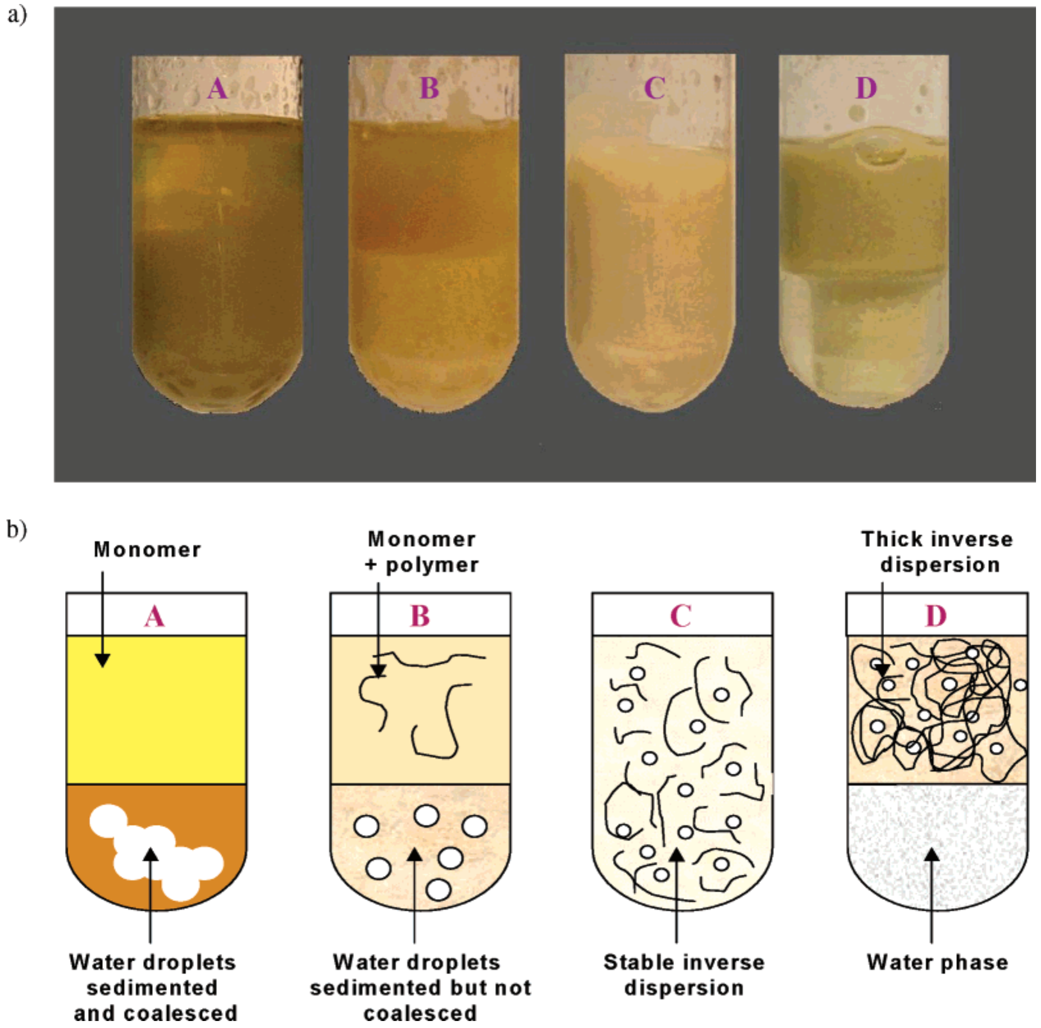


Figure 2. Macroscopic evolution of the inverse emulsion with conversion for a typical run (run 2, Table 1): (a) photographs at (A) 0%, (B) 41%, (C) 70%, and (D) 91% conversion; (b) schematized situation.

2). In all the experiments described here, inverse emulsions were generated due to the high content of salt introduced in the recipe as well as the rapid and systematic generation of LASC as a low-HLB surfactant.

The monomer-to-water ratio was first changed in recipes where high content of trivalent salt were used (Table 1 runs 2, 4, and 5). At equivalent DBSA concentration, there is no or little influence of the monomer content on the polymerization rate, so long as the state of emulsion was the same at the beginning (Figure 4). On the other hand, decreasing the water phase content allows longer chains to be produced, a result anticipated from decreased termination/transfer events by water.

It is also of interest to compare runs carried out at increasing content of salt (Table 1, runs 3−8). According to the kinetics given above for various solid contents (Figure 4a), the conversion/time curves are independent of the monomer ratio. On the other hand, increasing the catalyst amount in the recipe has a sharp impact on the polymerization rate (Figure 5). The S-shaped curve may correspond to a transition in the state of the emulsion, but that could not be clearly identified by the naked eye. The variations in molar masses with conversion both depend on the ytterbium triflate and monomer contents (Table 1, runs 3−8). The general trend is again that less water (or more saturated one) in the system leads to higher molar masses.

A key point to inspect the livingness or control on the polymerization is to change the content of initiator, i.e., protons, all things being equal in the recipe. As expected, the rate of polymerization increasing proportionally to the content of DBSA introduced (Table 1, runs 1 and 3), a result already observed in all IPE situations.[2−7] On the contrary, the molar masses neither vary with DBSA content nor follow the expected theoretical curve, a clear denial of molar mass control[7a−d] in such systems (Figure 6).

A last set of experiments have been carried out in the presence of toluene (Table 1, runs 9−11) to match experiments[7a−c] where fair amounts of bromobenzene, as internal standard for CPV, and CCl_4, to dissolve ytterbium triflate, were systematically used. The addition of toluene destabilized in some ways the emulsions, presumably because this solvent may solubilize the LASC surfactant and thus prevent to some degrees its stabilizing action. The rate of polymerization and maximal average molar masses are also smaller in the presence of added organic solvent than without it (see runs 8, 9 and 4, 10, respectively). In addition, kinetics is much faster at 60 °C than at 30 °C, so that polymerization proceeds in a day (Figure 7). Molar masses are however slightly less important in these conditions due to increasing water solubility at the interface.

Molar mass distributions, though difficult to interpret, may reveal typical features of polymerization process.

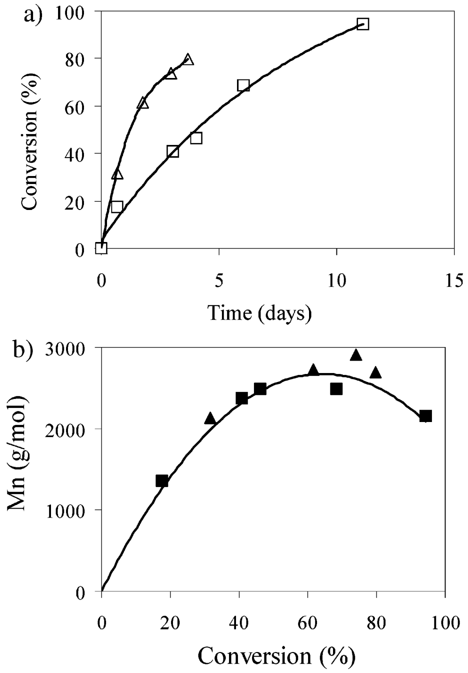


Figure 3. kinetics (a) and molar mass variation with conversion (b) for experiments with conventional recipes but different volumes of emulsion (Table 1, runs 2 (▲) and 3 (■)). Lines are only guides for the eyes.

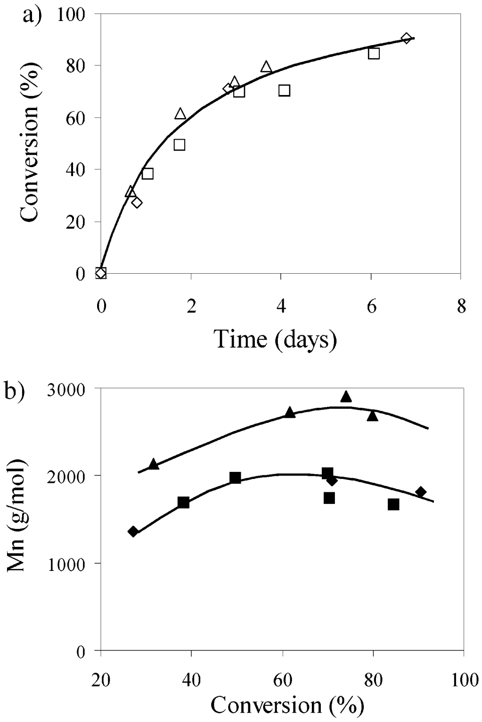


Figure 4. Kinetics (a) and molar mass variation with conversion (b) for experiments done at high ytterbium content and various monomer content (Table 1, runs 4 (◆), 5 (■), and 2 (▲)). Lines are only guides for the eyes.

These latter increase with the average molar masses (Figure 8, plotted from final values compiled in Tables 1 and 2) but are restricted to values of typically less than 1.8. Transfer reactions with water should theoretically lead to a molar mass distribution of 2, which was not observed here. The reason for that lies in the small length of the polymer chains. According to Figure 8, chains of about 5000 g/mol or more would exhibit the expected distribution.

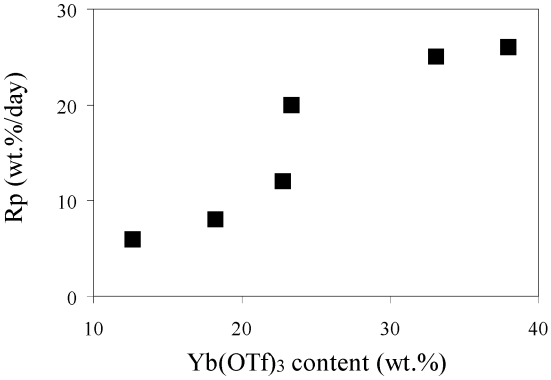


Figure 5. Influence of the content of ytterbium triflate in the recipe on the rate of polymerization.

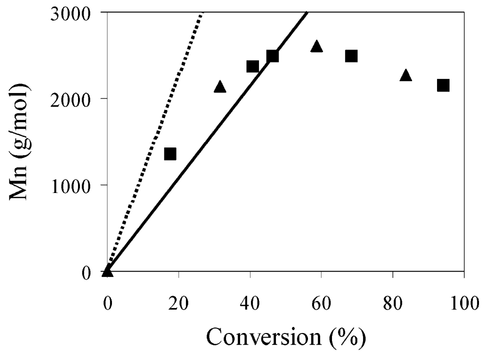


Figure 6. Influence of the content of DBSA in the recipe on the molar mass variation with conversion. Lines represent the theoretical M_n for runs 1 (▲, —) and 3 (■, - - -).

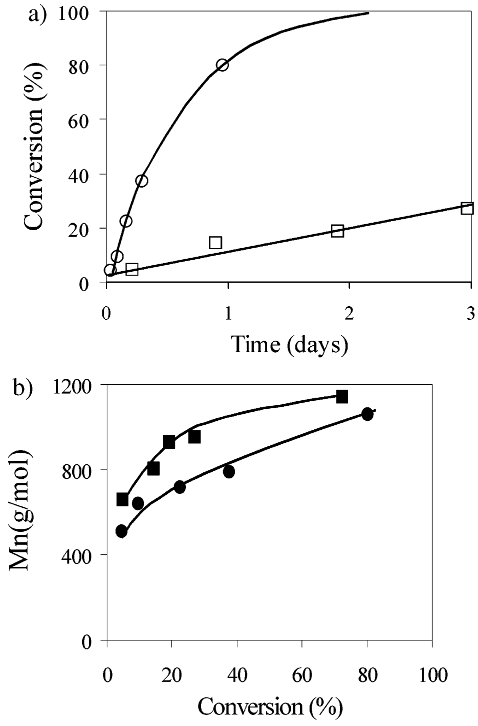


Figure 7. Kinetics (a) and molar mass variation with conversion (b) for experiments done in the presence of toluene and at two temperatures (Table 1, runs 9 (■, 30 °C), 11 (●, 60 °C)). Lines are only guides for the eyes.

Mechanism of Polymerization. Table 2 compiles the various experiments carried out here to better understand the role of each component in the recipe, in agreement with previous study on direct (mini)emulsion polymerization.[7g] Among the blank experiments, we

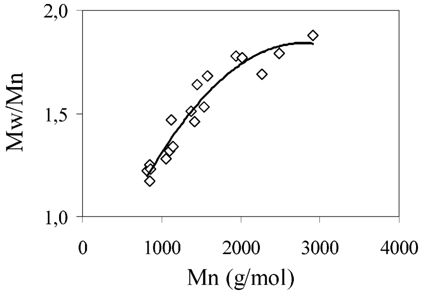


Figure 8. Final molar mass distributions vs average molar masses for all experiments described in Tables 1 and 2. The line is only guide for the eyes.

tested the role of ytterbium ions alone (by adding $YbCl_3$) and triflate alone (adding the sodium triflate salt in similar excess) as well as the influence of ionic strength by adding a noncatalyst trivalent salt (alun salt). The initial states of emulsion were generally really bad compared to recipes where ytterbium triflate is present. Consequently, polymerization rates (Table 2) and average molar masses (Figure 9) are much lower, whatever the conversion.

Clearly, increasing solely the ionic strength, by adding either ytterbium chloride or alun salt, has no effect on the polymerization scheme and even worst destabilizes the emulsion and consequently slows the rate of polymerization. This result confirms that most of the released ytterbium ions have no effects on the polymerization, except on binding to surfactant sulfonate groups and stabilizing the inverse emulsion. Note that it was recently demonstrated that a LASC prepared purposely from ytterbium chloride and SDS could not play the role of catalyst in similar conditions whereas it effectively participated in the stabilization of the miniemulsion.[10d]

The role of triflate ions is more complex. The latter, by trapping protons in the water phase, can better penetrate the interface and produce longer chains than using only DBSA. Similar results are obtained by adding triflic acid instead of DBSA. This phenomenon has also been observed in direct systems[7g] and has been interpreted in terms of the superacid hydrophobicity.[5a]

From these results, a similar mechanism scheme as provided before in direct emulsions and in the presence of ytterbium triflate[7g] applies. Basically, triflate ion captures a proton and an ytterbium triflate molecule to generate a bulky (Lewis acid-assisted) Brönsted acid, $HYbOTf_4$, that initiates a fast cationic polymerization. Chains grow rapidly until water transfer/termination reaction occurs. This reaction is retarded compared to direct emulsion processes, simply because the interface is rather apolar. The fact that the average molar mass increases with conversion is due to a modification of the interface by the small hydroxylated oligomers that are first generated, whereas the decrease in molar mass at high conversion is due to chain degradation catalyzed by the large amount of protons that ceased to catalyze the polymerization reaction.[7e]

Complementary Analyses. The possibility of forming a bulky counteranion such as $Yb(OTf)_4^-$ was indirectly confirmed by solution polymerization. As pointed out by Sawamoto,[14] sufficiently dried ytterbium triflate (containing only 0.25 mol of water per mole of catalyst) is able to initiate THF polymerization, as observed by a blur appearing after 1 h mixing. Although it is not clear in these conditions what species initiate the polymerization,[15] it is generally accepted that active chains propagate with $Yb(OTF)_4^-$ as a counterion. The polymer recovered by drying and washed with acetonitrile still entrapped $Yb(OTF)_4^-$ as seen by electrospray mass spectrometry (Figure 10a) where the expected isotopic content of each atom fits with the ISOPRO simulation of the bulky anion. ^{19}F NMR analyses of the same sample in d_6-DMSO was also compared with signals for triflic acid, sodium triflate, and ytterbium triflate (Figure 10b).[16] All species readily dissolved in the deuterated solvent and exhibit sharp signals, except for ytterbium triflate ($\delta = -78.30$ ppm) presumably because of partial aggregation.[7d] Triflic acid shows up at -78.44 ppm, whereas triflate and $Yb(OTF)_4^-$ anions are closed from each others ($\delta = -78.21$ and -78.16 ppm, respectively). Previous ^{19}F NMR analyses of ytterbium triflate in THF/water aimed at demonstrating that the catalyst keeps its structure, and thus its catalytic power, in the presence of water.[7d] From our own experience and from others,[11] it seems that the typical sharp peak they assigned to the ytterbium triflate may rather be attributed to the triflate anion, indeed shifted from the triflic acid as shown here.

Comparison with Previous Studies. It seems now evident that controlled cationic polymerization in water of *p*MOS is a priori not possible at this stage, albeit using the ytterbium triflate catalyst. The present data fit perfectly in terms of kinetics and molar evolution with conversion with previous results using *p*-toluenesulfonic acid as a proton source, all other things being equal (see for instance in Figure 11 a compilation of molar masses vs conversion for polymerizations performed in similar conditions as in ref 7c). It seems thus that the proposed polymerization scheme also applies to these polymerization conditions.

When the monomer/HCl adduct is added in the dispersion,[7a,b] rapid hydrolysis occurs, and the released HCl serves as the proton source.[10d] The use of conventional ammonium surfactants decreases the size of the dispersion of water in the monomer phase, but again does not affect the polymerization scheme, as shown from analogous average molar mass evolutions with conversion. Other metals, such as zinc or copper, as well as other ligands, such as BF_4^-, have shown to work in a similar way,[7d] the only prerequisite being that these are water-resistant Lewis acids, i.e., that the metal cations do not give hydroxides at acidic pH.[9]

The report of Storey and co-workers on cationic polymerization of *p*MOS in aqueous emulsion using phosphonic acids and ytterbium triflate is less easy to interpret.[7f] Most probably, the polymerization proceeds via a similar inverse emulsion process, since large quantities of ytterbium triflate and monomer were used in their recipe. The authors also noted that the polymerization was not controlled and termination arose from water, in agreement with the proposed mechanism scheme. The reason for their obtaining larger molar masses than here (on the order of 10 000 g/mol) may be found in the size of the Brönsted acid involved. Phosphonate anions are indeed known to complex more strongly than triflates on rare earth atoms[17] and may produce bigger counteranions. Complementary results are needed to state on this point, a work that we are currently performing in the laboratory.

Conclusion

The cationic polymerization of *p*-methoxystyrene in water using dodecylbenzenesulfonic acid as a surfactant

Table 2. Inverse Emulsion Polymerization Experiments Carried Out To Understand the Mechanism of Polymerization[a]

run	w_{H_2O} (g)	w_{pMOS} (g)	w_{DBSA} (g)	type of additive[b]	w_{add} (g)	M_n (g/mol)	M_w/M_n	R_p (% conv/day)	initial state of emulsion
12	1.60	1.01	0.12	$YbCl_3$	0.51	850	1.17	10	A
13	1.78	1.78	0.13	$YbCl_3$	0.50	860	1.23	6	A
14	0.83	1.92	0.06	$YbCl_3$	0.50	850	1.25	6	A
15	1.89	1.90	0.12	CF_3SO_3Na	0.66	1120	1.47	8	B
16	1.81	3.81	0.12	CF_3SO_3Na	0.81	1580	1.68	9	B
17	0.85	1.91	0.07	alun salt	0.63	820	1.22	3	A
18[c]	0.82	1.93	0.06	alun salt	0.66	1100	1.32	8	B

[a] All experiments were done at 30 °C. Same conventions as in Table 1. [b] Alun salt: trivalent salt of general formula $AlKS_2O_8 \cdot 12H_2O$. [c] Triflic acid (0.06 g) was added.

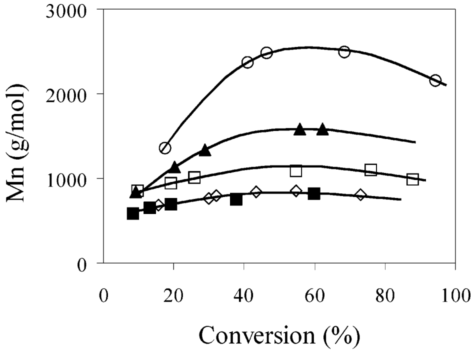


Figure 9. Molar mass variation with conversion for blank experiments (see recipes Table 2) compared to a model one (○, run 3). Additives: $YbCl_3$ (◇, run 14), alun salt (■, run 17), alun salt + triflic acid (□, run 18), CF_3SO_3Na (▲, run 16). Lines are only guides for the eyes.

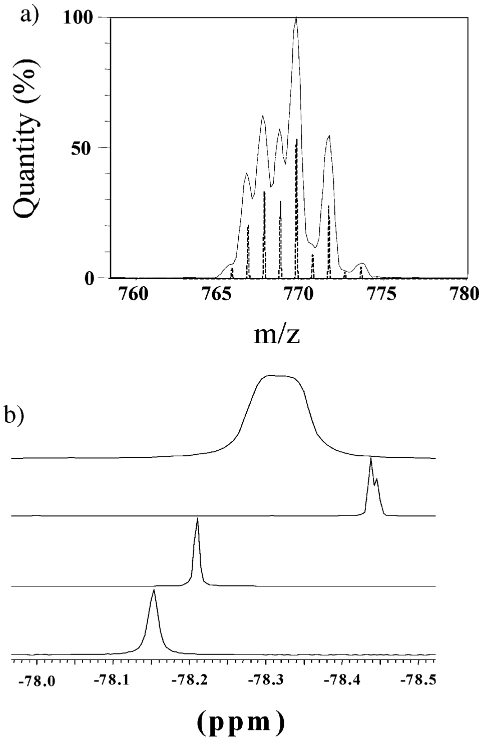


Figure 10. Evidence for the generation of $Yb(OTf_4)^-$ in the polymerization of THF by extremely dried $Yb(OTf)_3 \cdot {}^1/_4H_2O$. (a) Electrospray analysis in negative mode. (—) experimental data; (- - -) simulated isotopic distribution using ISOPRO ($MM_{YbOTf_4^-}$ = 769.4 g/mol). (b) ^{19}F NMR in d_6-DMSO. From top to bottom: ytterbium triflate, triflic acid, sodium triflate, and $Na^+Yb(OTf_4)^-$.

and ytterbium triflate as a catalyst was studied in terms of kinetics and physicochemistry. The polymerization proceeds through an inverse (water in monomer) emulsion process; i.e., the continuous phase is polymerized.

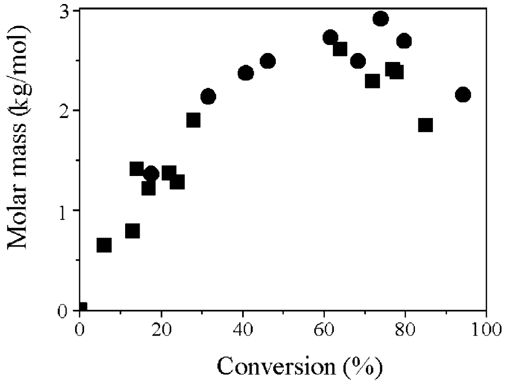


Figure 11. Number-average molar mass evolution with conversion for experiments performed here (●, runs 2 and 3 in Table 1) and by Sawamoto (■, ref 7c).

It was demonstrated that the emulsion evolved with conversion to finally give a thick and stable cake of polymer where water droplets are dispersed. Conversions were slow, typically at 30 °C, but the average molar masses could, in the best instances, go up to 3000 g/mol. The various blank experiments carried out here showed that the initiation was performed at the interface by a bulky (Lewis acid-assisted) Brönsted acid, typically $HYb(OTf)_4$. The present conventional polymerization scheme also applies to data from previous studies, definitively setting out that cationic polymerization of *p*MOS cannot, albeit at this stage, be controlled by rare earth catalysts. Those inverse emulsions, altough generating polymers of larger molar masses than in direct emulsion, may not find an industrial outlet by their large content of catalyst required and the difficulty to extract a pure polymer from these. We will soon report conditions to generate polymers of high molar masses from ytterbium-assisted cationic polymerization in direct emulsion.

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References and Notes

(1) Ganachaud, F. *Adv. Polym. Sci.*, in preparation.
(2) (a) Couvreur, P.; Kante, B.; Roland, M.; Guiot, P.; Bauduin, P.; Speiser, P. *J. Pharm. Pharmacol.* **1979**, *31*, 331. (b) Vauthier, C.; Couvreur, P. In *Handbook of Biopolymers*; Matsumara, J. P., Steinbuchel, A., Eds.; Wiley-VHC: New York, 2002; Vol. 9, Chapter 21, p 457. (c) Gallardo, M.; Couarraze, G.; Denizot, B.; Treupel, L.; Couvreur, P.; Puisieux, F. *Int. J. Pharm.* **1993**, *100*, 55. (d) Behan, N.; Birkinshaw, C. *Macromol. Rapid Commun.* **2000**, *21*, 884. (e) Behan, N.; Birkinshaw, C.; Clarke, N. *Biomaterials* **2001**, *22*, 1335. (f) Limouzin, C.; Caviggia, A.; Ganachaud, F.; Hémery, P. *Macromolecules* **2003**, *36*, 667.
(3) (a) De Keyser, J.-L.; Poupaert, J. H.; Dumont, P. *J. Pharm. Sci.* **1991**, *80*, 67. (b) Lescure, F.; Seguin, C.; Breton, P.;

Bourrinet, P.; Roy, D.; Couvreur, P. *Pharm. Res.* **1994**, *11*, 1270. (c) Breton, P.; Guillon, X.; Roy, D.; Lescure, F.; Riess, G.; Bru, N.; Roques-Carmes, C. *Biomaterials* **1998**, *19*, 271. (d) Bru-Magniez, N.; Guillon, X.; Breton, P.; Couvreur, P.; Lescure, F.; Roy, D.; Roques-Carmes, C.; Riess, G. US Patent 6,211,273, 2001.

(4) (a) Adamek, S. British Patent GB 1,123,801, 1968. (b) Kutch, E. L.; Osborn, S. W.; Wells, T. F. US Patent 3,337,513, 1967. (c) Adamek, S. British Patent GB 1,109,164, 1968. (d) Amerik, Y. B.; Shirokova, L. A.; Toltchinsky, I. M.; Krentsel, B. A. *Makromol. Chem.* **1984**, *185*, 899; (d) Rehor, A.; Tirelli, N.; Hubbell, J. A. *Macromolecules* **2002**, *35*, 8688.

(5) (a) Maitre, C.; Ganachaud, F.; Ferreira, O.; Lutz, J.-F.; Paintoux, Y.; Hémery, P. *Macromolecules* **2000**, *33*, 7730. (b) Walker, F. H.; Dickenson, J. B.; Hegedus, C. R.; Pepe, F. R. *Prog. Org. Coat.* **2002**, *45*, 291.

(6) (a) Becker, R. R.; Stahmann, A. *J. Biol. Chem.* **1953**, *204*, 737. (b) Miwa, K.; Stahmann, A. In *Polyamino acids, Polypeptides and Proteins*; University of Wisconsin Press: Madison, WI, 1961; p 81. (c) Taillades, J.; Collet, H.; Garrel, L.; Beuzelin, I.; Boiteau, L.; Choukroun, H.; Commeyras, A. *J. Mol. Evol.* **1999**, *48*, 638. (d) Taillades, J.; Collet, H.; Garrel, L.; Beuzelin, I.; Boiteau, L.; Choukroun, H.; Commeyras, A. *J. Chromatogr., A* **2002**, *952*, 239.

(7) (a) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1999**, *32*, 3827. (b) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 4660. (c) Satoh, K.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2728. (d) Satoh, K.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **2000**, *33*, 5836. (e) Cauvin, S.; Sadoun, A.; Dos Santos, R.; Belleney, J.; Ganachaud, F.; Hémery, P. *Macromolecules* **2002**, *35*, 7919. (f) Scheuer, A. D.; Storey, R. F. *Polym. Prepr.* **2002**, *43*, 932. (g) Cauvin, S.; Ganachaud, F. *Macromol. Symp.*, in press. (h) Cauvin, S.; Ganachaud, F. *e-Polym.* **2003**, No. 50.

(8) (a) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W.-L. *Chem. Rev.* **2002**, *102*, 2227. (b) Kobayashi, S.; Nagayama, S.; Busujima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8287. (c) Fringelli, F.; Pizzo, F.; Vaccaro, L. *J. Org. Chem.* **2001**, *66*, 4719.

(9) (a) Waller, F. J.; Barrett, A. G.; Braddock, D. C.; McKinnell, R. M.; Ramprasad, D. *J. Chem. Soc., Perkin Trans. 1* **1999**, 867. (b) Barrett, A. G.; Braddock, D. C.; Henschke, J. P.; Walker, E. R. *J. Chem. Soc., Perkin Trans. 1* **1999**, 873.

(10) (a) Kobayashi, S.; Wakabayashi, T. *Tetrahedron Lett.* **1998**, *39*, 5389. (b) Kobayashi, S. *Eur. J. Org. Chem.* **1950**, *15*, 5. (c) Kobayashi, S.; Manabe, K. *Synlett* **1999**, *5*, 547. (d) Touchard, V.; Boisson, C.; D'Agosto, F.; Graillat, C.; Spitz, R. *Macromolecules*, in press.

(11) van Loon, A. M.; van Bekkum, H.; Peters, J. A. *Inorg. Chem.* **1999**, *38*, 3080.

(12) Beeby, A.; Clarkson, I. M.; Eastoe, J.; Faulkner, S.; Warne,B. *Langmuir* **1997**, *13*, 5816.

(13) In course of preparing stable inverse miniemulsions, the aristonic acid, a doubled-tailed surfactant from the Pilot Chemical Co. (see ref 7h), was tested. The obtained LASC was so hydrophobic that it stayed in the organic phase and did not proceed to the dispersion and polymerization of *p*MOS.

(14) Satoh, K.; Katayama, H.; Kamigaito, M.; Sawamoto, M. *ACS Symp. Ser.* **1997**, *665*, 106.

(15) A triflic acid molecule can complex with ytterbium triflate, as we proposed before,[7g] to form $HYb(OTf)_4$. Dismutation processes between two catalyst molecules, e.g. $Yb(OTf)_2^+$, $Yb(OTf)_4^-$, were also invoked to explain "spontaneous" initiation (see for instance: Gandini, A.; Yang, Y.-H. *ACS Symp. Ser.* **1997**, *665*, 113).

(16) ^{19}F NMR chemical shifts are averages from at least three spectra obtained on two different apparatus, with precision on the values better than 0.01 ppm.

(17) Teramoto, M.; Sakuramoto, T.; Koyama, T.; Matsuyama, H.; Miyake, Y. *Sep. Sci. Technol.* **1986**, *21*, 229.

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