Cationic Polymerization of Styrene in Solution and Aqueous Suspension Using $B(C_6F_5)_3$ as a Water-Tolerant Lewis Acid

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Introduction. The discovery of the living cationic polymerization opened new possibilities in the synthesis of well-defined polymers with controlled molecular weight (M_n), polydispersity (MWD), terminal functionality, and different polymer architectures such as block copolymers, star, branched, and hyperbranched polymers and copolymers.[1−3] Unfortunately, the field of living cationic polymerization has not produced significant industrial outcomes so far, mainly because of high sensitivity to traces of water of commonly used Lewis acids, including (for the styrene) $SnC1_4$,[4] $BC1_3$,[5] $TiCl_4$,[6] $TiC1_3$(O-*i*-Pr),[7] and $AlCl_3$.[8]

$Yb(OTf)_3$ was recently claimed to be a water-tolerant Lewis acid that could catalyze the cationic polymerization of *p*-methoxystyrene in the presence of tosylic acid or HCl−monomer adduct.[9−11] Other initiators included dodecylbenzenesulfonic acid, whether without[12,13] or with[14,15] ytterbium triflate as a cocatalyst, and phosphonic acids/ytterbium triflate systems.[16] In all instances, it was shown that the polymerization in direct or inverse (micro)suspension proceeded at the interface and that physicochemical issues governed molecular weights; i.e., the polymerization is not controlled.[12,15] Some experiments were also driven with so-called Lewis acid-supported catalysts,[17,18] which in some instances conducted to long molar masses, namely when using an electrosteric surfactant and carefully chosen initiator.[17]

Recently, another Lewis acid ($BF_3{\cdot}OEt_2$) was successfully used for controlling the cationic polymerization of styrene and its derivatives in the presence of small amounts of water, albeit in larger concentration compared to the Lewis acid.[19−22] However, this catalyst is ineffective when huge excess of water is present, and all our attempts at polymerizing styrene or *p*-methoxystyrene in aqueous dispersions (emulsion or suspension) failed.[23] On the other hand, $B(C_6F_5)_3$ has been widely used in organic chemistry, for its renown water-tolerant Lewis acidity.[24,25] Both theoretical and experimental physicochemical studies showed that $B(C_6F_5)_3$ does not decompose in water but is able to form two types of stable adducts with water, including the strong Brønsted acid $B(C_6F_5)_3{-}H_2O$.[26−29] Such Lewis acid[30] and diborane derivative[31] were already used in the polymerization of isobutene, in the latter case in the presence of water, but were not applied to the polymerization of conventional monomers. In this paper we report for the first time the quasi-living (in the sense of B. Ivan)[32] cationic polymerization of styrene with $B(C_6F_5)_3$ in combination with an aromatic alcohol in solution, i.e., CH_2Cl_2 in open air and in the presence of water, as well as in aqueous suspension.

Results. The adduct of water and *p*-methoxystyrene [CH_3-$CH(C_6H_4$-*p*-$OCH_3)$-OH] (**1**) was used as an initiator for the cationic polymerization of styrene coupled with $B(C_6F_5)_3$ in CH_2Cl_2 at 20 °C, in air atmosphere, and without any drying of reactants. The data in Figure 1a clearly evidence that the polymerization of styrene with **1** as the initiator is essentially faster than with adventitious water. The $\ln([M]_0/[M])$ vs time, also given in Figure 1a, indicates a linearity only in the absence of initiator. In the experiments including **1**, the larger ionization rate of the initiator relative to the polymer chain ends has recently been put forward to explain the nonlinearity of plots such as those given in Figure 1a.[33−35]

Figure 1b shows the M_n and M_w/M_n variations with conversion for styrene polymerization with a **1**/$B(C_6F_5)_3$ initiating system. The molecular weight of the polymer increases with monomer conversion, but the experimental M_n's approach the calculated values only at the later stage of the polymerization. Since **1** is cationized by $B(C_6F_5)_3$ much faster than the hydroxylpolystyrene chains, slow initiation relative to propagation seems not likely. The discrepancy between theoretical and experimental molar mass evolution may rather be ascribed to a slow interconversion between the reversible-terminated and active species, i.e., fast addition of monomer units during the ionization−propagation−termination cycles, as clearly seen in the kinetics (Figure 1a). Moreover, at lower initiator concentration, the experimental M_n's are below the theoretical ones, presumably because proton initiation via water operates competitively. The MWD's stay relatively narrow ($M_w/M_n \sim 1.5{-}1.6$) during the styrene polymerization with the **1**/$B(C_6F_5)_3$ initiating system for both initiator concentrations. Also, it should be noted that styrene polymerization without initiator is not controlled: the molecular weight of polymers decreases and MWD broadens with monomer conversion (Figure 1b).

The living nature of styrene polymerization in the **1**/$B(C_6F_5)_3$ initiating system was also examined in a separate chain extension experiment (Figure 1c). Basically, a second feed of monomer was added to the reaction mixture just before the first load had completely polymerized. The additional monomer smoothly polymerize in about one night because of the sluggish ionization of polymer chain ends. The molecular weight of the obtained polymers double whereas the molecular weight distribution stays relatively narrow. In this experiment, polymers with slightly lower M_n ($M_n = 7600$ g/mol) than the calculated one ($M_{n,theor} = 8400$ g/mol) are produced due to simultaneous initiation by protic impurities as well as the presence of dead chains, revealed by the shoulder in the low molar mass SEC region (Figure 1c).

We also extended our study on the investigation of styrene polymerization in aqueous suspensions (see a typical optical micrograph in Figure 2). Small droplets of few microns in size slowly polymerize under severe agitation (typically 800 rpm). At low conversion (less than 30%), the organic phase creams at the top of the tube, whereas at larger conversions, the bigger density of the organic phase makes it drop at the rear of the test tube.

In opposition with the polymerization in CH_2Cl_2, the proton initiation via water is very slow and negligible under aqueous suspension conditions (Figure 3a), although the pH of the continuous medium is naturally set below 2. As also evidenced in Figure 3a, the increase in the initiator concentration leads to

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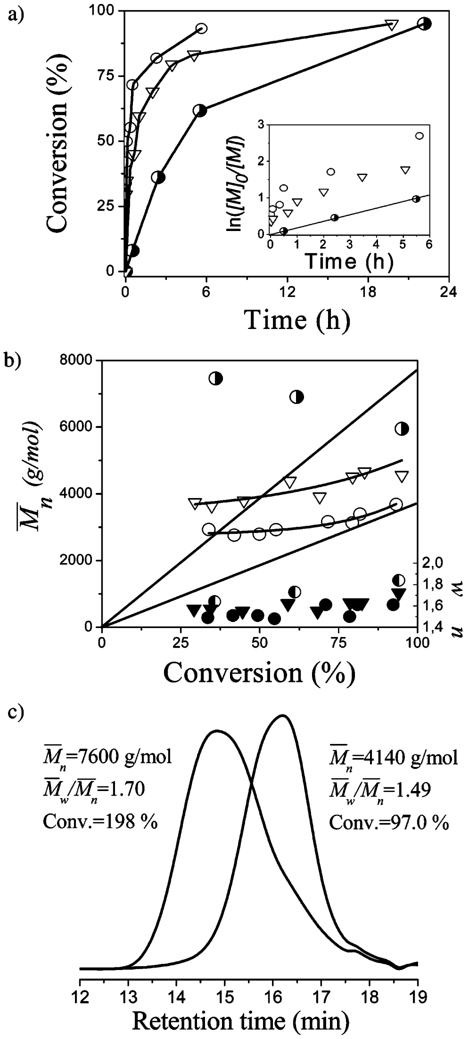

Figure 1. (a) Conversion (insert: $\ln([M]_0/[M])$) vs time. (b) M_n and M_w/M_n vs conversion for the polymerization of styrene with $B(C_6F_5)_3$ at 20 °C in CH_2Cl_2: $[B(C_6F_5)_3] = 0.052$ M; [St] = 0.65 M. Initiator concentrations: (○, ●) [**1**] = 0.019 M; (▽, ▼) [**1**] = 0.009 M; (◑, ◐) no initiator. The straight lines in (b) correspond to theoretically calculated M_n values. (c) SEC traces of polystyrenes obtained in a monomer addition experiment in the styrene polymerization with the **1**/$B(C_6F_5)_3$ initiating system in CH_2Cl_2 at 20 °C: [**1**] = 0.019 M; $[B(C_6F_5)_3] = 0.052$ M; $[St]_1 = [St]_2 = 0.65$ M.

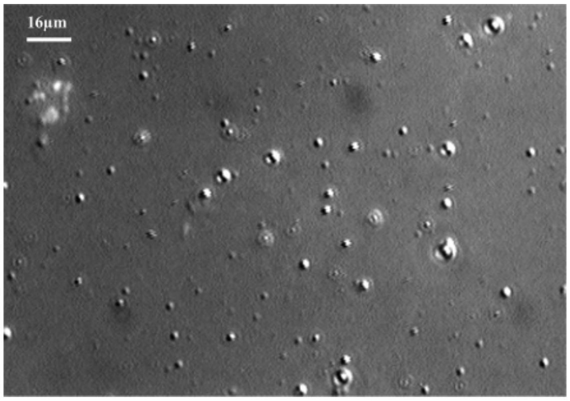

Figure 2. Optical micrograph of suspension of polystyrene obtained during the polymerization of styrene with $B(C_6F_5)_3$ at 20 °C in excess water. $[B(C_6F_5)_3] = 0.05$ M; [**1**] = 0.033 M; [St] = 1.0 M. A differential interference contrast was applied to enhance the volume observation of the droplets.

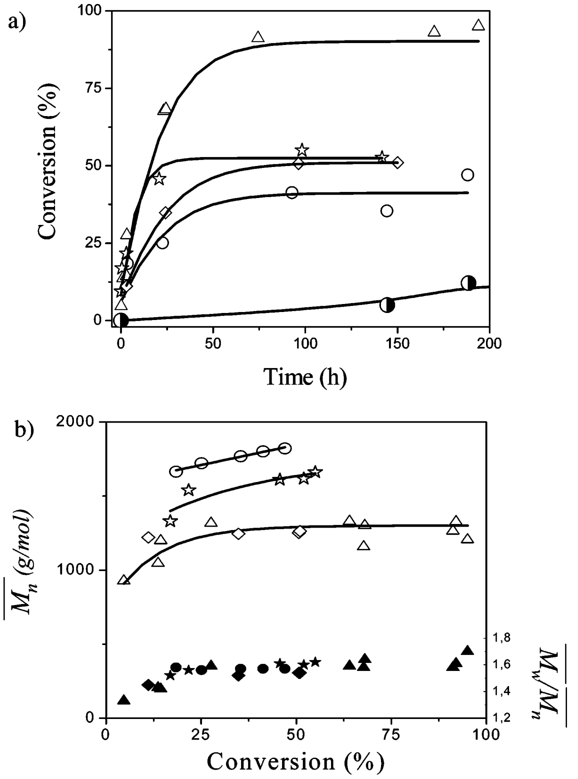

Figure 3. Conversion−time and M_n− and M_w/M_n−conversion dependences for the polymerization of styrene with $B(C_6F_5)_3$ at 20 °C in water: $[B(C_6F_5)_3] = 0.05$ M; [St] = 1.0 M. Initiator concentration: (△, ▲) [**1**] = 0.074 M; (☆, ★) [**1**] = 0.033 M; (○, ●) [**1**] = 0.017 M; (◇, ◆) [**1**] = 0.033 M + [**2**] = 0.033 M; (◑) no initiator.

the increase in the polymerization rate as well as in the maximum monomer conversion, up to almost full conversion at [**1**] = 0.074 M. The molecular weights of polymers are rather low in these conditions and hardly change with conversion for all initiator concentrations (Figure 3b). On the other hand, the maximum value of M_n decreases and maximum value of MWD slightly increases with the increasing initiator concentration.

A rational explanation for these results may be found in the physicochemistry of the system. Molecular weights are thought to be controlled by the interfacial polarity, not by the [M]/[I] ratio: the increase in the (polar) initiator content results in larger water concentration at the interface. In turn, this leads to faster transfer/termination rate with water and to the formation of shorter chains.[12] To verify that this feature, previously named the "critical DP hypothesis",[12−15] again applies in this system, we investigated the polymerization of styrene with **1**/$B(C_6F_5)_3$ in the presence of a polar additive (1-phenylethyl alcohol (**2**)), which we checked does not initiate the polymerization of styrene in aqueous suspension (not shown). As observed in Figure 3a, the addition of **2** slightly reduces the rate of polymerization of styrene, without major changes in the final monomer conversion; on the other hand, substantial decreases in the molecular weight as well as in the molecular weight distribution of the obtained polymers are observed (Figure 3b). Since the maximum values of M_n's of polystyrenes obtained with same concentration of **1** or **1** + **2** are the same (Figure 3b), one can consider that water content at the interface is exclusively controlling the molar mass. It should also be noted that the MWD's are relatively narrow ($M_w/M_n \sim 1.6$) in all experiments but broaden with monomer conversion in comparison with those obtained while polymerizing the styrene in CH_2Cl_2. This result may be an evidence that transfer/termination by water is irreversible under these conditions.

For both processes, the characterization of reprecipitated polystyrenes was performed by SEC and ^{1}H NMR, and results

Table 1. M_n(SEC), M_n(NMR), $F(\beta)$, and $F(\omega)$ of the Polystyrenes, Obtained in Aqueous Dispersion and Solution (See Text for Details)

run	M_n(SEC), g/mol	M_n(NMR), g/mol	$F(\beta)^a$	$F(\omega)^{a,b}$	process
1	2660	2900	0.90	0.85	solution
2	3960	4420	0.94	0.85	solution
3	1370	1370	1.07	1.0	suspension
4	1990	1990	1.00	1.0	suspension
5	2300	2420	1.05	0.91	suspension

[a] $F(\beta)$ ($F(\omega)$) are calculated as the ratio of integrals (normalized to one hydrogen) of β (ω) vs α NMR peaks: $F(\beta) = I(\beta)/I(\alpha)$; $F(\omega) = (3I(\omega))/I(\alpha)$. [b] The ^{13}C satellites of the methoxy group at 3.5 ppm appear at 4.14 and 3.44 ppm (see ref 12). The integral of the peak set at 3.44 ppm was subtracted from $I(\omega)$ to give a more accurate value of $F(\omega)$.

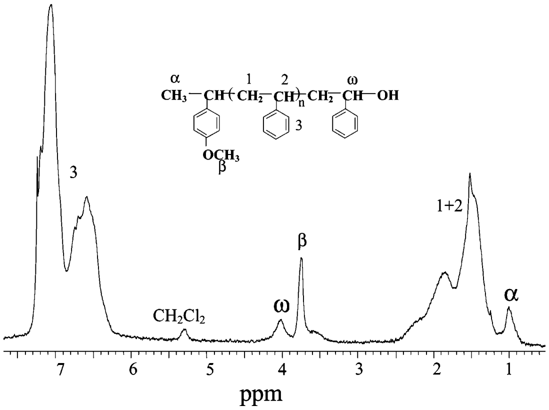

Figure 4. ^{1}H NMR spectrum of polystyrene obtained with **1**/B$(C_6F_5)_3$ in water at 20 °C: [**1**] = 0.017 M; [B$(C_6F_5)_3$] = 0.05 M; [St] = 1.0 M.

are given in Table 1. A typical ^{1}H NMR spectrum of a polystyrene obtained with the **1**/B$(C_6F_5)_3$ initiating system in aqueous suspension is also shown in Figure 4. In addition to the large absorption of the main-chain methylene (1), methine (2), and phenyl (3) protons of the polystyrene units, the signals ascribed to the end groups are clearly separated, namely, CH_3- (α; 1.0 ppm) and CH_3O- group (β; 3.75 ppm) at the α-end and $-CH-OH$ (ω; 3.9−4.2 ppm) at the ω-end. The number-average molecular weights of the polymer were determined by ^{1}H NMR from the peak intensity ratio of the well-resolved methyl (α) to the phenyl protons (3) (Table 1). The values are in good agreement with M_n's measured by size exclusion chromatography, except for large polymer chains obtained in solution, for which the α-methyl signal is low. Moreover, the functionalities of both chain ends ($F(\beta)$ and $F(\omega)$) were calculated and show clear differences between solution and suspension processes. For the polystyrenes obtained in CH_2Cl_2 (runs 1 and 2, Table 1), slightly lower values of $F(\beta)$ in comparison with $F(\alpha)$ can be connected with some loss of methoxy functionality due to the initiation by the protic impurities, as well as some production of dead chains when molar masses become significantly high (*vide infra*). In aqueous suspension, $F(\beta)$ and $F(\omega)$ exhibit values close to 1 (runs 3−5, Table 1). This feature confirms that water does not generate new polymer chains and side reactions, which would lead to the methyne or indanyl termini, are absent. Such results clearly indicate that the aqueous suspension process must be preferred when one seeks for producing polystyrene chains of almost perfect functionality but low molar mass.

Conclusive Discussion. The main reactions in the polymerization process described above are given in Scheme 1, including initiation by **1**/B$(C_6F_5)_3$ or B$(C_6F_5)_3-H_2O$, the fast propagation step and transfer reaction by water which ensures the necessary equilibrium between living and nonpropagating chains, as well as other transfer reactions leading to dead chains (such as hydroxyl abstraction or indanyl cyclizations), which were not specifically studied here but are known to occur in cationic polymerization. Table 2 summarizes the extent to which all steps occur in solution and suspension.

Scheme 1. Proposed Mechanism for Styrene Polymerization Catalyzed by B$(C_6F_5)_3$ in Solution in Dichloromethane and in Aqueous Suspension. Probability That Each Steps Occurs in Both Processes Is Given in Table 2

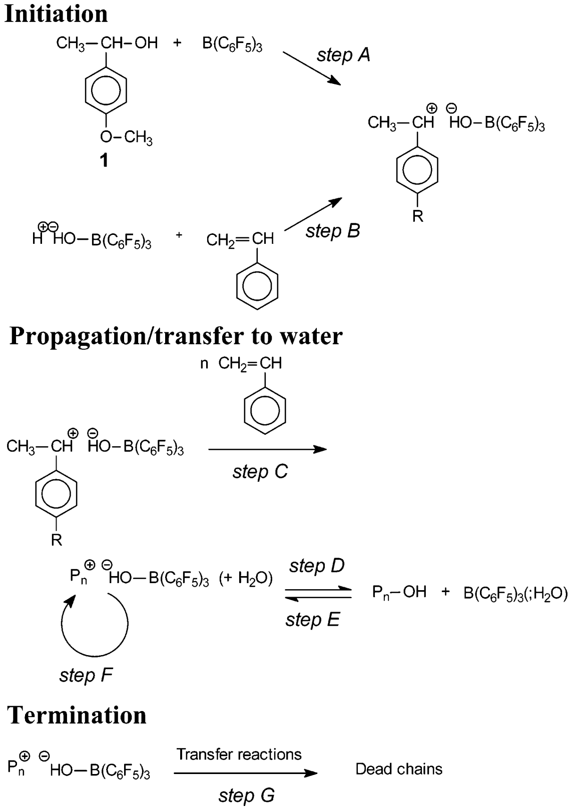

Table 2. Influence of the Polymerization Process on the Probability of Reaction Steps To Occur

process	step A	step B	step C	step D	step E	step F	step G
solution	fast	slow	very fast	slow	slow	very fast	slow
suspension	very slow	—[a]	very fast	fast	—[a]	—[a]	—[a]

[a] Not operating.

In solution, both the initiating complex **1**/B$(C_6F_5)_3$ and B$(C_6F_5)_3-H_2O$ initiate the polymerization, but the former is faster than the latter, particularly at larger contents of initiator. In aqueous suspension, initiation is much slower (compare for instance kinetics plots given in Figures 1a and 3a), but only the initiating complex is able to start a chain, thus giving rise to polystyrene chains with one methoxyphenyl extremity.

Once a chain is initiated, propagation is very fast in both solution and suspension until water transfer to the carbocation to generate a nonpropagating chain P_n-OH. In aqueous suspension, reactivation of the chains does not occur, according to the inactivity of the **2**/B$(C_6F_5)_3$ system. The length of the polymer chains is "controlled" by the ratio of monomer to water at the interface between organic and aqueous phase, not the content of initiating agent. On one hand, no side reactions, such as transfer to monomer or to adjacent phenyl group, occur, which thus leads to chains with an almost perfect functionality. On the other hand, chains are short, and full conversion only occurs when sufficient initiating agent has been introduced in the recipe. Note that even if oligomer chains could be reactivated, the entry into organic droplets for a critical degree of polymerization nevertheless limit the final molar mass of the polystyrene chains: this so-called "critical DP effect" has extensively been recorded in previous studies.[12−15]

In solution, the chains terminated by an hydroxylated moiety can cationize to give back the active center that goes on propagating. The ionization step (E) and transfer reaction (D) are rather slow, compared to propagation (F), which explains that the M_n vs conversion plot does not follow the theoretical line. However, polymerization proceeds even after addition of a second monomer shot, which confirms that in solution the polymerization is quasi-living. Some side reactions are also believed to occur according to the nonperfect ω-functionality measured by NMR (Table 1), but these are seldom and without important consequences for the process.

To summarize, the quasi-living cationic polymerization of styrene in open air and without any drying of the reagents was achieved using the 4-methoxy-α-methylbenzyl alcohol/$B(C_6F_5)_3$ initiating system in CH_2Cl_2 at 20 °C. The polymerization proceeds via reversible activation of C−OH terminus and hydroxyl-terminated polystyrenes with controlled molecular weight, and a relatively narrow molecular weight distribution were obtained. We have also succeeded for the first time in promoting the cationic polymerization of styrene in aqueous suspension to produce hydroxyl-terminated polystyrenes with high purity. Although the polymer chains are generated only from the initiator, still the molecular weight is controlled exclusively by interfacial polarity. This brief comparison between the two processes has shown that livingness can be achieved in solution, albeit at the expense of the functionality which is perfect in suspension. Current works are devoted to the detailed investigation of polymerization of styrene and derivatives with $B(C_6F_5)_3$ as the catalyst in aqueous emulsion as well as to the search for ligands that could drive the catalyst inside the droplets, hopefully completing quasi-living cationic polymerization of these monomers in aqueous dispersions.

Experimental Part. a. Materials and Methods. 4-Methoxy-α-methylbenzyl alcohol (Aldrich, 99%), 1-phenylethyl alcohol (Aldrich, 98%), $B(C_6F_5)_3$ (Lancaster, 97%), CH_2Cl_2 (Carlo-Erba, 99.5%), and methanol (Fluka, 99.8%) were used as received. Styrene (Acros, 99%) was distilled under reduced pressure before use. Size exclusion chromatography was performed on a Spectra Physics apparatus with two columns (PL gel, 5 μm, 300 mm, 500 and 100 Å) and one precolumn (PL gel 5 μm guard) thermostated at 30 °C. The detection was achieved with a SP8430 differential refractometer. THF was eluted at a flow rate of 1.0 mL/min. The calculations of molecular weight and polydispersity were based on polystyrene standards. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AC 200 spectrometer. Optical micrographs were taken on a DMRX Leika polarizing microscope. A drop of suspension was deposited on a glass slide and directly observed using a ×63 magnifier. Pictures were observed using a differential interference contrast.

b. Polymerization Procedures. Polymerizations were carried out under an air atmosphere in glass tubes. A typical example for styrene polymerization in CH_2Cl_2 is given below. The polymerization was initiated by adding a solution of $B(C_6F_5)_3$ in CH_2Cl_2 (1 mL, 0.26 M) to a mixture of a total volume 4.4 mL consisting of styrene (0.4 mL), 4-methoxy-α-methylbenzyl alcohol (1×10^{-4} mol, 0.015 g), and CH_2Cl_2 (4 mL). The polymerization of styrene in aqueous suspension was carried out as follows: a solution of $B(C_6F_5)_3$ and diethyl ether (0.1 g) in H_2O (1 mL, 0.26 M) was added to a mixture of a total volume 4.6 mL consisting of styrene (0.6 mL), an appropriate amount of 4-methoxy-α-methylbenzyl alcohol, and H_2O (4 mL). After a predetermined time, ~0.5 mL aliquots were withdrawn and poured out into excess methanol. The polymer was separated by centrifugation and dried in a vacuum to give the product polymer. Monomer conversions were determined gravimetrically.

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