Controlled/Living Cationic Polymerization of *p*-Methoxystyrene in Solution and Aqueous Dispersion Using Tris(pentafluorophenyl)borane as a Lewis Acid: Acetonitrile Does the Job[†]

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ABSTRACT: The living cationic polymerization of *p*-methoxystyrene using the 1-(4-methoxyphenyl)ethanol/$B(C_6F_5)_3$ initiating system in solution and in aqueous dispersion is reported. Solution experiments first showed that the molar mass of the obtained polymers increases in direct proportion to the monomer conversion and the molar mass distribution stays narrow in the course of the polymerization ($M_w/M_n \sim 1.2$). The living nature of the growing chains was confirmed by sequential monomer addition experiments, although matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-TOF-MS) revealed some hydroxyl elimination under monomer-starved conditions. Aqueous suspension polymerization of *p*-methoxystyrene using the same initiating system did not show a good control of molar masses, since after polymerization has proceeded at the interface up to critical DP, oligomers terminated by water penetrate inside the particles where they stop propagating. This limitation was leveled off for the first time by polymerizing *p*-methoxystyrene in an aqueous dispersion, i.e., in a mixture of H_2O:CH_3CN 3:2 (v/v). Under these conditions, the hydroxyl-terminated poly(*p*-methoxystyrene)s can be reactivated by $B(C_6F_5)_3$ located inside the particles to reinitiate the polymerization; molar masses thus increase with conversion, up to 3000 g mol^{-1}, and exhibit a narrow molar mass distribution ($M_w/M_n \sim 1.3$) and an almost pure hydroxylated functionality.

Introduction

The "controlled/living" (which in the following will be quoted "living") cationic polymerization process of vinyl monomers and heterocycles is an important tool for the precision synthesis of macromolecules with predetermined number-average molar mass (M_n), terminal functionality, and narrow molar mass distribution (MWD, otherwise referred to as M_w/M_n)[1−3] to be used in a wide range of applications.[4−7] However, most of the conventional Lewis acids are decomposed when excess water, relative to Lewis acid content, is introduced. Such a drawback imposes one to carry out polymerizations under strictly anhydrous conditions (dried solvents and inert atmosphere); these conditions have so far clearly limited the practical use of living cationic polymerization from the industrial viewpoint.

The living cationic polymerization of *p*-methoxystyrene has already been achieved using initiating systems based on weak Lewis acids (I_2, ZnI_2, $SnBr_4$) (see ref 8 and references therein), at the time only under high-purity conditions. In recent publications, the controlled cationic polymerization of *p*-alkoxystyrenes[9] as well as styrene and its derivatives[10−12] in the presence of water and using BF_3OEt_2 as a co-initiator was reported by Sawamoto and co-workers. Although a precision control of the polymerization was clearly achieved in solutions containing small contents of water, we observed that BF_3OEt_2 could not be used in high excess of water to Lewis acid because of catalyst decomposition.[13]

Aqueous suspension and emulsion polymerizations are widely used in the industry due to their environmental friendliness, moderate viscosity of latices even at high solids content, easier control of the reactions, and handling of the products. However, industrially these techniques are confined exclusively to radical polymerization because free radicals are tolerant to the water. In recent years, catalytic polymerizations in aqueous medium have developed intensively. Indeed, reports about anionic,[14,15] ring-opening metathesis polymerization,[16,17] and homo- and copolymerization of ethylene[18,19] using metallocenes have emerged recently.

Sawamoto and co-workers described cationic polymerization of *p*-methoxystyrene in the presence of rare earth triflates as water-tolerant Lewis acids with HCl adduct of monomer[20,21] or tosylic acid[22] as the initiators in aqueous suspension. Dodecylbenzenesulfonic acid alone[23,24] or with ytterbium triflate[25,26] and phosphonic acids/$Yb(OTf)_3$[27] systems as well as so-called Lewis acid supported catalysts[28,29] were also used for the *p*-methoxystyrene polymerization in suspension or miniemulsion. However, even though M_n increased with conversion at the beginning of the polymerization (up to 30−40% conversion), the final M_n typically did not exceed 3000 g mol^{-1} regardless of initiator concentration. Furthermore, considerable deviation of $M_{n,exp}$ vs conversion curve from the theoretical slope takes place. Later, it was clearly shown that in all above-mentioned systems the polymerization is not controlled, and molar masses are governed exclusively by interfacial polarity.[23,25,26] When the polymerization proceeded inside monomer droplets[28] or phosphonic acids/$Yb(OTf)_3$[27] systems was used, high molar mass hydroxyl-terminated poly(*p*-methoxystyrene)s were generated, but polymerization was still not controlled. A recent article finally described cationic polymerization of isobutylene in aqueous suspension co-initiated by 1,2-$C_6F_4[B(C_6F_5)_2]_2$.[30]

Contrary to the ionic polymerization, there are many examples concerning living/controlled radical polymerization in aqueous dispersed media in the literature.[31] Most of these processes begin

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[†] This paper is dedicated to professor Pierre Sigwalt for his 50 years commitment in the field of cationic polymerization.

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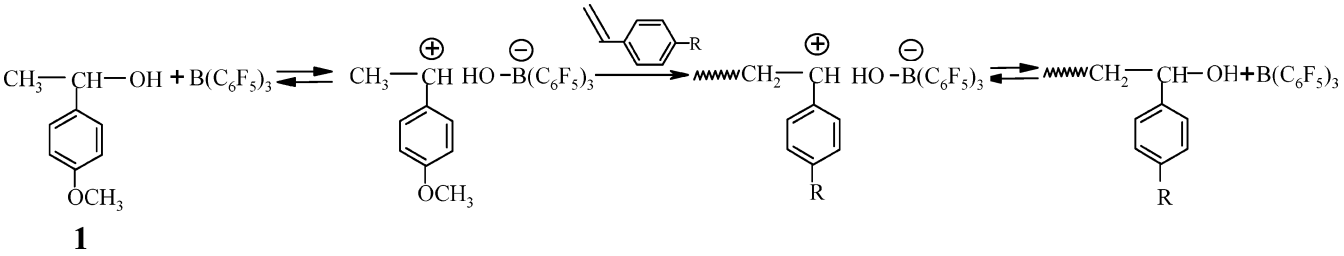
Scheme 1. Main Polymerization Reactions of Styrene (R = H)[32] and *p*-Methoxystyrene (R = OCH$_3$) (This Work) Using the 1/B(C$_6$F$_5$)$_3$ Initiating System in Solution



in the aqueous phase to form oligoradicals, which can enter the organic phase and, then, the polymerization proceeds inside of monomer droplets. In our opinion, this is the key stage in achieving control over M_n of these polymerization systems in aqueous media. A main feature of almost all ionic polymerization processes in dispersed media is the systematic limitation of the molar masses. This so-called "critical DP" effect was related to the entry in the particles of chains with low surface tensions.[23,26] Once buried, they stop propagating because catalyst usually remained in the aqueous phase. We assume therefore that for the completing of living cationic polymerization it is necessary to drive the catalyst inside the monomer droplets.

We recently showed that the living cationic polymerization of styrene could be performed using the 1-(4-methoxyphenyl)-ethanol (**1**)/B(C$_6$F$_5$)$_3$ initiating system in CH$_2$Cl$_2$ at +20 °C.[32] The living polymerization proceeds through the generation of a carbocation by hydroxide abstraction of the corresponding initiating monomer derivative and of the hydroxy-terminated chains by the borane agent (Scheme 1). Even when water transfers to the propagating carbocation, a hydroxyl-terminated chain, which can be reactivated, is produced, thus implementing a long-lived polymerization process. Water in all proportions does not decompose tris(pentafluorophenyl)borane; rather, it forms a Brönstedt acid-like adduct ($H^+[B(C_6F_5)_3OH]^-$ or $H_3O^+[B(C_6F_5)_3OH]^-$)[33−36] that competes with the conventional initiation system. Styrene was also polymerized in an aqueous suspension.[32] The presence of excess water slowed down significantly the reactivity of the Brönstedt acid toward styrene, thus allowing exclusive initiation by **1**/B(C$_6$F$_5$)$_3$. However, the polymerization in suspension was not living, since after propagation and transfer from water the hydroxyl-terminated polystyrene chains could not be reactivated, at least under these conditions.

Motivated by these recent findings, we extended our study to the polymerization of other styrene derivatives. In this paper, the living cationic polymerization of *p*-methoxystyrene initiated by 1-(4-methoxyphenyl)ethanol (**1**) using B(C$_6$F$_5$)$_3$ as a co-initiator in various solvents, at +20 °C, in open air and without thorough drying of reactants, as well as in aqueous suspension and dispersion, is presented.

Experimental Part

Materials and Methods. 1-(4-Methoxyphenyl)ethanol (Aldrich, 99%), B(C$_6$F$_5$)$_3$ (Lancaster, 97%), *p*-methoxystyrene (pMOS, Lancaster, 98%), CH$_2$Cl$_2$, acetonitrile, toluene (Carlo-Erba, 99.5%), and methanol (Fluka, 99.8%) were used as received.

Size exclusion chromatography (SEC) 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 by a SP8430 differential refractometer and tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany). ^{1}H NMR (400 MHz) spectra were recorded in CDCl$_3$ at 25 °C on a Bruker AC-200 spectrometer calibrated relative to the solvent peak in reference to tetramethylsilane standard. ^{19}F NMR (200 MHz) spectra were recorded on a Bruker AC-250 instrument at 25 °C, using CDCl$_3$, acetonitrile-d_3, or a mixture of acetonitrile-d_3 and D$_2$O as the solvents and CFCl$_3$ as the reference. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) analyses were performed on a Ultraflex (Bruker Daltonik, Bremen, Germany) time-of-flight mass spectrometer, equipped with a 337 nm, 50 Hz N$_2$ laser, a delayed extraction, and a reflector. The apparatus was operated at an accelerating potential of 20 kV in reflected mode. The polymer solution (1 μL of 10 g L^{-1} in THF) was mixed with 10 μL of matrix solution (DHB (2,5-dihydroxybenzoic acid), 20 g L^{-1} in THF). A solution of sodium iodide (10 mg L^{-1}) was utilized as a cationizing agent. The final solution (1 μL) was deposited onto the target and dried in air at room temperature before irradiation. The mass spectra represent averages over 250 consecutive laser shots. External calibrations were performed with peptide calibration standard (Bruker Daltonic, Brenem, Germany).

Polymerization Procedures. The polymerization reactions were carried out under air atmosphere in glass tubes, without further drying and purification of reactants. As an example of a typical procedure in solution, polymerization was initiated by adding a solution of B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ (1 mL, 0.14 M) to a mixture of a total volume of 4.3 mL consisting of *p*-methoxystyrene (0.3 mL, 2×10^{-3} mol), 1-(4-methoxyphenyl)ethanol (1×10^{-4} mol, 0.015 g), CH$_2$Cl$_2$ (1.5 mL), and acetonitrile (2.5 mL). Results were as follows: conversion = 79.8% (t = 40 min); number-average molar mass (M_n) = 2710 g mol^{-1}; molar mass distribution (M_w/M_n) = 1.21.

The polymerization in aqueous suspension was carried out as follows: a solution of B(C$_6$F$_5$)$_3$ (65 mg, 1.3×10^{-4} mol) in 1 mL of CH$_3$CN was added to a mixture of total volume 4.6 mL consisting of *p*-methoxystyrene (0.6 mL), 1-(4-methoxyphenyl)ethanol (1×10^{-4} mol, 0.015 g), CH$_3$CN (1 mL), and H$_2$O (3 mL). After a predetermined time, ~0.3 mL aliquots were withdrawn and poured into excess of methanol. The precipitated polymer was separated from the solution by centrifugation and dried in vacuum before SEC analyses. Monomer conversions were determined gravimetrically. The final results were as follows: conversion = 95% (t = 18.2 h); M_n = 2770 g mol^{-1}; M_w/M_n = 1.32.

Results and Discussion

A. Polymerization in Solution. *Preliminary Tests. p*-Methoxystyrene was first polymerized using the **1**/B(C$_6$F$_5$)$_3$ initiating system in different solvents. The content of water in the investigated systems was estimated from the manufacturer safety sheet, giving 0.05 wt % in acetonitrile and 0.02 wt % in CH$_2$Cl$_2$ and taking into account the fact that the catalyst forms a complex with H$_2$O (B(C$_6$F$_5$)$_3$·nH$_2$O (n = 1−3)) (vide infra). In these conditions, the ratio of water to catalyst is typically more than 1.5, which however has no consequences on the kinetics of polymerization, as shown below.

The polymerization of *p*-methoxystyrene in dichloromethane, using similar conditions as those reported for styrene,[32] proceeded very rapidly to produce polymers with higher molar

Table 1. Cationic Polymerization of *p*-Methoxystyrene (pMOS) in Various Solvents with the 1-(4-Methoxyphenyl)ethanol (1)/B(C_6F_5)$_3$ Initiating System[a]

run	solvent	time (min)	conversion (%)	$M_{n,exp}$[c] (g mol^{-1})	$M_{n,theor}$[c] (g mol^{-1})	M_w/M_n	I_{eff}[d] (%)
1	CH_2Cl_2[b]	0.5	100	6100	3115	2.50	51
		50	100 + 100	9190	6075	2.45	66
2	toluene	6	99	9700	3085	3.75	32
		90	100 + 100	11400	6075	2.80	53
3	CH_3CN	30	100	4380	3115	1.30	71
		270	100 + 98	7000	5960	1.65	85

[a] Reaction conditions: [**1**] = 0.019 M, [pMOS]$_1$ = [pMOS]$_2$ = 0.42 M, [B(C_6F_5)$_3$] = 0.026 M; temperature 20 °C. [b][B(C_6F_5)$_3$] = 0.05 M. [c] Experimental number-average molar mass ($M_{n,exp}$) obtained by GPC. Theoretical number-average molar mass ($M_{n;theor}$); $M_{n;theor}$ = [pMOS]$_0$/[**1**]$_0$ × 134 × conv + 135(head group) + 17(tail group). [d] Initiation efficiency: percentage of chains effectively produced from **1**; I_{eff} = [P$_n$]/[**1**]$_0$.

masses than theoretically expected, broad molar mass distribution (MWDs) and low initiating efficiencies (I_{eff}) (entry 1 in Table 1). Similarly, polymers with uncontrolled molar masses, very broad MWDs, and low I_{eff} are formed in toluene (entry 2 in Table 1). When acetonitrile was employed, controlled molar masses (entry 3, Table 1), with an increase of number-average molar masses (M_ns) with monomer conversion and relatively narrow MWDs, i.e. $M_w/M_n \sim 1.25-1.28$, were obtained (Figure S1). Still the experimental M_ns were higher than the theoretical ones (Table 1, entry 3).

Addition of a fresh monomer aliquot before monomer completion is a conventional trick to check whether polymer chains are living, even if polymerization is not controlled (e.g., systems with low initiation rate). In all cases, slow polymerizations and a gradual increase in molar masss were observed, even though the molar mass was not doubled as theoretically awaited (Table 1). Besides, molar mass distributions narrowed slightly compared to the end of the batch shots, when using CH_2Cl_2 and toluene, while in acetonitrile, the larger MWD than the one given at 100% conversion is ascribed to a partial reactivation of the chains, thus producing a bimodal distribution (Figure S2). These data indicate that in the polymerization system studied here most of the growing chains, whether they are initiated by water or the **1**/B(C_6F_5)$_3$ complex, are long-lived; however, either too fast (CH_2Cl_2, toluene) or too slow (CH_3CN) polymerizations lead to substantial loss of living chains, particularly when adding a second shot of monomer.

Mixed Solution Polymerization. Taking into account these preliminary results, we inferred that the mixture of CH_2Cl_2 and acetonitrile could be a compromise solution to achieve living cationic polymerization of *p*-methoxystyrene. Figure 1a shows the conversion−time relationship for the *p*-methoxystyrene polymerization with the **1**/B(C_6F_5)$_3$ initiating system in a 1:1 (v/v) mixture of CH_3CN and CH_2Cl_2 at various initiator concentrations. The data in Figure 1a clearly evidence that the polymerization of *p*-methoxystyrene proceeds without initiator but that polymerization with **1** as the initiator is essentially faster. Indeed, adventitious water complexed to the Lewis acid induces a competitive proton initiation, far to be negligible at low initiator concentration. The first-order plots, ln([M]$_0$/[M]) vs time shown in Figure 1b, are linear and start at the origin in the absence and presence of the initiator; this indicates the absence of irreversible termination during the polymerization.

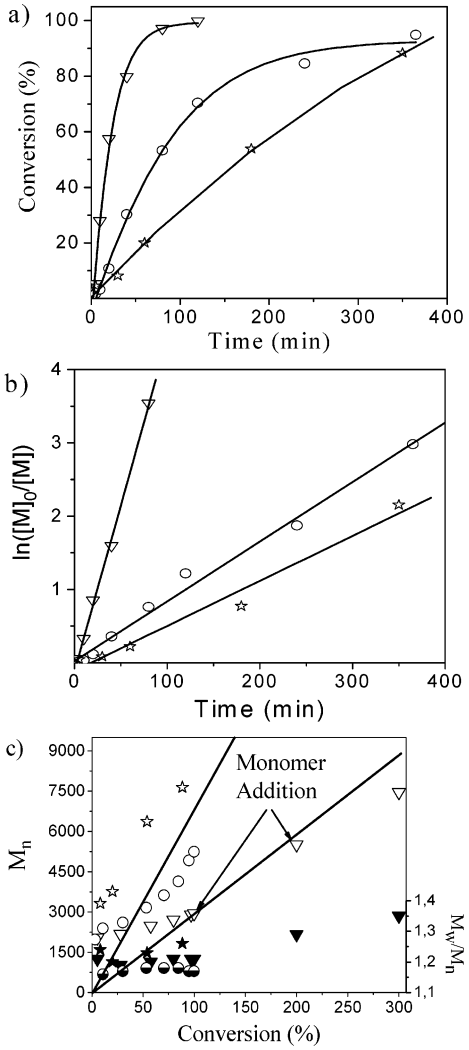


Figure 1. (a) Conversion vs time (b) ln([M]$_0$/[M]) vs time (where M is the monomer) and (c) number-average molar mass (M_n), molar mass distribution (M_w/M_n) vs conversion plots for the polymerization of *p*-methoxystyrene (pMOS) with 1-(4-methoxyphenyl)ethanol (**1**)/B-(C_6F_5)$_3$ initiating system in CH_3CN:CH_2Cl_2 1:1 (v/v) at 20 °C: [B(C_6F_5)$_3$] = 0.026 M; [pMOS] = 0.43 M. Initiator concentrations: (▽, ▼) [**1**] = 0.019 M, [pMOS]$_2$ = [pMOS]$_3$ = 0.41 M; (○,◒) [**1**] = 0.0085 M; (☆,★) no initiator. The straight lines correspond to theoretically calculated M_n values.

The number-average molar mass and molar mass distribution vs conversion are shown in Figure 1c. Contrary to the styrene case,[32] the polymerization of *p*-methoxystyrene is living even in the absence of initiator; i.e., M_n of polymers increases with conversion (Figure 1c). When adding an initiator, the M_ns of the poly(*p*-methoxystyrene)s increased in direct proportion to monomer conversion, but experimental M_ns were closer to the calculated values only at the later stage of the polymerization, indicating that slow initiation relative to propagation or slow interconversion between reversible terminated and active species take place. Indeed, even if initiator consumption is slow, **1** has almost the same structure (reactivity) as the reversible terminated polymer chains; the polymerization is thus first order with respect to monomer[37,38] even if the experimental M_ns are considerably higher than the theoretical ones at the early stages of the reaction.[38] (It was shown before that a first-order plot cannot be linear if more or less active initiators than the reversible terminated polymer chains were used.[39,40]) Consider-

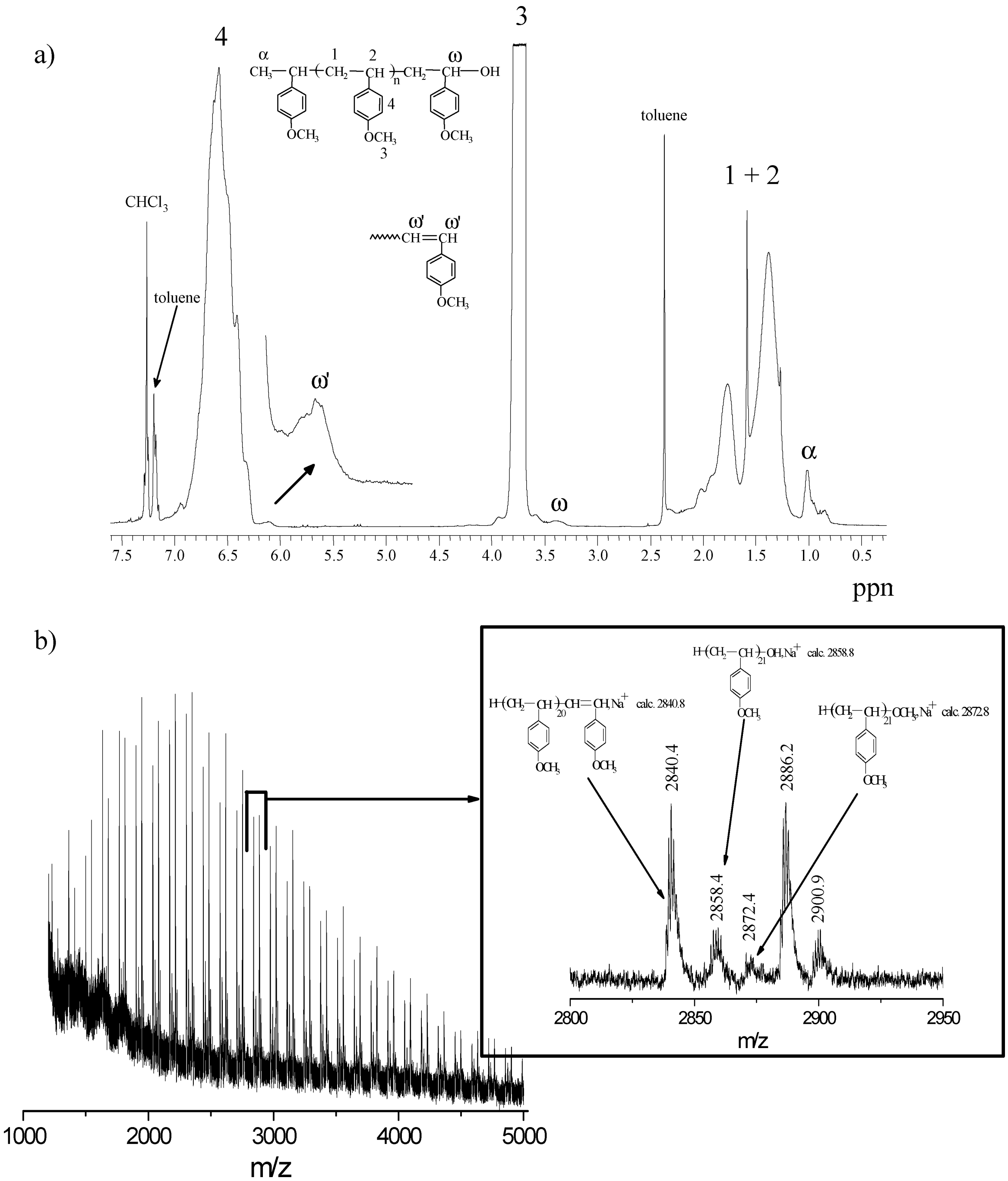


Figure 2. (a) ^{1}H NMR and (b) matrix-assisted laser desorption ionization time-of-flight mass spectra of poly(*p*-methoxystyrene) obtained by *p*-methoxystyrene (pMOS) polymerization with the 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ initiating system in CH_3CN:CH_2Cl_2 1:1 (v/v) at 20 °C: [**1**] = 0.019 M; [$B(C_6F_5)_3$] = 0.026 M; [pMOS] = 0.43 M. M_n(SEC) = 2800 g mol^{-1}.

ing the well-known ability of $B(C_6F_5)_3$ and its derivatives to form weakly coordinating counteranions,[41] it is obvious that rate constant of ion-pair collapse should be considerably smaller than the rate constant for propagation; i.e., slow interconversion between reversible terminated and active species indeed operates in the investigated system.

At the beginning of the polymerization the experimental M_ns for different initiator concentrations are very similar (below 30% conversion, Figure 1c), which seems to indicate that the same number of monomer units (about 15) were added to the initiating complex during the first ionization−propagation−termination cycle; indeed, it was previously shown that the number of monomer molecules (run number, RN) added to the initiator during one ionization−termination cycle, i.e., the initial M_n, only slightly increases with the decrease in the initiator concentration, at least at "high" polymerization temperature.[42] Slightly higher run number in the case of polymerization of *p*-methoxystyrene without initiator (RN ~ 20) can be due to the low initial concentration of active species arising from water.

At the lowest initiator concentration, the experimental M_ns are always below the theoretical line, probably because of competitive proton initiation via water, whereas for a larger initiator content, the molar masses reach the corresponding line at final conversion (Figure 1c). In addition, polymers exhibited very narrow molar mass distribution ($M_w/M_n \leq 1.2$) for both initiator concentrations. Besides, MWD slightly broadens with monomer conversion, probably because initiation by water is slow relative to propagation but still running throughout polymerization.

Table 2. Cationic Polymerization of *p*-Methoxystyrene (pMOS) in Dispersed Media with the 1-(4-Methoxyphenyl)ethanol (1)/$B(C_6F_5)_3$ Initiating System[a]

entry	V_{H_2O} (mL)	V_{CH_3CN} (mL)	W_{pMOS} (g)	time (h)	temp (°C)	conv (%)	$M_{n,exp}$[e] (g mol^{-1})	$M_{n,theor}$[e] (g mol^{-1})	M_w/M_n
1	5		0.48	23	20	99	2880	4435	1.75
2[b]	5		0.6	2	20	92	3800	5080	1.85
3[b]	5[c]		0.6	20	20	100	4380	5510	1.77
4	5[c]		0.59	23	20	100	3480	5410	1.86
5[d]	5[c]		0.59	21	20	98	3440		2.00
6[b]	5[c]	1	0.6	20	20	8	2500	580	2.81
7[b]	5[c]	1	0.3	20	35	19	1050	660	1.68
8	3[c]	2	0.58	50	40	8	1730	575	2.00
9	2	3	0.59	48	40	64	1440	3525	1.21
10	3	2	0.59	18	40	95	2830	5155	1.32

[a] Reaction conditions: **1** = 0.017 g; $B(C_6F_5)_3$ = 0.06 g. [b] $B(C_6F_5)_3$ = 0.14 g. [c] Buffer pH = 7 (NaH_2PO_4 3.6 g/L, Na_2HPO_4 7.2 g/L, NaCl 4.3 g/L, H_2O 1 L) instead of H_2O. [d] Without initiator. [e] Experimental ($M_{n,exp}$) and theoretical ($M_{n,theor}$) number-average molar mass; $M_{n,theor} = [pMOS]_0/[\mathbf{1}]_0 \times 134 \times$ conv + 135(head group) + 17(tail group).

The living nature of the *p*-methoxystyrene polymerization with the **1**/$B(C_6F_5)_3$ initiating system was further studied by investigating chain extension experiments; two feeds of *p*-methoxystyrene were sequentially added to the polymerization mixture before the initial charge of the monomer had been completely consumed. The additional monomer smoothly polymerized without any significant changes in the polymerization rate. As shown in Figure 1c, the molar mass doubled and tripled after addition of second and third feed of *p*-methoxystyrene and kept close from the theoretical values. The molar mass distribution also remains narrow ($M_w/M_n \sim 1.2-1.35$) but slightly broadens after the addition of the new feeds of the monomer, indicating that some irreversible termination reactions start to occur under monomer-starved conditions.

To summarize, the polymerization of *p*-methoxystyrene by the **1**/$B(C_6F_5)_3$ initiating system in CH_2Cl_2:CH_3CN 1:1 (v/v) at 20 °C, in open air and without any drying of the reagents, is living, since in these conditions chain transfer and termination reactions are not visible, at least up to 4000 g mol^{-1}. We also assume that acetonitrile can coordinate with $B(C_6F_5)_3$ to tune the Lewis acidity of the catalyst, allowing a better control of the polymerization rate and thus the livingness of the polymerization (a detailed discussion about the role of acetonitrile in polymerization is given below).

Polymer Characterization. The microstructure of the obtained polymers was studied by ^{1}H NMR spectroscopy and matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS). Figure 2a shows the ^{1}H NMR spectrum of poly(*p*-methoxystyrene) obtained by polymerization in the mixture of CH_2Cl_2 and acetonitrile. The resonances at 1.15−2.4, 3.6−3.9, and 6.2−7.1 ppm are ascribed to the main-chain methylene and methine (1 + 2), $-OCH_3$ (3), and phenyl (4) protons, respectively. The resonance at 0.8−1.1 ppm arises from the CH_3- (α) protons at the α-end, and the resonance at 3.4 ppm corresponds to $-CH-OH$ (ω) protons at the ω-end.[23,29] The number-average molar mass of the polymer, determined by ^{1}H NMR from the peak intensity ratio of the well-resolved methyl (α) to the phenyl protons (4) (M_n = 2815 g mol^{-1}), is in good agreement with M_n measured by size exclusion chromatography (M_n = 2800 g mol^{-1}) and with the calculated value based on the assumption that one chain is formed from one molecule of initiator (M_n = 2745 g mol^{-1} at 96% final conversion).

MALDI-TOF-MS spectroscopy analyses were then performed to investigate the effect of long time aging on the chain-end structure of poly(*p*-methoxystyrene). The same polymer was kept during an additional 6 h under monomer-starved conditions (Figure 2b).

The main population corresponds to polymer chains cationized by sodium and bearing a double bond as terminal group (M_n = 2840.4 g mol^{-1}). The two next populations are easily attributed to polymer chains bearing an hydroxyl (M_n = 2858.4 g mol^{-1}) and methoxy (arising from methanol precipitation of propagating chains, 2872.4 g mol^{-1}) ω-end groups.[29] The two last peaks, located at M_n = 2886.2 and 2900.9 g mol^{-1}, are ascribed to the acetonitrile adducts (≈+41 g mol^{-1}) of polymers again terminated by a double bond and an hydroxyl group, respectively.[43] We also confirmed the decay of the chain ends after the complete consumption of monomer by taking **1** as a model molecule for the growing poly(*p*-methoxystyrene) chains and looking at its decomposition in the presence of $B(C_6F_5)_3$ in a CH_3CN:CH_2Cl_2 mixture. ^{1}H NMR spectroscopy revealed that **1** forms *p*-methoxystyrene and oligomeric chains bearing both hydroxyl and double bond at the ω-end (Figure S3).

B. Polymerization in Dispersed Media. Table 2 summarizes the data obtained for the *p*-methoxystyrene polymerization with the **1**/$B(C_6F_5)_3$ initiating system in aqueous dispersed media. We chose here to work in surfactant-free conditions, to simplify the plot of reactions, and discriminated polymerizations carried out in suspension, i.e., only in mixtures of monomer and water (or buffer, vide supra), from those in dispersion, where a water-miscible solvent, i.e., acetonitrile, has been introduced. In terms of colloidal aspect and stability, the former system gave poorly stable emulsions, which phase-separate rapidly when stopping stirring. The dispersion systems gave milky solutions, entailing very slow creaming at zero agitation.

Polymerization in Aqueous Suspension. When the polymerization proceeded in water or in a phosphate buffer set at pH = 7, used as an attempt for suppressing protic initiation,[29] polymers with lower M_n than theoretical ones ($M_{n,theor} \sim 5500$ g mol^{-1}) and broad MWD ($M_w/M_n \sim 1.8$) were formed (entries 2−4 in Table 2).

The polymerization is slower in buffer in comparison with water, but the polymerization still proceeds even in the absence of an initiator, which means that protic initiation can be only partially suppressed in these conditions (entry 5 in Table 2, Figure 3a). However, in all these instances polymerization is not living: the molar mass rises quickly to a maximum value (at about 20−30% conversion) and then almost does not change (or even decreases) with conversion. MWDs of obtained polymers are near two, indicating that initiation and transfer reactions via water take place (Figure 3b). SEC traces of various samples normalized by their conversion are shown in Figure 3c. The peak maximum does not shift with conversion, and molar mass distributions broaden during polymerization. These data again clearly evidence that only oligomers were formed

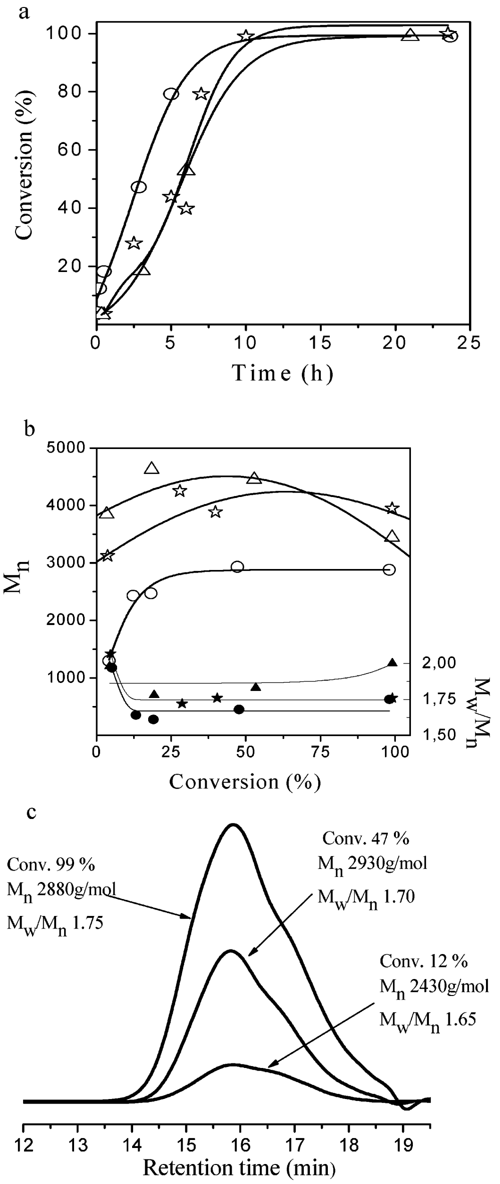


Figure 3. (a) Conversion vs time, (b) number-average molar mass (M_n), molar mass distribution (M_w/M_n) vs conversion dependences for the *p*-methoxystyrene (pMOS) polymerization with 1-(4-methoxyphenyl)ethanol (**1**)/B(C_6F_5)$_3$ at 20 °C: [**1**] = 0.018 M; [pMOS] = 0.78 M ([pMOS] = 0.65 M for the polymerization in water); [B(C_6F_5)$_3$] = 0.022 M. Solvent: (○, ●) water; (☆, ★) buffer pH = 7; (△, ▲) buffer pH = 7, no initiator. (c) SEC traces for the *p*-methoxystyrene polymerization with **1**/B(C_6F_5)$_3$ initiating system in water.

by interfacial polymerization similarly to previously reported systems;[23,24,26,29] i.e., polymerization is not living.

Polymerization in Aqueous Dispersion. Different reaction conditions were tested to establish the influence of the concentration of the cosolvent, namely acetonitrile, on the polymerization (entries 6−10 in Table 2). The polymerization was slowed down considerably when a small amount of acetonitrile was introduced (entries 6 and 7 in Table 2). Typically, in the mixture of water, or buffer pH = 7, with acetonitrile, the polymerization proceeds significantly only at higher temperature ($T \sim 40$ °C), and an inhibition period and polymers with low molar mass are obtained. Interestingly, the M_ns slightly increase, but MWDs of polymer broaden with conversion (see Figure S4). The peak maximum shifts with conversion, but distributions overlap in the low molar mass region: again, conventional chain transfer-dominated cationic polymerization takes place here.

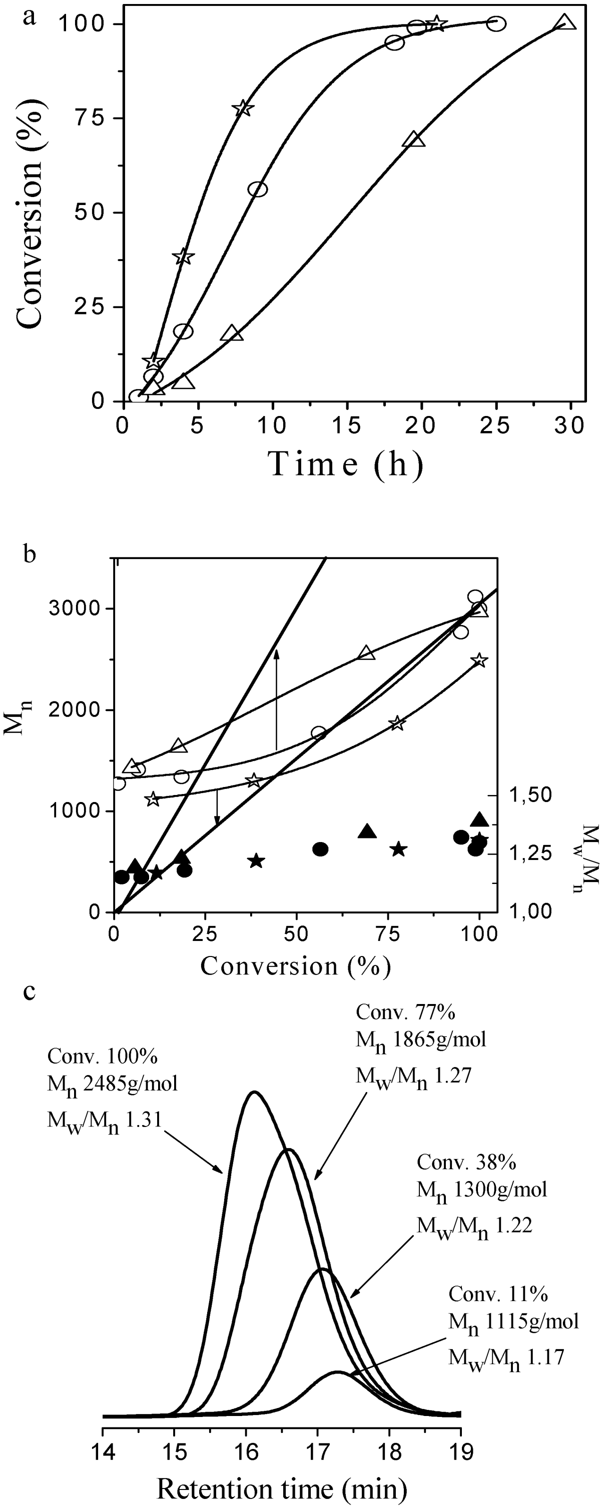


Figure 4. (a) Conversion vs time, (b) number-average molar mass (M_n), molar mass distribution (M_w/M_n) vs conversion plots for the *p*-methoxystyrene polymerization with 1-(4-methoxyphenyl)ethanol (**1**)/B(C_6F_5)$_3$ at 40 °C in water:acetonitrile 3:2 (v/v): [pMOS] = 0.78 M; [B(C_6F_5)$_3$] = 0.022 M. Initiator concentrations: (○, ●) [**1**] = 0.018 M; (☆, ★) [**1**] = 0.034 M; (△, ▲) no initiator. The straight lines correspond to theoretically calculated M_n values. (c) SEC traces of poly(*p*-methoxystyrene)s for increasing conversion with **1**/B(C_6F_5)$_3$ at 40 °C in water:acetonitrile 3:2 (v/v): [**1**] = 0.034 M; [pMOS] = 0.78 M; [B(C_6F_5)$_3$] = 0.022 M.

The most promising results have been obtained when larger acetonitrile vs water contents (2:3 v/v) were introduced in the recipe. Figure 4a shows the conversion−time variations for *p*-methoxystyrene polymerization with the **1**/B(C_6F_5)$_3$ initiating

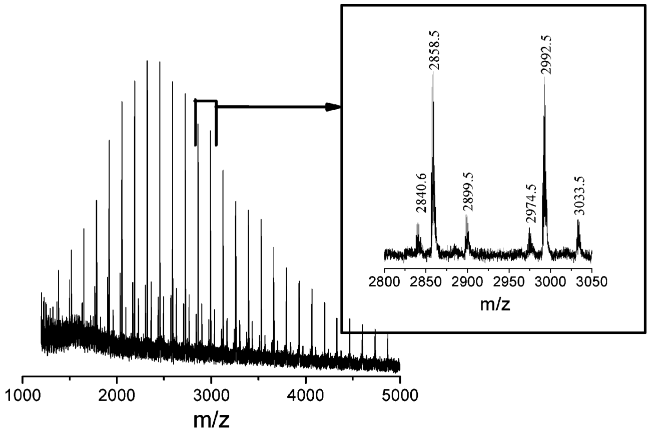


Figure 5. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry spectrum of poly(*p*-methoxystyrene) obtained by *p*-methoxystyrene (pMOS) polymerization with 1-(4-methoxyphenyl)-ethanol (**1**)/$B(C_6F_5)_3$ initiating system in H_2O:CH_3CN 3:2 (v/v) at 40 °C: [**1**] = 0.017 M; [$B(C_6F_5)_3$] = 0.023 M; [pMOS] = 0.78 M. M_n(SEC) = 2830 g mol^{-1}.

system in this solvent mixture and at different initiator concentrations. Basically, the polymerization proceeds with an induction period of ~1−2 h, and the polymerization rate increases with increasing the initiator concentration. Again, the polymerization occurs in the absence of initiator, indicating that proton initiation via water takes place. Therefore, it is not surprising that experimental M_ns are systematically below the theoretical ones, especially at lower initiator concentration (Figure 4b), due to competitive proton initiation via water. Besides, the molar mass of the polymers hardly changes at the beginning but increases slowly but continuously at the end of the polymerization. On the contrary, the MWDs of the obtained polymers increase up to ~50% conversion and then remains almost constant up to full conversion (Figure 4b).

The SEC traces of polymers normalized by their conversion overlap in the low molar mass region at the beginning of the reaction, although the peak maximum shifts with conversion (Figure 4c). According to the literature,[23,24,26,29] this, along with observed M_n and MWD evolutions with conversion at the beginning of the polymerization, is the typical feature of the interfacial polymerization, when the chains rapidly grow to the critical DP at the interface and then penetrate inside the droplets and stop propagating.[23,26,28,29] However, in opposition to all systems previously described,[20−26,29] the polymerization then goes on in a living manner, *inside* the monomer droplets, up to M_n 3000 g mol^{-1}. Indeed, the hydroxyl-terminated chains are reactivated by the Lewis acid to give back the active center and to maintain propagation. The overall shift of the SEC curves (without overlapping over 50% conversion) as well as the sharp increase of M_n with conversion without any significant changes in MWD (Figure 4b,c) confirms this polymerization scheme. To our knowledge, this is the first example of living cationic polymerization in aqueous media.

Polymer Characterization. MALDI-TOF-MS spectroscopy analyses were performed to investigate the chain-end structure of poly(*p*-methoxystyrene)s obtained in aqueous dispersion. Almost pure hydroxyl-terminated poly(*p*-methoxystyrene)s were formed even after aging during several hours under monomer-starved conditions, contrary to solution polymerization systems, where a considerable chain degradation was observed under similar time conditions (see Figures 2 and 5). The main population corresponds to polymer chains cationized by sodium and bearing an hydroxyl as terminal group (M_n = 2858.5 g mol^{-1}). The other two minor populations are attributed to polymer chains bearing a double bond at the ω-end (M_n = 2840.6 g mol^{-1}) and adduct of acetonitrile with poly(*p*-methoxystyrene) possessing an hydroxyl as terminal group (M_n = 2899.5 g mol^{-1}), respectively.[25]

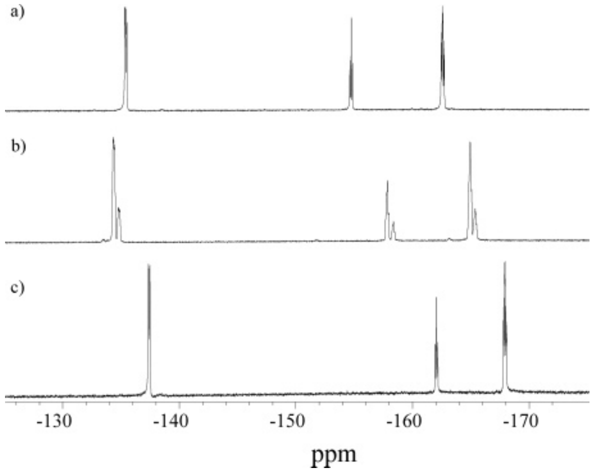
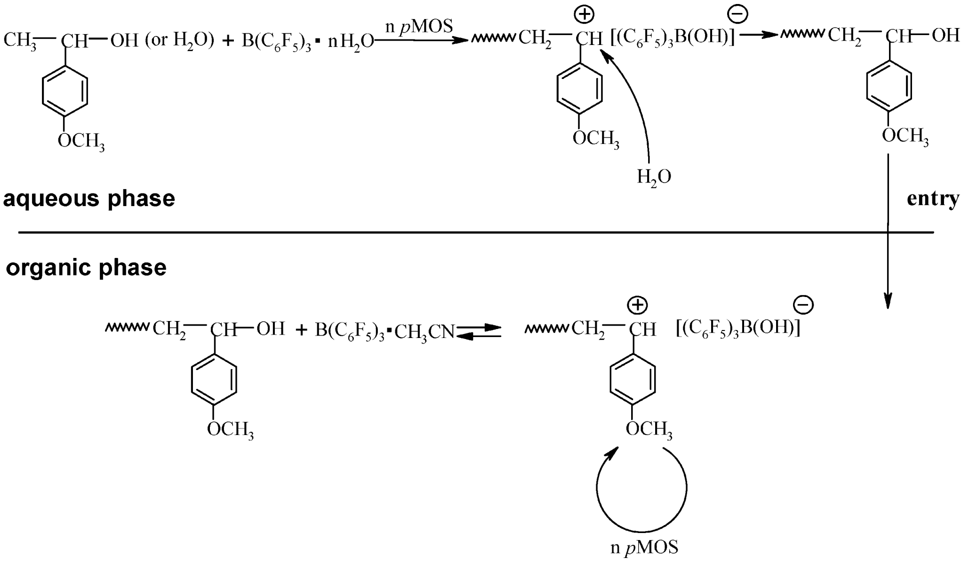


Figure 6. ^{19}F NMR spectra of $B(C_6F_5)_3$ in (a) $CDCl_3$, (b) acetonitrile-*d*$_3$, and (c) mixture of acetonitrile-*d*$_3$ and D_2O (2:3 v/v).

C. Polymerization Mechanism. $B(C_6F_5)_3$ is a strong Lewis acid;[33,35,36] therefore, the polymerization of *p*-methoxystyrene in solution (CH_2Cl_2, toluene) proceeds rapidly and in uncontrolled fashion. Considering that $B(C_6F_5)_3$ complexes adventitious water in the system ($B(C_6F_5)_3 \cdot nH_2O$),[36] the water-free Lewis acid remaining in the system leads to fast polymerization and numerous side reactions (hydroxyl abstraction, indanyl cyclizations, etc.). Generally, the polymerization of the reactive monomers such as vinyl ethers and *p*-methoxystyrene proceeds in a living fashion in the presence of weak Lewis acids.[8,44] Another popular method to modulate the Lewis acidity of the co-initiator is the addition of electron donor components to the system[2,45−50] (excess of electron donor is often required for the polymerization of reactive monomers[48−50]). Acetonitrile clearly plays this important role in both solution and aqueous suspension by competing with water in complexing the Lewis acid, without much decrease of the catalytic activity of the final complex.

To confirm this point, ^{19}F NMR analyses of the Lewis acid in $CDCl_3$, acetonitrile-*d*$_3$, and mixture of CD_3CN with D_2O were performed and are presented in Figure 6. There are three signals in the spectrum of $B(C_6F_5)_3$ in $CDCl_3$ due to the *ortho* (δ −135.35 ppm), *para* (δ −154.77 ppm), and *meta* (δ −162.6 ppm) fluorine atoms, respectively (Figure 6a). However, the signals of *ortho* and *para* fluorines show a significant shift upfield (3-7 ppm) in comparison with the resonances of anhydrous $B(C_6F_5)_3$ in dry CD_2Cl_2.[35] The comparison of our spectrum with the spectra of $B(C_6F_5)_3 \cdot H_2O$ and $B(C_6F_5)_3 \cdot 2H_2O$[35] (almost identical) allows us to conclude that $B(C_6F_5)_3 \cdot nH_2O$ (n = 1−3[35]), not $B(C_6F_5)_3$, is actually present primarily in the polymerization system when undried reactants are utilized. The use of acetonitrile-*d*$_3$ instead of $CDCl_3$ leads to the further upfield shift of signals of the *meta* and *para* fluorines (the signal of *ortho* fluorines often remains almost constant or showing a smaller shift in the opposite direction[36]) due to the complexation of acetonitrile with Lewis acid. The splitting of the signals in CD_3CN indicates that the $B(C_6F_5)_3 \cdot CD_3CN$ complex exists in equilibrium with the complex of $B(C_6F_5)_3$ with water. In the spectrum of the mixture of D_2O with acetonitrile-*d*$_3$ the peaks were progressively shifted upfield in comparison with the spectrum in acetonitrile-*d*$_3$, indicating the formation of a much stronger complex in the presence of a huge amount of water.

Scheme 2. Proposed Mechanism for the *p*-Methoxystyrene Polymerization with 1/B(C_6F_5)$_3$ Initiating Systems in a Water:Acetonitrile 3:2 (v/v) Mixture



We have shown that a high excess of strongly coordinating solvent as acetonitrile to the Lewis acid is required for the living polymerization of *p*-methoxystyrene with the **1**/B(C_6F_5)$_3$ initiating system to occur in solution. Taking into account that the complexes of B(C_6F_5)$_3$ with H_2O and CH_3CN are labile and the ligands exchange proceeds by dissociative mechanism,[36] we assume that the main function of acetonitrile in the investigated system is to suppress the dissociation of the complexes of B(C_6F_5)$_3$. In this case, only a small amount of B(C_6F_5)$_3$, resulting from the dissociation of B(C_6F_5)$_3$·CH_3CN or B(C_6F_5)$_3$·$n$$H_2O$, takes part in the initiating and propagating steps. This leads to a slowdown of the polymerization rate and to a suppression of side reactions. Similar conclusions have been proposed for the styrene polymerization co-initiated by $TiCl_4$[51] and $AlCl_3$[52] where an excess of electron donor to the Lewis acid was added.

Using acetonitrile in excess also responds to three other requirements to implement living polymerization. First, when a high excess of acetonitrile compared to water is present in the system (for instance, in the case of *p*-methoxystyrene polymerization in a mixture CH_3CN:CH_2Cl_2 1:1 v/v), acetonitrile can displace the water in the B(C_6F_5)$_3$·$n$$H_2O$ complexes, thereby suppressing the competing protic initiation from the strong Brönstedt acid $H_3O^+[B(C_6F_5)_3OH]^-$. Also, the complexation of the Lewis acid by acetonitrile is surely in favor of its partitioning toward the organic phase. Finally, acetonitrile or its complex with B(C_6F_5)$_3$, can interact with growing chains to modify their reactivity. According to Iván,[2,53] the interaction of the Lewis acid−nucleophile complex with active centers plays a critical role in the achievement of living cationic polymerization.

A proposed mechanism for the polymerization of *p*-methoxystyrene in aqueous dispersion, i.e., in a mixture of water with acetonitrile, using the **1**/B(C_6F_5)$_3$ initiating system is proposed in Scheme 2. Initiation of chains occurs either from **1** or water at the particle interface. Once initiated, each chain propagates until termination by water molecule.[23,26] When the oligomers terminated by water become too hydrophobic, they enter inside the particles.[23,26,54] Basically, at this stage of the polymerization only short oligomers are formed (DP ~ 8−10, see also for detail Figure 4b). However, in contrast to all previously described systems,[20−26,29] the polymerization of *p*-methoxystyrene can proceed further inside monomer droplets due to the reactivation of hydroxyl-terminated chains. Such a striking result was achieved due to the possibility to drive the catalyst inside the particles in the form of its complex with acetonitrile, less hydrophilic that the complexes of B(C_6F_5)$_3$ with water with which it competes. Such penetration of the catalyst in the organic phase is surely facilitated by the fact that acetonitrile partitions equally between the water and the monomer phases. More investigations are needed to evaluate the multiple roles that acetonitrile plays in this formulation.

Conclusion

The **1**/B(C_6F_5)$_3$ initiating system induces the living cationic polymerization of *p*-methoxystyrene in a mixture of CH_2Cl_2 and acetonitrile at 20 °C in open air and in the presence of water. The polymerization proceeds via reversible activation of C−OH terminus and poly(*p*-methoxystyrene)s with controlled molar mass and narrow molar mass distribution were obtained, although undesirable initiation by protic impurities takes place. However, the polymer chain ends are unstable and undergo acid-catalyzed dehydration under monomer-starved conditions, which leads to some loss of functionality.

The controlled/living aqueous dispersion polymerization of *p*-methoxystyrene using the same initiating system was successfully performed in a mixture H_2O:CH_3CN 3:2 (v/v) for the first time. Basically, the polymerization proceeds in two stages. The process begins at the interface where the chains propagate up to critical DP and then penetrate inside the particles on the first stage. On the second one, the hydroxyl-terminated poly(*p*-methoxystyrene)s are reactivated by B(C_6F_5)$_3$, which enters into monomer droplets, most probably, in the form of complex with acetonitrile. Even if undesirable initiation by protic impurities lowered the molar mass in comparison with theoretical ones, the M_n of polymers increased with conversion, albeit up to 3000 g mol^{-1}. In addition, almost pure hydroxyl-terminated poly(*p*-methoxystyrene)s were formed by aqueous polymerization in contrast to the solution process.

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Supporting Information Available: Plot of M_n and M_w/M_n vs conversion, SEC traces of poly(*p*-methoxystyrene)s, ^{1}H NMR spectra of pristine and degraded 1-(4-methoxyphenyl)ethanol, and SEC traces for poly(*p*-methoxystyrene) chains obtained in aqueous suspension. This material is available free of charge via the Internet at http://pubs.acs.org.

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