Cationic Polymerization of Styrene Derivatives and Cyclopentadiene Catalyzed by $B(C_6F_5)_3$ in Aqueous Media: Comparison of Suspension, Emulsion and Dispersion Processes

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Summary: The cationic polymerization of styrene derivatives [*p*-methoxystyrene (*p*MOS), *p*-hydroxystyrene (*p*HS), styrene (St)] and cyclopentadiene (CPD) using $B(C_6F_5)_3$-based initiating systems in aqueous media is reported, focusing specifically on the influence of various additives (surfactant, solvent) on the control of the polymerization rate and molar masses. 1-(4-Methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ system induced living *dispersion* (in solvent/water mixture, without surfactant) cationic polymerize-tion of *p*MOS and *p*HS, affording polymers which M_n*s* increased in direct proportion to monomer conversion ($M_n \leq 4500\ g\ mol^{-1}$) and which exhibited rather narrow molecular weight distributions ($M_w/M_n \leq 1.5$). Polymerization of St and CPD in *suspension* (in water without surfactant) proceeded uniquely through activation of the initiator followed by irreversible termination by water giving oligomers with $M_n \leq 2000\ g\ mol^{-1}$ and $M_w/M_n \leq 2.0$. Besides, *p*HS also polymerized in a living fashion under *emulsion* (in micellar aqueous solutions) conditions ($M_n \leq 4500\ g\ mol^{-1}$; $M_w/M_n \leq 1.5$) using either BRIJ® 97 or hexa-decyltrimethyl-ammonium bromide (CTAB) as surfactants, whereas conventional non-living cationic polymerization occurred with *p*MOS (using BRIJ® 97 or CTAB as surfactants) and CPD (using dodecylbenzenesulfonic acid, DBSA).

Keywords: $B(C_6F_5)_3$; cationic polymerization; emulsion polymerization; suspension and dispersion polymerization

Introduction

Water has long been used as an initiator in conventional cationic polymerization of various vinyl monomers in conditions where the concentration of Lewis acid (LA) co-initiator was much higher than water concentration.[1,2] For instance, water is known to initiate the living cationic polymerization of such monomers as isobutyl vinyl ether[3] or *p*-methoxystyrene.[4] On the other hand, when water is in similar contents as the proper initiator in living polymerization systems, control over molecular weight (M_n) diminishes and bimodal molecular weight distributions (MWD*s*) are observed.[5] Moreover, since most of conventional LA*s* are decomposed in the presence of excess water, strictly anhydrous conditions are generally required to conduct controlled cationic polymerizations.

This pessimistic outlook was shattered by the discovery of the cationic polymerization of *p*-methoxystyrene (*p*MOS) in *aqueous media* using $Yb(OTf)_3$ as catalyst in 1999 by Sawamoto's team.[6] Since this first report, considerable advances in the field of cationic

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polymerization in aqueous media have emerged during the past ten years. In a recent review,[7] we have described the chronological evolution of the catalytic systems and proposed to divide them into five main groups: (i) strong Brønsted acids; (ii) lanthanide triflates; (iii) Lewis acid surfactant combined catalysts (LASC); (iv) $BF_3.OEt_2$; (v) aromatic borane-based catalysts. Fatty strong acids, so-called INISURF for their concomitant role of *ini*tiator and *surf*actant, and lanthanide triflates were first used to tailor the suspension and emulsion cationic polymerizations of such reactive monomers as *p*MOS and vinyl ethers. The main features of these polymerization processes were found to be: (i) the location of all reactions (initiation, propagation and termination) at the particle interface; (ii) the observed limitation of molecular weight of synthesized polymers ($M_n < 4{,}000\,g\,mol^{-1}$), assigned to the "critical DP" effect and related to the entry of oligomers inside the particles when they become too hydrophobic. The next generation of catalysts (LASC), allowed shifting the polymerization locus from the interface to the inside of the monomer droplets and, in turns, to produce quite high molecular weight poly(*p*-methoxystyrene)s ($M_n \sim 40{,}000\,g\,mol^{-1}$). The fourth generation, $BF_3.OEt_2$-based initiating systems, showed great potential in controlling the cationic polymerization of styrene derivatives in "wet" solution ($1 < [H_2O]/[LA] < 100$), but, however, could not be applied in aqueous media due to catalyst decomposition.[8]

In this article we present our recent results on the cationic polymerization of styrene derivatives and cyclopentadiene in the presence of such water-tolerant Lewis acid as $B(C_6F_5)_3$ in aqueous media, i.e. in suspension, dispersion and emulsion processes. Particularly, the *p*-hydroxystyrene polymerization is described for the first time using $B(C_6F_5)_3$ as the catalyst.

Experimental Part

Materials

1-(4-Methoxyphenyl)ethanol (Aldrich, 99%), $B(C_6F_5)_3$ (Alfa Aesar, 97%), *p*-methoxystyrene (Alfa Aesar, 98%), *p*-acetoxystyrene (Aldrich, 97%), acetonitrile (Carlo-Erba, 99.5%), BRIJ®97 (Aldrich), hexadecyltrimethylammonium bromide (CTAB, Aldrich, 99%), Pluronic® F-68 (Aldrich), dodecylbenzenesulfonic acid (DBSA, Aldrich, ~90%), buffer pH = 7 (Carlo-Erba, composition: NaH_2PO_4 3.6g/L, Na_2HPO_4 7.2g/L, NaCl 4.3g/L, H_2O 1L) and methanol (Fluka, 99.8%) were used as received. *p*-Hydroxystyrene (*p*HS) was prepared from *p*-acetoxystyrene as reported previously[9] and then recrystallized from *n*-hexane. The purity of *p*HS was checked by ^1H NMR spectroscopy. Styrene (Acros, 99%) was distilled under reduced pressure before use. Cyclopentadiene (CPD) was obtained by the retro Diels-Alder reaction of dicyclopentadiene (Aldrich; > 95%) at 220 °C over calcium hydride.

Polymerizations

Polymerizations were carried out under air atmosphere in glass tubes. The polymerization in aqueous suspension or emulsion was carried out as follows: a suspension 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 containing appropriate amounts of initiator (1-(4-methoxyphenyl)ethanol), monomer, surfactant (for emulsion processes) and water. Specific reaction conditions for each monomer studied in this work are quoted in the figure captions. After a predetermined time, approximately 0.5 mL aliquots were withdrawn and poured out into excess methanol. The polymer was separated by centrifugation and dried in vacuum. Monomer conversions were determined gravimetrically. In the case of *p*HS polymerization, monomer conversion was determined from the concentration of residual monomer by ^1H NMR.

Characterization

Size-exclusion chromatography (SEC) was performed on a Spectra Physics apparatus with two columns (PL gel, 5 μm, 300 mm, 500 Å and 100 Å) and one pre-column (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 spectra were recorded in DMSO-d_6 or acetone-d_6 at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the solvent peak in reference to tetramethylsilane standard.

Results

p-Methoxystyrene

Figure 1 summarizes the data obtained when polymerizing *p*-methoxystyrene with 1-(4-methoxyphenyl)ethanol (**1**)/B(C_6F_5)$_3$ initiating system in aqueous suspension and emulsion, i.e. without or with surfactants, respectively.

We first compared the suspension cationic polymerization of *p*MOS in water or in a phosphate buffer set at pH = 7, which was thought to suppress protic initiation.[10] The polymerization was slower in buffer in comparison with water (lines 1 and 2 in Figure 1a), but the reaction still proceeded even in the absence of initiator,[11] which means that protic initiation was only partially suppressed in these conditions.

Cationic (hexadecyltrimethylammonium bromide (CTAB)) or such nonionic surfactant as BRIJ®97 almost did not influence the polymerization rate (lines 3 and 4 in Figure 1a), while Pluronic® F-68 retarded the polymerization significantly (line 5, Figure 1a), most probably through a strong complexation with B(C_6F_5)$_3$. The M$_n$*s* of obtained polymers, regardless of experimental conditions, increased at the beginning of the polymerization (up to 20–30% of conversion) and then leveled off at values in-between 4000–5000 g mol^{-1} (~2000 g mol^{-1} for CTAB and Pluronic® F-68) or even decreased with increasing monomer conversion (Figure 1b) because of chain transfer reactions. Molecular weight distributions were typically below 1.8 and did not change with monomer conversion (Figure 1b). Otherwise saying, only physicochemical issues governed the molecular weight of the polymers obtained, i.e. all above mentioned polymerizations were not controlled.

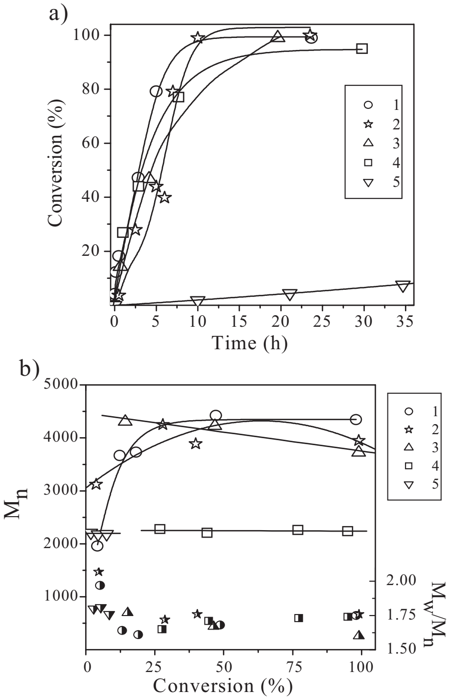

Figure 1.
(a) Conversion vs. time, (b) M$_n$ and MWD vs. conversion dependences for the *p*-methoxystyrene (pMOS) polymerization with 1-(4-methoxyphenyl)ethanol (**1**)/B(C_6F_5)$_3$ system at 20 °C in aqueous suspension or emulsion: [**1**] = 0.018 M; [pMOS] = 0.78 M; [B(C_6F_5)$_3$] = 0.05 M. Surfactant: (1) no surfactant; (2) no surfactant, buffer pH = 7 as reaction media (3) BRIJ®97, [BRIJ®97] = 0.016 M; (4) hexadecyltrimethylammonium bromide (CTAB), [CTAB] = 0.024 M; (5) Pluronic® F-68, [Pluronic® F-68] = 0.0033 M.

More promising results have been obtained in aqueous dispersion, i.e. in a water/acetonitrile (3:2 v/v) mixture: after an induction period of 1–2 h, the polymerization proceeded in a living fashion within one day affording polymers whose M$_n$*s* increased in direct proportion to monomer conversion up to 3000 g mol^{-1} with fairly narrow MWD*s* (M$_w$/M$_n$ ≤ 1.3) (see[11] for detailed conditions and results).

p-Hydroxystyrene

Taking into account the remarkable effect of acetonitrile in the achievement of the living cationic polymerization of *p*MOS in aqueous media,[11] the dispersion polymerization of *p*-hydroxystyrene (*p*HS) was performed in a mixture of phosphate buffer (pH = 7) and acetonitrile. According to Figure 2a, the polymerization of *p*HS with **1**/$B(C_6F_5)_3$ initiating system proceeded smoothly up to 80% conversion in 25 h, while in the absence of initiator the reaction was very slow and not completed even after 400 h. Importantly, in both cases the polymerization proceeded in a living fashion affording polymers whose M_n*s* increased in direct proportion to monomer conversion with relatively narrow MWD*s* ($M_w/M_n \leq 1.4$) (Figure 2b).

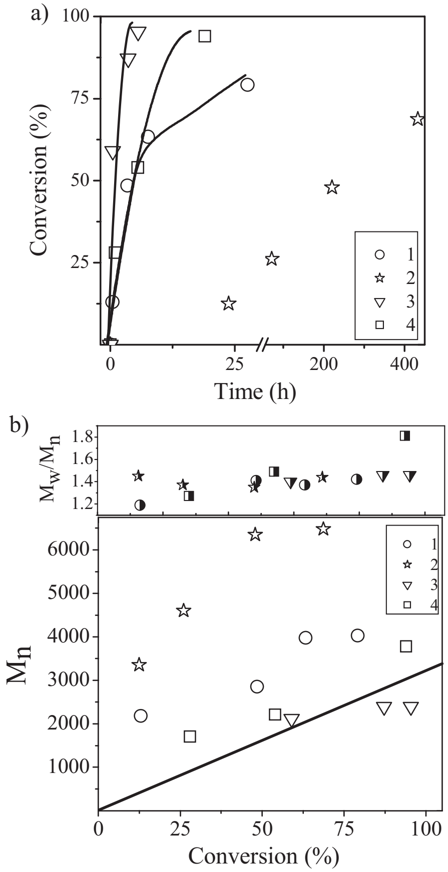

Figure 2.

(a) Conversion vs. time, (b) M_n and MWD vs. conversion dependences for the *p*-hydroxystyrene polymerization with 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ at 20 °C in aqueous dispersion or emulsion: [**1**] = 0.0125 M; [pHS] = 0.34 M; [$B(C_6F_5)_3$] = 0.04 M. Conditions: (1) buffer pH = 7/CH_3CN = 4/1 (v/v); (2) buffer pH = 7/CH_3CN = 4/1 (v/v), no initiator; (3) [BRIJ®97] = 0.028 M; (4) [CTAB] = 0.013 M. The straight line in (b) corresponds to theoretically calculated M_n values.

In contrast to *p*MOS emulsion polymerization, using cationic (CTAB) or nonionic (BRIJ®97) surfactant allowed to increase significantly the reaction rate (Figure 2a); this results is consistent with an increase of the surface area of droplets facilitating the transfer of co-initiator into the organic phase where the polymerization would take place. As shown in Figure 2b, the molecular weight of poly(hydroxystyrene)s obtained in aqueous emulsion increased in direct proportion to monomer conversion and experimental values of M_n correlated well with calculated ones, assuming that each initiator molecule generated one polymer chain. In addition, MWD stayed relatively narrow ($M_w/M_n \sim 1.4$) throughout the reaction. These results indicate that **1**/$B(C_6F_5)_3$ initiating system induced living cationic polymerization of *p*HS under aqueous emulsion conditions.

Styrene

The **1**/$B(C_6F_5)_3$ initiating system was also tested in the aqueous suspension polymerization of styrene (Figure 3).[12]

The increase in the initiator concentration led to an increase in the polymerization rate as well as in the maximum monomer conversion, up to almost full conversion at [**1**] = 0.074 M (Figure 3a). The molecular weights of polymers were rather low in these conditions and hardly changed with conversion for all initiator concentrations (Figure 3b). On the other hand the maximum value of M_n decreased and maximum value of MWD slightly increased with increasing initiator concentration (Figure 3b). A key observation here is related to the virtual absence of undesirable protonic initiation in aqueous suspension (line 4 in Figure 3a): this means that all

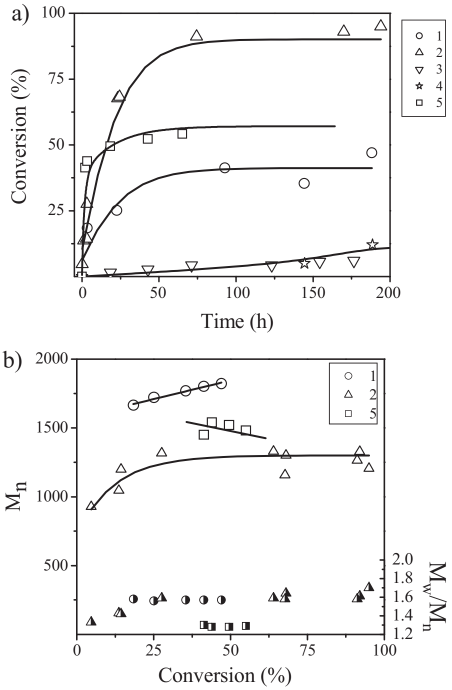

Figure 3.

(a) Conversion vs. time, (b) M_n and MWD vs. conversion dependences for the polymerization of styrene with **1**/$B(C_6F_5)_3$ initiating system at 20 °C in aqueous media: $[B(C_6F_5)_3] = 0.05$ M; [St] = 1.0 M; Initiator concentration: (1), (3) [**1**] = 0.017 M; (2), (5) [**1**] = 0.074 M; (4) no initiator. Surfactant: (1), (2), (4) no surfactant; (3) [BRIJ®97] = 0.016 M; (5) [DBSA] = 0.02 M. M_n and M_w/M_n were not reported for conditions (3) and (4), since the conversions in polymer were too low to perform SEC analyses.

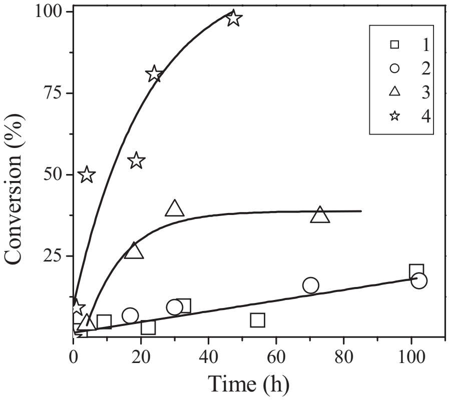

Figure 4.

Conversion vs. time dependences for the polymerization of cyclopentadiene at 20 °C with different initiating systems in aqueous media: [**1**] = 0.018 M; [CPD] = 1.0 M; $[B(C_6F_5)_3] = 0.027$ M; [DBSA] = 0.02 M. Initiating systems: (1) $B(C_6F_5)_3$ alone; (2) DBSA alone; (3) **1**/$B(C_6F_5)_3$; (4) DBSA/$B(C_6F_5)_3$.

macromolecules possess fragment of initiator at the α-end and hydroxy group at the ω-end, i.e. $F_n(\alpha) = F_n(\omega) \sim 1.0$.[12]

As shown in Figure 3a, the use of dodecylbenzenesulfonic acid (DBSA) as surfactant depressed the polymerization rate significantly (compare lines 2 and 5 in Figure 3a), while the addition to the system of such nonionic surfactant as BRIJ®97 led to no reaction (line 3, Figure 4). Moreover, the addition of DBSA did not influence significantly the molecular weight, but led to considerable narrowing of molecular weight distribution of obtained polymers (see Figure 3b). Note that the DBSA/$B(C_6F_5)_3$ catalytic system, i.e. without utilization of **1** as initiator, did not induce the cationic polymerization of styrene under aqueous emulsion conditions (~5% of conversion for 200 h).

To summarize, latexes of poly(styrene) with M_n up to 2000 g mol^{-1} and relatively narrow MWD ($M_w/M_n < 1.7$) were prepared during the styrene polymerization with **1**/$B(C_6F_5)_3$ initiating system under aqueous suspension and emulsion conditions.

Cyclopentadiene

Finally, $B(C_6F_5)_3$-based initiating systems were also investigated in the polymerization of cyclopentadiene (CPD) in aqueous suspension[13] or emulsion. Figure 4 shows that $B(C_6F_5)_3$ alone induced very slow cationic polymerization of CPD in aqueous suspension (>5% of conversion for 50 h). 1-(4-Methoxyphenyl)ethanol (**1**) in conjunction with $B(C_6F_5)_3$ initiated considerably faster suspension cationic polymerization of CPD; however, the monomer conversion did not exceed 40% due to a competitive dimerization reaction of the monomer into dicyclopentadiene.[13]

In order to suppress the extent of dimerization reaction of CPD we have

Chart 1.

Polymerization types (**A**: living polymerization; **B**: conventional non-living polymerization; **X**: controlled initiation, **Y**: competitive water co-initiation) and M_n and M_w/M_n typical values (in brackets) for $B(C_6F_5)_3$-catalyzed cationic polymerization of styrene derivatives and cyclopentadiene in aqueous media.

	*p*MOS	*p*HS	St	CPD
suspension	**B, Y**	–[b]	**B, X**	**B, X**
	(<5000; ≤1.8)		(<2000; ≤1.7)	(<1000; ≤2.2)
dispersion[a]	**A, Y**	**A, X**	–[c]	–[c]
	(<3000; ≤1.3)	(<4500; ≤1.5)		
emulsion	**B, Y**	**A, X**	**B, X**	**B, Y**
	(<5000; ≤1.8)	(<4500; ≤1.5)	(<2000; ≤2.0)	(<1500; ≤2.0)

[a] Mixture of acetonitrile with water or buffer pH=7.
[b] Polymerization was not investigated.
[c] Polymerization did not proceed.

tried to increase the reaction rate by using surfactants. In some instances, the addition of surfactants to the system indeed allowed to increase the rate of polymerization due to an increase of the surface area of droplets facilitating the transfer of co-initiator into the organic phase (see Figure 2). As shown in Figure 4, DBSA in combination with $B(C_6F_5)_3$ induced faster emulsion cationic polymerization of cyclopentadiene (~100% for 50 h), while DBSA alone (DBSA is known to initiate emulsion cationic polymerization of such reactive monomer as *p*MOS[14]) was not effective initiator under investigated conditions (>10% for 50 h).

Typically, during the cyclopentadiene polymerization in aqueous suspension or emulsion, oligomers with $M_n \leq 1500\,g\,mol^{-1}$ and broad MWD ($M_w/M_n < 2.2$) were obtained, but no regioselectivity of reaction (the content of [1,4] units in the polymer chains is around 50%) were observed under investigated conditions (not shown).

Conclusive Discussion

In this study, the cationic polymerization of styrene derivatives, namely *p*-methoxystyrene (*p*MOS), *p*-hydroxystyrene (*p*HS) and styrene (St), as well as cyclopentadiene (CPD) in the presence of $B(C_6F_5)_3$-based initiating systems in aqueous media (suspension, dispersion, emulsion) was described. Basically, 1-(4-methoxyphenyl)-ethanol (**1**)/$B(C_6F_5)_3$ initiating system induced living *dispersion* cationic polymerization of such reactive monomers as *p*MOS and *p*HS, while the less reactive monomers St and CPD did not polymerize at all under these conditions (see Chart 1). The same catalytic system initiated conventional cationic polymerization of *p*MOS in aqueous *suspension*, whereas in the case of St and CPD, polymerization was tailored by controlled initiation via **1**, fast propagation followed by irreversible termination by water. Besides, *p*HS could be also polymerized in a living fashion under aqueous *emulsion* conditions using both BRIJ®97 and hexadecyltrimethylammonium bromide (CTAB) as surfactants, whereas conventional non-living cationic polymerization occurred with *p*MOS (BRIJ®97, Pluronic® F-68 or CTAB were used as surfactants) and CPD (DBSA) (Chart 1).

Acknowledgements: This work was supported by a INTAS fellowship grant for young scientists (grant Nr 06-1000014-6127), NATO scientific and technical grant for exchange between east European countries and France and Belarusian Foundation for Fundamental Research (grant Nr X05MC-034).

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