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Cationic Polymerization of Vinyl Monomers in Aqueous Media: From Monofunctional Oligomers to Long-Lived Polymer Chains

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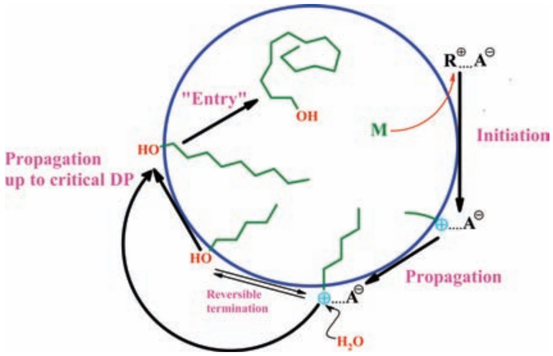

Polymer latexes are easily prepared on a multimillion ton scale in industry using free radical initiated emulsion and suspension polymerizations in water, a cheap, nonviscous, heat-controlling, and environmentally benign solvent. Until recently, researchers had done little investigation into ionic polymerization because even a small amount of water would easily deactivate the conventional catalysts used in these processes. In the last decade, however, cationic polymerization in aqueous media has emerged as a new and attractive method for controlling the polymerization reactions using mild experimental conditions.

This Account reviews the current science of and future outlook for cationic polymerization of vinyl monomers in aqueous media. We particularly emphasize the design and evolution of catalytic systems and the precision synthesis of functional polymers. Early work to tailor the suspension and emulsion cationic polymerizations of reactive monomers such as *p*-methoxystyrene and vinyl ethers used long-chain strong acids, called INISURF for their dual roles as initiators and surfactants, and lanthanide triflates. These polymerization processes shared two main features: (i) all reactions (initiation, propagation, and termination) occurred at the particle interface; (ii) synthesized polymers have limits on their molecular weight, attributed to the "critical DP" effect, related to the entry of oligomers inside the particles as they become increasingly hydrophobic.

The next generation of catalysts, named "Lewis acid—surfactant combined catalysts" (LASC), shifted the polymerization locus from the interface to the inside of the monomer droplets, allowing for the production of long polymer chains. Recently, catalytic systems based on boranes, (BF_3OEt_2, $B(C_6F_5)_3$, (C_6F_4-1,2-[$B(C_6F_5)_2$]), and (C_6F_4-1,2-[$B(C_{12}F_8)$]$_2$)), have shown great potential in controlling the cationic polymerization in "wet" solution, containing an excess of water relative to Lewis acid, or aqueous media of such industrially important monomers as styrene, cyclopentadiene, and even isobutylene.

Introduction

Since the discovery of the controlled/living cationic polymerization in the middle of the 1980s by the Higashimura[1] and Kennedy[2] groups, considerable attention has been paid to the utilization of this promising technique in the synthesis of well-defined homopolymers as well as different macromolecular architectures using three main groups of monomers: isobutylene, styrene and derivatives, and vinyl ethers.[3−7] A main drawback of

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the controlled cationic polymerization technique is the necessity to carry out the polymerization under strictly anhydrous conditions, since most conventional Lewis acids (LA) are decomposed in the presence of excess of water toward Lewis acid. Besides, the chlorinated solvents typically used in cationic polymerization are very toxic, and their utilization should be avoided.

Ionic polymerization in aqueous media may seem like a contradiction at a first sight with respect to the high water sensitivity of commonly used polymerization catalysts, such as Lewis acids, alkyllithiums, and Grignard reagents. Such drawback may not appear as a deadlock, according to the variety of organometallic catalysts that have been developed during the last two decades for the (co)polymerization of olefins (ethylene, α-olefins, dienes, norbornenes) in aqueous media.[8,9] Likewise, a number of catalytic systems were recently reported to promote the anionic polymerization of various cyclic and vinyl monomers in aqueous media (see refs 10−13 and references therein). Since the first report on the cationic polymerization of *p*-methoxystyrene (*p*MOS) in *aqueous media* using $Yb(OTf)_3$ in 1999 by Sawamoto et al.,[14] considerable advances in the field of cationic polymerization in aqueous media have emerged during the past ten years.

This Account presents the most recent developments in this field according to the nature of catalysts used: (i) INISURFs (for initiator/surfactant); (ii) lanthanide triflates; (iii) Lewis acid−surfactant combined catalysts (LASC); (iv) $BF_3 \cdot OEt_2$; (v) aromatic borane-based catalysts.

General Mechanism of Ionic Polymerization in Aqueous Media

The main feature of almost all ionic polymerizations in aqueous media is the fact that all main reactions, that is, initiation, propagation, and termination, first (and often exclusively) proceed at the particle interface (Figure 1).[10,11,15,16] Aqueous cationic polymerization is initiated by proton or carbocation derived from a strong/super acid or an initiator−Lewis acid pair, respectively. Propagation is very fast until water transfers to the growing carbocation to generate a nonpropagating chain $P_n{-}OH$ (Figure 1). Small oligomers accumulate at the interface at the beginning of the reaction and decrease the water content at the interface. This effect is responsible for the observed increase in molecular weight with increasing monomer conversion[10,15−17] and not a controlled polymerization process as first thought in early studies.[14,18−20] In rare cases however, the termination reaction via water is reversible and the polymerization proceeds in a controlled fashion (vide infra).[21]

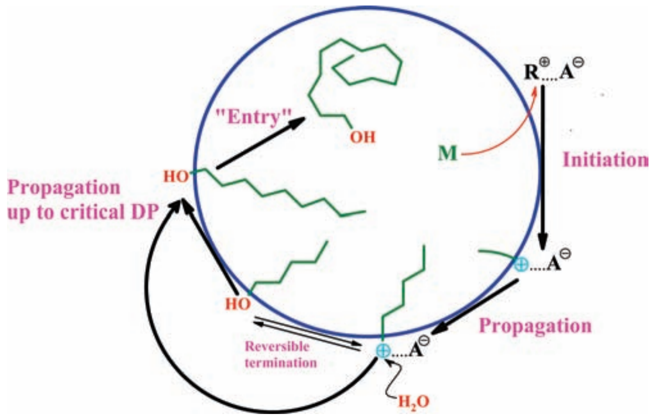


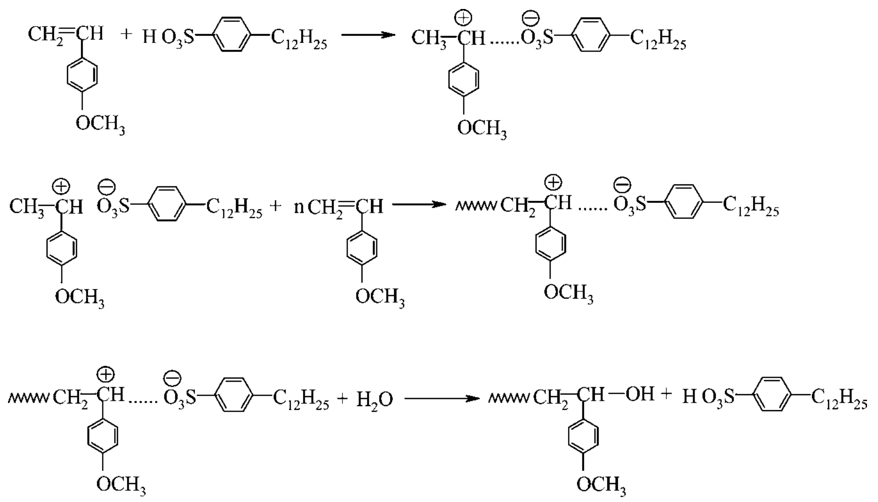
FIGURE 1. Simplified mechanism of the cationic polymerization in aqueous media [R = H, 1-(4-methoxyphenyl)ethyl; A = $C_{12}H_{25}(C_6H_4)SO_3^-$, $LA \cdot OH^-$; M = monomer].

Another striking feature of ionic polymerization in aqueous media is the systematic limitation of the polymer molecular weights, in best cases set at about 3000 g/mol. This so-called "critical DP" effect is ascribed to the entry of oligomers inside the particles when they become too hydrophobic and lose their surface activity (Figure 1).[10,11,15−17] In most cases, once the chains have penetrated inside the particles, they cannot undergo further propagation steps, since the catalyst is "locked" at the interface. We will show in this Account that recent works aimed (and sometimes succeeded) at driving the catalyst toward the core of the droplet/particle while keeping its Lewis acidity as high as possible to reactivate the oligomer chain-ends and produce living polymer chains.

First Generation: Strong Brønsted Acid Catalysts

In a series of publications,[16,22] dodecylbenzenesulfonic acid (DBSA) was used as an INISURF (initiator and surfactant combined) in the cationic polymerization of *p*-methoxystyrene in miniemulsion. Basically, the reaction is initiated by the proton (the true initiator), and resultant active centers associate with the pendant aromatic sulfonate moiety (the surfactant and counterion). The bulky ion pairs propagate further until transfer/termination reactions by water occur to generate hydroxyl-terminated oligomers (Scheme 1). All above-mentioned reactions proceed at the particle interface (see Figure 1 for details) providing oligomers with typical $M_n \leq 1000$ g/mol. To separate the propagating center from the surfactant counterion, a superacid, trifluoromethanesulfonic acid or triflic acid, was used as an initiator in conjunction with a nonionic surfactant.[22] M_n's of up to 1700 g/mol were produced here, at the expense of the polymerization rate (about ten times slower). Indeed, triflic acid may enter with difficulty the

SCHEME 1. Proposed Mechanism for *p*-Methoxystyrene Polymerization in the Presence of DBSA



monomer droplets because of the steric hindrance of the nonionic surfactant molecules, but once done, it apparently goes deeper inside the interface and suffers slower transfer reaction by water than in the INISURF system.

Second Generation: Lanthanide Triflate Cocatalysts

Polymerization of *p*-Methoxystyrene. Sawamoto et al.[14] were the first to show that $Yb(OTf)_3$ in conjunction with 1-chloro-1-(*p*-methoxyphenyl)ethane (*p*MOS-HCl)[14] induces slow cationic polymerization of *p*MOS at 30 °C in aqueous suspension, while the rate of the reaction considerably increases in the presence of sulfonic acid-based initiators[18] (Figure 2a). The use of cationic surfactant (dodecyltrimethylammonium bromide) also allowed the polymerization rate to increase[19] (Figure 2a), which 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.[19] In contrast, anionic surfactant (sodium laurylbenzenesulfonate) or nonionic polymer dispersant (poly(vinyl methyl ether)) retarded the polymerization, as explained by the probable complexation of $Yb(OTf)_3$ with these stabilizers.[19] The M_n's of obtained polymers, regardless of experimental conditions, increased at the beginning of the polymerization (up to ~30% of conversion) and then leveled off at values between 2500 and 3500 g/mol (Figure 2b) because of chain transfer reactions.[14,18,19] Molecular weight distributions (MWD) were typically below 1.5 and did not change with monomer conversion (Figure 2b).[14,18,19]

Later on, different metal triflates[19,20] and tetrafluoroborates[20] in conjunction with *p*MOS-HCl as an initiator were tested by Sawamoto's team. The reaction rate critically depended on the nature of metal: $Yb(OTf)_3 > Sn(OTf)_2 > Zn(OTf)_2 \approx Cu(OTf)_2$.[20] Moreover, $Sn(OTf)_2$ was found to be unstable in water and to hydrolyze into inactive hydroxides, while zinc tetrafluoroborate ($Zn(BF_4)_2$) induced a very slow polymerization rate.[20] Among the various lanthanide triflates tested ($Ln(OTf)_3$; Ln = Dy, Sm, Gd, Yb, and Nb) together with $Sc(OTf)_3$, the higher activity in suspension polymerization

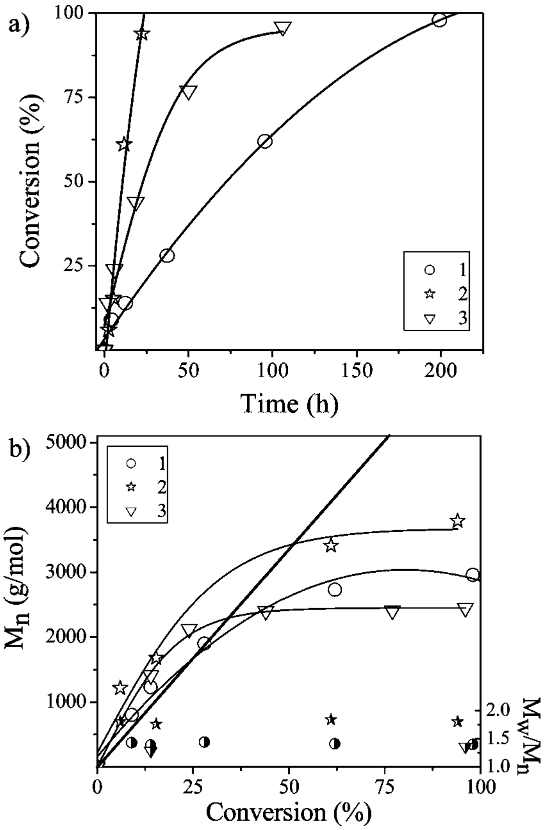
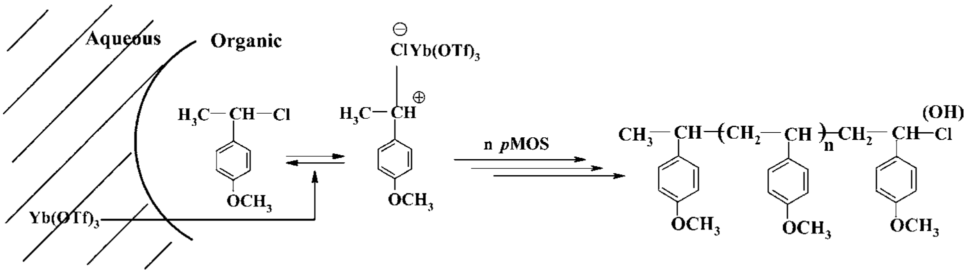


FIGURE 2. (a) Conversion vs time and (b) M_n and M_w/M_n vs conversion plots for the *p*-methoxystyrene polymerization with $Yb(OTf)_3$ in aqueous media at 30 °C. Initiator: (1, 3) *p*MOS-HCl; (2) $HOSO_2PhNO_2$. Surfactant: (1, 2) none; (3) dodecyltrimethylammonium bromide.

SCHEME 2. Mechanism for *p*-Methoxystyrene Polymerization in the Presence of $Yb(OTf)_3$ Proposed by Sawamoto et al.



(without surfactant) pertained to catalysts with central metal of the smallest ionic radius ($Sc(OTf)_3$, $Yb(OTf)_3$), whereas in emulsion (i.e., using a colloidal stabilizer), $Yb(OTf)_3$ was the most active co-initiator.[19] However, the nature of co-initiator did not influence significantly either the M_n or the MWD evolution with conversion.[19,20]

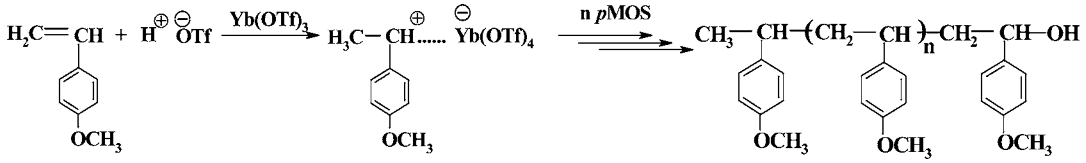
The analysis of poly(*p*-methoxystyrene)s chain-ends by ^1H NMR spectroscopy was at first revealing the presence of $-CH(C_6H_4OCH_3)-Cl$ ω-terminal group ($F_n(Cl) \approx 0.3-0.5$).[14,19,20] Later, Sawamoto et al.[18] and other research teams[16,23−25] showed unambiguously that almost all polymer chains were terminated by hydroxyl groups, originating from chain transfer via water. The low stability of terminal $-CH(C_6H_4OCH_3)-Cl$ groups, even in organic solvents, was also observed by Faust et al.[26] Originally, it was proposed[14,18−20] that the polymerization proceeds inside monomer/organic solvent droplets via carbocationic species generated from initiator located in organic phase through its *reversible* activation by $Yb(OTf)_3$. Due to the high hydrophilicity of $Yb(OTf)_3$, only a small amount of co-initiator would be able to penetrate into monomer droplets (Scheme 2). This fact, in the view of the authors,[14] explained the necessity to use high amounts of $Yb(OTf)_3$ to reach complete monomer conversion within a reasonable polymerization time.

In a recent work, Storey at al.[23] reported on the polymerization of *p*MOS using phosphonic acid initiators [$(HO)_2P(O)R$, R = Ph or Ph-*o*,*m*,*p*-NO_2] and $Yb(OTf)_3$ as co-initiator in conditions similar to those proposed by Sawamoto's team. It was claimed that polymerization proceeds at the aqueous/organic interface and is not controlled since changing the concentration of initiator did not influence the M_n evolution with conversion.[23] The main feature of this initiating system is the possibility to generate poly(*p*-methoxystyrene)s with high molecular weight ($M_n \leq 20\,000$ g/mol).

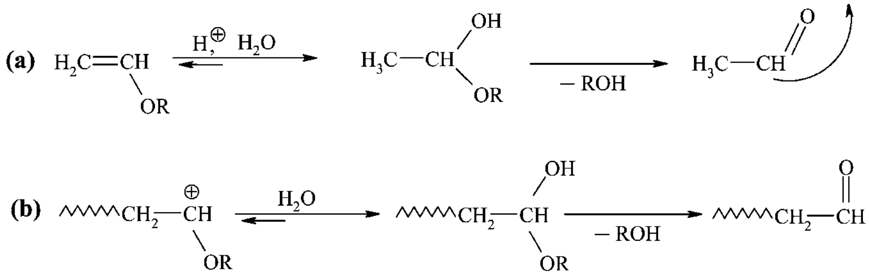
An exhaustive mechanistic study of the polymerization of *p*MOS in the presence of $Yb(OTf)_3$ with special emphasis on the colloidal parameters of the reaction media was performed by Ganachaud et al.[17,27] First, conductometric measurements clearly evidenced that ytterbium triflate salt totally dissociates in water into its ionic counterparts (Yb^{3+} and $CF_3SO_3^-$) but does not form nonreactive hydroxides below pH 7, unlike conventional Lewis acids, such as $AlCl_3$ or $TiCl_4$.[27] By saturating the water with the catalyst salt, the authors suspected that a few nondissociated $Yb(OTf)_3$ molecules would subsist and reach the interface to co-initiate the polymerization.[27] Second, the polymerization was shown to proceed in *direct* emulsion if an electrosteric-type surfactant such as polyoxyethylene(8) lauryl sulfate sodium was used[27] or in *inverse* (mini)emulsion in the presence of dodecylbenzenesulfonic acid (DBSA).[17] In inverse emulsion, polymers with M_n up to 3000 g/mol could be prepared, while in direct emulsion only oligomers with M_n of maximum 1250 g/mol were formed. Moreover, the rate of the polymerization was considerably slower in inverse compared with direct emulsion processes. According to Ganachaud et al.,[17,27] the polymerization of *p*-methoxystyrene in the presence of $Yb(OTf)_3$ proceeds at the interface regardless of the nature of dispersion. Presumably, triflate anion, which arises from the dissociation of $Yb(OTf)_3$, captures a proton and an ytterbium triflate molecule to generate a bulky, strong Brønsted superacid, $H^+Yb(OTf)_4^-$, which initiates the polymerization. Once a chain is created, propagation is very fast until water transfer/termination reaction occurs to generate hydroxyl-terminated dead oligomeric chains (Scheme 3). In this mechanism, the observed increase of molecular weight at the beginning of the polymerization can be explained by the decrease in the rate of transfer/termination by water due to the increasing hydrophobicity of interface saturated by small oligomers (Figure 1). Otherwise saying, only physicochemical issues govern the molecular weight of the polymers obtained.

Polymerization of Vinyl Ethers. The polymerization of isobutyl vinyl ether (IBVE) was initiated by adding a solution of monomer and initiator (adduct of IBVE with HCl, IBVE−HCl) in CCl_4 to an aqueous solution of $Yb(OTf)_3$.[14] Since $Yb(OTf)_3$ or IBVE−HCl alone did not induce polymerization at all, it was proposed that reaction proceeds via the formation of cationic species through activation of IBVE−HCl by $Yb(OTf)_3$.[14] Polymers (61−83% of conversion) with M_n's scattered around

SCHEME 3. Mechanism for *p*-Methoxystyrene Polymerization in the Presence of $Yb(OTf)_3$ Proposed by Ganachaud et al.



SCHEME 4. Side Reactions of (a) Protonated Monomer and (b) Growing Species during IBVE Polymerization in Aqueous Media



3000−6000 g/mol and broad MWD ($M_w/M_n = 2.0-3.4$) were synthesized in, however, a non-reproducible manner.

Another study reported the photoinitiated cationic polymerization of vinyl ethers in a mixture of water and acetonitrile, in the presence of $Yb(OTf)_3$ as co-initiator and diphenyliodonium iodide, which generated monomer−HX adduct during photolysis.[28] Oligomers ($M_n = 1800-2600$ g/mol) with monomer conversion of 30−50% and narrow MWD ($M_w/M_n = 1.1-1.3$) were produced but again with broad scattering on experimental results.[28] A rational explanation for such random polymerization results lies in the irreversible consumption of protonated monomer[29] or degradation of carbocationic growing species,[14,30] because of their high reactivity toward water and the low stability of hemiacetals formed in such aqueous environment (Scheme 4).

Third Generation: Lewis Acid−Surfactant Combined Catalysts (LASC)

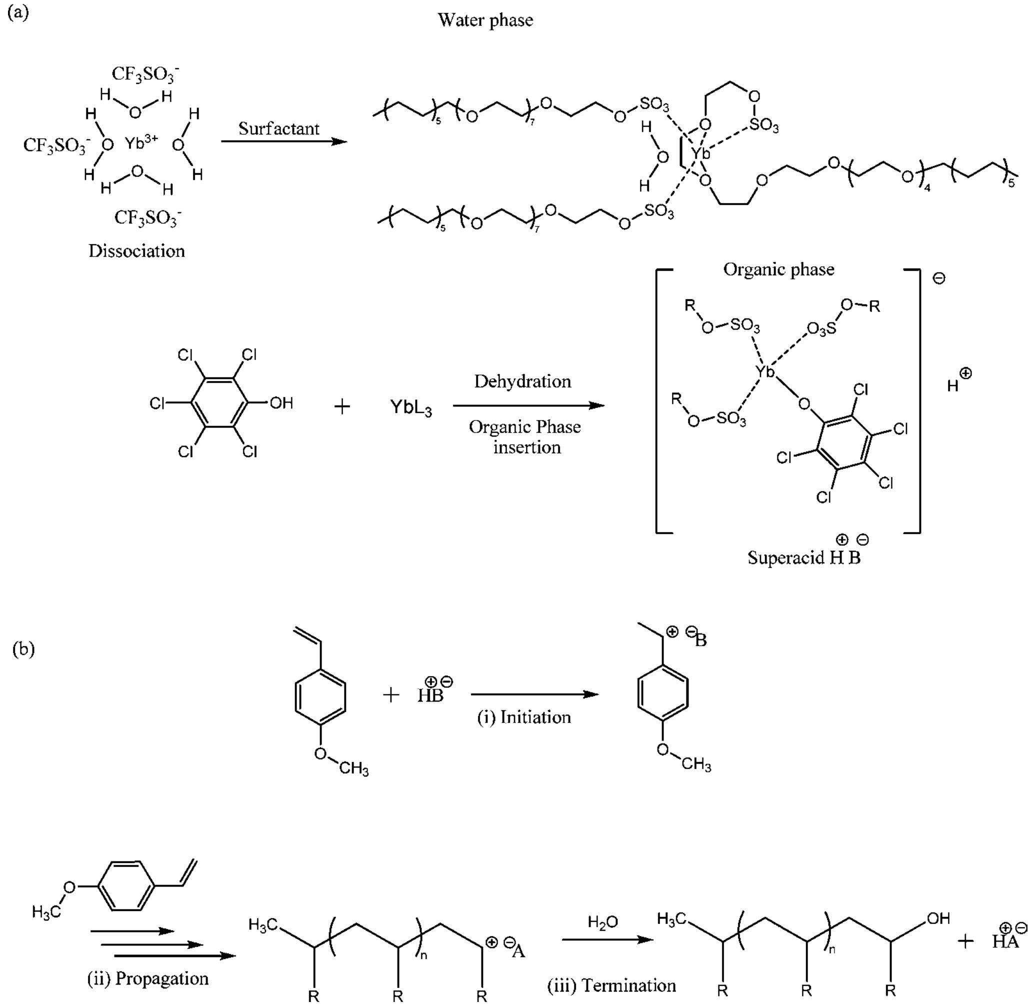
Since all polymerizations of *p*MOS discussed above proceed at the interface, the "critical DP" effect limits the molecular weight at values around 1000 g/mol (direct emulsion) or 3000 g/mol (suspension, inverse emulsion), respectively. To produce longer polymer chains, it is necessary to find conditions where the polymerization locus could be displaced from the interface to the core of the monomer droplets.[16] For this purpose, a complex of Lewis acid with surfactant, that is, so-called Lewis acid−surfactant combined catalyst (LASC) was investigated in miniemulsion polymerization of *p*MOS.[24] Typically, the tris(dodecyl sulfate)ytterbium LASC was recovered after precipitation in an aqueous mixture of $Yb(OTf)_3$ and dodecyl sulfate sodium salt (1:3).[24] Unfortunately, the authors undoubtedly showed that this particular LASC stayed at the interface and did not affect the polymerization process, that is, it acts only as a surfactant together with dodecyl sulfate sodium salt.[24]

Later on, another LASC was (unwittingly) generated under aqueous miniemulsion conditions, by *in situ* coupling between an electrosteric surfactant and ytterbium but (purposely) associated with a weak organic acid as an initiator to generate large molar mass polymer chains (Scheme 5a).[25] According to the authors,[25] only small oligomers were formed at the beginning of the reaction by interfacial polymerization. In strong contrast to previous studies however, high molecular weight polymers (M_n up to 40000 g/mol) started to appear after ca. 100 h. At this stage, the reaction media also changed from a two-phase mixture to a fine emulsion (Figure 3). It was proposed that, in this second stage, the polymerization proceeds *inside* the monomer droplets through the following steps: (i) in situ LASC formation; (ii) association with the weak acid to generate a bulky superacid and initiate the polymerization; (iii) fast propagation; (iv) (moderate) transfer due to the low content of water inside the droplets, thus allowing chains to grow significantly.[25] Since no variation of molecular weight with conversion was observed during the reaction, it was concluded that the polymerization was not controlled under these conditions.

Fourth Generation: $BF_3 \cdot OEt_2$ Cocatalyst

Along with $Yb(OTf)_3$, another strong Lewis acid, $BF_3 \cdot OEt_2$, was tested as a possible water-tolerant co-initiator for the cationic polymerization of styrene and its derivatives.[31−36] We describe here mainly the results obtained in "wet" solution, that is, where (an excess of) water (against Lewis acid) was introduced as a polymerization controlling agent.

SCHEME 5. (a) LASC Formation in Water and Superacid Generation in the Organic Phase and (b) Proposed Cationic Polymerization Mechanism inside the Monomer Droplets



***p*-Hydroxystyrene and *p*-Alkoxystyrenes Polymerization.** The cationic polymerization of such active monomers as *p*-hydroxystyrene (*p*HS)[31] and *p*-alkoxystyrenes[32] was first studied by Sawamoto et al. using different adducts of *p*-methoxystyrene as initiators (Scheme 6) and $BF_3 \cdot OEt_2$ as a co-initiator in acetonitrile or its mixture with CH_2Cl_2. It was found that alcohol (**4**) or ether *p*MOS-derived initiators (**3**) induced faster polymerization in contrast to chloride (**1**) and acetate (**2**) functionalized initiators, typically used in common metal chloride-mediated controlled cationic polymerizations. Importantly, the addition of *excess* water toward Lewis acid is necessary to control *p*HS polymerization with the **4**/BF_3OEt_2 initiating system, advantageously without the constraint of protecting the hydroxy groups.[31] Increasing the water concentration in the system led to more controlled polymerization in terms of M_n and MWD evolution with conversion, however at the expense of the reaction rate (Figure 4): the optimal $[H_2O]/[BF_3OEt_2]$ ratio was found to be 100 (CH_3CN/H_2O 250:1 v/v) (Figure 4). The living nature of *p*HS polymerization was confirmed by a monomer postaddition experiment: the M_n increased from 3000 to 6000 g/mol and MWD stayed relatively narrow (M_w/M_n < 1.4). Basically, poly(*p*-hydroxystyrene)s with molec-

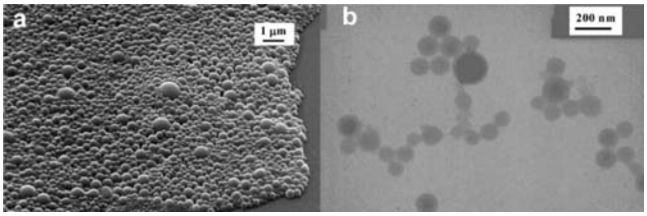
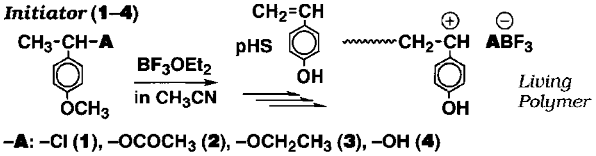


FIGURE 3. (a) Scanning and (b) transmission electron microscopy photographs of one example of final polymer dispersion.

SCHEME 6. *p*-Hydroxystyrene Polymerization Co-initiated by BF_3OEt_2 in Acetonitrile and in the Presence of Excess Water



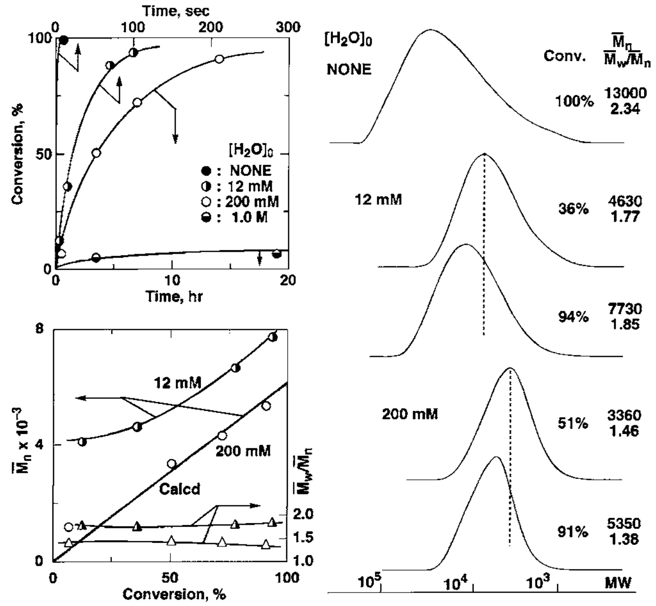


FIGURE 4. Effects of Water on the *p*HS Polymerization with **4**/BF_3OEt_2 in Acetonitrile at −15 °C: [*p*HS] = 0.20 M; [**4**] = 4.0 mM; [BF_3OEt_2] = 2.0 mM.

ular weight up to 15000 g/mol ($M_w/M_n \sim 2.0$) and 6000 g/mol ($M_w/M_n < 1.4$) could be synthesized by *p*HS polymerization with the **4**/BF_3OEt_2 initiating system at [H_2O]/[BF_3OEt_2] ratio of 6 and 100, respectively.[31]

The same initiating system was also successfully applied to the polymerization of *p*-alkoxystyrenes (*p*-methoxystyrene, *p*-*tert*-butoxystyrene (*t*BOS)).[32] The polymerization rate strongly depended on the nature of the *para* substituent: *t*BOS<*p*MOS<*p*HS.[32] As in the case of *p*HS polymerization, **4**/BF_3OEt_2 initiating system induced controlled cationic polymerization of *p*-alkoxystyrenes and allowed to synthesize polymers with M_n up to 6000 g/mol and narrow MWD ($M_w/M_n < 1.3$), but using much lower contents of water ([H_2O]/[BF_3OEt_2] = 20). In a following step, random and block copolymers of *p*HS and *p*MOS with molecular weight as high as 6000 g/mol and narrow MWD ($M_w/M_n < 1.5$) were prepared using BF_3OEt_2-based initiating system.[32] The analysis of poly(*p*-hydroxystyrene)s by ^{1}H NMR spectroscopy and MALDI-TOF-MS revealed that almost all macromolecules possess a fragment of initiator at the α-end and methoxy group at the ω-end, this latter arising from termination of the growing chains with methanol. Since the functionality of the ω-end was less than unity ($F_n(\omega) \geq 0.7$), it was proposed that some hydroxyl terminal groups derived from the initiator would be formed via chain transfer/termination by counterion.[31] On the contrary, for poly(*p*-alkoxystyrene)s and their copolymers were reported the formation of hydroxy terminal groups exclusively.[32]

Styrene and *p*-Substituted Styrenes Polymerization. BF_3OEt_2 was also tested as a water-tolerant co-initiator in the polymerization of styrene[33,35] and different *p*-substituted styrenes (*p*-methylstyrene (*p*MS),[33] *p*-chlorostyrene (*p*ClS),[33] *p*-chloromethylstyrene (*p*CMS)[34]) using CH_2Cl_2 as solvent. The 1-phenylethyl alcohol (**5**)/BF_3OEt_2 initiating system induced slow (~90% conversion for 20 h) and poorly controlled cationic polymerization of styrene in the presence of a slight excess of water toward Lewis acid ([H_2O]/[BF_3OEt_2] = 1.6).[33] More efficient initiators than **5**, namely, 2-phenyl-2-propanol (**6**) and 1-(4-methoxyphenyl)ethanol (**4**), allowed achievement of considerably better control over the reaction: M_n increased in direct proportion to monomer conversion up to 10000 g/mol, and MWD*s* became narrower during the polymerization ($M_w/M_n \approx 1.8$). Finally, the livingness of the styrene polymerization with **4**/BF_3OEt_2 initiating system was confirmed by a monomer postaddition experiment.[35] The **5**/BF_3OEt_2 initiating system was also effective in controlling the polymerization of such substituted styrenes as *p*MS, *p*ClS, and *p*CMS under experimental conditions close to those for styrene polymerization.[33,34] Polymers with controlled M_n up to 15000 g/mol and relatively narrow MWD ($M_w/M_n = 1.5-2.0$) were synthesized using a small excess of water ([H_2O]/[BF_3OEt_2] ≤ 1.6). The interesting feature of BF_3OEt_2-based initiating systems is the high tolerance of BF_3OEt_2 toward the −CH−Cl bond, which allows *p*CMS to polymerize without concurrent side reaction of the chloromethyl functional groups.[34] Finally, all synthesized polymers, according to ^{1}H NMR and MALDI-TOF-MS data, possess a fragment of initiator at the α-end ($F_n(\alpha) \leq 0.9$) and a hydroxy group ($F_n(\omega) \geq 0.7$) at the ω-end.[33,34]

Mechanism of BF_3OEt_2-Mediated Polymerization. The polymerization of styrene and its derivatives in solution proceeds via the reversible activation of the terminal C−OH bond by BF_3OEt_2 to give living polymers even in the presence of excess water toward Lewis acid.[31−36] The added water may serve here as a reversible chain transfer agent providing control over the polymerization reaction.[33] It was also assumed that under a high excess of water, less reactive H_3O^+, compared with free protons formed under vigorously dry conditions, is suppressing thereby the initiation via water.[31] Also, acetonitrile, which was used as solvent for the *p*HS[31] and *p*MS[32] polymerization, can suppress the protonic initiation by working as a proton trap.[37] Table 1 summarizes the possibilities and limitations of using BF_3OEt_2-based initiating systems for the controlled cationic polymerization of styrene and derivatives in the presence of water. Finally, we reported recently[35] that BF_3OEt_2 slowly hydrolyzes in an aqueous environment, preventing its use in aqueous suspension conditions.

TABLE 1

	*p*HS	*p*MOS	St	*p*MS	*p*ClS	*p*CMS
M_n (kg/mol)	6	6	10	15	15	8
M_w/M_n	$\leq$1.4	$\leq$1.3	$\geq$1.8	$\geq$1.5	$\geq$1.5	1.5−2.0
$[H_2O]/[BF_3OEt_2]$	100	20	2.2	1.6	0.8	0.8

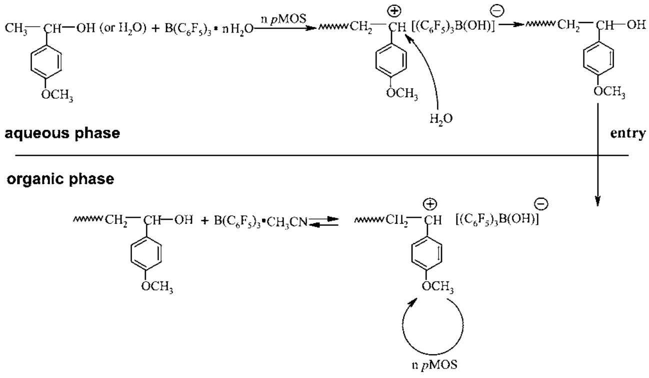
Fifth Generation: Aromatic Borane-Based Cocatalysts

Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, is a commercially available, air-stable, water-tolerant Lewis acid catalyst.[38,39] Both theoretical and experimental physicochemical studies showed that $B(C_6F_5)_3$ does not decompose in water; rather, it forms different stable adducts with water of general formula $B(C_6F_5)_3 \cdot nH_2O$.[40,41] This compound as well as the noncommercial C_6F_4-1,2-$[B(C_6F_5)_2]$,[42] and C_6F_4-1,2-$[B(C_{12}F_8)]_2$[43] were recently tested as co-initiators for cationic polymerization of *p*-methoxystyrene,[21,37] styrene,[44] cyclopentadiene,[45] and isobutylene[46,47] in "wet" solutions and in different aqueous dispersion processes.

Polymerization of *p*-Methoxystyrene. The polymerization of *p*-methoxystyrene was first studied in solution (CH_3CN/CH_2Cl_2) at different water concentrations ($[H_2O]/[B(C_6F_5)_3] = 0-20$) using the **4**/$B(C_6F_5)_3$ initiating system.[21,37] Whatever the water concentration, the polymerization proceeded in a controlled fashion via reversible activation of the terminal C−OH bond by $B(C_6F_5)_3$ to afford polymers whose M_n increased in direct proportion to monomer conversion up to 10000 g/mol with fairly narrow MWDs ($M_w/M_n \leq 1.3$). The controlled polymerization of *p*MOS occurred only in the presence of a sufficient amount of acetonitrile, which both entails the possible stabilization of growing carbocations and the suppression of the competitive protonic initiation.[21,37]

The same initiating system, **4**/$B(C_6F_5)_3$, was tested under aqueous suspension conditions.[21] Stable suspensions were generated only after the conversion reached 30%. The polymerization was completed in 10 h giving polymers with final M_n of 5000 g/mol and broad MWD ($M_w/M_n = 1.8-2.0$). The authors claimed[21] that under investigated conditions the polymerization is not controlled and proceeds exclusively at the interface similarly to previously reported studies.[14,16−20,22−24] More promising results have been obtained in aqueous dispersion, that is, in a water/acetonitrile (3:2 v/v) mixture.[21] After an induction period of 1−2 h, the polymerization proceeded within one day and M_n's increased in direct proportion to monomer conversion up to 3000 g/mol with narrow MWDs ($M_w/M_n \leq 1.3$). MALDI-TOF-MS analysis showed that almost all poly(*p*MOS) chains bear a hydroxyl group at their ω-end.[21] To explain such results, the mechanistic scheme shown in Scheme 7 was proposed. Initiation of chains occurs either from **4** or from water at the particle interface. Once initiated, each chain propagates until transfer to water occurs. The hydroxyl-terminated chains can be reactivated by the catalyst and further propagate and terminate until the dormant oligomers become too hydrophobic and penetrate inside the particles. Basically, at this stage of the reaction only short chains were formed by interfacial polymerization (DP $\approx$ 8−10). However, in contrast to all previously described systems,[14,16−20,22−24] the polymerization of *p*-methoxystyrene can proceed further *inside* the monomer droplet in a *controlled* fashion by the reactivation of hydroxyl-terminated chains in the organic core of the droplet. Such a striking event was made possible by the entry inside the particles and polymerization catalysis of $B(C_6F_5)_3$, presumably in the form of its complex with acetonitrile, which is less hydrophilic than while complexed with water.[21] However, even in these long-lived conditions, molar masses reached 3000 g/mol and hardly exceeded this value, a feature that we attributed to the polymerization locus becoming too hydrophobic to retain the catalyst or to leave it active.

SCHEME 7. Proposed Mechanism for the *p*-Methoxystyrene Polymerization with **4**/$B(C_6F_5)_3$ Initiating Systems in a Water/Acetonitrile 3:2 (v/v) Mixture



Polymerization of Styrene. The **4**/$B(C_6F_5)_3$ initiating system was also tested in the aqueous suspension polymerization of styrene.[44] Latexes of poly(styrene) (Figure 5) with M_n up to 2000 g/mol and relatively narrow MWD ($M_w/M_n < 1.7$) were thus prepared. Again, the reaction proceeded at the particle interface, and molecular weight was controlled exclusively by the interfacial polarity.[44] A key observation in this article was related to the virtual absence of undesirable protonic initiation in aqueous suspension ($\sim$10% for 250 h) in contrast to solution process ($\sim$99% for 20 h). All macromolecules from the former process possess a fragment of initiator at the α-end and a hydroxy group at the ω-end, that is, $F_n(\alpha) = F_n(\omega) \approx 1.0$.[44]

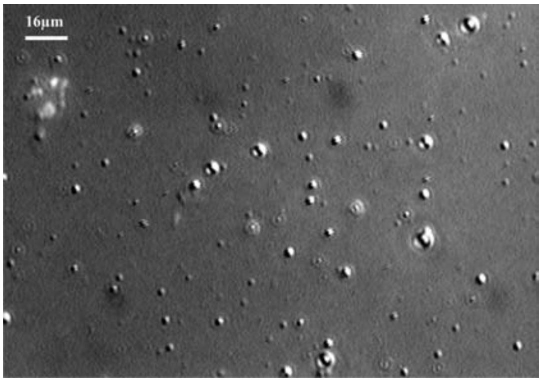


FIGURE 5. Optical micrograph of suspension of a polystyrene obtained during the polymerization of styrene with $B(C_6F_5)_3$ at 20 °C.

Polymerization of Cyclopentadiene. An original study on the controlled polymerization of cyclopentadiene using the **4**/$B(C_6F_5)_3$ initiating system in different CH_2Cl_2/CH_3CN mixtures was recently reported.[45] Well-defined poly(cyclopentadiene)s with controlled molecular weight ($M_n \leq 5000$ g/mol), high regioselectivity ([1,4] up to 70%) and reasonable MWD ($M_w/M_n = 1.2-1.6$) could thus be prepared in the presence of excess water ($[H_2O]/[B(C_6F_5)_3] \leq 4$). Aqueous suspension polymerization of cyclopentadiene using the same initiating system proceeded at the particle interface and allowed synthesis of primarily hydroxyl-terminated oligomers ($F_n(\omega) = 0.8-0.9$) with $M_n \leq 1000$ g/mol but broad MWD ($M_w/M_n \approx 2.2$).[45] In these conditions however, the monomer conversion did not exceed 40% due to competitive dimerization of the cyclopentadiene monomer; besides, no regioselectivity of the reaction ([1,4] ≈ 50%) was observed.[45]

Polymerization of Isobutylene. A number of model studies showed that diborane (C_6F_4-1,2-$[B(C_6F_5)_2]$) and diborole (C_6F_4-1,2-$[B(C_{12}F_8)]_2$) catalysts entail sufficiently high Lewis acidity to effectively ionize various cumyl derivatives (CumX, X = Cl, OCH_3, N_3) and play the role of co-initiators in the cationic polymerization of isobutylene (IB).[47,48] Indeed, C_6F_4-1,2-$[B(C_6F_5)_2]$ in combination with both CumCl and adventitious water induced fast cationic polymerization of isobutylene even in apolar media to afford polymers with high molecular weight ($M_n \approx 778000$ g/mol) but broad MWD ($M_w/M_n = 1.7-4.6$).[47,48] Suspension polymerizations of IB with either co-initiator were carried out in eutectic aqueous solutions, using strong electrolytes such as LiCl (23 wt %), H_2SO_4 (38 wt %), or HBF_4 (48 wt %) at −60 °C to give poly(isobutylene)s (yield 20−90%) of moderate to high molecular weight ($M_w = 10000-100000$ g/mol) and broad MWD ($M_w/M_n = 2-4$).[46,47] High molecular weight polymers ($M_w = 102000$ g/mol, $M_w/M_n = 3.3$) could also be prepared in a $MeOH/H_2O$ (68:32 v/v) mixture but in low yield (<10%).[46]

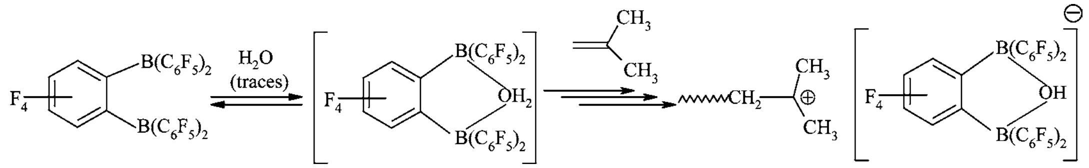
Since these suspensions were very unstable, the effect of different surfactants, namely, sodium dodecylsulfate, dodecyltrimethylammonium bromide, triflate, or tetrafluoroborate, on the isobutylene polymerization was studied: all of them led to a decrease in monomer conversion. Such tendency was tentatively attributed to an increase of the water concentration at the interface or inside monomer droplets in these "emulsion" polymerizations in comparison with suspension ones.[46,47] The decrease in polymer yield with increasing reaction temperature was likely explained by an increase of the water solubility in the organic phase.[47]

Concerning the polymerization mechanism, monodentate aquo complexes formed from either diborane or diborole molecules are insufficiently acidic to initiate the polymerization of isobutylene according to Collins et al.[47] For example, $B(C_6F_5)_3$ or $(o\text{-}C_6F_4H)B(C_6F_5)_2$, which are stronger Lewis acids than (C_6F_4-1,2-$[B(C_6F_5)_2]$), failed to initiate the cationic polymerization of isobutylene in aqueous suspension.[47] Instead, it was proposed that the μ-aquo complex (Scheme 8), which formed from diborane and one molecule of water, irreversibly protonates isobutylene. Note finally that polymers synthesized in aqueous suspension contain both *exo*- and *endo*-olefinic terminal groups (60:40 molar ratio), which is consistent with a chain transfer to monomer, that is, polymerization is not controlled.[47]

Conclusion

Cationic polymerization in aqueous media has emerged during the past decade as a new and very attractive method for controlling the polymerization of various cationically polymerizable monomers using such cheap and environmentally benign solvent as water or under mild experimental conditions (room temperature, open air, etc.). Lanthanide triflates were first reported as water-tolerant Lewis acids for suspension and emulsion cationic polymerizations. However, due to

SCHEME 8. Mechanism for the Aqueous Isobutylene Polymerization Co-initiated by C_6F_4-1,2-$[B(C_6F_5)_2]$



the complete dissociation of these salts in water, too large quantities were necessary to only slightly improve the polymerization rate and average molar mass. In contrast to $\mathrm{Ln(OTf)_3}$, borane-based catalysts showed greater potential in the synthesis of well-defined macromolecules by cationic polymerization in aqueous media from such industrially important monomers as styrene, cyclopentadiene, and even isobutylene. To date, however, with the exception of isobutylene polymerization, mainly low molecular weight ($M_n \leq 5000$ g/mol) polymers were prepared in a controlled fashion. We imagine that further fundamental research has to be done before this promising technique be transferred to industry.

BIOGRAPHICAL INFORMATION

Sergei Kostjuk, born in Kobrin, Belarus (1977), received his Ph.D. degree in polymer chemistry in 2002 from Belarusian State University. In 2002, he joined Research Institute for Physical Chemical Problems of the Belarusian State University as a Research Fellow (2002−2005) and then Senior Research Scientist (2005−2008). Since 2008, he has been heading the laboratory of catalysis of polymerization processes in the same institute. From 2005, he has also spent several periods as invited scientist in the team of F. Ganachaud, in the Institut Charles Gerhardt, ENSCM (France). His research interests lie in the fields of polymer design and synthesis (cationic and anionic polymerization, metallocene catalysis).

Francois Ganachaud, 40 years old, studied chemistry at CPE Lyon before receiving his Ph.D., supervised by Christian Pichot, in 1997. After one year as a postdoctoral fellow in Sydney in Prof. R. G. Gilbert's laboratory, he took a CNRS research position in Paris with Prof. Hémery from 1999 to 2003. He then moved to Montpellier in the laboratory of Prof. Boutevin, now part of the Institute Charles Gerhardt, where he completed his habilitation in 2004. His main research interests are (i) ionic polymerization in aqueous dispersed media, (ii) functional silicones and related materials, (iii) emulsification by "Ouzo effect".

FOOTNOTES

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