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Carbocationic Polymerization of Isoprene Co-initiated by $B(C_6F_5)_3$: An Alternative Route toward Natural Rubber Polymer Analogues?

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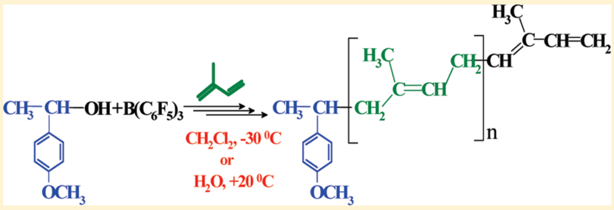
S Supporting Information



ABSTRACT: The cationic polymerization of isoprene using the 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ initiating system in solution (dichloromethane or α,α,α-trifluorotoluene) and in aqueous media (suspension, dispersion, or emulsion) is reported. In organic solvents the reaction proceeded by controlled initiation via **1**, followed by irreversible termination, thus affording polymers with a number-average molar mass $M_n \leq 5000$ g mol^{-1} and a molar mass distribution or MMD ($M_w/M_n \leq 2.5$) and rather high content of intact double bonds (≥70%) in the polymer backbone. In particular, using α,α,α-trifluorotoluene as polymerization solvent in place of dichloromethane promoted the synthesis of polyisoprene chains with $M_w/M_n \sim 1.4$ and larger content of intact double bonds (up to 88%). In the absence of **1**, polyisoprenes with fairly high molar mass (M_n up to 18 000 g mol^{-1}) and $M_w/M_n < 2.4$ were synthesized through adventitious water/$B(C_6F_5)_3$-initiated cationic polymerization of isoprene. In aqueous media, the cationic polymerization of isoprene with **1**/$B(C_6F_5)_3$ proceeded without any side reactions (cyclization, branching). However, aqueous conditions afforded only moderate yield (up to 60% monomer conversion) and polyisoprenes with low M_n (≤1200 g mol^{-1}) and $M_w/M_n \leq 1.7$ were obtained. By comparing different characterization data (NMR, mass spectrometry), it was demonstrated that under appropriate conditions (in organic solvents at −30 °C or in aqueous media) polyisoprenes carrying the initiator fragment from **1** at the α-end and an olefinic terminal group can be produced almost exclusively in a *trans*-1,4 configuration (92−96.5%).

INTRODUCTION

Natural rubber (NR) is composed of *cis*-1,4-polyisoprene chains with more than 99% of *cis*-enchainment, number-average molar masses (M_n) of 10^5-10^6 g mol^{-1}, and molar mass distributions or MMD (M_w/M_n) of 2−10. It is the most important natural polymer used as raw material in the manufacture of tires as well as medical and other rubber products.[1] Today, there is only one important commercial source of natural *cis*-1,4-polyisoprene (*Hevea brasiliensis*). Polyisoprenes with rather high *cis*-1,4-content (up to 96%) have been synthesized by anionic polymerization.[2] Ziegler−Natta-type catalysts, such as rare earth metal-based catalysts, showed very high stereoselectivity, affording polymers with as high as 99% *cis*-1,4-repeat units.[3] Despite such advances, there are no synthetic equivalents capable of competing with natural rubber-based materials in terms of mechanical properties.

Meanwhile, *trans*-1,4-polyisoprene, also called Gutta Percha or Balata (extracted from *Palaqium gutta* or *Mimusops balata* lattices, respectively), has attracted renewed interest thanks to peculiar mechanical properties (e.g., longer fatigue life, lower rolling resistance).[4] Industrially, *trans*-1,4-polyisoprene was produced mainly using vanadium (V) or V−Ti-based Ziegler−Natta catalysts, although they have low activity toward isoprene polymerization.[5] Recently, it was shown that certain lanthanide-based complexes were very effective catalysts for the *trans*-stereospecific polymerization of isoprene (>95% *trans*-1,4-units).[6] These catalysts, however, are multicomponent systems, too expensive nowadays to be of significant interest for industry. Isoprene can

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also be polymerized by radical mechanism in a living fashion but without control of the polymer microstructure: typically about 80% of 1,4-repeat units (in both *cis*- and *trans*-configurations) and about 20% of 1,2- and 3,4-structures were quantified by NMR spectroscopy.[7]

It was recently proposed that NR enzymatic biosynthesis resembles a cationic step-growth/chain-growth polycondensation reaction initiated by allylic carbocations, where the monomer (isopentenyl pyrophosphate) can only react with the activated allylic carbocation at the polymer chain end.[1] In order to investigate this concept, the cationic polymerization of isoprene initiated by dimethylallyl cations generated through the ionization of dimethylallyl bromide or dimethylallyl alcohol by $TiCl_4$[8] or $BF_3 \cdot OEt_2$[9] was investigated by Puskas and Deffieux et al. Under these conditions, polyisoprenes carrying a dimethylallyl headgroup and terminal double bond were synthesized almost exclusively via 1,4-addition, yielding repeating units mostly in the *trans*-configuration.[8,9] Unfortunately, it was also shown that chain transfer and cyclization/branching reactions yielded polymers with low M_ns (500−2000 g mol^{-1}) and broad MMD (M_w/M_n = 4−6) as well as ~50% loss of unsaturation (or ~50% intact double bonds content).[8,9] Such results are not surprising in light of the well-described cationic polymerization of dienes (for a recent review on cationic polymerization topic, see ref 10). For example, the carbocationic copolymerization of isoprene with isobutylene co-initiated by BCl_3 led to cyclization and loss of unsaturation.[11] However, co-initiation with $TiCl_4$ did not yield cyclization, and the copolymerization of 2,4-dimethyl-1,3-pentadiene with isobutylene was living.[12] Blocking of isoprene from high molar mass living polyisobutylene produced short linear blocks in *trans*-1,4 enchainment with no loss of unsaturation.[13] On the other hand, the polymerization of isoprene[14,15] and 1,3-pentadiene[15,16] in the presence of $AlCl_3$ or $TiCl_4$ co-initiators produced concomitantly insoluble cross-linked chains and soluble linear and grafted macromolecules. The soluble polyisoprenes were characterized by low number-average molar mass ($M_n \leq 5000$ g mol^{-1}), broad and often multimodal molar mass distribution, and significant loss of unsaturation (50−70% intact double bonds content) due to the occurrence of numerous side reactions such as cyclization, double-bond isomerization, or termination.[14,15] The microstructure analysis by ^{1}H and ^{13}C NMR revealed the preferable 1,4-*trans* enchainment of the monomer units in the cationically prepared polyisoprene chains.[14b,c]

It is a common feature in cationic polymerization that the rate of side reactions is strongly affected by the basicity of the counteranion; these can be minimized using anions that are weakly nucleophilic.[17] For example, high molar mass polyisobutylene or its copolymers with isoprene could be obtained at "high" temperatures (−8 to −35 °C) in the presence of tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, a unique Lewis acid generating weakly basic, noncoordinating, and non-nucleophilic anion $[B(C_6F_5)_3X]^-$ ($X = C_6F_5$, CO_2R, etc.).[18,19] Most importantly, up to 8.5 mol % of IP could be incorporated into copolymer without any gel formation (only 1−2 mol % with conventional Lewis acids[17]) in the $Et_3Si^+B(C_6F_5)_4^-$-initiated copolymerization of isobutylene with isoprene.[19] Recently, we developed a new initiating system, 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$, for the living cationic polymerization of *p*-methoxystyrene,[20,21] styrene,[22] and cyclopentadiene (a cyclic diene)[23] under mild reaction conditions, i.e., at room temperature, in open air and in the presence of fairly large amounts of water. Particularly, we could generate high molar mass poly(*p*-methoxystyrene)s (M_n ~ 50 000 g mol^{-1}) at room temperature[21] and succeeded at controlling the regiochemistry of monomer insertion during the polymerization of cyclopentadiene.[23] In related studies, the **1**/$B(C_6F_5)_3$ initiating system was also successfully applied to the cationic polymerization of styrene derivatives and cyclopentadiene in aqueous media (suspension, dispersion, or emulsion).[24,25]

The main goal of this paper is to define the best conditions for the synthesis of linear *trans*-1,4-polyisoprenes through the cationic polymerization of isoprene in various media. Thus, we report the *trans*-1,4-stereoselective cationic polymerization of isoprene co-initiated by $B(C_6F_5)_3$ as a Lewis acid under mild conditions, e.g., in polar solvents (CH_2Cl_2, α,α,α-trifluorotoluene) and at moderate temperatures (typically ≥−30 °C) giving polymers with relatively large molar mass and close to 90% intact double bonds content. The cationic polymerization of isoprene in aqueous media is also reported here for the first time.

EXPERIMENTAL PART

Materials. Isoprene (Aldrich, 99%), dichloromethane (CH_2Cl_2, Carlo-Erba, 99.5%), α,α,α-trifluorotoluene (BTF, Aldrich, 99%), and nitromethane (CH_3NO_2, Aldrich, >95%) were distilled from CaH_2 under an inert atmosphere prior to use. $B(C_6F_5)_3$ (Lancaster, 97%), dodecylbenzenesulfonic acid (DBSA, Aldrich, ~90%), pyridine (Carlo-Erba, 99%), acetic anhydride (Carlo-Erba, 99%), tetrahydrofuran (THF, Aldrich, 99.9%), diethyl ether (Aldrich, 99.5%), methanol (Fluka, 99.8%), and $CDCl_3$ (Euriso-top) were used as received. 1-(4-Methoxyphenyl)ethanol (**1**) (Aldrich, 99%) was purified by distillation from CaH_2 under reduced pressure. 1-(4-Methoxyphenyl)ethyl acetate (**2**) was synthesized by the reaction of **1** and acetic anhydride in pyridine at 100 °C for 1 h and purified by double distillation from CaH_2 under reduced pressure. *n*-Octadecanoic acid ($C_{17}H_{35}COOH$, Fluka, 98.5%) was purified by recrystallization from hexane. *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, Fluka, ≥99%), silver trifluoroacetate (TFA, Aldrich, 98%), and CuCl (Aldrich, ≥99.99%) were used as purchased. The purity of 1-(4-methoxyphenyl)ethyl acetate, $C_{17}H_{35}COOH$, and $B(C_6F_5)_3$ was checked by ^{1}H or ^{19}F NMR, for the latter.

Methods. Size exclusion chromatography (SEC) was performed on a PL-GPC 50 integrated GPC system 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 differential refractometer. THF was eluted at a flow rate of 1.0 mL min^{-1}. The calculations of molar mass and polydispersity were first based on polystyrene standards (Polymer Laboratories, Germany); all thus-obtained values were then compared to the corresponding NMR data and literature values[26] in order to check on the linearity of the polymer chains (vide infra). ^{1}H NMR and ^{19}F NMR (400 MHz) spectra were recorded in $CDCl_3$ at 25 °C on a Bruker AC-400 spectrometer calibrated relative to the solvent peak in reference to tetramethylsilane (^{1}H NMR) or $CFCl_3$ (^{19}F NMR) standards. MALDI-TOF MS was performed on a Voyager mass spectrometer (AB Sciex). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. Spectra were recorded in the positive-ion mode using the reflectron and with an accelerating voltage of 20 kV. Samples were dissolved in THF at 10 mg mL^{-1}. The DCTB matrix (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) solution was prepared by dissolving 10 mg in 1 mL of THF. A solution of cationization agent (AgTFA or CuCl, 10 mg mL^{-1}) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationization agent. 1−2 μL of the obtained solution was deposited onto the sample target and vacuum-dried. The instrument was calibrated externally using poly(ethylene glycol) standards at the appropriate molar mass. All mass-to-charge ratios (*m*/*z*) quoted are monoisotopic; i.e., they include the most abundant isotopes of the elements present in the corresponding ion. DSC measurements were performed on a NETZSCH DSC 200 F3Maia instrument calibrated with indium. Samples of poly(isoprene) (10−15 mg) were analyzed using the following steps: heating at 20 °C/min from 20 to 100 °C and, after 2 min at 100 °C isothermally, cooling at 20 °C/min from 100 to −100 °C, and, finally, heating at 20 °C/min from −100 to 100 °C to obtain the glass transition temperature (T_g).

Polymerization Procedures. The polymerization reactions were carried out in glass Schlenk tubes equipped with a stopcock in an argon atmosphere (in solution) or in open air (in aqueous media). As an example of a typical procedure in solution, polymerization was initiated by adding $B(C_6F_5)_3$ (1.35×10^{-4} mol, 0.07 g) dissolved in 0.5 mL of CH_2Cl_2 to a mixture consisting of 1-(4-methoxyphenyl)ethanol (6.8×10^{-5} mol), isoprene (1×10^{-2} mol, 1 mL), and CH_2Cl_2 (4.5 mL) for a total volume of 5.5 mL. After a predetermined time, ∼0.3−0.5 mL aliquots were withdrawn and poured into excess methanol. The precipitated polymer was separated from the solution by centrifugation and dried in vacuum. Monomer conversions were determined gravimetrically. The polymerization in aqueous suspension was carried out as follows: a suspension of $B(C_6F_5)_3$ (2.7×10^{-4} mol, 0.14 g) and diethyl ether (0.1 g) in water was added to a mixture consisting of 1-(4-methoxyphenyl)ethanol (10.8×10^{-4} mol, 0.16 g), isoprene (1×10^{-2} mol, 1 mL), and water (4 mL) for a total volume of 5.2 mL. After a predetermined time, ∼0.3−0.5 mL aliquots were withdrawn and poured into an excess of methanol. The precipitated polymer was separated from the aqueous phase by centrifugation and dried in vacuum. Monomer conversions were determined gravimetrically.

For the polymerization experiments in organic solvents at −30 °C or in aqueous media, the maximal conversion (C_{max}) attainable after consuming all initiator **1** was calculated according to the average molar mass of samples (M_n, given by SEC), the moles of initiator (n_1), and the mass of monomer consumed (m_{IP}) according to

$$C_{max} = n_1(M_n - 135)/m_{IP} \qquad (1)$$

Here, C_{max} was used only for the cases when initiation occurs exclusively through the ionization of an initiator (**1**) and irreversible termination is a main chain breaking process.

■ RESULTS

A. Polymerization in Solution. *Effect of Temperature and Initiator Nature.* The first experiments of the cationic polymerization of isoprene (IP) with the 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$ initiating system were conducted in CH_2Cl_2 at 20 °C. As shown in Figure 1a, the polymerization was fast and exothermic. At high monomer conversions, the experimental values of molar masses of polymers prepared at 20 °C deviated from the theoretical line, which was constructed assuming the formation of one chain per initiator (**1**) molecule, indicating that chain transfer reaction operated under these conditions (Figure 1b). In addition, the polymers exhibited broad and bimodal (at >50% conversion) molar mass distributions (Figure S1), high glass transition temperatures (e.g., T_g = 56.6 °C), and a moderate content of surviving double bonds (e.g., 50%, Figure 1c). From these last facts, we concluded that numerous side reactions involving the double bonds of the polymer chains (branching and/or cross-linking, intramolecular cyclizations) have taken place.

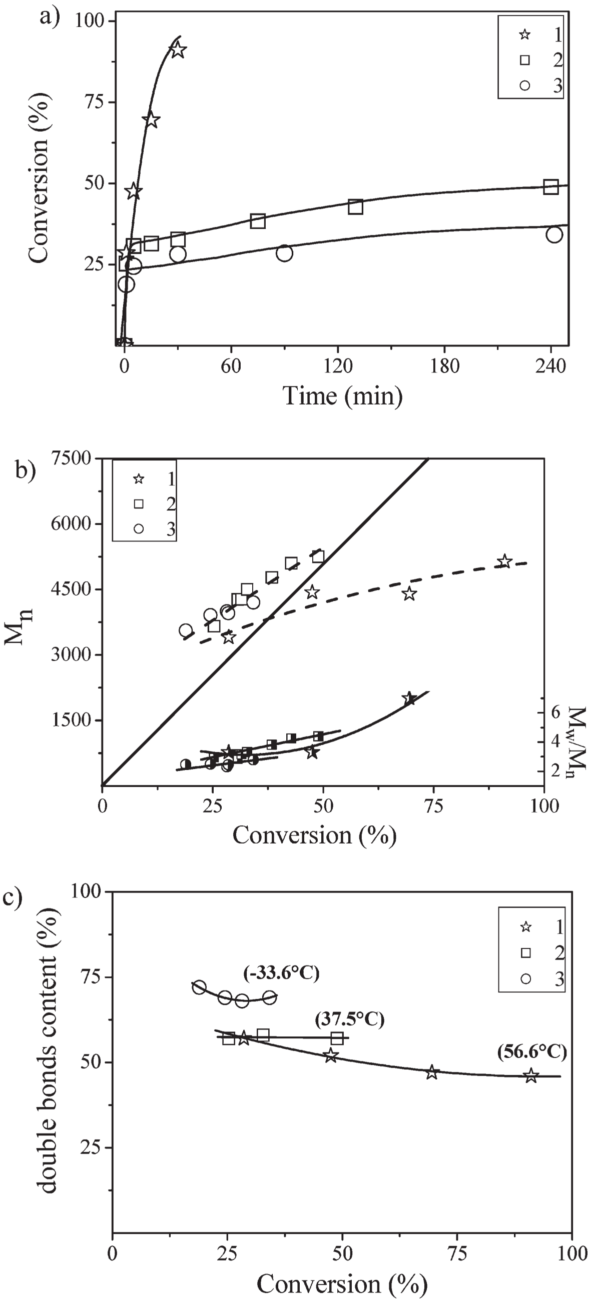


Figure 1. (a) Conversion vs time, (b) M_n vs conversion, and (c) double bonds content vs conversion plots for cationic polymerization of isoprene with **1**/$B(C_6F_5)_3$ initiating system at different temperatures: [I] = 0.011 M; [$B(C_6F_5)_3$] = 0.023 M; [IP] = 1.67 M; CH_2Cl_2 5 mL. Temperature: (1) 20 °C; (2) −10 °C; (3) −30 °C. The straight line in (b) corresponds to theoretically calculated M_n values. The numbers in parentheses in (c) are T_g values.

At lower polymerization temperatures (−10 and −30 °C), the reaction proceeded in two stages, i.e., an initial period of fast polymerization (up to about 30% of conversion) followed by a period of very slow monomer consumption (Figure 1a). The number-average molar mass of the polymers obtained at −10 and −30 °C slightly increased with increasing monomer conversion, apparently correlating with the theoretically calculated M_n values assuming that one molecule of initiator generates one polymer chain (Figure 1b). Importantly, decreasing the polymerization temperature led to a progressive increase of the intact double bonds content in polymer (∼70% at −30 °C) accompanied by a lowering of its glass transition temperature down to T_g = −33.6 at −30 °C (T_g = −62.7 °C[27] for *trans*-1,4-polyisoprene obtained from Gutta Percha). These results indicate that the formation of

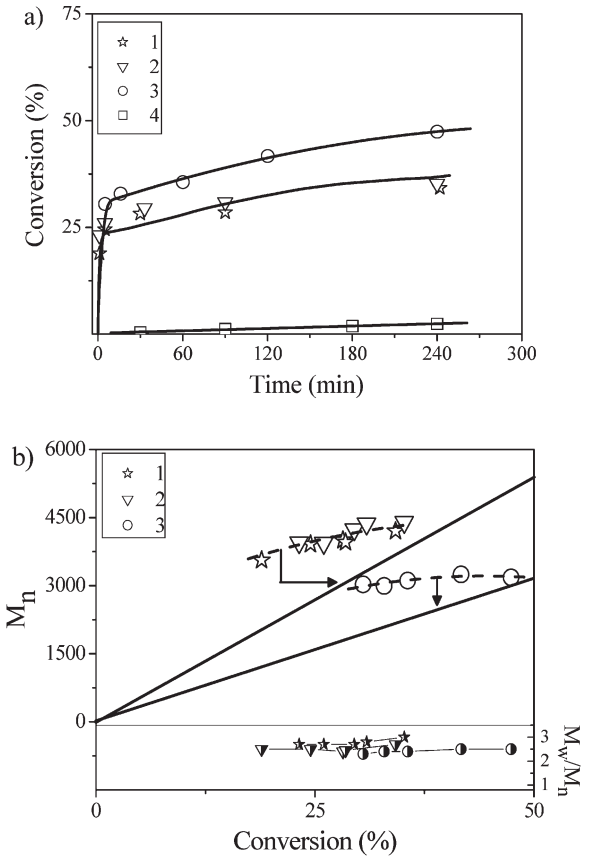


Figure 2. (a) Conversion vs time and (b) M_n vs conversion plots for the cationic polymerization of isoprene co-initiated by $B(C_6F_5)_3$ using different initiators: $[B(C_6F_5)_3]$ = 0.023 M; [IP] = 1.67 M; CH_2Cl_2 5 mL. Type of initiator: (1, 3) 1-(4-methoxyphenyl)ethanol; (2) 1-(4-methoxyphenyl)ethyl acetate; (4) $C_{17}H_{35}COOH$. Initiator concentration: (1, 2, 4) [I] = 0.011 M; (3) [I] = 0.023 M. The straight lines in (b) correspond to theoretically calculated M_n values.

cyclized sequences in the polyisoprene chains was significantly depressed at low temperatures (see Figure 1c).

The cationic polymerization of isoprene, at −30 °C, with the **1**/$B(C_6F_5)_3$ initiating system and at two different initiator concentrations, was also studied (Figure 2). Figure 2b shows that M_ns slightly increased with monomer conversion and were inversely proportional to initiator concentration, while the molar mass distributions laid in the range of M_w/M_n = 2.3−2.7. However, the polymerization stopped at ca. 35% and 50% conversion at [I] = 0.011 and 0.023 M (Figure 2a), respectively, i.e., after full consumption of initiator (estimated to 42% and 58%, respectively, by eq 1; see Experimental Part). The influence of the type of initiator on the cationic polymerization of isoprene co-initiated by $B(C_6F_5)_3$ is also presented in Figure 2. Basically, using 1-(4-methoxyphenyl)ethyl acetate (**2**) in place of **1** did not influence significantly either the reaction rate (Figure 2a) or M_n and MMD evolutions against monomer conversion (Figure 2b). In addition, the $C_{17}H_{35}COOH/B(C_6F_5)_3$ initiating system, which was previously shown to be highly effective in the synthesis of ultrahigh molar mass polyisobutylenes or isobutylene-2,3-dimethyl-1,3-butadiene copolymers ($M_w \sim$ 3 000 000 g mol^{-1}),[28] proved to have low activity in the cationic polymerization of isoprene at −30 °C (~2.5% conversion in 4 h; see Figure 2a). These data confirm the assumption that initiation occurs predominantly through the ionization of purposely added initiator (**1** or **2**), while protogenic compounds (H_2O, $C_{17}H_{35}COOH$) do not initiate efficiently the polymerization reaction under these conditions.

Polymerization in α,α,α-Trifluorotoluene. The cationic polymerization of isoprene with **1**/$B(C_6F_5)_3$ initiating system in α,α,α-trifluorotoluene or benzotrifluoride (BTF), previously claimed as an "environmentally benign" solvent for the cationic polymerization of styrene and isobutylene,[29] was then investigated. Compared to CH_2Cl_2, BTF has a similar dielectric constant (9.04 and 9.18, respectively), but a higher dipole moment (1.89 and 2.86 D, respectively).[30]

The polymerization of isoprene at −30 °C proceeded at a considerably higher rate in BTF than in CH_2Cl_2 under the same conditions, affording polymers with relatively broad MMD and low intact double bonds content (runs 1 and 2, Table 1). At lower co-initiator concentration, the polymers had molar masses varying with the [M]/[I] ratio, high contents of intact double bonds (up to 88%), low T_gs, and rather narrow and unimodal molar mass distributions (runs 3 and 4, Table 1 and Figure S2). As quoted also in Table 1, the **1**/$B(C_6F_5)_3$ initiating system is characterized by a high *trans*-1,4 selectivity affording polyisoprenes with 93−94% of *trans*-1,4-units. Note that, similarly to dichloromethane, conversions were limited to low values since termination reactions were not reversible here (see Figure S3).

Polymerization in the Absence of Initiator. In the cationic polymerization of isoprene in the absence of initiator (carried out here as blank experiments), the formation of a gel fraction, composed of cross-linked polymer chains insoluble in common organic solvents (THF, CH_2Cl_2), was generally observed after ~1 h of polymerization when the transparent reaction mixture started to become cloudy. By quenching the reaction at low monomer conversions (typically ≤40%), however, the formation of relatively high molar mass polymers (M_n up to 18 000 g mol^{-1}) with relatively narrow MMD (Figure S2) and relatively high intact double bonds content was observed (runs 5−7, Table 2). An increase in monomer concentration led to polymers with higher M_n, while at low isoprene concentration, polymers with lower M_ns and lower intact double bond contents were obtained (runs 5−7, Table 2). Moreover, using BTF instead of CH_2Cl_2 as a solvent did not influence significantly the M_n and MMD of the polymers. However, up to 80% of the double bonds remained intact (runs 5 and 8, Table 2). Under the best conditions, the polymers were characterized by low T_g values (Table 2) and high *trans*-1,4-content (see Table 2).

To summarize the data obtained here on the investigation of the cationic polymerization of isoprene in organic solvents (CH_2Cl_2, BTF) with **1**/$B(C_6F_5)_3$ initiating system (at −10 and −30 °C), we can conclude that the reaction proceeds in two stages in a partially controlled fashion. During the first stage of reaction a fast polymerization occurs due to the ionization of **1** followed by the addition of ca. 50−60 molecules of monomer up to ion pair collapsing with the formation of unsaturated (irreversible termination, major process) or hydroxyl-terminated (reversible termination, minor process) polyisoprene chains. On a second stage, a slow polymerization occurs through the reactivation of hydroxyl-terminated chain ends and/or competitive protonic initiation. The fact that very little amount of (if no) hydroxyl-terminated chains was detected by ^1H NMR spectroscopy or MALDI-TOF-MS (vide infra) could be ascribed to the low stability of such kind of terminal groups. In addition, the sole

Table 1. Results on the Cationic Polymerization of Isoprene Using the 1/$B(C_6F_5)_3$ Initiating System in α,α,α-Trifluorotoluene (BTF) as a Solvent[a]

run	solvent	time (min)	conv (%)	M_n (g mol^{-1})	M_w/M_n	unsaturation[b] (%)	*trans*-1,4[c] (%)	T_g[d] (°C)
1	CH_2Cl_2	360	30	4910	2.9	72	94.0	−33.6
2	BTF	2	82	5580	3.9	63	93.4	
3[e]	BTF	120	21	3460	1.9	83	92.9	−25.8
4[e,f]	BTF	360	26	2660	1.4	88	92.9	−32.4

[a] Polymerization conditions: [$B(C_6F_5)_3$] = 0.023 M; [IP] = 1.67 M; initiator: [**1**] = 0.011 M; solvent (BTF or CH_2Cl_2) 5 mL; temperature −30 °C. [b] Determined by ^{1}H NMR: 100% corresponds to linear polyisoprene with one unsaturation per isoprene units. [c] Determined by ^{1}H NMR and ^{13}C NMR spectroscopies. [d] Measured by DSC. [e] [$B(C_6F_5)_3$] = 0.01 M. [f] [**1**] = 0.023 M.

Table 2. Cationic Polymerization of Isoprene Co-initiated by $B(C_6F_5)_3$ without Initiator[a]

run	solvent	time (min)	conv (%)	M_n (g mol^{-1})	M_w/M_n	unsaturation[b] (%)	*trans*-1,4[c] (%)	T_g[d] (°C)
5	CH_2Cl_2	15	16	11 940	2.3	71	93.2	−21.1
6[e]	CH_2Cl_2	30	11	18 050	2.4	74	94.1	
7[f]	CH_2Cl_2	30	38	8 790	3.2	61	93.8	
8[g]	BTF	30	9	10 990	1.9	81	92.9	−24.6

[a] Polymerization conditions: [$B(C_6F_5)_3$] = 0.023 M; [IP] = 1.67 M; solvent (BTF or CH_2Cl_2) 5 mL; temperature −30 °C. [b] Determined by ^{1}H NMR: 100% corresponds to linear polyisoprene with one unsaturation per isoprene units. [c] Determined by ^{1}H NMR and ^{13}C NMR spectroscopy. [d] Measured by DSC. [e] [IP] = 3.35 M. [f] [IP] = 0.8 M. [g] [$B(C_6F_5)_3$] = 0.01 M.

protonic initiation typically led to branching and cross-linking reactions (see Table 2 and discussion therein).

B. Polymerization in Dispersed Media. In this part, we summarize the data obtained during the investigation of isoprene polymerization in aqueous suspension (i.e., monomer:water with vigorous agitation), in aqueous dispersion (monomer:water: solvent with vigorous agitation), or in aqueous emulsion (monomer:water + surfactant, gentle stirring).

Polymerization in Aqueous Suspension. Three concentrations of initiator **1** were tested; a blank experiment in absence of initiator was also performed (Figure 3). According to Figure 3a, the polymerization did not proceed at all without initiator under these aqueous suspension conditions, although the pH of the continuous medium was below 2. An increase in the initiator concentration led to an increase of the polymerization rate as well as of the maximum monomer conversion, up to 60% at [**1**] = 18.6×10^{-2} M. It should also be noted that the highest monomer conversion was slightly lower than predicted by eq 1 (see Experimental Part for C_{max} calculation): C_{exp} = 31%, 46%, 58% and C_{max} = 34%, 52%, 67% for [**1**] = 4.7×10^{-2}, 9.4×10^{-2}, 18.6×10^{-2} M, respectively.

The number-average molar mass of the polymers was rather low in these conditions ($M_n \leq 1200$ g mol^{-1}) and slightly increased with increasing monomer conversion, while the MMDs slightly broadened (Figure 3b). In addition, the maximum M_n decreased with an increase of initiator concentration, while MMDs did not depend significantly on the concentration of **1**. A more hydrophobic initiator (1-(4-methoxyphenyl)ethyl acetate, **2**) was also tested and compared with the results obtained with **1**. At the beginning of the reaction (up to 35% conversion), the polymerization of isoprene with **2** as an initiator proceeded at a lower rate, and higher molar mass polymers were formed in comparison with polymerizations initiated by **1** (see Figure S4). However, at the later stage of the polymerization, the reaction rates as well as the molar masses of the polymers were the same for both initiators studied (Figure S4). These results indicate that the more hydrophobic initiator could penetrate deeper into the interface layer, thus leading to an increase of molar mass due to a decreasing amount of water surrounding the propagating carbocation (irreversible chain termination/transfer agent). However, when the chains reached a critical length (15−16 monomer units, i.e., "critical DP"), they lost their surface activity and penetrated inside the particles. Once the chains were trapped in the particles, they could not undergo further propagation steps, since the catalyst was "locked" at the particle interface.[24] This effect is responsible for the observed flattening of M_ns values at the later stages of polymerization using both initiators.

Comparison with Other Processes. Figure 4 summarizes the results obtained during the investigation of the cationic polymerization of isoprene in suspension, emulsion (using DBSA as a surfactant), and dispersion (H_2O/CH_3NO_2 mixture). First of all, a blank experiment showed that dodecylbenzenesulfonic acid in combination with $B(C_6F_5)_3$ and without initiator did not initiate the cationic polymerization of isoprene. The highest (∼60%) and lowest (∼30%) monomer conversions as well as the highest ($M_n \sim 1200$ g mol^{-1}) and smallest ($M_n < 700$ g mol^{-1}) molar masses were obtained in suspension and emulsion polymerizations, respectively (see Figure 4a,b). The polymerization in aqueous dispersion proceeded almost at the same rate as in suspension (Figure 4a), however, generating polyisoprene chains with slightly lower molar masses and narrower molar mass distribution (Figure 4b).

Logically, the suspensions were not stable and phase separation rapidly occurred after the agitation was stopped; the colloidal stability of these, however, increased with monomer conversion and increasing initiator concentration. On the other hand, stable emulsions were produced with DBSA as a surfactant, with a mean particle size of typically 250 nm as measured by quasi-elastic light scattering.[31]

C. Polymer Characterization. *^{1}H NMR Spectroscopy.* Figure 5 shows the ^{1}H NMR spectra of polyisoprenes synthesized in solution (top) and in aqueous suspension (bottom). Basically, the presence of resonances arising from all three major isomeric repeat units was assigned:[7−9,32] the majority of repeat units was the *trans*-1,4 microstructure, whereas the 1,2- and 3,4-isomers are present as minor components (Figure 5). Among the signals of

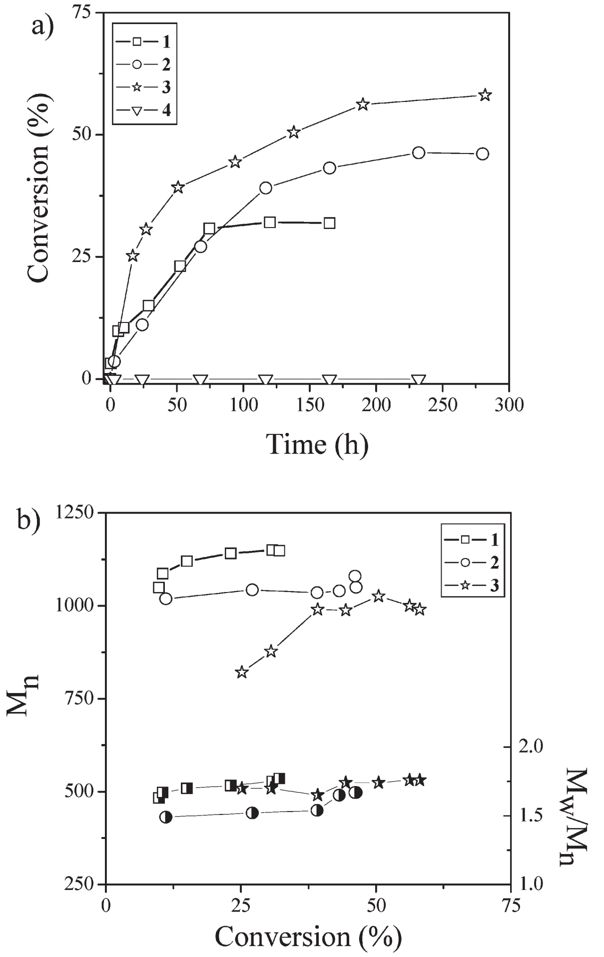


Figure 3. (a) Conversion vs time and (b) M_n, M_w/M_n vs conversion plots for isoprene polymerization with the **1**/$B(C_6F_5)_3$ initiating system in aqueous suspension at 20 °C and at various initiator concentrations: [IP] = 1.72 M; $[B(C_6F_5)_3] = 4.7 \times 10^{-2}$ M. Initiator concentration: (1) 4.7×10^{-2} M; (2) 9.4×10^{-2} M; (3) 18.6×10^{-2} M; (4) no initiator.

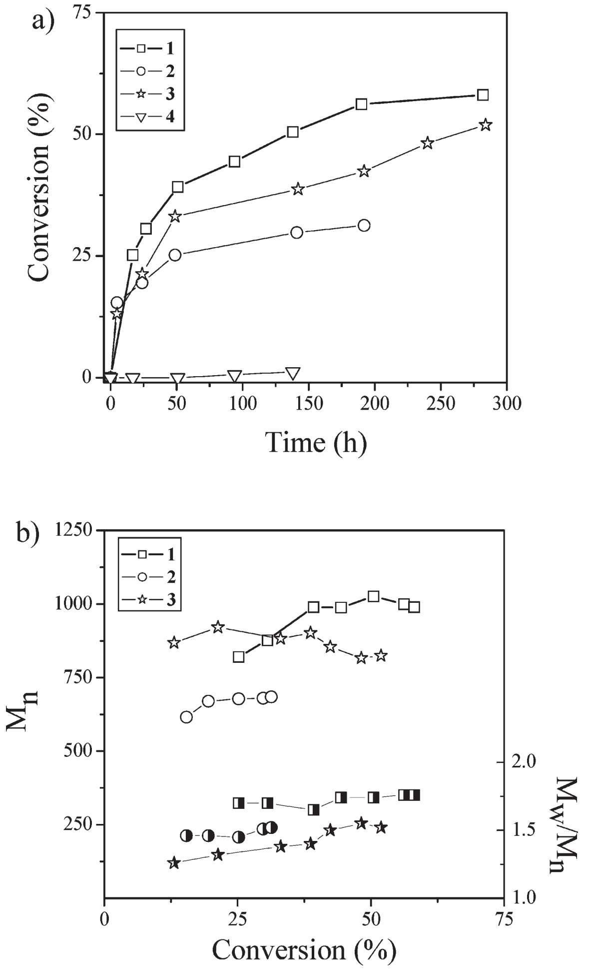


Figure 4. (a) Conversion vs time and (b) M_n, M_w/M_n vs conversion plots for the isoprene polymerization with the **1**/$B(C_6F_5)_3$ initiating system in different dispersed media at 20 °C: [IP] = 1.72 M; $[B(C_6F_5)_3] = 4.7 \times 10^{-2}$ M; [**1**] = 1.86×10^{-1} M. Dispersed media: (1) suspension; (2) emulsion, DBSA 10% to monomer; (3) dispersion, H_2O/CH_3NO_2 3 mL/2 mL; (4) emulsion, DBSA 10% to monomer; no initiator was added.

the main chain protons, i.e., CH_3- (*f*, ∼1.6 ppm), $-CH_2-$ (*d*, ∼2 ppm), olefinic protons of 3,4-(*a*, 4.6−4.7 ppm), 1,2-(*b*, 4,85−4.95 ppm; *c*, ∼5.75 ppm) and 1,4- (*e*, 5.1 ppm) units, the resonances corresponding to the chain ends are also detected in the spectrum: CH_3- (α, 1.15 ppm), CH_3O- (β, 3.8 ppm), $CH_3O-C_6H_4-$ (ε, 6.8, 7.1 ppm) at the α-end and $-CH{=}CH_2$ (ω, 4.6−4.7 ppm) at the ω-end. The absence of the signal corresponding to a $-CH_2-OH$ end group at ∼4.1 ppm,[26] generally observed in the cationic polymerization of other vinyl monomers with the **1**/$B(C_6F_5)_3$ initiating system,[20,22,23] seems to indicate that β-H elimination operates systematically under the investigated conditions (vide infra).

The comparison of ^1H NMR spectra of polyisoprenes synthesized in solution and in aqueous suspension (see Figure 5) revealed the absence of resonances corresponding to branched/cyclic structures (0.85−1.0 ppm) in the latter. Moreover, the cationic polymerization of isoprene in aqueous media discriminates from the solution process by a slightly higher regioselectivity of monomer insertion: the 1,4-, 1,2-, and 3,4-content (mol %) was 96.4%, 2.1%, 1.5% in aqueous suspension and 92.9%, 4.0%, 3.1% in the organic solvent, respectively. Importantly, the double bonds content was 96−99% for all samples obtained in dispersed media (suspension, emulsion, dispersion) while for the polymerization in solution the maximum intact double bonds content was found to be 88% (compare Table 1 and Table 3). This indicates that side reactions (cyclization, branching), which were shown to take place during the cationic polymerization of isoprene with the **1**/$B(C_6F_5)_3$ initiating system in organic solvents, were almost totally suppressed when polymerization proceeded in aqueous media (vide infra).

^{13}C NMR Spectroscopy. ^{13}C NMR spectroscopy (Figure 6) confirmed the *trans*-1,4 microstructure of all polyisoprenes synthesized in this work (Scheme 1): the major signal of the methyl carbon atom (5) of the *trans*-1,4-unit is detected at 16.0 ppm, while minor signals of the methyl carbon atoms of 3,4- (b) and 1,2-units (c) appeared at 18.8 and 22.1 ppm, respectively; note that the signal of methyl carbon atom of *cis*-1,4-unit (23.5 ppm) was totally absent in the spectrum.[32] The resonances corresponding to the methylene carbon atoms (4, 1) of *trans*-1,4 units appeared at 26.7 and 39.7 ppm, respectively, while the signals of the olefinic methylene (3) and methine (2) groups were observed at 124.2 and ∼135 ppm (see full spectrum in Figure S6), respectively. The low intensity signal at 17.7 ppm (a) was attributed to the head methyl group of *trans*-1,4-units

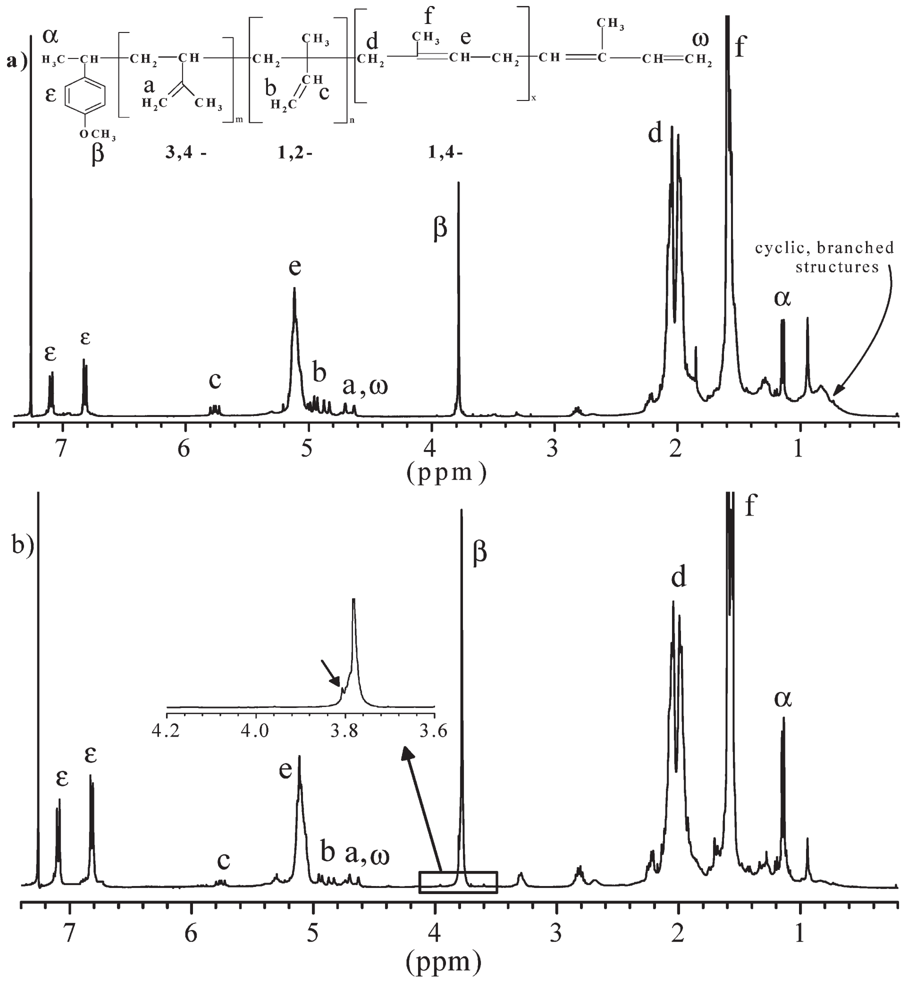


Figure 5. ^{1}H NMR spectra of polyisoprene obtained with the **1**/B(C$_6$F$_5$)$_3$ initiating system: (a) in solution at −30 °C (M_n(SEC) = 2660 g mol^{-1}; double bonds content 88%; run 4, Table 1); (b) in aqueous suspension (M_n(SEC) = 1040 g mol^{-1}; double bonds content 97%; run 9, Table 3).

Table 3. Results from the Cationic Polymerization of Isoprene Using the 1/B(C$_6$F$_5$)$_3$ Initiating System in Aqueous Media[a]

run	process	time (h)	conv (%)	M_n (g mol^{-1})	M_w/M_n	unsaturation[b] (%)	*trans*-1,4[c] (%)
9	suspension	138	51	1040	1.7	97	96.4
10	dispersion	142	39	900	1.4	99	96.2
11	emulsion	141	30	680	1.5	97	96.7

[a] Polymerization conditions: [IP] = 1.72 M; [B(C$_6$F$_5$)$_3$] = 4.7 × 10^{-2} M; [**1**] = 1.86 × 10^{-1} M; temperature 20 °C. [b] Determined by ^{1}H NMR: 100% corresponds to linear polyisoprene with one unsaturation per isoprene units. [c] Determined by ^{1}H NMR and ^{13}C NMR spectroscopy.

forming due to the protonic initiation, whereas the resonance at 22.9 ppm (d) was assigned to the methylene carbon atom of a 3,4-unit.[32] In addition, the low-intensity resonances of the methylene carbons corresponding to inverse tail-to-tail and head-to-head addition of *trans*-1,4-unit appeared at 28.3 ppm (e) and 38.5 ppm, respectively.[32] The signal at 40.4 ppm (g) corresponds to the quaternary carbon atom of the 1,2-structure, while the small signal at 44.9 ppm (h) was assigned to the methine carbon atom of a 3,4-unit.[32] Finally, the signals marked by asterisks correspond to methyl (21.3 ppm) and methine (36.9 ppm) carbon atoms of the initiator.

From the comparison of ^{13}C NMR spectra of polyisoprenes synthesized in solution (Figure 6a) and aqueous suspension (Figure 6b), we can conclude that the polymers obtained in aqueous suspension are characterized by a more regular structure than those prepared in organic solvents. Indeed, the ^{13}C NMR spectrum of polyisoprene prepared in aqueous suspension shows only signals corresponding to the carbon atoms of *trans*-1,4 units (see 1, 4, and 5 in Figure 6b) as well as the methyl (21.3 ppm) and methine (36.9 ppm) carbon atoms of the initiator, while the resonances of the carbon atoms of 1,2- or 3,4-units are almost absent in the spectrum. This observation correlates well with the ^{1}H NMR data, i.e., with higher regioselectivity of monomer insertion in aqueous media in comparison with the organic solvents. In addition, the concentration of regioirregular head-to-head (f) isoprene units is strongly decreased when the polymerization proceeds in aqueous media (compare parts a and b of Figure 6).

Mass Spectrometry. The chain end structures of polyisoprenes obtained in solution and in aqueous media were systematically analyzed by MALDI-TOF-MS. The MALDI-TOF spectrum of a typical polyisoprene synthesized in solution (run 1, Table 1), given in Figure 7, shows a narrow distribution of peaks separated by 68 g mol^{-1}, corresponding to one isoprene unit. Only one series of peaks corresponding to polymer chains cationized by silver and bearing the initiator fragment at the α-end and a double bond at the ω-end (M_n = 1604.0 g mol^{-1}) are observed in the spectrum (Figure 7). However, the mass difference between one initiator fragment (135 g mol^{-1}) and two monomer units (136 g mol^{-1}) being only 1 g mol^{-1}, it is difficult to separate the chains initiated by **1** from those generated by protonic initiation.

On the other hand, it is known that the multiplicity of the signals in the MALDI-TOF mass spectrum (arising from the isotopic distribution) can provide additional information on the chemical composition of investigated polymers by comparing the distribution of the natural isotopic cluster with the theoretical one.[33] Figure 8a shows a zoom of MALDI-TOF mass spectrum centered onto a single peak as well as two theoretical isotopic clusters for the chains initiated by protic impurities (Figure 8b) and by **1** (Figure 8c), respectively. For instance, identical peaks at 1627 g mol^{-1}, against one peak at 1628 g mol^{-1}, for theoretical (Figure 8b,c) and measured isotopic clusters (Figure 8a), respectively, indicates that the initiation of the polymerization under the conditions investigated (temperature −30 °C) proceeds mainly through the ionization of **1**, while initiation by protic impurities is negligible. The absence of peaks at 1633 and 1634 g mol^{-1} in the experimental spectrum (Figure 8a) confirms the above-mentioned suggestion: indeed, these peaks would appear in case of initiation by protic impurities (see Figure 8b).

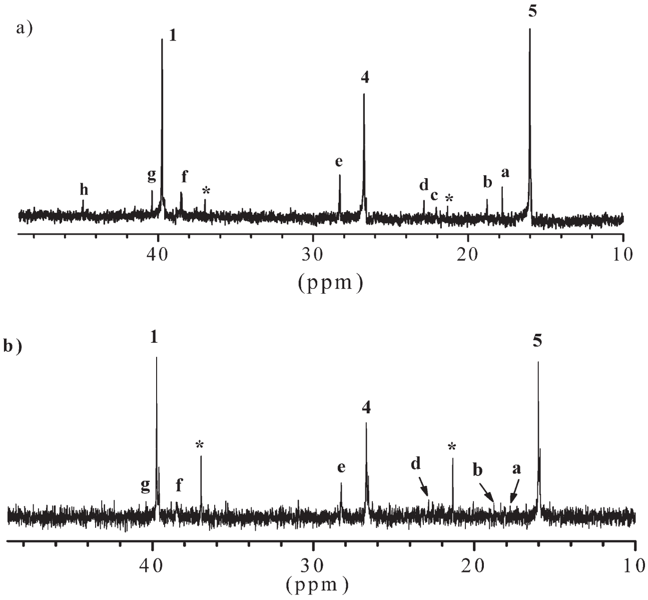
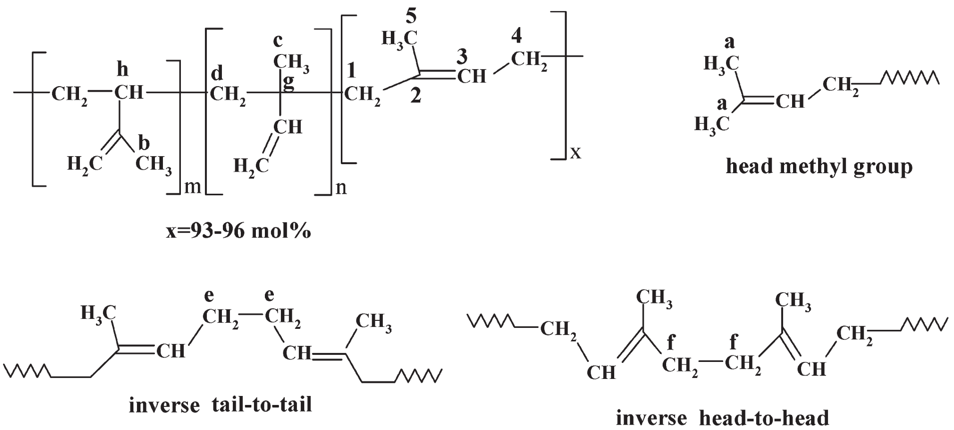


Figure 6. Aliphatic chemical shift region of the ^{13}C NMR spectrum of polyisoprenes obtained with the **1**/B(C_6F_5)$_3$ initiating system: (a) in solution at −30 °C (M_n(SEC) = 2660 g mol^{-1}; double bonds content 88%; run 4, Table 1); (b) in aqueous suspension (M_n(SEC) = 930 g mol^{-1}; double bonds content 97%; run 9, Table 3).

Polyisoprenes prepared in aqueous media entail more complicated MALDI-TOF mass spectra in comparison with those synthesized in solution (Figure 9). The main population (e.g., M_n = 785.3 g mol^{-1}) corresponds to chains cationized by silver and bearing the initiator fragment at the α-end and a double bond at the ω-end. The minor population (e.g., M_n = 803.3 g mol^{-1}) is assigned to hydroxyl-terminated polyisoprene chains containing the initiator fragment at the α-end. Interestingly, these latter were not detected by the less sensitive ^{1}H NMR spectroscopy technique (see Figure 5). Finally, the small peaks centered at e.g. M_n = 1123.5 g mol^{-1} and overlapping with the front of the main population (Figure S7) are attributed to polyisoprenes bearing two molecules of initiator per chain and one double bond at the ω-end. This type of chains could arise from the copolymerization of isoprene with one or few molecules of *p*-methoxystyrene, generated by partial decomposition of the initiator. One fact in favor of this explanation could be the slightly lower experimental monomer conversion obtained in comparison with the predicted value (see subsection Polymerization in Aqueous Suspension). Besides, the small shoulder of the methoxy peak at 3.81 ppm in the ^{1}H NMR spectrum of polyisoprene obtained in aqueous media (Figure 5b) is another indication of the presence of *p*-methoxystyrene unit(s) in the polyisoprene chains.[34]

Functionality and Molar Mass Correction. Table 4 summarizes the results of functionality (initiator fragment at the α-end) calculations using MALDI-TOF-MS and ^{1}H NMR spectroscopy data. The functionality of polyisoprenes synthesized at room temperature are far less than 100%, indicating that under these conditions a competitive protonic initiation takes place (Table 4). On the contrary, the polyisoprene chains obtained in organic solvents at −30 °C possess primarily one fragment of initiator at the α-end and one double bond at the ω-end (run 14, Table 4). In addition, for both temperatures studied, a decrease

Scheme 1. Possible Structures for Polyisoprenes Obtained by Cationic Polymerization of Isoprene with the 1/B(C_6F_5)$_3$ Initiating System



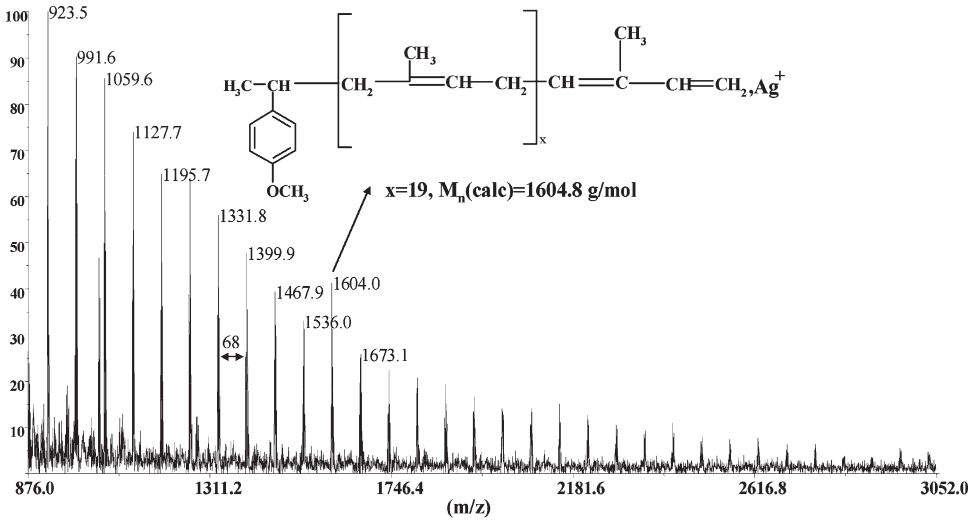


Figure 7. MALDI-TOF MS of polyisoprene obtained with the **1**/B(C_6F_5)$_3$ initiating system at −30 °C in CH_2Cl_2 (run 1, Table 1).

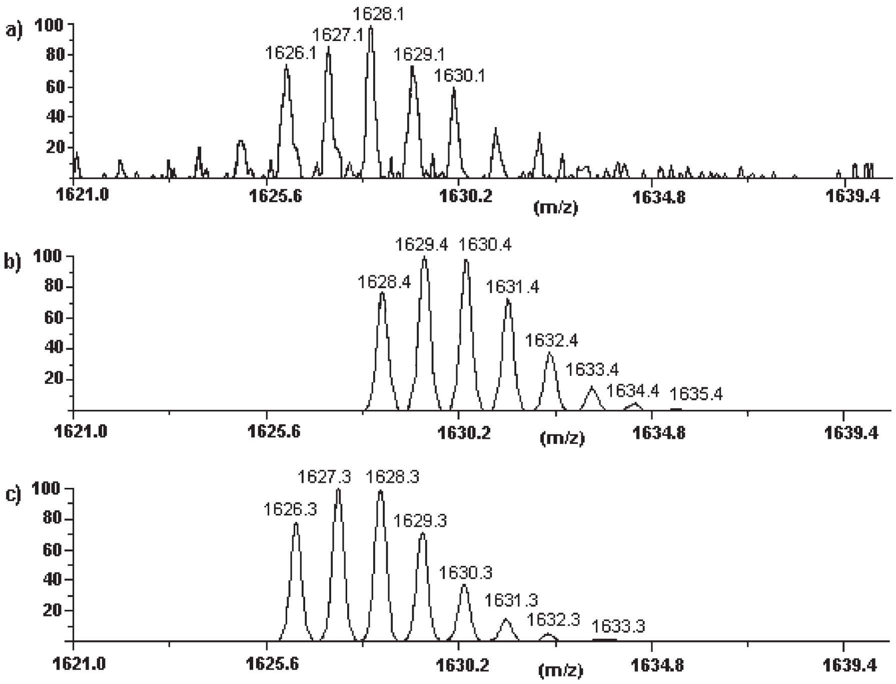


Figure 8. (a) Expansion of MALDI-TOF mass spectrum between m/z = 1621 and 1640 g mol^{-1} and theoretical isotopic clusters for (b) H−(polyisoprene) and (c) $CH_3O-C_6H_4$−(polyisoprene).

in $F_n(\alpha)$ value with increasing reaction time is observed, since protonic initiation is responsible for the slow consumption of monomer after the first, fast stage of polymerization (see Figures 1 and 2 and discussion therein). Finally, polyisoprenes obtained in aqueous media are characterized by a high functionality; i.e., virtually all chains possess an initiator fragment at the α-end. The observed overestimation of F_n (F_n = 107%) could be explained by the presence of *p*-methoxystyrene units in some polyisoprene chains (vide supra).

The number-average molar mass of the polymers were also determined by ^{1}H NMR spectroscopy from the peak intensity ratio of the main chain aliphatic protons to the phenyl protons of the initiator ($M_n = [2(I(d) + I(f))/5I(\varepsilon)] \times 68 + 135$ (head-group)). In the example given above (Figure 6), the obtained values M_n(NMR) = 2320 g mol^{-1} (in solution) and M_n = 910 g mol^{-1} (in aqueous media) were slightly lower than those calculated from SEC data, M_n(SEC) = 2660 g mol^{-1} and M_n(SEC) = 1050 g mol^{-1}, respectively. Overestimation of the M_n values by SEC is certainly due to the error arising from column calibration by polystyrene standards. We then built a curve of M_n(SEC) vs M_n(NMR) and compared our data with those obtained by Grubbs et al.,[26] who carried out the ring-opening metathesis polymerization of 1,5-dimethyl-1,5-cyclooctadiene, affording linear telechelic polyisoprene. As shown in Figure 10, most data fall on the same parallel of the bisectrix curve, indicating that mostly linear poly(isoprene) chains are formed in the course of isoprene polymerization with the **1**/B(C_6F_5)$_3$ initiating system in organic solvents (CH_2Cl_2, BTF) at −30 °C or in aqueous media. This

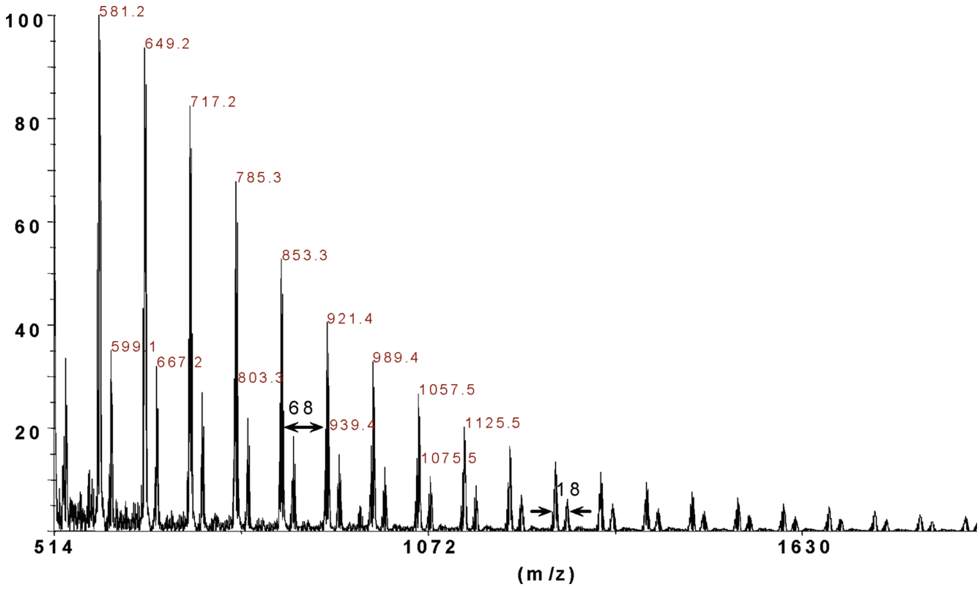


Figure 9. MALDI-TOF MS of poly(isoprene) obtained with the **1**/B(C_6F_5)$_3$ initiating system at 20 °C in aqueous suspension (run 9, Table 3).

Table 4. Functionality at the α-End of Polyisoprenes Synthesized with the 1/B(C_6F_5)$_3$ Initiating System[a]

run	media	*T* (°C)	time (min)	$F_n(\alpha)^b$	$F_n(\alpha)^c$
12	CH_2Cl_2	20	5	58	56
13[d]	CH_2Cl_2	20	45	39	31
14	CH_2Cl_2	−30	90	83	90
15[d]	CH_2Cl_2	−30	240	74	73
16	H_2O	20	138	–[e]	107

[a] Polymerization conditions: For polymerization in solution: [B(C_6F_5)$_3$] = 0.023 M; [IP] = 1.67 M; initiator: [**1**] = 0.011 M; CH_2Cl_2 5 mL. For polymerization in aqueous media: [IP] = 1.72 M; [B(C_6F_5)$_3$] = 4.7×10^{-2} M; [**1**] = 1.86×10^{-1} M. [b] Calculated from MALDI-TOF-MS data. [c] Determined by ^{1}H NMR. [d] 1-(4-Methoxyphenyl)ethyl acetate was used as initiator. [e] Peaks overlapping prevents one from carrying out any calculation.

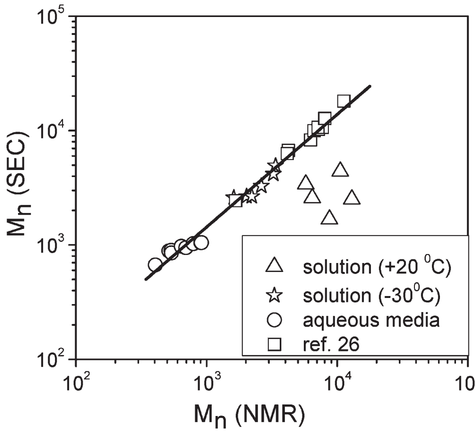


Figure 10. Correlation between M_n values obtained by ^{1}H NMR spectroscopy and SEC (in log−log scale).

relationship seems to strengthen the idea that, under these conditions, almost all polymer chains contain one initiator fragment at the α-end; i.e., undesirable protic initiation is suppressed. In contrast, M_n(NMR) ≫ M_n(SEC) for the polyisoprenes synthesized at +20 or −10 °C, since protic initiation or/and branching operate(s) at these temperatures (Figure 10).

DISCUSSION ON POLYMERIZATION MECHANISM

The main reactions in the polymerization processes described above are given in Scheme 2, including initiation by **1** or by adventitious H_2O, propagation, and β-H elimination as well as side reactions such as cyclization or branching. Table 5 summarizes which steps effectively occur in solution (at −30 °C or at room temperature (+20 °C)) and in aqueous media.

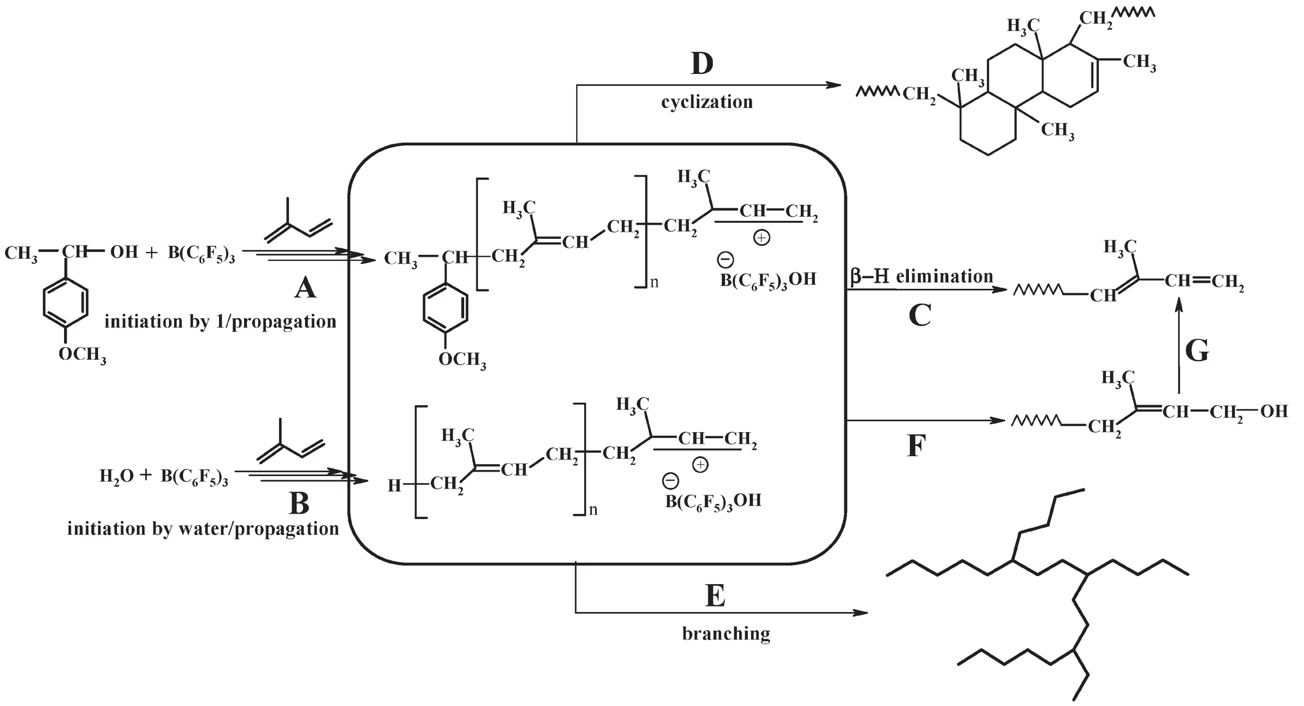
In solution and at room temperature, initiation both by **1** and H_2O occurs, followed by propagation until β-H elimination results in a chain transfer reaction (steps A, B, and C in Scheme 2). Side reactions such as cyclization (D) and branching (E), leading to polymers with high T_g and broad and multimodal MMD, also take place at this temperature. At lower reaction temperature (−30 °C), side reactions are moderated (but not fully suppressed); i.e., protonic initiation is negligible, while β-H elimination (step C) gives rise to irreversible termination under these conditions. The observed behavior of the **1**/B(C_6F_5)$_3$ initiating system at low temperatures can be attributed to an initial fast addition of ca. 50−60 molecules of isoprene to the ionized initiator molecule ($MeOPhCH(CH_3)^+ ... B(C_6F_5)_3OH^-$) in a sole ionization−monomer addition−ion pair collapse cycle, followed by a considerably slower chain growth through a competitive protonic initiation (see Table 4). The analysis of molar mass distributions of polyisoprenes prepared at −10 °C shows

Table 5. Proposed Elementary Steps in the Carbocationic Polymerization of Isoprene Initiated by the 1/B(C_6F_5)$_3$ System in Organic Solvents and in Aqueous Media[a]

process	step A	step B	step C	step D	step E	step F
solution (+20 °C)	(+)	(+)	(+)	(+)	(+)	(−)
solution (−30 °C)	(+)	(±)	(+)	(±)	(±)	(−)
aqueous media	(+)	(−)	(+)	(−)	(−)	(±)

[a] Symbols: (+) operating; (−) suppressed; (±) moderated.

Scheme 2. Proposed Mechanism for the Cationic Polymerization of Isoprene with the $1/B(C_6F_5)_3$ Initiating System in Organic Solvents and in Aqueous Media



that MMDs progressively broadened with monomer conversion (Figure 1b) becoming almost bimodal at the end of reaction (Figure S1b). This observation, in conjunction with the fact that the double bonds content did not change during the reaction (Figure 1c), indicates that most probably "parasitic" protonic initiation maintained a slow isoprene polymerization throughout the second stage of the reaction. On the contrary, at −30 °C, M_ns increased with monomer conversion without noticeable changes in their MMDs (Figure 1b and Figure S1c), whereas polymerization stopped at intermediate conversion (~35%). We assume that in this case controlled initiation via **1** took place, followed by irreversible termination most likely due to proton elimination, whereas competitive protonic initiation was strongly (almost fully) suppressed under these conditions. The propagation through the reactivation of dormant hydroxyl-terminated polyisoprene chains, which were formed in the course of reversible deactivation of the chain ends by collapse of counterion, can however not be fully excluded. The fact that no (or very little amount of) hydroxyl-terminated chains were detected by ^{1}H NMR spectroscopy or MALDI-TOF-MS could be explained by the elimination of water from the unstable hydroxyl-terminated polyisoprene chains (step G, in Scheme 2).

Neither side reactions leading to a loss of double bonds (steps D, E) nor "parasitic" protic initiation (step B) occurs in aqueous media (suspension, dispersion, or emulsion). The cationic polymerization of isoprene, similarly to the polymerization of other vinyl monomers, proceeds at the particle interface.[24] Thus, the reaction proceeds through initiation by **1** (step A) followed by irreversible β-H elimination (step C) as a major process or termination/transfer reaction via water (step F) as a minor process. Note that double-bond-terminated polyisoprenes could be also formed through the elimination reaction of the unstable hydroxyl chain ends during the work-up procedure (step G). The observed decrease of M_n with increasing initiator concentration can easily be explained by an increase of the interfacial polarity and, correspondingly, a faster termination reaction due to larger interfacial water contents. Such decrease of molar mass is also observed while decreasing monomer droplet sizes, from suspension to emulsion, again entailing higher interfacial water content in the latter. Under the best polymerization conditions, the so-called "critical DP" effect, provoked by the entry of oligomers inside the particles after they lose their surface activity, took place at around 1000 g mol^{-1} molar masses.[24] Once the chains have penetrated the particles, they cannot undergo further propagation steps, since the catalyst is "locked" at the particle interface. In conclusion, the proposed mechanism for isoprene polymerization with $1/B(C_6F_5)_3$ initiating system is fully consistent with a general polymerization mechanism in aqueous media.[24]

CONCLUSIONS

In conclusion, we have shown that the polymerization of isoprene using the $1/B(C_6F_5)_3$ initiating system proceeded in solution (CH_2Cl_2, α,α,α-trifluorotoluene as solvents) at −30 °C in a partially controlled fashion; i.e., controlled initiation via **1** followed by irreversible termination takes place, affording polymers with $M_n \leq 5000$ g mol^{-1} and $M_w/M_n \leq 1.4-2.5$, and rather high intact double bonds content (≥70%) in the polymer chains. High molar mass polymers (M_n up to 18 000 g mol^{-1}) with reasonable MMD ($M_w/M_n < 2.4$) were also synthesized through adventitious water/$B(C_6F_5)_3$-initiated cationic polymerization of isoprene. Most importantly, the cationic polymerization of isoprene with the $1/B(C_6F_5)_3$ initiating system in aqueous media (suspension, dispersion, or emulsion) proceeded without any side reactions (cyclization, branching) affording *trans*-1,4-polyisoprenes in moderate yield with $M_n \leq 1200$ g mol^{-1} and relatively narrow MMD ($M_w/M_n \leq 1.7$).

The formation of low-molar-mass polymers in aqueous media is consistent with the so-called "critical DP" effect, provoked by the entry of oligomers inside the particles after they lose their surface activity. The carbocationic polymerization of isoprene both in organic solvents and in aqueous media led to polyisoprenes possessing predominantly 1,4-*trans* microstructure (92−96.7%). To switch from 1,4-*trans* to 1,4-*cis* configuration, we now test new bulky though water-tolerant Lewis acids in the carbocationic polymerization of isoprene in organic solvents. In addition, these new Lewis acids will also be tested in aqueous media, since they should be hydrophobic enough to penetrate inside the monomer particles and promote fast polymerization, in order to synthesize high-molar-mass polyisoprenes.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Figures showing SEC traces, ^{13}C NMR spectrum of obtained poly(isoprene)s, conversion vs time and M_n, M_w/M_n vs conversion plots, and particle size distribution. This material is available free of charge via the Internet at http://pubs.acs.org.

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(31) To be precise, as shown in Figure S5, the emulsions (after diluting by 5−10-fold excess of water) exhibited a bimodal particle size distribution. This observation was tentatively attributed to the simultaneous coexistence of polymer particles (smaller size, around 270 nm) and monomer droplets (larger size, around 1090 nm) in the emulsion. Indeed, for this particular example, the percentage of smaller polymer particles was calculated to be 36%, in good correlation with the monomer conversion determined gravimetrically (32%).

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(34) Another possibility to explain the presence of more than one initiator fragment inside the polymer backbone would be some grafting reactions of one or few propagating chains onto free double bonds of a core chain. Several arguments nevertheless refute this hypothesis: (i) the extra methoxy groups are shifted downfield on the ^{1}H NMR spectrum (Figure 5b); (ii) monomodal distributions are observed in SEC traces of poly(isoprene)s obtained in aqueous media; (iii) the content of double bonds is 96% or higher for these chains.