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ORIGINAL PAPER

BF_3OEt_2-coinitiated cationic polymerization of cyclopentadiene in the presence of water at room temperature

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Abstract The cationic polymerization of cyclopentadiene (CPD) with 1-(4-methoxyphenyl)ethanol (**1**)/BF_3OEt_2 initiating system in CH_2Cl_2:CH_3CN 4:1 (v/v) mixture at room temperature and in the presence of water ($[H_2O]/[BF_3OEt_2]$ up to 8) is reported. The number-average molecular weights of obtained polymers increased in direct proportion to monomer conversion or initial monomer concentration ($M_n \leq 4{,}000$ g mol^{-1}) in agreement with calculated values, and were inversely proportional to initiator concentration. Polymer MWDs were relatively narrow ($M_w/M_n = 1.4$–1.7) up to 60% of monomer conversion. It was also shown that regioselectivity of CPD polymerization with **1**/BF_3OEt_2 initiating system did not depend significantly on water, monomer, or initiator concentration (1,4-structures content was nearly 60% in all cases).

Keywords Cationic polymerization · Cyclopentadiene · Poly(cyclopentadiene) · Water-tolerant coinitiators

Introduction

Cyclopentadiene (CPD) is one of the most active monomers in cationic polymerization leading to polymers with rigid cyclic repeated units and one double bond in every monomer unit [1]. Therefore, poly(cyclopentadiene)s exhibit attractive thermal and electronic properties such as low dielectric constants, excellent transparency, and high glass transition temperatures [1, 2], on the one hand. On the other hand, poly(cyclopentadiene)s easily crosslink into stable films by heat or air [2]. The first study on the cationic polymerization of cyclopentadiene with different

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Lewis acids ($SnCl_4$, $FeCl_3$, BCl_3, and $TiCl_4$) was performed by Staudinger et al. in the middle of 1920s [1]. In the late 1960s, important kinetic investigations were carried out by Imanishi et al. using BF_3OEt_2 alone or CCl_3COOH in conjunction with $SnCl_4$ or $TiCl_4$ [3]. Detailed investigations on the microstructure of polycyclopentadienes (polyCPD*s*) were performed by Aso et al. at the same time [4]. The very interesting studies were also performed in this period by Sigwalt and Vairon, who used such weak Lewis acids as $TiCl_3OBu$ [5, 6] and $Ph_3C^+SbCl_6^-$ [7] to synthesize poly(cyclopentadiene)s with high molecular weights (up to $M_n \sim 200{,}000$ g mol^{-1}). However, no sufficient control over cationic polymerization of CPD was attained so far due to the low stability of growing cations and the high reactivity of polymer double bonds [1]. Poor controllability was also seen in recent reports on the polymerization of CPD catalyzed by transition metal complexes [8, 9] or methylaluminoxane [2].

The possibility to control the molecular weight of poly(cyclopentadiene)s was first reported by Sigwalt and Vairon at the beginning of 1980s [10, 11]. Recently, Sawamoto et al. reported the possibility to control the molecular weight (up to $M_n \leq 12{,}000$ g mol^{-1}) and molecular weight distribution ($M_w/M_n = 1.2$–1.4) of poly(cyclopentadiene)s obtained by cationic polymerization of CPD using adduct of CPD with hydrogen chloride as an initiator and $SnCl_4$ as a coinitiator [12]. The same authors showed that weak Lewis acids such as $ZnBr_2$ or ZnI_2 allowed to control the regioselectivity in cationic polymerization of CPD: 70 and 76% of 1,4-structures in a polymer chain were obtained, respectively [13]. However, in all these systems, strict anhydrous conditions and very low temperatures (e.g. –78 °C) were required [10–13].

During the last decade, the cationic polymerization in aqueous media has attracted considerable attention [14]. This promising process allowed to overcome the two main problems of the cationic polymerization, i.e. the necessity to conduct polymerizations (i) in anhydrous conditions and (ii) at low temperatures. Particularly, we developed an efficient initiating system, 1-(4-methoxyphenyl)ethanol (**1**)/$B(C_6F_5)_3$, for the cationic polymerization of *p*-methoxystyrene [15], *p*-hydroxystyrene [16], styrene [17], and also cyclopentadiene [16, 18] in aqueous media. However, to date only low molecular weight polymers ($M_n \leq 3{,}000$ g mol^{-1}) could be obtained using this technique [14]. An alternative to the polymerization in aqueous media is the cationic polymerization in undried organic solvents, i.e. in the presence of excess water toward Lewis acid (LA). Two water-tolerant Lewis acids, i.e. BF_3OEt_2 [19–23] and $B(C_6F_5)_3$ [15, 17, 24], were effective in quasi-living cationic polymerization of styrene and its derivatives in CH_2Cl_2 or its mixtures with CH_3CN at $[H_2O]/[LA] = 1$ to 100, and between 0 and 20 °C. Polymers with $M_n \leq 15{,}000$ g mol^{-1} and relatively narrow molecular weight distribution ($M_w/M_n \leq 1.8$) could be obtained under these conditions. The main advantage of this technique is the simplification of the polymerization procedure, working with solvents that do not require any purification or drying.

We have recently shown that quasi-living cationic polymerization of cyclopentadiene could be performed using **1**/$B(C_6F_5)_3$ initiating system in the presence of excess water toward Lewis acid ($[H_2O]/[B(C_6F_5)_3] = 0$–5.5) at 20 °C in a CH_3CN/CH_2Cl_2 mixture [18]. Since BF_3OEt_2 is a cheaper and more widely used Lewis acid than $B(C_6F_5)_3$, we investigate in this work the cationic polymerization of cyclopentadiene with BF_3OEt_2 as a coinitiator. Particularly, the effect of water, initiator, and monomer concentrations on the cationic polymerization of the cyclopentadiene is discussed.

Experimental

Materials

Cyclopentadiene (CPD) was obtained by the retro Diels–Alder reaction of dicyclopentadiene at 180 °C over calcium hydride and then distilled in argon atmosphere over CaH_2 and kept at −30 °C. 1-(4-Methoxyphenyl)ethanol (Alfa Aesar, 95%) was distilled over CaH_2 under reduced pressure. CH_2Cl_2 was treated with sulfuric acid until the acid layer remained colorless, then washed with aqueous $NaHCO_3$, dried over $CaCl_2$, refluxed for 3 h with CaH_2, and distilled twice from CaH_2 under an inert atmosphere. Acetonitrile (Carlo Erba, 99.5%) was refluxed with P_2O_5 for 4 h, distilled over P_2O_5 and finally distilled in argon atmosphere over CaH_2. BF_3OEt_2 (Fluka) was distilled twice under reduced pressure before use. Ethanol (Sigma-Aldrich, ≥96%) was used as received.

Polymerization

The polymerization reactions were carried out under argon atmosphere at 20 °C in glass tubes. As an example of a typical procedure, polymerization was initiated by adding a solution of BF_3OEt_2 (0.061 g, 2.8×10^{-4} mol) in 0.5 mL of CH_3CN to a mixture of a total volume of 10.3 mL consisting of cyclopentadiene (0.66 g, 1×10^{-2} mol), 1-(4-methoxyphenyl)ethanol (0.031 g, 2×10^{-4} mol), CH_2Cl_2 (8 mL), acetonitrile (1.5 mL), and water (0.023 g, 1.3×10^{-3} mol). After a predetermined time, 1.0–1.5 mL aliquots were withdrawn and poured into an excess of ethanol containing a small amount of ammonia. The precipitated polymer was separated from the solution by centrifugation and dried in vacuum. Monomer conversions were determined gravimetrically. Polymer samples were stabilized by *N*-phenyl-2-naphthylamine and kept under argon atmosphere at −30 °C [12, 13].

Polymer characterization

Size-exclusion chromatography (SEC) was performed on a Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7 column thermostated at 30 °C. The detection was achieved by a differential refractometer and tetrahydrofuran (THF) was eluted at a flow rate of 1.0 mL/min. The calculation of molar mass and polydispersity was based on polystyrene standards (Polymer Labs, Germany). The molecular weights measured by SEC were corrected using the following equation: $M_n = (M_n(\text{SEC}) - 684)/1.28$ [18]. ^1H 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 standard (^1H NMR).

Results

In our previous article on the $B(C_6F_5)_3$-coinitiated cationic polymerization of cyclopentadiene, we have shown that control over molecular weight (M_n) and molecular weight distribution (MWD) could be achieved only if a mixture of CH_2Cl_2 with CH_3CN was used as a polymerization solvent [18]. Moreover, the optimal ratio (in terms of reaction rate as well as the molecular weight control) of CH_2Cl_2 to CH_3CN was found to be 4:1 v/v [18]. Therefore, the cationic polymerization of cyclopentadiene coinitiated by BF_3OEt_2 was investigated in the same solvent mixture.

Influence of water

In this series of experiments, the influence of added water concentration ($[H_2O] = 0$ to 0.31 M) on the BF_3OEt_2-coinitiated cationic polymerization of cyclopentadiene was investigated in order to find an optimal $[H_2O]/[BF_3OEt_2]$ ratio.

The cationic polymerization of CPD was extremely fast (Fig. 1a) and exothermic ($\Delta T = 20$–30 °C, up to boiling) in the absence of additional water ($[H_2O] = 0$ M). The addition of water ($[H_2O] = 0.12$ M; $[H_2O]/[BF_3OEt_2] = 3:1$) allowed to depress the polymerization rate and control the reaction exotherm ($\Delta T \leq 8$ °C). Importantly, the reaction proceeded with a reasonable rate even at $[H_2O]/[BF_3OEt_2] = 8:1$ ($[H_2O] = 0.31$ M), although the monomer conversion in this particular case did not exceed 50% (see Fig. 1a). In all cases, the polymerization processes were characterized by an initial period of high reaction rate followed by considerably slower monomer consumption (Fig. 1a). This observation is consistent with larger ionization rate for initiator relative to polymer chain ends [25–27]. A similar behavior was observed by us earlier during the investigation of the cationic polymerization of styrene with **1**/BF_3OEt_2 [23], **1**/$B(C_6F_5)_3$ [17], and 2-phenyl-2-propanol/$AlCl_3OBu_2$ [28, 29] initiating systems, respectively. On the other hand, the irreversible termination through β-H elimination as well as due to slow hydrolysis of Lewis acid [23], which operated under investigated conditions, is also responsible for the observed decrease in the reaction rate.

Figure 1b shows the evolution of M_n and MWD with conversion for the CPD polymerization with **1**/BF_3OEt_2 initiating system at different water concentrations. The molecular weights of the obtained poly(cyclopentadiene)s were directly proportional to the conversion and followed the theoretical line in all experiments, i.e. the cationic polymerization of cyclopentadiene using **1**/BF_3OEt_2 initiating system proceeded in a quasi-living (in the sense of Ivan [30]) fashion even in the presence of excess of water toward Lewis acid. In addition, the water concentration in the reaction mixture almost did not influence the molecular weight distribution evolution with conversion (Fig. 1b); MWD remained relatively narrow ($M_w/M_n \leq 1.6$) up to 60% of monomer conversion but some broadening of MWD was observed at higher conversions (Fig. 1b).

SEC traces, normalized by their conversion, of polymers obtained with **1**/BF_3OEt_2 initiating system are shown in Fig. 1c. The peak maximum shifts with conversion to high molecular weight region but distributions overlap in the low

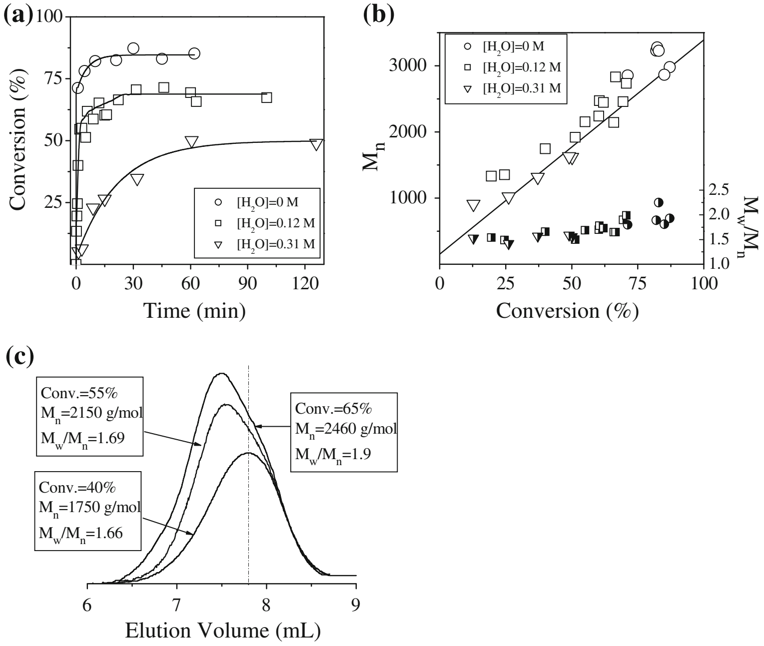


Fig. 1 **a** Conversion vs. time, **b** M_n and M_w/M_n vs. conversion dependences and **c** SEC traces for CPD polymerization with **1**/BF_3OEt_2 initiating system at different water concentrations and at 20 °C in CH_2Cl_2:CH_3CN 4:1 (v/v): [BF_3OEt_2] = 0.04 M; [CPD] = 0.93 M; [**1**] = 0.019 M. The straight line in **b** corresponds to theoretically calculated M_n. [H_2O] for **c** is 0.12 M

molar mass range. This observation also indicates that irreversible termination (but at a low extent) leading to the formation of dead chains took place under investigated conditions.

From the obtained results, we can conclude that optimal concentration of water in the systems is 0.12 M ([H_2O]/[BF_3OEt_2] = 3:1). At this water concentration, the polymerization proceeded at a high reaction rate while keeping a good control over M_n. Interestingly, almost the same amount of water is contained in wet (not purified) mixture of CH_2Cl_2 with CH_3CN [24]. These results also suggest that the added water serves as a reversible chain transfer agent providing an efficient interconversion of the active species into dormant hydroxyl-terminated species [19–23]. Further investigations were conducted at [H_2O] = 0.12 M.

Effect of initiator concentration

To confirm the quasi-living nature of cyclopentadiene polymerization with **1**/BF_3OEt_2 initiating system, the influence of initiator concentration on the polymerization process was studied. As shown in Fig. 2a, the rate of reaction increased with increasing initiator concentration, while the polymerization was very slow in the absence of an initiator. Besides, at low initiator concentrations, the polymerizations

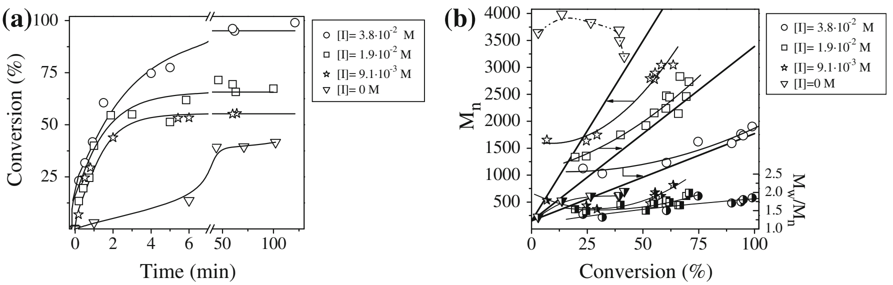


Fig. 2 **a** Conversion vs. time, **b** M_n and M_w/M_n vs. conversion dependences for CPD polymerization with **1**/BF_3OEt_2 initiating system at different initiator concentrations and at 20 °C in CH_2Cl_2:CH_3CN 4:1 (v/v): [BF_3OEt_2] = 0.04 M; [CPD] = 0.93 M; [H_2O] = 0.12 M. The *straight lines* in **b** correspond to theoretically calculated M_n

terminated at incomplete monomer conversion indicating that irreversible termination took place (Fig. 2a).

According to Fig. 2b, the molecular weights of synthesized poly(cyclopentadiene)s increased with monomer conversion irrespective of the initiator concentration in contrast to cyclopentadiene polymerization with H_2O/BF_3OEt_2 initiating system (without an addition of initiator) where M_n*s* decreased with increasing monomer conversion. Moreover, for cyclopentadiene polymerization with **1**/BF_3OEt_2 initiating system the M_n*s* were inversely proportional to initiator concentration, while experimental values of M_n correlated well with theoretical ones. In contrast, for polymerization done at low initiator concentration, the deviation of M_n from calculated value was observed due to competitive initiation by water (Fig. 2b). The observed deviation of experimental values of M_n from the theoretical line at the earlier stages of the polymerization could be attributed to a fast addition of ca. 20 molecules of CPD to ionized **1** during the first *ionization-propagation-ion pair collapse* cycle leading to higher DP_n than predicted by [*M*]/[*I*] ratio [28, 29]. In addition, the molecular weight distribution almost did not depend on the initiator concentration and leveled off at $M_w/M_n \leq 1.95$ for higher initiator concentrations ([**1**] = 3.8×10^{-2} and 1.9×10^{-2} M, respectively), while broader MWD ($M_w/M_n \sim 2.2$) was obtained at low initiator concentration (Fig. 2b). These data indicated that the cationic polymerization of cyclopentadiene with **1**/BF_3OEt_2 initiating system proceeded in a quasi-living fashion, at least for [**1**] $\geq 1.9 \times 10^{-2}$ M.

Influence of monomer concentration

Most quasi-living cationic polymerizations are successfully carried out at low monomer concentrations to avoid a high exothermicity of the reaction. However, from a practical point of view, a high monomer concentration would be desired. Therefore, the influence of monomer concentration on the cationic polymerization of cyclopentadiene with **1**/BF_3OEt_2 initiating system was investigated.

According to Fig. 3a, the reaction rate slightly decreased with increasing monomer concentration, most probably, due to the decrease of solvent polarity

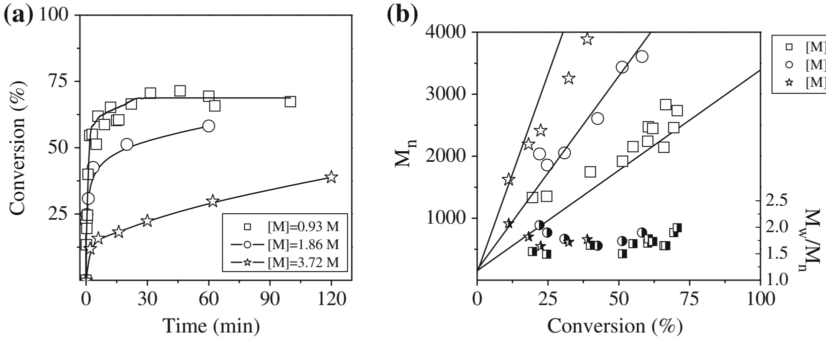


Fig. 3 **a** Conversion vs. time, **b** M_n and M_w/M_n vs. conversion dependences for CPD polymerization with **1**/BF_3OEt_2 initiating system at different monomer concentrations and at 20 °C in CH_2Cl_2:CH_3CN 4:1 (v/v): [BF_3OEt_2] = 0.04 M; [**1**] = 0.019 M; [H_2O] = 0.12 M ([H_2O] = 0.31 M for experiment with [M] = 3.72 M). The *straight lines* in **b** correspond to theoretically calculated M_n

through replacing part of solvent by less polar monomer. The number-average molecular weights and molecular weight distributions versus conversion plots are shown in Fig. 3b. The molecular weights of poly(cyclopentadiene)s were directly proportional to the conversion and followed the theoretical lines, with the exception of polymerizations performed at high monomer concentration ([M] = 3.72 M), where slight deviation of M_n from calculated value was observed. Note, in order to control the polymerization reaction at highest monomer concentration ([M] = 3.72 M), the higher concentration of water ([H_2O = 0.31 M]) was used (polymerization is uncontrolled and highly exothermic at [H_2O] = 0.12 M). Whatever the monomer concentration, the molecular weight distribution of obtained polymers almost did not change with conversion and typically lied below 1.95 (Fig. 3b). These results indicate that polymerization proceeds in a quasi-living fashion even at high monomer concentration ([M] = 3.72 M).

Polymer characterization

The microstructure of the obtained polymers was analyzed by ^{1}H NMR spectroscopy (Fig. 4). Characteristic signals appear in two regions, one for the olefinic protons (D; $a^{1,2}$ and $a^{1,4}$) in the region 5.4–6.0 ppm and the other one for the aliphatic protons, between 1.4 and 2.9 ppm. The latter region consists of three well-resolved parts: 1.4–1.8 ppm (A; $c^{1,4}$), 1.8–2.2 ppm (B; $d^{1,2}$), and 2.2–2.9 ppm (C; $c^{1,2}$, $b^{1,2}$, and $b^{1,4}$). The 1,4-structures content ([1, 4]) was calculated by the following equation: [1, 4], % = [2A/(A + B + C)] × 100, where A, B, C, and D corresponding peak intensities [4, 12, 13, 18]. The olefinic/aliphatic proton ratio (D/A + B + C) can be easily calculated from ^{1}H NMR spectrum and should equal 0.5 when the polymer chains contain only 1,2- and 1,4-structures. If the olefinic/aliphatic proton ratio deviates from 0.5, the polymer chain contains other structures formed due to the side reactions.

The chain-end structure of poly(cyclopentadiene)s obtained with **1**/BF_3OEt_2 initiating system was also examined by ^{1}H NMR spectroscopy (Fig. 4). The signals

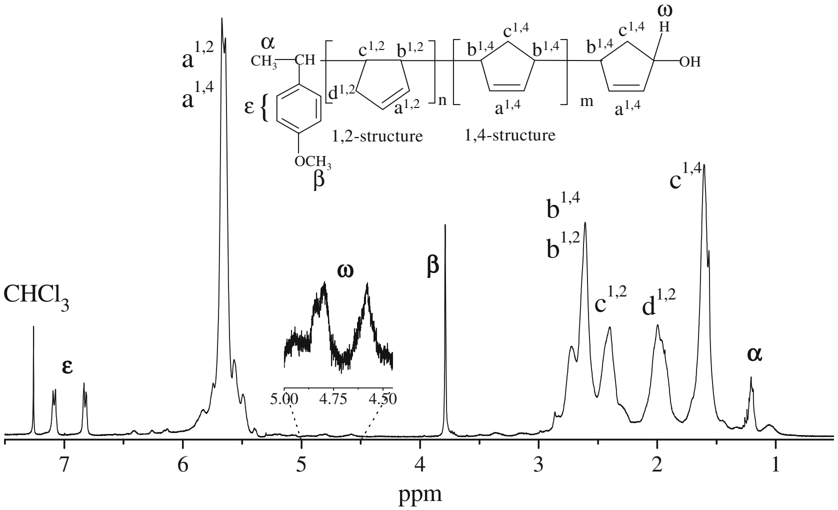


Fig. 4 ^{1}H NMR spectrum of poly(cyclopentadiene) obtained by cyclopentadiene polymerization with **1**/BF_3OEt_2 initiating system in CH_2Cl_2:CH_3CN 4:1 (v/v) at 20 °C: [CPD] = 0.93 M; [BF_3OEt_2] = 0.04 M; [1] = 0.019 M; [H_2O] = 0.12 M; Conv. = 43%; $M_n = 2710$; $M_w/M_n = 1.82$

ascribed to the end groups are clearly separated from the large characteristic signals of main-chain olefinic (D) and aliphatic (A, B, C) protons: CH_3– (α; 1.2 ppm), CH_3O– (β; 3.8 ppm); CH_3O–C_6H_4– (ε; 6.8, 7.1 ppm) at the α-end; the signals at 4.6 ppm and 4.8 ppm were attributed to the –C*H*–OH (ω) with 1,2- and 1,4-chain-end structure of the last monomeric unit, respectively [18].

Discussion

In this section, the scope and limitation of **1**/BF_3OEt_2 initiating system in the cationic polymerization of cyclopentadiene will be discussed. Table 1 summarizes the main results from this work in terms of chain-end functionality and microstructure of the poly(cyclopentadiene)s synthesized at different reaction conditions. As it is evident from Table 1, at low initiator concentration the functionality at the α-end is considerably lower than unity (see runs 1 and 2 in Table 1) indicating that under these conditions competitive initiation by H_2O takes place. This conclusion is in agreement with the observed deviation of experimental M_ns from the theoretical line at low initiator concentration (see Fig. 2b and discussion therein). Moreover, the functionality at the ω-end is less than 0.1 at medium monomer conversion and decreases down to 0 at higher conversions (see runs 1 and 2 in Table 1), i.e. an irreversible β-H elimination (see Scheme 1) is predominant under these conditions. At higher initiator concentrations, the functionality at the α-end is close to unity (runs 3–8, Table 1), indicating that protic initiation is negligible. A better functionality at the ω-end ($F_n(\omega)$ = 0.6–0.65) was obtained at low monomer conversions and at [H_2O] = 0.12 M (see runs 4, 5 in Table 1). No hydroxyl groups at the ω-end were

Table 1 Functionality and microstructure of poly(cyclopentadiene)s obtained with **1**/BF_3OEt_2 initiating system

Run	[I] (mM)	$[H_2O]$ (M)	Time (min)	Conv. (%)	$F_n(\alpha)$[a]	$F_n(\omega)$[b]	[1, 4][c] (%)	D/A + B + C[d]
1	9.1	0.12	2	44	0.65	0.05	57	0.47
2	9.1	0.12	121	64	0.45	0	55	0.48
3	19	0	1	71	0.80	0	51	0.50
4	19	0.12	2	55	1.05	0.65	56	0.49
5	19	0.31	3	6	1.15	0.60	57	0.49
6	19	0.31	32	36	0.90	0.25	57	0.50
7[e]	19	0.31	128	43	0.80	0.30	59	0.50
8	38	0.12	1	60	0.90	0.35	60	0.51

Polymerization conditions: CH_2Cl_2:CH_3CN 4:1 (v/v); temperature 20 °C; [CPD] = 0.93 M; $[BF_3OEt_2] = 0.04$ M.

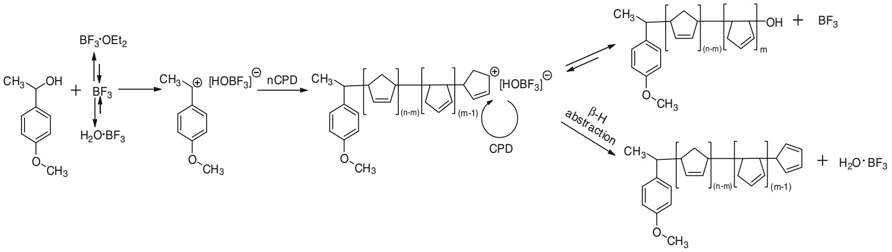
[a] Functionality at the α-end, calculated based on ^{1}H NMR data as follows: $F_n(\alpha) = [2I_\alpha \times DP_n(SEC)/3D] \times 100\%$, see "Polymer characterization" section for details

[b] Functionality at the ω-end, calculated based on ^{1}H NMR data as follows: $F_n(\omega) = [2I_\omega \times DP_n(SEC)/D] \times 100\%$.

[c] The content of 1,4-structures, calculated from ^{1}H NMR spectroscopy data.

[d] The olefinic/aliphatic proton ratios by ^{1}H NMR spectroscopy.

[e] [CPD] = 1.86 M



Scheme 1 Proposed mechanism for cyclopentadiene polymerization with **1**/BF_3OEt_2 initiating system

observed when polymerization proceeded without an addition of water (run 3, Table 1).

With respect to polymer microstructure, almost all polymers contain 55–60% of 1,4-structures in a polymer chain, i.e. the regioselectivity of the polymerization of cyclopentadiene coinitiated by BF_3OEt_2 does not depend significantly on water, initiator, or monomer concentrations. However, in the absence of an additional water (run 3, Table 1), an equal amount of 1,2- and 1,4-enchainment ([1, 4] = 51%) was found. In addition, the olefinic/aliphatic proton ratio is close to 0.5 for all polymers investigated (with the exception of those obtained at low initiator concentration) indicating that such side reactions as crosslinking, isomerization or double bond migration are absent under the investigated conditions.

A tentative polymerization mechanism is presented in Scheme 1. The main feature of this mechanism is the fact that free Lewis acid, which is formed by the dissociation of BF_3OEt_2 or BF_3OH_2 complexes, participates in the initiating and propagating steps (see Scheme 1) similarly to the styrene polymerization coinitiated by $AlCl_3OBu_2$ [28, 29] or $TiCl_4OBu_2$ [31, 32]. At appropriate reaction conditions ($[I] \geq 1.9 \times 10^{-2}$ M; $[H_2O] \geq 0.12$ M), the polymerization proceeds in a quasi-living fashion through the reversible activation of C–OH bond of initiator or dormant polymer chains. An excess of water toward Lewis acid under investigated conditions serves as a reversible chain transfer agent providing an efficient interconversion of the active species into dormant hydroxyl terminated species. At the same time, however, the polymerization is accompanied by irreversible β-H elimination leading to the loss of desired C–OH functionality at the ω-end. This side reaction becomes predominant under monomer-starved conditions. In addition, BF_3OEt_2 is not really water-tolerant Lewis acid and it slowly hydrolyzed in the presence of excess water [23]. This process also leads to irreversible termination leading to incomplete monomer conversion.

Conclusions

We have shown here that BF_3OEt_2 in conjunction with 1-(4-methoxyphenyl)ethanol (**1**) could be used for the quasi-living cationic polymerization of cyclopentadiene under mild experimental conditions, i.e. at room temperature and in the presence of excess of water toward Lewis acid ($[H_2O]/[BF_3OEt_2] = 3$–8). Poly(cyclopentadiene)s with molecular weight ($M_n \leq 4{,}000$ g mol^{-1}) and reasonable MWD ($M_w/M_n \leq 1.9$) could be prepared under these conditions. It was shown that the polymerization proceeded through reversible activation of C–OH terminal group, but the reaction was also accompanied by irreversible β-H elimination, which became predominant under monomer-starved conditions. The investigation of cyclopentadiene polymerization at different monomer concentrations revealed that the reaction proceeded in a quasi-living fashion even at monomer concentration as high as 3.72 M. We have also shown that the regioselectivity of the polymerization of cyclopentadiene using **1**/BF_3OEt_2 initiating system did not depend significantly on water, initiator, or monomer concentration: all obtained polymers contain 55–60% of 1,4-structures in a polymer chain.

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