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Chlorinated Solvent-Free Living Cationic Ring-Opening Polymerization of Epichlorohydrin Using BF_3•OEt_2 as Co-initiator: Towards Perfectly Functionalized Poly(epichlorohydrin) Diols

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ABSTRACT: The cationic ring-opening polymerization of epichlorohydrin co-initiated by $BF_3 \bullet Et_2O$ has been investigated here. Fast synthesis of pure poly(epichlorohydrin) diols ($F_n(OH) \sim 2.0$) with controlled molar mass (M_n up to 4000 g mol^{-1}) and low dispersity (Đ < 1.25) were performed both in toluene and in bulk. An original approach was developed here, consisting in first generating *in situ* the initiator through $BF_3 \bullet Et_2O$ -catalyzed reaction of ECH with water, leading to a mixture of oligomers with better solubility in the reaction medium than conventional initiators previously used. Then, through a second monomer starved-feed step, polymerization proceeds exclusively through the activated monomer mechanism, allowing perfect control of the polymer growth. The developed procedure was successfully upscaled to 100 g of polymer to validate a future industrial production of PECH, as well as its derivative glycidyl azide polymer

(GAP), the most important energetic binder for solid propellants. Additionally, a separate study was performed to elucidate the reasons for coloration of the polymer observed in the course of polymerization and/or under storage.

INTRODUCTION

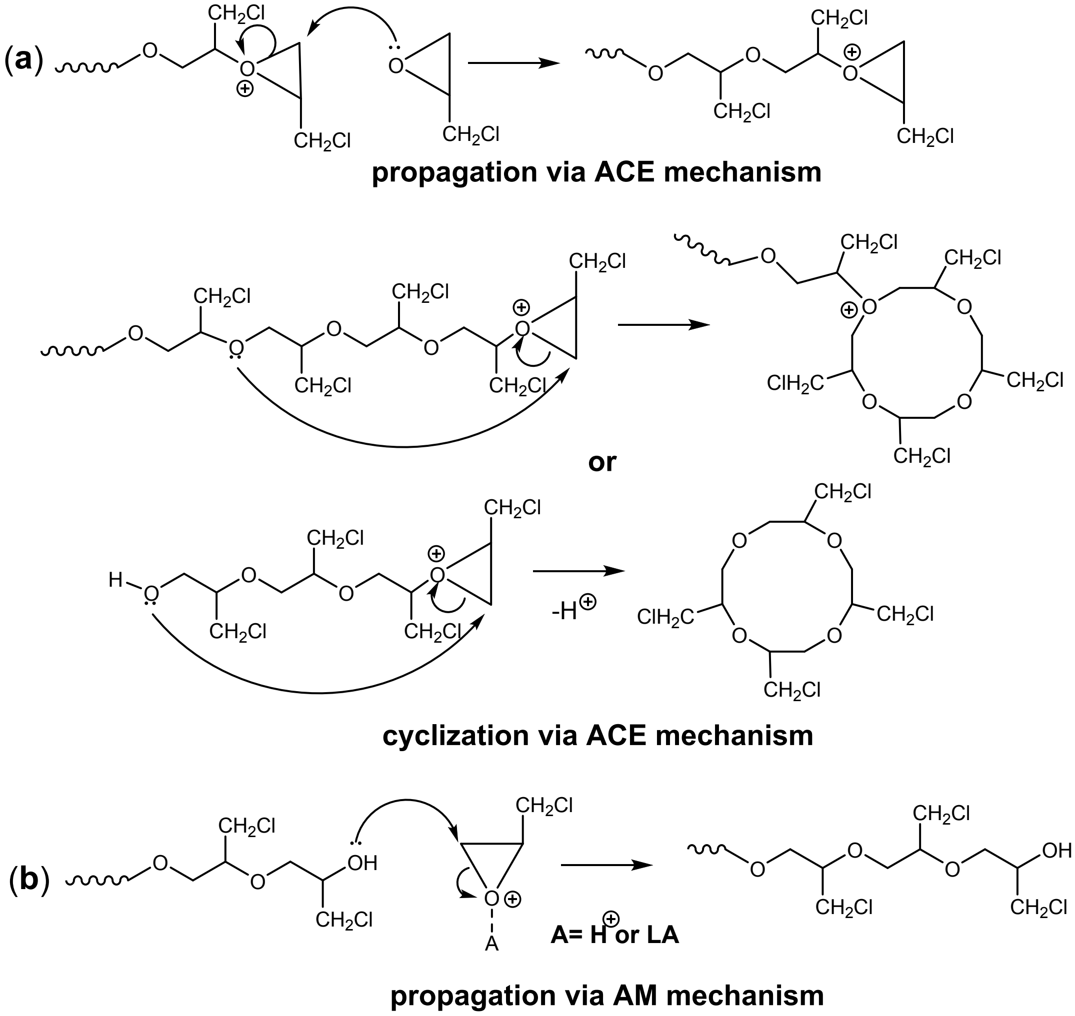
Epichlorohydrin (ECH) homopolymers (PECH) and copolymers represent an important class of functional polymeric materials for wide range applications such as in automotive industry,[1] biomedical field,[2] or energy storage.[3,4] PECH is also the starting polymer to prepare glycidyl azide polymer (GAP), the most important energetic binder for solid propellants.[5,6,7] This polymer is currently intensively used in place of hydroxyl-terminated polybutadiene, since it provides much higher specific impulse and burn rate.[7] For the preparation of such propellants, hydroxyl-terminated liquid GAP polymer is mixed with inorganic oxidizer and cured by reaction with isocyanates of functionality ≥ 2. As a result, a three-dimensional cross-linked polyurethane network with elastomeric properties is formed.[7] To ensure efficient chain extension in parallel to few crosslinking reactions, the functionality in hydroxyl groups of GAP, and thus of synthesized PECH, should be strictly equal to 2.[8] Also, because of environmental concerns, all fuels used in aviation and aerospace industries should not contain any banned molecules, in particular chlorinated solvents.

ECH can be polymerized via coordinative,[9,10,11,12,13,14] anionic[4,15,16,17] and cationic[18,1920,21,2223,24,25,2627,28,2930] mechanisms. Catalytic ring-opening polymerization (ROP) of

ECH was originally discovered by Vandenberg.[1,9,10] Vandenberg's catalyst is prepared by mixing 1 eq. of trialkyl aluminum with 0.5 eq. of H_2O and 0.5 eq. of acetylacetone to generate, as it was proposed recently, a bis(μ-oxo)dialkylaluminum active species.[31] It allows synthesizing high molar mass PECH ($M_n > 50,000$ g mol^{-1}) often with isotactic configuration of a polymer chain. Many other monometallic[12,13,14] and bimetallic[32] multicomponent catalytic systems for the synthesis of high molar mass PECH were later reported. Despite of the possibility to prepare high molar mass and often stereoregular (co)polymers of ECH, catalytic ROP of ECH suffers from some difficulties in controlling the molar mass and chain-end functionality. In some instances also, incomplete monomer conversion was observed.[9,10,11,12,13,14,31,32] It was reported recently about the catalytic regioselective polymerization of ECH using Zn-Co(III) double metal cyanide complex, which favors formation predominantly of PECH diols, albeit of low molar masses (M_n<3,500 g mol^{-1}) and relatively high dispersity (Đ>1.5) with semi-crystalline properties (solid-liquid transition around 100 ˚C).[33]

Living anionic ROP of ECH was achieved by Carlotti et al.[15,16] using $Oct_4NBr/^iBu_3Al$ initiating system. This initiating system allows preparing well-defined heterofunctional PECH with controlled molar masses (up to M_n=80,000 g mol^{-1}) and low dispersity (Đ<1.23) as well as random and block copolymers of ECH and propylene oxide.[15,16] Triethylaluminum adduct of (2-dibenzylamino)ethoxydiethylaluminum induces slow living anionic ROP of ECH (several days to complete conversion) affording heterofunctional PECHs with low dispersity (Đ<1.3) and molar masses ranging between 14 and 44 kg mol^{-1}.[34] Note that direct living anionic ROP of glycidyl azide was recently successfully performed using triethyl borane in conjunction with Bu_4NBr as an initiator, to generate heterofunctional GAP.[35]

Clearly, PECH*s* synthesized by catalytic or anionic means are not ideal tools for the preparation of GAP, principally because of the lack of desired functionality. In stark contrast, the cationic ROP of ECH in conjunction with a molecular diol as an initiator results systematically in dihydroxy-terminated PECH.[18,19,20,21,22,23,24,25,26,27,28,29] Two different mechanisms, i.e. activated chain end (ACE) and activated monomer (AM) mechanisms, simultaneously operate during the ROP of ECH, depending on the reaction conditions (Scheme 1).[18] In ACE mechanism, the active propagating species are oxonium ions located at the chain ends and propagation occurs through the addition of neutral monomer molecules to these oxonium ions (Scheme 1a). Since the main chain (or terminal) oxygen atoms can also attack the propagating oxonium ion, macrocyclic by-products (Scheme 1a) are generated that finally lead to ill-defined mixture of linear PECH diol and cyclic oligomers.



Scheme 1. ACE (a) and (b) AM Mechanisms.

In contrast to ACE mechanism, in AM mechanism, the chain end is neutral and propagation occurs through the nucleophilic attack of the hydroxyl group at the chain end onto activated (i.e. protonated) monomer. Since cyclization is not possible in the AM mechanism, pure PECH diols form under these conditions. ACE mechanism is prominent in conditions where i) the concentration of co-initiator (Lewis acid or Brönsted acid) is higher than the concentration of initiator (alcohols or other protogenic species) and ii) the concentration of monomer is much higher than the content of initiator. Therefore, to shift the propagation from ACE to AM mechanism and to suppress the formation of cyclic oligomers, the cationic ROP of ECH should proceed at low instantaneous concentration of monomer.[18]

Cationic ROP of ECH was already largely described in the literature, using catalytic systems based on such Lewis acids as $BF_3{\bullet}Et_2O$,[18,19,20,21,22,23,24,25,26] $SnCl_4$[27] $Et_3O^+PF_6^-$ [28] as well as 1,4-butanediyl ditriflate[29] and some acidic clays.[30] The ROP of ECH in the presence of acidic clays was done in bulk, so that the resulting polymer was characterized by low M_n, broad multimodal molar mass distribution and contains a large fraction of cyclic by-products.[30] 1,4-Butanediyl ditriflate initiates slow polymerization of ECH to afford the expected PECH diol with M_n from 3400 to 15,000 g mol^{-1} and relatively high dispersity (Đ ~1.5) at moderate yields (20–50%).[29]

Triethyloxonium hexafluorophosphate ($Et_3O^+PF_6^-$) in conjunction with ethylene glycol allowed to synthesize well-defined PECH diol (Đ ~ 1.3) of low molar masses ($M_n < 1,000$ g mol^{-1}).[28]

The comparison of efficiency of $BF_3•Et_2O$ and $SnCl_4$ in the cationic ROP of ECH revealed that $BF_3•Et_2O$ afforded PECH with higher functionality in chain-end hydroxyl groups and lower dispersity, even if the corresponding polymerizations were performed at slightly different ECH/1,4-butanediol (BD) ratios.[27] The best control of the synthesis of PECH diols free of cycles with controlled molar mass (M_n≤2500 g mol^{-1}) and low dispersity (Đ<1.20) was published by Penczek et al. in 1991.[18] They used an ethylene glycol (EG)/$BF_3•Et_2O$ initiating system in CH_2Cl_2 or in bulk and proceeded by slow addition of ECH (48 h) at 20 °C. Since then, many other diols such as BD,[20,21,22,27] diethylene glycol,[21,23] 1,2-propanediol,[23] hexylene diol,[23] 1,4-cyclohexanediol[23] and even polyethylene glycols (M_n= 200 – 600 g mol^{-1})[24] were used as initiators of cationic ROP of ECH in conjunction with $BF_3•Et_2O$, mainly at 0 °C. However, PECH*s* obtained with these different initiators are often characterized by relatively high dispersity (Đ = 1.40 – 2.15) and a functionality lower than 2.0; moreover, their SEC traces display shoulder or even a separate peak in the low molar mass region, indicating the formation of cyclic by-products.[20,21,22,23,24,25,26,27] The main differences between these works and Penczek's one[18] lie in the nature of initiator, the polymerization temperature as well as the initiator to co-initiator ratio ($[EG]/[BF_3•Et_2O] \sim 50$).

Recently, Kim et al.20,[21]observed an induction period during ROP of ECH with $BD/BF_3•Et_2O$ initiating system ($[BD]/[BF_3•Et_2O] = 1 – 5$) at temperatures below 10 °C, followed by highly exothermic polymerization raising significantly the reaction temperature. Such induction period was rationally attributed to the poor solubility of initiator (BD) in dichloromethane at low reaction temperature. Interestingly, the decrease of $BF_3•Et_2O$ concentration (below $[BD]/[BF_3•Et_2O] = 2$) resulted in an increase of exothermicity during the polymerization, after the induction period ceased.[20,21]

The main purpose of this study was originally to better understand the mechanisms of ECH ROP to find conditions avoiding the use of chlorinated solvents. In this contribution, we report detailed mechanistic study of $BF_3•Et_2O$-catalyzed ROP of ECH in toluene solution and bulk conditions. A simple and efficient initiating system was developed for fast synthesis of perfectly-functionalized PECH diols ($F_n(OH) \sim 2.0$) of controlled molar masses (M_n up to 4000 g mol^{-1}) and low dispersity (Đ < 1.25). Such procedure was easily upscaled to 100 g of polymer. Additionally, a detailed characterization of the synthesized PECHs was performed with the aim to elucidate the reasons leading to the coloration of the polymers during the storage of non-purified samples. Coloration in the course of polymerization was observed before by some authors,[18,20,21,22] but never explained.

EXPERIMENTAL SECTION

Materials and methods

Epichlorohydrin (Aldrich, ≥ 99%), 1,4-butanediol (BD, Aldrich, 99%), 3-chloro-1,2-propanediol (CLPD, Aldrich, 99%) were dried with CaH_2 and then distilled from CaH_2 under reduced pressure. Boron trifluoride diethyl etherate ($BF_3 \bullet Et_2O$, Merck, for synthesis) was distilled under reduced pressure. Toluene (Aldrich, 98%) and CH_2Cl_2 (Ecos-l, reagent grade) were treated with concentrated H_2SO_4 (Ecos-l, technical grade), sodium carbonate solution (Ecos-l, reagent grade), distilled water until reaching neutral pH, dried over $CaCl_2$ (Sigma-Aldrich, anhydrous, ≥ 97%), refluxed and distilled over sodium (Sigma-Aldrich, ≥ 99%) (for experiments done in toluene) and CaH_2 (Sigma-Aldrich, ≥ 97%) (for experiments done in CH_2Cl_2), respectively. Nitromethane (Aldrich, ≥ 95%) was dried and distilled over CaH_2. Acetonitrile (Carlo Erba, 99.5%) was refluxed with P_2O_5 (Ecos-l, reagent grade), distilled over P_2O_5 and finally distilled under argon atmosphere over CaH_2. In some experiments, monomer, solvent (toluene) and

BF_3•Et_2O were used without any purification (*vide infra*). $CDCl_3$ (Sigma-Aldrich, ≥ 99.8%), dimethyl sulfoxide-d_6 (Sigma-Aldrich, 99.9%), tetrahydrofuran (anhydrous, Sigma-Aldrich, ≥ 99.9%), trifluoroacetic anhydride (Aldrich, ≥ 99%), 4,4′-methylenebisphenyl isocyanate (Sigma-Aldrich, 98%), 1,8,9-anthracenetriol or dithranol (Alfa Aesar, 97+%) and sodium iodide (Aldrich, 99.9%) were used as received.

Size exclusion chromatography (SEC) was performed on an Agilent 1200 apparatus with Nucleogel GPC LM-5, 300/7,7 column and one precolumn (PL gel 5 µm guard) and an Ultimate 3000 Thermo Scientific apparatus with Agilent PL gel 5 µm MIXED-C column and one precolumn (PL gel 5 µm guard 50 × 7.5mm) thermostated at 30˚C. The detection was achieved with a differential refractometer thermostated at 35˚C. Tetrahydrofuran was eluted at a flow rate of 1.0 mL/min. The calculations of molar mass and dispersity are based on polystyrene standards (Polymer Labs, Germany).

^{1}H NMR spectra were recorded in $CDCl_3$ at 25˚C on a Bruker AC-500 spectrometer. ^{13}C and ^{13}C DEPT-135 NMR spectra were recorded in DMSO-d_6 at 25˚C on a Bruker AC-500 spectrometer. A pulse delay of 10 s was given for recording the ^{13}C NMR spectra and about 15000 scans were accumulated.

MALDI-TOF MS was performed on a Voyager mass spectrometer (AB Sciex) 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 a reflectron and with an accelerating voltage of 20 kV. Solutions of dithranol (20 mg/mL), polymer sample (10 mg/mL) and sodium iodide (10 mg/mL) were prepared in THF. These solutions were then mixed in the ratio of matrix/sample/cationizing salt = 10:2:1 and 0.5 μL aliquots were applied to a MALDI sample target for analysis. The instrument was calibrated externally using poly(ethylene glycol) standards of appropriate molar masses. 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.

The content of H_2O in some reactants was determined by a semi-micro method on an automatic titrator Titrino 848/877 using the Karl-Fischer method. Determination of the hydroxyl number of PECH samples was performed via acid-base titration according to ASTM D4274 -16.

Polymerization procedures

Polymerizations were carried out in a 50 mL three-necked flask, connected with a vacuum system, equipped with a magnetic (solution polymerization) or mechanical (bulk polymerization) stirrer, a thermocouple to control the reaction temperature and a rubber septum to introduce the reagents. Before polymerization, the flask was systematically vacuumed and filled with argon three times.

In a typical polymerization experiment in toluene with *in situ* prepared initiator, the flask was charged with 0.05 mL of H_2O, 0.034 mL of BF_3•Et_2O and 0.43 mL of ECH ($ECH/H_2O = 2/1$ mol/mol) and plunged in a water bath at 20 °C. This heterogeneous mixture was stirred for 1 – 1.5 h until it became a homogeneous transparent viscous liquid. Then 17.3 mL of toluene/ECH mixture (1/2 v/v) was added by a syringe pump at a rate of 2.6 mL/h (in respect to pure ECH) for 4.5 h. After the completion of monomer addition, the mixture was stirred for an additional 2.5 hours. The reaction was then quenched by addition of distilled water. The reaction mixture was washed with sodium bicarbonate solution (5 wt.%), then several times with distilled water until the washing water comes back to neutral pH. The solvent was evaporated using a rotary evaporator under reduced pressure and the resulting polymer was dried in vacuum at 60°C. The monomer conversion was determined gravimetrically.

Polymerization of epichlorohydrin in bulk with *in situ* prepared initiator was carried as followed. The flask was charged with 0.05 mL of H_2O, 0.023 mL of BF_3•Et_2O and 0.46 mL of ECH ($ECH/H_2O = 2/1$ mol/mol) and placed in a water bath at 20 °C. This heterogeneous mixture was stirred for 1 – 1.5 h until forming a transparent viscous liquid. Then the water bath was heated to 40 °C and 5.4 mL of ECH was added via a syringe pump at a rate of 1 mL/h during 5.4 h. After monomer feeding, the mixture was stirred for one additional hour. Finally, the polymer was dried in vacuum at 60 °C. The monomer conversion was determined gravimetrically.

Chain-end titration

The number average functionality on hydroxyl groups (F_n) was calculated as the ratio of molar mass determined by size-exclusion chromatography to molar mass calculated from ^{1}H NMR spectrum based on the content of hydroxyl groups (Figure S1), which is sensitive to the presence of cyclic by-products.

The molar mass as well as the content of secondary and primary hydroxyl groups at the chain ends were determined from ^{1}H NMR spectra of synthesized PECH*s* (Figure S1). Because of the overlapping of protons of methylene ($–CH_2–OH$) and methine ($–CH(CH_2Cl)–OH$) end-groups with the signals of main chain protons, the hydroxyl end-groups were converted into ester end-groups by reaction with excess of trifluoroacetic anhydride.[18] This reaction was performed directly in the NMR tube containing the solution of PECH in $CDCl_3$. The content of secondary hydroxyl groups was calculated from ^{1}H NMR spectrum (Figure S1) according to the following equation:

$$\%\ \text{secondary OH} = \int(d) / [\int(d) + \int(d')/2] \qquad (1)$$

All PECH samples synthesized in this work were found to bear mainly secondary terminal hydroxyl groups (≥ 96 mol%).

The molar mass of the PECHs ($M_{n,NMR}$) was calculated from ^{1}H NMR spectrum (Figure S1) according to equation presented below:

$$M_{n,NMR} = [\int(a+b+c)/5] / [\int(d')/4 + \int(d)/2] \times 92.5 + M_I \qquad (2)$$

where M_I is the molar mass of the fragment of initiator introduced in the polymer chain, if any (*vide infra*).

Since $M_{n,SEC}$ is calculated against polystyrene standards, it is not absolute and must be corrected. To do so, some polymers known to be perfectly difunctional and not containing any macrocycles (confirmed by MALDI TOF MS for certain samples) were titrated to calculate their hydroxyl number and deduce their absolute molar mass (Table S1). The obtained values ($M_{n,titration}$) were close to M_n determined by ^{1}H NMR according to chain-end versus main chain proton integration (eq. (2)), thus confirming the perfect functionality of analyzed samples. Finally, $M_{n,SEC}$ was plotted against $M_{n,titration}$ and a correction coefficient of 0.93 was deduced from this plot (Table S1, Figure S2). Considering the fact that molar masses determined by ^{1}H NMR spectroscopy are sensitive to the presence of macrocyclic chains, that have no end-groups, the difference between $M_{n,NMR}$ and corrected $M_{n,SEC}$ values were later used for the calculation of the number average functionality on hydroxyl end groups (F_n(OH)) without the need for chemical titration. Then, in the following, the number average functionality of the chains was calculated as $F_n = [M_n(SEC)/M_n(NMR)]\times2\times0.93$.

RESULTS AND DISCUSSION

Solution Polymerization

Preliminary experiments with butanediol as an initiator

An initial series of experiments was conducted using 1,4-butanediol/BF_3•Et_2O initiating system in conditions similar to those reported by Kim et al, i.e. [BD]/[BF_3•Et_2O] = 6:1, temperature: 0 °C for a theoretical M_n of ≈ 2500 g mol^{-1}.[20,21] Firstly, the effect of solvents of different polarities such as CH_2Cl_2, toluene, acetonitrile and nitromethane on the cationic ROP of ECH was briefly investigated. Toluene was selected as the most suited substitute to CH_2Cl_2, since this solvent led to polymers with the closest properties from CH_2Cl_2-prepared ones (Table S2). Still here, PECH*s* synthesized in these two solvents showed bimodal molar mass distribution (MWD) (Figure S3) and the functionality at the chain end was typically much lower than expected for an ideal telechelic hydroxyl-terminated poly(epichlorohydrin) ($F_n \approx 1$ against an expected value of 2, Table S2). Both the presence of a low molar mass peak in SEC curves and the observed low number average functionality on hydroxyl groups indicate that ACE mechanism competes with AM one, thus leading to the formation of macrocyclic by-products.[18,19,20,21,22,23,24,25] We also looked at the effect of temperature of reaction: raising the temperature from 0 to 30 ˚C increases the solubility of initiator (BD) as well as its complex with BF_3•Et_2O in toluene (Figure S4), as also reported by Kim et al.; this in turn allowed preparing better-defined PECH with improved MWD and functionality (Table S3, Figure S5).[20,21,22]

Next, the ratio [BD]/[BF_3•Et_2O] was systematically decreased (Table S4). In all cases, an induction period of several hours followed by exotherms of different magnitudes were observed. The induction period can be ascribed to slow initiation and/or polymerization of ECH due to the poor solubility of initiator (BD) and/or its complex with BF_3•Et_2O in toluene (Figure S4). The accumulation of monomer in the reaction mixture then results in a significant runaway of polymerization after BD has been fully consumed, responsible for the exotherm. Again, the ACE mechanism operating here (Scheme 1) decreases the functionality and increases the dispersity of synthesized PECH chains (Table S4). This loss of control is particularly obvious when decreasing $[BF_3•Et_2O]/[BD]$ down to 1/25 or less. In addition, the slower polymerization at low $BF_3•Et_2O$ concentration led to incomplete monomer conversion at $[BF_3•Et_2O]/[BD]<1/25$ (Table S4).

In order to gain deeper insight into the mechanism of ROP of ECH with $BD/BF_3•Et_2O$ initiating system, PECH synthesized under the best conditions at this stage (run S17, Table S4) was characterized by MALDI TOF MS. The spectrum shows the presence of several populations of polymer chains of different structures in low and high molar mass regions, respectively (Figure 1, full spectrum in Figure S6). The major population of chains in the low molar mass region corresponds to the diol $HO–(ECH)_n–OH$ cationized by Na^+ (e.g. for $n = 15$, $m/z = 1428.8$ g mol^{-1}), i.e. which does not embed any fragment of initiator in the polymer chain (Figure 1a). The small population with slightly lower molar mass (–18 m/z) can be assigned to cyclic chains $(ECH)_n$ (e.g. for $n = 15$, $m/z = 1410.9$ g mol^{-1}). The two minor peaks that appear in the low molar mass region at –37 m/z and –69 m/z in Figure 1a correspond to $HO–(ECH)_n–OH$ oligomers that lost one and two HCl molecules per chain, respectively (*vide infra*) (Figure 1a).

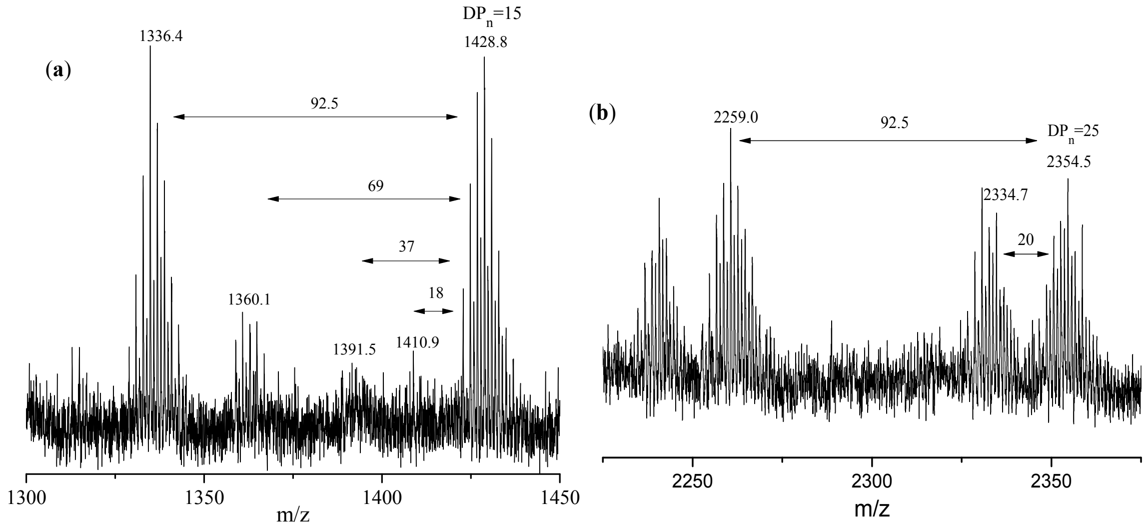


Figure 1. Zooms of (**a**) low molar mass and (**b**) high molar mass parts of MALDI TOF MS spectrum of PECH synthesized with BD/BF$_3$OEt$_2$ initiating system (run S17, Table S4). Full spectrum is given in Figure S6.

In contrast, two major populations of chains of almost equal intensities are present in the high molar mass region of the MALDI TOF MS spectrum (Figure 1b). One family of chains again corresponds to HO–(ECH)$_n$–OH cationized by Na$^+$ (for n =25, m/z = 2354.5 g mol^{-1}). Another population (m/z = 2334.7 g mol^{-1}) could be assigned either to cyclic polymer chains (ECH)$_n$ or PECH diol chains containing one fragment of initiator, i.e. HO-(ECH)$_k$–BD–(ECH)$_m$–OH: the peak difference between these two structures is only 2 m/z. The formation of cyclic chains of high molar mass is unlikely, while the presence of 1,4-butanediol fragment in a polymer chain was confirmed by ^{1}H NMR on the PECH sample reacted with trifluoroacetic anhydride (Figure S7). Indeed,^{1}H NMR spectrum shows a clear signal at 1.67 ppm assigned to the protons of the $–C\underline{H_2}–$ group of BD fragment in the polymer chain. Moreover, the molar mass calculated from ^{1}H NMR spectrum assuming one initiator fragment in the polymer chain (M_n=2960 g mol$^{–1}$) is higher than the theoretical one (M_n=2470 g mol$^{–1}$), the latter which is higher than the one based on the terminal hydroxyl groups (M_n=2370 g mol$^{–1}$). These data confirm the presence of a mix of both types of poly(epichlorohydrin) diols in the sample, i.e. with and without the initiator fragment inside the polymer chain.

One reasonable explanation for the presence of a significant fraction of HO–(ECH)$_n$–OH chains could be the competition brought by adventitious water, as efficient an initiator as BD. Indeed, as determined by Karl Fisher titration, the content of H_2O in BD (28.2 mM) and in monomer (9.2 mM) is quite high, even after drying with CaH_2, and anyhow much higher than in toluene (2.9 mM). In addition, the presence of only HO–(ECH)$_n$–OH chains in the low molar mass region indicates that at least part of adventitious water comes from the monomer slowly added into the reactor during the polymerization.

Using toluene as a solvent and applying temperatures at 20 °C or above seem to give as good conditions for cationic ROP of ECH with BD as initiator as reported before in CH_2Cl_2. However, the use of $BD/BF_3•Et_2O$ initiating system still shows several limitations: (i) a high amount of $BF_3•Et_2O$ is required to moderate the polymerization exotherm ($BD/BF_3•Et_2O$ =1/6); (ii) synthesized PECHs exhibit relatively high dispersity (Đ=1.3 – 1.4) and too low a functionality (F_n(OH)=1.80–1.90); (iii) competitive initiation via adventitious H_2O prevents the synthesis of well-defined PECH diols; and finally (iv) the induction period followed by the sharp, uncontrolled increase of the temperature are detrimental to industrial application.

Living polymerization of ECH in toluene

In the following, we decided to use H_2O as the initiator of $BF_3•Et_2O$-catalyzed cationic ROP of ECH. A first test in presence of adventitious H_2O as initiator has shown that the polymerization is slow because of the relatively low concentration of initiator. This led to an accumulation of monomer in the medium during the starved addition and promoted the ACE mechanism, generating predominantly low molar mass macrocyclic poly(epichlorohydrin)s (Table 1, Table S5, Figure S8). Although it is out of the scope of the present study, this method could be considered as a cheaper and more efficient alternative to $B(C_6F_5)_3$-catalyzed synthesis of macrocyclic polyethers.[36]

Table 1. Effect of the Type of Initiator (I) on the BF_3•Et_2O-Catalyzed Cationic ROP of Epichlorohydrin.[a]

run	initiator[b]	T_{max} (˚C)	conv. (%)	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	Đ	$F_n(OH)$[d]
1[e]	none	25	19	–	2790	630	1.51	0.43
2	H_2O	25	99	2475	2380	2510	1.16	2.00
3	CLPD	25	94	2350	2340	2370	1.20	1.98
4	BD	74	92	2300	1980	1940	1.32	1.86

[a] Conditions: [ECH]/[I] = 26; [BF_3•Et_2O]/[I] = 1/15; T = 25 °C; ECH/toluene=1/1 v/v; V(ECH)= 12.7 mL; time = 7 h. Rate of monomer addition (in respect to pure monomer): 2.5 mL/h; [b] Abbreviations: BD: butanediol; CLPD: 3-chloro-1,2-propanediol; [c] Theoretical M_n calculated as M_n = [ECH]/[initiator]×92.5×conv.; [d] Number average functionality at the chain end determined as F_n = ([M_n(SEC)/M_n(NMR)]×2×0.93); [e] Reaction time: 4.5 h; V(ECH)=3.95 mL; ECH/toluene = 2/1 v/v; [ECH]/[BF_3•Et_2O] = 623. Rate of monomer addition (with respect to pure monomer): 1.5 mL/h.

Then, a precise amount of H_2O was added to the polymerization system. In this case, the polymerization proceeded in two stages: (i) *in situ* preparation of initiator in aqueous suspension (ECH/H_2O from 1.5:1 to 1.05:1 mol/mol) (1.5 – 4h) followed by (ii) slow addition of monomer/toluene mixture (rate of addition: 2.5 mL/h, ~ 5 h). The chosen molar ratio of ECH to water is crucial and should be well below 1.5 to control the temperature during *in situ* initiator preparation (Table S6), especially in a view of a scale up (*vide infra*). During this stage, a mixture of CLPD, the monoadduct of ECH with water, and ECH oligomers are generated, the content of the former increasing with decreasing ECH/H_2O ratio (Figure S9). Note that for successful *in situ* initiator preparation, ECH should be added into the system just after premixing of BF_3•Et_2O with water. Indeed, postponing the monomer addition to 4.5 h resulted in significant slowing down of the polymerization (Table S7), most probably, because of partial hydrolysis of BF_3 in aqueous environment, as we showed it in a previous study.[37] In ideal conditions, H_2O/BF_3•Et_2O initiating system allows synthesizing well-defined PECH ($M_n \approx 2500$ g mol^{-1}) of low dispersity (Đ ≤ 1.2) and perfect chain-end functionality ($F_n(OH) \approx 2.0$) without any visible change in the reaction temperature (Table 1). Similar results in terms of control of M_n, dispersity and functionality were obtained introducing directly commercial CLPD as the initiator whereas, in strong contrast, BD initiator led to an induction period accompanied by a high reaction exotherm in the same reaction conditions (Table 1).

The living nature of the polymerization was then investigated by building M_n and Đ vs. [M]/[I] plots (Figure 2a). The molar mass increases in direct proportion to [M]/[I] ratio and a good correlation between theoretical and experimental values of M_n (both determined by SEC and ^{1}H NMR spectroscopy) is observed up to $M_n \approx 3500$ g mol^{-1} (Figure 2a).

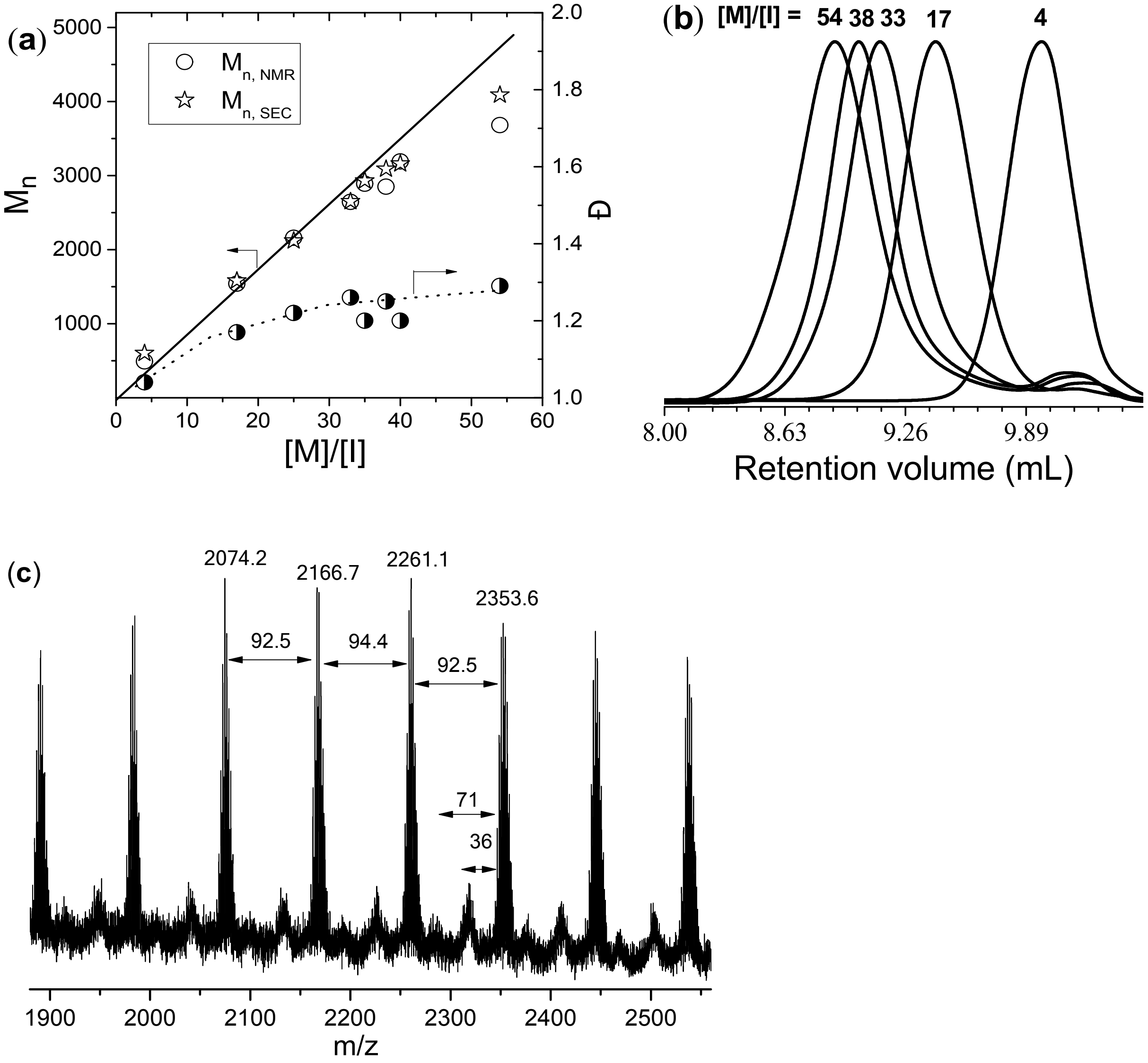


Figure 2. (**a**) M_n and Đ vs. [M]/[I] plot, (**b**) SEC traces at different [M]/[I] ratios for cationic ROP of ECH with $H_2O/BF_3{\bullet}Et_2O$ initiating system (see Table S8 for detailed experimental conditions). (**c**) Fragment of MALDI TOF MS spectrum of PECH (M_n=2510 g mol^{-1}; Đ=1.16) synthesized with $H_2O/BF_3{\bullet}Et_2O$ initiating system in toluene (run 2, Table 1). Series of peaks are mainly separated either by 92.5 or 94.5 m/z depending on the majority of stable chlorine isotopes Cl^{35} and Cl^{37} the ECH units contains, respectively.[33]

Some deviation from the theoretical line was noted at higher molar masses because of competitive initiation of polymerization by water supplied continuously with the monomer; severe drying of reactant by molecular sieves increased to some extent the molar mass of synthesized polymers (see Table S8). The dispersity of synthesized poly(epichlorohydrin)s only slightly increased with increasing [M]/[I] ratio (Figure 2a, Table S8), while SEC traces shifted towards larger molar masses as [M]/[I] ratio increased (Figure 2b). In addition, the number average functionality of hydroxyl group was measured close to 2 and did not depend on [M]/[I] ratio for all ratios studied (Table S8). These results indicate that cationic ROP of ECH with $H_2O/BF_3{\bullet}Et_2O$ initiating system proceeds in a living fashion, allowing synthesizing fully functionalized poly(epichlorohydrin) diols without visible traces of macrocyclic side compounds.

MALDI TOF MS analysis of PECH samples of different molar masses was performed to confirm the exclusive presence of PECH diols (two full spectra in Figure S10, zoom on one spectrum in Figure 2c). The major population of chains corresponds to HO–(ECH)$_n$–OH cationized by Na$^+$. Similarly to previous MALDI TOF MS spectrum (Figure 1), the two other minor populations were assigned to HO–(ECH)$_n$–OH that lost one or two HCl molecules per chain. No signals of macrocyclic PECH chains (ECH)$_n$ were tracked here (Figure 2c and Figure S10).

The preparation of pure PECH diol was finally confirmed by reacting a PECH diol sample (M_n = 3160 g mol^{-1}, Đ = 1.20) with 4,4′-methylenebis(phenyl isocyanate) to readily generate a high molar mass polyurethane (M_n = 17,900 g mol^{-1}; Đ = 2.48) (Figure S11). In addition, PECH diol distribution almost completely disappeared in the SEC spectrum, thus confirming the perfect chain-end functionality (Figure S11).

To summarize, H_2O/BF_3•Et_2O is a simple but very efficient initiating system for living cationic ROP of ECH, affording macrocyclic-free PECH*s* with M_n between 500 and 4100 g mol^{-1}, low dispersity (Đ ≤ 1.25) and exceptionally high chain-end functionality (F_n(OH) ≈ 2.0).

Towards industrially-suitable conditions

Previously-reported monomer-starved conditions to obtain PECH with high chain-end functionality are typically between 20 and 48 h, that is too long for an industrial process.[18,19,20,21,22] We then investigated the influence of the rate of monomer addition on the cationic ROP of ECH so as to optimize the reaction time. As shown in Table 2, the increase of rate of monomer addition from 0.7 to 3.5 mL/h allowed to shorten significantly the polymerization time (from 18 down to 3.5 h), without impairing the monomer conversion and polymer functionality. Dispersity of synthesized polymers only slightly increased when increasing the rate of monomer addition. Faster monomer addition (4.5 mL/h) resulted in incomplete monomer conversion (~80%), but led anyway to well-defined macrocyclic-free PECH diols with perfect functionality (Table 2, Figure 3a).

Table 2. Effect of the Rate of Monomer Addition on the Cationic ROP of Epichlorohydrin.[a]

run	ECH addition rate (mL/h)[b]	Time (h)	conv. (%)	$M_{n,theo}$[c] (g mol^{-1})	$M_{n,NMR}$ (g mol^{-1})	$M_{n, SEC}$ (g mol^{-1})	Đ	F_n(OH)[d]
5	0.7	18.0	96	3370	2890	3060	1.21	2.01
6	1.5	8.0	94	3300	3190	3130	1.20	1.96
7	2.5	3.3	88	3110	2650	2790	1.25	2.01

8	3.5	3.6	93	3280	2645	2750	1.25	1.99
9	4.5	2.6	81	2860	2450	2460	1.27	1.97

[a] Conditions: [ECH]/[H_2O]=38; [H_2O]/[BF_3•Et_2O]=15; toluene/ECH=1/2 v/v; $V(ECH)_{total}$=8.3 mL; temperature: 25 °C. [b] With respect to pure monomer. [c] Theoretical M_n calculated as M_n = [ECH]/[H_2O]×92.5×conv. [d] Number average functionality at the chain end determined as F_n = ([M_n(SEC)/M_n(NMR)]×2×0.93).

Interestingly, when more dilution was applied (toluene/ECH = 2/1 instead of 1/2 vol/vol) together with a higher rate of monomer addition (4.5 mL/h), the polymerization proceeded at lower rate, affording PECH with lower than quantitative functionality (Table S9) and containing macrocyclic by-products (Figure 3b). This result indicates that under "concentrated" conditions, the monomer is consumed faster by propagation, allowing maintaining the instantaneous concentration of ECH at very low level. Logically, reducing the rate of monomer addition under "diluted" conditions resulted in living cationic ROP of ECH to receive macrocycle-free PECH chains (Figure 3b, Table S9).

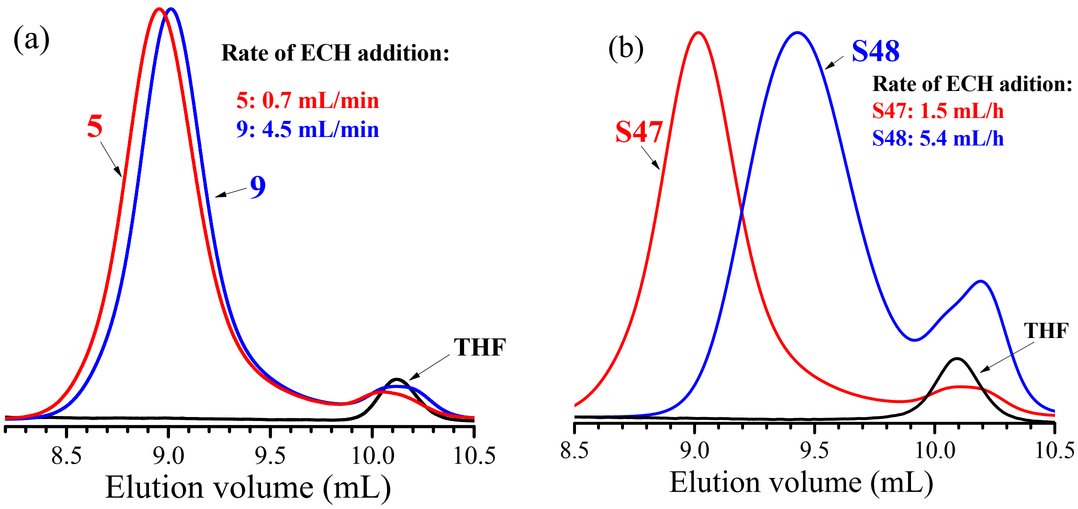


Figure 3. SEC traces of poly(epichlorohydrin) synthesized using the $H_2O/BF_3{\bullet}Et_2O$ initiating system in toluene, at different toluene/ECH ratios and different rates of monomer addition. Conditions: $[ECH]/[H_2O] = 38$; $[H_2O]/[BF_3{\bullet}Et_2O] = 15$; temperature: 25 °C. Toluene/ECH ratio (vol/vol): (**a**) 1:2; (**b**) 2:1. Numbers in Figure 3a correspond to runs in Table 2, while numbers in Figure 3b correspond to runs in Table S9, respectively.

Then, the effect of temperature was briefly investigated in the $H_2O/BF_3{\bullet}Et_2O$ initiating system. In general, similarly to ECH polymerization with $BD/BF_3{\bullet}Et_2O$ initiating system (Table S3, Figure S5), the decrease of reaction temperature below 20 °C led to a slowing down of the reaction as well as to the generation of a fraction of macrocyclic by-products (Table S10, Figure S12). On the contrary, increasing the temperature from 20 to 40 °C did not have any negative effects on the reaction rate and preserved the properties of the synthesized PECHs (Table S10).

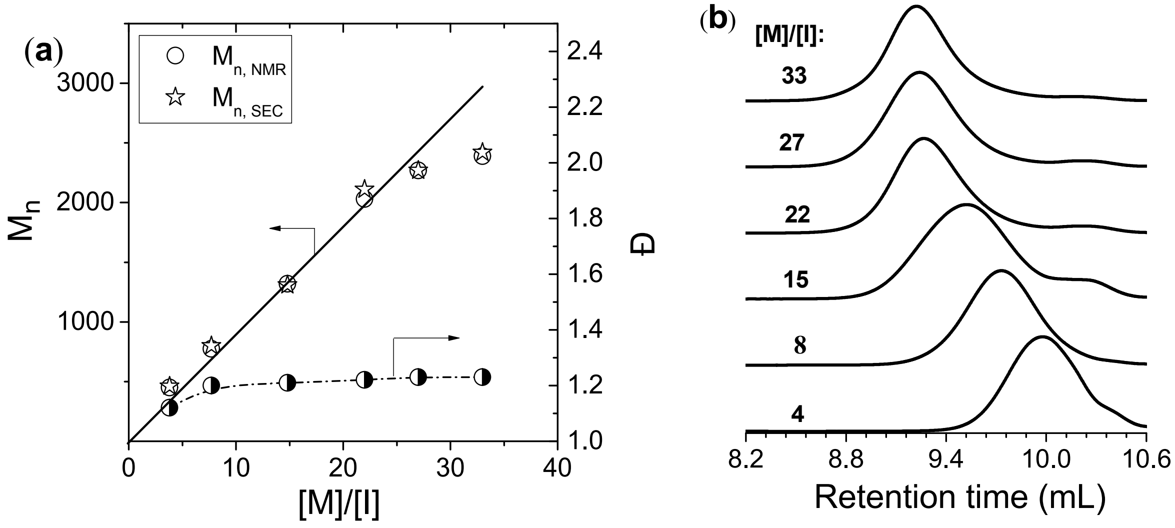
In all studies related to cationic, anionic or coordinative ROP of ECH, extensive drying and purification of all reagents and monomer are generally done because of the known sensitivity of used co-initiators/catalysts towards even traces of water. On the other hand, our team[37] and others[38] showed that $BF_3•Et_2O$ could be considered as a water-tolerant Lewis acid, as it slowly hydrolyzes in aqueous environment. Well-defined PECH diols ($M_n \approx 2500$ g mol^{-1}, $F_n(OH) \approx 2.0$) with quite low dispersity (Đ<1.2) were obtained using non-purified reagents and monomer, as shown in Table 3. Moreover, neither the reaction rate, the molar mass, the dispersity nor the chain-end functionality were affected in these raw conditions (Table S11, Figure S13).

Intermediate conclusion on ECH polymerization in toluene solution

H_2O/BF_3OEt_2 initiating system where the initiator is prepared *in situ* by reaction of ECH with water allowed synthesizing well-defined PECH diols at much faster rate that $BD/BF_3•Et_2O$[20,21] and ethylene glycol/$BF_3•Et_2O$[18] initiating systems. This achievement is indebted to the much better solubility of both CLPD and low molar mass oligomers formed in the course of *in situ* initiator preparation in the reaction media, as compared to BD and ethylene glycol (Figure S4, Figure S14, see also section “Scale-up of ECH polymerization” for more details). Polymerizations performed under “concentrated” conditions are more efficient than in “diluted” conditions (compare Figure 3a and Figure 3b) thanks again to the better solubility of CLPD or ECH oligomers in monomer than in toluene (Figure S14). An increase of polymerization temperature also results in enhanced solubility of initiator/low molar mass oligomers and, in turn, facilitates the preparation of well-defined PECH diols via a fast living ROP of ECH using $H_2O/BF_3•Et_2O$ initiating system. In optimized conditions (temperature $\geq$ 25 °C; toluene/ECH 1:2 vol/vol), $H_2O/BF_3•Et_2O$ initiating system allows synthesizing well-defined macrocycle-free PECH diols ($F_n(OH) \approx 2.0$) with M_n up to 4000 g mol^{-1} and low dispersity ($Đ \leq 1.25$) at relatively high rate of monomer addition and a total polymerization time of 3 – 4 h. The robustness and high potential for industrial use of this initiating system is also strengthened by the possibility to conduct the polymerization using unpurified reagents and monomer.

Bulk Polymerization

Motivated by the much better solubility of ECH oligomers in monomer than in toluene (Figure S14), the cationic ROP of ECH in bulk using $H_2O/BF_3•Et_2O$ initiating system was then investigated. To account for the relatively high viscosity of PECH with $M_n \approx 2000$ g mol^{-1} at 20 °C,[18] the ROP of ECH at $[ECH]/[H_2O] > 15$ was performed at 40 °C under mechanical stirring (all previous experiments in toluene were performed using a magnetic stirrer) (Table S12). The bulk cationic ROP of ECH using $H_2O/BF_3•Et_2O$ initiating system proceeds in a living fashion: the experimental values determined by both SEC and ^1H NMR correlate well with the theoretical line up to $M_n \approx 2500$ g mol^{-1}, while dispersity remains low ($Đ \leq 1.23$) (Figure 4a). SEC traces of PECH samples are symmetrical at all [M]/[I] ratios studied here and shift towards higher molar masses with increasing [M]/[I] ratio (Figure 4b).



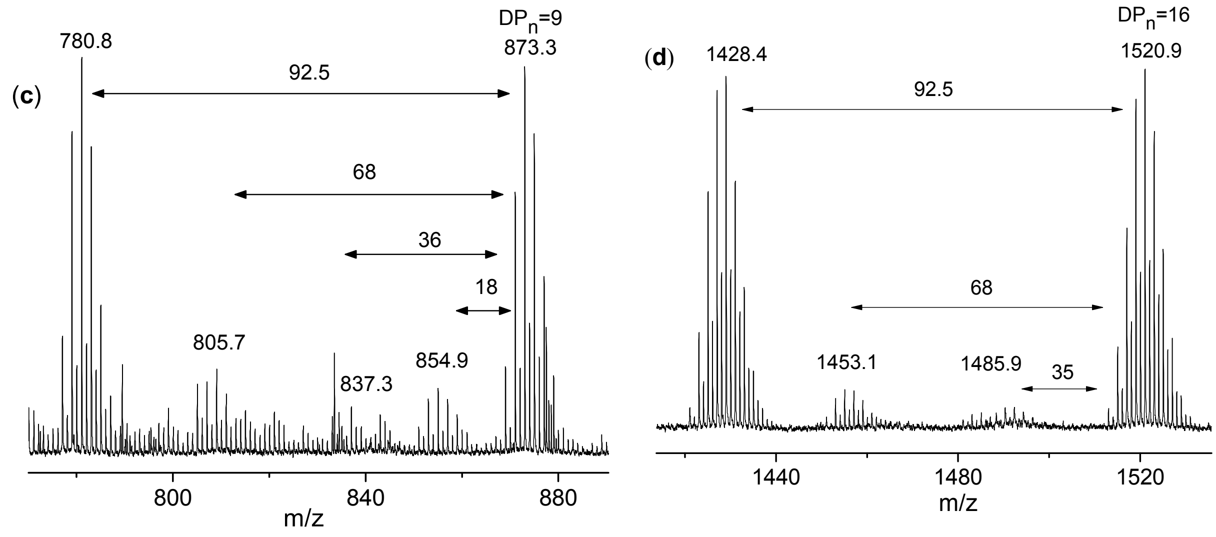


Figure 4. **(a)** M_n and Đ vs. [M]/[I] plot, **(b)** SEC traces at different [M]/[I] ratios for cationic ROP of ECH with $H_2O/BF_3•Et_2O$ initiating system in bulk (see Table S12 for detailed experimental conditions). Zooms of (**c**) low molar mass and (**d**) high molar mass parts of MALDI TOF MS spectrum of PECH ($M_n = 2270$ g mol^{-1}; Đ = 1.23; run S61 in Table S12) synthesized with $H_2O/BF_3•Et_2O$ initiating system in bulk.

Importantly, the functionality of the chain-ends does not depend on [M]/[I] ratio and is close to quantitative for all [M]/[I] ratios studied (Table S12). In order to confirm the absence of macrocyclic PECH chains and other side products in polymers obtained via bulk polymerization, MALDI TOF MS was performed (Figure 4c,d, full spectrum in Figure S15). The major population of chains in both low and high molar mass regions corresponds to polyepichlorydrin diol HO–(ECH)$_n$–OH cationized by Na$^+$. Minor peaks (–36 and –68 m/z) can be assigned to PECH diol chains that lost one and two HCl molecules, respectively. Finally, a small massif of peaks corresponding to cyclic PECH (–18 m/z) is present only in the low molar mass part of MALDI TOF MS spectra. Thus, bulk cationic ROP of ECH with $H_2O/BF_3•Et_2O$ initiating system produces predominantly PECH diol and a negligible fraction of cyclic by-products.

It should be noted that the synthesis of PECH of similar molar mass in bulk and using ethylene glycol/$BF_3•Et_2O$ initiating system, was reported previously by Penczek et al.[18] The main improvement achieved in the present work using $H_2O/BF_3•Et_2O$ initiating system is the successful reduction of the polymerization time (from 48 to 5 – 6 h) without any deleterious effect on the dispersity and functionality at the chain end of synthesized PECH*s*. This is ascribed to the much better solubility of *in situ* prepared initiator in reaction medium as compared to ethylene glycol.

Reasons for polymer coloring

PECH*s* synthesized both in solution and in bulk are transparent viscous liquids just after reaction, but then become slightly yellow (especially those obtained in bulk) upon storage for several months. The conditions of storage influence strongly the color intensity: a sample stored at –20 °C remains transparent, while the strongest coloration is observed for the same sample stored at 45 °C (FigureS16). The extension of the storage time also increases the intensity of the color, especially for the sample stored at 45 °C (Figure S17). The coloration of PECH*s* prepared in bulk is tentatively associated with the presence of traces of co-initiator in the samples that were not purified (Figure S16). Indeed, a PECH sample obtained in bulk and washed with Na_2CO_3 and water is still transparent even after 2 months of storage (compare samples 2 and 5, Figure S16).

The coloration of the sample upon storage does not affect the molar mass and the dispersity of the synthesized polymers (Figure S18). Moreover, PECH*s* samples stored at –20 °C (sample 1, Figure S16) and 45 °C (sample 4, Figure S16) show almost identical MALDI TOF MS spectra (Figure S19), i.e. the functionality at the chain end is not affected with time. Based on these observations, we can conclude that changes inside the main chain are most probably responsible for the observed coloration of PECH samples. To check so, the structure of the PECH stored at 45 °C was investigated by ^{13}C and ^{13}C-DEPT NMR spectroscopy (Figure 5). The signals at 44.2 and 78.1 ppm were assigned to the main chain carbon atoms of chloromethyl (**c**) and methine (**b**) groups in ^{13}C NMR spectrum, respectively, while the carbon signal of the methylene groups of the main chain (**a**) is splitting into three signals corresponding to regular head-to-tail (68.7 ppm, H-T), inverse tail-to-tail (70.2 ppm, T-T) and head-to-head (70.6 ppm, H-H) units. The carbon signals of terminal epichlorohydrin unit connected to hydroxyl group were identified with the help of ^{13}C DEPT-135 NMR spectroscopy (Figure 5b) at the following chemical shifts: 47.1 (**c’**), 69.3 (**b’**) and 70.8 ppm (**a’**). In addition to these signals, a resonance at 15.2 ppm (**d**) in the aliphatic part of ^{13}C NMR spectrum was assigned to the carbon of the methyl group close to an internal main chain double bond (Figure 5). The signals at ca. 101.5 ppm (**e**) on both ^{13}C NMR and ^{13}C DEPT-135 NMR spectra can be assigned to carbon atoms of internal olefinic methine group in the main chain (Figure 5b). Another signal in the olefinic part of ^{13}C NMR spectrum at 162.0 ppm (**f**) corresponds to the signal of the tertiary carbon atom connected to an external main chain double bond, as confirmed by ^{13}C DEPT-135 NMR (Figure 5b). Note that the signal of the carbon atom of olefinic methylene group (CH_2=) is theoretically assigned at ca. 77 ppm and, therefore, surely overlaps with the resonances of main chain carbon atoms.

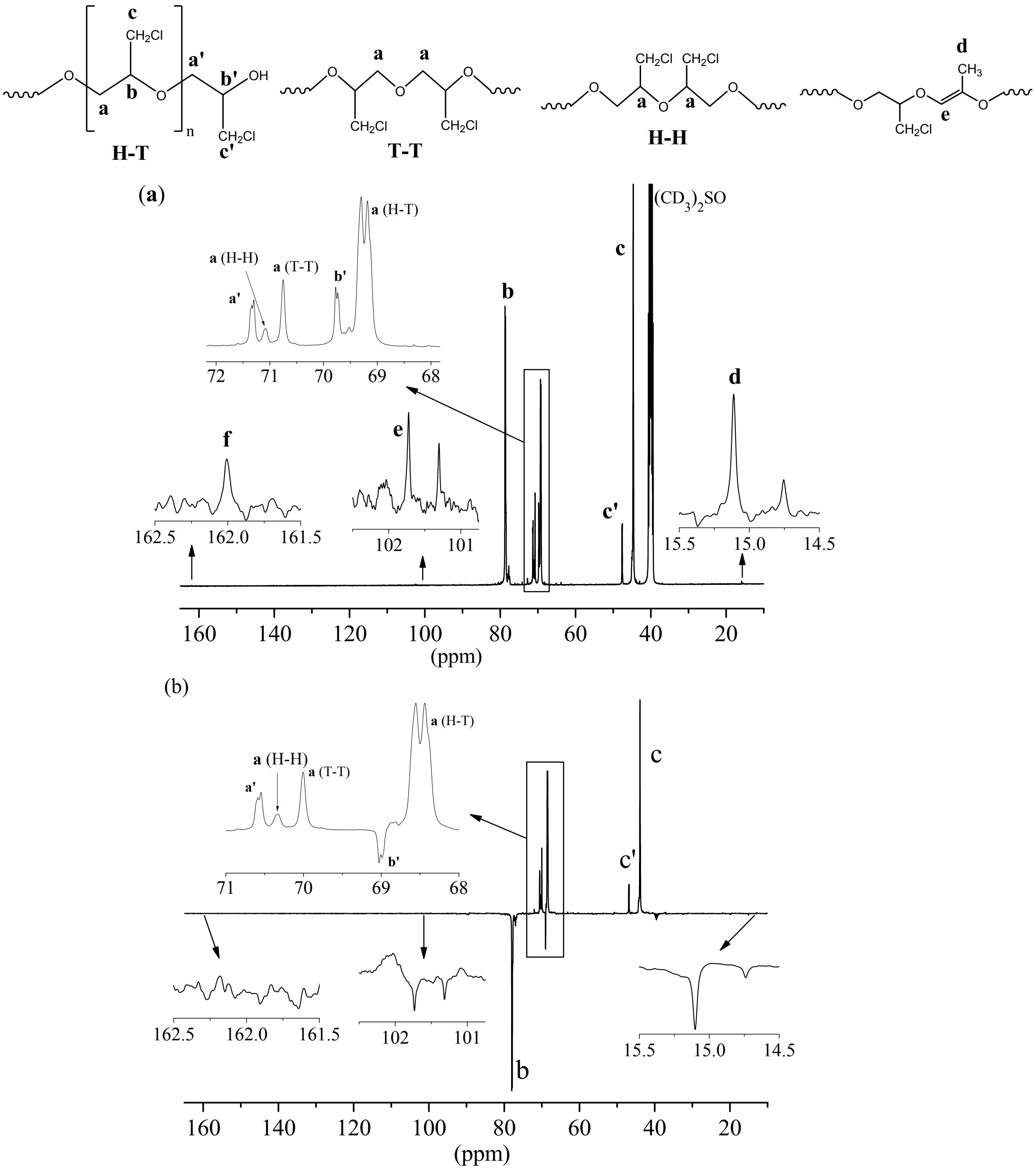
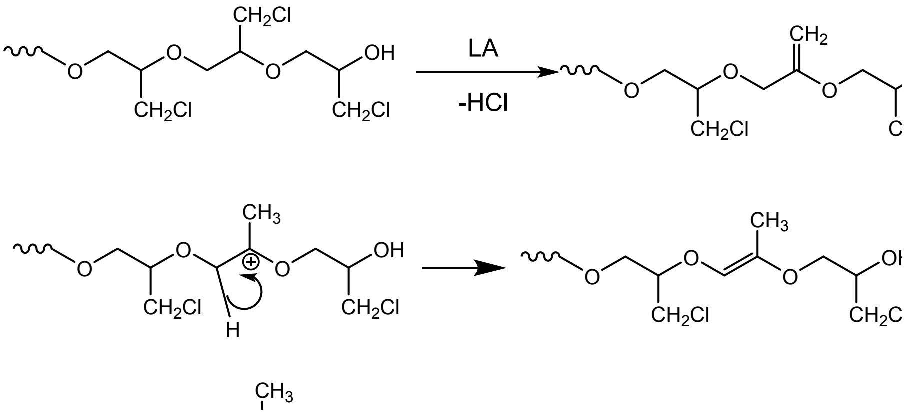


Figure 5. (**a**) ^{13}C and (**b**) ^{13}C DEPT-135 NMR spectra of PECH (M_n = 2230 g mol^{-1}; Đ = 1.22) synthesized with H_2O/BF_3•Et_2O initiating system in bulk and stored at 45 °C for 2 months.

Based on these data, the following mechanism for the sample yellowing is proposed (Scheme 2). HCl abstraction by a trace of Lewis acid, together with temperature and/or sunlight irradiation, can occur during the polymerization or storage of the bulk sample, leading to the formation of a *side* olefinic group in a main chain. Then, this double bond is protonated by water with the formation of a stable tertiary cation. The elimination of proton from the neighboring methylene group leads to the formation of a thermodynamically stable *internal* double bond. Similar repetition of reactions with neighboring chloromethyl group results in formation of conjugated double bonds (through the oxygen), which, most probably, are responsible for the observed coloration of PECH samples under long storage.



Scheme 2. Proposed mechanism for the formation of side and internal double bonds in poly(epichlorohydrin).

Note that for GAP application, the loss of HCl groups in the course of polymerization or during the storage of PECH decreases the degree of functionalization by azide, which means undesirable loss of energetic properties of solid propellants. Therefore, for the preparation of high quality PECH diol, not only the polymerization process should be mastered, but also the conditions of storage and/or transportation of polymer need controls.

Scale-up of ECH polymerization

The solution process in toluene was first successfully upscaled to 200 g of PECH using a low [BF_3•Et_2O]/[H_2O] ratio (1:26 mol/mol) and a slow monomer addition (Table S13). The *in situ* initiator preparation as well as polymerization proceeded smoothly under such conditions since reaction temperature did not exceed 35°C. Final results are a conversion above 98% after 23 h of polymerization, PECH chains of M_n of 2300 g mol^{-1}, low dispersity ($Đ < 1.15$) and quantitative functionality ($F_n(OH) \approx 2.0$) (Table S13).

An attempt to decrease the polymerization time, using the best conditions found in small-scale batch experiments (10 g ECH, run 9, Table 2) led to the following difficulties: i) an uncontrolled reaction with a high temperature jump during *in situ* initiator preparation when [BF_3•Et_2O]/[H_2O]

was increased from 1:26 to 1:15; and ii) a significant temperature increase (up to 70°C) rapidly after the beginning of the polymerization of ECH (typically in less than 1 h). This uncontrolled rise of temperature was attributed to the much faster ROP of ECH than the initiator formation under these homogeneous conditions. To solve this problem, we added some solvent (toluene) into the reaction mixture to maintain the heterogeneity of the system during the *in situ* initiator preparation. Doing so, the reaction mixture remained heterogeneous all along this first step, as shown in Figure S20, and no temperature change was observed, even when preparing about 50 g of initiator solution (for about 1 kg of final PECH content). Increasing the rate of addition of ECH also resulted in an increase of the reaction temperature up to 75°C approximately after 30 min since the beginning of the polymerization (Table S14). This temperature jump coincided with the change of the state of reaction mixture from heterogeneous to homogeneous. Still, apart from this exotherm, the characteristics of the final polymers were basically the same.

To better understand this solubility issue, oligomers of ECH with degree of polymerization (DP_n) from 1 to 5 were synthesized (Table S15) and introduced in toluene or ECH. Oligo(ECH)s with $DP_n \leq 3$ are poorly soluble in toluene, while perfect solubility was observed for oligoECHs with $DP_n \geq 4$ (Figure S21a). All oligomers were fully soluble in ECH (Figure S21b).

In order to avoid the temperature rise during ROP of ECH, it was proposed to conduct a two-stage polymerization consisting first in slow monomer addition in heterogeneous conditions (in solution), followed by fast monomer addition in homogeneous conditions (in bulk). This approach allowed controlling the exothermicity of polymerization with a maximal temperature not exceeding 35°C (Table 3). The total reaction time was reduced from about 20 h (Table S14) to 8 – 9 h (Table 3), while well-defined PECHs with controlled molar mass ($M_n \sim 2600$ g.mol^{-1}), low dispersity (Đ < 1.2) and ideal functionality were obtained (Table 3).

Another strategy to prepare well-defined PECH at large scale under fast polymerization rate without any temperature jump was tested: it consisted in using toluene-soluble oligoepichlorohydrin ($DP_n \geq 4$) as macroinitiator of ROP of ECH in conjunction with BF_3OEt_2 as co-initiator. The desired PECH chains with controlled molar mass and low dispersity were obtained in less than 6 h (Table 3). Implementing the same protocol as in solution (conducting the polymerization in two stages) allowed controlling the reaction temperature during the polymerization and synthesizing well-defined PECH of $M_n \sim 2500$ g mol^{-1}, low dispersity and expected functionality (Table 3). It should be noted that thanks to the excellent solubility of both CLPD and low molar mass PECH in ECH (Figure S21b), the polymerization in bulk could be easily upscaled to 100 g of polymer and did not require a two-stage monomer addition and/or using ECH oligomers as initiator (Table 3).

Table 3. Scale-up of Cationic ROP of ECH with H_2O/BF_3OEt_2 Initiating System in Toluene and in Bulk.[a]

run	process	1st stage ECH rate addition (mL/h)	Time (h)	2nd stage ECH rate addition (mL/h)	Time (h)	conv. (%)	$M_{n,NMR}$ (g mol^{-1})	$M_{n,SEC}$ (g mol^{-1})	Đ
14	solution	1.5	3.6	13.6	9	97	2510	2580	1.18
15	solution	3.2	2.8	13.6	8	97	2430	2480	1.18
16[c]	solution	–	–	20.4	6	99	2560	2710	1.19
17[d]	bulk	–	–	13.6	8	99	2590	2610	1.21

[a] Conditions: $[BF_3{\bullet}Et_2O]/[H_2O] = 1/15$; $[ECH]/[H_2O] = 28$; ECH_{total}: 100 g; ECH/toluene = 2:1 v/v for polymerization in solution; T = 25 °C; $V(ECH)_{total} = 85$ mL. F_n at chain-ends determined as $F_n=[M_n(SEC)/M_n(NMR)]\times2\times0.93$ was 1.99±0.2 for all experiments. No temperature jump was observed, the temperature of reaction continuously increased from 25 to 31 °C during the polymerization. $M_{n,theo} = 2500$ g mol^{-1}. [b] Total reaction time for 2 stages. [c] Oligoepichlorohydrin ($DP_n = 4$) was used as an initiator. [d] CLPD was used as an initiator.

CONCLUSIONS

In this work, a detailed fundamental mechanistic study of BF_3•Et_2O-catalyzed cationic ring-opening polymerization of epichlorohydrin was performed to reach industrially-relevant polymerization conditions. First of all, the possibility to conduct the living cationic ROP of ECH in non-chlorinated solvents (typically toluene) or in bulk was demonstrated. The solubility of initiating complex in the reaction medium is a key issue for providing fast and living ROP of ECH. It was unambiguously showed that the poor solubility in toluene of both molecular initiators (BD, CLPD) and low molar mass oligomers (up to $DP_n = 3$) resulted in retardation of the initiating process and accumulation of monomer in the reaction mixture at the beginning of the polymerization. This monomer accumulation gave rise to an induction period, followed by a fast polymerization accompanied by a significant increase of reaction temperature (up to boiling of reaction mixture).

To solve this problem, we proposed a simple and efficient initiation approach consisting in first forming the initiator through reaction of ECH with water ($ECH/H_2O=1:1.05$ or 1.5:1 mol/mol) in the presence of the water-tolerant BF_3•Et_2O co-initiator. Doing so, CLPD and longer oligomers displaying perfect solubility in reaction media were prepared *in situ*. As a result, the induction period was reduced and, thereof, ROP of ECH could proceed at much faster rate (4 – 8 h) as compared to previously described processes (20 – 48 h). The proposed initiating system ($H_2O/BF_3{\bullet}Et_2O$) could be efficiently used in a non-chlorinated solvent such as toluene as well as in bulk conditions. In best conditions, fast synthesis of pure PECH diols ($F_n(OH) \approx 2.0$) with controlled molar mass (M_n up to 4000 g mol^{-1}), low dispersity ($Đ < 1.25$) was achieved. The developed procedure for fast synthesis of PECH diol was successfully scaled-up to 100 g of polymer, either in solution or in bulk, eventually using prepared oligoECHs as initiators. The developed procedure was successfully upscaled to 100 g of polymer as an incentive to industrial production of PECH as well as its derivative glycidyl azide polymer (GAP).

Finally, detailed characterization of the synthesized PECH was performed with the aim to elucidate the reasons leading to the coloration of the polymers in the course of polymerization observed by some authors[18,20,21,22] or during the storage of non-purified samples (this work). Such process occurs via the abstraction of HCl by Lewis acid with formation of side double bond followed by its protonation/proton abstraction with the formation of internal conjugated double bonds.

ASSOCIATED CONTENT

Supporting Information. Tables with polymerization data, ^{1}H and ^{13}C NMR spectra, SEC traces, photos of initiator/solvent (monomer) mixtures, reaction mixture and obtained polymers, MALDI TOF MS spectra. The following files are available free of charge.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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Chlorinated Solvent-Free Living Cationic Ring-Opening Polymerization of Epichlorohydrin Using BF_3•OEt_2 as Co-initiator: Towards Perfectly Functionalized Polyepichlorohydrin Diols

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