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PAPER

Regio-selective Synthesis of Polyepichlorohydrin Diol using Zn-Co (III) Double Metal Cyanide Complex

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A simple one-pot ring-opening polymerization (ROP) of epichlorohydrin (ECH) was successfully performed by a heterogeneous Zn-Co (III) double metal cyanide complex (Zn-Co (III) DMCC) catalyst, affording regio-regular poly(ECH) diol with a head-to-tail content of > 99% in the absence of organic solvent and/or protic compound. No cyclic or oligomers by-product was observed, and the employed Zn-Co (III) DMCC catalyst was recyclable. ROP of (*R*)- or (*S*)-ECH led to the generation of semi-crystalline poly(ECH) diol with a melting point of 81°C or 102°C, respectively. These regio-regular poly(ECH)s with two end hydroxyl groups are versatile platform for ECH-based functionalized polymers.

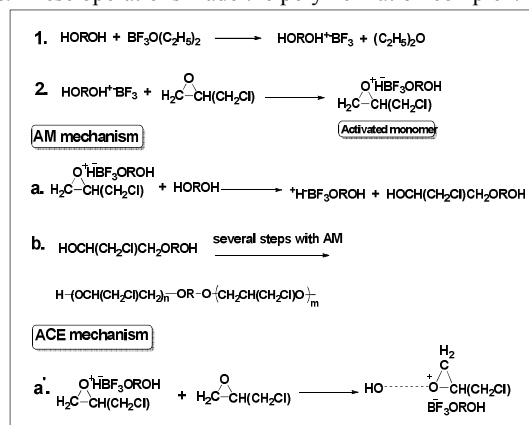
Introduction

Due to the chloromethyl and two terminated hydroxyl groups, polyepichlorohydrin [poly(ECH)] diol is widely used as a precursor for making functionalized polymers. The terminated hydroxyls could take reaction with di- or tri-isocyanates to give linear or cross-linked polyurethane materials,¹ while the nucleophilic substitution of -Cl by azide (-N₃) would result in the formation of glycidylazide polymer, which could be used as an energetic binder.²

For most of the disclosed catalysts, like Lewis acids of BF₃ etherate³, SnCl₄⁴ or SbCl₅⁵, inorganic acid of sulfuric acid⁶, trialkyl oxonium salt of triethyloxonium tetrafluoroborate⁷, and super acid esters of CF₃SO₃R or FSO₃R⁸, generally, a protic compound co-initiator is essentially required. These co-initiators could be water, alcohol and organic carbonic acid, which were responsible for the generation of the end hydroxyl groups. Also, by adjusting the ratio of catalyst/co-initiator, the added protic compound could control the catalytic activity, molecular weight (MW) and microstructure of the product. Organometallic catalysts such as AlEt₃ were also employed for the ECH ROP by a Vandenberg process, affording elastomeric poly(ECH) with high molecular weights.⁹ However, most of the produced poly(ECH) diols from the aforementioned catalysts had irregular-microstructure.

There are two ECH ROP mechanisms for the binary Lewis acids/protic compounds, as shown in Scheme 1^{3b, 3c, 10}. One is the activated monomer (AM) mechanism, and the other is called the activated chain end (ACE) mechanism. Take Lewis acid BF₃(OCH₂CH₃)/alcohol as an example, firstly, the alcohol combined with the Lewis acid catalyst to produce an oxonium salt, then reacted with ECH to generate activated monomer (AM). Herein, if AM reacted with the alcohol, a hydroxyl-terminated macro-monomer would be produced, and further reacted with AM to result in a higher molecular weight poly(ECH) diol (a and b in Scheme 1). On the other hand, since AM was a secondary

oxonium ion, it also could react with the oxygen atom of neutral ECH monomer, and form an activated chain end (ACE, a[□] in Scheme 1). The ACE could be terminated by reaction with protic compounds such as water and alcohol, to give poly(ECH) with end hydroxyl groups. However, if there were no adequate protic compounds, as an oxonium ion, the ACE could take intramolecular back biting reaction with any of the oxygen atom in the polymer chain, resulting in the generation of cyclic or oligomers by-product. Therefore, in order to improve the polyether diol selectivity, the instantaneous ratio of ECH monomer/alcohol was always kept very low, which favours the chain growth by AM mechanism.^{3g} General method was that ECH was added drop by drop into the binary Lewis acid/alcohol system during ECH ROP.^{3a, 3b, 7b} Because of the acidity of the employed Lewis acid, the product was required post-treatment of neutralizing with weak base solution and pure water for several times. These operations made the polymerization complex.



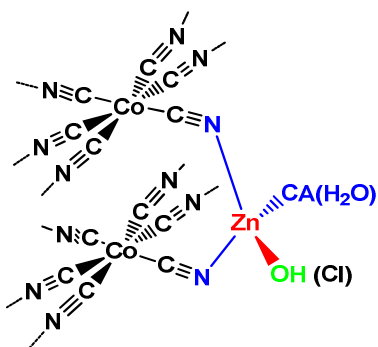
Scheme 1. The typical ECH ROP mechanism for the binary Lewis acid/protic compound (BF₃O(C₂H₅)₂/diol) catalyst system.

In addition, these reported Lewis acid catalysts had to be performed at relatively low temperatures of < 70°C for improving poly(ECH) selectivity^{3f}, which largely depressed the catalyst

activity, because the ROP of epoxides was thermodynamically beneficial.¹¹ So mostly, organic solvents such as toluene, dichloromethane were employed to reduce the reaction viscosity and improve the catalytic activity at low reaction temperatures.

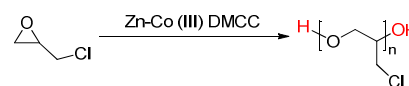
The recovery of the solvent is energy-consuming process and causes the release of the solvents. Importantly, under the binary Lewis acids/co-initiator system, the produced poly(ECH) diol only showed a head-to-tail content of up to 80% at the optimized conditions^{3e, 3g, 7b}, which is far from satisfaction.

Therefore, it is necessary to seek a simple catalytic way to circumvent the above problems and efficiently produce regio-regular poly(ECH) diol without using solvents. Zinc-cobalt (III) double metal cyanide complex (Zn-Co (III) DMCC), a typical heterogeneous catalyst, has been proved to be a highly efficient catalyst for the epoxide-involved polymerization, such as epoxides ROP¹¹ and (regio-)selective epoxides/CO₂ copolymerization¹², is expected to be a suitable catalyst for ECH ROP. This catalyst is traditionally prepared from the reaction of the excess ZnCl₂ and K₃Co(CN)₆ in the presence of organic complexing agent *tert*-BuOH. The chemical formula of Zn-Co (III) DMCC catalyst could be noted as Zn₃[Co(CN)₆]₂·xZnCl₂·y*t*-BuOH·zH₂O. In this work, the employed Zn-Co (III) DMCC catalyst was prepared at 75°C, and had nanolamellar structure with a very high BET area of 653 m²/g, which enabled its better dispersion and exposure of active sites in the reaction systems.^{12a} The initiating centre of this catalyst has been confirmed to be Zn-OH bond (Scheme 2), which triggers the polymerization and generates one terminated hydroxyl group for the resultant polymer.^{12a, 13} Since there is trace water in the reaction system, the propagating polymer chain transfers to water and produces a dormant polymer chain with two terminal hydroxyl groups and a renewed Zn-OH initiating site.



Scheme 2. The proposed structure of the active site of Zn-Co (III) DMCC catalyst. The Zn-OH structure is proposed as the initiating group of this catalyst (CA represents the complexing agent used during the preparation of the catalyst).

In the present work, we applied a nanolamellar Zn-Co (III) DMCC catalyst for efficiently producing regio-regular ECH ROP with a simple one-pot reaction process without using external organic solvent and protic compound co-initiators. The effect of various reaction conditions such as temperatures, amounts of catalyst and reaction times on the polymerization was investigated. The two end hydroxyl groups were characterized by an electrospray ionization-tandem mass spectrometry (ESI-MS) test and the regio-regular chain structure was confirmed by the ¹³C NMR spectrum.



Scheme 3. The ECH ROP catalyzed by Zn-Co(III) DMCC catalyst.

Experimental

Materials

K₃Co(CN)₆ (Yixing City Lianyang Chemical Co., Ltd, China, 99%) was recrystallized in de-ionized water before use. ZnCl₂, *tert*-BuOH were analytical grade and used without further purification. Epichlorohydrin (ECH), (*R*)-/(*S*)-ECH (Sigma) were refluxed over calcium hydride for 12 hours and then distilled.

Zn-Co (III) DMCC preparation

This catalyst was synthesized according to our recent published work^{12d}: an amount of ZnCl₂ (8.0 g) was dissolved in the solution of de-ionized water (10 ml) and *tert*-BuOH (10 ml). K₃Co(CN)₆ (6.6 g) dissolved in 10 ml de-ionized water and was added dropwisely into ZnCl₂ solution over 30 min at 30°C under vigorous stirring. Afterward, the precipitation reaction was heated to 75°C and agitated for 3h. The resulting white precipitate was separated by pressure filtration and reslurried in a mixture of *tert*-BuOH and water (v/v=1/1) with vigorous stirring over 2h. Once again, the precipitation was isolated and reslurried in a mixture of *tert*-BuOH and water. With increasing proportion of *tert*-BuOH over water, the precipitate was washed several times to remove potassium ion completely. Finally the wet precipitate was reslurried in neat *tert*-BuOH, separated and dried at 70°C under vacuum to a constant weight. The elemental analysis result of the catalyst (weight %): Co: 12.48; Zn: 27.29; N: 16.57; C: 23.34; H: 2.27; Cl: 9.50.

ECH ring-opening polymerization (ROP)

A 60ml autoclave with a small magnetic stirrer was dried at 120°C for 3 h, and cooled to the room temperature in a closed desiccator. Appropriate Zn-Co(III) DMCC catalyst and ECH were transferred into the autoclave. The reactor was then heated to a desired temperature for the whole reaction time. After the polymerization, the autoclave was cooled with ice-water bath. A small amount of crude product was collected for NMR spectroscopy and GPC tests. The residual product was purified by the removal of unreacted ECH monomer under reduced pressure, then the polymer was dried at 60°C under vacuum to a constant weight.

Characterization

Infrared spectra were measured by using a Bruker Vector 22 FT-IR spectrophotometer. Elemental analyses were performed by using an ICP-AES instrument (Leeman Labs) and a Vario MACRO instrument (Elementar). ¹H NMR and ¹³C NMR spectra of the products were obtained on a Bruker Advance DMX 400-MHz and 125-MHz spectrometer with TMS as internal reference respectively. Average-number molecular weight (*M_n*) and molecular weight distribution (*M_w*/*M_n*) were determined by using a PL-GPC 220 chromatograph (Polymer Laboratories Ltd.) equipped with an HP 1100 pump from Agilent Technologies. The GPC columns were eluted with tetrahydrofuran at 1.0 ml/min at

40°C. The sample concentration was approximately 0.3wt% and the injection volume was 50µl. Calibration was performed using monodispersed polystyrene standards covering the molecular weight ranging from 500 to 500000 Da. Differential scanning calorimetric (DSC) tests were conducted on a TAQ200 instrument (New Castle, DE) with a heating rate of 10°C/min under N₂ atmosphere, and the data from the second heating curve were collected. Electrospray ionization-tandem mass spectrometry (ESI-MS) analysis was performed on an Esquire3000 plus mass spectrometer, using mixed methylene chloride/methanol as solvent for dissolving the copolymer.

Result and discussion

Series of one-pot ECH ROP catalyzed by Zn-Co (III) DMCC catalyst were performed in a sealed 10ml autoclave with 5.0ml ECH. The results of the reaction temperature, the amount of catalyst and reaction time on ECH ROP were collected in Table 1. Figure 1 shows the selected ¹H NMR spectrum of the crude resultant from entry 1 in Table 1. It is found that there is a group of multiple peaks at 3.4-3.9ppm, which could be ascribed to the protons of methine and methylene of poly(ECH) and were hard to separate. The other three chemical shifts of 2.6, 2.9 and 3.2ppm were clearly attributed to the unreacted oxirane protons of ECH monomer in the crude polyether. Figure 2 shows the FT-IR spectrum of the resultant poly(ECH) diol. The peak at 3500 cm⁻¹ was derived from the stretching vibration of hydroxyl group, which indicates the formation of terminal -OH of the resultant. Moreover, the strong peak at 1120 cm⁻¹ was ascribed to the ether linkages in the polymer.

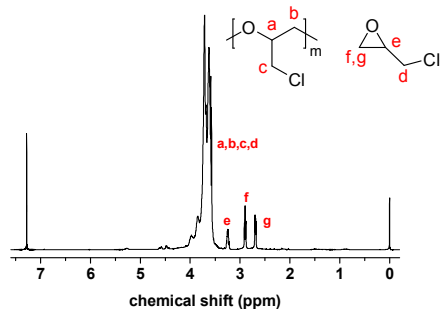


Fig. 1. ¹H NMR spectrum of the crude poly(ECH) of entry 1 in Table 1 (CDCl₃)

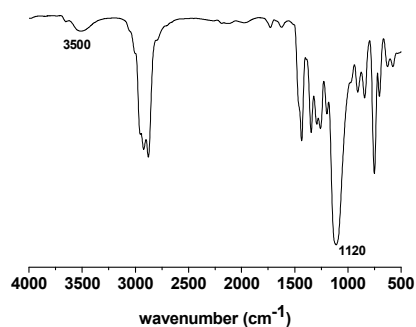


Fig. 2. FT-IR spectrum of the crude poly(ECH) diol (entry 1, Table 1).

Since ROP of the epoxide was considered to be a typical thermodynamically favourable polymerization,^{12a} relatively high temperatures would result in enhanced poly(ECH) productivity. As shown in Table 1, when ECH ROP was carried out at 40°C for 7.0 h using 3.0 mg Zn-Co (III) DMCC catalyst (entry 1), the productivity was 550g polyether/g catalyst and the yield was only 30%. With elevating the reaction temperature up to 120°C, the productivity was sharply improved to 1653 g polymer/g catalyst, and the yield increased to 84% (entry 6), which was about three times of that at 40°C. The corresponding M_n s of entries 1-6 increased from 0.9 to 3.6 kg/mol along with the temperatures from 40 to 120°C, while the M_w/M_n s of these samples kept relatively narrow and in a range of 1.42-1.72 despite of the heterogeneous catalysis and one-pot reaction mode. Figure 3 showed GPC curves of these crude resultants under various reaction temperatures and displayed single elution peaks, which indicated that no cyclic or less-molecular-weight oligomer was produced even at a high temperature of 120°C.^{3d-3e}

Table 1. The ECH ROP catalyzed by Zn-Co (III) DMCC catalyst. ^a

Entry	catalyst (mg)	Temp. (°C)	Time (h)	M_n^b (kg/mol)	M_w/M_n^b	Productivity ^c	Yield (%)
1	3.0	40	7	0.9	1.42	550	30
2	3.0	60	7	1.9	1.56	743	38
3	3.0	80	7	2.5	1.62	1180	60
4	3.0	90	7	2.9	1.68	1265	64
5	3.0	100	7	3.1	1.70	1468	75
6	3.0	120	7	3.6	1.72	1653	84
7	3.0	80	3	1.3	1.52	526	27
8	3.0	80	5	2.0	1.55	945	48
9	3.0	80	10	3.4	1.63	1268	65
10	3.0	80	15	4.2	1.70	1427	73
11	1.0	80	7	0.9	1.43	534	9
12	5.0	80	7	2.7	1.62	845	72
13	7.0	80	7	2.9	1.65	710	84
14 ^d	7.0	80	7	2.8	1.66	695	83
15 ^e	7.0	80	7	2.7	1.64	690	82
16 ^f	7.0	80	7	2.7	1.64	683	81
17 ^g	3.0	80	7	-	-	900	46
18 ^h	3.0	80	7	-	-	825	42

^aReaction condition: ECH 5.0ml; ^bDetermined by gel permeation chromatography in THF, 40°C, calibrated with standard monodispersed polystyrene; ^cThe productivity was defined as the g poly(ECH)/g catalyst. ^{d(e,f)}: Zn-Co(III) DMCC catalyst employed came from entry 13 (14, 15); ^{g,h}: the ECH monomer employed was R-ECH and S-ECH respectively.

The effect of reaction time on the ECH ROP was also studied, as shown in Figure 4 and Figure 5. It is found that the yield increased from 27% to 73% with increasing reaction times from 3 to 15h (entries 3 and 7-10 in Table 1, Figure 4). Correspondingly, M_n increased from 1.3 to 4.2 kg/mol in an approximately linear fashion with increasing reaction time from 3 to 15h, as shown in Figure 4. The M_w/M_n s kept at 1.52-1.70 and stable, this was caused by the fast chain transfer reaction.^{12a} At the early polymerization stage, M_n was relatively low, as shown in Figure 5. While that fast chain transfer reaction brought the dormant polyether with low molecular weight into propagating species, ensuring its continuous propagation, thus increased the M_n and eliminated low-molecular-weight oligomers that could be easily produced in a binary Lewis acids/protic compound system. Because Zn-Co (III) DMCC was acted as an effective initiator for ECH ROP, in which Zn-OH initiated the polymerization¹², the rate of ECH ROP was determined by the amounts of Zn-Co (III) DMCC. This was evident by the relationship of the amounts of

the catalyst with ECH conversion under the same polymerization condition. When a low loading of 1.0mg catalyst was employed, the yield and M_n were only 9% and 0.90 kg/mol respectively (entry 11). A higher loading of 5.0mg catalyst was added, the yield was increased to 72%, while higher loading of 7.0 mg catalyst was used, 84% of ECH conversion was achieved (entries 12-13). However, the M_n and M_w/M_n kept nearly unchanged.

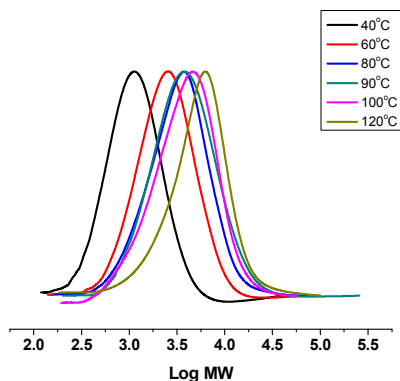


Fig.3. GPC curves of the ECH ROP resultants at various temperatures (entries 1-6, Table 1).

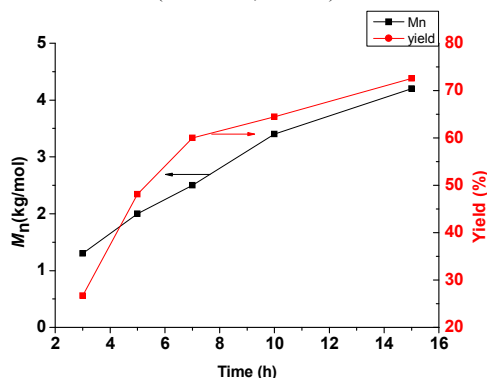


Fig.4. Plots of M_n (black) and Yield% (red) vs Time. Reaction conditions: 80°C; catalyst, 3.0mg; ECH, 5.0ml.

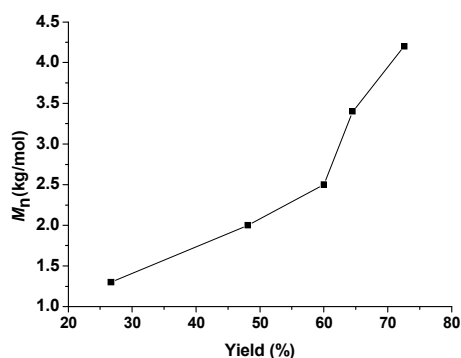


Fig. 5. Plots of Yield% vs M_n . Reaction conditions: 80°C; catalyst, 3.0mg; ECH, 5.0ml. (In this work, Yield was about equal to the ECH conversion)

The recycle of Zn-Co (III)DMCC catalyst was tested as well, as shown in entries 14-16 in Table 1. After ECH ROP of the entry 13 in Table 1, the crude product was dissolved into dichloromethane, the dilute solution was then centrifuged at a rate of 15000r/min. At the bottom of the centrifuge tube, it was observed that Zn-Co (III) DMCC catalyst was deposited. After

removal of the upper solution, Zn-Co (III) DMCC catalyst was washed and centrifuged several times. Afterwards, it was dried and applied to ECH ROP again. From entries 14-16 in Table 1, it is found that the M_n s and M_w/M_n s of the resultant poly(ECH)s were nearly unchanged, and the productivities kept almost the same. The recycle of this catalyst could be explained by the regeneration of Zn-OH of the catalyst via chain transfer reaction, through which the initiating structure and the catalytic performance of this catalyst could be preserved.

Since the chloromethyl of ECH is a strong electron-withdrawing group, we thought that chloromethyl could induce the sole attack of propagating species to the CH site of ECH and expected to produce regio-regular poly(ECH). In order to understand the chain microstructure of the resultant poly(ECH) via Zn-Co (III) DMCC catalysis, poly(*R*-ECH) and poly(*S*-ECH) were also synthesized as the controls under the same conditions as entry 3 in Table 1. These three poly(ECH)s were characterized by ^{13}C NMR spectra, as shown in Figure 6. The common chemical shifts at $\delta=43.6$, 69.5 and 79.0ppm could be ascribed to the methylene carbon of pendant group $-\text{CH}_2\text{Cl}$, the methylene and methine carbons in the polyether backbone, respectively, while the chemical shifts at $\delta=51.2, 46.8$ and 45.1ppm were responsible for the methine and methylene carbons of the residual ECH. We observed that the ^{13}C NMR spectroscopy of the poly(*rac*-ECH) presented two split symmetrical peaks at $\delta=69.3$ and 69.8ppm, while poly(*R*-ECH) and poly(*S*-ECH) presented only one single peak at 69.7ppm and 69.6ppm respectively. These chemical shifts could be clearly ascribed to the carbon of $-\text{O}-\text{CH}_2-$ in the head-to-tail (H-T) diad.^{3b, 3d, 3g, 10} No peaks at $\delta=70.8-71.8\text{ppm}$ were observed in these three spectra, which were attributed to the head-to-head (H-H) and tail-to-tail (T-T) diads of poly(ECH).^{3b, 3d, 3g, 10} These results suggested that the resultant poly(ECH) exhibited a complete regio-regular structure as our expectation.

Both poly(*R*-ECH) and poly(*S*-ECH) were solid powder (Figure 7) and were not soluble in THF due to their enantiomorphous state, while poly(*rac*-ECH) was viscous liquid with a much low T_g of -38°C (entry 10, Table 1). Moreover, both poly(*R*-ECH) and poly(*S*-ECH) were semi-crystalline, with melting points of 81 and 102°C respectively, as shown in Figure 8.

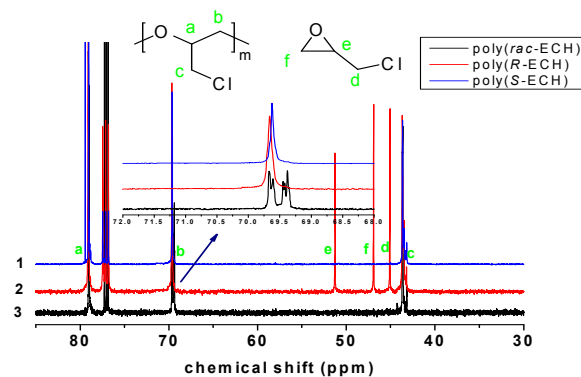


Fig.6. ^{13}C NMR spectra of the resultant polyepichlorohydrins (lines 1-3 represented the samples of poly(ECH)s derived from *rac*-ECH, *R*-ECH and *S*-ECH, entries 3, 17-18, Table 1).



Fig.7. The photos of the produced solid poly(R-ECH) (1) and poly(S-ECH) (2).

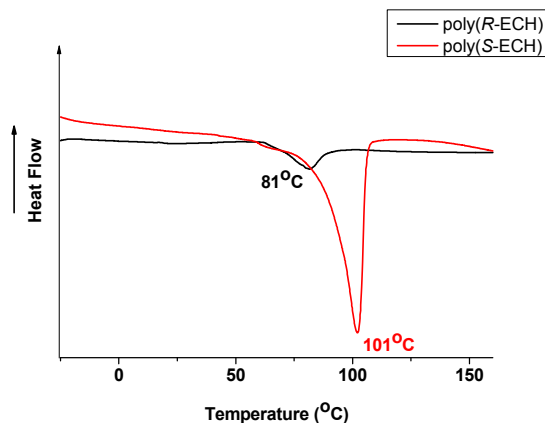


Fig.8. The DSC curves of the poly(R-ECH) and poly(S-ECH).

The two end hydroxyl groups of the resultant poly(ECH) were confirmed by the electrospray ionization–tandem mass spectrometry (ESI–MS) test with various positive ion sources such as H^+ , K^+ , as shown in Figure 9. The polyether sample had low molecular weight of 1150 g/mol and PDI of 1.5 under Zn-Co (III) DMCC catalysis. All of m/z species in the spectrum were assigned and summarized in Table 2. Because of the two stable chlorine isotopes Cl^{35} and Cl^{37} , the MS spectrum had two kinds of ether linkages of $(ECH)^{92}$ and $(ECH)^{94}$. Three kinds of species of (1) $[(ECH)_m^{94}-(ECH)_n^{92}+K^+]$, (2) $[HO-(ECH)_m^{94}-(ECH)_n^{92}-H+H^+]$, and (3) $[HO-(ECH)_m^{94}-(ECH)_n^{92}-H+K^+]$ covered all m/z regions in the spectrum. It was found that all of the m/z species of (2) and (3) had two terminal hydroxyl groups. Species (1) was considered to be the species derived from (2) or (3) by a neutral loss of H_2O during ESI-MS test condition. This is because the terminal secondary hydroxyl groups of poly(ECH) would be easily dissociated to form neutral H_2O under the test environment due to the strong electron-withdrawing ability of $-CH_2Cl^{12d}$. Moreover, the probability of that species (1) was crown ethers could be minimized during the ROP^{12a} because such crown ethers with big rings ($m+n=6, 7, \dots, 17$) was prohibited to form by backbiting mechanism.

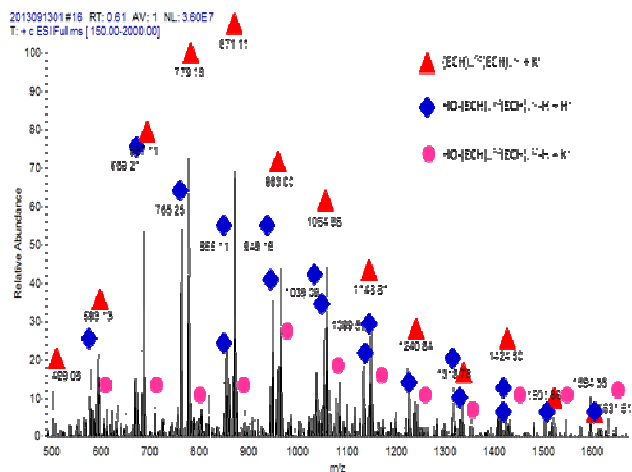
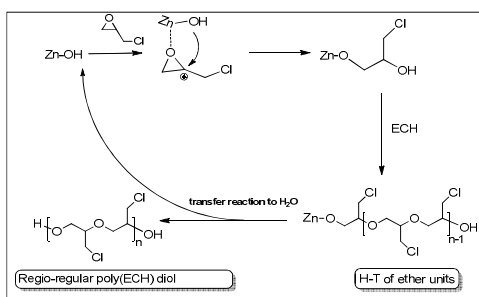


Fig.9. ESI-MS spectrum of the polyepichlorohydrin diol. (Due to the two stable chlorine isotopes of Cl^{35} and Cl^{37} , the ether linkages have two different molecular weights determined by the introduction of either of the chlorine. When Cl^{35} was anchored, the molecular weight of ether linkage is 92, marked as $(ECH)^{92}$. By the similar manner, when Cl^{37} was employed, the corresponding ether linkage is noted as $(ECH)^{94}$).

Table 2. The m/z species of the resultant poly(ECH) diol.

Species	m/z
$(ECH)_m^{94}-(ECH)_n^{92}+K^+$	
($m=0, 1, 2; n=5$)	(499, 593, 687)
($m=2; n=6, 7, 8, 9$)	(779, 871, 963, 1055)
($m=3; n=9, 10, 11, 12, 13, 14$)	(1149, 1241, 1333, 1425, 1517, 1609)
$HO-(ECH)_m^{94}-(ECH)_n^{92}-H+H^+$	
($m=3; n=3, 4, 5, 6, 7$)	(577, 669, 761, 853, 945)
($m=4, 5, 6, 7, 8, 9, 10, 11, 12; n=5$)	(855, 949, 1043, 1137, 1231, 1325, 141, 1513, 1607)
($m=4, 5; n=7$)	(1039, 1133)
($m=5; n=8$)	(1225)
($m=6; n=8, 9, 10, 11, 12$)	(1319, 1411, 1503, 1595, 1687)
$HO-(ECH)_m^{94}-(ECH)_n^{92}-H+K^+$	
($m=4; n=2, 3, 4$)	(617, 709, 801)
($m=5; n=4, 5, 6, 7, 8, 9, 10, 11, 12$)	(895, 987, 1079, 1171, 1263, 1355, 1447, 1539, 1631)

Based on the above results, a polymerization mechanism was proposed for the selective ECH ROP under Zn-Co (III) DMCC catalysis, as shown in Scheme 4. Due to the strong electron-withdrawing chloromethyl group, the methine carbon of ECH has more electron-positivity than the methylene carbon, and was predominantly attacked by propagating species (and the initiating species of $-OH$), realized regio-selective ring-opening reaction of ECH. Then followed by the continuous insertion of ECH, a regio-regular polyether chain with one terminal hydroxyl group of $-CH(CH_2Cl)OH$ was obtained. Afterward, the other end hydroxyl group of $-CH(CH_2Cl)CH_2OH$ was generated by the chain transfer reaction of Zn-alkoxide intermediate to trace water during the polymerization. Finally, the poly(ECH) diol was achieved.



Scheme 4. Proposed mechanism of the ECH ROP under Zn-Co(III) DMCC catalysis.

Conclusion

In conclusion, a simple one-pot ECH ROP was successfully catalyzed by a heterogeneous Zn–Co (III) DMCC. The catalyst was highly active and could be reused without the loss of the productivity. Moreover, the resultant poly(ECH) showed regioregular microstructure with a H-T content of >99% as well as two end hydroxyl groups. These poly(ECH)s are excellent platform for further synthesizing azide-containing polymers, block copolymers and so on.

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Notes and references

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Regio-selective Synthesis of Polyepichlorohydrin Diol using Zn-Co (III) Double Metal Cyanide Complex

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This work describes the first regio-selective synthesis of poly(epichlorohydrin) diol via a simple one-pot bulk polymerization with a heterogeneous catalyst.

