

Online Monitoring of Reaction Temperature During Cationic Ring Opening Polymerization of Epichlorohydrin in Presence of BF_3 and 1,4-Butanediol

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ABSTRACT: This work introduces cationic ring opening polymerization of polyepichlorohydrin (PECH) produced under various reaction conditions (set temperature: -10 to 40°C , $[\text{C}]/[\text{I}]$ ratio: 0.1–1, monomer feed rate: 1–4 mL/min). In addition, a correlation between the exothermic reaction temperature and the performance of the PECH was obtained by utilizing a reaction temperature monitoring system, GPC, $^1\text{H-NMR}$, and FTIR. During the polymerization, an induction period which affects the polydispersity was observed below 10°C . At lower temperatures and lower $[\text{C}]/[\text{I}]$ ratios, a higher induction period was observed. The monomer feed rate did not affect the induction period but it highly affected the polydispersity when the induction period occurred. The total molecular weight of PECH increased with decreasing set temperature even though the amount of low molecular weight cyclic oligomer increased. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2013**, *000*, 39912.

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INTRODUCTION

Polyepichlorohydrin (PECH) and ECH copolymers are major functional polymeric materials with reactive pendent chloromethyl groups for modification via nucleophilic substitution and have been utilized in applications such as energetic polymeric binders, catalyst contained binders for solid propellants, and liquid crystal alignment layers.^{1–8}

van den Berg first prepared high molecular weight PECH through a cationic coordination mechanism in the presence of organometallic catalysts.⁹ Well-defined PECH ($1.08 \leq \text{PDI} \leq 1.24$) was also prepared by Stéphane Carloti through anionic polymerization using a tetraoctylammonium bromide-triisobutyl aluminum initiating system.¹⁰

Ring opening polymerization (ROP) for hydroxyl-terminated PECH has been studied for many years.^{11–19} Two different propagation mechanisms for ROP have been reported and are shown in Figure 1.^{11,12} The active propagating centers of the active chain end mechanism (ACE) are located at the chain end of the polymer. On the other hand, the active centers of the active monomer (AM) mechanism are located on the monomer, while the chain end of the polymer is neutral hydroxyl.^{13–15} Both mechanisms can coexist in the reaction media. For instance, when there are $\text{H}^+ \text{BF}_4^-$, 1,4-butanediol, and excess ethylene oxide in a methylene chloride solution, one of ethylene oxides is

protonated by $\text{H}^+ \text{BF}_4^-$. Then, the reaction proceeds through the two propagation mechanisms depending on whether the protonated monomer reacts with the hydroxyl group of 1,4-butanediol (1,4-BD) (AM mechanism) or nonprotonated monomer (ACE mechanism).

A high performance of the polymer can be obtained depending on the mechanism. Figure 2 shows the side reactions in the AM and ACE mechanism reactions. In the AM mechanism, the tertiary oxonium ion can be formed by reacting with the protonated monomer and oxygen atom in the polymer.^{12–14} However, the side reaction of the AM mechanism rarely occurs due to steric hindrance of the monomer and polymer structure.¹² In the ACE mechanism, the cyclic oligomer can be formed by an intermolecular back biting reaction with the oxonium ion and oxygen atom in the polymer. And, in the presence of diethyl ether, the polymers that have ethoxy end groups can also be formed by an exchange reaction with the diethyl ether of BF_3 -etherate.^{12,16} Thus, the polymerization should be carried out via the AM propagation mechanism to obtain a linear polymer with a controlled molecular weight.

The polymerization conditions for the AM mechanism have been studied for many years since Kubisa and Penczek demonstrated the polymerization of cyclic ether via the AM mechanism by slowly adding monomer (monomer-starved conditions).^{11,12,17–19}

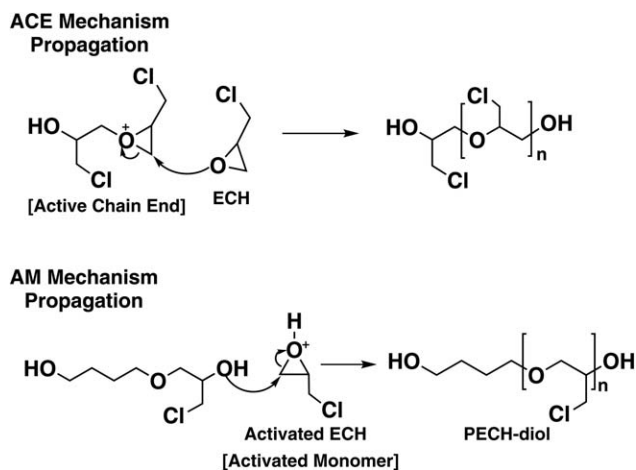


Figure 1. The ACE and AM polymerization mechanisms.

Francis et al. investigated the effect of catalysts (BF_3 -etherate and SnCl_4) on the hydroxyl structure and functionality of PECH. The hydroxyl functionality (1.7%) and secondary hydroxyl group contents (91.3%) of PECH prepared using BF_3 -etherate-1,4-BD was higher than that prepared from SnCl_4 1,4-BD.¹⁸

Recently, Guanaes et al. investigated the influence of the polymerization conditions on the performance of PECH by utilizing experimental design.¹⁹ They suggested that the polymerization should be carried out under a slow monomer addition rate at 25°C to obtain a polymer with the highest molecular weight and lowest polydispersity.

Various polymerization parameters affecting the performance of PECH have been investigated. To the best of our knowledge, however, online temperature monitoring of the reaction state under various polymerization conditions has not been reported. The monitored temperature during the reaction would be beneficial for scientific and industrial situations to determine reaction rates and mechanisms and to explore the effects of different reaction conditions. The results can also be used for the design of scaled-up reactors.

In this work, we monitored the reaction temperature during the cationic ring opening polymerization of ECH while varying the reaction conditions including the temperature, $[\text{BF}_3]/[1,4\text{-BD}]$ ($[\text{C}]/[\text{I}]$) ratio, and monomer feed rate. The focal point of our study was to obtain a correlation between the online monitored temperature and the performance of PECH as a function of the various reaction conditions.

EXPERIMENTAL

Materials

Boron trifluoride diethyl etherate (BF_3 -etherate, Aldrich) and sodium bicarbonate (NaHCO_3 , Samchun, 99.0%) were used as purchased. Epichlorohydrin (ECH, Samchun 99.0%), methylene chloride (MC, Samchun 99.5%), and 1,4-BD (Aldrich 97%) were kept over molecular sieve (4 Å) for 1 week before use.

Reactor System

The reactor system was designed for the polymerization of ECH where temperature monitoring was employed. The system con-

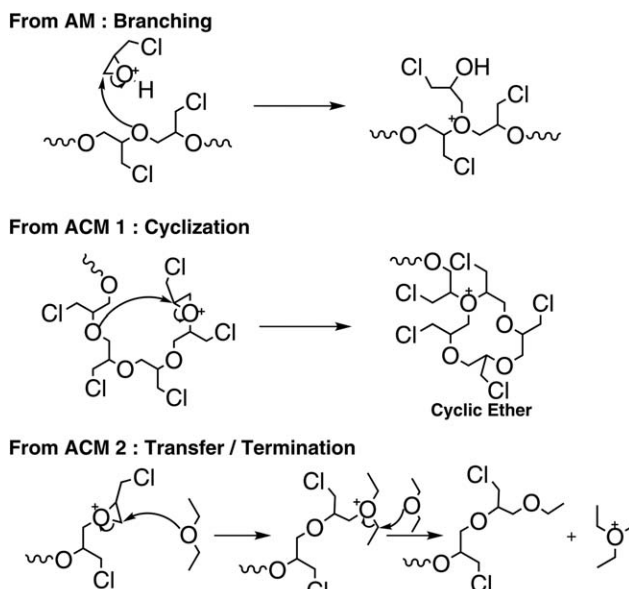


Figure 2. Side reactions in AM and ACE mechanism reactions.

sisted of a micropump, cooler, cooling jacket, 1000 mL flask, computer controller, and stirrer, as shown in Figure 3. During the reaction, the temperature was controlled and measured by the computer connected to the cooler. To keep the reactor at a set temperature, LabTracer® (JEIO TECH) software was used for monitoring the temperature in the reactor and communicating with cooler (JEIO TECH, RW-2025G).

Polymerization

The PECH diol polymerization process is shown in Figure 4. To avoid the exchange side reaction with the diethyl ether of BF_3 -etherate, as detailed in Figure 2, an active condensate catalyst (AC) consisting of boron trifluoride and 1,4-BD was obtained by the evaporation of diethyl etherate from a BF_3 -etherate and 1,4-BD solution at low pressure (1×10^{-3} torr). Calculated amounts of BF_3 -etherate and 1,4-BD were introduced in the two-neck round-bottom glass flask equipped with a vacuum line and thermocouple. The mixture was maintained at room temperature for 1 h while being stirred by a magnetic bar. Then, diethyl ether was removed from the solution under stirring at 40°C by vacuum distillation for 6 h. After the distillation time, a light brown transparent AC liquid was obtained.

All polymerizations were performed in a 1000-mL four-neck glass reactor that was equipped with a mechanical stirrer, monomer feeding equipment, a thermometer, a condenser, and a cooler. Before the polymerization, the reactor was dried at 90°C for 24 h in an Ar atmosphere. The ECH solution (100 g, 1.08 mol, 21 wt %) was introduced in the monomer flask that was connected to a micropump by tygon tubing. Calculated amounts of AC and MC (10 g) were added to the reactor. After cooling down, the temperature recording started. After 45 min, the ECH solution was fed into the reactor by the micropump. When the ECH solution feeding was complete, the reaction solution was stirred for one additional hour before washing with a sodium bicarbonate solution (10 g, 5 wt %), followed by several washings with distilled water until it was neutral, as

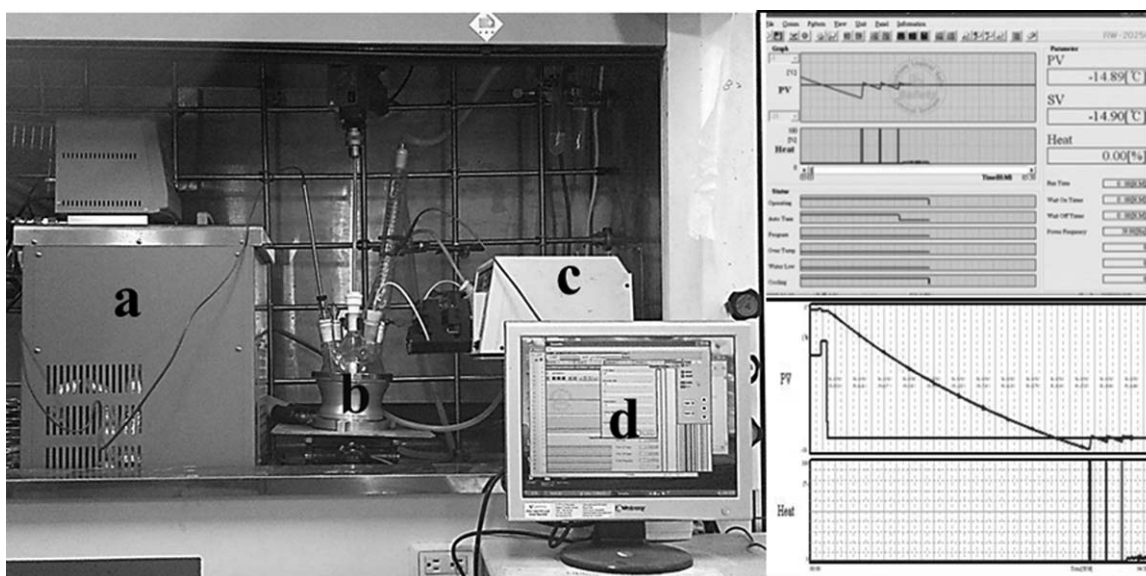


Figure 3. Cationic ring opening polymerization reactor system for temperature monitoring [(a) temp. sensing and contouring; (b) reactor; (c) micro-pump; (d) temperature monitoring].

determined by using pH paper. The solvent was removed by evaporation. The obtained polymer was characterized by its molecular weight as well as FTIR and $^1\text{H-NMR}$ spectra. The detailed polymerization conditions are shown in Table I.

Characterization

The average relative molecular weights and the polydispersity index ($\text{PDI} = M_w/M_n$) were determined by a gel permeation chromatography (GPC) system equipped with four Waters Styragel® columns (5- μm beads: HR 1, 100 Å; HR 2, 500 Å; HR 3, 1000 Å; HR 4, 10,000 Å) and a 2410 differential refractive index detector. The operating temperature was 40°C, the mobile phase was THF, the flow rate was 1.0 mL/min, and the raw data were calibrated using a universal calibration with polystyrene standards ($M_w = 162\text{--}2,400,000$).

The FTIR spectra of PECH were obtained from samples on a KBr cell using a Varian 800 series instrument. $^1\text{H-NMR}$ spectra were recorded on a Digital Avance III-400 NMR spectrometer (Bruker Co.) at 400 MHz in deuterated chloroform.

RESULTS AND DISCUSSION

Based on the polymerization of PECH, the aim of this study was to investigate the correlation between the monitored reaction temperature and performance of the polymer obtained under various reaction conditions.

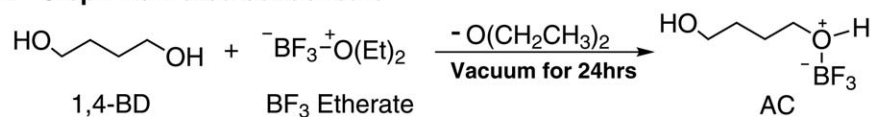
The Effect of Reaction Temperature

The effect of the reaction temperature on the ECH cationic ring opening polymerization was investigated by a temperature monitoring system, GPC, $^1\text{H-NMR}$, and FTIR. The AC_1ri_γT_2 mL PECH series was polymerized at various temperatures (−10 to 40°C) while holding the other reaction conditions constant ($[\text{BF}_3]/[1,4\text{-BD}]$ ratio = 1, monomer feed rate = 2 mL/min). The monitored reaction temperature results are shown in Figure 5.

An increase of the temperature was observed as soon as the monomer was added into the reactor at set temperatures above 20°C. On the other hand, below a set temperature of 10°C, an

Synthesis of PECH-diol

1st Step : Activated condensate



2nd Step : Polymerization of ECH

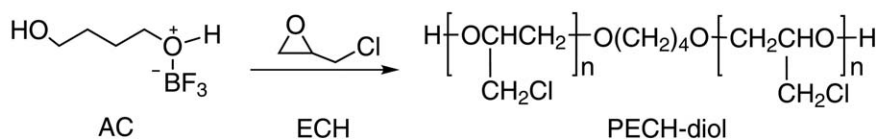


Figure 4. Synthesis process of PECH.

Table I. Experimental Conditions Applied in the PECH Synthesis^a

Sample code ^b	Set temp. (°C)	[C]/[I] ratio ^c	Feed rate (mL/min)	Feed time (h)
AC_1ri_40T_2 mL	40	1	2	4
AC_1ri_30T_2 mL	30	1	2	4
AC_1ri_20T_2 mL	20	1	2	4
AC_1ri_10T_2 mL	10	1	2	4
AC_1ri_0T_2 mL	0	1	2	4
AC_1ri_-10T_2 mL	-10	1	2	4
AC_0.1ri_0T_1 mL	0	0.1	1	8
AC_0.2ri_0T_1 mL	0	0.2	1	8
AC_0.5ri_0T_1 mL	0	0.5	1	8
AC_1ri_0T_1 mL	0	1	1	8
AC_1ri_10T_1 mL	10	1	1	8
AC_1ri_20T_4 mL	20	1	4	2
AC_1ri_20T_1.4 mL	20	1	1.4	6
AC_1ri_20T_1 mL	20	1	1	8
AC_1ri_-10T_1 mL	-10	1	1	8

^a 1,4-BD: 0.033 mol; ECH: 1.08 mol; calculated M_n : 3000 g/mol.

^b ri: ratio of [catalyst]/[initiator]; T: set temperature; mL: monomer feeding rate.

^c Ratio of $[BF_3]/[1,4-BD]$.

induction period was observed followed by very rapid thermally accelerated polymerization. As the set temperature was decreased, the induction period increased. In particular, the induction period was half the time of the monomer solution addition time at a set temperature of -10°C after which an exothermic temperature (ΔT_{max}) was clearly observed. The maximum exothermic temperature (ΔT_{max}) and induction period obtained at the different set temperatures are shown in Table II. Above a set temperature of 20°C , the maximum exothermic temperatures (ΔT_{max}) were lower than $+3^\circ\text{C}$. On the contrary, below a set temperature 10°C , the maximum exothermic temperature (ΔT_{max}) increased from $+6^\circ\text{C}$ to $+30^\circ\text{C}$ accompanied by an increasing induction period. This indicates that the

monomer was concentrated due to the lower polymerization rate compared to the monomer feeding rate during the induction period.

The GPC chromatograms of the AC_1ri_γT_2 mL PECHs are shown in Figure 6. The low molecular weight peak observed in Figure 6 (right side shoulder peak of the curve) belongs to cyclic oligomer, which is a side reaction product of the ACE mechanism polymerization.^{20,21} With increasing set temperature from -10 to 10°C , the low molecular weight peak decreased. Above a set temperature of 20°C , the peak was also observed but the intensity did not change. The molecular weight characterization of the AC_1ri_γT_2 mL PECHs is summarized in Table III. Even though the low molecular weight cyclic oligomer increased, the molecular weight of the resulting polymers increased with decreasing set temperature with the exception of -10°C . The polydispersity (PDI) was minimized at a set

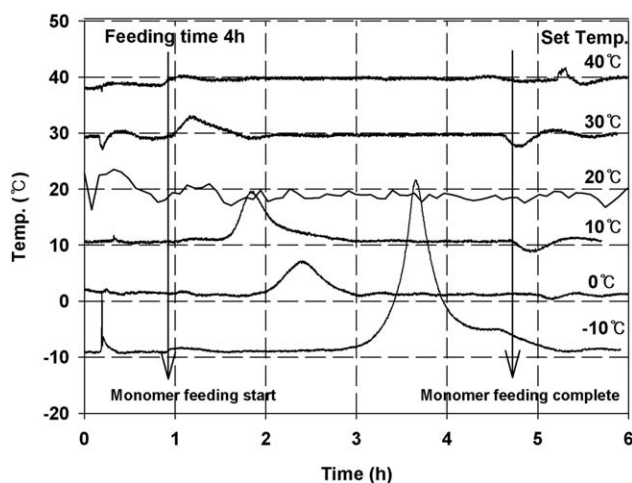


Figure 5. Reaction temperature as a function of reaction time for the various reaction set temperatures for AC_1ri_γT_2 mL.

Table II. Maximum Exothermic Temperatures (ΔT_{max}) and Start Times of the Temperature Deviations for the Different Set Temperatures for AC_1ri_γT_2 mL

Set temp. (°C)	Max. exothermic temp. (ΔT_{max} , °C) ^a	Induction period (min)
-10	+30.3	120
0	+6.2	50
10	+8.7	30
20	+3.2	-
30	+3.5	-
40	+2.7	-

^a ΔT_{max} = Maximum temp. – set temp.

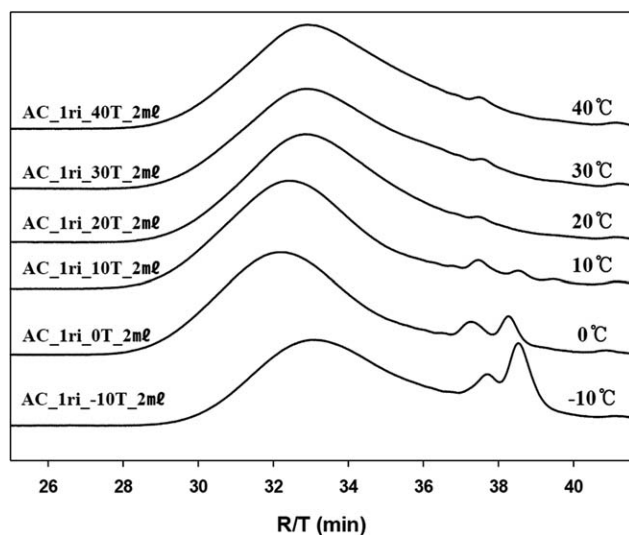


Figure 6. GPC chromatograms of AC_{1ri}γT₂ mL.

temperature of 20°C. From 20 to 40°C, the PDI slightly increased, which may be caused by the side reaction of the AM and ACE mechanism, as shown in Figure 2.

From -10 to 20°C, the PDI decreased due to the decreasing cyclic oligomer peak. This phenomenon could be explained by the existence of an induction period, as shown in Figure 5. The induction period leads to an increased monomer concentration in the reaction media. In addition, the concentrated monomer can be polymerized easily through the ACE mechanism, which is associated with the low molecular weight cyclic oligomer.^{12,22,23} As a result, the induction period strongly affects the cationic ring opening polymerization mechanism and the molecular weight distribution.

The ¹H-NMR spectra are shown in Figure 7. The polymers show signals in the range of 3.6–3.8 ppm due to the protons of the -O-CH₂-, -O-CH-, and -CH₂-Cl units.¹⁸ The FTIR spectra of the PECHs of the AC_{1ri}γT₂ mL series show typical bands of PECH, as assigned in Figure 8. All of the PECH spectra show absorption peaks due to hydroxyl at 3450 cm⁻¹, C-O-C at 1120 cm⁻¹, and C-Cl at 748 cm⁻¹.^{18,24} The PECH formation was confirmed by ¹H-NMR and FTIR. However, typical differences at the various set temperatures were not observed.

Table III. Molecular Weight and Polydispersity Obtained for the Various Set Temperatures for AC_{1ri}γT₂ mL

Set temp. (°C)	M _n (g/mol)	M _w (g/mol)	PDI	Yield (%)
40	1480	2590	1.75	>90
30	1450	2600	1.79	>90
20	1600	2690	1.68	>90
10	1720	3100	1.80	>90
0	1630	3190	1.96	>90
-10	910	1950	2.15	88

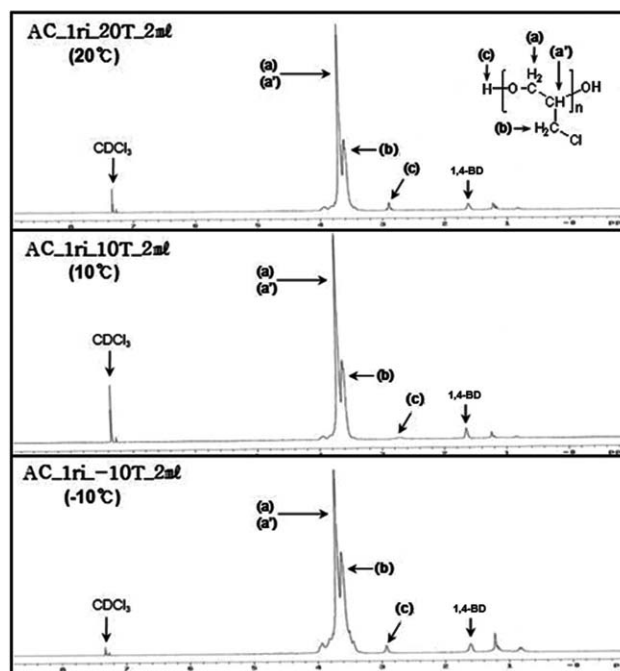


Figure 7. ¹H-NMR spectra of AC_{1ri}γT₂ mL.

The Effect of [BF₃]/[1,4-BD] Ratio

The effect of the [BF₃]/[1,4-BD] ratio ([C]/[I] ratio) on PECH cationic ring opening polymerization was investigated by the temperature monitoring system, GPC, and ¹H-NMR.

The AC_{γri}0T₁ mL PECH series was polymerized under various [C]/[I] molar ratios while holding the other reaction conditions constant (set temperature = 0°C, monomer feeding rate = 1 mL/min). The [C]/[I] ratio was varied from 0.1 to 1 and the monitored reaction temperatures are shown in Figure 9. The maximum exothermic temperature and induction period are summarized in Table IV. In particular, at a [C]/[I] ratio of 0.2, a highly exothermic reaction ($\Delta T_{\text{max}} = +33^\circ\text{C}$) appeared 1 h after completing the monomer feed. The maximum

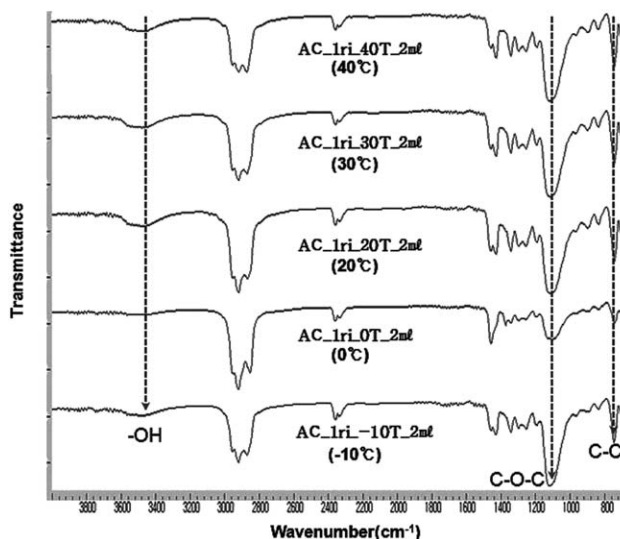


Figure 8. FTIR spectra of AC_{1ri}γT₂ mL.

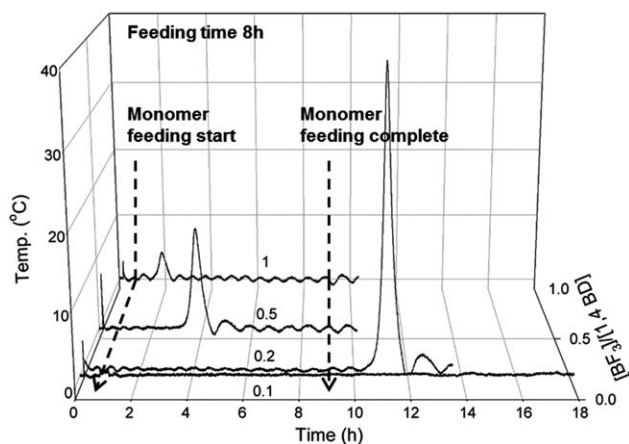


Figure 9. Reaction temperature as a function of the reaction time for the various molar ratios of $[\text{BF}_3]/[1,4\text{-BD}]$ for $\text{AC}_\gamma\text{ri}_0\text{T}_1$ mL.

exothermic temperature (ΔT_{max}) and induction period decreased with increasing $[\text{C}]/[\text{I}]$ ratio with the exception of $\text{AC}_{0.1\text{ri}_0\text{T}_1}$ mL. At a $[\text{C}]/[\text{I}]$ ratio of 0.1, there was not an exothermic reaction peak even though the reaction was carried out for additional time.

The GPC chromatograms and molecular weight characterizations of $\text{AC}_\gamma\text{ri}_0\text{T}_1$ mL PECHs are shown in Figure 10 and Table V, respectively. The cyclic oligomer shoulder peak (right side of the main curve) was observed and the intensity of the cyclic oligomer peak decreased with decreasing induction period, as shown in Figure 10. The molecular weight and yield of the resulting polymers typically increased when the $[\text{C}]/[\text{I}]$ ratio increased. The PDI of all of the PECHs was relatively broad due to the effect of the induction period, which depends on the monomer concentration in the reaction media. At a $[\text{C}]/[\text{I}]$ ratio of 0.1, the peak intensity of the GPC curve and yield was smaller than the others due to the low polymerization rate.

The $^1\text{H-NMR}$ spectra are shown in Figure 11. The unreactive ECH monomer in the $^1\text{H-NMR}$ spectra of $\text{AC}_{0.1\text{ri}_0\text{T}_1}$ mL and $\text{AC}_{0.2\text{ri}_0\text{T}_1}$ mL showed signals at 2.38 and 2.63 ppm (due to $-\text{O}-\text{CH}_2-$), 2.85 ppm (due to $-\text{O}-\text{CH}-$), and 3.38 and 3.63 ppm (due to $\text{CH}_2-\text{Cl}-$).⁸

This indicates that the $[\text{C}]/[\text{I}]$ ratio affected the initiation and propagation rate of the cationic ring opening polymerization and induction period. And the induction period may be caused by low initiation rate. Thus, the polymerization rarely occurs dur-

Table IV. Maximum Exothermic Temperature and Induction Period for the Various Molar Ratios of $[\text{BF}_3]/[1,4\text{-BD}]$ for $\text{AC}_\gamma\text{ri}_0\text{T}_1$ mL

$[\text{C}]/[\text{I}]$ ratio ^a	Max. exothermic temp. (ΔT_{max} , °C)	Induction period (min)
1	+4	40
0.5	+18	120
0.2	+33	510
0.1	-	-

^aThe ratio of $[\text{BF}_3]/[1,4\text{-BD}]$.

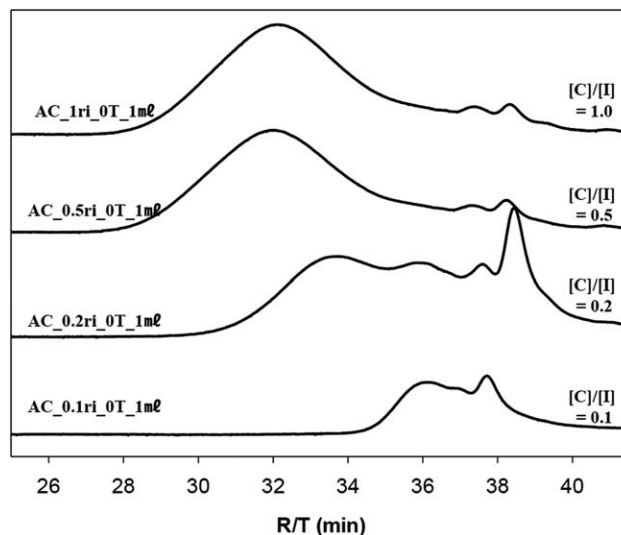


Figure 10. GPC chromatograms of $\text{AC}_\gamma\text{ri}_0\text{T}_1$ mL.

ing the induction period. As a result, the concentration of accumulated monomer which led to thermally accelerated exothermic reaction increased due to decreasing the initiation rate with decreasing $[\text{C}]/[\text{I}]$ ratio.

The Effect of Monomer Feeding Rate

The effect of the monomer feed rate on the PECH cationic ring opening polymerization was investigated by the temperature monitoring system, GPC, and $^1\text{H-NMR}$. The $\text{AC}_{1\text{ri}_\chi\text{T}_\chi}$ mL PECH series was polymerized under various monomer feed rates and reaction temperatures while maintaining a constant $[\text{C}]/[\text{I}]$ ratio of 1. Figure 12 shows the monitored reaction temperatures at set temperatures of 0°C and -10°C . Table VI shows the summary of the maximum exothermic temperature and induction period at set temperatures of 20°C and -10°C . The maximum exothermic temperature (ΔT_{max}) increased with increasing monomer feed rate. The induction period was 40 min at 2 mL/min and 50 min at 1 mL/min with a set temperature of 0°C . The period was 130 min at 2 mL/min and 120 min at 1 mL/min with a set temperature of -10°C . There was not a significant disparity between $\text{AC}_{1\text{ri}_\chi\text{T}_1}$ mL and $\text{AC}_{1\text{ri}_\chi\text{T}_2}$ mL at the same set temperature in terms of the induction period. This indicates that the induction period was not affected by the monomer feed rate.

The GPC curves and molecular weight characterization of $\text{AC}_{1\text{ri}_\chi\text{T}_\chi}$ mL PECHs are shown in Figure 13 and Table

Table V. Molecular Weight and Polydispersity Results for $\text{AC}_\gamma\text{ri}_0\text{T}_1$ mL

$[\text{C}]/[\text{I}]$ ratio ^a	M_n (g/mol)	M_w (g/mol)	PDI	Yield (%)
1	1950	3530	1.81	>90
0.5	1820	3290	1.81	87
0.2	780	1410	1.81	71
0.1	640	780	1.22	10

^aThe ratio of $[\text{BF}_3]/[1,4\text{-BD}]$.

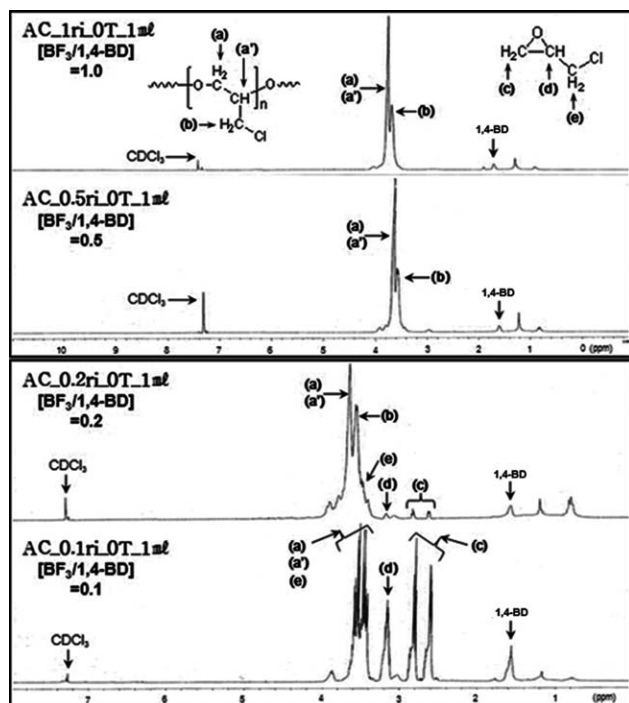


Figure 11. $^1\text{H-NMR}$ spectra of $\text{AC}_\chi\text{ri_OT}_1$ mL.

VII, respectively. The effect of the monomer feed rate on the molecular weight and PDI of the PECHs was insignificant at a set temperature of 20°C . But below a set temperature of 0°C , the molecular weight increased and the PDI became narrow with decreasing feed rate due to the decreasing intensity of the cyclic oligomer peak, as shown in Figure 13.

According to monitored reaction temperature and GPC data, the monomer feeding rate affected the molecular weight of PECH and their PDI when an induction period was observed. To the best of our knowledge, the existence of the induction period in cationic ring opening polymerization of ECH with a BF_3 catalyst and 1,4-BD initiator has not been reported in the literature. An induction period in the ring opening polymerization with metal alkoxides and a photo initiator catalyst has often been observed.^{25–27} Stridsberg et al. gave an overview of the induction period. An induction period was often observed during which the initiator rearranges to form the active species

Table VI. Maximum Exothermic Temperature and Onset Time of the Temperature Deviations with Various Feed Rates for $\text{AC}_\chi\text{ri}_\chi\text{T}_\chi$ mL

Set temp. ($^\circ\text{C}$)	Feed rate (mL/min)	Max. exothermic temp. (ΔT_{max} , $^\circ\text{C}$)	Induction period (min)
20	1	+2	–
20	2	+3.2	–
0	1	+4	40
0	2	+6.2	50
-10	1	+10.2	130
-10	2	+30.3	120

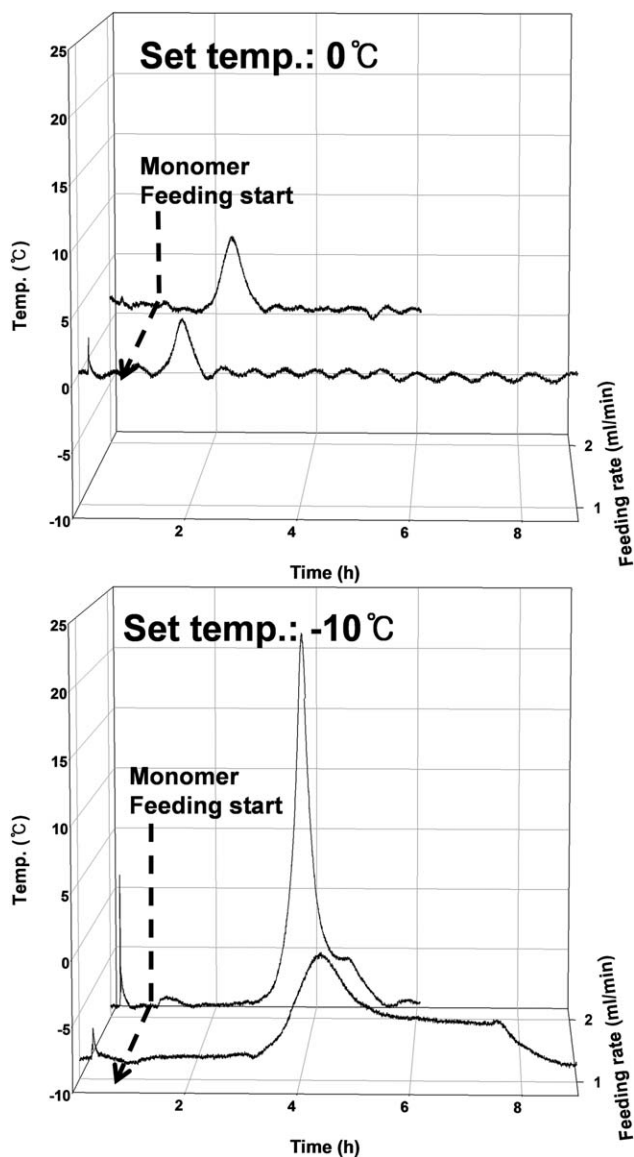


Figure 12. Reaction temperature as a function of the reaction time for the various feed ratio (top: set temperatures of 0°C ; bottom: -10°C).

for polymerization. The aggregated initiators are less reactive than nonaggregated initiators for propagation.²⁸ In the presence of amines and alcohols, the solvent polarity affects the aggregation of the initiators.^{29–31} In our experiment, the phenomenon was similar to the induction period reported by Stridsberg et al. The length of the induction period was influenced by the reaction temperature and $[\text{C}]/[\text{I}]$ ratio, where a higher reaction temperature and $[\text{C}]/[\text{I}]$ ratio resulted in a shorter induction period. In our case, the existence of the induction period may be explained by the melting point (mp: 20.1°C) and solubility of 1,4-BD. The results in Figure 14 show appearances of 1,4-BD in the MC solvent at -10 and 20°C . 1,4-BD and MC were separated in layers at 25°C and the 1,4-BD layer was frozen at -10°C . This implies that 1,4-BD could be aggregated with the catalyst in MC and the aggregation may cause the induction period below a set temperature of 10°C .

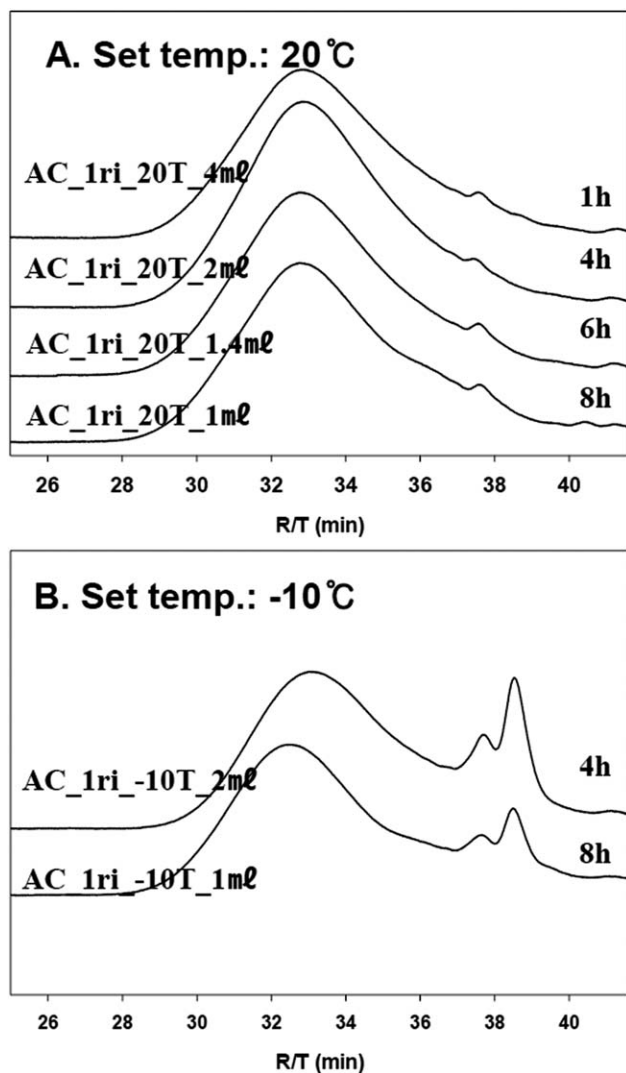


Figure 13. GPC chromatograms for AC_{1ri_20T_γ} mL and AC_{1ri_10T_γ} mL PECHs (A: 20°C; B: -10°C).

CONCLUSIONS

In this work, a correlation between the online monitored temperature and the performance of PECH as a function of the various reaction conditions were investigated. A competition reaction between AM and ACE mechanisms had been reported

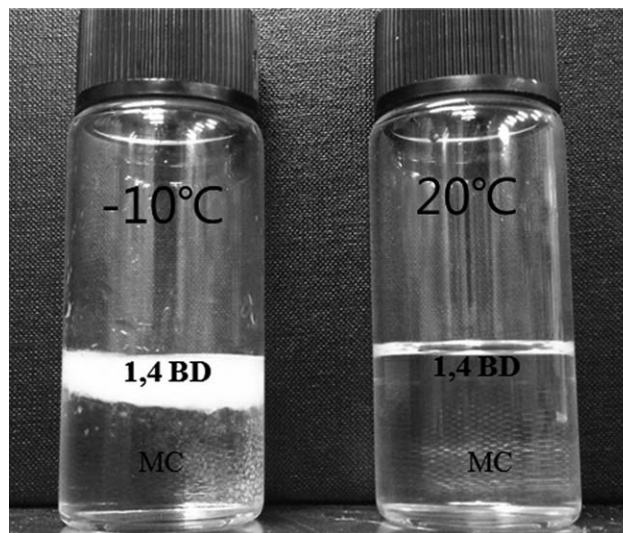


Figure 14. Appearances of 1,4-BD in MC (left: at -10°C; right: at 20°C).

for cationic ring opening polymerization.^{11,12} To enhance the contribution of AM, monomer starved condition in a reactor should be kept during the polymerization. In our investigation, however, during the polymerization, temperature and $[C]/[I]$ ratio-dependent induction periods which implies the monomer accumulated condition were observed. The amount of cyclic oligomer which is due to ACE mechanism and molecular weight distribution increased with increasing induction period. Under conditions (20–40°C) in which the induction period does not occur, the molecular weight and molecular weight distribution of resulting polymer decreased and became boarder with increasing the set temperature. And we suggested that this phenomenon is possible due to the solubility and physical properties of an initiator.

The online reaction temperature monitoring technique affords better understanding of the BF_3 -catalyzed ring opening polymerization of ECH in presence of 1,4-BD. And based on these results, it should be clear that the ring opening polymerization in the presence of 1,4-BD and BF_3 must be carried out under condition (20°C) in which the induction period does not occur to obtain the high performance of PECH.

Table VII. Molecular Weight and Polydispersity Results for AC_{1ri_γT_γ} mL

Set temp. (°C)	Feed rate (mL/min)	M_n (g/mol)	M_w (g/mol)	PDI	Yield (%)
20	4	1500	2700	1.74	>90
20	2	1600	2690	1.68	>90
20	1.4	1600	2700	1.74	>90
20	1	1600	2700	1.68	>90
0	2	1630	3190	1.96	>90
0	1	1950	3530	1.81	>90
-10	2	910	1950	2.15	88
-10	1	1190	2530	2.12	>90

In a future study, we will design a 5 L scale reactor and investigate the effects of different initiators that are soluble in MC on the ECH cationic ring opening polymerization in the presence of BF_3 .

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