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Ring-opening polymerization of various oxirane derivatives using organotin phosphate condensate; Selective synthesis of the polyether containing oxirane ring in the side chain

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Summary

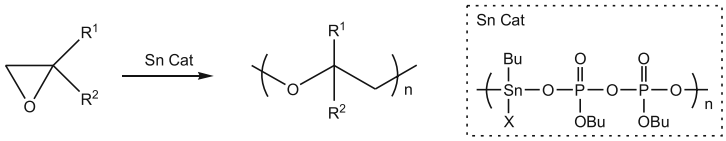
Ring-opening polymerization (ROP) of various oxirane derivatives of the type, 2,2-R^1,R^2-CCH_2O [R^1 = H (**1**), CH_3 (**2**); R^2 = CH_3 (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)], using organotin phosphate (Bu_2SnO-Bu_3PO_4) condensate has been explored. The ROP of monosubstituted oxiranes (**1a-c**) afforded ring-opened polymers in high yields (**1a, 1c** = 99% and **1b** = 69%); the resultant polymers from monomers **1a** and **1b** possessed high molecular weights (M_n = 9.49 × 10^4, 10.60 × 10^4, respectively). In contrast, both polymer yields and molecular weights for resultant polymers in the polymerization of disubstituted oxiranes (**2a-c**) were considerably lower than those in the polymerization of monosubstituted monomers (**1a-c**). ROP of glycidyl 2-methylglycidyl ether (**3**) possessing two oxirane groups with different reactivity was thus conducted by organotin catalyst; the high molecular weight polyether (M_n = 9.17 × 10^4) containing oxirane ring in the side chain has successfully been obtained in moderate yield.

Introduction

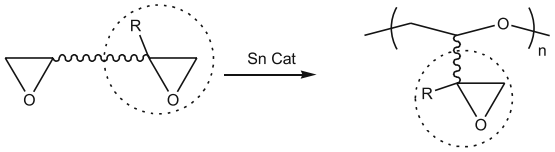
Ring-opening polymerization (ROP) of oxiranes has recently emerged as a subject of substantial interest since the initial report on the polymerization of propylene oxide (PO) using a catalyst system composed of $FeCl_3$ with PO in 1955 by Pruitt [1], which enhanced a rapid development in the design of catalyst systems/initiators for the ROP of a wide variety of monomers [2-30]. Above-mentioned Pruitt-Baggett catalyst [1, 10] was followed by the development of aluminum- and zinc-based catalyst systems (for example; $AlEt_3$-H_2O-acetylacetone and Et_2Zn-H_2O, respectively) [2-9], double metal cyanide (DMC) catalysts [11-14] and organotin phosphate condensate catalysts such as Bu_2SnO-Bu_3PO_4 [16-17]. Among various oxirane monomers, ROP of PO has been often studied from the viewpoint of stereochemical control during the polymerization [1-10, 15-17]. Recently, Coates and coworkers achieved the synthesis of isotactic poly(PO) ([*mm*] > 99%) with high molecular weight by using cobalt catalyst [15]. However, the catalytic activity was not so high in comparison with Fe-, Al-, Zn- and Sn-based catalyst. Moreover, the application of the cobalt catalyst was restricted to PO, because other oxirane monomers were not polymerizable with this

system. The polymerization of oxirane monomers other than PO is highly desirable because of attractive properties and promising applications in the resulting polymers; many effective catalysts for this purpose have been thus reported [18-24]. High molecular weight poly(isobutylene oxide) was prepared by using a ternary catalyst system composed of $ZnEt_2$, H_2S and cyclohexylamine [19]. Moreover, various organotin phosphate condensate catalysts were effective for ROP of epichlorohydrin [20]; the ROP of 3,3,3-trifluoro-1,2-epoxypropane using organozinc compound [22-23] or aluminate complex [24] afforded polyether which possessed unique properties derived from fluorine atoms.

In the present work, the effect of steric bulk of various oxirane monomers toward their reactivity in the ROP using the organotin phosphate condensate catalyst has been examined (Scheme 1). Moreover, we wish to demonstrate a selective synthesis of polyether containing oxirane ring in the side chain by adopting selective ROP of the bifunctional monomer containing two oxirane moieties with different reactivity (Scheme 2).



Scheme 1. The effect of steric bulk of various oxirane monomers on their reactivity toward catalyst system of organotin phosphate condensate in ROP



Scheme 2. Synthesis of the polyether containing oxirane ring in side chain by selective ROP

Experimental

General Procedures

Dibutyltin oxide, tributyl phosphate, 2-propen-1-ol and 3-chloro-2-methyl-1-propene were purchased from Aldrich Chemical Co. and were used as received. Racemic propylene oxide (**1a**) and 2,2-dimethyloxirane (**2a**) were refluxed over a mixture of potassium hydroxide and calcium dihydride, and then fractionally distilled under nitrogen atmosphere. Epichlorohydrin (**1b**), β-methylepichlorohydrin (**2b**), 2-methyl-glycidyl ether (**2c**) and glycidyl 2-methylglycidyl ether (**3**) were transferred into bottles containing molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox under N_2 stream, the solution was shaken for 10 min, and passed through a short alumina column. Glycidyl methyl ether (**1c**) was purified by vacuum distillation using fractionating column and the same purification procedure was employed for **1b, 2b,** and **2c**. All other chemicals used were of reagent grades and purified by standard purification procedures. ^{1}H NMR spectra of the resultant polymers were measured in benzene-d_6 at 50ºC on a JEOL ECP-400 spectrometer

(^{1}H 400MHz). Chemical shifts were referred to the peak of benzene-d_6 at 7.15 ppm. ^{13}C NMR spectra were measured under the same conditions on the ECP-400 spectrometer (^{13}C 100MHz) and chemical shifts of ^{13}C NMR spectra were referenced to the central peak of benzene-d_6 at 128.0 ppm. Gel permeation Chromatography (GPC) measurements were performed on an Shimadzu gel permeation chromatography system equipped with the columns Shodex KD807, KD806, KD806M and KD803 at 60ºC using DMF as the eluent with a flow rate of 1.0 mL/min. All measurements were calibrated vs polystyrene standards. Infrared spectroscopy (IR) spectra were measured on a FT-730 spectrometer (HORIBA) at room temperature. Differential scanning calorimetry (DSC) thermograms were measured on Perkin-Elmer 7 Series Thermal Analysis System. High resolution mass spectrometry (HRMS) was measured using positive electrospray ionization (m/z values are given) on JMS-700 (JEOL).

Preparation of Bu_2SnO-Bu_3PO_4 condensates

A mixture of Bu_2SnO (4.0 g, 16 mmol) and Bu_3PO_4 (8.5 g, 32 mmol) was stirred and heated at 250ºC for 20-30 min under dry nitrogen atmosphere. Removal of the by-products (butane, butene, 1-butanol, and dibutyl ether) from the mixture afforded the titled condensate (white solid) until the by-products didn't evolve any more. The condensate was insoluble in a variety of organic solvents because of the formation of network structure. The condensate is assumed to have the following structure (Figure 1) [20].

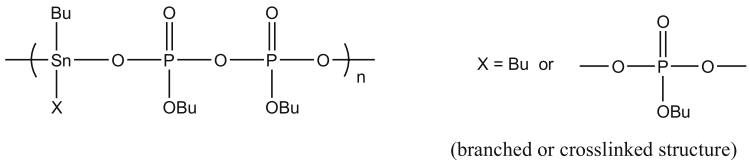


Figure 1. Structure of organotin phosphate condensate

*Synthesis of methyl 2-methylglycidyl ether (**2c**)*

Into a 3L separable flask containing MeOH (481 g, 15.0 mol) and $BF_3{\cdot}Et_2O$ (4.74 g, 30.0 mmol), which was precooled to 10 ºC, β-methylepichlorohydrin (**2b**) (320 g, 3.0 mol) was added dropwise over a period of 2 h. The solution was stirred for 8 h at the same temperature (10 ºC), and the organic solvents in the mixture were then removed *in vacuo* using rotary evaporator. The resultant liquid was added CH_2Cl_2 (980 mL) and cooled to 10 ºC, and 48% NaOH aq. (292 g, 3.5 mol) was then added dropwise over 2 h; the resultant suspension was stirred for 4 h at the same temperature. The organic layer was then separated and the aqueous layer was extracted with CH_2Cl_2 (150 mL × 3). All organic layers were combined and washed with 3% HCl aq. (200 mL × 2). Removal of CH_2Cl_2 afforded the crude product **2c**, which was further purified by distillation *in vacuo* equipped with a fractionating column (yield 49%).
Purified **2c** was a colorless liquid (boiling point 39ºC/47 mmHg).
^{1}H NMR ($CDCl_3$) δ = 1.17 (s, 3H, *Me*), 2.18 (d, J = 5 Hz, 1H, CH_2 in epoxy ring), 2.34 (d, J = 5 Hz, 1H, CH_2 in epoxy ring), 3.03 (d, J = 11 Hz, 1H, CH_2OCH_3), 3.09 (s, 3H, OCH_3), 3.17 (d, J = 11 Hz, 1H, CH_2OCH_3).
^{13}C NMR ($CDCl_3$) δ = 18.3, 50.7, 55.4, 58.7, 76.3.

IR (neat) 806, 899, 1115, 1196, 1263, 2927, 2987, 3047 cm^{-1}.
HRMS Calcld for $C_5H_{10}O_2$, 102.0681; Found, 101.0604 $[M-H]^+$.

*Synthesis of glycidyl 2-methylglycidyl ether (**3**)*

Preparation of 3-allyloxy-2-methyl-1-propene
3-Propenol (482 g, 8.3 mol) and KOH (628 g, 11.2 mol) were added into a 3L separable flask and the mixture was stirred at room temperature for 1 h. The resultant suspension was heated upto 70ºC and 3-chloro-2-methylpropene (996 g, 11.0 mol) was added slowly over a period of 5 h. The reaction mixture was further stirred under the same reaction conditions for 3 h, and the flask was cooled to room temperature. The salt formed was filtered off using a glass filter, and the filtrate was rinsed with diethyl ether (200 mL). The filtrate was washed with water (100 mL × 3) and the organic layer was dried over Na_2SO_4. 3-Allyloxy-2-methyl-1-propene with pure form was obtained by distillation (Yield 67%).

*Preparation of glycidyl 2-methylglycidyl ether (**3**)*
Into a 3L separable flask, 3-allyloxy-2-methyl-1-propene (150 g, 1.34 mol), acetonitrile (330 g, 8.04 mol), $KHCO_3$ (107 g, 1.07 mol) and methanol (300 mL) were added. The mixture was heated upto 50ºC, and 27 % H_2O_2 (438 g, 3.48 mol) aq. was then added slowly over a period of 6 h. The resulting heterogeneous mixture was stirred for 3 h under the same reaction conditions, and the solution was cooled to room temperature. Cold water (300 mL) was then added into the mixture, and the resulting suspension was extracted with CH_2Cl_2 (150 mL × 2); the organic layer was washed with water (100 mL × 3), and then 0.1N $NaHSO_3$ aq. (100 mL × 3) and was dried over Na_2SO_4. The vacuum distillation of the crude **3** afforded a pure sample in 63% yield as colorless liquid (boiling point 85ºC/8 mmHg).
^1H NMR ($CDCl_3$) δ = 1.16 (s), 1.18 (s, total 3H), 2.13-2.19 (m, 2H), 2.26-2.28 (m, 1H), 2.35-2.38 (m, 1H), 2.78-2.84 (m, 1H), 3.06-3.21 (m, 2H), 3.29-3.47 (m, 2H).
^{13}C NMR ($CDCl_3$) δ = 18.27, 18.30, 43.37, 43.40, 50.52, 50.58, 50.68, 50.78, 55.48, 55.52, 72.07, 72.30, 74.79, 75.08.
IR (neat) 800, 899, 1105, 1261, 1286, 2927, 2964, 3054 cm^{-1}.
HRMS Calcld for $C_7H_{12}O_3$, 144.0786; Found, 143.0707 $[M-H]^+$.

*Polymerization of **1a-c** and **2a-c***

Polymerizations of monomers **1a-c** and **2a-c** were conducted as follows: Bu_2SnO-Bu_3PO_4 condensate (40 mg) was dried in a glass ampoule at 150 ºC for 1 h *in vacuo* prior to use. Into a Schlenk tube containing the pretreated Bu_2SnO-Bu_3PO_4 condensate (40 mg), *n*-hexane (9.1 mL) and **1a** (4.0 g) were added at room temperature. Polymerization was conducted at 40 ºC for 24 h. The polymerization was then terminated by adding methanol, and the resultant polymer was dissolved in benzene and insoluble initiator residue was removed by centrifugation. The ring-opened polymer was then collected from the benzene solution by removing the volatiles *in vacuo*.

*Polymerization of glycidyl 2-methylglycidyl ether (**3**)*

Polymerization of glycidyl 2-methylglycidyl ether (**3**) was conducted as follows: Bu_2SnO-Bu_3PO_4 condensate (60 mg) was dried in a glass ampoule at 150 ºC for 1 h

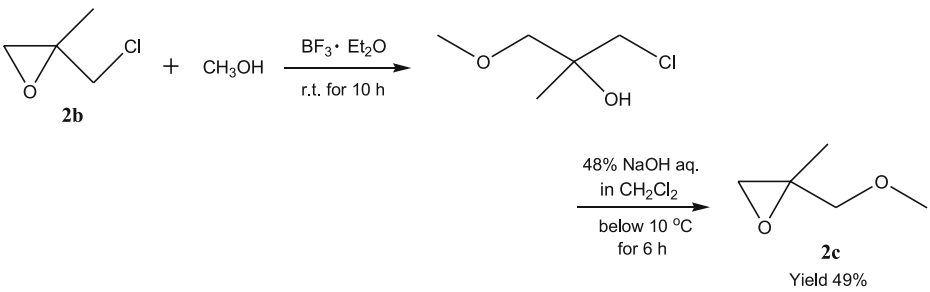
in vacuo prior to use. Into a Schlenk tube containing the pretreated condensate, *n*-hexane (9.1 mL) and **3** (4.0 g) were added, and polymerization was performed at 30ºC for 12 h. The polymerization was quenched by adding methanol, and the resultant polymer was dissolved in benzene and insoluble initiator residue was removed by centrifugation. The polymer was collected from the benzene solution by removing volatiles *in vacuo*.
^{1}H NMR ($CDCl_3$) δ =1.29 (s, 3H), 2.32 (d, 1H), 2.52 (d, 1H), 3.33-3.49 (m, 2H), 3.62-3.80 (m, 5H).
^{13}C NMR ($CDCl_3$) δ = 18.59, 51.04, 55.72, 70.72, 72.20, 75.31, 79.59.
IR (solid) 804, 897, 1082, 1105, 1261, 2924, 2958 cm^{-1}.

Results and Discussion

1. Synthesis of oxirane monomers

1-1. Synthesis of methyl 2-methylglycidyl ether (2c)

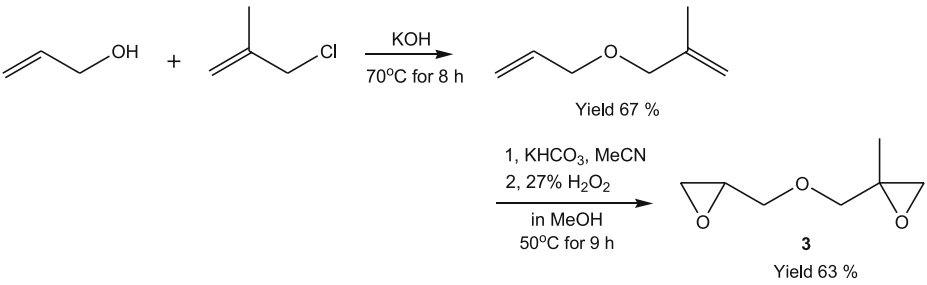
Methyl 2-methylglycidyl ether (**2c**) was prepared by acid-catalyzed ring-opening of oxirane (**2b)** with methanol and subsequent intramolecular nucleophilic substitution leading to ring closure (Scheme 3). The product resulting from the nucleophilic substitution of Cl atom was by-produced if reaction of **2b** with methanol is carried out in alkaline medium leading to the lower yield of **2c**. Monomer **2c** was characterized by ^{1}H and ^{13}C NMR spectra, FT-IR spectrum and mass spectrometry. The IR spectrum showed characteristic vibrations of epoxide; ν_{asym} = 899, ν_{sym} = 1263 cm^{-1}.



Scheme 3. Synthesis of monofunctional oxirane (**2c**)

1-2. Synthesis of glycidyl 2-methylglycidyl ether (3)

Allyl methallyl ether, the product in the first step, was prepared in 67% yield by Williamson ether synthesis, and the subsequent epoxidation with hydrogen peroxide afforded glycidyl 2-methylglycidyl ether (**3**) in 63% yield (Scheme 4). The yield decreased (yield 43%) if the epoxidation of allyl methallyl ether was conducted by using peracetic acid. The monitoring the epoxidation by gas chromatography revealed that no significant differences were seen in the epoxidation rates of both allyl ether and methallyl ether (Figure 2). The structure of **3** was confirmed by ^{1}H and ^{13}C NMR spectra, FT-IR spectrum and mass spectrometry. The IR spectrum showed characteristic vibrations of epoxide; ν_{asym} = 899, ν_{sym} = 1261 cm^{-1}.



Scheme 4. Synthesis of bifunctional oxirane (**3**)

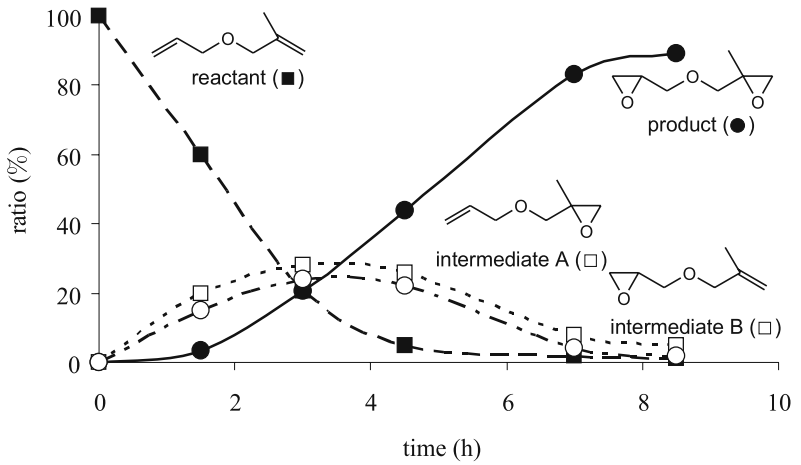


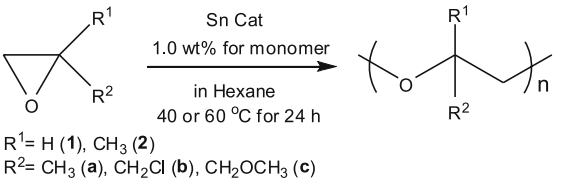
Figure 2. Monitoring of epoxidation by GC (■: reactant, □: intermediate A, ○: intermediate B, ●: product)

2. Ring-opening polymerization (ROP) of various epoxide monomers using organotin phosphate condensates

As depicted in Scheme 5, polymerizations of various epoxide monomers of the type, 2,2-R^1,R^2-CCH_2O [R^1 = H (**1**), Me (**2**); R^2 = Me (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)] were conducted in the presence of organotin phosphate condensate. The results are summarized in Table 1. The resultant polymers possessed ring-opened structure confirmed by ^1H and ^{13}C NMR spectra.

Ring-opening polymerization (ROP) of monosubstituted epoxide **1a** reached to completion after 24 h, affording high molecular weight polymer ($M_n = 9.49 \times 10^4$). In contrast, the polymer yield as well as the molecular weight in the resultant polymer was considerably lower in ROP of disubstituted monomer **2a**, which would be explained due to the greater steric bulk of **2a** than that of **1a**. The steric effect was pronounced in the ROP of disubstituted monomers **2b**, **2c** with increased steric bulk; the ROP did not take place with the present catalyst system (Run 4,7), moreover at the higher temperature (Run 5,8). Although it was widely known that the ROP of oxiranes strongly depends on the temperature [31-32], the effect of the temperature was not

seen in this range (40-60 ºC). On the other hand, ROP of monosubstituted monomers **1b** and **1c** afforded the polymers in 69% and 99% yields, respectively. The results clearly suggest that monosubstituted oxirane monomers display higher reactivity toward the present catalyst system than their disubstituted counterparts. The molecular weights of poly(**1a**) and poly(**1b**) were close, whereas the M_n value for poly(**1c**) was much low, although we do not have any appropriate reason to explain the observed difference at this moment.



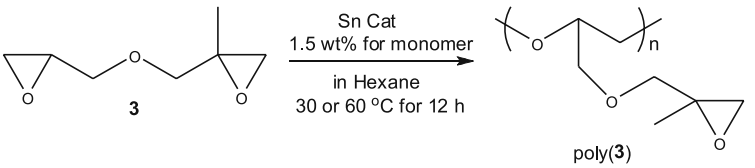
Scheme 5. Ring-opening polymerization of monofunctional oxiranes

Table 1. Ring-opening polymerization of oxiranes, 2,2-R^1,R^2-CCH_2O [R^1 = H (**1**), Me (**2**); R^2 = Me (**a**), CH_2Cl (**b**), CH_2OCH_3 (**c**)] and glycidyl 2-methylglycidyl ether (**3**) by organotin phosphate condensate.[a]

Run	Monomer (R^1, R^2)	Temp / ºC	Time / h	Yield / g (%)	M_n[b] $\times 10^{-4}$	M_w/M_n[b]
1	**1a** (CH_3, H)	40	24	3.95 (99)	9.49	4.9
2	**2a** (CH_3, CH_3)	40	24	0.66 (17)	0.25	2.0
3	**1b** (CH_2Cl, H)	40	24	2.76 (69)	10.60	4.8
4	**2b** (CH_2Cl, CH_3)	40	24	trace	--	--
5	**2b** (CH_2Cl, CH_3)	60	24	trace	--	--
6	**1c** (CH_2OCH_3, H)	40	24	3.94 (99)	1.63	3.0
7	**2c** (CH_2OCH_3, CH_3)	40	24	trace	--	--
8	**2c** (CH_2OCH_3, CH_3)	60	24	trace	--	--
9	**3**	30	12	3.40 (85)	9.17	3.6
10	**3**	60	12	3.83 (96)	5.60	5.7

[a]Conditions: Sn cat 1.0 wt% for monomers (Runs 1-8), 1.5 wt% (Runs 9-10), monomer 4.0 g, initial monomer conc.= 4.2 mol/L, *n*-hexane.
[b]GPC data in DMF vs polystyrene standards.

Taking into account the above results, selective synthesis of polyethers containing epoxy ring in the side chain was considered by the selective ROP of bifunctional monomer containing both mono- and disubstituted epoxide moieties in the presence of organotin catalyst. The ROPs of **3** were thus examined in *n*-hexane and polymers were obtained in 85 % (30ºC, Run 9) and 96 % (60ºC, Run 10), respectively (Scheme 6).



Scheme 6. Ring-opening polymerization of bifunctional oxirane (**3**)

The both resultant polymers were almost easily soluble in common organic solvents such as, benzene, toluene and DMF. The solubility of the poly(**3**) in DMF allowed the determination of its M_n by GPC {9.17×10^4 (Run 9), 5.60×10^4 (Run 10)}, and the M_n value (9.17×10^4) was not very different from those of poly(**1a**) and poly(**1b**). The result suggests that polymer is formed by ring opening of (most probably the less bulky) one oxirane group selectively. On the other hand, the lower M_n value (5.60×10^4) would be due to increased active sites for the ROP by higher temperature (60ºC), not cross-linking by the ring-opening of both mono- and disubstituted epoxide, because the ROP of both **2b** and **2c** at 60 ºC (Runs 5,8) afforded negligible amount of polymer. In addition, the better solubility of the resultant polymer should rule out the possibility of any cross-linking accompanied due to ring opening of both the oxirane moieties. The fact was also confirmed by the ^{1}H and ^{13}C NMR spectra as well as the FT-IR spectrum of the polymer (Figure 3, Figure 4).

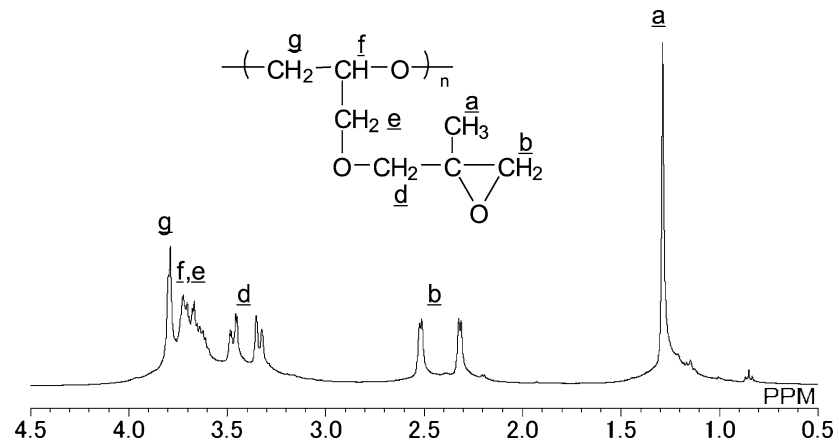


Figure 3. ^{1}H NMR spectrum of poly(**3**) (400 MHz, benzene-d_6, 50ºC).

The two doublet peaks around 2.32 and 2.52 ppm are observed in ^{1}H NMR spectrum of the polymer with integration ratio of 1:1. The presence of these peaks clearly indicates the presence of disubstituted oxirane moiety in the resulting polymer thus suggesting the selective ROP of the bifunctional monomer **3**.

Moreover, the peak at 51.0 ppm in ^{13}C NMR is also assigned to methylene carbon in the intact epoxy ring. IR spectrum of the polymer furnished further evidence for the presence of epoxy ring the polymer as showed by the presence of peaks around

ν_{sym} = 1261, ν_{asym} = 897 cm^{-1}. DSC of the resultant polymer indicated that ΔH_m could not be detected and glass transition point (T_g) was found to be -48ºC. The polyether is expected to act as the precursor for the formation of various functional polymers by the introduction of a variety of substitutents in the side chain using the reaction chemistry of epoxide moiety. Moreover, this kind of polymer is anticipated to find application as elastomer without the requirement of cross-linkers.

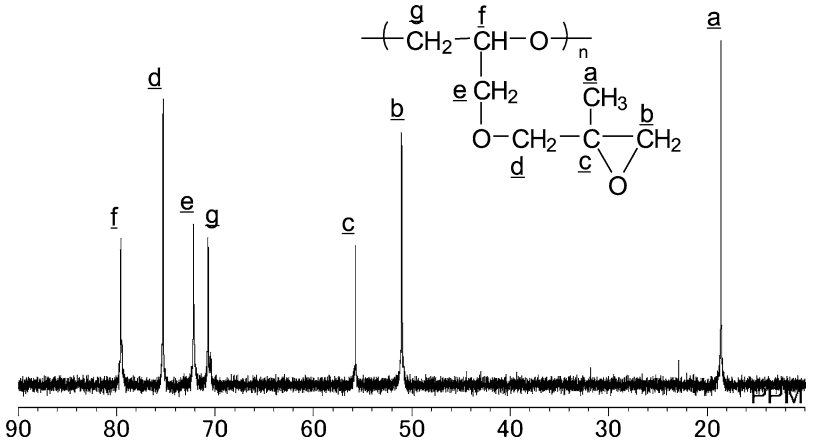


Figure 4. ^{13}C NMR spectrum of poly(**3**) (100 MHz, benzene-d_6, 50ºC).

Conclusions

Organotin phosphate (Bu_2SnO-Bu_3PO_4) condensate mediateded the ring-opening polymerization of **1a-c** and **2a-c**. The ROP of monosubstituted oxiranes (**1a-c)** reached to high conversion, whereas the conversion of the bisubstituted (**2a-c**) was considerably lower. Consequently, the polymerization of glycidyl 2-methylglycidyl ether (**3**) with both mono- and disubstituted oxirane groups was carried out resulting in the formation of polyether containing oxirane ring in the side chain in moderate yield.

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