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Articles

Copolymerization of Epoxides by Aluminum Porphyrin. Reactivity of (Porphinato)aluminum Alkoxide as Growing Species

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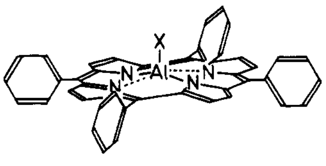
ABSTRACT: (5,10,15,20-Tetraphenylporphinato)aluminum chloride ((TPP)AlCl, 1, X = Cl) effectively brings about the copolymerization of epoxides to give copolyethers with narrow molecular weight distribution. The effect of the substituent of epoxide on the reactivity of the growing species, (porphinato)aluminum alkoxide, is much more significant than on the reactivity of the epoxide. A much higher reactivity of the primary alkoxide (TPP)Al–OCH_2CH_2– over that of the secondary alkoxide (TPP)Al–$OCH(CH_3)CH_2$– is clearly demonstrated in the competitive reactions toward 3,3-dimethyl-1,2-epoxybutane having little homopolymerizability.

Introduction

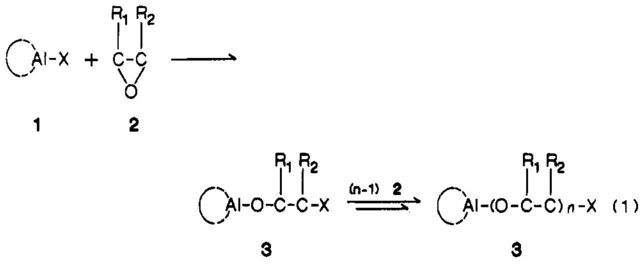
The copolymerization of the cyclic ether with a variety of catalyst systems has been studied in order to design polymer materials of desirable properties as well as to gain a better understanding of the polymerization mechanism.[1] However, the mechanistic interpretations have suffered the ambiguities coming from appreciable side reactions together with a multiplicity of active centers.

Recently, we have developed the aluminum porphyrin system as an excellent initiator for the polymerization of epoxide to give polyethers of controlled molecular weight with narrow distribution.[2] Typically, (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, 1, X = Cl) brings about the polymerization of 1,2-epoxypropane effectively even at room temperature where the molecular weight of the polymer increases linearly as the polymerization progresses, retaining a ratio of weight-average and number-average molecular weights ($\bar{M}_w/\bar{M}_n$) close to unity.[3-5] In contrast, anionic systems such as alkali metal alkoxide produce polymers of lower molecular weight due to appreciable side reactions involving the substituent of the epoxide.[1,6] Coordinate anionic catalysts such as organoaluminum or organozinc systems give polymers of high molecular weight but often with very broad or variable molecular weight distribution.[7,8] The successful formation of block copolymers of controlled chain lengths by the successive polymerization of epoxides catalyzed by aluminum porphyrin confirms the "living" character without chain transfer and termination.[3,5] Together with the excellent agreement between the degree of polymerization of polyether and the mole ratio of epoxide to aluminum porphyrin, the above observations demonstrate the uniformity of polymerization: the polymer molecules grow simultaneously from every molecule of the initiator without any side reactions.



(TPP)AlX (1)

Another advantage of the present system from an analytical viewpoint is that the porphyrin ring provides a strong magnetic shielding in its proximity, which allows us to "see" directly the process of reaction on the aluminum by means of NMR spectroscopy.[3b] By virtue of this, the polymerization of epoxide with aluminum porphyrin ((TPPAlX, 1) has been concluded to be initiated by the insertion of epoxide into the Al–X bond and to proceed via (porphinato)aluminum alkoxide (3) as the sole growing species:



Further developments are the living polymerization of β-lactone,[9] the living alternating copolymerization of epoxide and cyclic acid anhydride[10,11] or carbon dioxide,[12] the observation that the exchange between growing species takes place much faster than chain growth,[13] and the new concept of "immortal" polymerization.[14]

This paper focuses attention on the reactivity of the alkoxide group bound to aluminum porphyrin as the growing species of the polymerization of epoxide initiated by (TPP)AlCl (1, X = Cl), as investigated by copolymerization taking advantage of the living character of polymerization. The NMR observation of the copolymerization system was made to evaluate directly the reactivity of (porphinato)aluminum alkoxide.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[15] *cis-* and *trans-*2,3-epoxybutanes were synthesized by the reaction of *cis-* and *trans-*2-butenes, respectively, with *N*-bromosuccinimide[16] followed by the ring closure of the resulting bromohydrin in a concentrated aqueous solution of potassium hydroxide.[17] 3,3-Dimethyl-1,2-epoxybutane was synthesized by a similar ring closure[17] of the bromohydrin derived from the reduction of 1-bromo-3,3-dimethylbutan-2-one[18] with sodium borohydride. Epoxyethane, stirred with a mixture of potassium hydroxide and calcium hydride, was collected in a trap cooled with liquid nitrogen. 1-Chloro-2,3-epoxypropane was distilled over calcium hydride under nitrogen. The other epoxides were distilled in nitrogen atmosphere after refluxing over a mixture of potassium hydroxide and calcium

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hydride. Dichloromethane (CH_2Cl_2), washed successively with concentrated sulfuric acid, water, and aqueous sodium bicarbonate, was dried with calcium chloride and then subjected to distillation after refluxing over calcium hydride under nitrogen. Deuteriated chloroform ($CDCl_3$) was refluxed with calcium hydride followed by distillation under nitrogen.

Procedures. Preparation of Aluminum Porphyrins ((TPP)AlX, 1). A round-bottom flask (50 mL) equipped with a three-way stopcock containing $TPPH_2$ (1 mmol) was purged with dry nitrogen, and dichloromethane (20 mL) was added by a hypodermic syringe in the nitrogen stream to dissolve the porphyrin. Diethylaluminum chloride (1.2 mmol) was added by a hypodermic syringe to this mixture, which was kept stirring for 1 h. Volatile fractions were removed from the reaction mixture to leave (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl, 1, X = Cl) as a purple powder.[3] For the preparation of (TPP)Al–$(OCH_2CH_2)_n$–Cl and (TPP)Al–$(OCH(CH_3)CH_2)_n$–Cl, epoxyethane and 1,2-epoxypropane were polymerized respectively by (TPP)AlCl in dichloromethane at room temperature overnight with a mole ratio of epoxide to (TPP)AlCl of 5.[3] After the removal of volatile fractions under reduced pressure in nitrogen atmosphere, the number of repeating oxyalkylene units in the oligomers formed, as determined by ^{1}H NMR,[3] was about 5.

Copolymerization. To a flask containing 0.5 mmol of aluminum porphyrin thus prepared was added dichloromethane (20 or 40 mL), followed by the introduction of a mixture of comonomers at room temperature using a hypodermic syringe in the nitrogen stream. Then the mixture was kept stirring under nitrogen in a water bath. After a definite time, a large amount of methanol was added to the reaction mixture, which was then immediately subjected to evaporation under reduced pressure to remove the volatile fractions (unreacted epoxides and solvent), and the residue was analyzed by ^{1}H NMR to obtain the composition of the copolymer.[19] The conversion was calculated from the weight of the residue divided by that of the total comonomer in the feed after subtracting the amount corresponding to (TPP)AlCl. The copolymerization of *cis*- and *trans*-2,3-epoxybutanes was carried out in a similar way in dichloromethane (5 mL), where the conversions of the respective isomers were determined by gas chromatography of the volatile fractions collected in a trap cooled with liquid nitrogen. For direct observation by ^{1}H NMR of the copolymerization system, a mixture of comonomers was added to the $CDCl_3$ solution of (TPP)AlCl (1, X = Cl) cooled with a dry ice/methanol bath. An aliquot of the mixture was transferred by hypodermic syringe in a nitrogen stream into a NMR glass tube (5-mm i.d.), which was then sealed off in a nitrogen stream and kept at the dry ice/methanol temperature until the NMR measurement was made at room temperature.

Measurements. The ^{1}H NMR spectrum was recorded on a JEOL Type 4H-A spectrometer at 100 MHz by using $CDCl_3$ as solvent, where the chemical shift was determined with respect to the $(CH_3)_3Si$–group as standard. Gas chromatographic analysis of *cis*- and *trans*-2,3-epoxybutanes was carried out by using a Shimadzu GC 4B PT type gas chromatograph with a column packed with poly(ethylene glycol) and helium as carrier gas. For the estimation of number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) of copolymer, gel permeation chromatography (GPC) of the reaction mixture was performed on a Toyo Soda Model 802-UR high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent with a flow rate of 1.1 mL·min^{-1}. The column sets consisted of four Polystyragel columns with pore sizes 7000–3000 Å (two), 3000 Å (one), and 2000 Å (one). A molecular weight calibration curve was made based on standard poly(oxyethylenes) from Toyo Soda Manufacturing Co., Ltd., $\bar{M}_n = 22000$ ($\bar{M}_w/\bar{M}_n = 1.14$), $\bar{M}_n = 39000$ ($\bar{M}_w/\bar{M}_n = 1.03$), and $\bar{M}_n = 72000$ ($\bar{M}_w/\bar{M}_n = 1.02$), and poly(propylene glycols) from Lion Fat & Oil Co., Ltd, $\bar{M}_n$ = 1000 and 2000 ($\bar{M}_w/\bar{M}_n \approx 1$).

Statistical Treatment. Monomer reactivity ratios r_1 and r_2 were evaluated from the composition of the comonomer in the feed and that of the copolymer formed at the early stage by applying the Kelen–Tüdös method.[20]

Results and Discussion

The copolymerization of epoxides using the aluminum porphyrin ((TPP)AlCl, 1, X = Cl; TPP, 5,10,15,20-tetraphenylporphinato) as initiator was examined in CH_2Cl_2 at room temperature with 1,2-epoxypropane (2, $R_1 = CH_3$, R_2 = H; PO) as counterpart of the comonomers.[21]

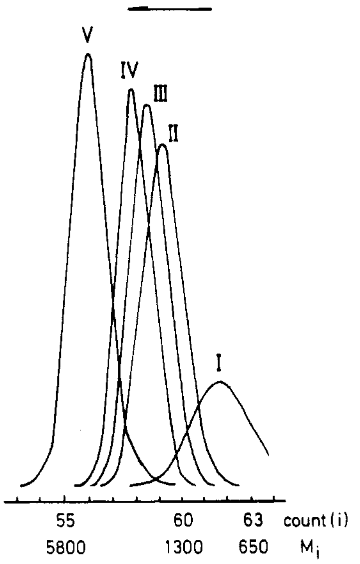

Figure 1. Copolymerization of 1,2-epoxypropane (PO) and epoxyethane (EO) with (TPP)AlCl (1, X = Cl) in CH_2Cl_2 (80 mL) at room temperature. $[PO]_0/[EO]_0/[(TPP)AlCl]_0 = 100/100/1$. $[(TPP)AlCl]_0 = 10.9$ mmol·L^{-1}; GPC profile of copolymerization: (I) time 30 min, conversion 5%; (II) 60 min, 7%; (III) 120 min, 12%; (IV) 180 min, 26%; (V) 24 h, 55%.

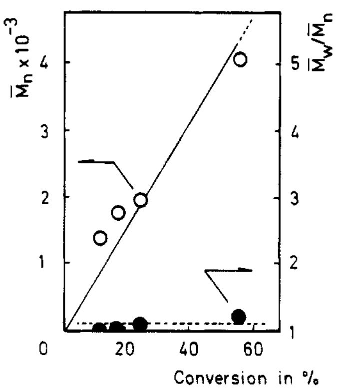

Figure 2. Copolymerization of 1,2-epoxypropane (PO) and epoxyethane (EO) with (TPP)AlCl (1, X = Cl). Relationship between $\bar{M}_n$ (○) ($\bar{M}_w/\bar{M}_n$ (●)) and conversion. Reaction conditions: see Figure 1.

The copolymerization of 1,2-epoxypropane with epoxyethane (2, $R_1 = R_2$ = H; EO) proceeded readily to give the corresponding copolymer, as shown in Figure 1. It is noteworthy that the resulting copolymer is of narrow molecular weight distribution as is the case in the homopolymerization of each comonomer.[3] The GPC profile of the reaction mixture showed a single and sharp elution curve, which was observed to shift toward the higher molecular weight region as the copolymerization progressed. A linear relationship was found between the number-average molecular weight ($\bar{M}_n$) of copolymer and the conversion of comonomers, while the ratio of the weight-average molecular weight to the number-average molecular weight ($\bar{M}_w/\bar{M}_n$) was close to unity throughout the copolymerization (Figure 2). 1,2-Epoxybutane (2, $R_1 = CH_2CH_3$, R_2 = H; 1BO) was also found to copolymerize with 1,2-epoxypropane to give copolymers of narrow molecular weight distribution, as shown in Figures 3 and 4. The number-average molecular weight ($\bar{M}_n$) of the copolymer increased linearly as the copolymerization progressed, retaining a $\bar{M}_w/\bar{M}_n$ ratio of about 1.1. Similarly,

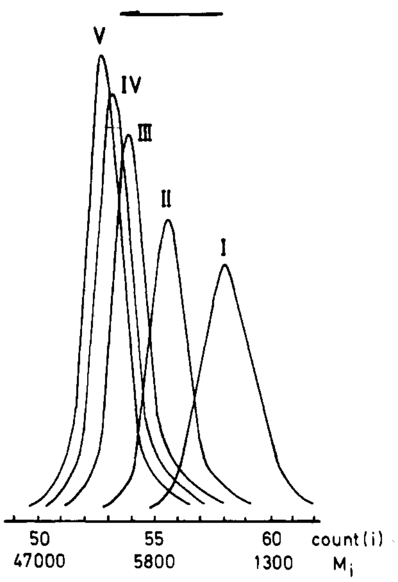

Figure 3. Copolymerization of 1,2-epoxypropane (PO) and 1,2-epoxybutane (1BO) in CH_2Cl_2 (20 mL) at room temperature $[PO]_0/[1BO]_0/[(TPP)AlCl]_0 = 270/200/1$, $[(TPP)AlCl]_0 = 18.6$ mmol·L^{-1}; GPC profile of copolymerization: (I) time 20 min, conversion 16.5%; (II) 35 min, 27%; (III) 120 min, 44%; (IV) 15.7 h, 60%.

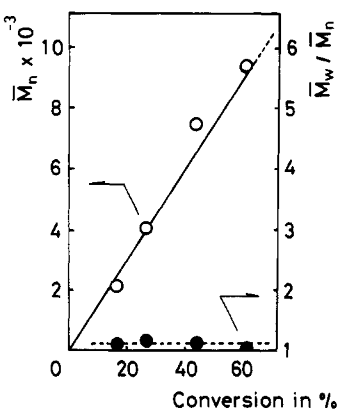

Figure 4. Copolymerization of 1,2-epoxypropane (PO) and 1,2-epoxybutane (1BO) with (TPP)AlCl (1, X = Cl). Relationship between $\bar{M}_n$ (○) ($\bar{M}_w/\bar{M}_n$ (●)) and conversion. Reaction conditions: see Figure 3.

the copolymerizations of 1,2-epoxypropane (PO) with 1-chloro-2,3-epoxybutane (2, $R_1 = CH_2Cl$, $R_2 = H$; ECH), 3,3-dimethyl-1,2-epoxybutane (2, $R_1 = C(CH_3)_3$, $R_2 = H$; tBuEO), and *cis*-2,3-epoxybutane (2, $R_1 = R_2 = CH_3$(cis); cis2BO) afforded the corresponding copolymer with narrow molecular weight distribution, the ratio $\bar{M}_w/\bar{M}_n$ ranging from 1.12 to 1.18.

Thus, the copolymerization of epoxide using the aluminum porphyrin (TPP)AlCl (1) as initiator is characterized by the living nature to give copolyethers with narrow molecular weight distribution. Uniform chain growth with respect to all molecules of the copolymer is considered to proceed via (porphinato)aluminum alkoxide as growing species.

Monomer Reactivity Ratio. Figure 5 shows the copolymerization diagram for the reaction of 1,2-epoxypropane (M_1) with another epoxide (M_2). In the copolymerization using epoxyethane (EO), 1,2-epoxybutane (1BO), or 1-chloro-2,3-epoxypropane (ECH) as a counterpart for 1,2-epoxypropane, the composition of copolymer formed at the early stage is very similar to that of the comonomers in the feed, indicating that the copolymerizabilities of these epoxides are not so much different from each other. On the other hand, when 1,2-epoxypropane was copolymerized with 3,3-dimethyl-1,2-epoxybutane (tBuEO) with a bulky *tert*-butyl group or *cis*-2,3-epoxybutane (cis2BO) with 1,2-disubstitution, preferential incorporation of 1,2-epoxypropane was observed over a wide range of the starting comonomer composition.

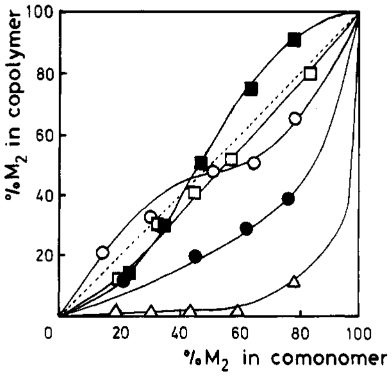

Figure 5. Copolymerization of epoxide catalyzed by (TPP)AlCl (1, X = Cl), in CH_2Cl_2 using 1,2-epoxypropane (PO) as M_1. Relationship between the composition of copolymer formed at the early stage and that of the comonomer in the feed. M_2: (○) epoxyethane; (□) 1,2-epoxybutane; (■) 1-chloro-2,3-epoxypropane; (●) *cis*-2,3-epoxybutane; (△) 3,3-dimethyl-1,2-epoxybutane.

Table I
Monomer Reactivity Ratio in the Copolymerization of Epoxide by (TPP)AlCl (1, X = Cl) Using 1,2-Epoxypropane (PO) as M_1

M_1 (PO)		M_2				
R_1	R_2	R_1	R_2	r_1	r_2	$1/r_1$
CH_3	H	H	H	0.5	0.3	2.0
		CH_2CH_3	H	1.4	0.9	0.7
		CH_2Cl	H	5.1	6.3	0.2
		cis-CH_3	*cis*-CH_3	1.8	*a*	0.6

[a] Very small, close to 0.

Since the steady state with respect to the concentration of growing species is realized in these copolymerizations with living character, the Kelen–Tüdös method[20] was applied to evaluate the monomer reactivity ratio (Table I). The value $1/r_1$ represents the relative reactivity of M_2 to M_1 toward the growing species derived from M_1.

Thus, the observed reactivity of epoxide toward (porphinato)aluminum alkoxide 3 ($R_1 = CH_3$, $R_2 = H$) decreased in the order epoxyethane > 1,2-epoxypropane, 1,2-epoxybutane ≈ *cis*-2,3-epoxybutane > 1-chloro-2,3-epoxypropane. Although the observed order appears to be parallel with the increasing bulkiness of the substituent on the epoxide ring, it is rather interesting that the lowest reactivity is observed for 1-chloro-2,3-epoxypropane, which has been reported to be highly susceptible to nucleophiles due to the electron-withdrawing substituent.[22,23]

Another interesting observation was made in the copolymerization of an equimolar mixture of *cis*- and *trans*-2,3-epoxybutanes, where the cis isomer was consumed preferentially over the trans isomer, although the homopolymerization of each isomer gives the polymer in almost the same yield.[4] A similar higher reactivity of the cis isomer has been reported in the copolymerization by a representative "coordinate" anionic catalyst composed of triethylaluminum, water, and acetylacetone,[7] while in a simple nucleophilic reaction the difference in the reactivity between these isomers is small.[24] Thus, the coordinative interaction between the oxygen atom of the epoxide and the aluminum atom is suggested to occur prior to ring opening of the epoxide in the polymerization by aluminum porphyrin. The Lewis acidic character of alu-

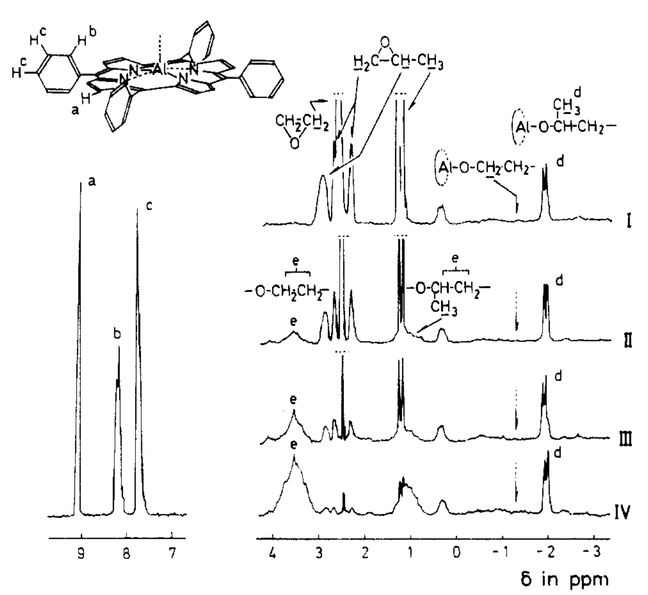

Figure 6. Copolymerization of 1,2-epoxypropane (PO) and epoxyethane (EO) with (TPP)AlCl (1, X = Cl) in $CDCl_3$ at room temperature. $[PO]_0/[EO]_0/[(TPP)AlCl]_0 = 7/7/1$, $[(TPP)AlCl]_0 = 48.0\ mmol{\cdot}L^{-1}$. ^1H NMR spectra of the copolymerization system: (I) 30 min; (II) 50 min; (III) 80 min; (IV) 3 days.

minum porphyrins has been noted by their ability to coordinate a nitrogenous base such as 1-methylimidazole[25] or the anionic species of some onium salts.[10,26]

Direct Observation of Growing Species. In the copolymerization of an equimolar mixture of 1,2-epoxypropane (PO) and 1,2-epoxybutane (1BO) by (TPP)AlCl (1, X = Cl) in $CDCl_3$, the ^1H NMR spectrum of the reaction mixture showed two signals characteristic of (TPP)Al-$OCH(CH_3)CH_2$– from 1,2-epoxypropane and (TPP)Al-$OCH(CH_2CH_3)CH_2$– from 1,2-epoxybutane with a comparable intensity at δ -2.0 (d)[3b] and δ -1.8 (t),[27] respectively. This result is consistent with the random tendency of copolymerization, as expected from the calculated sequence distribution of copolymer based on monomer reactivity ratios: $f_{PO\text{-}PO}$, 32.5%; $f_{PO\text{-}1BO} + f_{1BO\text{-}PO}$, 46.5%; and $f_{1BO\text{-}1BO}$, 21.0 % ($[PO]_0/[1BO]_0 = 1$). Thus, either of the growing species should be regenerated with almost the same probability as the result of chain growth without any preference of comonomers.

On the other hand, a rather unexpected but interesting observation was made in the copolymerization of an equimolar mixture of 1,2-epoxypropane and epoxyethane, as shown in Figure 6. The signal due to (TPP)Al-$OCH(CH_3)CH_2$– (d) from 1,2-epoxypropane appeared at δ -2.0,[3b] while the growing species from epoxyethane (TPP)Al-OCH_2CH_2–, which is expected to be observable at δ -1.4,[3b] could hardly be detected throughout the reaction, although the signal of epoxyethane at δ 2.5 decreased and disappeared in copolymerization. Since the intensity of the signal (d) was close to $^3/_8$ that of the signal of the pyrrole-β proton of aluminum porphyrin (a, 8 H), the $-OCH(CH_3)CH_2-$ group is a single observable alkoxide bound to the aluminum porphyrin throughout the copolymerization. When epoxyethane alone was added to the present copolymerization system from which both comonomers had been removed, a triplet signal due to (TPP)Al-OCH_2CH_2– did appear at δ -1.4 quantitatively with the disappearance of the signal (d).

However, when epoxyethane was added together with 1,2-epoxypropane to the mixture of (TPP)Al-$(OCH_2CH_2)_n$-Cl and (TPP)Al-$(OCH(CH_3)CH_2)_n$-Cl ($n \simeq 5$), separately prepared from each comonomer, the signal at δ -1.4 due to (TPP)Al-$(OCH_2CH_2)_n$-Cl disappeared, whereas the signal (d) at δ -2.0 remained unchanged. When the alternating tendency of chain growth between 1,2-epoxypropane and epoxyethane (Figure 5) is taken into consideration, the reaction of (TPP)Al-OCH_2CH_2– and 1,2-epoxypropane is considered to proceed much faster than the reaction of (TPP)Al-$OCH(CH_3)CH_2$– and epoxyethane due to the pronounced reactivity of the primary alkoxide as growing species.

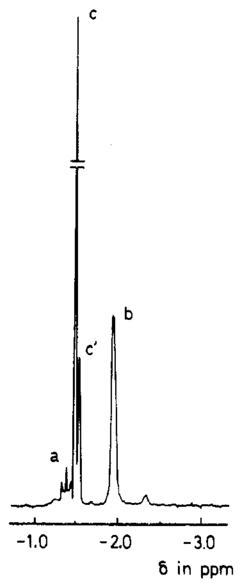

Figure 7. Reaction of the equimolar mixture of (TPP)Al-$(OCH_2CH_2)_n$-Cl and (TPP)Al-$(OCH(CH_3)CH_2)_n$-Cl ($n \simeq 5$) (1 mmol/1 mmol) with 3,3-dimethyl-1,2-epoxybutane (5 mmol) in $CDCl_3$ (20 mL) at room temperature under N_2. ^1H NMR spectrum of the reaction mixture.

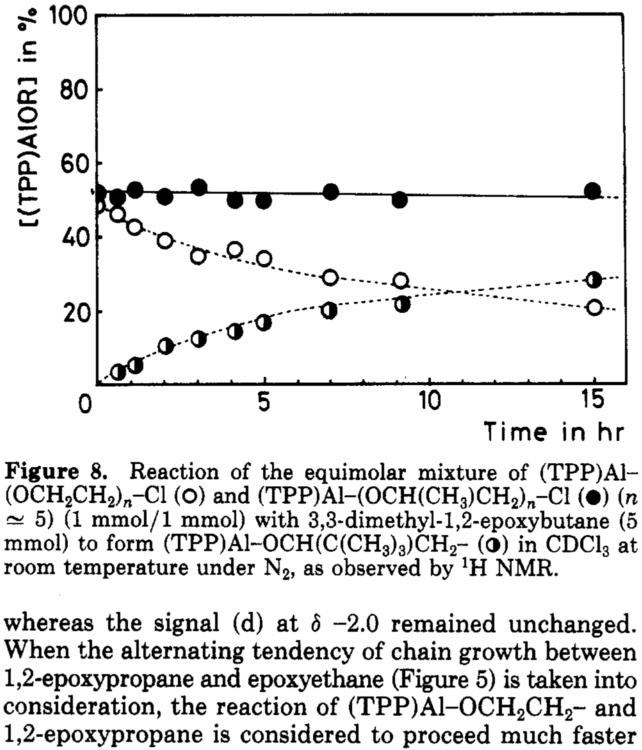

Figure 8. Reaction of the equimolar mixture of (TPP)Al-$(OCH_2CH_2)_n$-Cl (○) and (TPP)Al-$(OCH(CH_3)CH_2)_n$-Cl (●) ($n \simeq 5$) (1 mmol/1 mmol) with 3,3-dimethyl-1,2-epoxybutane (5 mmol) to form (TPP)Al-$OCH(C(CH_3)_3)CH_2$– (◑) in $CDCl_3$ at room temperature under N_2, as observed by ^1H NMR.

In fact, the difference in the reactivity between the primary and the secondary alkoxides was much more explicit in the reaction toward 3,3-dimethyl-1,2-epoxybutane with little homopolymerizability.[28] In the reaction of this epoxide (5 equiv) with an equimolar mixture of (TPP)-Al-$(OCH_2CH_2)_n$-Cl and (TPP)Al-$(OCH(CH_3)CH_2)_n$-Cl ($n \simeq 5$) (1 equiv/1 equiv) in $CDCl_3$ at room temperature (Figure 7), a singlet signal (c) at δ -1.58 assignable to the adduct (TPP)Al-$OCH(C(CH_3)_3)CH_2$-$(OCH_2CH_2)_n$-Cl appeared to grow at the expense of (TPP)Al-$(OCH_2CH_2)_n$-Cl (a, δ -1.4), while the insertion of 3,3-dimethyl-1,2-epoxybutane into the (TPP)Al-$OCH(CH_3)CH_2$– bond (b, δ -2.0) to give (TPP)Al-$OCH(C(CH_3)_3)CH_2$-$(OCH(CH_3)CH_2)_n$-Cl (c′, δ −1.67 (s)) was observed to be very slow (Figure 8).

Even when a large excess (10 times) of epoxyethane was employed for the copolymerization with 1,2-epoxypropane, the ^{1}H NMR signal due to (TPP)Al–OCH_2CH_2– was observable only with very low intensity. This is quite surprising since epoxyethane is twice as reactive as 1,2-epoxypropane toward (TPP)Al–$OCH(CH_3)CH_2$–, as indicated by the value $1/r_1$. The growing species (TPP)Al–OCH_2CH_2– was also undetectable by ^{1}H NMR in the copolymerization of epoxyethane with 1,2-epoxybutane, again demonstrating the pronounced reactivity of the growing species from epoxyethane.

Conclusion

The copolymerization of epoxides initiated by aluminum porphyrin is of a living character and gives copolyethers of narrow molecular weight distribution irrespective of the difference in the reactivities of the epoxide and/or growing species involved. The effect of the substituent of the epoxide ring is much more remarkable on the reactivity of the growing species, (porphinato)aluminum alkoxide, than on the reactivity of epoxide. The reactivity of the primary alkoxide on aluminum porphyrin toward epoxide is much higher than that of the secondary alkoxide. The preference of cis isomer in the copolymerization of geometrically isomeric epoxides indicates a similarity between aluminum porphyrin and the so-called "coordinate" anionic system in respect to monomer activation. However, the formation of copolymer as well as the homopolymer of epoxide with narrow molecular weight distribution by the present system emphasizes the significance of the highly isolated structure of the active site by the porphyrin ring to assure the uniformity of every elementary step associated with the chain growth of all polymerizing molecules.

Registry No. 1 (X = Cl), 71102-37-9; (PO)(EO) (copolymer), 9003-11-6; (PO)(IBO) (copolymer), 25549-07-9; (ECH)(PO) (copolymer), 24969-08-2; (*cis*-2BO)(PO) (copolymer), 106213-32-5; (*t*-BuEO)(PO) (copolymer), 106213-33-6; EO, 75-21-8; IBO, 106-88-7; ECH, 106-89-8; *cis*-2BO, 1758-33-4; PO, 75-56-9.

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