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Living Polymerization of Epoxides with Metalloporphyrin and Synthesis of Block Copolymers with Controlled Chain Lengths

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ABSTRACT: The 5,10,15,20-tetraphenylporphine–diethylaluminum chloride system has been found to polymerize ethylene oxide, propylene oxide, and 1,2-butene oxide to produce "living" polymers having narrow molecular weight distributions. Binary and ternary block copolymers could be synthesized from these epoxides with very high blocking efficiency (almost 100%). The length of the blocked chain could be controlled by changing the amounts of the monomers reacted. The block copolymers are also characterized by a narrow molecular weight distribution.

"Living" polymerization is of great importance in the preparation of polymers with narrow molecular weight distributions and block copolymers with well-defined block lengths. However, examples have been limited mainly to polymerization of nonpolar vinyl monomers. As for ring-opening polymerization of epoxides, only ethylene oxide was reported to form living polymer with some alkaline catalysts.

Recently, in the course of our studies on the copolymerization of carbon dioxide and epoxide using metalloporphyrins as a catalyst, the 5,10,15,20-tetraphenylporphine ($TPPH_2$)–diethylaluminum chloride (Et_2AlCl) system was found to show particularly high catalytic activity for the homopolymerization of propylene oxide to give a polymer with a narrow molecular weight distribution.[1] Further investigation has revealed that the molecular weight of the poly(propylene oxide) can be controlled by the initial mole ratio of monomer to catalyst or by changing the conversion.[2] Therefore, the polymerization of propylene oxide with this catalyst system is considered to proceed without any appreciable chain transfer reaction or deactivation of the propagating end. In accordance with this, a high blocking efficiency was achieved in the block copolymerization of ethylene oxide with poly(propylene oxide) prepared by the $TPPH_2$–Et_2AlCl system.[3] The block copolymer obtained was also characterized by a narrow molecular weight distribution. These findings prompted us to apply this excellent catalyst for the polymerization of other epoxides in order to extend the procedures to prepare various polyethers and their block copolymers having narrow molecular weight distributions.

Experimental Section

Materials. $TPPH_2$ was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol. This crystalline material was found from the visible spectrum to be contaminated with 2–3% $\alpha,\beta,\gamma,\delta$-tetraphenylchlorin.[4] Propylene oxide and 1,2-butene oxide were purified by refluxing over a mixture of potassium hydroxide and calcium hydride and then fractionally distilled twice under a nitrogen atmosphere. Ethylene oxide, stirred with a mixture of potassium hydroxide and calcium hydride at room temperature, was degassed to remove air and then collected in a trap cooled in a liquid nitrogen bath. Dichloromethane, washed with concentrated sulfuric acid and neutralized with sodium bicarbonate, was dried over calcium chloride and then fractionally distilled over calcium hydride under a nitrogen atmosphere. Et_2AlCl was purified by fractional distillation under reduced pressure.

Measurements. ^1H NMR spectra of the polymers were measured in deuterated benzene or chloroform, using a JEOL Type 4H-A spectrophotometer operating at 100 MHz. Hexamethyldisiloxane was used as an internal standard. The signal due to the methylene proton (δ 1.6) of the side chain was employed for calculation of the content of the oxy(ethylethylene) unit from 1,2-butene oxide in block copolymer. The contents of the oxy(methylethylene) unit from propylene oxide and oxyethylene unit from ethylene oxide were calculated on the basis of the signals due to methine and/or methylene protons (δ 3.4) of the main chain and methyl proton (δ 1.1) of the side chain. Gel permeation chromatography (GPC) was performed on a Toyo Soda Model HLC-802UR gel permeation chromatograph equipped with a differential refractometer detector. The eluent was tetrahydrofuran, and the flow rate was 1.2 $mL \cdot min^{-1}$. The column set consisted of four columns (60 cm) of porosity ratings 7000–3000 Å (two), 3000 Å (one), and 2000 Å (one). A molecular weight calibration curve was obtained by using standard poly(propylene glycols) for the lower molecular weight region and standard poly(ethylene oxides) for the high molecular weight region. Standard poly(propylene glycols) were obtained from Lion Fat and Oil Co., Ltd.: $\bar{M}_n$ = 1000 and 2000 ($\bar{M}_w/\bar{M}_n \approx 1$). Standard poly(ethylene oxides) were obtained from Toyo Soda Manufacturing Co., Ltd.: $\bar{M}_n$ = 22 000 ($\bar{M}_w/\bar{M}_n$ = 1.14), $\bar{M}_n$ = 39 000 ($\bar{M}_w/\bar{M}_n$ = 1.03), and $\bar{M}_n$ = 72 000 ($\bar{M}_w/\bar{M}_n$ = 1.02). From GPC results, the number-average and weight-average molecular weights ($\bar{M}_n$ and $\bar{M}_w$) were calculated by standard procedures based on the molecular weight calibration curve.

Procedures. Preparation of Catalyst. The reaction of $TPPH_2$ with Et_2AlCl was carried out in a Pyrex flask fitted with a three-way cock. The flask containing $TPPH_2$ (0.61 g, 1 mmol) was purged with dry nitrogen, and dichloromethane (20 mL) was added to dissolve the $TPPH_2$. To this solution was added Et_2AlCl (1.2 mmol) in 20% excess to $TPPH_2$. After about 2 h, the volatile materials were removed from the reaction mixture to give a purple solid, which was used as the catalyst.

Polymerization. A prescribed amount of dichloromethane was added to the flask in which the catalyst was prepared. Then the purified monomer was degassed and introduced by distillation to this flask, cooled with a liquid nitrogen bath (trap-to-trap method). Polymerization was carried out under a nitrogen atmosphere at room temperature. After the polymerization, a large amount of methanol was added to the reaction mixture and volatile materials were removed under reduced pressure. The conversion was calculated from the weight of the residue by subtracting the amount corresponding to the catalyst.

For block copolymerization, homopolymerization of the first monomer was carried out with the $TPPH_2$–Et_2AlCl system in dichloromethane. After the monomer was completely polymerized, a portion of the polymerization system was subjected to GPC analysis and the second monomer was introduced to the remainder by a trap-to-trap method. Ternary block copolymerization was carried out by a procedure similar to that described above.

For GPC measurement, part of the obtained polymer was dissolved in tetrahydrofuran, and a Teflon filter was used to filter off the insoluble part (catalyst residue) from this solution.

Results and Discussion

Reaction of $TPPH_2$ with Et_2AlCl. In the equimolar reaction of $TPPH_2$ with Et_2AlCl, rapid evolution of about 2 equiv of ethane with respect to $TPPH_2$ was observed. Therefore, this reaction is considered to proceed as illustrated in Scheme I. A similar reaction of $TPPH_2$ with $AlEt_3$ gives (tetraphenylporphinato)ethylaluminum.[5] In this paper, the reaction product of $TPPH_2$ with Et_2AlCl

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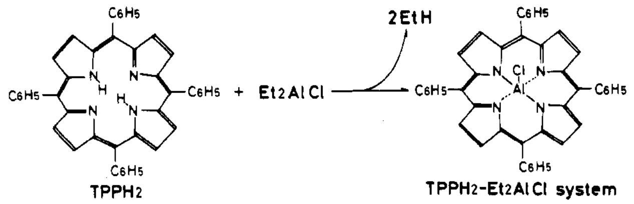
Scheme I



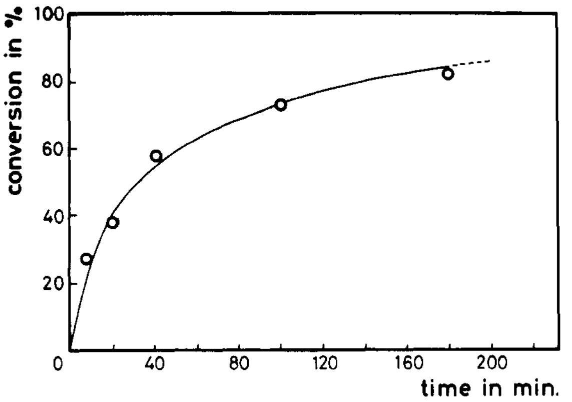


Figure 1. Polymerization of ethylene oxide (EO) with the $TPPH_2$-Et_2AlCl system (room temperature; solvent, CH_2Cl_2; $[cat]_0 = 16.7\ mmol{\cdot}L^{-1}$; $[EO]_0/[cat]_0 = 400$).

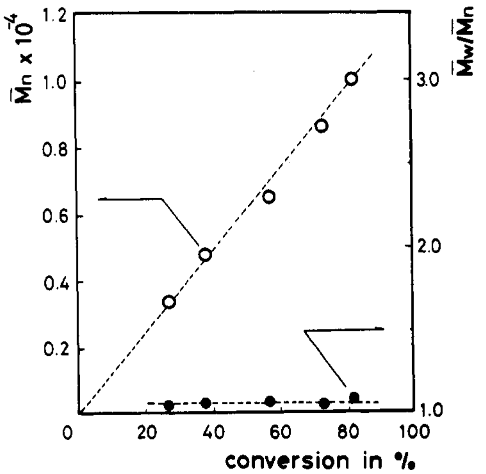


Figure 2. Polymerization of ethylene oxide (EO) with the $TPPH_2$-Et_2AlCl system. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and conversion ($[EO]_0/[cat]_0 = 400$).

(polymerization catalyst) is denoted as the "$TPPH_2$-Et_2AlCl system".

Polymerization of Ethylene Oxide. The time-conversion curve for the polymerization of ethylene oxide with the $TPPH_2$-Et_2AlCl system at room temperature is shown in Figure 1, where the initial mole ratio of monomer to catalyst was 400 ($[EO]_0/[cat]_0 = 400$). The polymerization proceeded with heat evolution and gave the polymer in good yield within a short time.

From GPC analysis, the molecular weight distribution of the polymer formed, as indicated by the ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$), was very narrow throughout the polymerization. Furthermore, a linear increase of number-average molecular weight with conversion was observed in this system, as shown in Figure 2.

The number of polymer molecules (N) calculated by eq 1, where (monomer) is the monomer in moles, conv is the

$$N = (\text{monomer}) \times \frac{\text{conv}}{100} \times \frac{1}{\bar{M}_n(\text{GPC})} \qquad (1)$$

conversion in percent, and $\bar{M}_n$(GPC) is the number-average molecular weight of the polymer estimated by GPC, is in fair agreement with the number of catalyst groups, indicating the very high efficiency of this catalyst.

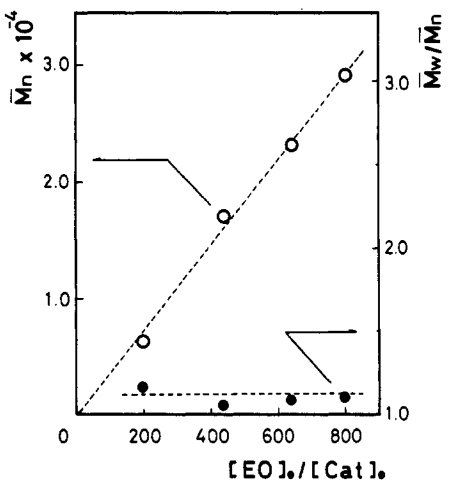


Figure 3. Polymerization of ethylene oxide (EO) with the $TPPH_2$-Et_2AlCl system. Dependence of $\bar{M}_n$ (○) and $\bar{M}_w/\bar{M}_n$ (●) upon $[EO]_0/[cat]_0$ (conversion ~100%).

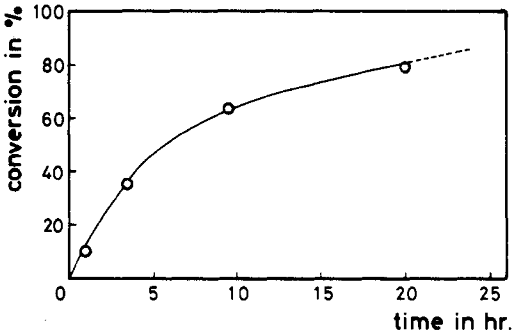


Figure 4. Polymerization of 1,2-butene oxide (1-BO) with the $TPPH_2$-Et_2AlCl system (room temperature; solvent, CH_2Cl_2; $[cat]_0 = 27.9\ mmol{\cdot}L^{-1}$; $[1\text{-}BO]_0/[cat]_0 = 300$).

The molecular weight of the polymer may be controlled by the mole ratio of monomer to catalyst. As shown in Figure 3, the number-average molecular weight of polymer obtained at 100% conversion increased linearly with the initial monomer-to-catalyst ratio, retaining the narrow molecular weight distribution.

Polymerization of 1,2-Butene Oxide. 1,2-Butene oxide also polymerized smoothly at room temperature with a lower rate than propylene oxide or ethylene oxide (Figure 4).

The number-average molecular weight increased linearly with conversion (Figure 5), while at each conversion, the molecular weight distribution of the polymer was very narrow.

In this case as well, the number of polymer molecules is calculated to be almost equal to the number of catalyst groups throughout the polymerization, as shown in Figure 6. Since a very low efficiency for catalyst has been reported in the polymerization of epoxide using other organometallic systems, such as the $ZnEt_2$-H_2O system, it is particularly noteworthy that the $TPPH_2$-Et_2AlCl system has a very high catalyst efficiency.

Block Copolymerization of Epoxide Catalyzed by the $TPPH_2$-Et_2AlCl System. The results mentioned above strongly indicate the living nature of the $TPPH_2$-Et_2AlCl-catalyzed polymerization of ethylene oxide, propylene oxide,[2] and 1,2-butene oxide. The living nature of the polymerization suggests the possibility of synthesizing

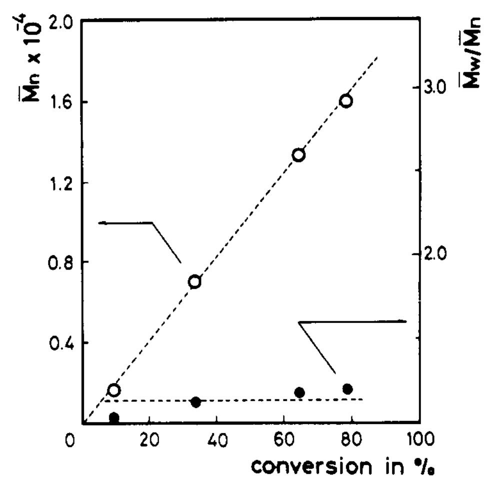


Figure 5. Polymerization of 1,2-butene oxide (1-BO) with the TPPH$_2$-Et$_2$AlCl system. Relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and conversion ([1-BO]$_0$/[cat]$_0$ = 300).

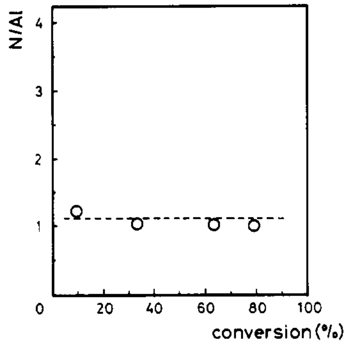


Figure 6. Polymerization of 1,2-butene oxide (1-BO) with the TPPH$_2$-Et$_2$AlCl system. Relationship between (number of polymer molecules)/(number of aluminum atoms) (N/Al) and conversion ([cat]$_0$ = 27.9 mmol·L^{-1}; [1-BO]$_0$/[cat]$_0$ = 300).

Table I
Prepolymers of 1,2-Butene Oxide (1-BO)[a] for the Block Copolymerization with Propylene Oxide

no.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	4200	1.21
2	4300	1.09
3	4600	1.17

[a] Polymerization was carried out in CH_2Cl_2 at room temperature; [1-BO]$_0$/[cat]$_0$ = 60; conversion 100%; [cat]$_0$ = 64.1 mmol·L^{-1}.

block copolymers from these epoxides. In this paper we report the synthesis of 1,2-butene oxide–propylene oxide and 1,2-butene oxide–ethylene oxide binary block copolymers and 1,2-butene oxide–propylene oxide–ethylene oxide ternary block copolymer.

The synthesis of propylene oxide–ethylene oxide block copolymer was briefly described in a previous communication.[3]

1,2-Butene Oxide–Propylene Oxide Block Copolymerization. As the first stage, the living polymer of 1,2-butene oxide was prepared by polymerization with the TPPH$_2$-Et$_2$AlCl system at 100% conversion, where the molar amount of monomer was 60 times that of the catalyst. Table I shows the number-average molecular weight ($\bar{M}_n$) and the ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$) of the prepolymers of 1,2-butene oxide thus obtained, employed for the block copolymerization. To this living prepolymer was added propylene oxide for the second stage of polymerization.

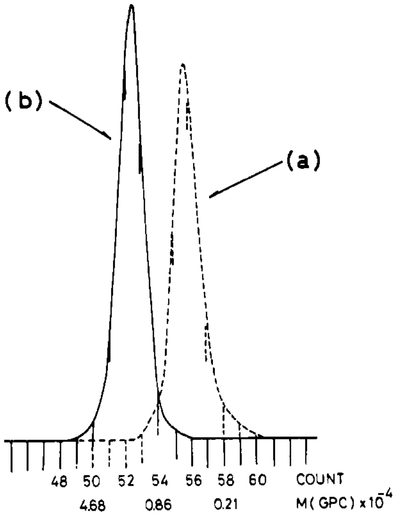


Figure 7. GPC chromatograms of a 1,2-butene oxide–propylene oxide block copolymer and of the corresponding prepolymer of 1,2-butene oxide: (a) prepolymer (no. 2), $\bar{M}_n$ = 4300, $\bar{M}_w/\bar{M}_n$ = 1.09; (b) block copolymer, $\bar{M}_n$ = 16000, $\bar{M}_w/\bar{M}_n$ = 1.19.

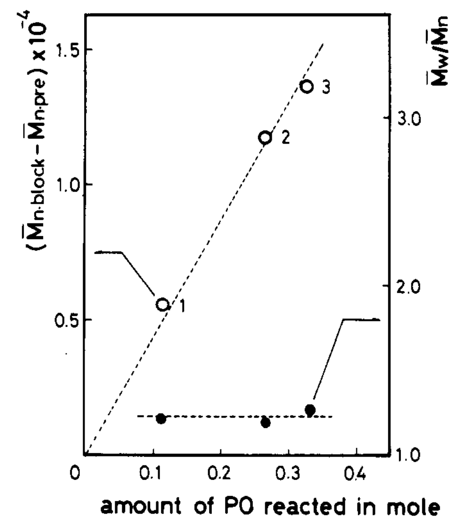


Figure 8. Relationship between the molecular weight of the oxy(methylethylene) blocks in 1,2-butene oxide–propylene oxide block copolymers and the amount of reacted propylene oxide (PO). The number on each plot represents the number of the used prepolymer (Table I).

Figure 7 shows typical GPC chromatogram patterns of the polymer obtained after the second stage of polymerization (block copolymerization) and that of the corresponding prepolymer. The GPC chromatogram of the polymer obtained after the second stage of polymerization clearly shifted toward the higher molecular weight region, retaining the narrow molecular weight distribution. Furthermore, neither the peak corresponding to the prepolymer of 1,2-butene oxide nor that corresponding to the homopolymer of propylene oxide was observed. Thus, the polymerization of propylene oxide occurred from the propagating end of poly(1,2-butene oxide) to produce 1,2-butene oxide–propylene oxide block copolymer with high blocking efficiency (almost 100%). This result conforms to the "living" behavior of the homopolymerization of 1,2-butene oxide described above.

In order to control the length of the blocked chain, various molar amounts of propylene oxide were added in the second stage of polymerization. As illustrated in Figure 8, the molecular weight of the blocked chain, calculated by subtracting the molecular weight of the prepolymer used from that of the block copolymer, increased linearly

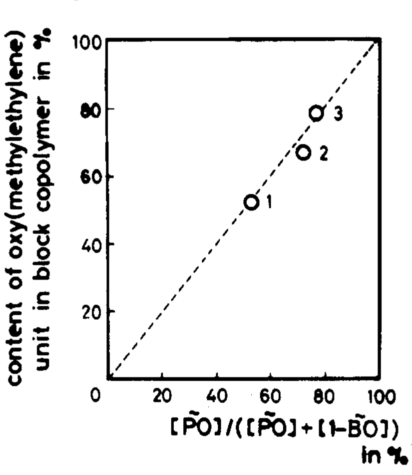


Figure 9. Relationship between the mole fraction of reacted propylene oxide (PO) and the composition of the 1,2-butene oxide (1-BO)–propylene oxide block copolymers ($[1\text{-}\tilde{\mathrm{B}}\mathrm{O}]$ = amount of 1,2-butene oxide prepolymer used (in moles with respect to repeating units); $[\tilde{\mathrm{P}}\mathrm{O}]$ = amount of propylene oxide reacted (in moles)).

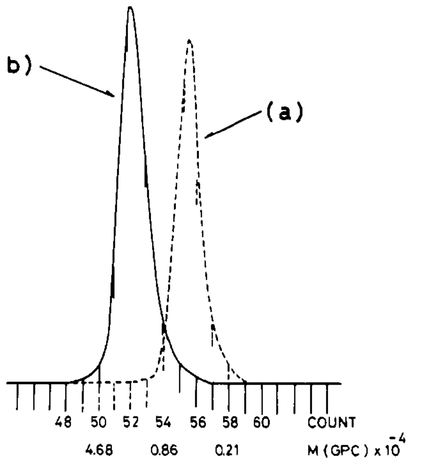


Figure 10. GPC chromatograms of a 1,2-butene oxide–ethylene oxide block copolymer and of the corresponding prepolymer of 1,2-butene oxide: (a) prepolymer (no. 5), $\bar{M}_n$ = 4000, $\bar{M}_w/\bar{M}_n$ = 1.10; (b) block copolymer, $\bar{M}_n$ = 17 000, $\bar{M}_w/\bar{M}_n$ = 1.17.

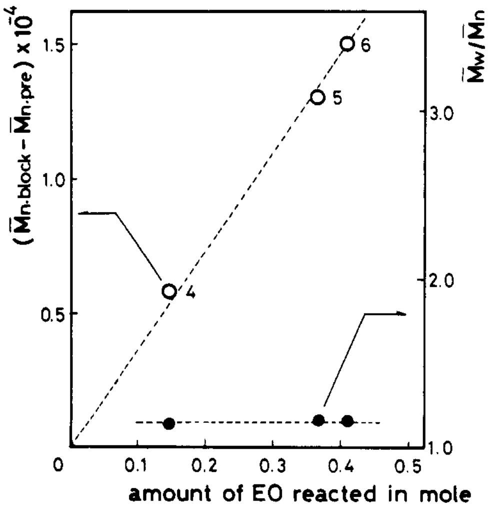


Figure 11. Relationship between the molecular weight of the oxyethylene blocks in 1,2-butene oxide–ethylene oxide block copolymers and the amount of reacted ethylene oxide (EO). The number on each plot represents the number of the used prepolymer (Table II).

with the amount of propylene oxide reacted, without broadening the GPC chromatogram.

Table II
Prepolymers of 1,2-Butene Oxide (1-BO)[a] for the Block Copolymerization with Ethylene Oxide

no.	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
4	4100	1.10
5	4000	1.10
6	4000	1.25

[a] Polymerization was carried out in CH_2Cl_2 at room temperature; $[1\text{-BO}]_0/[\text{cat}]_0$ = 60; conversion 100%; $[\text{cat}]_0$ = 64.1 mmol·L^{-1}.

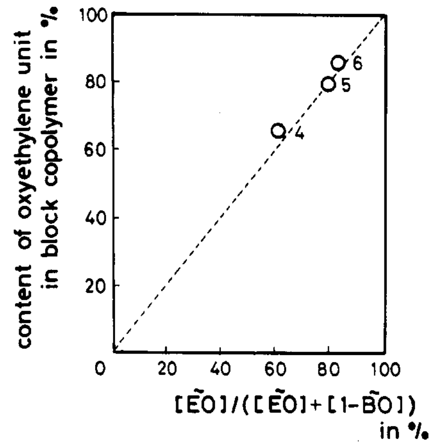


Figure 12. Relationship between the mole fraction of reacted ethylene oxide (EO) and the composition of the 1,2-butene oxide (1-BO)–ethylene oxide block copolymers ($[1\text{-}\tilde{\mathrm{B}}\mathrm{O}]$ = amount of 1,2-butene oxide prepolymer used (in moles with respect to repeating units); $[\tilde{\mathrm{E}}\mathrm{O}]$ = amount of ethylene oxide reacted (in moles)).

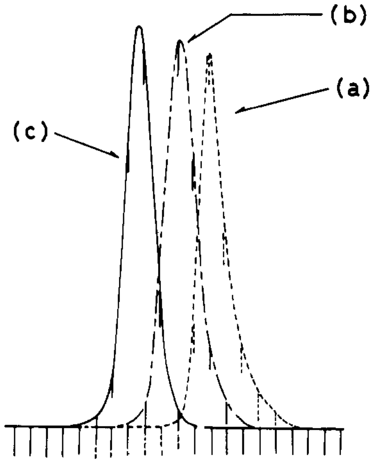


Figure 13. GPC profile of the ternary block copolymerization (1-BO–PO–EO system): (a) prepolymer of 1,2-butene oxide (no. 1), $\bar{M}_n$ = 4200, $\bar{M}_w/\bar{M}_n$ = 1.21; (b) 1,2-butene oxide–propylene oxide diblock copolymer, $\bar{M}_n$ = 9800, $\bar{M}_w/\bar{M}_n$ = 1.22; (c) 1,2-butene oxide–propylene oxide–ethylene oxide triblock copolymer, $\bar{M}_n$ = 32 000, $\bar{M}_w/\bar{M}_n$ = 1.16.

A proportional relation was observed between the composition (NMR) and mole ratio of the two epoxides reacted, as shown in Figure 9.

1,2-Butene Oxide–Ethylene Oxide Block Copolymerization. Since it is very interesting to synthesize block copolymer having blocks with different crystallinities and solubilities, the block copolymerization of ethylene oxide with the living poly(1,2-butene oxide) prepared by the $TPPH_2$–Et_2AlCl catalyst system was investigated. Living poly(1,2-butene oxides) employed as the prepolymer for the block copolymerization with ethylene oxide had $\bar{M}_n$

and $\bar{M}_w/\bar{M}_n$ values as shown in Table II.

The GPC curves exemplified in Figure 10 clearly indicate an increase in the molecular weight of the block copolymer relative to that of the prepolymer of 1,2-butene oxide, retaining the narrow molecular weight distribution, and the absence of either the remaining prepolymer or the homopolymer of ethylene oxide. Thus, ideal block copolymerization with very high blocking efficiency was also achieved in this system. This block copolymer is characterized by having a crystalline and water-soluble block (oxyethylene chain) and a noncrystalline and water-insoluble block [oxy(ethylethylene) chain].

The length of the oxyethylene chain blocked and the composition of the block copolymer could be controlled without broadening the molecular weight distribution by changing the amount of ethylene oxide reacted in the second stage, as shown in Figures 11 and 12.

1,2-Butene Oxide–Propylene Oxide–Ethylene Oxide Block Copolymerization. Since the successful binary block copolymerization described above suggests the possibility of multiplying the sequences of blocked chain with controlled molecular weight, the binary block copolymer of 1,2-butene oxide–propylene oxide was used as the prepolymer in order to carry out a ternary block copolymerization by blocking ethylene oxide from this propagating end. As mentioned above, the prepolymer, 1,2-butene oxide–propylene oxide block copolymer, shows a unimodal sharp elution curve in the GPC (Figure 13b). To this system was introduced ethylene oxide and the third stage of polymerization was carried out. This polymerization proceeded with heat evolution and the average molecular weight of the final product showed a sharp and unimodal peak (Figure 13c), indicating that the living nature of the first stage of polymerization of 1,2-butene oxide was followed by subsequent block copolymerizations.

The ^{1}H NMR analysis of the final product also confirmed the formation of a ternary block copolymer, the contents of oxy(ethylethylene), oxy(methylethylene), and oxyethylene units being 16, 17, and 67%, respectively.

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Living Polymerization of Epoxide Catalyzed by the Porphyrin–Et_2AlCl System. Structure of the Living End

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ABSTRACT: Systems obtained from diethylaluminum chloride and 5,10,15,20-tetraphenylporphine, its para-substituted derivatives, or etioporphyrin I were demonstrated to polymerize propylene oxide to form "living" polymers having narrow molecular weight distributions. By detailed ^{13}C and ^{1}H NMR investigations, the structure of the propagating end of the living polymer of propylene oxide or ethylene oxide was concluded to be a (porphinato)aluminum alkoxide.

Introduction

Living polymerization is very important for the synthesis of polymers and block copolymers having narrow molecular weight distributions with well-defined chain lengths. Recently, we found that a reaction mixture of 5,10,15,20-tetraphenylporphine ($TPPH_2$) with diethylaluminum chloride (Et_2AlCl) exhibits a high catalytic activity for the polymerizations of propylene oxide, ethylene oxide, and 1,2-butene oxide to form the corresponding "living" polymers.[1,2] Furthermore, the successful block copolymerizations of these epoxides with very high blocking efficiency (almost 100%) were achieved by taking advantage of the living nature of the polymerization.[2,3] These characteristics could not be achieved by using Et_2AlCl alone as the catalyst.

In this paper we report the polymerization of propylene oxide catalyzed by the systems from Et_2AlCl and various porphyrins ($TPPH_2$, *p*-Cl$TPPH_2$, *p*-OCH_3TPPH_2, and etioporphyrin I). For the $TPPH_2$–Et_2AlCl system, the polymerization mechanism is discussed in detail, based mainly on the NMR analysis of the structure of the "living" oligomer.

Experimental Section

Materials. $TPPH_2$, *p*-Cl$TPPH_2$, and *p*-OCH_3TPPH_2 were synthesized from pyrrole and the corresponding benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[4] Etioporphyrin I was synthesized from *tert*-butyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate as reported by Barnett and Smith.[5] Propylene oxide was purified by refluxing over a mixture of potassium hydroxide and calcium hydride and then fractionally distilled twice under a nitrogen atmosphere. Ethylene oxide, stirred with a mixture of potassium hydroxide and calcium hydride at room temperature, was degassed to remove air and then collected in a trap cooled in a liquid nitrogen bath. Dichloromethane, washed with concentrated sulfuric acid and neutralized with sodium bicarbonate, was dried over calcium chloride and then fractionally distilled over calcium hydride under a nitrogen atmosphere. Et_2AlCl was purified by fractional distillation under reduced pressure under a nitrogen atmosphere. Propylene chlorohydrin was obtained from Tokyo Kasei Kogyo Co., Ltd. Poly(propylene glycol) ($\bar{M}_n$ = 300) was obtained from Lion Fat & Oil Co., Ltd.

Measurements. The ^{1}H NMR spectrum of the reaction mixture (living oligomer) was measured in dichloromethane in a sealed tube under nitrogen, using a JEOL Type 4H-A spectrometer operating at 100 MHz. ^{13}C NMR measurement of the reaction mixture (living oligomer) was performed in deuterated dichloromethane in a sealed tube under nitrogen, using a JEOL PFT-100 spectrometer equipped with a JEOL data terminal, Model SILENT 700 ASR. The spectra were recorded at 25.03 MHz with 10-μs pulse widths applied at 1.5-s intervals. Complete proton decoupling ($^{13}C\{^1H\}$ NMR) and single-frequency off-resonance decoupling were employed for the ^{13}C NMR measurement of the living oligomeric propylene oxide prepared by the

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