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*-$ClTPPH_2$, *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*-$ClTPPH_2$, 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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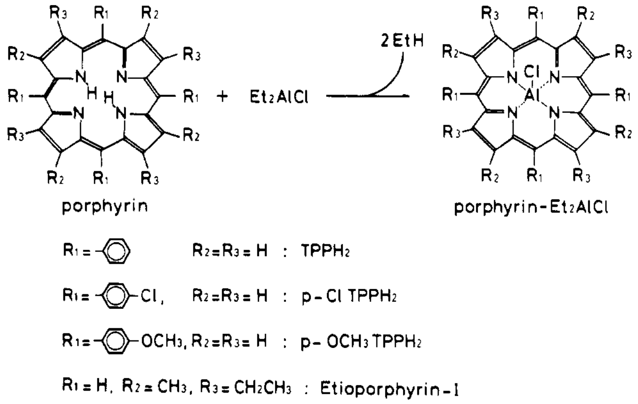
Scheme I



TPPH$_2$–Et$_2$AlCl system. For the assignment of each signal, the spectra of 1-chloro-2-propanol, 2-chloro-1-propanol, and poly(propylene glycol) ($\bar{M}_n$ = 300) were employed. Gel permeation chromatography (GPC) measurement 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·min^{-1}. The column set consisted of four columns (60 cm) with pore sizes 7000–3000 (two), 3000 (one), and 2000 (one) Å. 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 relatively high molecular weight region. Standard poly(propylene glycols) were obtained from Lion Fat & Oil Co., Ltd.: $\bar{M}_n$ = 1000 and 2000 ($\bar{M}_w/\bar{M}_n \simeq 1$). 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). On the basis of this molecular weight calibration curve, the number-average and weight-average molecular weights were calculated by standard procedures, using the gel permeation chromatogram.

Procedures. Preparation of Catalyst. The reaction of porphyrin with Et$_2$AlCl was carried out in a Pyrex flask fitted with a three-way cock. The flask containing the porphyrin (1 mmol) was purged with dry nitrogen, and dichloromethane (20 mL) was added to dissolve the porphyrin. To this solution was added Et$_2$AlCl (1.2 mmol) in 20% excess to the porphyrin. After about 4 h, the volatile materials were removed under reduced pressure from the above reaction mixture to leave crystalline materials, which were used as the polymerization catalyst, denoted as the "porphyrin–Et$_2$AlCl system".

Polymerization. Dichloromethane (20 mL) was added to the flask containing the catalyst. To this catalyst solution, cooled with a liquid nitrogen bath, was introduced purified propylene oxide by distillation (trap-to-trap method). The initial mole ratio of propylene oxide to catalyst was 200. Polymerization was carried out under a nitrogen atmosphere at room temperature. After a definite time, a large amount of methanol was added to the polymerization system 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 GPC analysis, a part of the obtained polymer was dissolved in tetrahydrofuran and the insoluble part (catalyst residue) was filtered off from this solution by a Teflon filter (pore size 0.45 μm).

Oligomerization. To the catalyst solution was added propylene oxide and/or ethylene oxide with a monomer to catalyst ratio of 2–7, and the mixture was polymerized for 1 week at room temperature. Then the volatile materials were removed from the reaction mixture under reduced pressure, and a prescribed amount of dichloromethane or deuterated dichloromethane was added to dissolve the "living" oligomer for NMR analysis.

Results and Discussion

The reaction between the porphyrins and Et$_2$AlCl is most likely to proceed as shown in Scheme I to form the corresponding (porphinato)aluminum chloride, similar to the reaction of TPPH$_2$ with Et$_2$AlCl.[1]

Table I
Polymerization of Propylene Oxide with Various Porphyrin-Et$_2$AlCl Systems[a]

porphyrin	$[PO]_0$/$[cat]_0$	time, days	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
TPPH$_2$	200	6	100	10200	1.13
p-ClTPPH$_2$	200	3	90	8400	1.15
p-OCH$_3$TPPH$_2$	200	3	93	9300	1.13
etioporphyrin I	200	9	30	2400	1.04
	200	8	43	3500	1.06

[a] Polymerization was carried out in CH$_2$Cl$_2$ at room temperature. $[cat]_0$ = 29.4 mmol·L^{-1}.

Polymerization of Propylene Oxide with the Porphyrin-Et$_2$AlCl Systems. As shown in Table I, systems from Et$_2$AlCl and TPPH$_2$, *p*-ClTPPH$_2$, or *p*-OCH$_3$TPPH$_2$ exhibited similar catalytic activity for the polymerization of propylene oxide. On the other hand, a lower catalytic activity was observed in the case with etioporphyrin I as the porphyrin component. The molecular weight distributions of the polymers obtained by these catalyst systems were all narrow, as indicated by the ratio of weight-average molecular weight to number-average molecular weight ($\bar{M}_w/\bar{M}_n$) (Table I). Thus the polymerizations with these catalyst systems are considered to be of a living type, as demonstrated in the polymerization with the TPPH$_2$–Et$_2$AlCl system.[1,3] In accordance with this, the number of polymer molecules, calculated on the basis of the amount of feed monomer, conversion, and $\bar{M}_n$(GPC), is in fair agreement with the number of catalyst groups.

Structure of the Living Propagating End of Oligomeric Propylene Oxide. In connection with the living nature of the polymerization, it is of particular interest to reveal the structure of the propagating end formed in the polymerization of epoxide with the porphyrin–Et$_2$AlCl system. As we have reported in the previous paper,[1] the equimolar reaction of propylene oxide with the TPPH$_2$–Et$_2$AlCl system gives 1-chloro-2-propanol as the main product. In accordance with this result, the oligomeric product obtained at a monomer to catalyst ratio of 8 has a structure with a chlorine attached to a terminal methylene group and a terminal hydroxyl group attached to a methine group. In order to obtain direct information on the structure of the propagating end, "living" oligomeric propylene oxide was subjected to NMR analysis. In the $^{13}C\{^1H\}$ NMR spectrum of the living oligomeric propylene oxide prepared by the TPPH$_2$–Et$_2$AlCl system illustrated in Figure 1, signals A, B, and E are assigned to methine, methylene, and methyl groups of the oligomer chain, respectively. Signals C and D are considered to be due to terminal OCH and CH$_2$Cl groups, respectively. Upon treatment of the living oligomeric propylene oxide with methanolic hydrochloric acid, the signal due to the terminal methine carbon appeared at a lower magnetic field (Figure 2a, C′, 67 ppm) than that of the living oligomer (Figure 1, C, 60 ppm), while no change was observed in the other signals. The shift of the signal due to the terminal methine carbon on treatment with acid suggests that an aluminum alkoxide, $-CH_2CH(CH_3)OAl$, is the living propagating species in the polymerization of propylene oxide with the TPPH$_2$–Et$_2$AlCl system.

More detailed information was obtained from the ^{1}H NMR spectrum of the living oligomeric propylene oxide prepared with the TPPH$_2$–Et$_2$AlCl system (Figure 3). The signals a, b, and c observed at 9.1, 8.2, and 7.8 ppm are assigned to the resonances due to the porphine protons and the phenyl protons, respectively. Signal d, observed at 3.4 ppm, is assigned to the resonances of the methine and methylene protons of the in-chain oxymethylethylene unit.

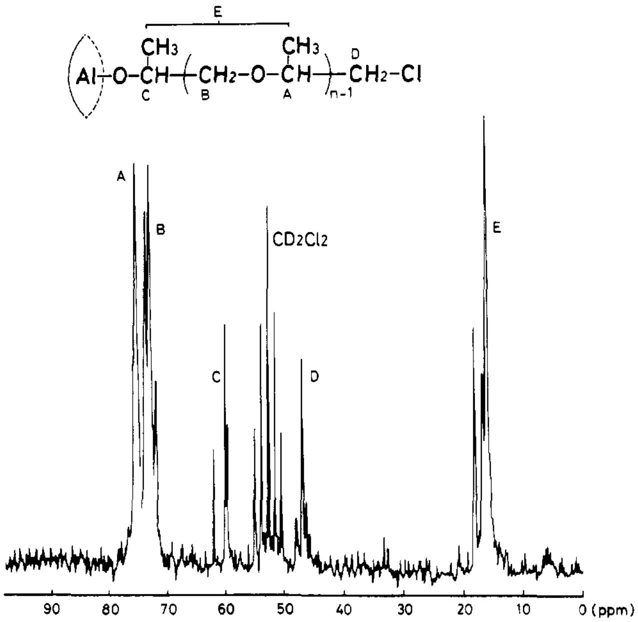


Figure 1. $^{13}C\{^1H\}$ NMR spectrum of living oligomeric propylene oxide (PO) prepared by the $TPPH_2$–Et_2AlCl system.

Table II
^1H NMR Intensity Data of Living Oligomeric Propylene Oxide (PO) Prepared by the $TPPH_2$-Et_2AlCl System

$[PO]_0/[cat]_0$		2	5
$\bar{P}_n$[a]		2.3	5.2
porphyrin a[b]:b[b]:c[b]	obsd	8:8:12	8:7.3:12
	calcd	8:8:12	8:8:12
porphyrin:terminal CH_3 a[b]:f[b]	obsd	8:2.9	8:3.4
	calcd	8:3	8:3

[a] $\bar{P}_n$ is the degree of polymerization calculated by the intensity ratio of signal e to signal f. [b] The symbols a, b, c, and f represent the signals illustrated in Figure 3.

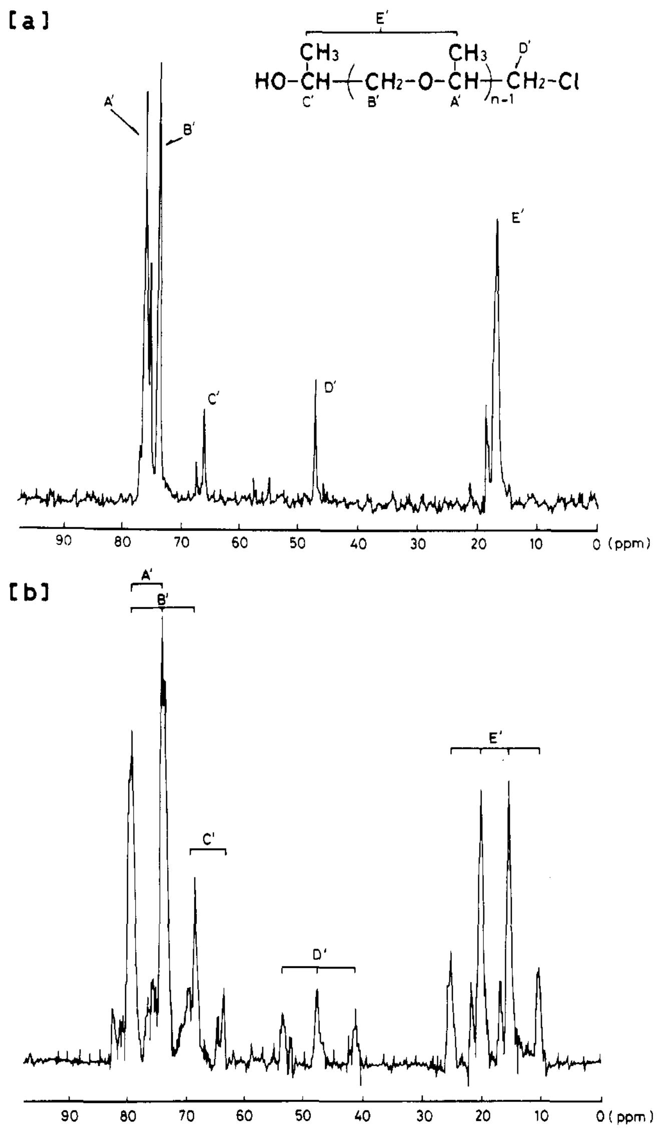


Figure 2. ^{13}C NMR spectra of oligomeric propylene oxide (PO) prepared by the $TPPH_2$–Et_2AlCl system treated with methanolic hydrochloric acid: (a) $^{13}C\{^1H\}$ NMR spectrum; (b) single-frequency off-resonance decoupled NMR spectrum.

Figure 3. ^1H NMR spectrum of living oligomeric propylene oxide (PO) prepared by the $TPPH_2$–Et_2AlCl system ($[PO]_0/[cat]_0$ = 2).

The signal due to the methyl proton of the in-chain oxymethylethylene unit appeared at 1.1 ppm (e). Furthermore, the signal due to the methyl proton (f) of the terminal group, influenced by the large magnetic effect of the prophyrin, was observed at unusually high magnetic fields (−2.0 ppm). From the intensity ratio of the terminal methyl proton (f, −2.0 ppm, 3 H) to the pyrrole proton of the porphyrin (9.1 ppm, 8 H), an equivalent amount of this terminal methyl group was calculated to be formed with respect to tetraphenylporphine, independent of the initial monomer to catalyst ratio (Table II). On the other hand, the number-average molecular weight of this "living" oligomeric propylene oxide calculated by the intensity ratio of the in-chain methyl proton (e, 1.1 ppm, 3H) to the terminal one (f) is in good agreement with the initial monomer to catalyst ratio. Therefore, the structure of the growing end is considered to be a (tetraphenylporphinato)aluminum alkoxide, $-CH_2CH(CH_3)OAlTPP$.

Structure of the Living Propagating End of Oligomeric Ethylene Oxide. In the ^1H NMR spectrum of the living oligomeric ethylene oxide prepared with the $TPPH_2$–Et_2AlCl systems illustrated in Figure 4, a few triplet signals due to methylene protons, besides the signal due to the usual resonance of the methylene proton of the oxyethylene chain (k, 3.4 ppm), appeared at higher magnetic field (g, h, i, and j at −1.4, −0.1, 1.9, and 2.6 ppm, respectively), probably because of the magnetic influence of the porphyrin ring. In this case as well, a quantitative relation between the terminal methylene group (g, −1.4 ppm, 2 H) and the porphyrin confirmed the structure of the living propagating end to be a (tetraphenylporphinato)aluminum alkoxide, $-CH_2CH_2OAlTPP$.

Block Copolymerization of Ethylene Oxide with the Living Poly(propylene oxide). In a previous paper,[3] we reported the synthesis of propylene oxide–ethylene oxide

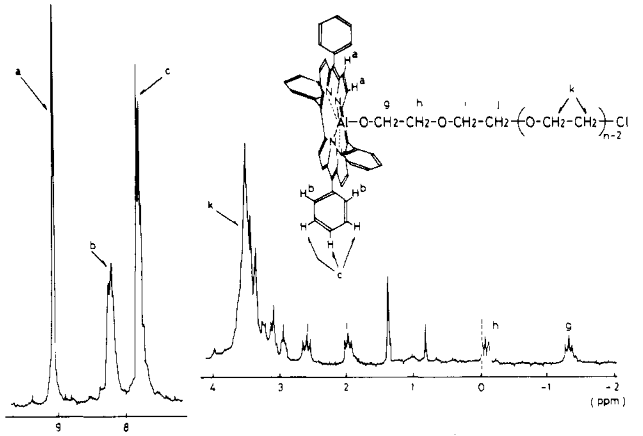


Figure 4. ^{1}H NMR spectrum of living oligomeric ethylene oxide (EO) prepared by the $TPPH_2$–Et_2AlCl system ($[EO]_0/[cat]_0$ = 7).

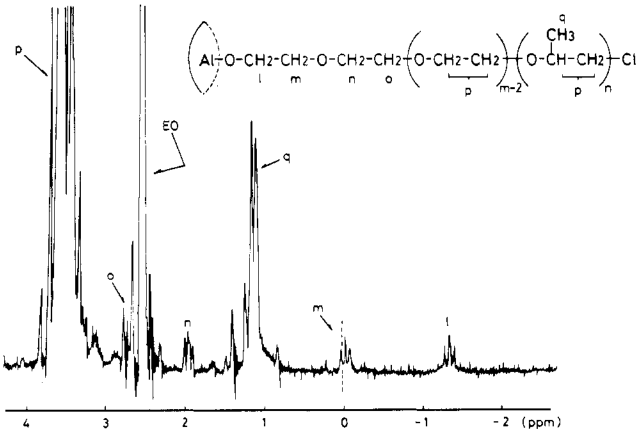
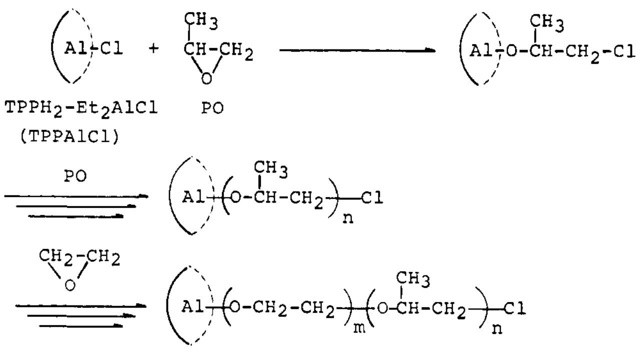


Figure 5. ^{1}H NMR spectrum of the polymerization system of ethylene oxide (EO) with living oligomeric propylene oxide.

block copolymer with controlled molecular weight by the polymerization of ethylene oxide with the living poly(propylene oxide) prepared by the $TPPH_2$–Et_2AlCl system. In order to obtain direct evidence for the transformation of the growing chain end in the block copolymerization, ethylene oxide was added to the living oligomeric propylene oxide (Figure 3), and the block copolymerization was investigated by ^{1}H NMR analysis (Figure 5). The signal due to the terminal methyl group observed at −2.0 ppm in Figure 3 (f) disappeared completely in Figure 5. Instead signals due to the terminal and other methylene protons of the oxyethylene unit (l, m, n, and o) were observed at the same position as those observed in the spectrum of living oligomeric ethylene oxide, shown in Figure 4 (g, h, i, and j). This finding clearly indicates that the insertion of ethylene oxide into the growing end of living oligomeric propylene oxide (block copolymerization) occurred with a blocking efficiency of 100%, as reported before,[3] to transform the end structure $-CH_2CH(CH_3)$-OAlTPP to $-CH_2CH_2OAlTPP$.

Scheme II



Mechanism. Together with the fact that the main product of the equimolar reaction between propylene oxide and the $TPPH_2$–Et_2AlCl system is 1-chloro-2-propanol,[1] the polymerization of propylene oxide is considered to proceed according to Scheme II. Propylene oxide reacts with the $TPPH_2$–Et_2AlCl system, probably TPPAlCl, to form a (tetraphenylporphinato)aluminum alkoxide, the living propagating species, where propylene oxide reacts successively to form a high molecular weight polymer, with quantitative efficiency of the $TPPH_2$–Et_2AlCl system. The addition of ethylene oxide to the living poly(propylene oxide) converts the living end to that of ethylene oxide quantitatively.

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