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# From Living to “Immortal” Polymerization

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# FROM LIVING TO "IMMORTAL" POLYMERIZATION

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## ABSTRACT

Aluminum porphyrin is an excellent initiator for the living polymerizations of a wide variety of monomers such as epoxide, β-lactone, δ-lactone, ϵ-lactone, and lactide, and also for the alternating copolymerization of epoxide and cyclic acid anhydride or carbon dioxide, to give polymers and copolymers with narrow molecular weight distribution. Aluminum porphyrin was recently found to initiate also the living polymerization of methacrylic ester. In the polymerizations of epoxides and lactones initiated with aluminum porphyrin in the presence of an appropriate protic compound, polymers with narrow molecular weight can be obtained with the number of the polymer molecules more than those of the initiator. This fact demonstrates the "immortal" nature of the polymerization due to unusual reactivities of aluminum prophyrin.

## INTRODUCTION

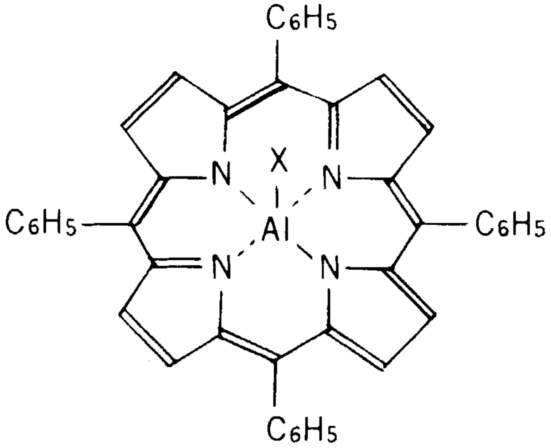
Control of molecular weight in polymer synthesis is of primary importance for the molecular design of polymeric materials. Although this has been accomplished by living polymerization of some vinyl and cyclic monomers, a particular type of initiator has been successfully applied only to a limited type of monomers. We have recently found that aluminum porphyrin (1) is an excellent initiator for the living polymerization of a variety of monomers such as epoxide [1], β-lactone [2], δ-lactone [3], ϵ-lactone [4], and lactide [5], and also for the alternating copolymerization of epoxide and cyclic acid anhydride [6] or carbon dioxide [7], to give polymers and copolymers with narrow molecular weight distributions.

In living polymerization, to give the product with narrow molecular weight distribution, uniform initiation and propagation with respect to all growing molecules are required, together with the absence of termination and chain-transfer reactions. As a result, the number of polymer molecules is the same as or less than that of the initiator molecule.

In contrast, "immortal" polymerization as described in the present article can afford polymers with narrow molecular weight distributions, with the number of the polymer molecules more than that of the initiator. This could be accomplished in the polymerization of epoxide [8]-[10] and some cyclic esters [3, 4] initiated by aluminum porphyrin in the presence of an appropriate protic compound. The present paper deals with the living and "immortal" polymerizations of some cyclic and vinyl monomers initiated with aluminum porphyrin.

## PREPARATION OF ALUMINUM PORPHYRIN

Representatives of aluminum prophyrins used as the initiator are (tetraphenylporphinato)aluminum chloride [(TPP)AlCl: Structure 1, X = Cl], -ethyl [(TPP)AlEt], -alkoxide [(TPP)AlOR], and -carboxylate [(TPP)$AlO_2CR$].



STRUCTURE 1.

(TPP)AlCl is prepared by the equimolar reaction between tetraphenylporphine [(TPP)$H_2$] and diethylaluminum chloride ($Et_2AlCl$). The reaction of (TPP)$H_2$ with triethylaluminum gives (TPP)AlEt, which reacts with protic compounds, such as alcohol, phenol, or carboxylic acid, to afford various (TPP)AlX (X = OR, OAr, $O_2CR$, etc.).

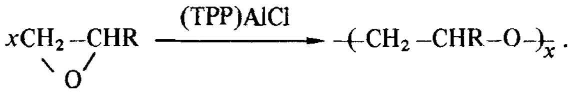
$$(\mathrm{TPP})\mathrm{H_2} + \mathrm{Et_2AlCl} \xrightarrow{\text{-EtH}} (\mathrm{TPP})\mathrm{AlCl}, \tag{1}$$

$$(\mathrm{TPP})\mathrm{H_2} + \mathrm{Et_3Al} \xrightarrow{\text{-EtH}} (\mathrm{TPP})\mathrm{AlEt}, \tag{2}$$

$$(\mathrm{TPP})\mathrm{AlEt} + \mathrm{XH} \xrightarrow{\text{-EtH}} (\mathrm{TPP})\mathrm{AlX}. \tag{3}$$

## LIVING POLYMERIZATION OF EPOXIDE

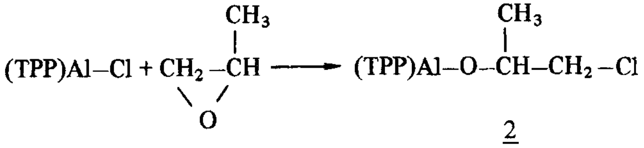
Living polymerization of epoxide with aluminum porphyrin can be conveniently carried out in an ordinary flask, differently from the living polymerization of styrene with an organoalkali metal compound, which usually requires an all-sealed glass apparatus. In the polymerization of ethylene oxide or propylene oxide with (TPP)AlCl in methylene chloride at room temperature, the reaction proceeds with heat evolution and is complete in a few hours. The reaction without solvent proceeds much more rapidly, and the reaction mixture becomes very viscous to make the stirring of the mixture impossible. Even under such conditions, the molecular weight distribution of the polymer is very narrow ($\bar{M}_w/\bar{M}_n$ = 1.05-1.1), and the molecular weight increases linearly with consumption of the monomer. By changing the ratio of epoxide to initiator, polyether with the desired molecular weight can be synthesized. Poly(propylene oxide) with molecular weight up to 50 000 has been synthesized so far.



$$x\,\mathrm{CH_2{-}CHR}\ (\text{epoxide, O}) \xrightarrow{(\mathrm{TPP})\mathrm{AlCl}} \mathrm{-\!\!(CH_2{-}CHR{-}O)\!\!-}_x\,. \tag{4}$$

Based on the molecular weight ($\bar{M}_n$) of the polymer and the conversion, the number of the polymer molecules ($N$) can be calculated. The ratio of $N$ to the number of the initiator molecules (Al) is close to unity throughout the reaction. Thus, every molecule of (TPP)AlCl can initiate the polymerization of epoxide, and all molecules of the polymer formed remain alive, without any side reactions.

Detailed studies revealed that the polymerization of epoxide is initiated by the reaction of (TPP)AlCl with epoxide to form a (porphinato)aluminum alkoxide, followed by the repeated reaction of the alkoxide with epoxide [11-14]:



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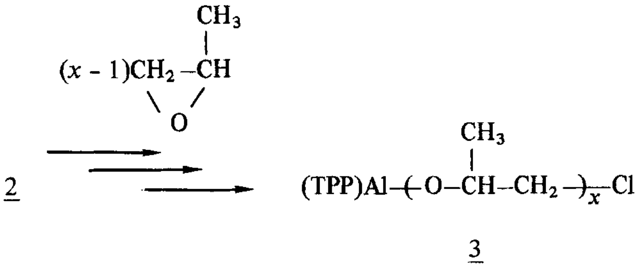


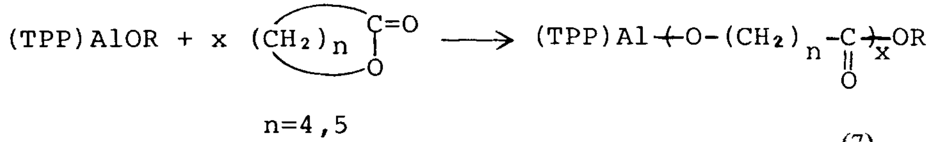
(6)

NMR spectral investigation of the reaction mixture has been particularly useful for the elucidation of the structure of the growing species since the nuclei in proximity above the porphyrin ring are strongly shielded by the ring current and exhibit the corresponding signals at unusually high magnetic field.

## LIVING POLYMERIZATION OF LACTONES

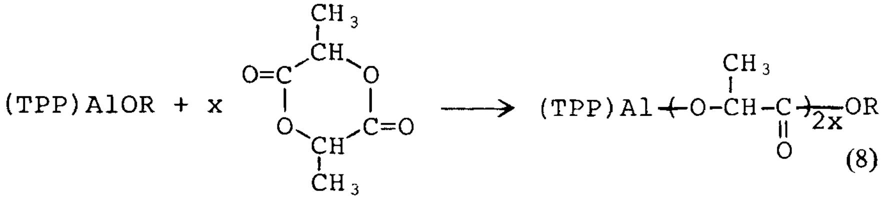
(Porphinato)aluminum alkoxide [(TPP)AlOR: Structure 1, X = OR] can initiate polymerization of δ-lactone (6-membered) and ϵ-lactone (7-membered). The reaction is slower than epoxide polymerization, but proceeds at a moderate temperature such as room temperature or 50°C. The polyesters formed have narrow molecular weight distribution, the degree of polymerization increases linearly with conversion and can be controlled by the monomer-to-initiator ratio; thus the reaction is of living nature. The most interesting and important characteristic is the fact that cyclic oligomers are not formed, different from the reported examples of the polymerization of these lactones with other initiators.

The polymerization proceeds by ring-opening at the acyl-oxygen bond of these lactones, and the growing species is a (porphinato)aluminum alkoxide.



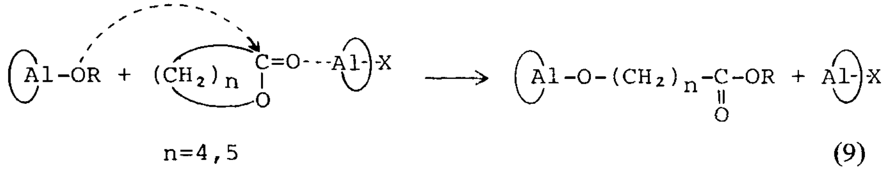
(7)

The living polymerization of lactide to give a product with narrow molecular weight distribution takes place similarly with (TPP)AlOR as initiator although a higher temperature, such as 100°C, is required.



(8)

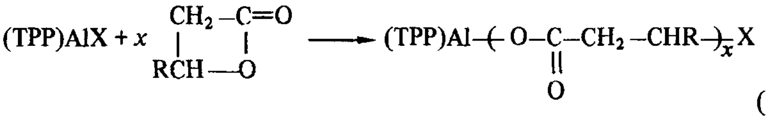
In contrast to the polymerization of epoxide, (TPP)AlCl cannot initiate the polymerization of δ-lactone, ε-lactone, and lactide. However, of particular interest is the fact that (TPP)AlCl exhibits a remarkable accelerating effect on the polymerization of these lactones initiated by (TPP)AlOR. On the other hand, the number of polymer molecules does not increase on addition of (TPP)AlCl but remains equal to the number of (TPP)AlOR molecules. Therefore, (TPP)AlCl is considered to participate in the reaction as a "catalyst." In conformity with this, the kinetic analysis of the reaction revealed that the rate of polymerization is first order with respect to the lactone, (TPP)AlOR, and (TPP)AlCl. Furthermore, the rate of polymerization initiated by (TPP)AlOR in the absence of (TPP)AlCl is second order with respect to (TPP)AlOR. Thus, two molecules of aluminum porphyrin are considered to participate in the reaction. One of them is, of course, (TPP)AlOR which reacts with the lactone, while the other, (TPP)AlX (X = Cl or OR), is considered to activate the lactone by the coordination as a Lewis acid.



(9)

In fact, the coordination of lactone to aluminum porphyrin, such as (TPP)AlCl, is indicated by NMR spectral investigation.

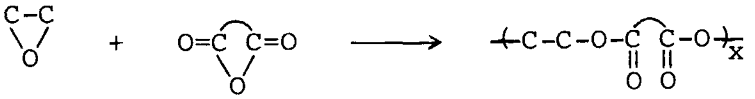
The living polymerization of β-lactone (4-membered) also proceeds at room temperature by aluminum porphyrin as initiator. (Porphinato)aluminum chloride [(TPP)AlCl], -carboxylate [$(TPP)AlO_2CR$], and -phenoxide [(TPP)-AlOAr] initiate the polymerization, while the reactivity of the alkoxide [(TPP)AlOR] toward β-lactone is low, in contrast to other lactones. The ring cleavage of β-lactone takes place at the alkyl–oxygen bond, and the growing species is a (porphinato)aluminum carboxylate.



$$\mathrm{(TPP)AlX} + x \begin{array}{l} \mathrm{CH_2-C{=}O} \\ \;\;|\qquad\;| \\ \mathrm{RCH-O} \end{array} \longrightarrow \mathrm{(TPP)Al}\!\left(\mathrm{O-\underset{\underset{\displaystyle O}{\|}}{C}-CH_2-CHR}\right)_{x}\mathrm{X} \tag{10}$$

## ALTERNATING COPOLYMERIZATION OF EPOXIDE AND CYCLIC ACID ANHYDRIDE OR CARBON DIOXIDE

Alternating copolymerization of epoxide and cyclic acid anhydride gives a polyester. Epoxide-carbon dioxide alternating copolymerization to afford aliphatic polycarbonate has been developed by the present author [15].



(11)

(12)

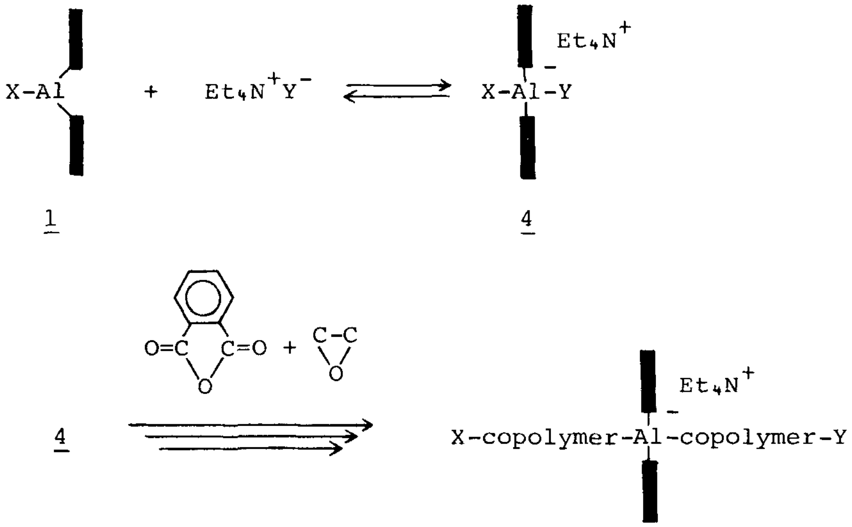
Although various initiator or catalyst systems have been developed for these copolymerization reactions, the synthesis of copolymers with controlled molecular weight have not been reported. In general, the control of molecular weight in copolymerization is considered difficult since monomers as well as growing species with different reactivities are involved, which leads to heterogeneity in the rate of propagation of each polymer molecule.

In this respect, aluminum porphyrin is a system of particular interest to give the above copolymers with narrow molecular weight distribution. For these copolymerizations, an equimolar mixture of aluminum porphyrin and a quaternary ammonium or phosphonium salt is effective. Typically, the combination of (TPP)AlCl and tetraethylammonium chloride or ethyltriphenylphosphonium bromide brings about the alternating copolymerization of phthalic anhydride and propylene oxide at room temperature, though slower than the homopolymerization of epoxide, to give the copolymer with $\bar{M}_w/\bar{M}_n \sim 1.1$.

These copolymerization reactions are of living nature, as indicated by the linear increase of the molecular weight with conversion and the formation of block copolymers upon further addition of a different pair of comonomers.

The most remarkable observation made in the copolymerization of phthalic anhydride and epoxide with the (TPP)AlX-quaternary salt system (1:1) is the fact that two molecules of the copolymer are formed per one molecule of aluminum porphyrin, different from the homopolymerization of epoxide and lactones with (TPP)AlX, where the number of polymer molecules is equal to that of aluminum porphyrin. Detailed studies revealed that a hexacoordinate complex 4 is formed from (TPP)AlX and the quaternary salt by the coordination of the anion of the salt to aluminum (Scheme 1).

Both axial groups Al–X and Al–Y have enough reactivity to initiate the copolymerization reaction. Thus, formation of copolymer takes place on both sides of the metalloporphyrin plane. In some cases, two growing polymer ends bound to one aluminum porphyrin can be observed by $^1$H NMR.

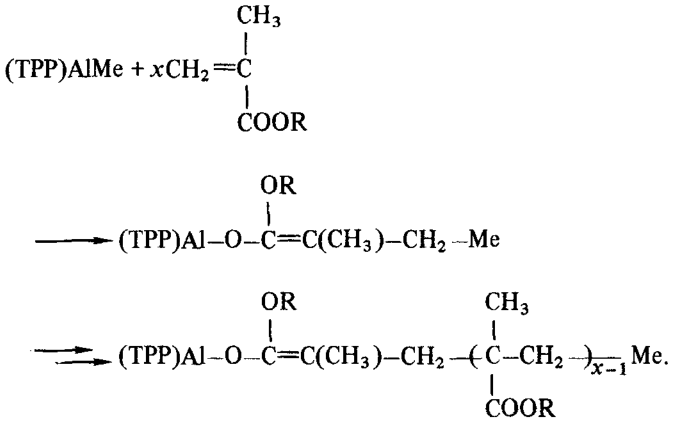


SCHEME 1.

## LIVING POLYMERIZATION OF METHACRYLIC ESTER

More recently, (tetraphenylporphinato)aluminum methyl [(TPP)AlMe: Structure 1, X = $CH_3$] was found to initiate the living polymerization of methacrylic ester upon irradiation with visible light at room temperature [16]. The reaction does not substantially proceed in the dark. The polymer of methyl methacrylate, for example, has a narrow molecular weight distribution ($\bar{M}_n$, up to 80 000; $\bar{M}_w/\bar{M}_n$, 1.06-1.20), and the block copolymer from different methacrylic esters can be synthesized with quantitative efficiency.

The polymerization is considered to proceed with a (porphinato)aluminum enolate as the growing species, and the effect of visible light is observed not only in the initiation reaction [addition of (TPP)AlMe to methacrylate] but also in every step of the propagation reaction (addition of the enolate to methacrylate).



$$(\mathrm{TPP})\mathrm{AlMe} + x\mathrm{CH_2}{=}\underset{\mathrm{COOR}}{\overset{\mathrm{CH_3}}{\mathrm{C}}} \longrightarrow (\mathrm{TPP})\mathrm{Al{-}O{-}}\overset{\mathrm{OR}}{\mathrm{C}}{=}\mathrm{C(CH_3){-}CH_2{-}Me} \rightrightarrows (\mathrm{TPP})\mathrm{Al{-}O{-}}\overset{\mathrm{OR}}{\mathrm{C}}{=}\mathrm{C(CH_3){-}CH_2}{-}\!\left(\underset{\mathrm{COOR}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}{-}\mathrm{CH_2}\right)_{x-1}\mathrm{Me}. \qquad (13)$$

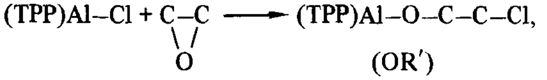
## "IMMORTAL" POLYMERIZATION

Although the polymerization of epoxide with (TPP)AlCl is of nucleophilic or anionic nature, as described above, the polymerization cannot be "killed" by the addition of a protic compound such as alcohol, water, phenol, carboxylic acid, or even hydrogen chloride.

For example, "living" polymer of ethylene oxide is prepared with (TPP)-AlCl as initiator, and added hydrogen chloride, followed by propylene oxide. If the "living" polymer is killed by hydrogen chloride as a strong acid, no further reaction will take place upon addition of propylene oxide. On the other hand, if hydrogen chloride does not participate in the reaction, the formation of ethylene oxide-propylene oxide block copolymer will result. In either case, the gel permeation chromatogram (GPC) of the reaction mixture will show a single unimodal peak. Of particular interest, two unimodal peaks are observed in the GPC of the reaction mixutre which moves to the higher molecular weight region with the progress of the reaction. On the other hand, the peak due to the original poly(ethylene oxide) disappears. The fractions corresponding to the two peaks can be separated by the different solubility in $CHCl_3$/hexane. The insoluble fraction is identified by $^1H$ NMR to be the block copolymer consisting of poly(ethylene oxide) and poly(propylene oxide), while the soluble fraction is the homopolymer of propylene oxide.

The molecular weight estimated for the poly(propylene oxide) segment in the block copolymer is substantially the same as that observed for the homopolymer. The total number of polymer molecules ($N_p$) as calculated on the basis of the molecular weight of the isolated homopolymer is in excellent agreement with the sum of the numbers of the molecules of the starting "living" poly(ethylene oxide) ($N_{Al}$) and of hydrogen chloride. The homopolymer of propylene oxide isolated is found by $^{13}C$ NMR to carry a chlorine terminal ($Cl{-}CH_2CH(CH_3)O{-}$). These observations indicate that the following sequence of reactions takes place, in addition to the repeated reaction of (TPP)-AlOR with epoxide to form polyether (Eq. 6).

$$(TPP)Al{-}OR + HCl \longrightarrow (TPP)Al{-}Cl + HOR, \qquad (14)$$



$$(TPP)Al{-}Cl + \underset{\diagdown O \diagup}{C{-}C} \longrightarrow \underset{(OR')}{(TPP)Al{-}O{-}C{-}C{-}Cl}, \qquad (15)$$

$$(TPP)Al{-}OR' + HOR \rightleftharpoons (TPP)Al{-}OR + HOR'. \qquad (16)$$

The reaction between the growing species (TPP)AlOR and hydrogen chloride gives (TPP)AlCl, which can initiate the polymerization of epoxide. Although Reaction (14) is irreversible, (TPP)AlOR′ formed by Reaction (15) exchanges with ROH, the "dead" polymer, which eventually revives to the growing species (Eq. 16). Thus, in the above experiments, the polymerization of propylene oxide takes place uniformly from all the molecules of the "living" poly(ethylene oxide) and hydrogen chloride.

Thus, the polymerization of epoxide by aluminum porphyrin may not be killed even by hydrogen chloride, and may be regarded as having an "immortal" nature. When compared, for example, with the corresponding polymerization of epoxide initiated with the alkali-metal alkoxide, an unusually high

TABLE 1. Polymerization of Epoxide with (TPP)AlCl (Structure 1, X = Cl) in the Presence of Methanol[a]

| Epoxide (E) | $\frac{[E]_0}{[\underline{1}]_0}$ | $\frac{[MeOH]_0}{[\underline{1}]_0}$ | Time, h | Conversion, % | $\bar{M}_n$[b] | $\frac{\bar{M}_w}{\bar{M}_n}$[b] | $\frac{N_p}{N_{Al}}$[c] |
|---|---|---|---|---|---|---|---|
| Ethylene oxide | 200 | 9 | 48 | 100 | 700 | 1.05 | 12.6 |
| Propylene oxide | 200 | 9 | 48 | 100 | 1300 | 1.08 | 8.9 |
| 1-Butene oxide | 200 | 9 | 96 | 100 | 1200 | 1.10 | 12.0 |
| Epichlorohydrin | 200 | 9 | 48 | 100 | 1500 | 1.04 | 12.3 |

[a] At room temperature without solvent.
[b] By GPC.
[c] Number of polymer molecules ($N_p$)/number of aluminum atoms ($N_{Al}$).

reactivity as nucleophile of the aluminum–chlorine bond of aluminum porphyrin (Structure 1, X = Cl) is most important to account for the origin of the "immortality" of the polymerization. In contrast, the polymerization with alkali-metal alkoxide is killed by hydrogen chloride, since a comparable reactivity can hardly be expected for alkali-metal chloride.

Taking advantage of the principle of "immortal" polymerization of epoxide with (TPP)AlCl in the presence of a protic compound, for example methanol, polymer of uniform molecular weight can be prepared with the number of the molecules ($N_p$) more than that of the initiator ((TPP)AlCl) ($N_{\mathrm{AL}}$). The reaction may be applied to the polymerization of various epoxides such as ethylene oxide, propylene oxide, 1-butene oxide, and epichlorohydrin (Table 1). In the present system the polymerization proceeds by the participation of Reactions (6), (15), and (16). The narrow molecular weight distribution of the product corresponds to the fact that the reversible exchange reaction (Eq. 16) proceeds much faster than the propagation reaction (Eq. 6). The same principle can be applied to the synthesis of polyester with narrow molecular distribution by the polymerization of β-lactone, δ-lactone, and ϵ-lactone initiated with aluminum porphyrin in the presence of an appropriate protic compound.

## CONCLUSION

Aluminum porphyrin is an excellent initiator for the living polymerization of a wide variety of monomers such as epoxide, lactones, and methacrylic ester, and also for the living alternating copolymerization of epoxide and cyclic acid anhydride or carbon dioxide. Although the growing species are of anionic or nucleophilic nature, the polymerization of epoxide and β-lactone cannot be terminated even by a strong acid such as hydrogen chloride. Thus, the reaction can be called "immortal" polymerization. Taking advantage of this, polyether and polyester having controlled molecular weight can be synthesized, with the number of polymer molecules more than that of the initiator. Living and "immortal" polymerizations with aluminum porphyrin permit the synthesis of a variety of block copolymers and end-reactive polymers with controlled chain lengths.

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