HIGHLIGHT

Immortal Polymerization: The Outset, Development, and Application

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ABSTRACT: The story of the outset of the concept of immortal polymerization is presented. Immortal polymerization is the polymerization that gives polymers with a narrow molecular distribution, even in the presence of a chain transfer reaction, because of its reversibility, which leads to the revival of the polymers once dead, that is, the immortal nature of the polymers. As a result, immortal polymerization can afford polymers with a controlled molecular weight, the number of polymer molecules being more than that of the initiator. The compound that plays a leading role is metalloporphyrin, in which the metal-axial ligand bond has an unusually high reactivity. Immortal polymerization can be carried out in the ring-opening polymerizations of epoxides, episulfides, and lactones by the selection of an appropriate metalloporphyrin as the initiator and a protic compound as the chain transfer agent. Immortal polymerization is an effective method for synthesizing end-functional polymers and oligomers with narrow molecular weight distributions. © 2000 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 38: 2861–2871, 2000

Keywords: immortal polymerization; living polymerization; metalloporphyrin; ring-opening polymerization

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He received the following: Chemical Society of Japan Progress Award, 1967; Society of Polymer Science Japan Award, 1974; Chemical Society of Japan Award, 1990; Toray Science and Technology Award, 1994; Society of Polymer Science Japan Award for Distinguished Accomplishments and Services, 1994; and Medal with Purple Ribbon from the Japanese Government for Accomplishments in Academic Research, 1998.

INTRODUCTION

A large variety of synthetic polymers are produced by addition polymerization, mostly with a radical mechanism. A reaction between radicals on the terminals of growing polymer molecules necessarily takes place, resulting in the "death" of the polymers. In contrast, in an ionic mechanism, the reaction between ions with the same sign of charge cannot occur, and there is a possibility that ions on the terminals of growing polymer molecules will stay "living" for a long time. The first example of this was discovered by Professor Szwarc in 1956.[1] The reaction was the polymerization of styrene initiated with organo-alkali metal compounds. The molecular weight of the polystyrene formed was of a very narrow distribution, and the number of polymer molecules was the same as that of the initiator molecules. Of particular interest is what was found when the second portion of styrene was added after completion of the consumption of the initially charged styrene. Polymerization again ensued, and the molecular weight of the polymer increased, retaining the number of the molecules, indicating that carbanion growing terminals were alive throughout the procedure. Thus, the polymer was called *living polymer.* Since then, the examples of living polymerization, which gives living polymers, have increased and have been utilized for the syntheses of polymers with controlled molecular weights, block copolymers, and end-reactive polymers, some of which have found practical applications.

Living does not mean *immortal.* In the aforementioned anionic polymerization of styrene, the living polymer can be instantly "killed" upon the addition of a protic compound such as water. In contrast, in the immortal polymerization[2] discussed here, the polymer cannot be killed even by the addition of a protic compound, although the growing active species is of an anionic nature, the monomer being epoxides and lactones. Furthermore, the number of polymer molecules, with a narrow molecular weight distribution, is more than that of the initiator molecules. This is advantageous in the synthetic aspect.

## DISCOVERY OF A NOVEL INITIATOR: WHY ALUMINUM PORPHYRIN?

The main actor in immortal polymerization is a porphyrin complex of aluminum as the initiator. Why aluminum porphyrin? The background dates to 1968, when I discovered the alternating copolymerization of carbon dioxide and epoxide.[3] This is the first example of the use of carbon dioxide as a monomer for polymer synthesis. The

product is an aliphatic polycarbonate, and much interest has been shown for possible practical applications.

The aforementioned discovery led me to a general interest in the fixation/utilization of carbon dioxide. Because a good catalyst for the copolymerization of carbon dioxide and epoxide is a system based on an organozinc compound, I started fundamental studies on the reaction of carbon dioxide with organozinc and related organoaluminum compounds. There was no relation to polymer synthesis. As is well-known, coordinating ligands greatly influence the reactivity of metal complexes. Some interesting effects of ligands were observed also in the reaction of organometallic compounds with carbon dioxide.[4]

Here appears porphyrin as a ligand. When we think about the chemical fixation of carbon dioxide, a related biological fixation of carbon dioxide—photosynthesis—is of particular interest. In photosynthesis, chlorophyll with a ligand of a similar structure to porphyrin is excited by visible light, and an electron is released that eventually reduces carbon dioxide to carbohydrate. It is of much interest to create an artificial system that acts similarly.

I started to examine the reaction of aluminum porphyrin. Trivalent aluminum leaves one valence bond as an axial ligand when incorporated into porphyrin. A porphyrin ring is excited by visible light, and this effect would bring about an increase in the reactivity of aluminum—axial ligand bond. An aluminum complex of tetraphenylporphyrin with an Al—Et bond (Fig. 1, **1,** X = Et) was synthesized, and the reactivity with carbon dioxide was examined, but the reaction did not take place. However, in the presence of 1-methylimidazale and under irradiation with visible light, the reaction proceeded:[5]

$$(1)$$
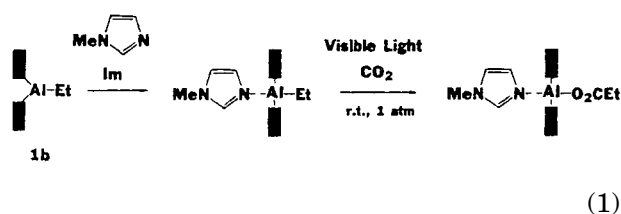
The reaction is stoichiometric, typical of organometallic compounds, but the confirmation of the effect of light was important.

To develop a catalytic process, the reaction of methoxide complex [(TPP)AlOMe: **1,** X = OMe] was examined. This complex reacts readily with carbon dioxide in the presence of 1-methylimidazole, even in the dark. Trapped carbon dioxide is activated. Upon the addition of epoxide, cyclic carbonate is formed, and the original complex is regenerated. Thus, the (TPP)AlOMe/1-methylimidazole system was found as a catalyst for the
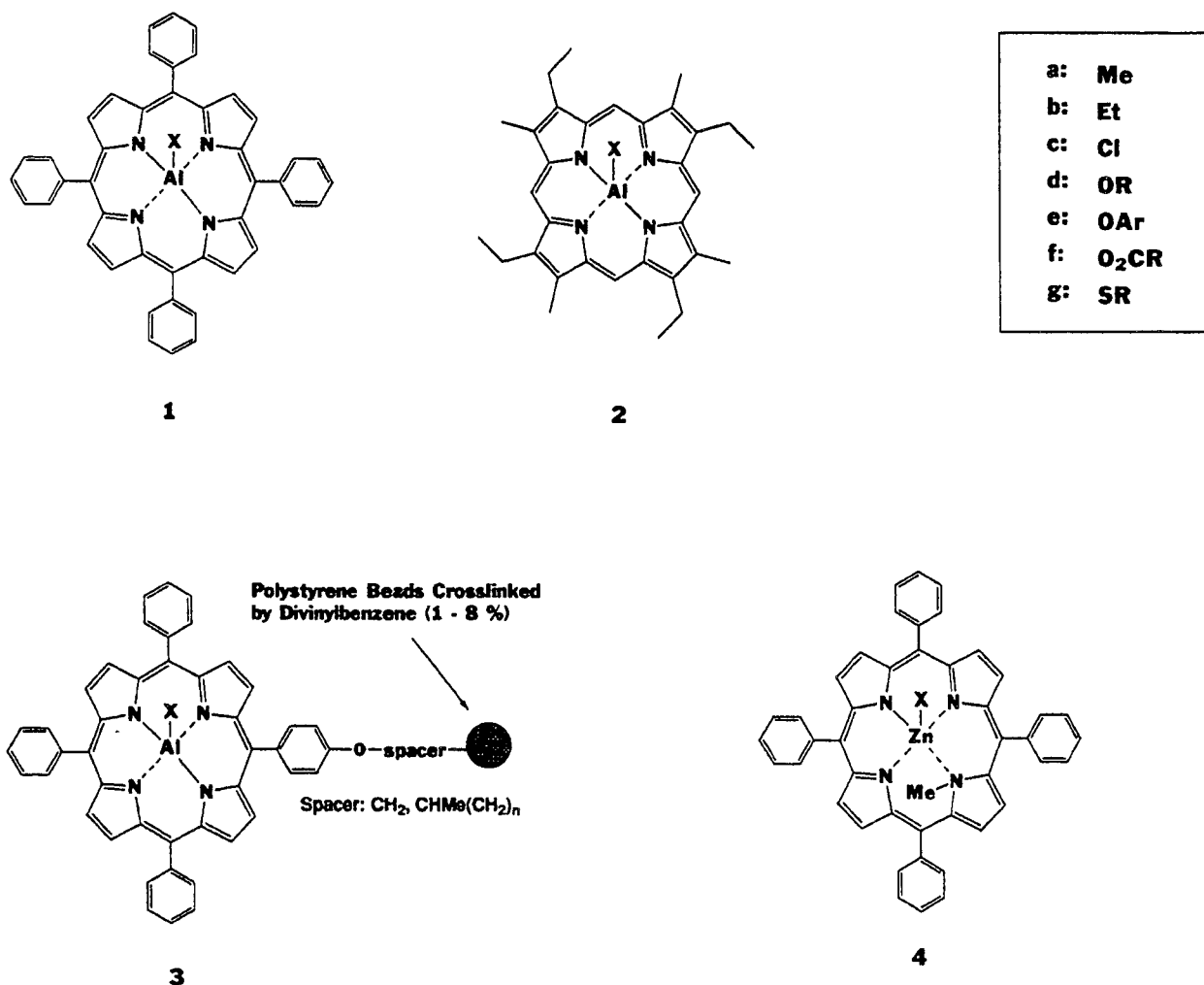
**Figure 1.**   Structures of the metalloporphyrins.

LIVING POLYMERIZATION WITH ALUMINUM PORPHYRIN

The reaction of carbon dioxide and epoxide with me-thoxide-aluminum porphyrin proceeds very slowly even in the absence of 1-methylimidazole. The product is not cyclic carbonate but linear copolymer. In the absence of carbon dioxide, the reaction of epoxide proceeds much faster to afford a polymer, a polyether:[7]

formation of cyclic carbonate from carbon dioxide and epoxide (Fig. 2).[6]

$$\text{Al-X} + n\ \underset{O}{\overset{R}{C-C}} \ \rightleftharpoons \ \text{Al}\left(\text{O-}\overset{R}{\text{C-C}}\right)_n\text{X} \qquad (2)$$
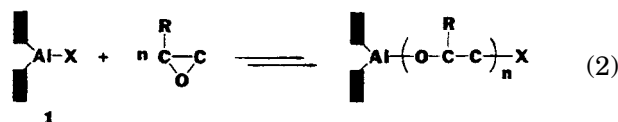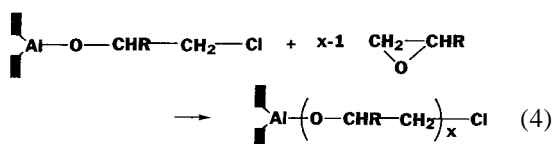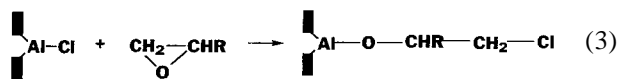
An examination of the molecular weight distribution of the polymer with gel permeation chromatography (GPC) revealed the very narrow distribution. This fact indicates the living character of the ring-opening polymerization of epoxide with aluminum porphyrin. Because there have been few examples of the living polymerization of ep-oxide, which is of fundamental and practical interest, the aforementioned reaction was investigated in detail.

Chloro complex [(TPP)AlCl: **1,** X = Cl] is also an excellent initiator.[8] The reaction proceeds smoothly at room temperature, and the molecular weight of the poly-mer can be controlled by the monomer-to-initiator ratio. The number of polymer molecules is equal to that of the initiator molecules. Block copolymers[9] and end-reactive polymers can be readily synthesized. Because the living polymer molecule is bound to all molecules of the com-plex, the structure of the growing species can be char-acterized well, e.g., by ^{1}H NMR of the reaction mixture
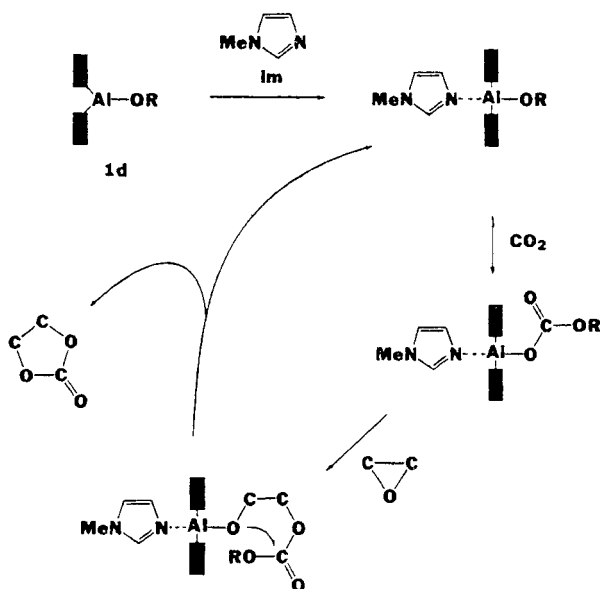
Figure 2.   Formation of cyclic carbonate from carbon dioxide and epoxide with aluminum porphyrin as the catalyst.

by the high field shift of the signal due to the H—C group close to the porphyrin ring. The polymerization initiated with chloro complex proceeds as follows, with alkoxide complex as the growing species:

$$\text{Al—Cl} + \text{CH}_2\text{—CHR} \longrightarrow \text{Al—O—CHR—CH}_2\text{—Cl} \quad (3)$$

$$\text{Al—O—CHR—CH}_2\text{—Cl} + \text{x-1 CH}_2\text{—CHR}$$
$$\longrightarrow \text{Al}\big(\text{O—CHR—CH}_2\big)_x\text{—Cl} \quad (4)$$

An extension to monomers other than epoxide has revealed so far that aluminum porphyrin can afford living polymers in the ring-opening polymerization of β-lactone,[10] δ-lactone,[11] ε-lactone,[12] and lactide.[13] It was a matter of course for us to examine the copolymerization of carbon dioxide and epoxide with aluminum porphyrin.[14] As a result, the system of chloro or carboxylate complex (**1,** X = O$_2$CR) combined with a quaternary phosphonium or ammonium salt was found to bring about alternating copolymerization with a moderate rate. The molecular weight distribution of the product was very narrow. This system is also effective for the alternating copolymerization of epoxide and cyclic acid anhydride to give a polyester with a narrow molecular

weight distribution.[15] These alternating copolymerizations are of a living nature.

Aluminum porphyrins can also bring about the living polymerization of acrylic monomers such as methacrylates,[16] acrylates,[17] and methacrylonitrile.[18] For methylaluminum porphyrin (**1,** X = Me), irradiation with visible light is necessary for initiation, whereas thiolate-aluminum porphyrin (**1,** X = SR) can initiate the polymerization without irradiation. Metalloporphyrins other than that of aluminum have been examined as polymerization initiators. Among these, the thiolate-zinc complex of *N*-methylporphyrin (Fig. 1, **4,** X = SR) is effective for the living polymerization of episulfide.[19] These examples are listed in Table I, together with examples developed by groups other than ours.[20–22]

UNEXPECTED MECHANISM

As mentioned earlier, the growing species of epoxide polymerization on aluminum porphyrin can be visualized by NMR studies of the reaction mixture. The question then arises whether a particular molecule of the growing polymer binds to a particular molecule of the complex throughout the polymerization, where the monomer successively inserts into the alkoxide–aluminum bond. This is a general question regarding ionic polymerization. There is present a counterion in the neighbor of the growing ionic species. For really ionic species, the exchange between counterions is expected to take place, whereas for species of a more covalent nature, no exchange would occur. However, no experimental data seem to have been provided for this matter, and there is no convenient method to know the truth.

Fortunately, for polymerization with aluminum porphyrin, there is a good methodology. It is to utilize the difference in the reactivity of the complex depending on the structure.[23] The aluminum complex of etioporphyrin I [Fig. 1, **2:** (Etio P)AlX] brings about the living polymerization of epoxide, but the reaction proceeds more slowly than for tetraphenylporphyrin complex (TPP)AlX **1.** Accordingly, when the reaction under otherwise identical conditions is carried out for the same period of time, the extent of the reaction and the molecular weight of the polymer are lower for **2.** What happens when the polymerization of epoxide is carried out with a mixture of (Etio P)AlX and (TPP)AlX? If these two porphyrin complexes take part independently in the reaction, a polymer with a low molecular weight and a polymer with a high molecular weight would be formed, both with narrow molecular weight distributions. Then, the GPC of the product should show two narrow peaks.

Unexpectedly, GPC of the product exhibited a single, narrow peak. The conversion and molecular weight of

Table I.   Monomers for Living Polymerization with Metalloporphyrins

(Amass[20])

(Höcker[21])

(Yoshinaga[22])

- -

**Alternating Copolymerization**

(long lived)
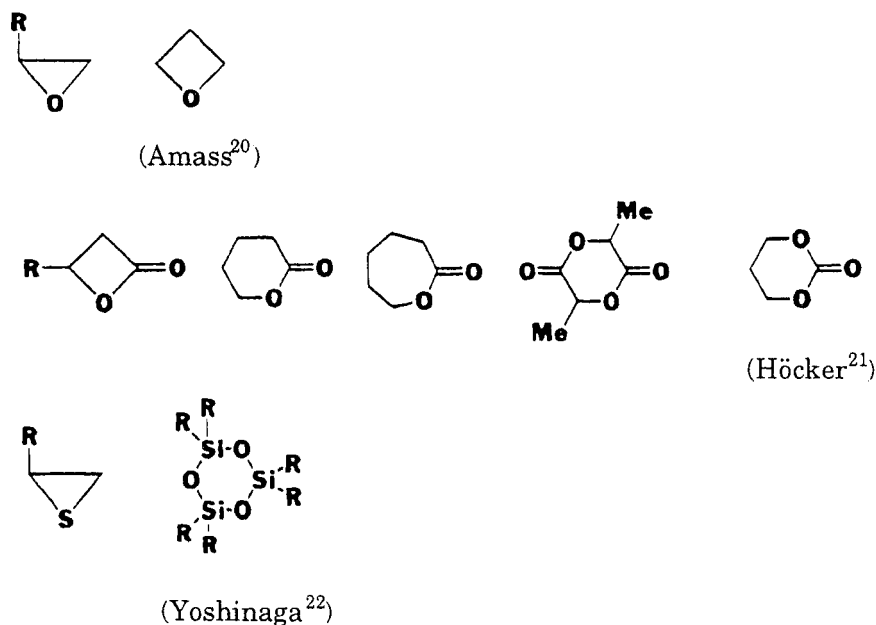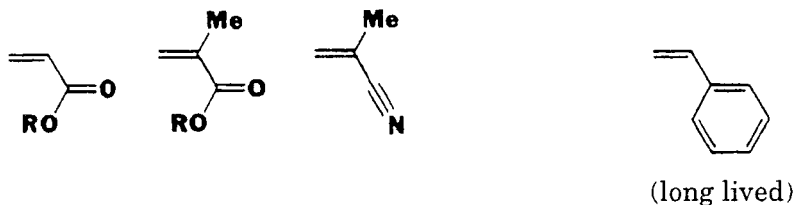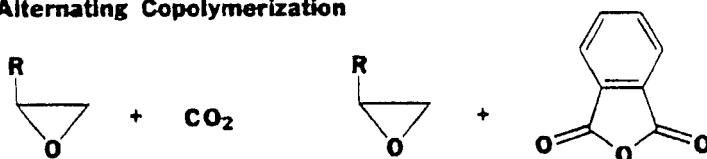
the product both had intermediate values compared with those expected for the independent participation of the two complexes. The number of polymer molecules was the same as the sum of the numbers of molecules of the two complexes. These facts indicate that a particular polymer molecule does not stay on a particular molecule of the complex, but rather a rapid exchange among these is taking place. In fact, a rapid intermolecular exchange of alkoxide groups on aluminum porphyrin was confirmed by the NMR spectrum of a mixture of two aluminum porphyrins with different alkoxide groups on aluminum:

$$(TPP)AlOR^1 + (EtioP)AlOR^2$$
$$\rightleftharpoons (TPP)AlOR^2 + (EtioP)AlOR^1 \qquad (5)$$
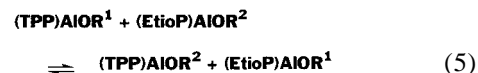
FROM LIVING POLYMERIZATION TO IMMORTAL POLYMERIZATION

In the course of the studies on the aforementioned exchange reaction, the alkoxide group on aluminum porphyrin was found to undergo a rapid exchange with alcohol:
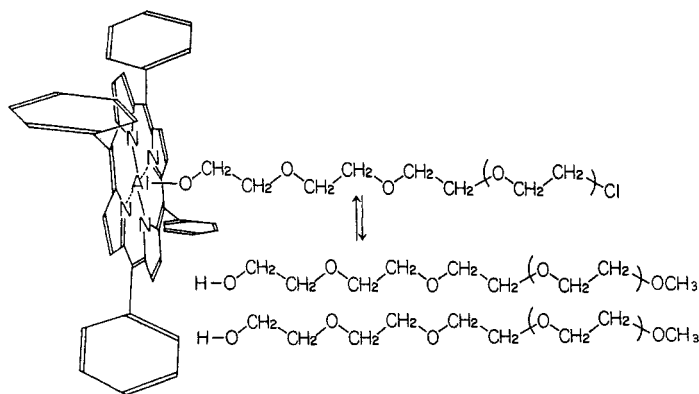
Figure 3.   Growing species of ethylene oxide polymerization on aluminum porphyrin exchanging with once dead species.

$$\text{Al-OR}^1 \; + \; \text{R}^2\text{OH} \; \rightleftharpoons \; \text{Al-OR}^2 \; + \; \text{R}^1\text{OH} \qquad (6)$$
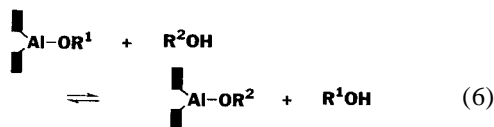
An exchange between metal alkoxide and alcohol is not unusual, but the rapid exchange is important, as explained next.

Because the growing species of epoxide polymerization is an alkoxide, alcohol is expected to behave as a chain transfer agent. The forward reaction of eq 6 is a chain transfer reaction in the usual sense. The growing polymer molecule (TPP)AlOR^1 is converted to a dead polymer, R^{1}OH, while the growth of a new polymer molecule starts from (TPP)AlOR^2. However, R^{1}OH is not really dead in this case. Because the reaction of eq 6 is reversible, R^{1}OH can revive to a growing species. If this exchange reaction is rapid enough compared with the polymer growth, the molecular weight distribution of the product formed is expected to remain narrow as in the absence of alcohol. This is in contrast to the general observation that a chain transfer reaction brings about the broadening of the molecular weight distribution of the polymer.

In fact, the polymerization of epoxide with the chloro complex (TPP)AlCl as the initiator proceeds smoothly even in the presence of methanol. The molecular weight of the polymer decreases with the amount of methanol. In other words, the number of polymer molecules increases. However, the molecular weight distribution remains narrow. The number of polymer molecules coincides with the sum of the number of the molecules of the initiator and that of the methanol. The reaction is initiated by eq 3. Upon the formation of alkoxide, a reversible exchange with methanol takes place by eq 6. Because this exchange is rapid, all alcohol molecules present in the system can act as growing species, from which the polymer forms by a reaction similar to eq 4. Among the polymer molecules, those corresponding to the number of molecules of the complex are present as growing species, and others are present in the form of alcohol, but the latter is not really dead but revives by the reaction of eq 6. Thus, the polymerization reaction has an immortal character (Fig. 3).[24]
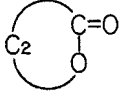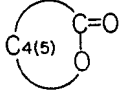
ACTIVE SPECIES RESISTANT TO HYDROCHLORIC ACID

What happens when a stronger acid is added to the polymerization mixture? The following experiment was carried out.[25] First, ethylene oxide was polymerized with aluminum porphyrin as the initiator, and the living polymer was formed. Then, hydrogen chloride was added, followed by the addition of propylene oxide. If hydrogen chloride kills the living polymer, nothing would take place afterward. If hydrogen chloride does not kill the living polymer, which is considered unlikely, ethylene oxide–propylene oxide block copolymer would be formed. In both cases, GPC of the final product should show a single peak. In reality, however, GPC showed two peaks. These two parts could be fractionated and were found to be ethylene oxide–propylene oxide block copolymer and the homopolymer of propylene oxide, respectively.

Thus, hydrogen chloride, a very strong acid, cannot kill this polymerization system. A living polymer of epoxide, an alkoxide complex, reacts irreversibly with hydrogen chloride:

$$\text{Al-OR} \; + \; \text{HCl} \; \longrightarrow \; \text{Al-Cl} \; + \; \text{ROH} \qquad (7)$$
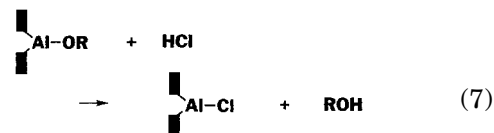
Table II.   Living and Immortal Polymerizations with Metalloporphyrins

Monomer	Initiator	Growing Species	Transfer Agent for Immortal Polymerization
(epoxide)	(P) AlOR (P) AlOAr (P) AlO$_2$CR (P) AlCl	(P)AlOR	ROH ArOH RCO$_2$H HCl
(β-lactone, C2)	(P) AlOAr (P) AlO$_2$CR (P) AlCl	(P)AlO$_2$CR	RCO$_2$H HCl
(lactone C4(5))	(P) AlOR	(P)AlOR	ROH
(episulfide)	(NMP)ZnSR	(NMP)ZnSR	RSH
CH$_2$=C(CH$_3$) | CO$_2$R	(P) AlMe/hν	(P) Al—O—C=(CH$_3$)—CH$_2$— | OR	—

(P) = porphyrin; (NMP) = N-methylporphyrin.

However, when epoxide is added to this reaction mixture, (TPP)AlCl can initiate the polymerization (eq 3). Then, alkoxide complex is formed, which undergoes an exchange with alcohol by eq 6. Accordingly, the once dead polymer ROH, by the irreversible reaction of eq 7, revives.

Therefore, the keys for immortal polymerization are the rapid exchange between the alkoxide complex and alcohol and the unusually high reactivity of the chloro–aluminum bond of the chloro complex.

The polymerization of ethylene oxide with sodium alkoxide as the growing species also proceeds with a living character. However, the addition of hydrogen chloride kills the living polymer without revival. Another product is sodium chloride, which has no ability to initiate the polymerization. Thus, the reactivity of the chloro–aluminum bond on aluminum porphyrin is surprisingly high.

DEVELOPMENT OF IMMORTAL POLYMERIZATION

The immortal polymerization of epoxide with aluminum porphyrin proceeds with phenols or carboxylic acids as chain transfer agent as well because phenolate-aluminum porphyrin, (P)AlOAr, and carboxylate-aluminum porphyrin, (P)AlO$_2$CR, can initiate the polymerization.

By the selection of the appropriate metalloporphyrin and protic compound, the immortal polymerization of lactones is also possible (Table II). As for β-lactone, four-membered cyclic esters, (P)AlOAr, (P)AlO$_2$CR, and (P)AlCl, but not (P)AlOR, are effective initiators for living polymerization. The polymerization proceeds by ring opening at the oxygen-β-carbon bond to give an aluminum carboxylate as the growing species:

$$\text{Al-X} + \underset{O=C-C\alpha}{\overset{O-C\beta}{|\quad|}} \longrightarrow \text{Al-O-C-C-C-X} \quad (8)$$
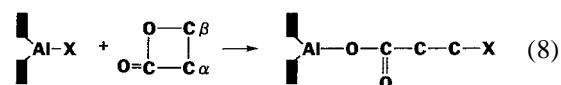
Carboxylic acids and hydrogen chloride as the transfer agent lead to immortal polymerization, whereas alcohols do not because alcohol cannot exchange with (P)AlO$_2$CR as the growing species.

For δ- (six-membered) and ε- (seven-membered) lactones, (P)AlOR can initiate the living polymerization that proceeds by ring opening at the oxygen–carbonyl bond to afford an aluminum alkoxide growing species:

$$\text{Al-X} + \underset{Cx}{O-C=O} \longrightarrow \text{Al-O-Cx-C-X} \quad (9)$$
$$x=4,5$$
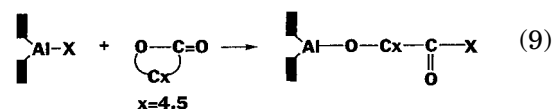
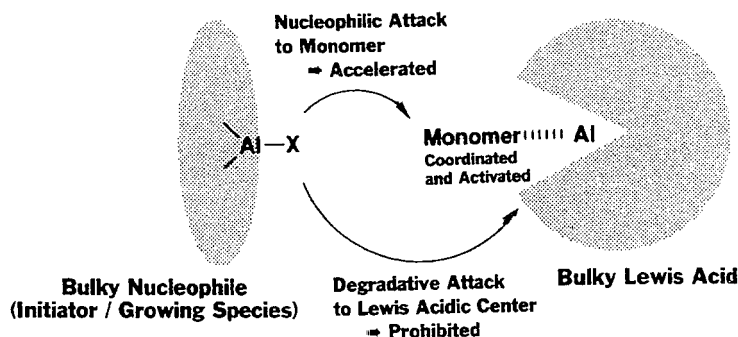Thus, immortal polymerization takes place with alcohol as the transfer agent. However, hydrogen chloride, car-

**Figure 4.** Basic concept of high-speed living polymerization.

boxylic acids, and phenols kill the living polymer because the resulting (P)AlCl, (P)O₂CR, and (P)AlOAr cannot initiate the polymerization of these lactones.

In the living polymerization of episulfide with zinc *N*-methylporphyrin with thiolate–zinc bond as the initiator, the addition of thiol leads to immortal polymerization[19]:

$$(10)$$
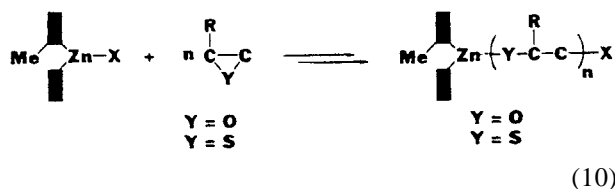
However, alcohols are not effective, with no ability to exchange with zinc thiolate growing species.

The polymerization of methacrylates and acrylates with aluminum porphyrin proceeds with an aluminum enolate growing species:

$$(11)$$

$$(12)$$
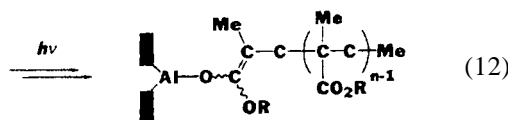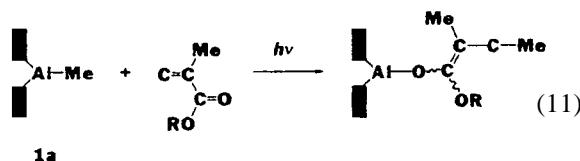
To realize the immortal polymerization of (meth)acrylic esters, (P)AlX is required, which can initiate the polymerization and abstract the α-hydrogen of ester to regenerate enolate. The development of such a compound awaits further studies.
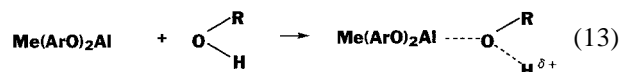
HIGH-SPEED IMMORTAL POLYMERIZATION

Immortal polymerization can afford polymers with controlled molecular weights, the number of molecules of which is more than that of the initiator. To increase the number of polymer molecules without a change in the amount of the initiator and the molecular weight of the product, the amounts of the monomer and transfer agent should be increased. However, this necessarily slows the rate of reaction, which is disadvantageous in practical aspects.

Fortunately, this disadvantage can be circumvented by the application of high-speed living polymerization, which has been developed in the course of our studies on polymerization with metalloporphyrin. The concept is based on the use of a Lewis acid, which can activate the monomer by coordination but is inert to the growing species (Fig. 4).[26] A typical Lewis acid satisfying these requirements is a methylaluminum di(phenoxide) with bulky substituents at ortho positions of the phenyl groups (Table III), which can dramatically accelerate the living polymerization of methacrylic esters,[26] epoxides,[27] and lactones[28] with aluminum porphyrin and episulfides with zinc *N*-methylporphyrin,[29] retaining the narrow molecular weight distributions of the products.

Similarly, the polymerization of propylene oxide with aluminum porphyrin in the presence of methanol could be much accelerated by the addition of a bulky Lewis acid, retaining the immortal character.[30] For example, the number of polymer molecules could be increased by 1000 times with respect to that of the initiator.[31] The formation of a polymer with a narrow molecular weight distribution under these conditions indicates the acceleration by the Lewis acid takes place not only in the polymer growth but also in the exchange between the growing species, (P)AlOR and alcohol. In fact, this has been confirmed by NMR studies.[31] The coordination of alcohol to the Lewis acid is thought to enhance the acidity of the alcohol, resulting in a more rapid exchange:

$$(13)$$

Table III. Lewis Acids for High-Speed Living Polymerization

Accelerator	Terminator

Ph$_3$Al

Me$_3$Al
Et$_3$Al
iso-Bu$_3$Al

R^1 = R^3 = ^{tert}Bu, R^2 = H
R^1 = R^2 = R^3 = ^{tert}Bu
R^1 = R^2 = ^{tert}Bu, R^3 = Me
R^1 = R^3 = Ph, R^2 = H

(C$_6$H$_5$)$_3$B
(C$_6$F$_5$)$_3$B

BF$_3$ · OEt$_2$
BCl$_3$

APPLICATIONS OF IMMORTAL POLYMERIZATION

Immortal polymerization enables the syntheses of a variety of end-functionalized polymers and oligomers by the appropriate selection of a protic compound as the transfer agent (Table IV).[32,33] For example, the use of a protic compound with an unsaturated group such as methacrylic acid and 2-hydroxyethyl methacrylate leads to the attachment of a polymerizable end group to the polymer with quantitative efficiency (i.e., the syntheses of macromonomers). When benzyl alcohol is used, benzyl group at the polymer terminal can be removed by hydrogenation to form a hydroxyl group. This method was applied to the synthesis of poly(propylene oxide) with primary hydroxyl groups at both ends, which is useful as the soft segments for polyurethane.[34] When diols and triols are used as the protic transfer agent, the resulting products are telechelic polymers and star polymers, respectively.

The immortal polymerization of propylene oxide in the presence of methanol can be carried out with aluminum porphyrin bound to crosslinked polystyrene (Fig. 1, **3**).[35] In this case, an equimolar amount of the polymer formed is bound to the insolubilized aluminum porphyrin, but all others with methoxy and hydroxyl groups at each end remain soluble and thus are readily separable from the insoluble initiator, which can be reused. In fact, the reaction could be repeated nine times without loss of the activity and broadening of the molecular weight distribution of the product.

CONCLUSION

Thus, immortal polymerization is a result of the unexpected development of my interest in the photochemical fixation of carbon dioxide with aluminum porphyrin. This is regarded as a byproduct of the initially intended research, but this by product has

Table IV.   End-Functionalized Polymers and Oligomers by Immortal Polymerization
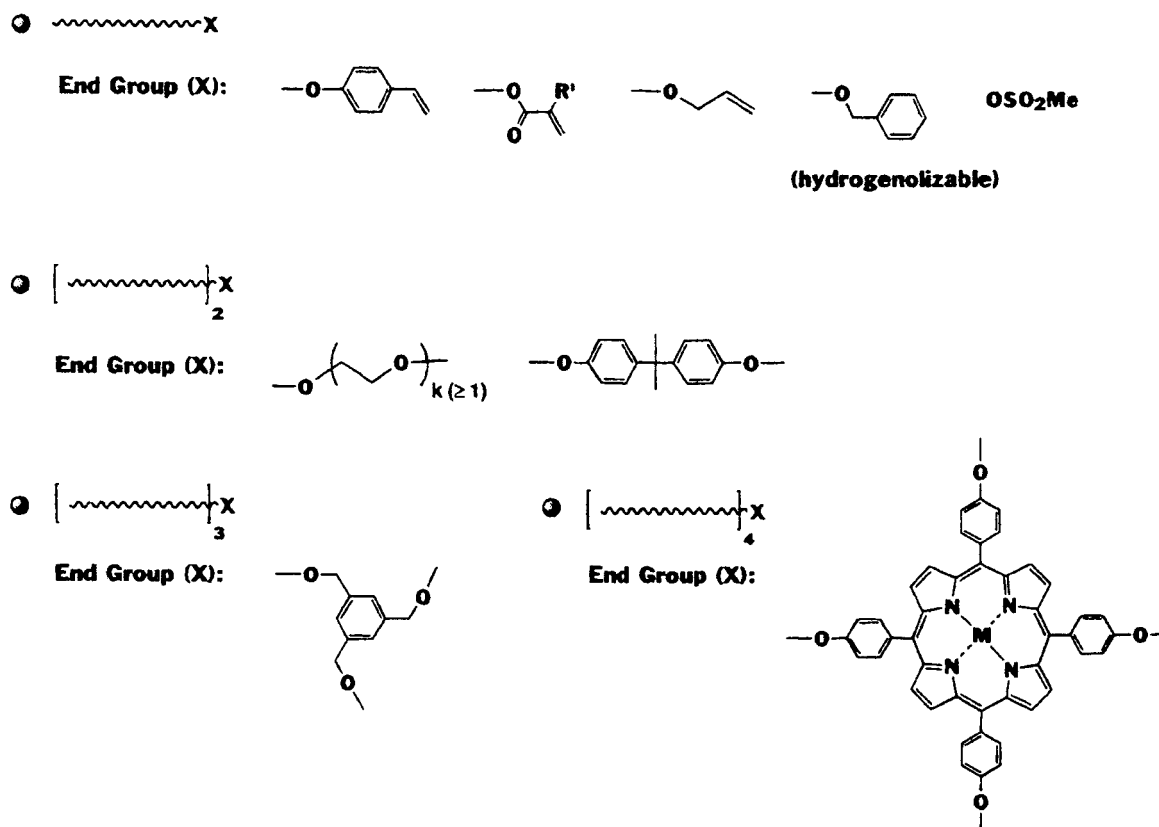
grown to the main topic of my research. As often observed in scientific research, the step for essential progress is the discovery of unexpected facts or the idea of combining separate facts that could not be correlated before. After a discovery, the development of the principle can be made for some time, but it is limited by the principle. Of course, research is planned and carried out with some expectation on the basis of a logic, but a breakthrough or essential progress comes from the unexpectedness of the fact. This is a contradiction intrinsic in research, but research is interesting because of this contradiction.

The research on metalloporphyrin hopefully will continue to be a source of unexpected facts leading to new ideas. I believe that our research remains "living" and "immortal".

REFERENCES AND NOTES

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