Metalloporphyrins as Initiators for Living and Immortal Polymerizations

TAKUZO AIDA AND SHOHEI INOUE*,†

Department of Chemistry and Biotechnology, Graduate School of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Received May 2, 1995

Needless to say, "molecular weight" is an essential factor to affect the fundamental properties of polymer materials. However, unlike some naturally occurring macromolecules such as proteins and nucleic acids, synthetic polymers, except those obtained by stepwise approach, are of broad molecular weight distribution (MWD); *i.e.*, they are mixtures of macromolecules with different molecular weights. MWD is caused by the heterogeneity of the growth of polymer chain. Figure 1 shows a schematic diagram of addition polymerization of unsaturated monomer (M) with I−☆ as initiator, where the chain growth of a polymer molecule starts by the reaction of I−☆ with M to generate the active species (I−M−☆) (initiation step), followed by repeated addition of M to I−M−☆ (propagation step) to furnish a higher molecular weight polymer (I−(M)$_n$−☆). In this case, if (1) the initiation is much faster than the propagation and (2) the propagation proceeds uniformly with respect to all growing polymer molecules (I−M)$_n$−☆), a polymer with uniform molecular weight should be formed. However, polymerization is generally accompanied by side reactions such as termination and chain transfer reactions, leading to irreversible deactivation of the growing species. Since these side reactions interfere with the uniform growth of polymer chains, broadening of polymer MWD will result.

In 1956, the first example of the formation of a narrow MWD polymer was discovered by M. Szwarc in his basic studies on the electron transfer process between organometallic reagents and unsaturated compounds under rigorously dry and inert conditions.[1,2] He noticed that the polymer formed from styrene in the presence of sodium naphthalide is of very narrow MWD, as indicated by the ratio of weight- to number-average molecular weights close to unity. Upon addition of a fresh feed of styrene to the completely polymerized system, the second-stage polymerization ensues, resulting in further growth of all growing polymer molecules. The polymerization with this character is named "living polymerization", since the growth pattern of polymer can be viewed as analogous to the growth of a biological organism.

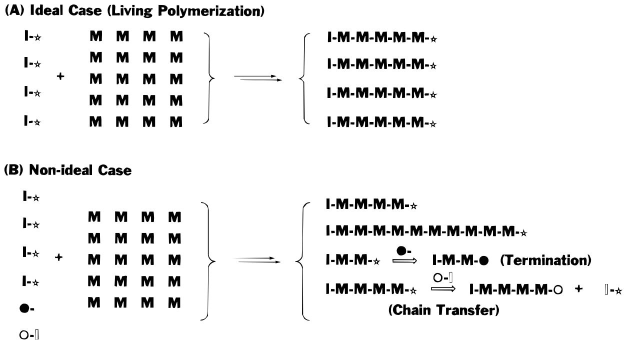


Figure 1. Schematic diagrams of addition polymerization.

A key to achieve "living polymerization" is to develop well-behaved initiators, since the initiator affects the relative rate of initiation to propagation and the potential for side reactions during chain growth. Great progress in the field of living polymerization was made in the 1980s thanks to the discovery of various new initiators.[3] We have discovered that some metalloporphyrin complexes serve as excellent initiators for living polymerization, where the most characteristic feature is their exceptionally wide applicability for a variety of monomers, listed in Table 1.[3,4] In these cases, the fate of the initiator can be directly followed by ^{1}H NMR, taking advantage of the ring current effect of the porphyrin ligand on the axially bonded species. This is particularly beneficial for understanding the polymerization mechanism, and we found that the polymerization takes place at the central metal atom of the initiator.

In the course of this study, we have discovered some interesting features of the polymerization, such as (1) the acceleration effect of visible light, (2) Lewis acid assisted high-speed living anionic polymerization, and (3) the immortal character of polymerization, all of which take advantage of the unique reactivities and structures of the metalloporphyrins. In the present Account, an overview of polymerization with metalloporphyrins and related systems will be described together with the background of its discovery and recent developments.

Takuzo Aida is an associate professor of the Department of Chemistry and Biotechnology at the University of Tokyo, where he received his Ph.D. in 1984. His research interests include controlled macromolecular synthesis by metal complexes and biomimetic application of porphyrins and related compounds. He has received the Chemical Society of Japan Award for Young Chemists and the Society of Polymer Science, Japan Award.

Shohei Inoue is a professor of synthetic organic chemistry at the Department of Industrial Chemistry, Science University of Tokyo and professor emeritus of the University of Tokyo. Besides polymerization with metal complexes, his research interests include chemical fixation of carbon dioxide and asymmetric catalysis by synthetic polypeptides. He is now on the Advisory Board of the *Journal of Polymer Science.* He obtained his Ph.D. from Kyoto University in 1962.

---

† Present address: Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.

[1] Szwarc, M.; Levy, M.; Milkovich, R. *J. Am. Chem. Soc.* **1956**, *78*, 2656.

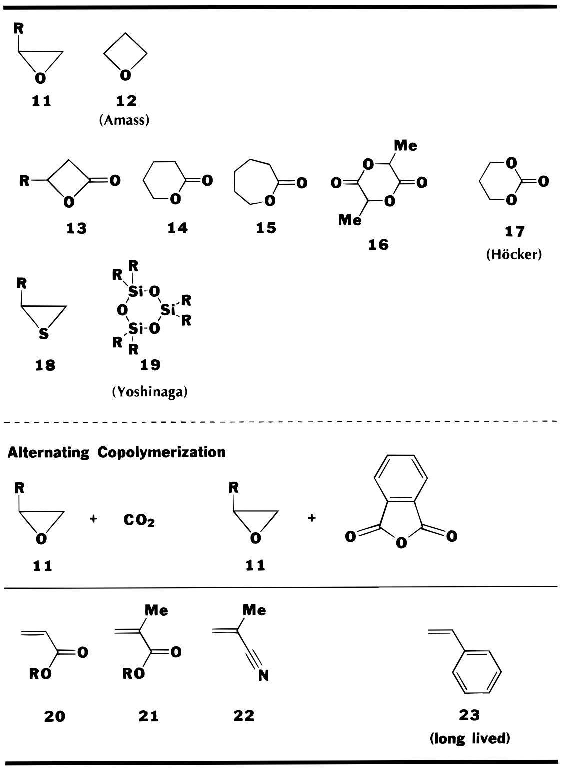
[2] Szwarc, M. *Nature* **1956**, *178*, 1168.

[3] Aida, T. *Prog. Polym. Sci.* **1994**, *18*, 469.

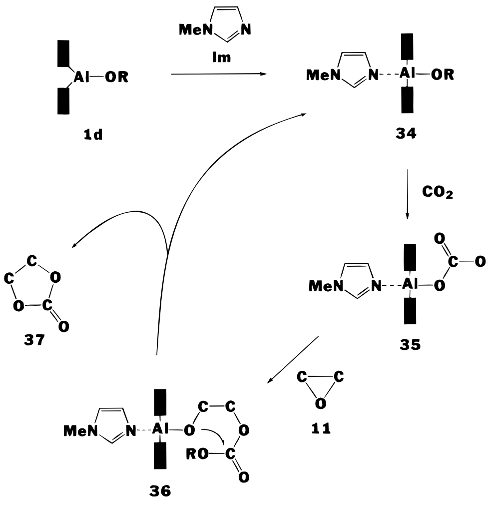
[4] Inoue, S.; Aida, T. Anionic Ring-Opening Polymerization. In *New Method for Polymer Synthesis*; Mijs, W. J., Ed.; Plenum: New York, 1992; p 33.

0001-4842/96/0129-0039$12.00/0

Table 1. Monomers for Living Polymerization with Metalloporphyrins



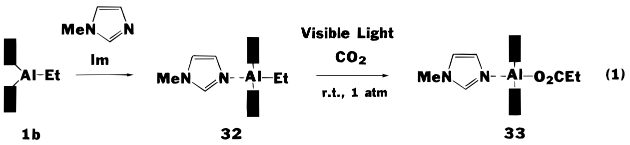
Scheme 1

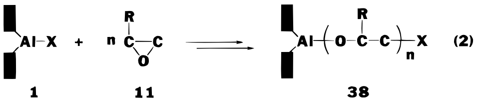


Background of the Discovery of the Unique Functions of Metalloporphyrins

Metalloporphyrins have attracted considerable attention because of their interesting biological functions as the active sites of hemoproteins and photosynthetic centers, where a mechanistic understanding and chemical modeling of their functions have been the central interests. In 1970s, we were exploring the chemical fixation of carbon dioxide by using some metalloporphyrins, with the intention of realizing the catalytic conversion of carbon dioxide by solar energy. Among a variety of metalloporphyrins, we chose metalloporphyrins of aluminum and zinc as the candidates, based on our discovery in 1968 of the alternating copolymerization of carbon dioxide and epoxides with some organoaluminum and zinc-based initiators.[5]

Unlike trialkylaluminums, an alkylaluminum porphyrin such as ethylaluminum tetraphenylporphyrin (**1b**) does not react with carbon dioxide under ambient conditions. On the other hand, under irradiation with visible light in the presence of an axially coordinating base such as 1-methylimidazole (MeIm), carbon dioxide is inserted into the aluminum−carbon bond in **32** to form the corresponding aluminum carboxylate species (**33**) (eq 1).[6] In contrast, an aluminum alkoxide complex (**1d**) reacts with carbon dioxide regardless of visible light irradiation when MeIm is present.[7] As shown in Scheme 1, the trapped carbon dioxide in the form of an aluminum carbonate (**35**) is catalytically transferred to epoxides, affording cyclic carbonates (**37**).[8] On the other hand, the reaction in the absence of MeIm results in the polymerization of epoxides without formation of cyclic carbonate. Further studies on this finding led us to the development of the living polymerization of epoxides (eq 2).[9]



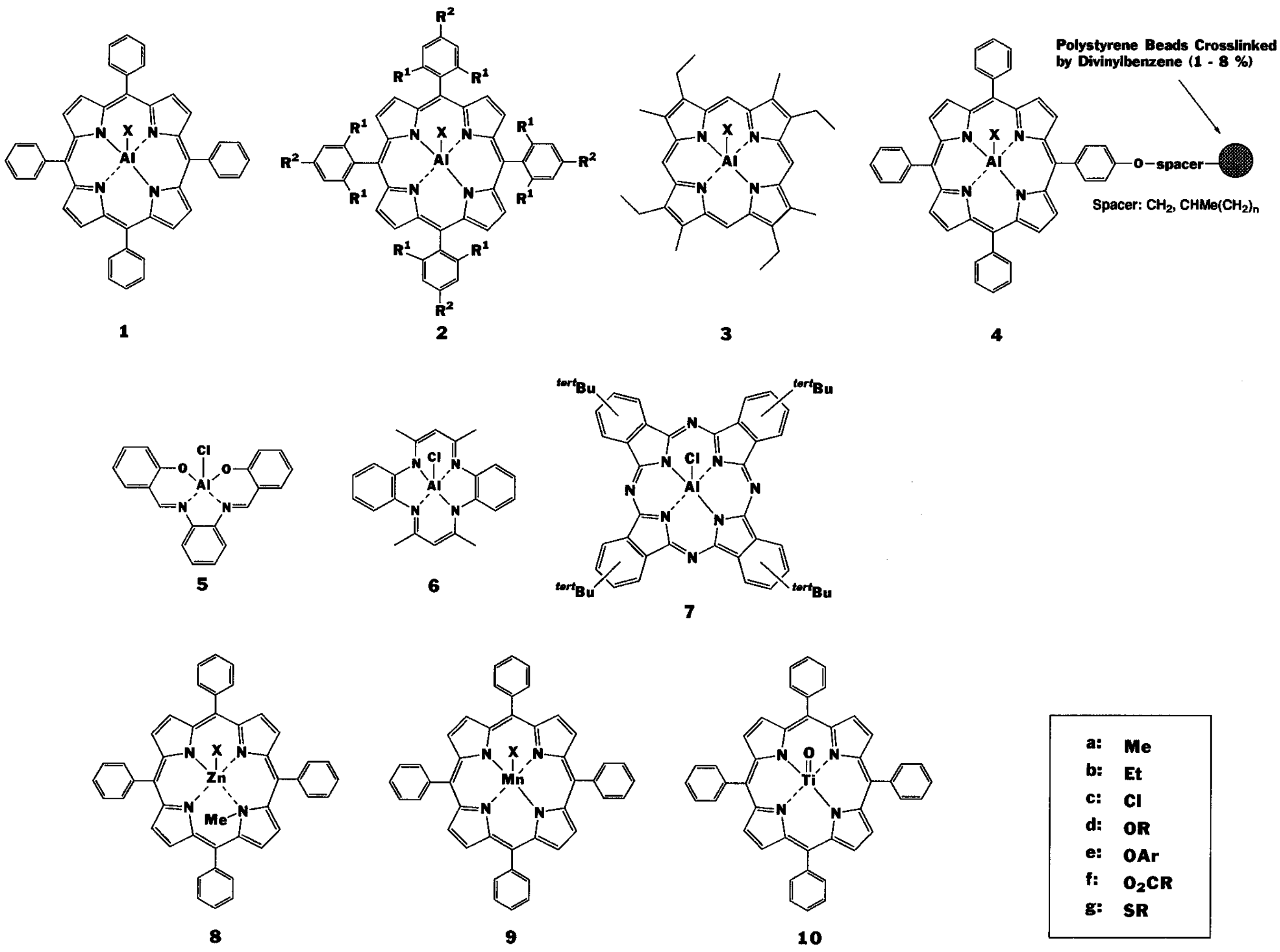


Applicability of Metalloporphyrin Initiators

The metalloporphyrins so far examined are aluminum porphyrins (**1**), zinc *N*-methylporphyrins (**8**), manganese porphyrins (**9**), and titanium porphyrins (**10**), in which aluminum porphyrins are the best initiators of wide applicability (Chart 1). In addition to epoxides (**11**), heterocyclic monomers such as lactones with four-, six-, and seven-membered rings (β-, γ-, and ϵ-lactones) (**13−15**)[10−12] and lactide (**16**)[13] are polymerized by aluminum porphyrin initiators to give narrow MWD polyesters (Table 1). The living polymerizations of a cyclic carbonate (**17**), cyclic siloxanes (**19**), and a four-membered cyclic ether (**12**, oxetane) with aluminum porphyrins (**1**) as initiators have been reported by Höcker,[14] Yoshinaga,[15] and Amass,[16] respectively. In the presence of ammonium or phosphonium salts, **1c** brings about the living alternating copolymerizations of epoxides with carbon dioxide or phthalic anhydride, affording polycarbonates[17] or polyesters[18,19] with narrow MWD. In addition to these

(5) Inoue, S. *CHEMTECH* **1976**, *6*, 588.
(6) Inoue, S.; Takeda, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 984.
(7) Takeda, N.; Inoue, S. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 3564.
(8) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1983**, *105*, 1304.
(9) Takeda, N.; Inoue, S. *Makromol. Chem.* **1978**, *179*, 1377.
(10) (a) Yasuda, T.; Aida, T.; Inoue, S. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 585. (b) Yasuda, T.; Aida, T.; Inoue, S. *Macromolecules* **1983**, *16*, 1792. (c) Yasuda, T.; Aida, T.; Inoue S. *Macromolecules* **1984**, *17*, 2217.
(11) Shimasaki, K.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 3076.
(12) Endo, M.; Aida, T.; Inoue, S. *Macromolecules* **1987**, *20*, 2982.
(13) Trofimoff, L. R.; Aida, T.; Inoue, S. *Chem. Lett.* **1987**, 991.
(14) Hovestadt, H.; Keul, H.; Höcker, H. *Polymer* **1992**, *33*, 1941.
(15) Yoshinaga, K.; Iida, Y. *Chem. Lett.* **1991**, 1057.
(16) Amass, A. J.; Perry, M. C.; Riat, D. S.; Tighe, B. J.; Colclough, E.; Steward, M. J. *Eur. Polym. J.* **1994**, *30*, 641.
(17) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8.
(18) Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1985**, *107*, 1358.
(19) Aida, T.; Sanuki, K.; Inoue, S. *Macromolecules* **1985**, *18*, 1049.

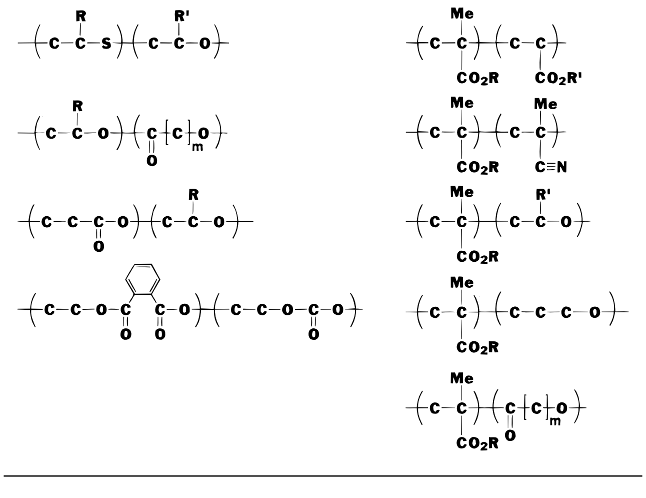
Chart 1



heterocyclic monomers, some polar vinyl monomers such as methacrylic[20] and acrylic esters[21] and methacrylonitrile[22] (**20**−**22**) are also polymerizable via a living mechanism. The living polymerization of methacrylic esters has been utilized by Kodaira *et al.* for the synthesis of liquid crystalline poly(methacrylic esters) with narrow MWD.[23] For the living polymerization of an episulfide (**18**) such as propylene sulfide (R = Me), a zinc complex of *N*-methylporphyrin such as **8** is effective,[24] whereas that by **1** is accompanied by desulfurization and lacks living character. **8** is also effective for the living polymerization of epoxides.[25] A manganese(III) porphyrin (**9**) serves as an excellent initiator for the living polymerization of epoxides.[26] Furthermore, an oxotitanium(IV) porphyrin such as **10** in conjunction with triethylaluminum gives rise to the polymerization of styrene, where a narrow MWD polymer is formed under optimal conditions.[27]

By virtue of the wide applicability of the metalloporphyrin initiators, a variety of tailored block copolymers with narrow MWD have been synthesized (Table 2), some of which are not obtainable by other initiators. Representative examples are the methacrylate−epoxide[28] and −oxetane[29] block copolymers, since no initiators other than aluminum porphyrins have been reported effective for the living polymerization of all three monomers.

Table 2. Tailored Block Copolymers by Metalloporphyrin Initiators



---

[20] Kuroki, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1987**, *109*, 4737.

[21] Hosokawa, Y.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1991**, *24*, 824.

[22] Inoue, S.; Aida, T.; Kuroki, M.; Hosokawa, Y. *Makromol. Chem., Macromol. Symp.* **1990**, *32*, 255.

[23] Kodaira, T.; Yamamoto, M.; Urushisaki, M.; Hashimoto, T. *Polym. Prepr. Jpn.* **1993**, *42*, 337.

[24] Aida, T.; Kawaguchi, K.; Inoue, S. *Macromolecules* **1990**, *23*, 3887.

[25] Watanabe, Y.; Aida, T.; Inoue, S. *Macromolecules* **1990**, *23*, 2612.

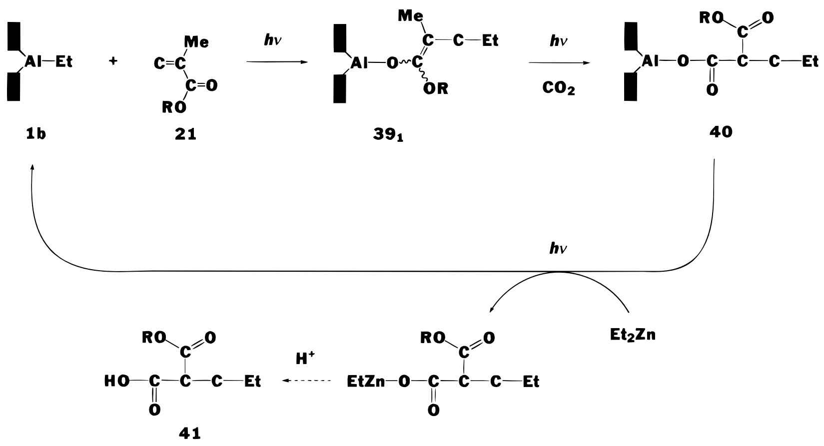
[26] Kuroki, M.; Aida, T.; Inoue, S. *Makromol. Chem.* **1988**, *189*, 1305.

[27] Shibata, K.; Aida, T.; Inoue, S. *Polym. Prepr. Jpn.* **1992**, *41*, 303.

[28] Kuroki, M.; Nashimoto, S.; Aida, T.; Inoue, S. *Macromolecules* **1988**, *21*, 3114.

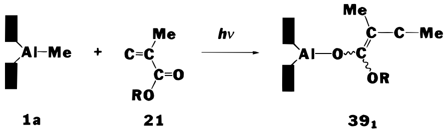
[29] Takeuchi, D.; Watanabe, Y.; Aida, T.; Inoue, S. *Macromolecules* **1995**, *28*, 651.

Scheme 2

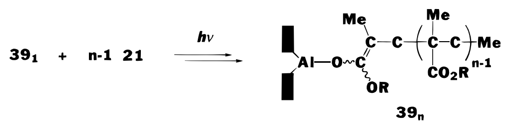


Effect of Visible Light

As mentioned above, our interest in metalloporphyrins has emerged from the possibility of the effect of visible light on their reactions. As for the polymerization reactions, this has been actually observed for the first time in the polymerization of methacrylic esters.[20] When an alkylaluminum porphyrin such as **1a** is used as initiator, the polymerization of methacrylic esters takes place only under irradiation with visible light, but not in the dark even at a high temperature such as 80 °C. The active species in the polymerization of methacrylic esters has been found to be an aluminum enolate (eqs 3-1 and 3-2). The initiation reaction (eq 3-1) does not take place in the dark, while the propagation reaction (eq 3-2) proceeds even in the dark, but is accelerated by visible light.



(3-1)

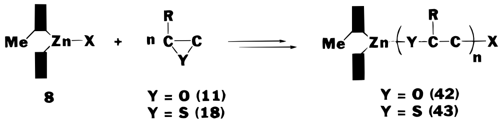


(3-2)

An aluminum thiolate complex such as **1g** is also an effective initiator for the living polymerization of acrylic and methacrylic esters, in which, however, the initiation does not require irradiation with visible light.[21] The acceleration effect of visible light on the chain growth step has been also observed for the polymerization of methacrylonitrile in the presence of an axially coordinating base such as pyridine.[22] In contrast with these two examples, where the polymer chains are formed by repeated C−C bond forming reactions, the effect of visible light has not been observed for the ring-opening polymerization of epoxides with aluminum porphyrins.

The discovery of the effect of irradiation on the polymerization of methacrylic esters has been successfully extended to the development of visible light driven catalytic formation of malonic ester derivatives (**41**) from carbon dioxide, methacrylic esters, and diethylzinc (Et_2Zn).[30,31] Scheme 2 shows the catalytic cycle of this reaction, where (1) **1b** first reacts with a methacrylic ester (**21**) to generate an aluminum enolate species (**39_1**), (2) which then reacts with carbon dioxide, (3) followed by ligand exchange of the resulting aluminum malonate species (**40**) with Et_2Zn, to regenerate the starting alkylaluminum porphyrin (**1b**) with elimination of the product from the active site of the catalyst. Similarly, methacrylonitrile (**22**) is also catalytically carboxylated to form an α-cyano carboxylic acid under irradiation with visible light. Also of interest to note here is the fact that the effect of visible light is observed for all three elementary reactions.

As already described, a *N*-substituted porphyrin (**8g**) is capable of initiating the living polymerizations of epoxides (**11**)[25] and episulfides (**18**)[24] (eq 4), where the former is accelerated by visible light, whereas the latter is not. This finding has been extended to the first synthesis of an epoxide−episulfide copolymer rich in the cross-propagation sequence.[32] Anionic copolymerization of epoxide and episulfide usually gives a copolymer rich in the homopropagation sequences, because the latter is much more reactive than the former toward nucleophiles. When the copolymerization initiated with **8g** is carried out in the dark, a copolymer with a lower content of the cross-propagation sequence is formed. In contrast, under irradiation, the reaction of the alkoxide growing species (originating from epoxide) with episulfide is accelerated, and the content of the cross-propagation sequence is increased. This is the first example of a copolymerizability change by visible light.



(4)

Structure−Reactivity Relationship of Aluminum Porphyrin Initiators

The polymerizations initiated with aluminum porphyrins proceed on the central metal atom of the porphyrin complex, so the reactivities of the initiating and propagating species are affected by the structure of the porphyrin ligand. For example, in the case of the polymerization of β-propiolactone (**13**), an aluminum tetraphenylporphyrin carrying methoxy groups at the ortho positions of the phenyl rings (**2**, $R^1 = R^2$

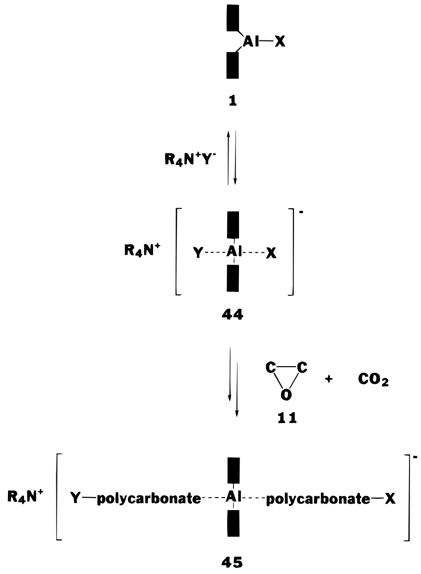
---

(30) Hirai, Y.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1989**, *111*, 3062.

(31) Komatsu, M.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1991**, *113*, 8492.

(32) Watanabe, Y.; Aida, T.; Inoue, S. *Macromolecules* **1991**, *24*, 3970.

Scheme 3



= OMe) is much more active than the nonsubstituted aluminum tetraphenylporphyrin (**1**), while that having methyl groups (**2**, $R^1 = R^2 =$ Me) in place of methoxy groups is much less active than **1**.[33] Furthermore, **2** bearing phenyl substituents at the ortho positions (R^1 = Ph, R^2 = H) is virtually inactive for the polymerization of β-propiolactone.

Of further interest to note is that the activities of aluminum complexes of a Schiff base (**5**),[34] a tetraazaannulene (**6**),[35] and a phthalocyanine (**7**) are much lower than those of aluminum porphyrins. For example, the polymerization of propylene oxide with **5** as initiator does not occur at room temperature, but requires a higher temperature such as 80 °C.

External Tuning of Nucleophilicity: Living Alternating Copolymerization of Epoxide with Carbon Dioxide or Cyclic Anhydride

As already described briefly, alkoxyaluminum porphyrins (**1d**) require the assist of an externally added Lewis base such as 1-methylimidazole for the reaction with carbon dioxide, where the base coordinates to **1d** from the back side to give a highly nucleophilic six-coordinate complex (**34**) (trans effect) (eq 1). The effect of an external ligand has been also observed for the anionic polymerization of methacrylonitrile (**22**) initiated from the living polymer of methyl methacrylate, in which the chain growth is promoted by pyridine to afford a narrow MWD block copolymer.[22] These facts indicate the possibility of external tuning of the nucleophilicity of aluminum porphyrins. In connection with these studies, we have also found that the anionic group of an onium salt coordinates to the back side of the aluminum porphyrin (**1**), to generate the corresponding six-coordinate aluminum porphyrin species (**44**) (Scheme 3).[18] Furthermore, the six-coordinate complex (**44**) formed here is capable of initiating the living alternating copolymerization of carbon dioxide[17] or phthalic anhydride[19] with epoxides, affording narrow MWD polycarbonates or polyesters. In contrast, the copolymerization in the absence of onium salts gives copolymers consisting mostly of polyethers, as expected from the very low reactivity of the alkoxide species toward carbon dioxide and phthalic anhydride. NMR and UV−vis studies have shown that the copolymerization proceeds on both sides, respectively, of an aluminum porphyrin plane, retaining the highly nucleophilic six-coordinate structure (**45**).[18] This is a good demonstration of the external tuning of the nucleophilicity of aluminum porphyrins. Advantage has been taken of the living character of these copolymerizations to successfully synthesize binary and ternary block copolymers consisting of polycarbonate and polyester segments (Table 2).[17]

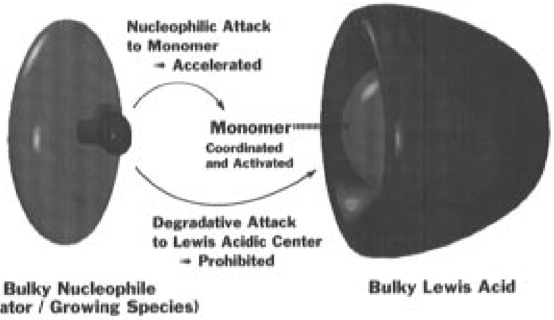


Figure 2. A schematic diagram of the concept of the Lewis acid assisted "high-speed" living anionic polymerization.

External Tuning of Lewis Acidity: Lewis Acid Assisted High-Speed Living Anionic Polymerization

It is well-known that nucleophilic reactions are promoted by Lewis acids through coordination and activation of substrates, in which, however, a side reaction such as degradative attack of nucleophiles to Lewis acids (neutralization) is usually inevitable. On the other hand, we have proposed Lewis acid assisted high-speed living anionic polymerization, in which the degradative nucleophile−Lewis acid neutralization is sterically suppressed by the combination of bulky Lewis acids with aluminum porphyrins as nucleophiles.[36] Figure 2 shows a schematic diagram of the Lewis acid assisted high-speed living anionic polymerization, where the nucleophile and Lewis acid are both so large that they are unable to react directly with each other, while monomer is able to coordinate to the Lewis acid and is activated for nucleophilic attack.

An example of high-speed living anionic polymerization is shown by the polymerization of methyl methacrylate (MMA, **21** (R = Me)) initiated with (TPP)AlMe (**1a**) ($[\mathrm{MMA}]_0/[\mathbf{1a}]_0 = 217$) in CH_2Cl_2, where the polymerization at 35 °C under irradiation with visible light (>420 nm) proceeds to only 6.1% conversion in 2.5 h, but proceeds dramatically rapidly upon addition of a sterically crowded methylaluminum diphenolate (**48** (Table 3), 0.14 mol % with respect to MMA) to the system and is completed within 3 s.[36] This corresponds to the acceleration of polymerization by a factor of at least 45 300. The produced polymer has a narrow MWD ($M_w/M_n = 1.09$), where the M_n value (25 500) is close to the theoretical one (21 700), as expected from the assumption that every molecule

---

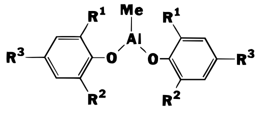
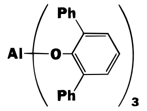
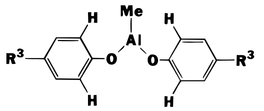
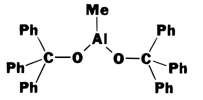
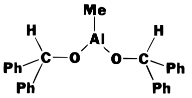
[33] Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1990**, *23*, 2869.

[34] Vincens, V.; Le Borgne, V.; Spassky, N. *Makromol. Chem., Rapid Commun.* **1989**, *10*, 623.

[35] Yoshida, Y.; Sano, S.; Inoue, S. *Polym. Prepr. Jpn.* **1980**, *29*, 141.

[36] Kuroki, M.; Watanabe, T.; Aida, T.; Inoue, S. *J. Am. Chem. Soc.* **1991**, *113*, 5903.

Table 3. Lewis Acids for High-Speed Living Polymerization of Methacrylic Esters[a]

Accelerator	Terminator
Ph_3Al	Me_3Al Et_3Al iso-Bu_3Al
 $R^1 = R^3 = {}^{tert}Bu$, $R^2 = H$ (46) $R^1 = R^2 = R^3 = {}^{tert}Bu$ (47) $R^1 = R^2 = {}^{tert}Bu$, $R^3 = Me$ (48) $R^1 = R^3 = Ph$, $R^2 = H$ (49)  50	 51
 52	 53
$(C_6H_5)_3B$ $(C_6F_5)_3B$	$BF_3{\cdot}OEt_2$ BCl_3

[a] Initiator: aluminum tetraphenylporphyrin (**1**).

of **1a** as initiator produces one polymer molecule. When the mole ratio of **48** to **1a** is increased while the mole ratio of methyl methacrylate to **1a** is held constant, the magnitude of the acceleration becomes much more pronounced, while the molecular weight of the produced polymer remains unchanged.[37] On the other hand, upon increment of the mole ratio $[MMA]_0/[\mathbf{1a}]_0$, the polymer molecular weight increases proportionally, and a monodisperse, high molecular weight polymer with $M_n > 10^6$ has been synthesized in a short polymerization time.[38] A thiolate complex of aluminum porphyrin such as (TPP)AlSPr (**1g**) is a more convenient initiator than (TPP)AlMe (**1a**) for the high-speed living polymerization of methyl methacrylate,[39] since **1g** does not require irradiation for initiating the polymerization.[21]

Lewis acid assisted high-speed living anionic polymerization can be applied not only to the accelerated synthesis of narrow MWD poly(methacrylic esters) but also to the ring-opening polymerizations of epoxides (**11**)[40] and lactones (**14** and **15**)[41] with aluminum porphyrins and of episulfides (**18**)[42] with zinc *N*-substituted porphyrins (**8**).

For realizing high-speed living polymerization, the choice of Lewis acids is very important. As for the Lewis acid component, methylaluminum diphenoxides with bulky ortho substituent(s) (**46**−**49**) are representative of the effective candidates (Table 3),[37,43] while diphenoxides without ortho substituent(s) (**51**) are ineffective because of concomitant occurrence of the degradative attack of the nucleophilic growing species toward the Lewis acidic center. An aluminum triphenoxide such as **50** is also effective, as reported by Yamamoto *et al.*[44] The steric bulk of the porphyrin ligand also plays a role. A good example of this can be seen in the polymerization of methyl methacrylate (**21**, R = Me) by three aluminum porphyrin initiators with different steric environments (**1a**, **2** ($R^1 = R^2 =$ Me), and **3**) (Figure 3),[45] where the polymerization initiated with the least bulky **3** is terminated as soon as triisobutylaluminum (i-Bu_3Al) is added, while that with the most bulky **2** ($R^1 = R^2 =$ Me) is not terminated by i-Bu_3Al but is accelerated to attain 100% monomer conversion, affording a narrow MWD polymer. On the other hand, the polymerization with **1a** having an intermediate steric bulk between that of **2** ($R^1 = R^2 =$ Me) and **3** is accelerated by i-Bu_3Al at the initial stage, but is terminated before completion.

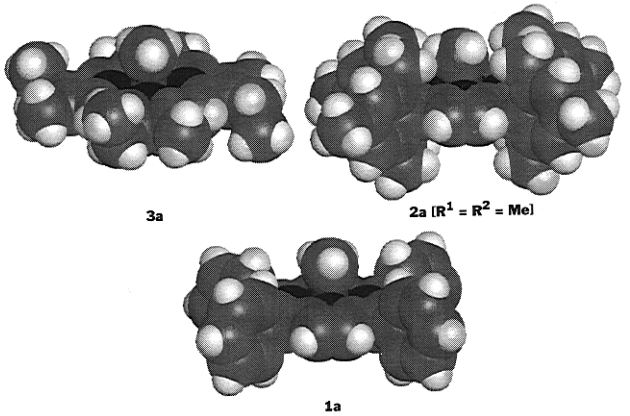


Figure 3. Space-filling representations of aluminum porphyrins **1a**, **2a** ($R^1 = R^2 =$ Me), and **3a**.

As for the Lewis acid component, organoboron compounds can also be used as excellent accelerators for the polymerization of methyl methacrylate initiated with **1a**, where triphenylboron and tris(perfluorophenyl)boron are very effective.[46] On the other hand, tributylboron bearing no particular steric hindrance does not terminate the polymerization. This is in sharp contrast with the case using trialkylaluminum as monomer activator and gives an indication that, in the case of organoborons as the accelerators, their lower reactivities toward nucleophiles are more important than the steric factors for suppressing the undesired degradative reaction between the nucleophile and the Lewis acid.

As already described, the aluminum complexes of a Schiff base (**5**), a tetraazaannulene (**6**), and a phthalocyanine (**7**) have much lower activities than aluminum porphyrins for the polymerization of propylene oxide. However, in the presence of an appropriate Lewis acid such as **48**, the polymerizations with these initiators proceed even at room temperature, affording polymers with fairly narrow MWD.[40]

---

(37) Sugimoto, H.; Kuroki, M.; Watanabe, T.; Kawamura, C.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 3403.

(38) Adachi, T.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1992**, *25*, 2280.

(39) Adachi, A.; Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 1238.

(40) Sugimoto, H.; Kawamura, C.; Kuroki, M.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 2013.

(41) Isoda, M.; Sugimoto, H.; Aida, T.; Inoue, S. *Polym. Prepr. Jpn.* **1992**, *41*, 2038.

(42) Sadamoto, R.; Watanabe, Y.; Aida, T.; Inoue, S. *Polym. Prepr. Jpn.* **1992**, *41*, 301.

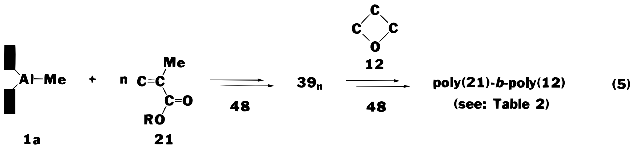
(43) Aida, T.; Kuroki, M.; Sugimoto, H.; Watanabe, T.; Adachi, T.; Kawamura, C.; Inoue, S. *Makromol. Chem., Macromol. Symp.* **1993**, *67*, 125.

(44) Maruoka, K.; Akakura, M.; Yamamoto, H. *Synlett* **1995**, 81.

(45) Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1994**, *27*, 3672.

(46) Sugimoto, H.; Aida, T.; Inoue, S. *Macromolecules* **1993**, *26*, 4751.

As a strategical extension of the principle of Lewis acid assisted high-speed living anionic polymerization, we have succeeded in the asymmetric selective polymerization of racemic 1-phenethyl methacrylate by aluminum porphyrin **1a** by using a sterically hindered, chiral Lewis acid, where (*R*)- or (*S*)-monomer is preferentially activated depending on the chirality of the Lewis acid.[47] Another interesting application is the achievement of living anionic polymerization of oxetane (**12**).[29] Oxetane is the most basic cyclic ether, with a low susceptibility toward nucleophiles, and has been categorized in the monomer as only cationically polymerizable. Due to the poor controllability of cationic polymerization, it is very difficult to synthesize a polyoxetane with narrow MWD. However, aluminum porphyrins (**1c** and **1d**) in conjunction with a Lewis acid such as **48** bring about the anionic polymerization of oxetane under mild conditions, affording a narrow MWD polymer. By virtue of this achievement, a novel polyvinyl–polyether block copolymer with narrow MWD has been synthesized by the sequential high-speed living polymerization of methyl methacrylate followed by oxetane with the **1a**–**48** system (eq 5).[29] Amass *et al.* have reported that oxetane is polymerizable with a chloroaluminum porphyrin (**1c**) alone as initiator at an elevated temperature such as 60 °C.[16] We have confirmed that the initiation of polymerization takes place even at room temperature in the absence of **48**, whereas the subsequent propagation does not occur. Further extensions of the high-speed living polymerization involve molecular design of an aluminum porphyrin initiator with a *built-in* Lewis acidic monomer activation site, which by itself is capable of causing a rapid polymerization of methyl methacrylate without the aid of external Lewis acid.[48]



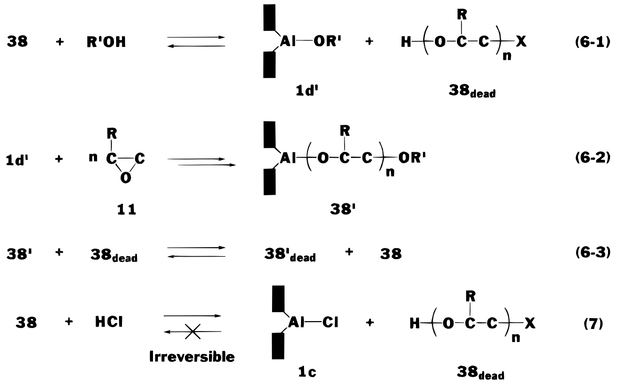
In relation to our studies, the polymerizations of methacrylic esters with alkyllithium–trialkylaluminum systems,[49] alkyllithium–bulky organoaluminum systems,[50] and enamine–bulky organoaluminum systems[51] have been reported by Hatada, Ballard, and Miyamoto *et al.*, respectively.

Rapid, Reversible Axial Ligand Exchange: Immortal Polymerization

As already mentioned, living polymerization requires the absence of termination and chain transfer reactions. As a consequence, a polymer with narrow MWD is formed with the number of molecules equal to the number of initiator molecules. However, it should be noted that the term "living" does not mean the "immortality" of the growing polymer. That is, the growth of a polymer molecule can be stopped intentionally or accidentally by terminating agents.

We have proposed "immortal" polymerization, in which a polymer with narrow MWD is formed with the number of molecules exceeding the number of initiator molecules.[3,4] Immortal polymerization involves a chain transfer reaction. In the usual sense, "chain transfer reaction" is a side reaction, by which the growth of a polymer molecule is irreversibly terminated, while a new polymer chain is formed to grow. On the contrary, in immortal polymerization, the chain transfer reaction involved is reversible and much more rapid than the chain growth. Consequently, a narrow MWD polymer is formed with the number of polymer molecules exceeding the number of initiator molecules. In this sense, immortal polymerization is the "catalytic" version of living polymerization. We noticed this possibility in the course of studies on the polymerization of epoxides with aluminum porphyrin initiators, proceeding via an aluminum alkoxide (**38**) as the growing species (eq 2).

A representative example is the polymerization of propylene oxide (**11**, R = Me) initiated with **1c** in the presence of alcohol as chain transfer agent.[52] In this case, the exchange between the growing alkoxide species and alcohol (eq 6-1) leads to chain transfer reaction, since the resulting aluminum alkoxide (**1d′**) is able to reinitiate the polymerization (eq 6-2). Furthermore, this exchange reaction (eq 6-1) takes place reversibly and much more rapidly than the reaction between **38** (**38′**) and epoxides (eqs 2 and 6-2), thereby allowing the catalytic formation of a narrow MWD polymer. The naming of "immortal" polymerization comes from the fact that the polymerization of epoxides is not terminated by a strong acid such as hydrogen chloride.[53] Although hydrogen chloride reacts with the growing alkoxide species irreversibly (eq 7), the resulting chloroaluminum porphyrin (**1c**) is capable of reinitiating the polymerization, so that an aluminum alkoxide (**38**), exchangeable with the dead polymer bearing a hydroxyl functionality ($\mathbf{38}_{\text{dead}}$), is regenerated and the polymerization ensues with immortal character. This is in sharp contrast with the anionic polymerization of epoxides with sodium or potassium hydroxide or alkoxide, where the polymerization is terminated by hydrogen chloride, because the resulting sodium chloride is unable to reinitiate the polymerization. Thus, the immortal character of



---

[47] Watanabe, Y.; Aida, T.; Inoue, S. *Polym. Prepr. Jpn.* **1994**, *43*, 173.

[48] Kinugawa, M.; Aida, T.; Inoue, S. *Polym. Prepr. Jpn.* **1993**, *42*, 2232.

[49] Kitayama, T.; Shinozaki, T.; Masuda, E.; Yamamoto, M.; Hatada, K. *Polym. Bull.* **1988**, *20*, 505.

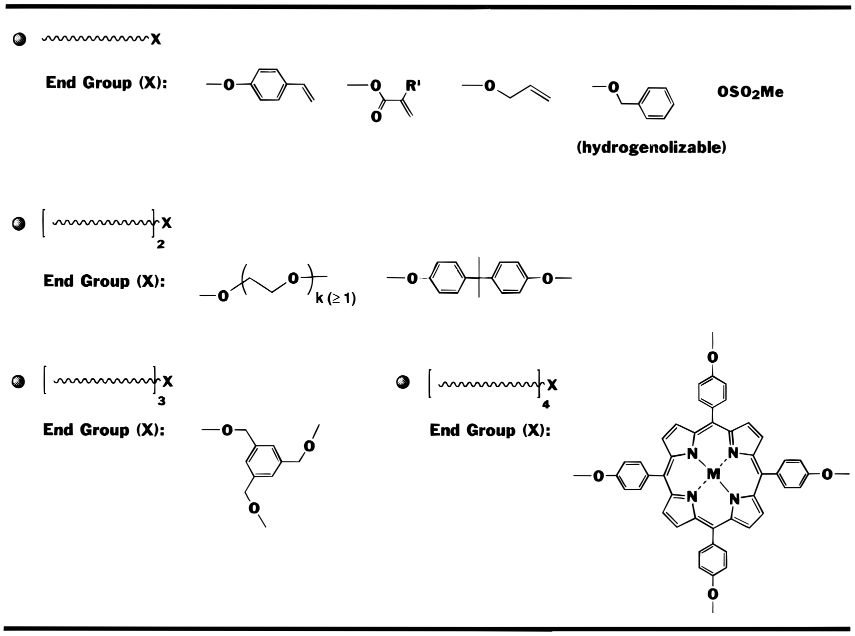
[50] Ballard, D. G. H.; Bowles, R. J.; Haddleton, D. M.; Richards, S. N.; Sellens, R.; Twose, D. L. *Macromolecules* **1992**, *25*, 5907.

[51] Kanetaka, S.; Miyamoto, M.; Saegusa, T. *Polym. Prepr. Jpn.* **1990**, *39*, 220.

[52] Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148.

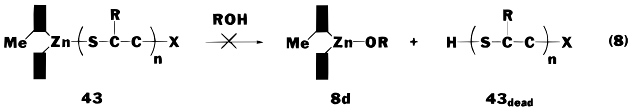
[53] Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. *Macromolecules* **1988**, *21*, 1195.

Table 4. End-Functionalized Polymers and Oligomers by Immortal Polymerization

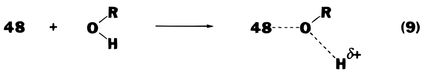


polymerization is due to the unusual reactivity of the aluminum–axial ligand bond in aluminum porphyrin **1**.

By selection of appropriate transfer agents, immortal polymerizations with metalloporphyrins can be applied also to lactones and lactide.[53] In addition to aluminum porphyrins (**1**), an acetate complex of manganese porphyrin (**9f**) gives rise to the immortal polymerization of propylene oxide (**11**, R = Me) by using alcohol as chain transfer agent.[26] A tholate complex of zinc *N*-substituted porphyrin (**8g**) also brings about the immortal polymerizations of epoxides (**11**) and episulfides (**18**) using alcohol and thiol, respectively, as chain transfer agents.[24,25] Interestingly, the polymerization of **18** with **8g** in alcohol does not display immortal character, since the propagating thiolate species (**43**) is not exchangeable with alcohol (eq 8).



In principle, the number of polymer molecules in immortal polymerization can be increased by increasing the mole ratio of chain transfer agent to initiator, but the polymerization at a higher concentration of chain transfer agent is unfortunately slower. However, on the basis of the principle of Lewis acid assisted high-speed living polymerization (Figure 2), the immortal polymerization of propylene oxide could be dramatically accelerated, retaining the immortal character, by the addition of a sterically crowded Lewis acid such as **48**, where an excess of 1000 polymer molecules relative to the initiator molecules has been achieved under appropriate conditions.[54] Formation of a narrow MWD polymer here indicates that not only the chain growth but also the reversible exchange between the aluminum alkoxide growing species with alcohol is accelerated by **48**. In fact, the exchange between the aluminum 2-propoxide complex (**1d**, R = $CHMe_2$) and 2-propanol ($[\text{2-propanol}]_0/[\mathbf{1d}]_0 = 13$, in CD_2Cl_2) is accelerated by **48** (3 equiv with respect to **1d**) by a factor of at least 50, as determined by the ^1H NMR saturation transfer method.[54] The accelerated alcoholate–alcohol exchange in the presence of **48** is considered as a consequence of the interaction of alcohol with **48** (eq 9).



Immortal polymerization is an effective method for the synthesis of end-functionalized polymers and oligomers with narrow MWD (Table 4). For example, use of unsaturated protic chain transfer agents such as acrylic acid, methacrylic acid, and 2-hydroxyethyl methacrylate for immortal polymerization leads to polymers carrying polymerizable end groups (macromonomers).[55] Multifunctional protic chain transfer agents such as diols and triols enable the synthesis of telechelic and star-shaped polymers. The novel amphiphilic porphyrin carrying four polyether side chains of the same chain length (**55**) has been synthesized from **54** by the immortal polymerization of epoxyethane (**11**, R = H) initiated with **1c** (eq 10), where the length of the four poly(oxyethylene) side chains can be controlled by the mole ratio of epoxyethane to **54**.[56] Due to its amphiphilic character, **55** spontaneously forms cofacial aggregates in aqueous media depending on the length of the water-soluble polyether side chains. McGrath *et al.* have shown the applicability of immortal polymerization to the synthesis of a poly(propylene oxide) with primary hydroxyl functionality at both terminals,[57] which is particularly useful as a prepolymer for the production of segmented polyurethane.

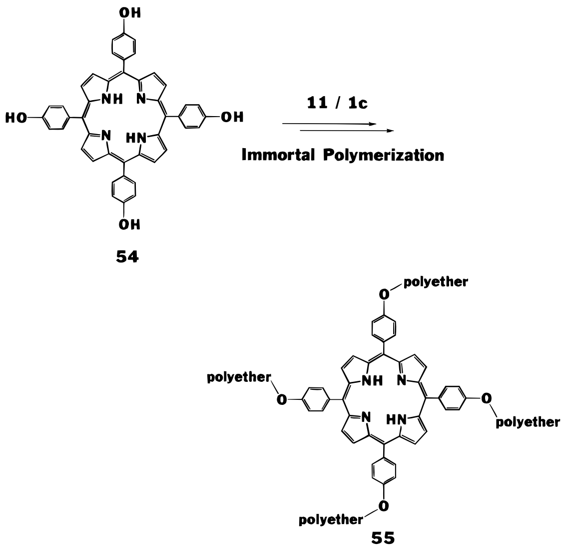
---

(54) Akatsuka, M.; Aida, T.; Inoue, S. *Macromolecules* **1995**, *28*, 1320.

(55) Inoue, S.; Aida, T. *Makromol. Chem., Macromol. Symp.* **1986**, *6*, 217.

(56) Aida, T.; Takemura, A.; Fuse, M.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1988**, 391.

(57) Yoo, Y.; McGrath, J. E. *Makromol. Chem., Macromol. Symp.* **1991**, *42/43*, 387.



54

55

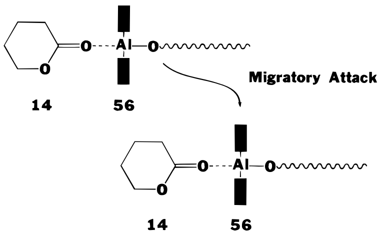
(10)

The principle of immortal polymerization indicates the possibility of recycling the aluminum porphyrin initiator. In order to facilitate the isolation of polymer and regeneration of initiator, an aluminum porphyrin bound to cross-linked polystyrene (**4**) has been developed by Mizutani *et al.*[58] For example, the immortal polymerization of propylene oxide (PO) initiated with **4** ($[PO]_0/[MeOH]_0/[\mathbf{4}]_0 = 200/7/1$) can be repeated nine times without any loss of the initiator activity and any broadening of the polymer MWD.

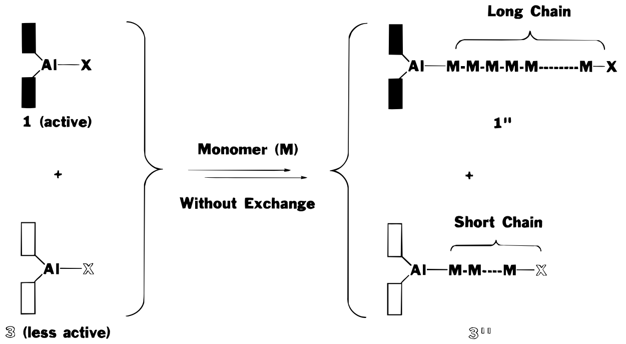
Mechanistic Consideration of the Controlled Polymerizations with Aluminum Porphyrin Initiators

It would be interesting to know why aluminum porphyrins are of wide applicability as initiators for living polymerization. Remember that the formation of a narrow MWD polymer requires (1) faster initiation than propagation, (2) absence of termination, (3) absence of chain transfer unless reversible and rapid, and (4) uniform chain growth with respect to all growing polymer molecules. For discussing the well-behaved activity of the aluminum porphyrin initiators, polymerization of epoxides is a good example.[59] It is well-known that alkali metal alkoxides bring about the living anionic polymerization of ethylene oxide, affording a poly(oxyethylene) with a desired molecular weight with narrow MWD.[60] On the contrary, the anionic polymerization of propylene oxide with these initiators is accompanied by side reactions such as proton abstraction from the methyl group of the monomer to the growing species (chain transfer reaction), resulting in the formation of a low molecular weight polymer with terminal unsaturation.[61] High molecular weight polymers can be synthesized both from ethylene oxide and from propylene oxide by some coordinate anionic initiators such as a triethylaluminum–water–acetylacetone system,[62] indicating a low probability of chain transfer and termination in the coordinate anionic process. However, polyethers formed by these initiators are generally of very broad MWD.[63] These contrastive examples indicate the importance of (1) well-balanced nucleophilic and Lewis acidic character and (2) uniform reactivity of all the growing polymer molecules for controlled polymerization: Alkali metal based initiators are so nucleophilic that they are likely to undergo various side reactions. On the other hand, organoaluminum-based initiators are characterized by their well-balanced nucleophilicity and Lewis acidity, but their high tendency of aggregation obstructs uniform chain growth of all the growing polymer molecules. Compared with these representative initiators, aluminum porphyrins appear to possess relatively weak nucleophilicity and moderately high Lewis acidity, as judged from, *e.g.*, the poor reactivity toward carbon dioxide and a high coordinating ability toward nitrogen bases. Therefore, coordinative activation of monomer prior to the nucleophilic attack of the growing species may be responsible for chain growth. Furthermore, the uniform reactivity of the growing species should be assured by the large, macrocyclic porphyrin ligand.

Scheme 4



Scheme 5



In relation to this chelation effect of the porphyrin ligand, it is also interesting to know whether the chain growth of a particular polymer molecule proceeds on the active site of a particular metalloporphyrin molecule. A kinetic study made on the polymerization of δ-valerolactone (**14**) via a (porphinato)aluminum alkoxide (**56**) (Scheme 4) has indicated that the polymerization rate is second-order with respect to **56** but first-order with respect to the monomer.[11] We have also found that this polymerization is considerably accelerated by a highly Lewis acidic chloroaluminum porphyrin (**1c**) with no capability of initiating the polymerization of **14**. A kinetic study on this accelerated polymerization system has shown that the polymerization rate is expressed by $k[\mathbf{56}]_0/[\mathbf{1c}]_0/[\text{monomer}]_0$.[11] These two results suggest that the polymerization proceeds via the linear transition state mechanism involving simultaneous participation of two aluminum porphyrin molecules, one of which serves as nucleophilic growing species, the other as Lewis acidic

---

[58] Uno, H.; Tanaka, K.; Mizutani, Y. *React. Polym.* **1991**, *15*, 121.

[59] Inoue, S.; Aida, T. Cyclic Ethers. In *Ring-Opening Polymerization*; Ivin, K. J., Saegusa, T., Eds.; Elsevier: London, 1984; Vol. 3, p 185.

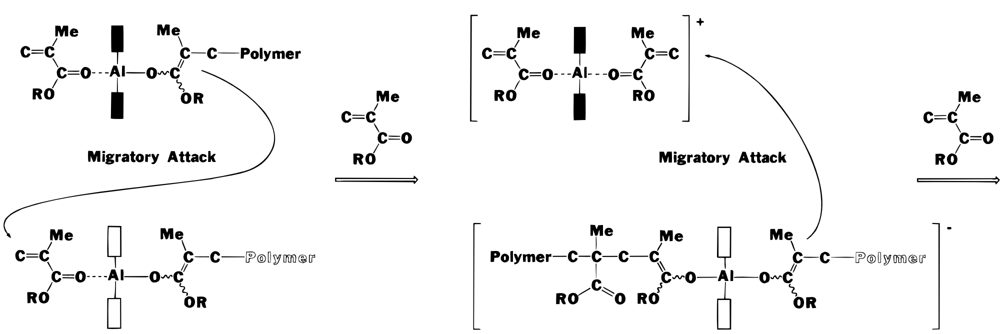
[60] Price, C. C.; Carmelite, D. D. *J. Am. Chem. Soc.* **1966**, *88*, 4039.

[61] Simons, D. M.; Verbanc, J. J. *J. Polym. Sci.* **1960**, *44*, 303.

[62] Vandenberg, E. J. *J. Polym. Sci.* **1960**, *47*, 486.

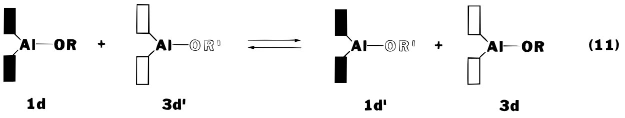
[63] Inoue, S.; Aida, T. Polyethers. In *Handbook of Polymer Synthesis*; Kricheldorf, H. A., Ed.; Dekker: New York, 1992; Part A, p 481.

Scheme 6



monomer activator (Scheme 4). The Lewis acid assisted high-speed living anionic polymerization (Figure 2) is a successful extension along the line of this study.

The linear transition state mechanism (Scheme 4) involves migratory attack of the active polymer end to the monomer coordinated with the other aluminum porphyrin molecule, resulting in the axial ligand (growing polymer) exchange between different aluminum porphyrin molecules. In relation to this possibility, we have investigated the polymerization of propylene oxide using two different aluminum porphyrins (**1** and **3**) with different reactivities, where **1** is much more reactive than **3**. In this case, if the growth of polymer molecules proceeds on individual active sites without exchange, a polymer with a bimodal MWD should result due to the difference in the rates of chain growth on **1** and **3** (Scheme 5). However, a polymer with a unimodal, sharp MWD is formed at a rate somewhere in between those with **1** and **3**, respectively, as initiators.[64] These results indicate the occurrence of the rapid alkoxide−alkoxide exchange during the polymerization. Later, this exchange reaction was found to take place even in the absence of the monomer, indicating the possibility of a direct exchange path (eq 11) in addition to the exchange as a consequence of the migratory chain growth (*e.g.*, Scheme 4). In addition to the alkoxides (**1d**), (porphinato)aluminum phenoxides (**1e**) and carboxylates (**1f**) are also subject to ligand exchange, indicating the highly ionic character of the aluminum−oxygen bonds in these complexes.



In contrast with these complexes, (porphinato)aluminum alkyls (**1a**,**b**) and enolates (**39**, eq 3) do not exchange their ligands, as determined from the ^{1}H NMR studies with appropriately labeled alkyl− and enolate−aluminum porphyrin complexes.[65] However, the polymerization of methyl methacrylate (**21**, R = Me) with a mixture of **1a** and **3a** (1/1) also results in the formation of a polymer with a single, sharp GPC pattern, where the rate of chain growth is intermediate between those with **1a** and **3a**, respectively, as initiators. When all of these observations are taken into account, the linear transition state mechanism (Scheme 6) seems most likely, where the growing enolate species migrates from one aluminum porphyrin molecule to the other whenever it adds to the monomer. This is in sharp contrast with the cyclic transition state mechanism proposed for the group transfer polymerization (GTP) of methacrylic esters via a silyl enolate as the growing species,[66] where the silyl group at the active end is transferred to the newly formed active end without exchange.[67]

The exchange phenomenon of the growing species is one of the important subjects worthy of discussion. Our study on this subject provides an indication that the multiplicity of the growing species, even though involved, does not always reflect the MWD of the produced polymer, when the growing species are transformed to each other reversibly and rapidly. Immortal polymerization, in which active and dormant species are simultaneously involved, is another good representation of this idea.

Conclusion

Metalloporphyrins of some nontransition metals such as aluminum and zinc and transition metals such as manganese and titanium bring about the controlled polymerization of a wide variety of heterocyclic and vinyl monomers, affording polymers and block copolymers with narrow MWD. The large, rigid macrocyclic porphyrin chelate assures the uniform reactivity of the growing polymer and also allows external tuning of the nucleophilicity/Lewis acidity balance of the active species without damaging the cleanness of the polymerization. Along the line of this work, one of the future interests would be the applicability of metalloporphyrin initiators to living “coordination” and “radical” polymerizations, which are not well explored to date. In this respect, an organocobalt porphyrin has recently been reported to bring about the living radical polymerization of acrylic monomers.[68]

We are grateful to the dedicated students of the University of Tokyo and researchers from Cao, Kansai Paint, Nippon Polyurethane, Tokuyama, and Unitika Co. Ltd., whose names appear in the references. We also thank the Ministry of Education, Science and Culture, Japan, and Science Foundations of Asahi Glass, ICI, Iketani, Ito, Izumi, Kawakami, Mazda, Nissan, Ogasawara, Tokuyama, Toray, and Yazaki for financial support.

AR950029L

---

(64) Asano, S.; Aida, T.; Inoue, S. *Macromolecules* **1985**, *18*, 2057.

(65) Aida, T.; Sugimoto, H.; Kuroki, M.; Inoue, S. *J. Phys. Org. Chem.* **1995**, *8*, 249.

(66) Sogah, D. Y.; Webster, O. W. In *Recent Advances in Mechanistic and Synthetic Aspects of Polymerization*; Fontanille, M., Guyot, A., Eds.; NATO ASI Ser. C215; Kluwer: Dordrecht, 1987; p 61.

(67) Recently, Quirk *et al.* have reported a possibility of silyl group exchange during GTP of methacrylic esters and claimed the presence of a dissociative species: Quirk, R. P.; Ren, J. *Macromolecules* **1990**, *23*, 4034.

(68) Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.