JOURNAL OF PHYSICAL ORGANIC CHEMISTRY, VOL. 8, 249–257 (1995)

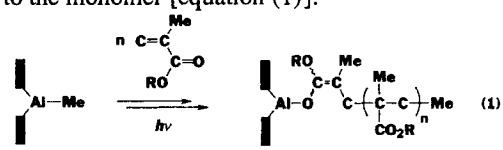
LIVING POLYMERIZATION OF METHACRYLIC ESTERS WITH ALUMINIUM PORPHYRIN INITIATORS. AXIAL LIGAND EXCHANGE ACTIVITIES OF ALKYL- AND ENOLATE-ALUMINIUM PORPHYRINS IN RELATION TO THE POLYMERIZATION MECHANISM

TAKUZO AIDA†, HIROSHI SUGIMOTO,* MASAKATSU KUROKI AND SHOHEI INOUE*,†
Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan

Polymerization of methacrylic esters such as benzyl methacrylate using as initiator an-equimolar mixture of methylaluminium 5,10,15,20-tetraphenylporphine [(TPP)AlMe] and 2,7,12,17-tetramethyl-3,8,13,18-tetramethylporphine [(EtioP)AlMe] proceeded from both initiators, affording a unimodal polymer of narrow molecular weight distribution, although the reactivities of (TPP)AlMe and (EtioP)AlMe are very different from each other. ^{1}H NMR studies on a mixture of two different (porphinato)aluminium enolates, the growing species, and a mixture of a (porphinato)aluminium enolate and an alcoholate, in the absence and presence of methyl methacrylate (MMA or MMA-d_8), indicated an acyclic transition state polymerization mechanism by the participation of two aluminium porphyrin molecules, where the growing species always exchange their enolate ligands whenever it grows.

INTRODUCTION

Aluminium porphyrins such as methylaluminium 5,10,15,20-tetraphenylporphine [(TPP)AlMe, **1a**], upon irradiation with visible light, initiate the living polymerization of methacrylic esters, where the growing species is a (porphinato)aluminium enolate (**1c**) formed by the conjugate addition of the Me-Al bond in **1a** to the monomer [equation (1)].[1,2]



(1)

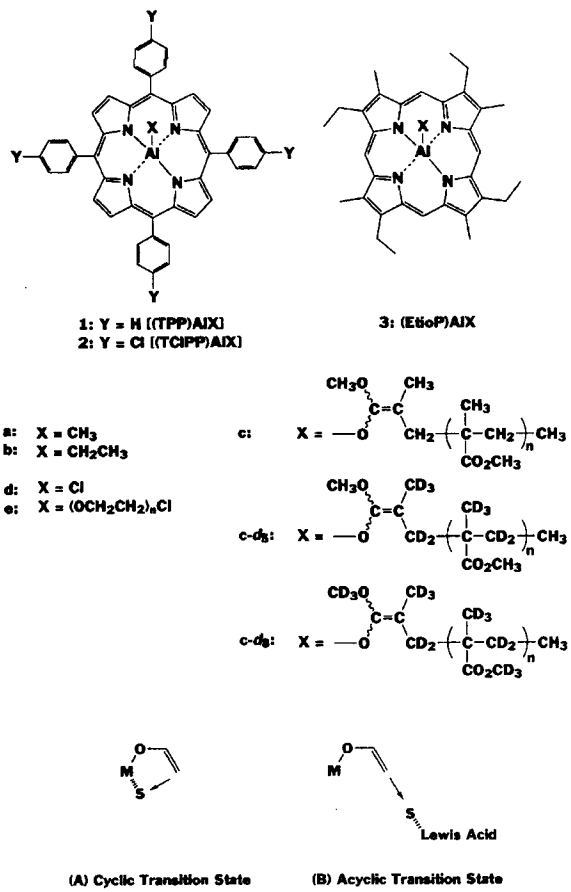
Metal enolates play an important role in carbon–carbon bond forming reactions,[3] for which the reaction mechanism involving a cyclic transition state [Scheme 1-(A)] has been generally accepted.[4] Exceptionally, an acyclic transition state mechanism [Scheme 1-(B)] has also been proposed when the metal enolates are used in conjunction with Lewis acids such as $TiCl_4$,[5–7] $SnCl_4$,[6,7] $BF_3{\cdot}OEt_2$,[7] Ph_3CClO_4[8] and $CF_3SO_3SiMe_3$,[9] where the Lewis acids possibly activate substrates through coordination. In the field of synthetic polymer chemistry, the group transfer polymerization (GTP) of methacrylic esters is a well known example of metal enolate—mediated polymerizations, where a cyclic transition-state mechanism involving a hypervalent silicon intermediate has long been accepted (Scheme 2).[10] This proposal is based on the observation that the trialkylsilyl group at the active polymer end exhibits an extremely low exchange activity during the polymerization. However, Quirk and Ren[11] have recently reinvestigated GTP of methacrylic esters, and claimed that the active-end trialkylsilyl group is easily exchangeable intermolecularly during the polymerization. Thus, the validity of the GTP mechanism via the cyclic transition state (Scheme 2) now needs to be re-examined.

We have also been interested in the exchange activities of the growing species in the metalloporphyrin—mediated polymerizations since the discovery of 'immortal' polymerization (Scheme 3).[12] Immortal polymerization involves a rapid, reversible

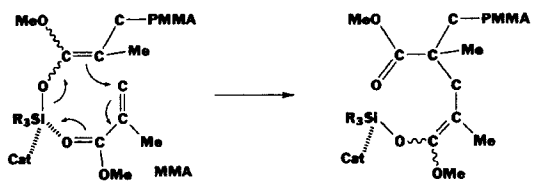
* Present address: Department of Industrial Chemistry, Faculty of Engineering, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo 162, Japan.
† Author for correspondence.

CCC 0894–3230/95/040249–09

Received 8 September 1994
Revised 24 October 1994

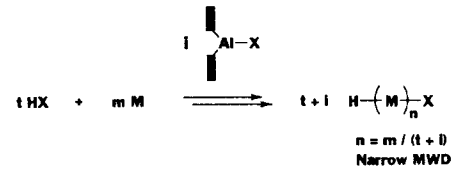


Scheme 1



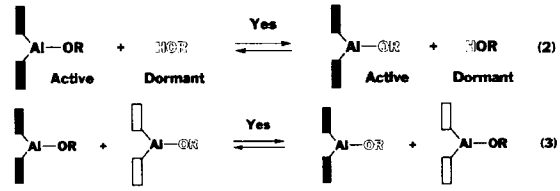
Scheme 2

exchange between the growing species and chain transfer agents (HX), thereby producing a narrow molecular weight distribution (MWD) polymer with the number of the polymer molecules exceeding that of the initiator molecules. A representative example is the immortal polymerization of epoxides using an alcohol as chain transfer agent, where the growing alcoholate species exchanges with alcohol reversibly and much more rapidly than the chain growth [equation (2)].[13] In connection with this exchange process, we have noted



Scheme 3

that the alcoholate–alcoholate exchange reaction [equation (3)]



also takes place during the polymerization of epoxides.[14] Similarly to equation (2), equation (3) also takes place much more rapidly than the propagation reaction, as evidenced by, e.g., the formation of a narrow MWD polyether initiated with a mixture of two aluminium porphyrin initiators with different reactivities. (Porphinato)aluminium carboxylates, the growing species of the polymerization of four-membered lactones,[14] and phenolates[15] are also susceptible to axial ligand exchange. The ligand-exchange activities of the aluminium porphyrin family are generally interesting, considering the bulkiness of the porphyrin ligand.

We report here axial ligand-exchange profiles of some alkyl and enolate aluminium porphyrins in relation to the mechanism of the living polymerization of methacrylic esters initiated with alkylaluminium porphyrins [equation (1)].

RESULTS AND DISCUSSION

Polymerization of benzyl methacrylate (BnMA) initiated with an equimolar mixture of two different aluminium porphyrins, (TPP)AlMe (1a) and (EtioP)AlMe (3a)

Similarly to the polymerization of epoxides and lactones initiated with aluminium porphyrins,[14,16] the rate of polymerization of methacrylic esters under appropriate conditions is strongly dependent of the structure of the porphyrin ligand. For example, the polymerization of benzyl methacrylate (BnMA, 25 mmol, 100 equiv. with respect to **1a**), carried out by using (TPP)AlMe (**1a**, 0·25 mmol) as initiator in CH_2Cl_2 (10 ml) at 35 °C under irradiation from a xenon arc lamp ($\lambda > 420$ nm), proceeded to 100% monomer conversion within 6 h [Figure 1(A)]. However, when (EtioP)AlMe (**3a**) was used in place

of **1a** under the same conditions, the polymerization proceeded much more slowly to attain 23 and 60% conversion in 6 and 40 h, respectively [Figure 1(B)]. In both cases, the polymers formed were of narrow MWD [Figure 2(A) and (B)], and the number-average molecular weights (M_n), as estimated by gel permeation chromatography (GPC) based on polystyrene standards [For evaluating the average molecular weights of poly(benzyl methacrylates), M_ws and M_ns, calibrated by polystyrene standards, were multiplied by a factor of 1·7 (molecular weight ratio of benzyl methacrylate to styrene)],[17] were close to the values expected from the assumption that every initiator molecule produces one polymer molecule [Figure 3(A) and (B)].

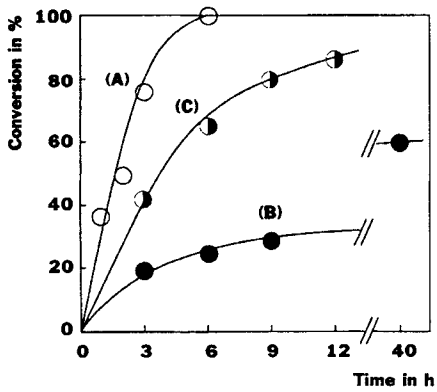


Figure 1. Polymerizations of benzyl methacrylate (BnMA, 50 mmol, 100 equiv.) initiated with (A), (TPP)AlMe (**1a**), (B) (EtioP)AlMe (**3a**) and (C) a mixture of **1a** and **3a** (0·5 equiv. each) in CH_2Cl_2 (10 ml) at 35 °C under irradiation with a xenon arc lamp ($\lambda > 420$ nm). Time–conversion relationships

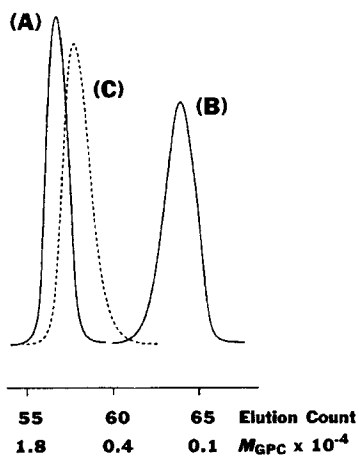


Figure 2. Polymerizations of benzyl methacrylate (BnMA, 50 mmol, 100 equiv.) initiated with (A) (TPP)AlMe (**1a**) (100% conversion, $M_n = 15{,}500$, $M_w/M_n = 1{\cdot}14$), (B) (EtioP)AlMe (**3a**) (23% conversion, $M_n = 3600$, $M_w/M_n = 1{\cdot}18$) and (C) a mixture of **1a** and **3a** (0·5 equiv. each) (64% conversion, $M_n = 12{,}900$, $M_w/M_n = 1{\cdot}14$) in CH_2Cl_2 (10 ml) at 35 °C under irradiation with a xenon arc lamp ($\lambda > 420$ nm). GPC profiles after 6 h

Figure 1(C) shows the time–conversion curve for the polymerization of BnMA initiated with an equimolar mixture of **1a** and **3a** ($[BnMA]_0 : [\mathbf{1a}]_0 : [\mathbf{3a}]_0 = 100 : 0{\cdot}5 : 0{\cdot}5$) under conditions otherwise identical with the above. The polymerization proceeded at an intermediate rate between those with **1a** and **3a**, respectively, where the monomer conversion reached 64% in 6 h [Figure 1(C)]. Of great interest to note is the fact that the polymer formed with this mixed initiator system was also of unimodal, narrow MWD ($M_w/M_n = 1{\cdot}14$) [Figure 2(C)]. As the polymerization proceeded, the M_n of the polymer increased linearly along the theoretical line expected when **1a** and **3a** both initiate the polymerization, while the M_w/M_n ratio remained narrow throughout the polymerization [Figure 3(C)]. In this case, if the ligand-exchange reaction does not take place, formation of a mixture of polymers with different molecular weights (bimodal MWD) should result, since the polymer molecule initiated from **1a** should grow much more rapidly than that from **1b**. On the other hand, if the ligand-exchange reaction takes place and is much more rapid than the chain growth, a unimodal, narrow MWD polymer should be formed. Therefore, the sharp GPC profile of the polymer formed with the **1a**–**3a** mixed initiator system [Figure 2(C)] suggests that the polymerization involves a rapid enolate–enolate exchange between the growing species.

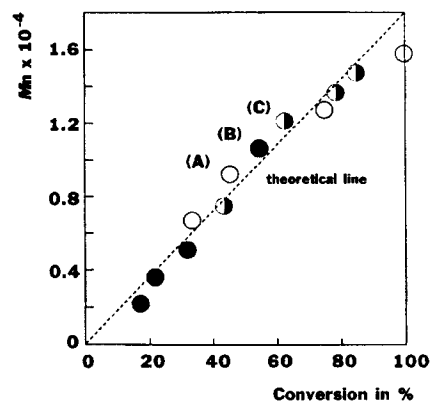
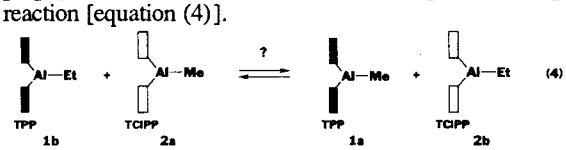


Figure 3. Polymerizations of benzyl methacrylate (BnMA, 50 mmol, 100 equiv.) initiated with (A) (TPP)AlMe (**1a**), (B) (EtioP)AlMe (**3a**) and (C) a mixture of **1a** and **3a** (0·5 equiv. each) in CH_2Cl_2 (10 ml) at 35 °C under irradiation with a xenon arc lamp ($\lambda > 420$ nm). M_n–conversion relationships

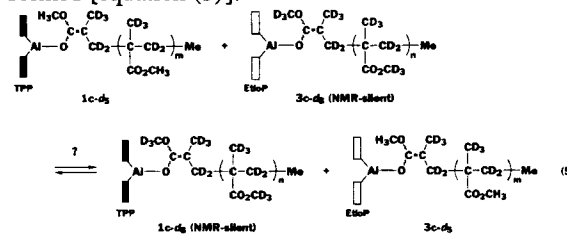
^{1}H NMR studies on the axial ligand exchange activities of alkyl- and enolate-aluminium porphyrins

^{1}H NMR studies were made on the ligand-exchange activities of the initiating and propagating species, where deuterated methyl methacrylates, MMA-d_5 [CD_2=C(CD_3)CO_2CH_3] and MMA-d_8 [CD_2=C(CD_3)CO_2CD_3], and alkylaluminium porphyrins, (TPP)AlMe (**1a**), (TPP)AlEt (**1b**), (TClPP)AlMe (**2a**), and (TClPP)AlEt (**2b**), and (EtioP)AlMe (**3a**) were used.

As summarized in Table 1, the chemical shift values of the axial groups are affected by the structure of the porphyrin ligand. The methylaluminium porphyrins, **1a** and **2a**, exhibit singlet signals due to Al-*Me* at δ −6·9 and −7·0 ppm, respectively (entries 1 and 5). Similarly, the signals due to the axial ethyl groups in **1b** and **2b** are distinguishable from each other (entries 2 and 6). If the axial alkyl groups in the alkylaluminium porphyrin family are exchangeable [equation (4)], mixing of, e.g, **1b** and **2a** should furnish a mixture of four different alkylaluminium porphyrins, **1a**, **2a**, **1b** and **2b**, where **1a** and **2b** are the exchanged products. However, the ^{1}H NMR spectrum in $CDCl_3$ at 22 °C of the equimolar mixture of **1b** and **2a** showed a simple superimposed image of the spectra of these two complexes, while no new signals assignable to **1a** and **2b** were detected throughout the observation over a period of 1 week. This result indicates that alkylaluminium porphyrins as initiators are not liable to ligand exchange reaction [equation (4)].



Next, the exchange activities of the growing enolate species were likewise studied by using living methacrylate oligomers, **1c**-d_5, **1c**-d_8, **3c**-d_5 and **3c**-d_8, prepared from the polymerizations of MMA-d_5 and MMA-d_8 initiated with **1a** and **3a** (from $[MMA]_0/[initiator]_0 = 10$, 100% conversion), respectively. Here, the enolate groups in **1c**-d_5 and **3c**-d_5 are clearly distinguishable from each other by the characteristic OMe signals (Table 1, entries 3 and 7), whereas those in **1c**-d_8 and **3c**-d_8 are NMR silent. Therefore, C_6D_6 solutions of **1c**-d_5 and **3c**-d_8 were mixed. If the axial ligand exchange takes place between these two enolate species, **1c**-d_8 and **3c**-d_5 should be newly formed [equation (5)].



However, throughout the observation over a period of 50 h at 35 °C, no new signals assignable to **3c**-d_5 appeared, while the signals due to **1c**-d_5 remained unchanged in intensity (Figure 4). No enolate exchange was also the result when the sample was continuously exposed to visible light (λ >420 nm) for 50 h at 35 °C. Therefore, differently from (porphinato)aluminium alcoholate, phenolate and carboxylate complexes having Al—O bonds but similarly to (porphinato)aluminium alkyls, the enolate complexes, **1c** and **3c**, are very reluctant to undergo ligand-exchange reaction. [Contrary to this result, a reversible enolate–enolate exchange was observed for (porphinato)aluminium enolates derived from ketones.[17]]

This observation is inconsistent with what was expected from the results of the polymerization of benzyl methacrylate (BnMA) with the **1a–3a** system,

Table 1. ^{1}H NMR data for aluminium porphyrins (C_6D_6, 22 °C)

Entry	Data[a]	Entry	Data[a]
1.*	(TPP)Al—CH_3 (1a) δ -6.9	5.*	(TClPP)Al—CH_3 (2a) δ -7.0
2.*	(TPP)Al—CH_2—CH_3 (1b) δ -6.4 δ -3.4	6.*	(TClPP)Al—CH_2—CH_3 (2b) δ -6.5 δ -3.5
3.	(TPP)Al—O—C(CH_3O)=C(CD_3)—CD_2—C(CD_3)(CO_2CH_3)—CH_3 (1c-d_5) δ 0.53 - 0.62 δ 0.82 - 1.02	7.	(EtioP)Al—O—C(CH_3O)=C(CD_3)—CD_2—C(CD_3)(CO_2CH_3)—CH_3 (3c-d_5) δ 0.18 - 0.33 δ 0.82 - 1.02
4.	(TPP)Al—O—CH_2—CH_2—(O—CH_2—CH_2)$_n$—Cl (1e) δ -0.45 δ 0.67	8.	(EtioP)Al—O—CH_2—CH_2—(O—CH_2—CH_2)$_m$—Cl (3e) δ -0.98 δ 0.46

TPP = tetraphenylporphinato; TClPP = tetrakis-(4′-chlorophenyl)porphinato; EtioP = etioporphyrinato.
* in $CDCl_3$.

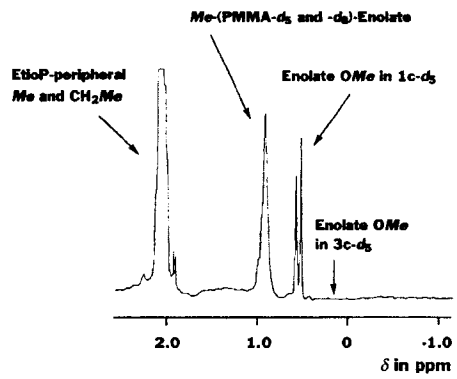
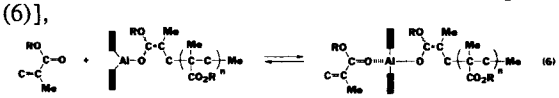


Figure 4. ^{1}NMR spectrum in C_6D_6 at 22 °C of an equimolar mixture of the living oligomers of **1c**-d_5 (from [MMA-d_5]$_0$/[**1a**]$_0$ = 10, 100% conversion) and **3c**-d_8 (from [MMA-d_8]$_0$/[**3a**]$_0$ = 10, 100% conversion) after 72 h on mixing at 35 °C

where a narrow MWD polymer with a degree of polymerization close to [BnMA]$_{reacted}$/[**1a** + **3a**]$_0$ [Figure 2(C)] indicates the occurrence of a rapid enolate exchange between the growing species. Taking this discrepancy into consideration, we investigated the system of an equimolar mixture of **1c**d_5 and **3c**-d_8 in the presence of MMA-d_8 ([MMA-d_8]$_0$: [**1c**-d_5]$_0$: [**3c**-d_8]$_0$ = 10 : 1 : 1) in C_6D_6. If the monomer is capable of promoting a direct enolate exchange between the growing species by, e.g., coordination to the central aluminium atom [equation (6)],



(6)

1c-d_8 and **3c**-d_5, should be newly formed. {Back-side coordination of Lewis bases such as 1-methylimidazole to aluminium porphyrins [(porph)AlX], producing six-coordinate aluminium porphyrin species, eventually leads to enhancement of the nucleophilic reactivity of the Al—X bond.[18] As for coordination of MMA to aluminium porphyrins, slight upfield shifts for the MMA signals were observed by ^{1}H NMR when the aluminium porphyrin was highly Lewis acidic (TPP)AlCl (**1d**), whereas the shifts were not detectable for less Lewis acidic enolate and alcoholate complexes.} When the above mixture was set at 35 °C under irradiation with visible light (λ > 420 nm), consumption of MMA-d_8 (monomer consumption was monitored by gas chromotography) and the decrease in intensity of the enolate OMe signal due to **1c**-d_5 [Figure 5(A)] were observed with time as a result of the nucleophilic attack of the enolate group in **1c**-d_5 to MMA-d_8, whereas no new signals assignable to **3c**-d_5 were detected [Figure 5(B)] throughout the observation over a period of 60 h. This result rules out the possibility of a direct enolate exchange in the presence of a methacrylate monomer.

Another possibility to result in the enolate exchange is a migratory chain growth mechanism via an acyclic transition state (Scheme 4), where the enolate growing species reacts with the activated monomer on coordination to the aluminium atom in another aluminium porphyrin molecule. If this mechanism is true, the results in Figure 5 using MMA-d_8 as the monomer are reasonable, since the migratory chain growth in that case always produces NMR-silent enolate species (**1c**-d_8' and **3c**-d_8'). Therefore, we investigated the possibility of this migratory chain growth mechanism (Scheme 4) by using an equimolar mixture of the enolate species **1c** (from [MMA]$_0$/[**1a**]$_0$ = 15, 100% conversion) and alcoholate species **3e** (from [epoxyethane]$_0$/[**3d**]$_0$ = 15, 100% conversion, entry 8 in Table 1) in the presence of MMA ([MMA]$_0$: [**1c**]$_0$: [**3e**]$_0$ = 15 : 1 : 1) in C_6D_6. The reactivity of the alcoholate species is different from that of the enolate species as it has no ability to attack MMA, but the Lewis acidic characteristics of the aluminium atoms in these two aluminium porphyrin complexes are considered to be not much different from each other. Therefore, if the polymerization of MMA proceeds via the acyclic transition state assisted by **3e** (Scheme 5), the enolate group bound to (EtioP)Al (**3c**) and the alcoholate group bound to (TPP)Al (**1e**) (entry 4 in Table 1) should be newly formed as a consequence of the migratory attack of the enolate group on the MMA molecule coordinated to **3e**. On the other hand, if the polymerization is not accompanied by the enolate group migration, only the enolate group bound to (TPP)A1 (**1c**) and the starting alcoholate species (**3e**) should be detected. Prior to this experiment, the system

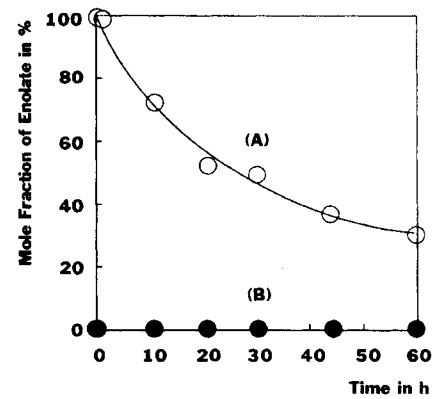
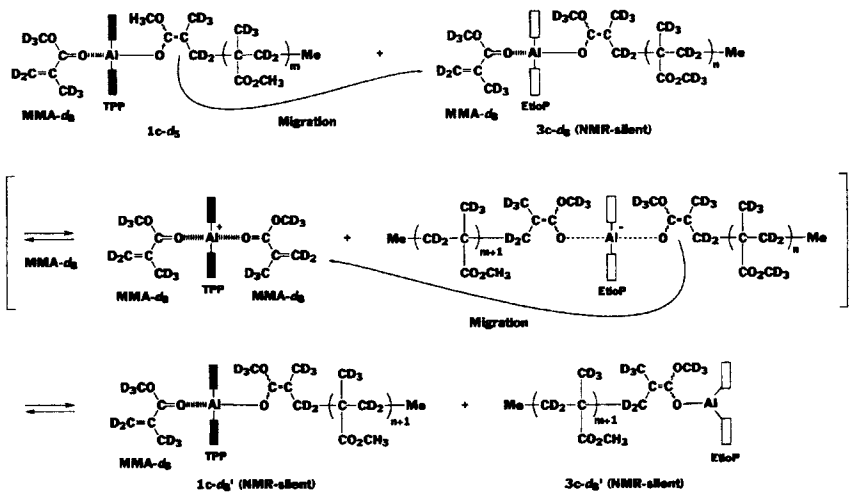
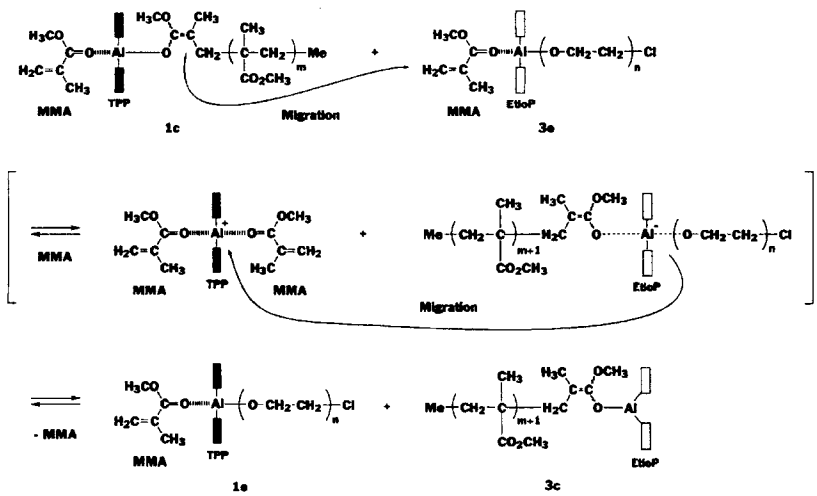


Figure 5. Polymerizations of methyl methacrylate-d_8 (MMA-d_8, 10 equiv.) initiated with an equimolar mixture of **1c**-d_5 and **3c**-d_8 in C_6D_6 at 35 °C under irradiation with a xenon arc lamp (λ > 420 nm). Change in the mole fractions of the enolate species, (A) **1c**-d_5 and (B) **3c**-d_5 with time



Scheme 4

of an equimolar mixture of **1c** and **3e** in the absence of MMA was investigated by ^{1}H NMR (C_6D_6, 35 °C), where no new signals due to the simple exchanged products, **3c** and **1e**, were detected both in the dark and under irradiation for 200 h. This result excludes the possibility of an enolate–alcoholate direct exchange path. In contrast, in the presence of MMA under conditions otherwise identical with the above, the signal assignable to the enolate OMe in **3c** and alcoholate Al-OCH_2 in **1e** newly appeared at the expense of **1c**, **3e** and MMA [Figure 6(B)], at 9% conversion of MMA; 1·5 equiv. with respect to **1c**], although the spectrum just after the addition of MMA [Figure 6(A)] showed only the signals due to **1c** and **3e** at the characteristic upfield region (δ 0–0·8 ppm). Together with the results of the polymerization of BnMA with the **1a**–**3a** system (Figures 1—3) and no direct ligand exchange path between **1c** and **3e**, formation of the ligand exchanged products, **3c** and **1e**, is considered to be a consequence of the migratory attack of the enolate group in **1c** to MMA on coordination to the aluminium atom in **3e** (Scheme 5).



Scheme 5

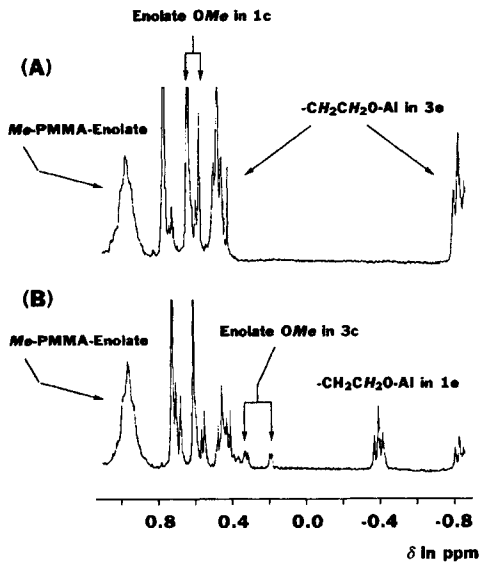


Figure 6. Polymerizations of methyl methacrylate (MMA, 15 equiv.) initiated with **1c** (from $[MMA]_0/[\mathbf{1a}]_0 = 15$, 100% conversion) in the presence of an equimolar amount of **3e** (from $[EO]_0/[\mathbf{3d}]_0 = 15$, 100% conversion) in C_6D_6 at 35 °C under irradiation with a xenon arc lamp ($\lambda > 420$ nm). ^1H NMR spectra (22 °C) (A) just after the addition of MMA and (B) at 9% conversion of MMA (after irradiation for 150 h at 35 °C)

CONCLUSION

The polymerization of methacrylic esters initiated with alkylaluminium porphyrins proceeds via an acyclic transition-state mechanism (Scheme 4) by the simultaneous participation of two aluminium porphyrin molecules. We have already proposed a similar chain-growth mechanism for the ring-opening polymerization of a six-membered lactone via a (porphinato)aluminium alcoholate growing species, where one of the aluminium porphyrin molecules functions as monomer activator for the nucleophilic chain growth. This mechanism is considered also to be operative for our recent discovery of the Lewis acid—assisted high-speed living polymerization of methacrylic esters initiated with aluminium porphyrins, where the Lewis acid component acts as a monomer activator through coordination.[19]

EXPERIMENTAL

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized from pyrrole and benzaldehyde in refluxing propionic acid. The crude product was recrystallized from $CHCl_3$–MeOH to give $TPPH_2$ as purple crystals in 20% yield.[20] In a similar way, 5,10,15,20-tetrakis-(4′-chlorophenyl)porphyrin ($TClPPH_2$) was synthesized from pyrrole and 4-chlorobenzaldehyde.

2,7,12,17-Tetraethyl–3,8,13,18-tetramethylporphine (etioporphyrin I, $EtioPH_2$) was synthesized from *tert*-butyl-4-ethyl-3,5-dimethylpyrrole-2-carboxylate via a dipyrromethene intermediate.[21] The crude product was subjected to column chromatography on silica gel using CH_2Cl_2–hexane (1 : 2) as eluent. A fraction with a reddish purple colour was collected and evaporated to dryness, and the residue was recrystallized from $CHCl_3$–MeOH (1 : 2) to give $EtioPH_2$ as reddish purple crystals in 30% yield.

Methyl methacrylate (MMA) and benzyl methacrylate (BnMA) were fractionally distilled under reduced pressure over CaH_2 in a nitrogen atmosphere.

Fully deuterated methyl methacrylate (MMA-d_8) was prepared as follows.[22] To a D_2O solution (82·6 ml) of NaCN (0·96 mol) was added acetone-d_6 (0·68 mol) at room temperature, followed by a mixture of D_2O (88·3 ml) and D_2SO_4 (62·6 g, 0·63 mol) at 0 °C. The resulting mixture was stirred at the same temperature for 1 h and the ether extracts combined were dried over $MgSO_4$ and subjected to fractional distillation under reduced pressure, affording acetone cyanohydrin-d_7 in 63% yield (39.4 g). The acetone cyanohydrin-d_7 thus obtained was added dropwise at 60 °C to H_2SO_4 (34·1 g, 0·35 mol) containing fuming H_2SO_4 (15.1 g) in the presence of a mixture of metallic Cu (1·5 g) and CuCl (0·5 g), and the mixture was stirred at 140 °C. After 1 h, the reaction mixture was allowed to cool to 100°C and MeOH-d_4 (0·78 mol) was added. The mixture was stirred for 20 h at the same temperature and then allowed to cool to room temperature. The organic layer, separated on addition of water (49.6 ml), was dried over molecular sieve 4A and fractionally distilled under nitrogen, affording MMA-d_8 in 10·4% yield (4·8 g), which was further distilled in the presence of Et_3Al under nitrogen prior to use. Partially deuterated methyl methacrylate (MMA-d_5) was prepared from acetone cyanohydrin-d_7 and MeOH similarly to the preparation of MMA-d_8.

Epoxyethane (ethylene oxide, EO), stirred with a mixture of KOH and CaH_2 at room temperature, was subjected to several thaw-to-flow cycles and distilled into a trap cooled in a liquid nitrogen bath.

CH_2Cl_2, after treatment with concentrated H_2SO_4, was neutralized with aqueous $NaHCO_3$ followed by washing with water, dried over $CaCl_2$ and fractionally distilled over CaH_2 under nitrogen. $CDCl_3$ was fractionally distilled after refluxing over CaH_2 under nitrogen. C_6D_6 was fractionally distilled over Na wire in the presence of benzophenone ketyl under nitrogen.

Me_3Al, Et_3Al and $ClEt_2Al$ were fractionally distilled under reduced pressure in a nitrogen atmosphere.

Preparation of alkyl- and chloro-aluminium porphyrins. Methylaluminium porphyrins, **1a–3a**, were

prepared by the reaction of Me_3Al and the corresponding free-base porphyrins as follows.[15] To a 100-ml round-bottomed flask fitted with a three-way tap, containing a CH_2Cl_2 solution (40 ml) of $TPPH_2$ (0·615 g, 1 mmol) under nitrogen, was added Me_3Al (0·13 ml, 1 mmol) by a hypodermic syringe and the mixture was stirred for 2 h. The reaction mixture was evaporated to dryness under reduced pressure, leaving **1a** as purple powder. Ethylaluminium porphyrins, **1b** and **2b**, and chloroaluminium porphyrins, **1d** and **3d**, were prepared by using Et_3Al (0·13 ml, 1 mmol) and $ClEt_2Al$ (0·16 ml, 1·2 mmol), respectively, in place of Me_3Al.

Preparation of enolate-aluminium porphyrins. Enolate-aluminium porphyrins, **1c**, **1c**-d_5, **1c**-d_8, **3c**-d_5 *and* **3c**-d_8, from **1a** and **3a** as initiators and MMA, MMA-d_5 and MMA-d_8 as monomers, were prepared according to the following representative procedure. To a 50-ml round-bottomed flask attached to a three-way stopcock, containing a C_6D_6 solution of **1a** (0·2 mmol) under nitrogen, were added by a hypodermic syringe 10 equiv. of MMA-d_5 in a nitrogen stream, and the mixture was irradiated with a xenon arc lamp ($\lambda > 420$ nm) at 35 °C. After 2 days, a portion of the reaction mixture was transferred to a NMR tube (diameter 5 mm) in a nitrogen stream and subjected to ^{1}H NMR analysis to confirm the complete conversion of **1a** and MMA-d_5 to **1c**-d_5 (monomer consumption was monitored by gas chromatography).

Preparation of alcoholate-aluminium porphyrins. Alcoholate-aluminium porphyrins, **1e** and **3e**, from **1d** and **3d** as initiators and EO as a monomer, were prepared according to the following representative procedure.[23] To a 50-ml round-bottomed flask attached to a three-way stopcock, containing a CH_2Cl_2 solution (4 ml) of **1d** (0·2 mmol) under nitrogen, was added by a hypodermic syringe a CH_2Cl_2 solution (1 ml) of EO (3 mmol, 15 equiv.) in a nitrogen stream. After 2 days, the polymerization mixture was evaporated to dryness, leaving **1e** as a reddish purple, viscous liquid, which was dissolved in C_6D_6 and subjected to ^{1}H NMR analysis.

Polymerization of benzyl methacrylates. Polymerizations of benzyl methacrylate (BnMA) initiated by using **1a**, **3a**, and an equimolar mixture of **1a** and **3a** were carried out according to the following representative example. To a 100-ml round-bottomed flask attached to a three-way stopcock, containing a CH_2Cl_2 solution (10 ml) of a mixture of **1a** and **3a** (0·125 mmol each) under nitrogen, was added BnMA (25 mmol) by a hypodermic syringe in a nitrogen stream, and the mixture was irradiated with a xenon arc lamp ($\lambda > 420$ nm) at 35 °C. An aliquot of the reaction mixture was periodically removed with a syringe in a nitrogen stream, and subjected to ^{1}H NMR analysis to determine the monomer conversion and to GPC for evaluating the average molecular weights (M_n, M_w) of the polymer produced.

Measurements. ^{1}H NMR measurements were performed in C_6D_6 and $CDCl_3$ using a JEOL GSX-270 spectrometer, where the chemical shifts were determined with respect to C_6H_6 (δ7·40) and $CHCl_3$ (δ7·28), respectively, as internal standards. GPC measurements were performed at 40 °C on a TOSOH Model 802A high-speed liquid chromatograph equipped with a differential refractometric detector, using tetrahydrofuran as eluent at a flow rate of 1·0 ml min^{-1}. The molecular weight calibration curve was obtained by using polystyrene standards (TOSOH) $M_n = 2{,}890{,}000$ ($M_w/M_n = 1{\cdot}09$), 422,000 (1·04), 107,000 (1·07), 43,900 (1·01), 16,700 (1·02), 9000 (1·06), 6200 (1·04), 4000 (1·10) and 2800 (1·05) [For evaluating the average molecular weights of poly(benzyl methacrylates), M_ws and N_n, calibrated by polystyrene standards, were multiplied by a factor of 1·7 (molecular weight ratio of benzyl methacrylate to styrene)].

ACKNOWLEDGEMENTS

The authors are grateful to Professor K. Hatada and Dr T. Kitayama of Osaka University for generous instruction on the preparation of deuterated methyl methacrylates.

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