Reactivity of (Porphinato)aluminum Phenoxide and Alkoxide as Active Initiators for Polymerization of Epoxide and Lactone

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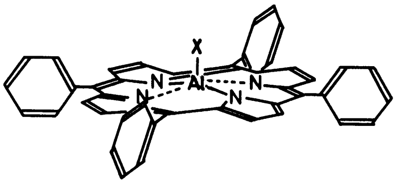
Reactivity of the axial aluminum-phenoxyl and -alkoxyl bond (Al-X) of aluminum porphyrin (**1**, (TPP)AlX, (TPP): (5,10,15,20-tetraphenylporphinato)) toward epoxide, β-lactone, and ε-lactone was examined in relation to the ring-opening polymerization of these cyclic compounds catalyzed by **1**. The reactivity of aluminum phenoxide was in the order, epoxide>β-lactone>ε-lactone, while that of the alkoxide, ε-lactone >β-lactone.



(TPP)AlX (**1**)

Control of molecular weight of polymer is a subject of primary importance for elaborate design of polymeric materials with desired function.[1] Recently, we found aluminum porphyrin such as (5,10,15,20-tetraphenylporphinato)aluminum chloride (**1**, X=Cl: (TPP)AlCl) to be an excellent initiator or catalyst for the ring-opening polymerization of epoxide[2] and β-lactone[3] to give polyether and polyester, respectively, of very narrow molecular-weight distribution.[4] This remarkable characteristics is due to unusually high reactivity of the aluminum-axial ligand bond (Al-X) of the aluminum porphyrin.[2-4] Typically, the reactivity of aluminum-chlorine bond in (TPP)AlCl is much higher than that expected for usual aluminum-chlorine bond, and (TPP)AlCl reacts readily with epoxide to initiate the polymerization which proceeds with a (porphinato)aluminum alkoxide as the growing species.[5]

(1)

1 (X = Cl) **2**

The reactivity of (porphinato)aluminum chloride toward epoxide is considered higher than, or at least the same as, that of (porphinato)aluminum alkoxide, taking into account the narrow molecular-weight distribution of the polymer formed. If the reactivity of (porphinato)aluminum chloride were lower than that of the alkoxide, slower initiation followed by faster propagation should result in the broad molecular-weight distribution of polymer. The reactivity of (porphinato)aluminum carboxylate (**1**, X=O_2CR) toward epoxide is also considered not lower than that of the alkoxide, on the basis of the fact that the polymerization of epoxide initiated by (porphinato)aluminum carboxylate affords the polymer with narrow molecular-weight distribution.[6]

Polymerization of β-lactone initiated by (TPP)AlCl proceeds by the ring cleavage at alkyl-oxygen linkage, with a (porphinato)aluminum carboxylate as the growing species.[7]

(2)

1 (X = Cl)

The narrow molecular-weight distribution of the polymer indicates that the reactivity of (porphinato)aluminum chloride toward β-lactone is higher than, or the same as, that of the carboxylate, on the basis of the same consideration as described above.

Corresponding to the above findings, (porphinato)aluminum alkoxide (**1**, (X=OR): **2**) and carboxylate (**1**, X=O_2CR) initiate the polymerization of epoxide[2,5] and β-lactone,[7] respectively. The latter can initiate also the polymerization of epoxide as mentioned above.[6] (Porphinato)aluminum phenoxide (**1**, X=OAr) was found to initiate the polymerization of epoxide and β-lactone to give the polymers with narrow molecular-weight distribution.[6]

These interesting findings prompted us to examine the reactivity of aluminum porphyrin in more detail by NMR analysis of the reaction system, which proved very useful to follow the reaction by virtue of the remarkable effect of the porphyrin ring current.[4-7] The present paper places emphasis on the reactivity of (porphinato)aluminum phenoxide, which is expected to exhibit an intermediate reactivity between the alkoxide and the carboxylate, toward epoxide, β-lactone, and ε-lactone.

Results and Discussion

Reaction of (Porphinato)aluminum Phenoxide. In the reaction of (tetraphenylporphinato)aluminum phenoxide (**1**, X=OPh: (TPP)AlOPh) with eight molar equivalents of β-propiolactone (PL) in $CDCl_3$ at

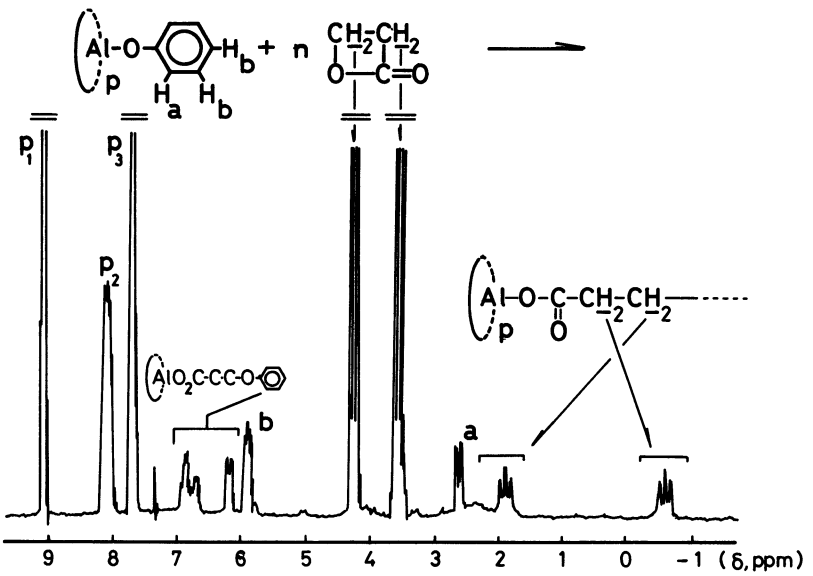
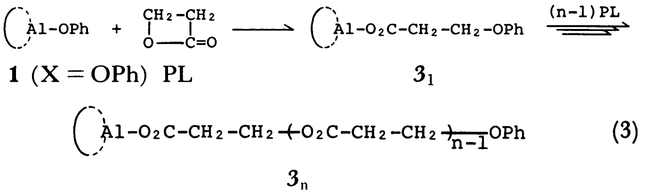


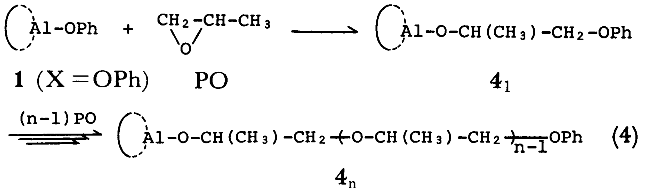
Fig. 1. ^1H NMR spectrum of the reaction mixture between (TPP)AlOPh (**1**, X=OPh) and β-propiolactone (PL) in $CDCl_3$. $[PL]_0/[(TPP)AlOPh]_0=8.1$; $[(TPP)AlOPh]_0=130\ \mathrm{mmol\ dm^{-3}}$; r.t.; 6 h.

room temperature (≈20 °C), the ^1H NMR spectrum of the reaction mixture (Fig. 1) showed that the signals at δ 2.6 (a, *o*-H) and δ 5.9 (b, *m*- and *p*-H) due to the phenoxyl group of (TPP)AlOPh[6] decreased in intensity. On the other hand, a new signal appeared at δ −0.66, which is assigned to a carboxylate $(TPP)AlO_2C\text{-}\underline{CH_2}\text{-}CH_2\text{-}$[7,8] formed by the ring opening of the β-lactone at alkyl-oxygen bond. Similarly, the formation of a (porphinato)aluminum alkoxide by the reaction of (TPP)AlOPh with an excess of 1,2-epoxypropane (PO) was confirmed by the ^1H NMR spectrum of the reaction mixture; $(TPP)AlOCH(\underline{CH_3})\text{-}CH_2\text{-}$, δ −1.86.[5]



$$\text{Al-OPh} + \underset{\text{O—C=O}}{\text{CH}_2\text{-CH}_2} \longrightarrow \text{Al-O}_2\text{C-CH}_2\text{-CH}_2\text{-OPh} \xrightleftharpoons{(n-1)\,\text{PL}} \text{Al-O}_2\text{C-CH}_2\text{-CH}_2\text{-}(\text{O}_2\text{C-CH}_2\text{-CH}_2)_{n-1}\text{-OPh} \quad (3)$$

1 (X=OPh) PL $\mathbf{3}_1$ $\mathbf{3}_n$



$$\text{Al-OPh} + \text{CH}_2\text{-CH-CH}_3\ (\text{O}) \longrightarrow \text{Al-O-CH(CH}_3\text{)-CH}_2\text{-OPh} \xrightleftharpoons{(n-1)\,\text{PO}} \text{Al-O-CH(CH}_3\text{)-CH}_2\text{-}(\text{O-CH(CH}_3\text{)-CH}_2)_{n-1}\text{-OPh} \quad (4)$$

1 (X=OPh) PO $\mathbf{4}_1$ $\mathbf{4}_n$

The reaction of (TPP)AlOPh with an excess (7—8 times) of β-lactone or epoxide at room temperature in $CDCl_3$ was followed by the change in the intensity of the signal for the phenoxyl group (δ 5.9 (b, 3H), *m*-, *p*-H) with respect to that due to the pyrrole β-proton of aluminum porphyrin (δ 9.1 (p_1, 8H)) as standard. In each case, the signal due to the corresponding polymeric unit[9] was hardly observed under the conditions examined, indicating that the observation made here can be related to the initiation step to give $\mathbf{3}_1$ and $\mathbf{4}_1$, respectively. As shown in Fig. 2, the reaction of (TPP)AlOPh with epoxide proceeded rapidly and was completed in about 4 h, while the reaction with β-lactone was rather slow to attain the complete consumption of (TPP)AlOPh after about 24 h. On the other hand, in the attempted reaction of (TPP)AlOPh with ε-caprolactone (6-hexanolide) under similar conditions, no change was observed in the ^1H NMR spectrum of the reaction mixture.

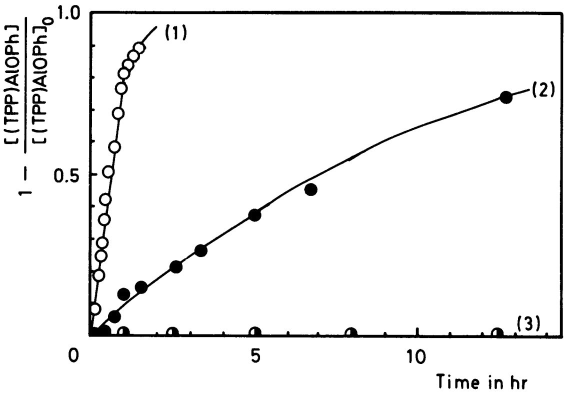


Fig. 2. Reaction of (TPP)AlOPh (**1**, X=OPh) with (1) 1,2-epoxypropane (PO), (2) β-propiolactone (PL), and (3) ε-caprolactone (CL). $[PO]_0/[(TPP)AlOPh]_0=8.0$, $[PL]_0/[(TPP)AlOPh]_0=8.1$, $[CL]_0/[(TPP)AlOPh]_0=7.2$; $[(TPP)AlOPh]_0=130\ \mathrm{mmol\ dm^{-3}}$; in $CDCl_3$; at r.t.

Reaction of (Porphinato)aluminum Alkoxide. The reaction of (tetraphenylporphinato)aluminum alkoxide (**1**, X=OR: (TPP)AlOR) with lactone was exam-

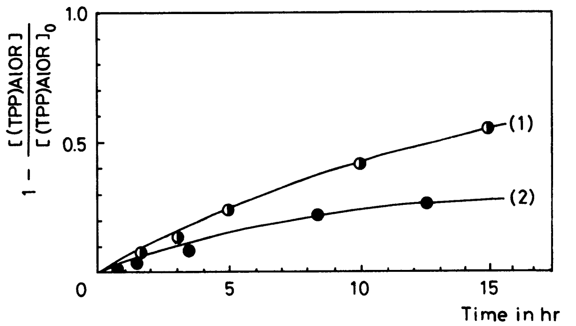
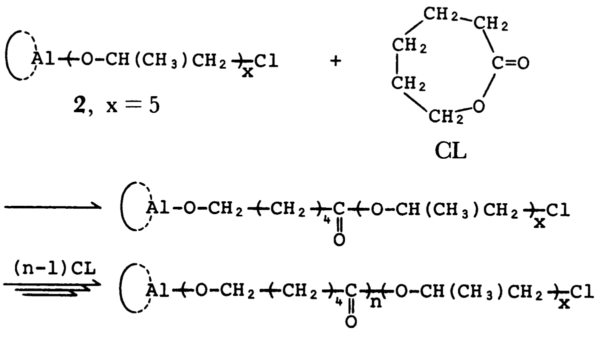


Fig. 3. Reaction of (TPP)AlOR (**2**) with (1) ε-caprolactone (CL), and (2) β-propiolactone (PL). $[CL]_0/[(TPP)AlOR]_0=8.2$, $[PL]_0/[(TPP)AlOR]_0=7.8$; $[(TPP)AlOR]_0=227\ \mathrm{mmol\,dm^{-3}}$; in $CDCl_3$; r.t.

ined by using an oligomeric alkoxide **2** prepared from 1,2-epoxypropane with (TPP)AlCl as initiator.[5,10] In contrast to (TPP)AlOPh, (TPP)AlOR exhibited a moderate reactivity toward ε-caprolactone (CL) (Fig. 3). In the ^1H NMR spectrum of the reaction mixture of (TPP)AlOR (**2**) with a large excess of the lactone, a new signal appeared at δ −1.09, at the expense of the signal at δ −1.86 due to (TPP)Al-OCH-($C\underline{H}_3$)-CH_2- of **2**. The former signal is assigned to an alkoxide (TPP)Al-O-$C\underline{H}_2(CH_2)_4$-CO-,[11] the product of ring opening at acyl-oxygen bond of ε-caprolactone.



(5)

On the other hand, the reaction of (TPP)AlOR with β-propiolactone proceeded much slower. The main product as detected by the ^1H NMR spectrum was a (porphinato)aluminum carboxylate resulting from the ring cleavage at alkyl-oxygen bond, similarly to the reaction of (TPP)AlOPh.

Thus, the reactivity of (porphinato)aluminum phenoxide is much different from that of the alkoxide, but is rather similar to the reactivity of the carboxylate, which does not react with ε-caprolactone. Much lower reactivity with ε-lactone than with β-lactone is of particular interest, since in many cases the reactivity of the former has been reported to be higher than the latter.[12]

Experimental

Materials. 5,10,15,20-Tetraphenylporphine ($TPPH_2$) was synthesized by the reaction of pyrrole with benzaldehyde.[13] (Tetraphenylporphinato)aluminum phenoxide (**1**, X=OPh: (TPP)AlOPh) and 3-phenoxypropionate[8] (**1**, X=O_2C-CH_2CH_2-OPh: (TPP)$AlO_2CCH_2CH_2OPh$) were synthesized, respectively, by the reaction of phenol[6] and 3-phenoxypropionic acid with ethyl(tetraphenylporphinato)aluminum (**1**, X=Et: (TPP)AlEt) which was obtained by the reaction of $TPPH_2$ and triethylaluminum.[14] Oligomeric (tetraphenylporphinato)aluminum alkoxide (**2**) was prepared by the reaction of (tetraphenylporphinato)aluminum chloride (**1**, X=Cl: (TPP)AlCl) with five molar equivalents of 1,2-epoxypropane.[5,10] 1,2-Epoxypropane was purified by refluxing over a mixture of potassium hydroxide and calcium hydride and then distilled twice under a nitrogen atmosphere. β-Propiolactone, dried by stirring with calcium hydride overnight at room temperature, was purified by fractional distillation under reduced pressure under a nitrogen atmosphere over calcium hydride. ε-Caprolactone was distilled over calcium hydride under reduced pressure. Deuterated chloroform ($CDCl_3$) was distilled after refluxing over calcium hydride under a nitrogen atmosphere.

Reaction. To a 50 cm^3 flask equipped with a three-way stop cock containing a $CDCl_3$ solution of an aluminum porphyrin, epoxide or lactone was added by syringe at room temperature under a nitrogen atmosphere with constant stirring. After an appropriate time, a portion of the reaction mixture was subjected to ^1H NMR spectroscopy with a JEOL JNM PS-100 spectrometer to follow the reaction. Chemical shift was separately determined with an improved accuracy by using a JEOL JNM GX-400 FT spectrometer operating at 399.7 MHz with $CHCl_3$ (δ 7.28) as standard.

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8) $(TPP)AlO_2CC\underline{H}_2CH_2OPh$ (see Experimental): δ= −0.66 in $CDCl_3$.

9) For ${+}O_2CC\underline{H}_2CH_2{+}_x$: δ=2.7 ($O_2CC\underline{H}_2$), δ=4.3 (CH_2); for ${+}OCH(CH_3)CH_2{+}_x$: δ=1.1 (CH_3), δ=3.5 (CH, CH_2), in $CDCl_3$.

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