

# Catalytic Reaction on Both Sides of a Metalloporphyrin Plane. Alternating Copolymerization of Phthalic Anhydride and Epoxypropane with an Aluminum Porphyrin-Quaternary Salt System

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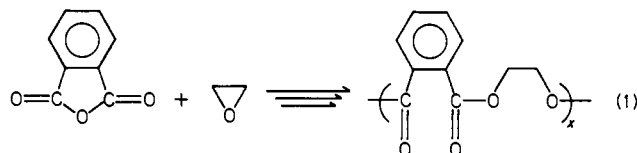
**Abstract:** The first example of the catalytic reaction occurring simultaneously on both sides of a metalloporphyrin plane was demonstrated in the copolymerization of phthalic anhydride and 1,2-epoxypropane by using the system of aluminum porphyrin coupled with quaternary ammonium or phosphonium salt as catalyst, to afford the copolymer with a highly regulated structure as to the sequence (alternating) and the number of the repeating units. The anion of the quaternary organic salt is activated as nucleophile by the metalloporphyrin, and the structure of the active growing species was confirmed by detailed spectroscopic investigations to be a novel six-coordinate aluminum porphyrin carrying one reactive axial ligand on both sides respectively of its square-planar  $N_4Al$  skeleton.

Recent years have seen dramatic advances in the chemistry of metalloporphyrins and related compounds in connection with their prominent functions in the living organism and in view of the utility as catalyst and/or reagent for organic syntheses.<sup>1</sup>

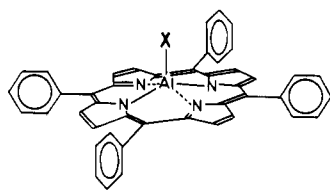
Metalloporphyrin is regarded as a molecular system with two structurally isolated sites linking back to back with each other through one metal atom. The information at one site can be transferred to the opposite site by an electronic interaction between two isolated sites via the metal (trans effect). A reaction takes place at one side of the metalloporphyrin plane, while on the other side an appropriate ligand coordinates to the metal and assists the reaction by affecting the rate and/or the equilibrium. A representative example is the  $O_2$ - or CO-binding ability of the porphyrin complex of the divalent metal, which is remarkably enhanced by the axial ligation with an electron-donating group such as imidazole.<sup>2</sup> Another interesting example has been found in the course of our studies on the fixation reaction of carbon dioxide with metalloporphyrin. A marked acceleration of the insertion reaction of carbon dioxide into the axial Al-O bond of (porphinato)aluminum alkoxide (**3**) was observed as the result

type of reaction involving metalloporphyrin with the assistance of a coordinating ligand has been considered similarly to proceed on either side of a metalloporphyrin plane.

In the present article we describe the first example of the catalytic reaction proceeding on both sides of a metalloporphyrin plane. The reaction is the alternating copolymerization of phthalic anhydride and 1,2-epoxypropane to form a polyester, catalyzed by the system of an aluminum porphyrin with a covalently bound axial ligand ((TPP)AlX) and a quaternary ammonium or phosphonium salt.



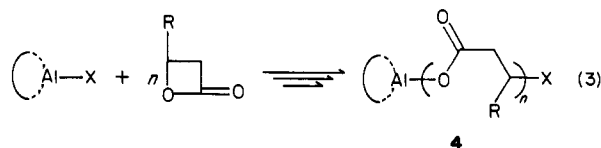
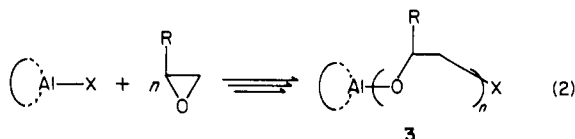
We have already found that the metalloporphyrin of aluminum gives rise effectively to the polymerizations of epoxide or  $\beta$ -lactone, producing corresponding polymers of a controlled number of repeating units with unusually narrow distribution, without any side reactions such as chain transfer or termination ("living" polymerization).<sup>5-8</sup> The repeated insertion of epoxide or  $\beta$ -lactone into the Al-X bond of the aluminum porphyrin, regenerating the alkoxide or the carboxylate of (porphinato)aluminum as the reactive species, was confirmed.<sup>9,10</sup>



(TPP)AlX

- |  |   |
|--|---|
| 1 -X = -Et                                   | 4a -X = +OCOCH <sub>2</sub> CHR <sub>2</sub> Cl                     |
| 2 = -Cl                                      | b = -OCOCH <sub>3</sub>   |
| 3 = +OCH(CH <sub>3</sub> )CH <sub>2</sub> Cl | c = -OCOC(CH <sub>3</sub> ) <sub>3</sub>                            |
|  | d = -O-C(=O)-C(=O)-OCH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> |

of the trans ligation of **3** with 1-methylimidazole.<sup>3,4</sup> The catalytic



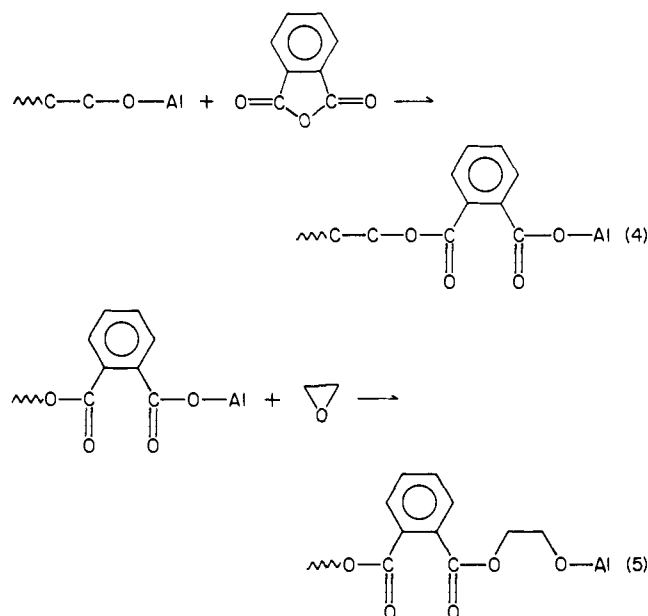
In the course of our studies to develop this excellent catalyst to other reactions, the system of aluminum porphyrin coupled with

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quaternary ammonium or phosphonium salt was found a novel, effective catalyst for the alternating copolymerization of cyclic acid anhydride and epoxide to give a polyester with narrow molecular weight distribution (eq 1). Taking into account the reaction mechanisms of the polymerization of epoxide (eq 2) and  $\beta$ -lactone (eq 3), the copolymerization of cyclic acid anhydride and epoxide is considered to involve the following two elementary steps



In this paper is described, through the mechanistic studies of the present copolymerization reaction, the evidences for the first example of the catalytic reaction simultaneously occurring on both sides of a porphyrin plane, involving a novel mode of activation of ionic species by metalloporphyrin. Detailed understanding of the mechanism of the reaction is much indebted to the analytical advantage characteristic of the polymer formation reaction that the locus or the history of the elementary reaction step is successively memorized along the polymer chain.

### Experimental Section

**Materials.** 5,10,15,20-Tetraphenylporphine (TPPH<sub>2</sub>) was synthesized from pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.<sup>11</sup> Propylene oxide was distilled after refluxing over a mixture of potassium hydroxide and calcium hydride. Phthalic anhydride was purified by recrystallization from benzene. Dichloromethane and deuterated chloroform were dried by refluxing over calcium hydride and distilled in a dry nitrogen atmosphere. Tetraethylammonium chloride was recrystallized from *N,N*-dimethylacetamide. Tetraethylammonium bromide was recrystallized from ethanol. Anhydrous tetraethylammonium acetate was obtained by dehydration of the commercial tetrahydrate complex by repeated azeotropic distillations with benzene. Ethyltriphenylphosphonium bromide and iodide were prepared by quaternization of triphenylphosphine with the corresponding ethyl halide and purified by recrystallization from water.<sup>12</sup> Tetraphenylphosphonium bromide was recrystallized from acetone. A mixture of 1-methyl-2-chloroethyl benzoate and 2-chloropropyl benzoate was prepared by the reaction of benzoyl chloride with the mixture of 1-chloro-2-propanol and 2-chloro-1-propanol (commercial propylene chlorohydrin) at reflux temperature, followed by distillation under reduced pressure.<sup>13</sup> A mixture of 1-methyl-2-bromoethyl benzoate and 2-bromopropyl benzoate was prepared, in a similar manner, from propylene bromohydrin (a mixture of 1-bromo-2-propanol and 2-bromo-1-propanol) and benzoyl bromide. Mono-1-propyl phthalate was synthesized by the reaction of phthalic anhydride and 1-propanol.<sup>14</sup> Triethylaluminum (Et<sub>3</sub>Al) and diethylaluminum chloride (Et<sub>2</sub>AlCl) were purified by distillation under reduced pressure in a nitrogen atmosphere. Commercial acetic acid and 2,2'-

dimethylpropanoic acid (pivalic acid) were used without further purification.

**Procedures.** (i) **Preparation of (TPP)AlX.** (TPP)AlEt (1) was prepared by the equimolar reaction between TPPH<sub>2</sub> and Et<sub>3</sub>Al in CH<sub>2</sub>Cl<sub>2</sub> at room temperature in a nitrogen atmosphere.<sup>15</sup> (TPP)AlOCOR (4b-4d) was prepared by the reaction of (TPP)AlEt (1) with the corresponding carboxylic acid.<sup>16</sup> (TPP)AlCl (2) was prepared by the reaction of TPPH<sub>2</sub> with Et<sub>2</sub>AlCl in CH<sub>2</sub>Cl<sub>2</sub> at room temperature in a nitrogen atmosphere.<sup>7</sup> (TPP)Al-(OCH(CH<sub>3</sub>)CH<sub>2</sub>)<sub>n</sub>-Cl (3) was prepared by the polymerization reaction of 1,2-epoxypropane with (TPP)AlCl (2).<sup>9</sup> The distribution as to the number of repeating oxyalkylene units of 3 has been confirmed to be narrow.

(ii) **Reaction of 1,2-Epoxypropane (PO) and Phthalic Anhydride (PhA).** To a 50-mL flask equipped with a three-way cock containing phthalic anhydride (25 mmol), 1,2-epoxypropane (25 mmol), and dichloromethane (10 mL) was added, by a hypodermic syringe, a dichloromethane or deuterated chloroform solution (20 mL) of the catalyst system, an equimolar mixture of (TPP)AlX and quaternary ammonium or phosphonium salt (1 mmol/1 mmol). Then, the reaction system was kept stirring at room temperature in nitrogen atmosphere. After an appropriate time, the volatile fraction was removed from the reaction system and the residue was subjected to repeated precipitation from chloroform/methanol to remove the catalyst. The precipitate, the polymeric product, was redissolved in benzene and freeze-dried in vacuo. The product was identified by NMR as the alternating copolymer of phthalic anhydride and 1,2-epoxypropane without containing the repeating oxy-(methylene) units from 1,2-epoxypropane.<sup>17</sup>

**Measurements.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the reaction system in CDCl<sub>3</sub> were measured in a sealed tube with a JEOL Type JNM GX-400 spectrophotometer operating at 399.7 and 100.5 MHz, respectively. Chemical shift was determined with respect to CHCl<sub>3</sub> ( $\delta$  7.28) for <sup>1</sup>H NMR and with respect to CDCl<sub>3</sub> ( $\delta$  77.102) for <sup>13</sup>C NMR. Infrared spectra of the reaction system were measured in a KBr fixed cell, with a Hitachi 260-30 infrared spectrophotometer. Visible spectra of the reaction system were measured in a quartz cell of 1-cm length with a Shimadzu RSP-7B spectrophotometer. Vapor-pressure osmometry, for the measurement of number-average molecular weight ( $\bar{M}_n$ ) of the polymer, was performed in benzene on a Corona 117 molecular weight apparatus, using as standard a polystyrene;  $\bar{M}_n = 2800$ ,  $\bar{M}_w/\bar{M}_n$  (ratio of weight-average molecular weight to number-average molecular weight) = 1.05, from Toyo Soda Manufacturing Co., Ltd. For the convenient estimation of molecular weight and molecular weight distribution of the polymer, gel permeation chromatography was performed on a Toyo Soda Model HLC-802A high-speed liquid chromatograph equipped with a differential refractometer detector. The eluent was tetrahydrofuran, and the flow rate was 1.1 mL·min<sup>-1</sup>. The column set consisted of four Styragel columns (60 cm) of porosity ratings 7000-3000 Å (two), 3000 Å (one), and 2000 Å (one). The molecular weight calibration curve was obtained by using standard polystyrenes;  $\bar{M}_n = 107\,000$  ( $\bar{M}_w/\bar{M}_n = 1.01$ ),  $\bar{M}_n = 16\,700$  ( $\bar{M}_w/\bar{M}_n = 1.02$ ),  $\bar{M}_n = 6200$  ( $\bar{M}_w/\bar{M}_n = 1.04$ ), and  $\bar{M}_n = 2800$  ( $\bar{M}_w/\bar{M}_n = 1.05$ ), from Toyo Soda Manufacturing Co., Ltd.

### Results and Discussion

**Copolymerization of Phthalic Anhydride and 1,2-Epoxypropane.** By using the system of aluminum porphyrin ((TPP)AlX) coupled with the quaternary salt of triethylamine (Et<sub>4</sub>N<sup>+</sup>Y<sup>-</sup>) or triphenylphosphine (RPh<sub>3</sub>P<sup>+</sup>Y<sup>-</sup>) as catalyst, the copolymerization of phthalic anhydride and 1,2-epoxypropane took place under mild conditions to give an alternating copolymer, a polyester (eq 1), in a quantitative yield (Table I, run 1-6). On the other hand, (TPP)AlX<sup>18</sup> or quaternary ammonium or phosphonium salt alone hardly gave the copolymer under similar conditions (run 7-9). The copolymer is characterized by the unusually narrow distribution as to the number of repeating units, as indicated by the ratio of weight-average molecular weight to number-average molecular weight ( $\bar{M}_w/\bar{M}_n$ ) close to one. Such a high degree of

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(17) For poly(methylene phthalate)  $\delta$  70.0 (CH), 68.5 (CH<sub>2</sub>), 16.0 (CH<sub>3</sub>), and 167.5 (CO) by <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>;  $\delta$  5.4 (CH), 4.4 (CH<sub>2</sub>), 1.34 (CH<sub>3</sub>) by <sup>1</sup>H NMR in CDCl<sub>3</sub>. For poly[oxy(methylene)ethylene]  $\delta$  75.3 (CH), 73.1 (CH<sub>2</sub>), and 17.3 (CH<sub>3</sub>) by <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>;  $\delta$  3.4 (CH and CH<sub>2</sub>) and 1.1 (CH<sub>3</sub>) by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

(18) The copolymerization of phthalic anhydride and 1,2-epoxypropane by (TPP)AlX (X = Cl, OR) took place very slowly to give the copolymer rich in ether linkage in a very low yield upon prolonged reaction time (unpublished result).

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**Table I.** Copolymerization of Phthalic Anhydride (PhA) and 1,2-Epoxypropane (PO) by Using the System of Aluminum Porphyrin Coupled with Quaternary Organic Salt as Catalyst<sup>a</sup>

run no.	porphyrin	salt	conversion of PhA, %	$\bar{M}_n^b$	$\bar{M}_w/\bar{M}_n^b$	$N_p^*/Al$
1	TPPAI OCOC(CH <sub>3</sub> ) <sub>3</sub> ( <b>4c</b> )	Et <sub>4</sub> N <sup>+</sup> CH <sub>3</sub> COO <sup>-</sup>	100	3000	1.1	1.7
2	TPPAI Cl ( <b>2</b> )	Et <sub>4</sub> N <sup>+</sup> Cl <sup>-</sup>	100	2700	1.1	1.9
3		Et <sub>4</sub> N <sup>+</sup> Br <sup>-</sup>	100	3000	1.1	1.7
4		EtPh <sub>3</sub> P <sup>+</sup> Br <sup>-</sup>	100	2500	1.1	2.1
5		EtPh <sub>3</sub> P <sup>+</sup> I <sup>-</sup>	100	3000 <sup>c</sup>	1.1	1.7
6		Ph <sub>4</sub> P <sup>+</sup> Br <sup>-</sup>	100	2300	1.1	2.2
7		none	trace	2400	1.1	2.1
8	none	Et <sub>4</sub> N <sup>+</sup> CH <sub>3</sub> COO <sup>-</sup>	0			
9		EtPh <sub>3</sub> P <sup>+</sup> Br <sup>-</sup>	0			

<sup>a</sup> [PO]<sub>0</sub> = [PhA]<sub>0</sub> = 25 mmol; [TPPAIX]<sub>0</sub> = [salt]<sub>0</sub> = 1 mmol; in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) at room temperature for 4–7 days. <sup>b</sup> By GPC calibrated with standard polystyrene. <sup>c</sup> By vapor-pressure osmometry.

regulation as to the molecular length as well as the sequence of a copolymer is the first achievement in the field of polymer synthesis and is rather surprising since two different elementary reaction steps are involved in the copolymerization reaction (eq 4 and 5). A clear increase in the molecular weight of the copolymer by successive addition of comonomers in the reaction system has confirmed that the reactive propagating species, (porphinato)aluminum alkoxide and carboxylate, are rather stable, and the present alternating copolymerization proceeds without chain transfer nor termination reaction ("living" polymerization).<sup>19</sup> Of particular interest is the fact that the number of the copolymer molecules ( $N_p^*$ ), calculated based on eq 6 from the yield ( $Y_p$ ) and the number-average molecular weight ( $\bar{M}_n$ ), is almost twice the number of aluminum porphyrin. This result is in clear contrast

$$N_p^* = Y_p \bar{M}_n^{-1} \quad (6)$$

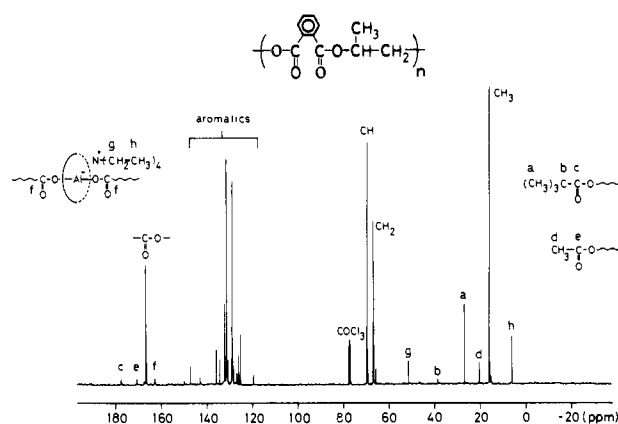
with the polymerization of epoxide or  $\beta$ -lactone by using the aluminum porphyrin (**2**) alone as catalyst (eq 2 and 3), where a good agreement was observed between the number of polymer molecules and that of aluminum porphyrin.<sup>7,8</sup> Thus, the addition of quaternary organic salt to aluminum porphyrin is considered to bring about a change in the mode of the reaction. Since  $N_p^*$  should be equal to the number of aluminum atoms in the reaction system in such a case that the polymerization proceeds by the insertion of the monomers into Al–X bond of every aluminum porphyrin molecule without any side reactions, the above observation indicates the quite unexpected and unusual fact that a two polymer chain grows on one aluminum atom in the present reaction.

**Structure of Growing Copolymer.** Taking advantage of the correspondence in numbers of the catalyst and the product and of the relatively stable nature of the reactive species, the investigation as to the structure of the reactive species, i.e., the growing (living) copolymer, can be made directly by spectroscopy of the reaction mixture.

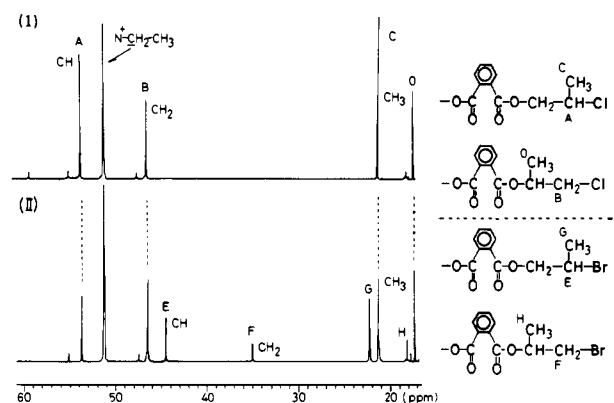
(i) <sup>13</sup>C NMR Studies. Figure 1 shows the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the reaction system of phthalic anhydride and 1,2-epoxypropane (25/25) by using (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> (**4c**) coupled with Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1/1) as catalyst. The signals appeared at  $\delta$  16.0, 68.5, 70.0, and 167.5, due respectively to methyl, methylene, methine, and carbonyl carbons of the repeating ester units in the copolymer.<sup>17</sup> A group of signals observed in the range from  $\delta$  120 to 150 are due to aromatic carbons involved in the copolymer and porphyrin. The signals due to methyl (h) and methylene (g) carbons of tetraethylammonium ion appeared at  $\delta$  7.5 and  $\delta$  51.5, slightly shifted from those of Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup>.<sup>20</sup> The signals other than the above are considered to reflect the structure of the terminal groups of the copolymer, since these are not observed in the spectrum of high molecular weight copolymer.

(19) Synthetic aspect of the present copolymerization reaction will be reported in: Aida, T.; Sanuki, K.; Inoue, S. *Macromolecules*, in press.

(20) For tetraethylammonium acetate  $\delta$  176.1 (CO), 25.0 (CH<sub>3</sub>CO), 52.6 (N<sup>+</sup>CH<sub>2</sub>), and 7.7 (N<sup>+</sup>CH<sub>2</sub>CH<sub>3</sub>) by <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>;  $\delta$  1.9 (CH<sub>3</sub>CO), 3.4 (N<sup>+</sup>CH<sub>2</sub>), and 1.3 (N<sup>+</sup>CH<sub>2</sub>CH<sub>3</sub>) by <sup>1</sup>H NMR in CDCl<sub>3</sub>.



**Figure 1.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the copolymerization system of phthalic anhydride and 1,2-epoxypropane (25/25) by using the catalyst system (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub>-Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1/1) in CDCl<sub>3</sub> at room temperature.



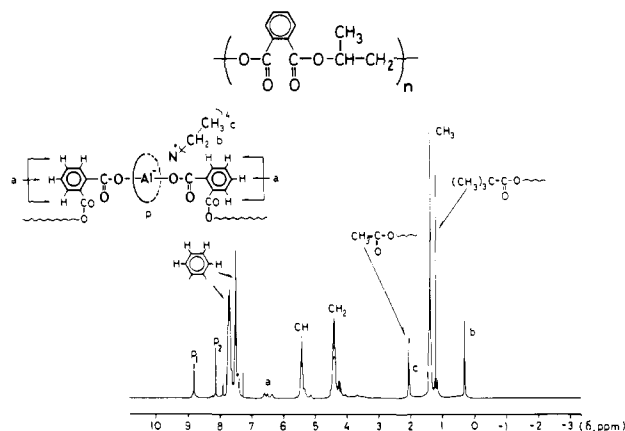
**Figure 2.** <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the copolymerization system of phthalic anhydride and 1,2-epoxypropane (25/25) in CDCl<sub>3</sub> at room temperature: (I) (TPP)AlCl-Et<sub>4</sub>N<sup>+</sup>Cl<sup>-</sup> (1/1) and (II) (TPP)AlCl-Et<sub>4</sub>N<sup>+</sup>Br<sup>-</sup> (1/1).

By reference to the spectra of methyl 2,2-dimethylpropanoate<sup>21</sup> and ethyl acetate,<sup>22</sup> two sets of signals, a ( $\delta$  27.5), b ( $\delta$  39.0), c ( $\delta$  178.0) and d ( $\delta$  20.5), e ( $\delta$  172.0), are assigned respectively to 2,2-dimethylpropanoate and acetate groups bound to one of the terminals of a copolymer molecule.

Similarly, the signals due to the unit from the epoxide attached to chlorine atom were observed in the copolymer prepared by the

(21) For methyl 2,2-dimethylpropanoate  $\delta$  26.8 ((CH<sub>3</sub>)<sub>3</sub>C), 38.3 ((C-H<sub>3</sub>)<sub>3</sub>C), 178.4 (CO), and 51.2 (OCH<sub>3</sub>) by <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>;  $\delta$  1.2 ((CH<sub>3</sub>)<sub>3</sub>C) and 3.7 (OCH<sub>3</sub>) by <sup>1</sup>H NMR in CDCl<sub>3</sub>.

(22) For ethyl acetate  $\delta$  20.0 (CH<sub>3</sub>CO), 170.0 (CO), 59.8 (OCH<sub>2</sub>), and 13.8 (OCH<sub>2</sub>CH<sub>3</sub>) by <sup>13</sup>C{<sup>1</sup>H} NMR in CDCl<sub>3</sub>;  $\delta$  2.0 (CH<sub>3</sub>CO), 4.1 (OCH<sub>2</sub>), and 1.2 (OCH<sub>2</sub>CH<sub>3</sub>) by <sup>1</sup>H NMR in CDCl<sub>3</sub>.



**Figure 3.**  $^1\text{H}$  NMR spectrum of the copolymerization system of phthalic anhydride and 1,2-epoxypropane (25/25) by the  $(\text{TPP})\text{AlOCOC}(\text{CH}_3)_3\text{-Et}_4\text{N}^+\text{CH}_3\text{COO}^-$  (1/1) system in  $\text{CDCl}_3$  at room temperature.

combination of  $\text{Et}_4\text{N}^+\text{Cl}^-$  with  $(\text{TPP})\text{AlCl}$  (A, C and B, D; Figure 2 (I)). On the other hand, the copolymerization reaction by using the system of  $(\text{TPP})\text{AlCl}$  coupled with  $\text{Et}_4\text{N}^+\text{Br}^-$  afforded the copolymer carrying a bromine atom (E, G and F, H; Figure 2, II) or a chlorine atom (A, C and B, D) at the terminal.<sup>23,24</sup> Thus, the axial group of aluminum porphyrin as well as the anion of the quaternary organic salt are confirmed to be introduced at the terminal of the copolymer.

Although both carboxylate and alkoxide of (porphinato)aluminum are considered as the growing species in the present copolymerization reaction (eq 4 and 5), the signals corresponding to the alkoxide **3** ( $\delta$  60 ppm<sup>9</sup>) were hardly observed in Figure 1, but the signal observed throughout the reaction was that due to the carboxylate group bound to (porphinato)aluminum (f) similar to the reaction product between **3** and phthalic anhydride ( $\delta$  162.1<sup>26</sup>). Considering the alternating nature of the present copolymerization reaction, this observation indicates that the reaction of the alkoxide with cyclic acid anhydride (eq 4) takes place much faster than the reaction of the carboxylate with epoxide (eq 5).

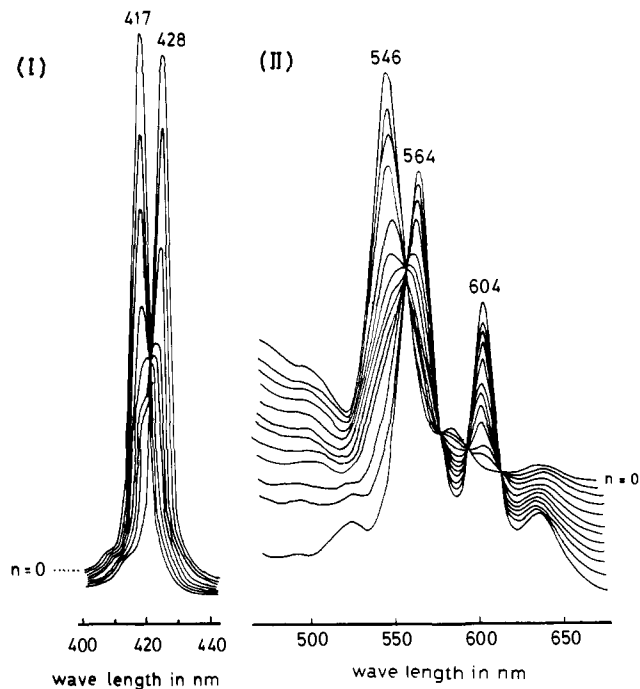
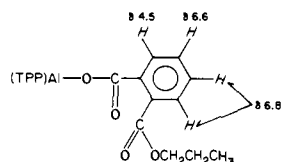
(ii)  $^1\text{H}$  NMR Studies. As to the investigation of the structure of the reactive species bound to aluminum porphyrin,  $^1\text{H}$  NMR spectroscopy is much more advantageous than  $^{13}\text{C}$  NMR, since the shielding effect of the porphyrin ring is very remarkable in the former.

Figure 3 shows the  $^1\text{H}$  NMR spectrum of the reaction system of phthalic anhydride and 1,2-epoxypropane by using  $(\text{TPP})\text{AlOCOC}(\text{CH}_3)_3$  coupled with  $\text{Et}_4\text{N}^+\text{CH}_3\text{COO}^-$  (1/1) as catalyst. The signals due to methyl, methylene, and methine protons of the oxy(methyl)ethylene unit in the copolymer were observed respectively at  $\delta$  1.34, 4.4, and 5.4, together with the aromatic protons of phthalate units at  $\delta$  7.5 and  $\delta$  7.7.<sup>17</sup> The signals at  $\delta$  1.2 and  $\delta$  2.0 are due respectively to 2,2-dimethylpropanoate and acetate groups bound to the terminal of the copolymer.<sup>21,22</sup> A group of signals (a) with three peaks at  $\delta$  6.3, 6.5, and 6.6 was assigned to the phthalate unit (3 H) bound to (porphinato)aluminum, by reference to the spectrum of **4d**<sup>25</sup> or the reaction

(23) For 1-methyl-2-chloroethyl benzoate  $\delta$  70.1 (CH), 46.9 ( $\text{CH}_2$ ), and 17.6 ( $\text{CH}_3$ ) in  $\text{CDCl}_3$ . For 2-chloropropyl benzoate  $\delta$  54.0 (CH), 68.9 ( $\text{CH}_2$ ), and 21.6 ( $\text{CH}_3$ ) in  $\text{CDCl}_3$ . For 1-methyl-2-bromoethyl benzoate  $\delta$  69.4 (CH), 35.3 ( $\text{CH}_2$ ), and 18.4 ( $\text{CH}_3$ ) in  $\text{CDCl}_3$ . For 2-bromopropyl benzoate  $\delta$  44.7 (CH), 68.9 ( $\text{CH}_2$ ), and 22.2 ( $\text{CH}_3$ ) in  $\text{CDCl}_3$ .

(24) Two types of structure observed respectively for chlorine-attached terminal (A, B) and for bromine-attached terminal (E, F) are due to the cleavage of the unsymmetrical epoxide ring at the O- $\text{CH}_2$  bond as well as the O-CH bond in the reaction.

(25) For **4d** in  $\text{CDCl}_3$ .



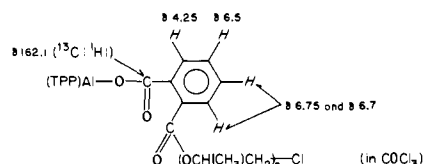
**Figure 4.** Visible spectra of the  $(\text{TPP})\text{AlOCOC}(\text{CH}_3)_3\text{-Et}_4\text{N}^+\text{CH}_3\text{COO}^-$  system in  $\text{CH}_2\text{Cl}_2$ .  $n$  represents the molar ratio of  $\text{Et}_4\text{N}^+\text{CH}_3\text{COO}^-$  to  $(\text{TPP})\text{AlOCOC}(\text{CH}_3)_3$ .

mixture between **3** and phthalic anhydride.<sup>26</sup> This and the signal  $p_1$  ( $\delta$  8.85) due to the  $\beta$ -pyrrole proton of porphyrin ring, which is highly sensitive to the axial ligation of metalloporphyrin, were observed at slightly higher magnetic field with respect to the corresponding signals of the reference samples, **4d** or the reaction product between **3** and phthalic anhydride ( $p_1$ ,  $\delta$  9.1). The integration of the signals a (3 H) and  $p_1$  (8 H) indicated the presence of 2 equiv of phthalate groups bound to aluminum atom in a porphyrin ring. Thus, the novel aluminum porphyrin carrying one carboxylate group on both sides of a porphyrin plane, respectively, is considered as the structure of a reactive (growing) species in the present copolymerization reaction. A large upfield shift observed for the signals due to methyl (b,  $\delta$  0.3) and methylene (c,  $\delta$  2.05) protons of tetraethylammonium ion<sup>20</sup> suggests that the cation of the organic salt in the reaction system is also located near the porphyrin ring, probably as the paired ion of the six-coordinate aluminum porphyrin.

**Structure of a (Porphinato)aluminum Carboxylate-Quaternary Ammonium Salt System.** Since the structure of the reactive species thus proposed for the copolymerization suggested a novel type of coordination of quaternary ammonium salt with aluminum porphyrin, detailed studies were performed on the system from  $(\text{TPP})\text{AlOCOR}$  (**4**) and  $\text{Et}_4\text{N}^+\text{RCOO}^-$ , which may be regarded as a simplified model for the reactive species of the present copolymerization reaction.

(i) **Visible, Infrared, and NMR Spectral Studies.** Upon mixing  $(\text{TPP})\text{AlOCOC}(\text{CH}_3)_3$  (**4b**) with  $\text{Et}_4\text{N}^+\text{CH}_3\text{COO}^-$  in  $\text{CHCl}_3$ , the color of the solution varied from reddish purple to bluish purple which is similar to the color of the copolymerization system. Figure 4 (I) shows the visible spectra at the region of the Soret band, in which the absorption maximum changed from 417 to 428 nm upon addition of  $\text{Et}_4\text{N}^+\text{CH}_3\text{COO}^-$  to  $(\text{TPP})\text{AlOCOC}(\text{CH}_3)_3$ . As for the

(26) The reaction of phthalic anhydride and **3** proceeds to form the following species:



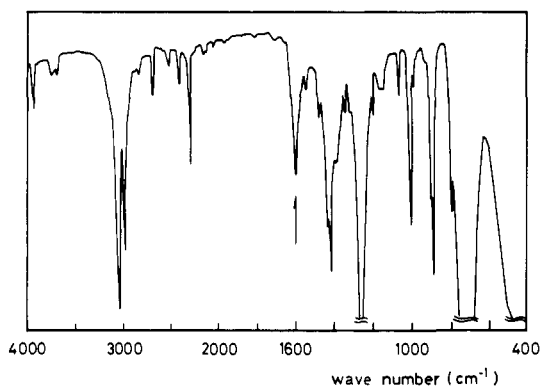


Figure 5. Infrared spectrum of the equimolar mixture of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub>.

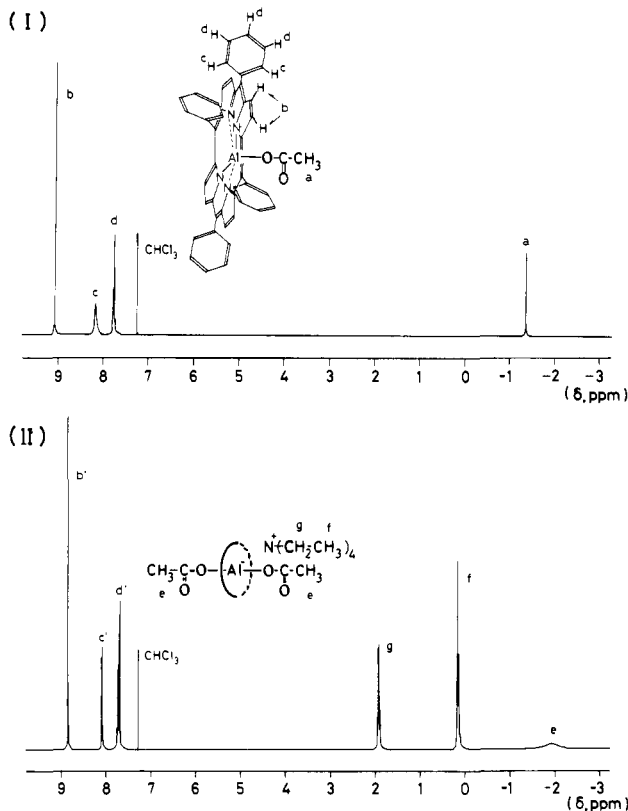


Figure 6. <sup>1</sup>H NMR spectra in CDCl<sub>3</sub> at 20 °C: (I) (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and (II) (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub>-Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1/1).

Q band of aluminum porphyrin, dramatic change in the absorption pattern was also observed as shown in Figure 4 (II), where the absorption at 546 nm decreased in its intensity with the mole fraction of Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> in the system, while new absorption bands appeared at 564 and 604 nm. The visible spectral profile thus observed is quite analogous to that observed in the coordination of 1-methylimidazole to (porphinato)aluminum alkoxide (3).<sup>4</sup>

In the infrared spectrum in CH<sub>2</sub>Cl<sub>2</sub> of the equimolar mixture of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> (4b) and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> was observed a sharp carbonyl absorption at 1600 cm<sup>-1</sup> (Figure 5), while the absorptions due to (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> (1550 cm<sup>-1</sup>) and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1570 cm<sup>-1</sup>) were hardly observed. This result indicates the formation of a single carboxylate species from two different sources of carboxylate group, (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup>. Thus, the formation of a six-coordinate aluminum porphyrin carrying one carboxylate group as the axial ligand on both sides, respectively, of a porphyrin plane is considered most likely in the system involving (TPP)AlOCOR and Et<sub>4</sub>N<sup>+</sup>RCOO<sup>-</sup>.

Figure 6 (I) shows the <sup>1</sup>H NMR spectrum of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub>, in which a characteristic signal due to the axial CH<sub>3</sub>COO

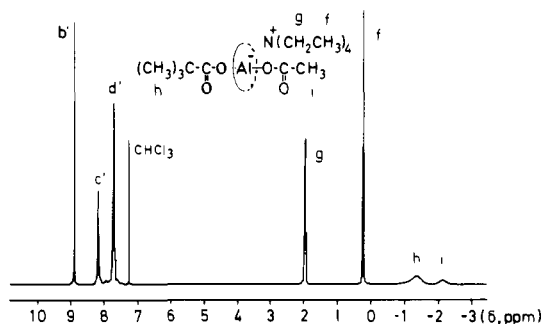
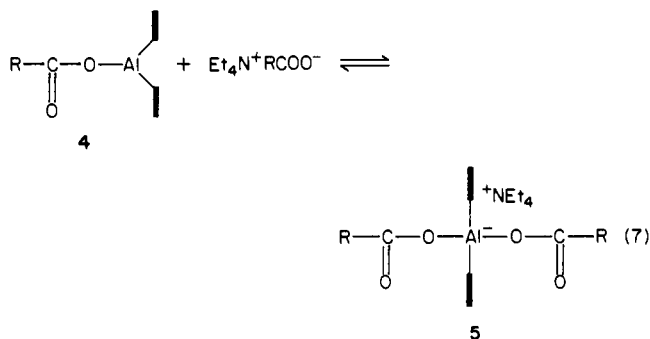


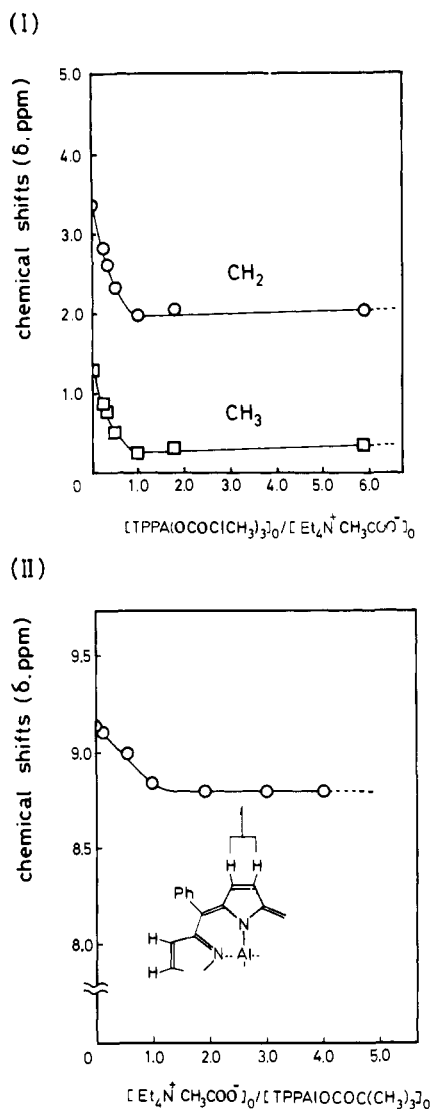
Figure 7. <sup>1</sup>H NMR spectra of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub>-Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1/1) system in CDCl<sub>3</sub> at 20 °C.

group appeared at  $\delta$  -1.4 (a)<sup>16</sup> together with the signals due to  $\beta$ -pyrrole (b,  $\delta$  9.1) and phenyl (c,  $\delta$  8.15 and d,  $\delta$  7.8) protons of the porphyrin ligand. Upon mixing (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> with an equimolar amount of Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (Figure 6 (II)), the signals due to the CH<sub>3</sub>COO groups of TPPAlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> ( $\delta$  1.9) disappeared. Instead, a broad signal (e) with the intensity corresponding to the sum of the above two carboxylate groups appeared at about  $\delta$  -2.0. On the other hand, an equimolar mixture of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> (4c) and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> showed two broad signals at about  $\delta$  -1.4 (h) and  $\delta$  -2.15 (i) (Figure 7), with the disappearance of the signals corresponding to the carboxylate groups of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> ( $\delta$  -1.1) as well as Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> ( $\delta$  1.9). The relative intensities of the signals h and i with respect to the  $\beta$ -pyrrole proton of the porphyrin ring (b') indicated that the signals h and i were due respectively to (CH<sub>3</sub>)<sub>3</sub>CCOO and CH<sub>3</sub>COO groups originating from (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup>. Furthermore, in this case was also observed an upfield shift for the signals due to methyl (f) and methylene (g) protons of the tetraethylammonium ion.<sup>20</sup> The shift increased with the mole ratio of (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> to Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> and reached a plateau at the equimolar ratio (Figure 8 (I)). Similar observation was made for the upfield shift of the signal due to  $\beta$ -pyrrole protons of porphyrin ring, as shown in Figure 8 (II).

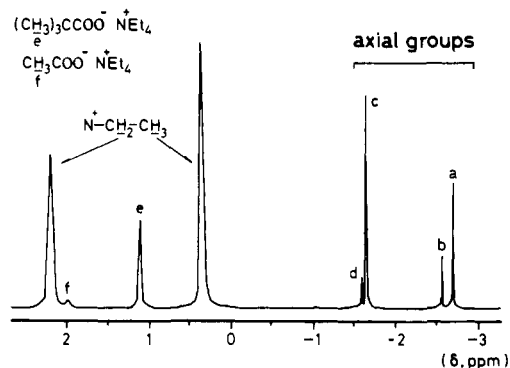
Thus, all the observed results described above clearly demonstrate the following equilibrium between five-coordinate aluminum porphyrin (TPP)AlOCOR and six-coordinate complex formed from (TPP)AlOCOR and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> carrying one carboxylate group as the axial ligand on both sides, respectively, of a porphyrin plane



(ii) **NMR Spectrum at Low Temperature.** In the <sup>1</sup>H NMR spectrum of the mixture of Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> and (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> at the mole ratio of 0.56 at -60 °C, the signal due to the porphyrin proton ( $\delta$  8.99) was observed to split into two signals,  $\delta$  9.1 and  $\delta$  8.84, assignable respectively to the five-coordinate and six-coordinate aluminum porphyrins. In such a case, similar resolved signals were observed as for the axial ligand. On the other hand, (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> in the presence of more than one equivalent amount of Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> shows only the signal due to six-coordinate species. In connection with this, a quite interesting observation was made in the <sup>1</sup>H NMR spectrum at -60 °C of the system from (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1/1.92) (Figure 9). Two singlet signals were observed

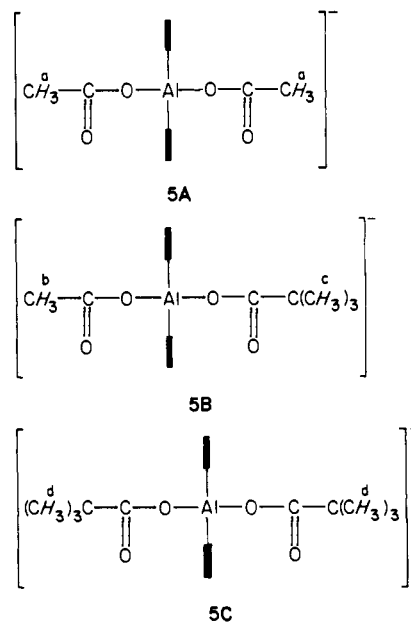


**Figure 8.** <sup>1</sup>H NMR chemical shift and the molar ratio in the system from (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> in CDCl<sub>3</sub> at 20 °C: (I) the ethyl group of the tetraethylammonium ion and (II) the β-pyrrole proton of the porphyrin.



**Figure 9.** <sup>1</sup>H NMR spectrum of the system from (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> (1/1.92) in CDCl<sub>3</sub> at -60 °C.

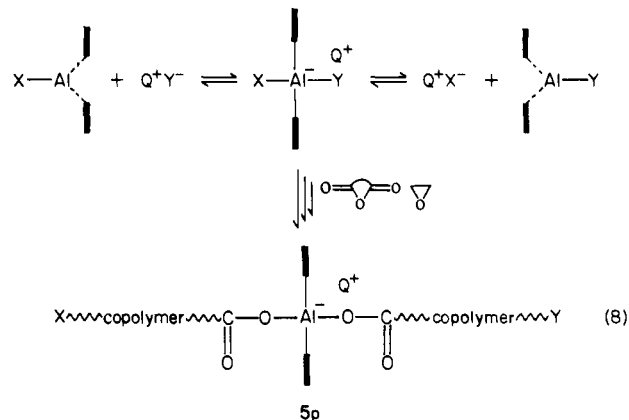
for CH<sub>3</sub>COO (a, δ -2.71 and b, δ -2.57), and the other two singlet signals for (CH<sub>3</sub>)<sub>3</sub>CCOO (c, δ -1.65 and d, δ -1.60), while the system from (TPP)AlOCOCH<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> showed a single signal at δ -2.70. This is in conformity with the proposed structure of six-coordinate aluminum porphyrin (5 in eq 7), since the following three different combinations as to the axial ligands on the front and the back sides of a porphyrin plane are considered possible when two types of carboxylate group are involved in the reaction system



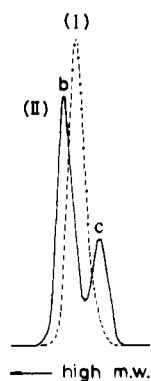
A slight difference in the chemical shift between the signals a and b or between c and d may be ascribed to the difference in the ability of an axial carboxylate group to coordinate toward aluminum porphyrin on the opposite side to another axial carboxylate, since the mole fraction of the less bulkier CH<sub>3</sub>COO group on the aluminum porphyrin estimated by the signal intensities (75%) is enhanced compared with that in Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> in the feed (65%). A pair of the signals b and c was found to have the intensity ratio of three corresponding to the mixed carboxylate complex 5B. The remarkable upfield shift observed for the signal due to the axial carboxylate group of aluminum porphyrin accompanied by the formation of six-coordinate species (eq 7) is ascribed to the structural change of the N<sub>4</sub>Al skeleton from the square pyramidal (4) to the square planar (5), by which the shielding effect of porphyrin on the axial group becomes more pronounced. Similar observation was also made for the reactive species in the copolymerization reaction (Figure 3, signal a).

Thus, the system from (TPP)AlOCOR and Et<sub>4</sub>N<sup>+</sup>R'COO<sup>-</sup> exhibits the spectral characteristics very similar to that of the copolymerization system.

**Mechanism of the Reaction.** Taking into consideration that the copolymer with a terminal group originating from the anion of quaternary ammonium (or phosphonium) salt or the axial group on aluminum porphyrin is formed and that the number of the copolymer molecule is twice with respect to aluminum porphyrin, the above spectral information as to the structure of aluminum porphyrin clearly demonstrates that the copolymerization reaction simultaneously takes place on both sides of a porphyrin plane, retaining the active six-coordinate structure of aluminum porphyrin

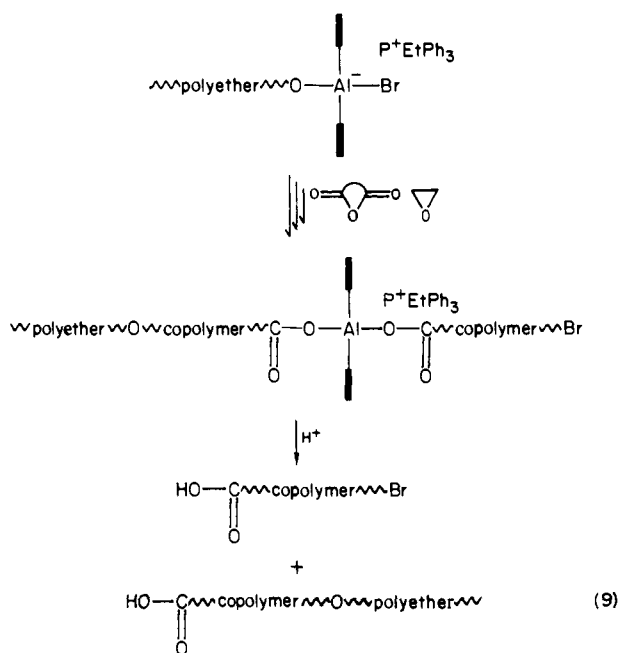


Other supporting evidence for the reaction proceeding on both sides of a metalloporphyrin plane was obtained by the co-



**Figure 10.** GPC profile of the copolymerization of phthalic anhydride and 1,2-epoxypropane (25/25) by using the system from (TPP)Al-(OCH(CH<sub>3</sub>)CH<sub>2</sub>)<sub>n</sub>-Cl and EtPh<sub>3</sub>P<sup>+</sup>Br<sup>-</sup> (1/1) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature: (I) -(O-CH(CH<sub>3</sub>)CH<sub>2</sub>)<sub>n</sub>-Cl in the catalyst and (II) reaction mixture.

polymerization of phthalic anhydride and 1,2-epoxypropane with aluminum porphyrin carrying a macromolecular axial ligand, a polyether with well-regulated chain length, (TPP)Al-(OCH(CH<sub>3</sub>)CH<sub>2</sub>)<sub>n</sub>-Cl (**3**,<sup>9</sup>  $\bar{M}_n = 3500$ ,  $\bar{M}_w/\bar{M}_n = 1.10$ ). When this aluminum porphyrin coupled with EtPh<sub>3</sub>P<sup>+</sup>Br<sup>-</sup> is used as catalyst, the product with an end group originating from the axial ligand of this aluminum porphyrin is expected to have a longer molecular chain than the product carrying bromine end group from the organic salt

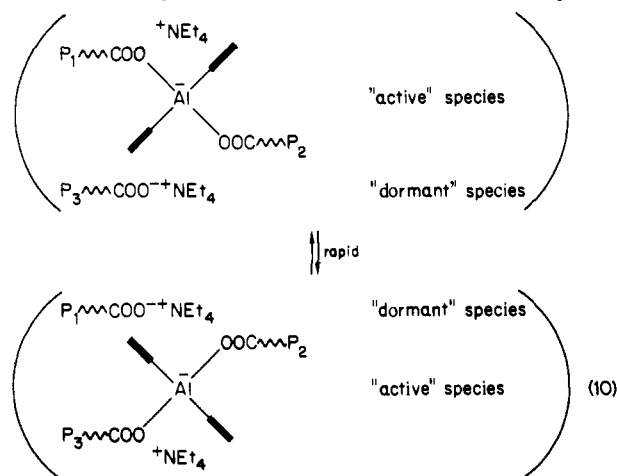


As shown by two narrow peaks in the gel permeation chromatogram (GPC) illustrated in Figure 10, the reaction mixture showed, as expected, a bimodal molecular weight distribution. Peak I corresponding to the axial ligand of **3** was no longer observed, confirming the quantitative reaction of **3**. Furthermore, the value calculated by subtracting the molecular weight corresponding to peak b from that corresponding to peak a was in fair

agreement with the number-average molecular weight of the axial ligand (polyether) of **3**.

Since five-coordinate aluminum porphyrin exhibits much less activity in the present copolymerization reaction,<sup>18</sup> the enhanced reactivity of the reactive species as the axial ligand of six-coordinate aluminum porphyrin (**5**) is ascribed to the "mutual" trans effect between the reactive species separated by a porphyrin plane.

Another aspect of general interest in the present reaction is the novel function of metalloporphyrin as an activator of the anion of quaternary ammonium or phosphonium salt as nucleophile. In connection with this was observed a decrease in the number average molecular weight of the copolymer in inverse proportion to the total number of carboxylate groups in the reaction system, retaining the narrow molecular weight distribution. An example was demonstrated by the copolymerization reactions with use of the system from (TPP)AlOCOC(CH<sub>3</sub>)<sub>3</sub> and Et<sub>4</sub>N<sup>+</sup>CH<sub>3</sub>COO<sup>-</sup> as catalyst with the ratios of 1/1 and 1/2, where the former afforded the product with the number-average molecular weight of 3000 (run 1 in Table), while the latter had a number-average molecular weight of 2200 ( $\bar{M}_w/\bar{M}_n = 1.1$ ). Thus, the copolymerization reaction in the latter case is considered to take place from every carboxylate group involved in the catalyst system, producing the reactive species the number of which is three-halves with respect to a molecule of aluminum porphyrin. This fact indicates that there exist an "active" species and a "dormant" species simultaneously, with a rapid interconversion between these two species



This interconversion is considered much faster than the reaction of chain growth (eq 4 and 5), considering the narrow distribution as to the number of repeating units in the resulting copolymer.

### Conclusion

The copolymerization reaction of phthalic anhydride and 1,2-epoxypropane with an aluminum porphyrin-quaternary ammonium or phosphonium salt system as catalyst disclosed the first example of the catalytic reaction simultaneously occurring on both sides of a metalloporphyrin plane, involving a novel type of activation of anionic species of quaternary ammonium or phosphonium salt as nucleophile by metalloporphyrin.

**Registry No.** Et<sub>4</sub>N<sup>+</sup>·CH<sub>3</sub>COO<sup>-</sup>, 1185-59-7; Et<sub>4</sub>N<sup>+</sup>·Cl<sup>-</sup>, 56-34-8; Et<sub>4</sub>N<sup>+</sup>·Br<sup>-</sup>, 71-91-0; EtPh<sub>3</sub>P<sup>+</sup>·Br<sup>-</sup>, 1530-32-1; EtPh<sub>3</sub>P<sup>+</sup>·I<sup>-</sup>, 4736-60-1; Ph<sub>4</sub>P<sup>+</sup>·Br<sup>-</sup>, 2751-90-8; TPPAlOC(O)CH<sub>3</sub>, 85709-47-3; TPPAlCl, 71102-37-9; TPPAlOC(O)C(CH<sub>3</sub>)<sub>3</sub>, 94348-17-1; (PhA)·(PO) (copolymer), 26009-60-9; poly(PhA)·(PO)(SRU), 9053-08-1.