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Living Polymerization of δ-Valerolactone with Aluminum Porphyrin. Trimolecular Mechanism by the Participation of Two Aluminum Porphyrin Molecules

Kazuhiro Shimasaki,[†] Takuzo Aida, and Shohei Inoue[*]

Department of Synthetic Chemistry, Faculty of Engineering, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan. *Received April 27, 1987;*
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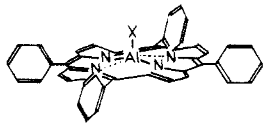
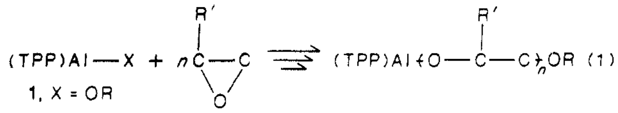
ABSTRACT: (5,10,15,20-Tetraphenylporphinato)aluminum alkoxide ((TPP)AlOR) brought about the "living" polymerization of δ-valerolactone, while no polymerization took place by (TPP)AlCl. The addition of (TPP)AlCl to the polymerization system initiated with (TPP)AlOR resulted in a remarkable acceleration without losing the "living" character. Spectroscopic and kinetic analyses revealed for the first time the simultaneous participation of two molecules of aluminum porphyrin for chain growth, involving a (porphinato)aluminum alkoxide as the growing species and another aluminum porphyrin molecule as a Lewis acid to coordinate with and activate the monomer.

Introduction

Aluminum porphyrin (1) is an excellent initiator for the polymerization of epoxide[1] and lactone[2] to give the corresponding polymer with very narrow molecular weight distribution. The polymerization proceeds by the repeated insertion of monomer into the aluminum–axial ligand bond of aluminum porphyrin (Al–X of 1). For example, the polymerization of epoxide or ε-caprolactone proceeds by the nucleophilic attack of a (porphinato)aluminum alkoxide (1, X = OR) as the growing species on the monomer[3] (eq. 1 and 2).



(TPP)AlX (1)



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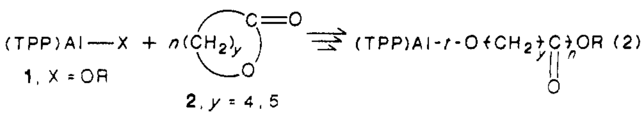

(2)

In this connection, some observations have been made which indicate the coordination of monomer to the aluminum atom. An example is the preferred polymerization of cis isomer to the trans isomer in the polymerization of geometrical isomers of 2,3-butene oxide by aluminum porphyrin.[4] This structural preference is typical of the polymerization by "coordinate" anionic catalyst such as the triethylaluminum–water–acetylacetone system.[5] In relation to this observation, the Lewis acidity of aluminum porphyrin is exemplified by its ability to coordinate with *N*-methylimidazole[6] or the counteranion of ammonium salt.[7] Therefore, the coordination and activation of monomer by the aluminum atom of aluminum porphyrin are considered to take place in the polymerization of lactone, although there has been no evidence.

In this paper evidence is given for the coordination to the aluminum atom and activation of lactone in the living polymerization of δ-valerolactone[8] initiated with (porphinato)aluminum alkoxide. Also evidence is presented for the first time that the mechanism involves two molecules of aluminum porphyrin.

Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ((TPP)H_2) was synthesized by the reaction of pyrrole and benzaldehyde in propionic acid and recrystallized from chloroform/methanol.[9] δ-Valerolactone was dried with calcium hydride and fractionally distilled under reduced pressure. Diethylaluminum chloride (Et_2AlCl) and triethylaluminum (Et_3Al) were fractionally distilled in nitrogen under reduced pressure, respectively.

Dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$), washed sequentially with concentrated sulfuric acid, water, and dilute aqueous solution of sodium bicarbonate, were dried with calcium chloride followed by distillation in a nitrogen atmosphere after refluxing with calcium hydride. Methanol was purified as follows: 100 mL of methanol was dried with calcium hydride followed by refluxing over the mixture of magnesium (5 g) and iodine (2.5 g) until all of the magnesium was converted to the methoxide, and then 1 L of methanol was added, refluxed, and distilled in a nitrogen atmosphere.

Preparation of Aluminum Porphyrin. (TPP)AlCl (1, X = Cl).[3a] A round-bottom flask (50 or 100 mL) equipped with a three-way stopcock containing $TPPH_2$ (1 mmol) was purged with dry nitrogen, and dichloromethane (20 mL) was added by a hypodermic syringe in a nitrogen stream to dissolve the porphyrin. To this solution was added Et_2AlCl (1.2 mmol), and the mixture was stirred for 2 h. Then, volatile fractions were removed from the reaction mixture to leave (5,10,15,20-tetraphenylporphinato)aluminum chloride ((TPP)AlCl (1, X = Cl)) as a purple powder.

(TPP)AlOMe (1, X = OMe).[10] To chloroform (20 mL) containing $TPPH_2$ (1 mmol) was added Et_3Al (1 mmol), and the mixture was stirred for 2 h. Then, methanol (10 mL) was added and the mixture was stirred for 16 h at 50 °C. Volatile fractions were removed from the reaction mixture to leave (5,10,15,20-tetraphenylporphinato)aluminum methoxide ((TPP)AlOMe (1, X = OMe)) as a purple powder.

Polymerization. To a round-bottom flask containing (TPP)AlOMe was added δ-valerolactone (2, n = 4) by a hypo-

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[†] On leave from the Tokuyama Soda Co., Ltd., Tokuyama, Japan.

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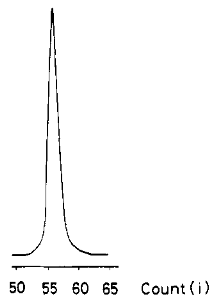


Figure 1. GPC curve of the polymerization mixture of δ-valerolactone (δ-VL) initiated with (TPP)AlOMe. Reaction conditions: $[\delta\text{-VL}]_0/[(\text{TPP})\text{AlOMe}]_0 = 200$; without solvent at 50 °C for 580 h; conversion 86%; $\bar{M}_w/\bar{M}_n = 1.12$.

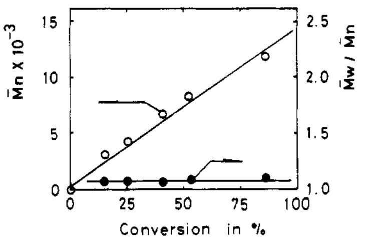


Figure 2. Polymerization of δ-valerolactone initiated with (TPP)AlOMe: relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (●) and the conversion; $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC.

dermic syringe in a nitrogen stream, and the mixture was stirred magnetically at 50 °C.

For the determination of the conversion of the monomer, an aliquot of the reaction mixture was taken out by a hypodermic syringe in a nitrogen stream and was subjected to gel permeation chromatography. The formation of polymer was confirmed by ^{1}H NMR of the reaction mixture; for poly(δ-valerolactone): δ 4.10 (t, 2 H, CH_2O), 2.35 (t, 2 H, $CH_2C(O)$), 1.70 (m, 4 H, $CH_2(\text{-}CH_2\text{-})_2CH_2$).

Kinetic analysis was carried out on the basis of the rate of monomer consumption at the initial stage of polymerization.

Measurements. ^{1}H NMR measurements were performed in $CDCl_3$ on a JEOL type JNM GX-400 spectrometer operating at 399.7 MHz. Chemical shift was determined with respect to $CHCl_3$ (δ 7.28). For the estimation of average molecular weight and molecular weight distribution, gel permeation chromatography (GPC) of the reaction mixture was performed on a Toyo Soda Model 802A high-speed liquid chromatograph equipped with a differential refractometer detector, using tetrahydrofuran as eluent at 38 °C. The flow rate was 1.1 mL·min^{-1}. The column set consisted of four Styragel columns (60 cm) of porosity ratings 7000–3000 (two), 3000 (one), and 2000 Å (one). The molecular weight calibration curve was obtained by using standard polystyrenes; 107 000 ($\bar{M}_w/\bar{M}_n = 1.01$), 43 900 (1.01), 39 000 (1.07), 18 000 (1.10), 16 700 (1.02), 6200 (1.04), and 2800 (1.05) (Toyo Soda Manufacturing Co., Ltd.).

Results and Discussion

Polymerization of δ-Valerolactone with (TPP)AlOMe (1, X = OMe). A typical gel permeation chromatogram of the polymerization mixture of δ-valerolactone with (TPP)AlOMe (1, X = OMe) is shown in Figure 1, where the polymerization was carried out with the mole ratio of monomer to (TPP)AlOMe of 200 for 580 h at 50 °C, and the monomer conversion was 86%. The molecular weight distribution of the polymer was very narrow ($\bar{M}_w/\bar{M}_n = 1.12$; $\bar{M}_n = 12\,000$). No peak due to the cyclic oligomer was detected in the low molecular weight region.

As shown in Figure 2, the number-average molecular weight ($\bar{M}_n$) of the polymer increased linearly with conversion, keeping the ratio of the weight- and the number-average molecular weights ($\bar{M}_w/\bar{M}_n$) almost constant at 1.06–1.10 throughout the polymerization. These facts indicate the living nature of polymerization without any chain transfer and termination reactions. In the reaction of δ-valerolactone with (TPP)AlOMe, two modes of ring cleavage, and two different growing species, accordingly, are considered possible; the acyl–oxygen cleavage to give (porphinato)aluminum alkoxide (a) and the alkyl–oxygen cleavage to give (porphinato)aluminum carboxylate (b).

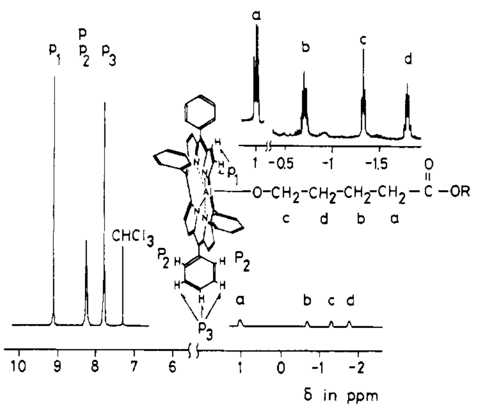
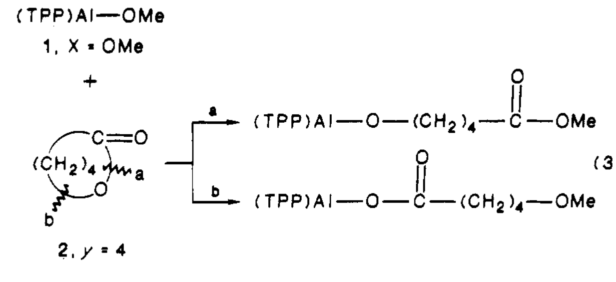


Figure 3. ^{1}H NMR spectrum of living oligomeric δ-valerolactone (δ-VL) prepared by (TPP)AlOMe ($[\delta\text{-VL}]_0/[(\text{TPP})\text{AlOMe}]_0 = 8$) in $CDCl_3$ at room temperature.



In this respect, the ^{1}H NMR analysis was made on the reaction mixture between (TPP)AlOMe and δ-valerolactone (1/8) in $CDCl_3$ at room temperature, since the signal at upfield region, if any, is informative of the structure of the growing species attached to the central aluminum atom. As shown in Figure 3, the extended spectrum in the upfield region clearly shows four signals (a, δ 1.0; b, δ -0.71; c, δ -1.34; d, δ -1.80) in which the triplet signal c at δ -1.34 is assignable to the methylene group of (TPP)Al-O-CH_2-CH_2-CH_2-CH_2-CO···.[11] If a (porphinato)aluminum carboxylate was formed by the ring cleavage at the alkyl–oxygen bond, the corresponding (TPP)Al-O-OC-CH_2-CH_2··· should be observable at δ -0.7 (t).[12] Thus, δ-valerolactone is cleaved at acyl–oxygen bond by (TPP)AlOMe to give a (porphinato)aluminum alkoxide as the growing species.

Polymerization of δ-Valerolactone with a Mixture of (TPP)AlOMe (1, X = OMe) and (TPP)AlCl (1, X = Cl). In contrast to (TPP)AlOMe, (TPP)AlCl (1, X = Cl) did not initiate the polymerization of δ-valerolactone. However, (TPP)AlCl was found to affect remarkably the polymerization of δ-valerolactone with (TPP)AlOMe. As shown in Figure 4, the polymerization was remarkably accelerated by the addition of (TPP)AlCl. In the reaction with the lactone to (TPP)AlOMe ratio of 200 at 50 °C, the conversion was 53% after 320 h, while the conversion dramatically increased to 51% after 1.3 h upon the addition of a half molar equivalent of (TPP)AlCl to (TPP)AlOMe.

Of particular interest is the fact that the addition of (TPP)AlCl does not affect the molecular weight of the polymer. The degree of polymerization is proportional to

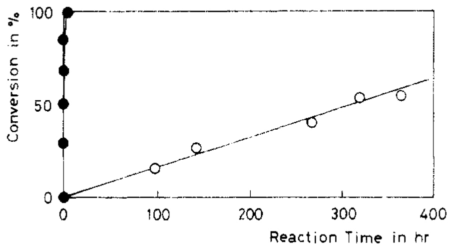


Figure 4. Time–conversion curve for the polymerization of δ-valerolactone (δ-VL) initiated with (TPP)AlOMe in the absence (○) and in the presence of (TPP)AlCl (●), at 50 °C without solvent ($[\delta\text{-VL}]_0/[(\text{TPP})\text{AlOMe}]_0 = 200$; $[(\text{TPP})\text{AlOMe}]_0/[(\text{TPP})\text{AlCl}]_0 = 2$).

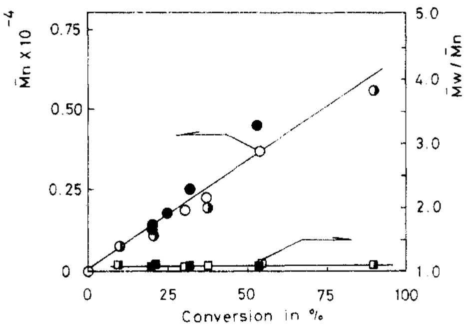


Figure 5. Polymerization of δ-valerolactone (δ-VL) initiated with (TPP)AlOMe in the presence of (TPP)AlCl: relationship between $\bar{M}_n$ (○) or $\bar{M}_w/\bar{M}_n$ (□) and the conversion; $\bar{M}_n$ and $\bar{M}_w$ as estimated by GPC ($[\delta\text{-VL}]_0/[(\text{TPP})\text{AlOMe}]_0 = 200$; $[(\text{TPP})\text{AlCl}]_0/[(\text{TPP})\text{AlOMe}]_0 = 0.5$ (●, ■), 1.0 (○, □), 2.0 (◑, ◧)).

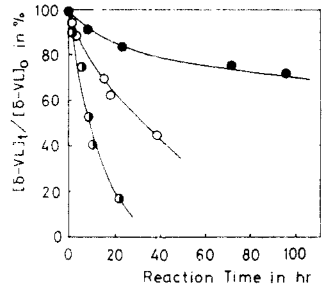


Figure 6. Polymerization of δ-valerolactone (δ-VL) initiated with various initial concentrations of (TPP)AlOMe in the presence of (TPP)AlCl in CH_2Cl_2 at 23 °C ($[\delta\text{-VL}]_0/[(\text{TPP})\text{AlOMe}]_0 = 400$ (●), 200 (○), 100 (◑); $[\delta\text{-VL}]_0/[(\text{TPP})\text{AlCl}]_0 = 200$; $[(\text{TPP})\text{AlCl}]_0 = 26.3$ mM).

the monomer to (TPP)AlOMe ratio taking the conversion into account. In other words, the number of polymer molecules is equal to that of (TPP)AlOMe, irrespective of the addition of (TPP)AlCl (Figure 5). These facts confirm that (TPP)AlCl does not initiate the polymerization but accelerates the reaction as a catalyst.

Kinetics of Polymerization. When the polymerization was initiated by various initial concentrations of (TPP)AlOMe in the presence of a constant initial concentration of (TPP)AlCl in CH_2Cl_2 at 23 °C, the rate of the monomer consumption increased as the initial concentration of (TPP)AlOMe was increased (Figure 6). When the reaction was carried out at a constant initial concentration of (TPP)AlOMe and various initial concentrations of (TPP)AlCl, the rate increased with the increase of the initial concentration of (TPP)AlCl (Figure 7). Therefore, the rate of polymerization is assumed to be expressed by the following equation

$$v = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k[(\text{TPP})\text{AlOR}]^{m}[(\text{TPP})\text{AlCl}]^{m'}[\mathrm{M}] \quad (4)$$

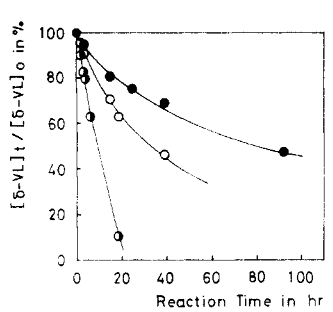


Figure 7. Polymerization of δ-valerolactone (δ-VL) initiated with a constant initial concentration of (TPP)AlOMe, in the presence of various initial concentrations of (TPP)AlCl in CH_2Cl_2 at 23 °C ($[\delta\text{-VL}]_0/[(\text{TPP})\text{AlCl}]_0 = 400$ (●), 200 (○), 100 (◑); $[\delta\text{-VL}]_0/[(\text{TPP})\text{AlOMe}]_0 = 200$; $[(\text{TPP})\text{AlOMe}]_0 = 26.3$ mM).

where [M] is the concentration of the monomer. [(TPP)AlOR] is constant throughout the polymerization, since the number of the living polymer molecules (growing species) is the same as that of (TPP)AlOMe as the initiator; that is, $[(\text{TPP})\text{AlOR}] = [(\text{TPP})\text{AlOMe}]_0$. [(TPP)AlCl] is also kept constant throughout the polymerization. Thus, eq 4 can be transformed as follows

$$\log v/[\mathrm{M}] = m \log [(\text{TPP})\text{AlOR}] + d \quad (5)$$

where $d = \log k + m' \log [(\text{TPP})\text{AlCl}]$, or

$$\log v/[\mathrm{M}] = m' \log [(\text{TPP})\text{AlCl}] + d' \quad (6)$$

where $d' = \log k + m \log [(\text{TPP})\text{AlOR}]$.

On the basis of the results of Figure 6, a linear relationship (correlation coefficient $r = 1.00$) was found to exist between $\log v/[\mathrm{M}]$ and $\log [(\text{TPP})\text{AlOR}]$. From the slope of the line, the value of m was found to be unity. Similarly, a linear relationship ($r = 1.00$) between $\log v/[\mathrm{M}]$ and $\log [(\text{TPP})\text{AlCl}]$ was confirmed, and the value of m' was found to be unity on the basis of the results of Figure 7.

Thus, the rate of reaction can be described as follows

$$v = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k[(\text{TPP})\text{AlOR}][(\text{TPP})\text{AlCl}][\mathrm{M}] \quad (7)$$

where $k = 2 \times 10^{-2}\ (\mathrm{dm}^3)^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$.

According to the rate equation, three molecules, (TPP)AlOR, (TPP)AlCl, and δ-valerolactone, are considered to participate in the polymerization. Similarly, in the polymerization of δ-valerolactone initiated by (TPP)AlOMe in the absence of (TPP)AlCl without solvent, the rate equation of the polymerization was found to be described as follows

$$v = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k'[(\text{TPP})\text{AlOR}]^2[\mathrm{M}] \quad (8)$$

where $k' = 6 \times 10^{-4}\ (\mathrm{dm}^3)^2\ \mathrm{mol}^{-2}\ \mathrm{s}^{-1}$.

Thus, even in the absence of (TPP)AlCl, two molecules of (TPP)AlOR are considered to be involved in the reaction. Since one of the two (TPP)AlOR molecules is the growing species to attack the monomer, the other molecule of (TPP)AlOR is considered to participate in the reaction as a catalyst. In view of the higher rate constant for the system containing (TPP)AlCl, the role of the second aluminum porphyrin molecule is considered to interact with the monomer as a Lewis acid and to activate the monomer for the nucleophilic attack by the growing species.

(TPP)AlCl is considered to be a stronger Lewis acid than (TPP)AlOR because of the stronger electron-attracting nature of the chlorine group compared to the alkoxy.

Interaction between (TPP)AlCl and Lactone. In order to obtain the information as to the interaction between (TPP)AlCl and δ-valerolactone, ^{1}H NMR measurement was carried out for a $CDCl_3$ solution containing (TPP)AlCl and δ-valerolactone at room temperature.

At the molar ratio of (TPP)AlCl to δ-valerolactone of 2:1, the mixture showed the spectrum as shown in Figure

Table I
^{1}H NMR Chemical Shifts of δ-Valerolactone (δ-VL), (TPP)AlCl, and δ-VL-(TPP)AlCl (1/2)^a

	porphyrin					
	p^1 pyrrole β	p^2 phenyl o	p_3 phenyl m, p	a OCH_2	b $C(O)CH_2$	c $CH_2(CH_2)_2CH_2$
δ-VL-(TPP)AlCl (1/2)	9.2	8.3	7.8	4.1	2.0	1.7
δ-VL				4.2	2.4	1.8
(TPP)AlCl	9.2	8.3	7.8			

^{a}In $CDCl_3$ at room temperature; for the assignments, see Figure 8.

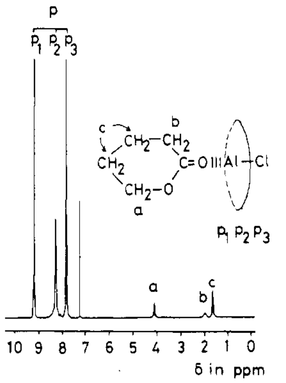


Figure 8. ^{1}H NMR spectrum of the $CDCl_3$ solution containing (TPP)AlCl and δ-valerolactone at room temperature ($[δ\text{-VL}]_0/[(TPP)AlCl]_0 = 2$; $[(TPP)AlCl]_0 = 50$ mM).

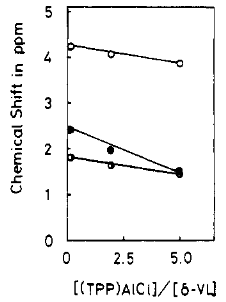


Figure 9. Relationship between the chemical shift of the signals due to δ-valerolactone (δ-VL) in (TPP)AlCl–δ-VL system in $CDCl_3$. For the assignment of the signals, see Figure 8.

8, where signals p are due to the porphyrin and the signals a, b, and c are assigned to CH_2O, CH_2CO, and other CH_2 groups of δ-valerolactone, respectively. When the spectrum of the mixture was compared with those of (TPP)AlCl alone and δ-valerolactone alone, respectively (Table I), each signal for δ-valerolactone in the mixture shifted to a higher magnetic field. The extent of the upfield shift was most remarkable in signal b. When the molar ratio of (TPP)AlCl to δ-valerolactone was increased (Figure 9), the shift to a higher magnetic field became more remarkable, particularly for signal b. Each signal due to the lactone was broadened with an increase of the ratio of (TPP)AlCl to δ-valerolactone, and the broadening was also most remarkable in signal b. These facts indicate that an interaction between δ-valerolactone and (TPP)AlCl takes place by the coordination of the carbonyl group to (TPP)AlCl.

As described in the previous section, (TPP)AlCl is considered to interact with and activate lactone more strongly than (TPP)AlOMe as a Lewis acid. In order to confirm this by ^{1}H NMR studies, we selected γ-butyrolactone (**2**, $y = 3$) as the lactone, since this lactone can be polymerized by neither (TPP)AlCl nor (TPP)AlOMe, and it is considered possible to compare the extent of the interaction of this lactone with (TPP)AlCl and with (TPP)AlOMe. Figure 10 shows the ^{1}H NMR spectra of the equimolar mixtures of (TPP)AlOMe and γ-butyrolactone (i) and of (TPP)AlCl and γ-butyrolactone (ii) in $CDCl_3$. The signals of γ-butyrolactone were observed at 4.36, 2.50, and 2.27 ppm, and those of the mixture of γ-butyrolactone and (TPP)AlOMe were observed at the almost same positions. On the other hand, each signal of γ-butyrolactone was shifted to upfield region in the mixture of γ-butyrolactone and (TPP)AlCl. These facts indicate that (TPP)AlCl interacts with lactone more strongly than (TPP)AlOMe.

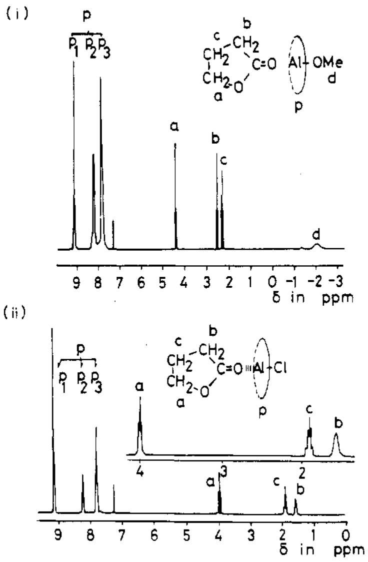
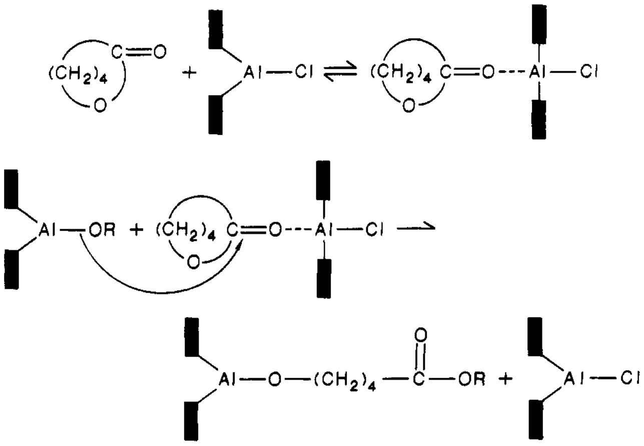


Figure 10. ^{1}H NMR spectra of the $CDCl_3$ solution containing (TPP)AlOMe and γ-butyrolactone (γ-BL) at room temperature (i) and (TPP)AlCl and γ-butyrolactone at 40 °C (ii) ($[γ\text{-BL}]_0/[(TPP)AlOMe]_0 = 1$; $[γ\text{-BL}]_0/[(TPP)AlCl]_0 = 1$; $[(TPP)AlOMe]_0 = [(TPP)AlCl]_0 = 100$ mM).

Scheme I



Conclusion

(Tetraphenylporphinato)aluminum alkoxide ((TPP)AlOR) is an excellent initiator for the living polymerization of δ-valerolactone. Kinetic analysis of the polymerization and ^{1}H NMR investigation of the reaction mixture indicate that the monomer coordinates to (TPP)AlX and is thereby activated. Thus, two aluminum porphyrin molecules participate in the polymerization (Scheme I).

By the virtue of such activation, the polymerization initiated with (TPP)AlOR is remarkably accelerated by the addition of (TPP)AlCl which itself cannot initiate the polymerization. The acceleration of polymerization by the addition of (TPP)AlCl is also observed in the polymerization of ε-caprolactone and D-lactide ((3(*R*), 6(*R*)-3,6-dimethyl-1,4-dioxacyclohexene-2,5-dione) initiated with (TPP)AlOR. For example, in the polymerization of D-lactide (9.33 mmol) initiated with (TPP)AlOMe (0.14 mmol) in CH_2Cl_2 (4.9 mL) at 100 °C for 2 h, the conversion was 26.1%, while upon addition of an equimolar amount of (TPP)AlCl to (TPP)AlOMe the conversion increased to 39.6%.

In conclusion, the results of the present study provide evidence that two metal atoms participate in the polymerization of lactone, and probably epoxide, with other organometallic catalyst systems as well.

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Registry No. 1 (X = Cl), 71102-37-9; 1 (X = OMe), 66945-43-5; 2, 542-28-9; 2 (*n* = 4, homopolymer), 26354-94-9; 2 (*n* = 4, SRU), 26499-05-8.

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Notes

Number of Entanglement Strands per Cubed Tube Diameter, a Fundamental Aspect of Topological Universality in Polymer Viscoelasticity

Y.-H. LIN

Exxon Chemical Company, Baytown Polymers Center, Baytown, Texas 77522. *Received February 17, 1987*

Polymer viscoelastic properties are strongly influenced by polymer chain entanglement. A strong indication of this is the modulus plateau that can be observed for nearly monodisperse high molecular weight (MW) samples.[1-3] Modeling chain entanglements as slip-links and chain diffusion as reptation,[4] Doi and Edwards[5-8] developed a very successful constitutive equation for monodisperse linear polymers in 1978. The deficiency of the Doi–Edwards theory to explain fully the experimentally observed MW dependence of the zero-shear viscosity ($\eta \propto M^3$ for theory; $\eta \propto M^{3.4}$ for experiment) has been removed by a proposed general linear viscoelastic theory.[9] An extensive quantitative line-shape analysis of the linear viscoelastic spectra has further strongly supported the validity of the proposed general theory.[10-12] It has been shown that the general theory is universal for all linear flexible polymers as long as the MW is expressed in terms of the reduced unit (M/M_e, where M_e is the entanglement MW). A constitutive equation[13] including the chain tension relaxation process[14] has been obtained from modifying the Doi–Edwards theory. It has been shown from analyzing experimental results in terms of the constitutive equation that the melt flow instability, i.e., slip–stick melt fracture, is a universal phenomenon for all linear flexible polymers.[13] It will occur to a polymer as long as its M/M_e value is high enough and its molecular weight distribution (MWD) is narrow enough. The proposed general linear viscoelastic theory and constitutive equation are unified in the terminal region.[15]

All these results summarized above support the universality of the topological constraint effect as described by the tube model, where the tube diameter, a, is equivalent to the distance between two adjacent slip links (entanglements). Then we ask the question whether there is a universal relation among the basic elements (physical quantities) in the tube model as described by Doi and Edwards. A similar motivation has led Graessley and Edwards[16] to propose a correlation among the basic elements.

The key elements in the tube model should be the bulk density of the polymer, the entanglement MW, the mass and length associated with each Kuhn segment, and the tube diameter. A difficulty encountered here is the lack of experiment to determine the Kuhn segment length and mass independently. Graessley and Edwards[16] used $l = C_\infty b$ (C_∞ is the characteristic ratio and b is the average length of the main chain chemical bonds of the average mass, m) for the Kuhn step length. There should be an approximation involved in their approach.

Here, we study this matter from a different viewpoint. Without linking the Kuhn segment with the characteristic ratio (C_∞) directly, we use the C_∞ value to calculate the tube diameter from the entanglement MW through the following equation[17]

$$a^2 = C_\infty \frac{M_e}{m} b^2 \tag{1}$$

This equation is totally consistent with the Doi–Edwards

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