Aluminum-Porphyrin 촉매계를 이용한 Propylene Oxide의 배위중합 : 중합속도론과 메카니즘

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(1994년 1월 4일 접수)

Coordination Polymerization of Propylene Oxide over Aluminum Porphyrin Catalyst System : Polymerization Kinetics and Mechanism

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(Received January 4, 1994)

요 약 : Aluminum porphyrin촉매를 이용한 propylene oxide의 배위중합 메카니즘을 이해하기 위하여 초기 단량체 농도, 촉매농도, 중합온도 등을 변수로 중합 반응속도를 측정하였다. 중합반응 속도는 단량체 및 촉매농도의 일차식에 비례하는 경향을 보였으며 성장단계의 활성화 에너지는 9.7~11.1 kcal/mole이 얻어졌다. 또한 비대칭 고리형 단량체인 propylene oxide는 methylene-oxygen 결합에서 활성점의 친핵성공격에 의해 개환되어 head to tail의 배열을 갖는 고분자가 합성되는 것을 ^{19}F-NMR실험을 통하여 확인하였다. 속도론 연구 및 Aluminum-27 NMR 실험결과를 종합할때 중합경로는 우선, Aluminum-porphyrin의 제6배위자리에 에폭시단량체가 결합하면 이는 음이온성 활성체의 탈배위를 유도하여 배위결합으로 여기된 단량체를 친핵성 치환반응으로 개환한 후 배위상태로 환원되는 것으로 보여진다.

Abstract : The kinetics of polymerization of propylene oxide by using aluminum porphyrin initiator system was investigated to elucidate the coordination polymerization mechanism. The rate of polymerization is first order with respect to monomer and initiator concentrations with an activation energy of 9.7~11.1 kcal/mole. Also, the polymerization proceeded through the exclusive cleavage of methylene-oxygen bond via a nucleophilic attack of growing species, yielding to head to tail configuration with asymmetric monomers according to the ^{19}F-NMR experiment. These observations in conjunction with ^{27}Al-NMR studies suggest that the polymerization route may be first, association of epoxide monomer to the sixth coordinate site of porphyrinatoaluminum followed by the generation of anionic growing species to maintain the penta-coordinated square pyramidal arrangements. Subsequently, this anionic active species open the coordinated epoxide rings by nucleophilic substitution maintaining penta-coordinated state.

INTRODUCTION

Some alkylene oxide can be polymerized to a very high molecular weight under moderate reaction conditions. This type of polymerization is called "coordinate anoinic polymerization", since its mechanism is characterized by the fact that the monomer first coordinates at a catalyst site prior to propagation, and that the propagating species, which are essentially anionic, metal alkoxide, then attacks the coordinated monomers.[1~3] This is analogous to the polymerization of olefins by Ziegler-Natta catalyst systems. The coordination catalyst may include partially hydrolyzed ferric alkoxide,[4] $ZnEt_2$ /H_2O,[5] $ZnEt_2$ /ROH, [6] Et_3Al-0.5H_2O,[7] and Et_3Al-0.5H_2O- 0.5AcAc,[7] where acetylacetone served as a chelating agent for the aluminum atom. The role of the chelating agent has been speculated that it may minimize an ordinary cationic polymerzation by lewis acid type catalyst by locking the fourth coordinate position of alumium and allowing the fifth and/or sixth coordinate positions of aluminum to function in a coordination/ propagation step.[7]

However, most coordinate catalyst systems tend to be highly aggregated and to form a variety of catalyst sites with different reactivities, which is responisble for the broad molecular weight distribution and uncontrolled chain length. It is rather difficult to investigate the structure of the active site, because of its extremely low effective metal concentration (0.05 -1% of total metal atom).[8]

Recently, some metalloporphyrins of aluminum and zinc have been recognized to be effective for the living polymerization of epoxide to give polymers with controlled chain length and narrow molecular weight distribution.[9~10] In the metalloporphyrin compound a central metal atom displaces two hydrogen atoms from the porphyrin ligand thus forms a symmetrical electrostatic field of four nitrogen atoms with which it may generate four almost equivalent coordi-

nate donor-acceptor bonds. The specific features of metalloporphyrins as intercomplex compounds are due to the polydentate nature of ligand and its rigidity, which is determined by the planar shape of large ring structure of porphyrin owing to the conjugation in it.[11] In addition, the steric hindrance is pronounced when the compound with bulky substituent approaches porphyrin moiety. This site isolation effect could be the most significant feature when it is used in catalyst application since homogeneity of all reactive site may be acquired.

The present paper deals with the mechanism and kinetics of propylene oxide polymerization employing aluminum-prophyrin catalyst system. Although the general concept of coordination polymerization has been postulated abundantly as was stated above, they were rarely substantiated with concrete experimental verifications. In the course of our study it was possible to examine a detailed route of polymerization of epoxide over aluminum-porphyrin catalyst on the basis of kinetic studies, ^{27}Al-NMR and ^{19}F- NMR experiments.

EXPERIMENTAL

Reagents. 5, 10, 15, 20-Tetraphenyl-porphyrin(TPPH$_2$)(Aldrich) was recrystallized from a chloroform/methanol mixture and dried under reduced pressure at 50°C. Dichloromethane (Mallinckrodt co. analytical grade) was dried and fractionally distilled from calcium hydride under nitrogen. Propylene oxide was obtained from Aldrich. The cyclic monomer was fractionally distilled from a mixture of calcium hydride and potassium hydroxide under a nitrogen atmosphere. Mild heating was provided and middle fraction was collected. To the middle fraction collected by the first distillation, 0.2~0.3wt % of triethyl aluminum in hexane solution (1 mole/liter) was added and stirred for 24 hours to remove residual moisture. The solution was fractionally distilled under an inert atmosphere.

Diethyl aluminum chloride (Et_2 AlCl) supplied by Ethyl Corporation(11.25 wt% in heptane) was used as received.

Preparation of Aluminumporphyrin. 5, 10, 15, 20-Tetraphenylporphyrinato aluminum chloride(TPPAl-Cl) was prepared by dissolving $TPPH_2$ in purified dichloromethane under 3~5 psig nitrogen atmosphere followed by the addition of equivalent of Et_2AlCl. Stirring was continued over a period of 5 hours, which affords a homogeneous purple solution. The reaction is described below. ^{1}H-NMR in $CDCl_3$: (δ : 8.25ppm, 8H, d) (δ= 7.81ppm, 12H, t), (δ =9.07ppm, 8H, d)

$$TPPH_2 + Et_2AlCl \longrightarrow TPPAl-Cl + 2 C_2H_6 \qquad (1)$$

Polymerization and Kinetic Study: The polymerization of propylene oxide was carried out by adding calculated amounts of purified monomer via a transfer needle to the TPPAlCl catalyst. High pressure Parr reactor equipped with overhead(magnetically driven) agitator, temperature control system(heating and cooling) and sampling valve was used. In the kinetic studies, catalyst and monomer concentrations were varied in the range of 17.2-43mmol/l and 7.1-10.3 mole/l, respectively. In order to determine the activation energy of polymerization the temperature of reaction mixture was maintained at 25, 30, 47 and 56°C. In the course of polymerization samples were taken from the reactor periodically and the polymerization was immediately terminated with a water/acetone mixture. Conversions were determine by gravimetric analysis after removing solvent and unreacted monomers by reduced pressure.

Analysis. Proton-NMR spectra were obtained for TPPAl-Cl using Jeol 270MHz spectrometer in a deutrated chloform solution. Tetramethylsilane was used as an internal standard for the proton spectra. ^{19}F-NMR spectra were obtained from 200MHz IBM FT-NMR multinuclear probe. The ^{19}F-NMR spectra were run to determine the primary and secondary
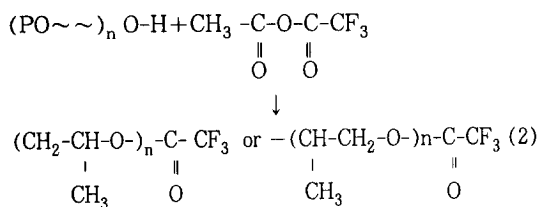
hydroxyl functionality of poly(propylene oxide). In this case, each hydroxyl end group was derivatized by trifluoroacetic anhydride. Fluorobenzene was added to the solution as an internal standard.

RESI;TS AND DISCUSSION

Mode of Cleavage. The mode of cleavage of a three-membered epoxide monomer is an important criteria to judge the propagation mechanism. It has been postulated that methylene-oxygen bonds of propylene oxides are exclusively cleaved in anionic polymerization,[13] whereas methylene-oxygen and methine-oxygen bonds are equally broken in cationic polymerization.[14] The latter mechanism results in a significant amount of head to head or tail to tail chain configuration, since ring opening occurs spontaneously due to the increased polarization effect upon coordination to the catalyst sites. If methylene-oxygen bonds are cleaved by the attack of growing alkoxide species, the end groups of poly(propylene oxide) will be secondary hydroxyls. However, after terminating the growing polymer chain, the poly(propylene oxide) prepared through the cationic route will possess a mixture of statistically determined secondary and primary hydroxyl end groups.

The hydroxyl terminals of poly(propylene oxide) prepared by the aluminum porphyrin catalyst were derivatized with trifluoroacetic anhydride and characterized by ^{19}F-NMR. One percent mono-fluorobenzene was added as an internal standard in the deuterated chloroform solution.

Due to the long range coupling of the trifluoromethyl with the methine or methylene protons, ^{19}F-NMR spectroscopy affords to differentiate the primary and secondary hydroxyls. In the ^{19}F-NMR spectra, two peaks are detected in addition to the peak from the internal standard. In Fig.1 the peak located at 36.7ppm downfield from the standard is assigned to trifluoroacetic

$(PO\sim\sim)_n$ O-H + CH$_3$ -C-O-C-CF$_3$
                              ‖   ‖
                              O   O
                              ↓

$(CH_2-CH-O-)_n-C-$ CF$_3$ or $-(CH-CH_2-O-)n-C-CF_3$ (2)
    | ‖ | ‖
   CH$_3$ O   CH$_3$ O

acid, a byproduct of the derivatization reaction. The second peak is located at 37.6ppm, which is confirmed as trifluoroacetate terminal derived from the reaction. As a reference, 2-propanol was analyzed by ^{19}F-NMR in the same manner. The peak from the trifluoroacetate derivative of the secondary hydroxyl end group was detected at exactly the same location as that of the poly (propylene oxide). The corresponding derivatives of the primary hydroxyl groups are detected at approxmately 0.3-0.4ppm downfield from the secondary hydroxy derivative. It may be concluded from ^{19}F-NMR experiments that the propagation is taking place through the cleavage of the methylene-oxygen bonds of propylene oxide by the nucleophilic attack of the alkoxide growing species.

Kinetic Studies. One aluminum-porphyrin catalyst molecule initiates one polymer in the absence of coinitiators. Moreover, all of the active sites considered to be of equal reactivity
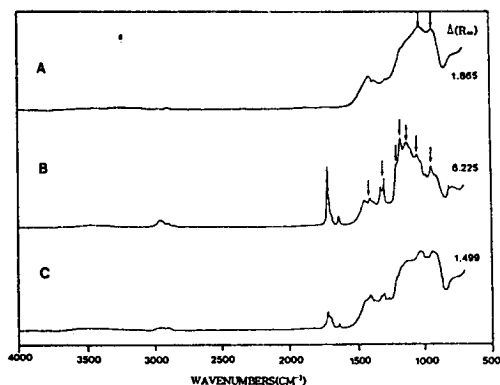
Fig. 1. DRIFT spectra of hydrolyzed BTE and γ-MPS on the E-glass fiber. A) hydrolyzed BTE, B) hydrolyzed γ-MPS and C) mixed silane
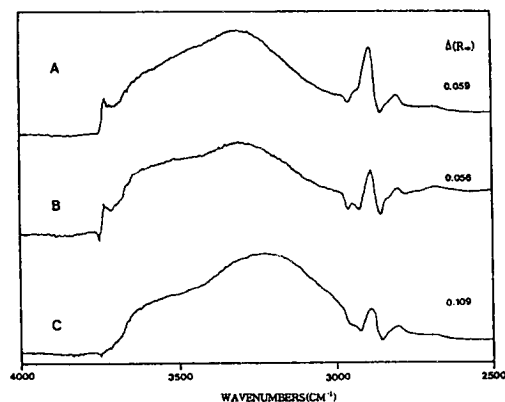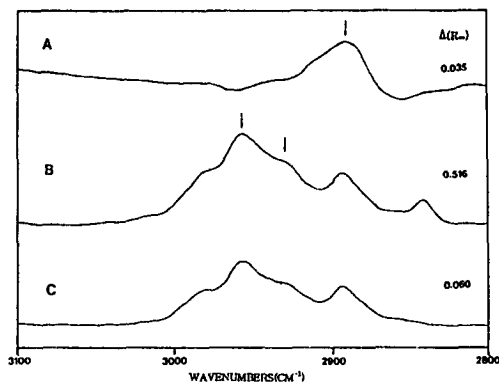

Fig. 2. DRIFT spectra of hydrolyzed mixed silane on the E-glass fiber in different solution pH.
A) pH 10.5, B) pH 7.0 and C) pH 3.5

toward the monomer due to their uniform structure as the observed molecular weights from GPC measuments correspond to the stastistically determined values from the monomer/catalyst charge ratios and very narrow molecular weight distributions of the polymer(~ 1.1).[9,10]

Effect of Momomer Concentration A series of polymerization were conducted under carefully controlled experimental conditions. The catalyst was prepared in a pressure reactor in methylene chloride solution and a calculated amount of monomer was added by a transfer needle. Conversion vs. time was plotted for three different initial monomer concentrations, as shown in Fig. 2. The conversion versus time curves for each experiments are similar for three monomer concentrations of 10.3mole/liter, 8.5mole/liter and 7.1mole/liter($\pm 2\%$ deviation). As illustrated in Fig. 3, this system was properly represented by the first order kinetics with respect to the monomer concentration within tested range.

Catalyst Concentration. The effect of catalyst concentration was examined in a similar manner. Three different catalyst concentrations (17, 32, 43mmole/liter) were employed, while maintaining the other reaction variables con
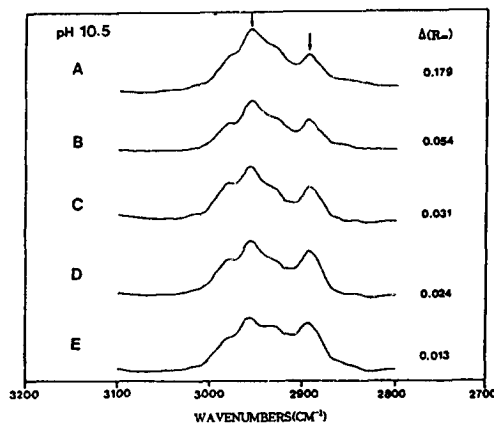
Fig. 3. DRIFT spectra of hydrolyzed γ-MPS and BTE on the E-glass fiber. A) hydrolyzed γ-MPS, B) hydrolyzed BTE and C) mixed silane.
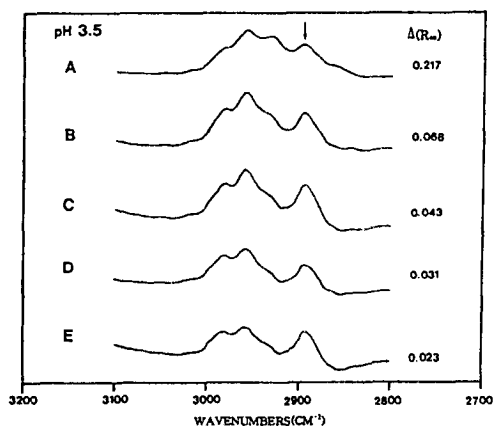
Fig. 4. DRIFT spectra of hydrolyzed mixed silane on the E-glass fiber as a function of BTE mol ratio (pH 3.5). A) γ-MPS itself, B) mol ratio 0.5 : 9.5, C) 1.0 : 9.0, D) 2.0 : 8.0 and E) 3.0 : 7.0.

stant. Initial monomer concentrations of all experiments were 7.1mole/liter and the reaction temperature was controlled at 25℃. -Ln(1-x) versus time curves at various catalyst concentrations are plotted as the polymerization follows first order kinetics with respect to the monomer concentration. As shown in the Fig. 4, the slope of each plot, which is a product of catalyst concentration and rate constant, has a linear dependency on the catalyst concentration.

Fig. 5. DRIFT spectra of hydrolyzed mixed silane on the E-glass fiber as a function of BTE mol ratio (pH 10.5). A) γ-MPS itself, B) mol ratio 0.5 : 9.5, C) 1.0, 9.0, D) 2.0:8.0 and E) 3.0:7.0.

Since the temperature was kept constant at 25 ℃ during the polymerization, only the catalyst concentration could contribute to the difference in slopes. As a result, the rate of polymerization appears to be proportional to the first order of the catalyst concentration(i.e., the concentration of the active centers in the propagation).

Effect of Polymerization Temperature. In order to determine the activation energy of the propagation, the polymerizations were carried out at various temperatures(30℃, 47℃, 56℃) in methylene chloride under the same initial monomer and catalyst concentrations. Conversion versus time curves at three different temperatures are plotted in Fig. 5. An accelerated propagation rate is observed at elevated temperatures. Both differential and integral methods were used to determine the activation energy. in the differential analysis the rates of polymerization were ratioed at the same conversion of polymerization among reactions at various temperatures. The activation energy of the polymerization is estimated from the tangent of ln(dx/dt) vs.(1/T), yielding 11.1±0.5kcal/mole.
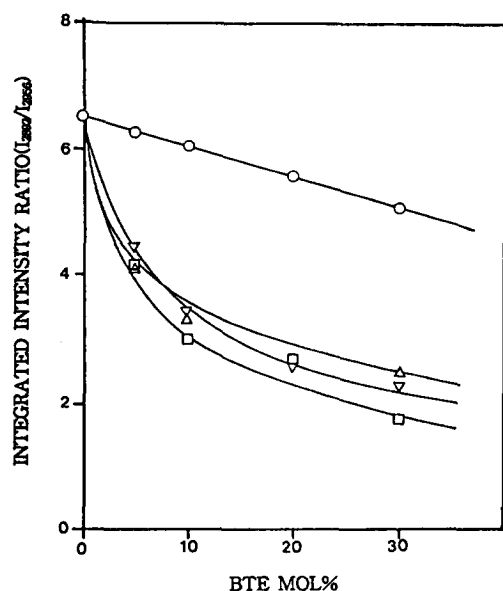
In the integral method, -ln(1-x) vs. reaction

Fig. 6. Integrated intensity ratio of I_{2892}/I_{2956} as a function of BTE mole% (○) theoretical, (□) pH 3.0, (▽) pH 7.0, and (△) pH 10.5.

Fig. 7. Integrated intensity ratio of $I_c = /I^{CH2}$ as a function of BTE mole% (○) aqueous solution and (△) aqueous alcoholic solution.

time was plotted for each experiment and the slopes of the plots i.e., k[cat], were determined. The rate constants were calculated after division by catalyst concentration. By plotting logarithm of rate constant versus reciprocal temperature, the activation energy was estimated as 9.7 ± 0.4 kcal/mole from the slope of the Arrehnius plot in Fig. 6.

Proposed Route of Polymerization. In the ^{27}Al-NMR spectra, the δ-values in the 250ppm range have been recognized as a tri-coordinated aluminum atom and δ-values of the tetra-coordinated aluminum atom have been established to be in the 140~180ppm region. For the penta-coordinated strate, the δ-value lies in the 30~120ppm range and hexa-coordinated aluminum atom have δ-values in the range of -40~20pm. [15~17]The penta-coordinated state of aluminum in TPPAl-Cl was evidenced by value of 54ppm in ^{27}Al-NMR spectra. Four coordination sites are identified with pyrrole rings within the macrocycle and the fifth one is from the association with chloride ligand. The aluminum-27 NMR

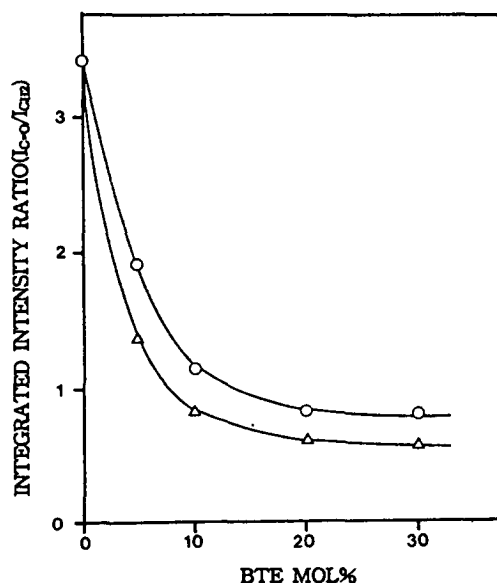collected during polymerization of propylene oxide shows two distinct signals as presented in Fig. 7. The major signal centered at 54ppm with a broad bandwidth is from the penta-coordinated aluminum and a new signal comes upfield at 20ppm is an indicative of hexa-coordinated arrangement.

The first order dependency of polymerization rate on both monomer and catalyst concentrations is an indicative of bimolecular interaction between epoxide and aluminum-porphyrin with either chloride or alkoxide ligand. Particularly, the first order dependency on catalyst concentration suggests that the number of coordination sites for monomers increases with the concentration of aluminum atom in a linear fashion. From the magnitude of penta and hexa-coordinated states of aluminum in the Al-NMR spectrum as can be seen in Fig. 7, the hexa-coordinated arrangements seem less favored. The stable hexa-coordinated states of aluminum have been reported on the cases that aluminum forms coordination bonding with identical li-
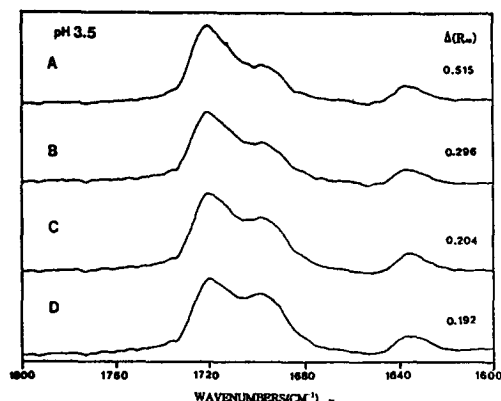
Fig. 8. DRIFT spectra of mixed silane on the E-glass fiber in the region of $1800-1600 cm^{-1}$ (pH 3.5). A) mole ratio 0.5 : 9.5, B) 1.0 : 9.0, C) 2.0 : 8.0 and D) 3.0 : 7.0.

gands, such as $Al(DMF)_6$, $Al(EtOH)_6$, $Al(acac)_3$ etc.[16] When an asymmetric coordination takes place on both phases of porphyrinatoaluminum, permanent hexa-coordinated arrangement is unlikely due to the electronegativity difference in ligands and/or other factors. The hexa-coordinated state may be converted to penta-coordinated by releasing extra ligand bound to the planar phase of porphyrinatoaluminum, by which active anionic species could be produced. One can speculate that the epoxide is substantially polarized through the coordination on the rear phase of porphyrinatoaluminum chloride. These correspond to the facts that polymerization can be initiated at room temperature and the activation energy of polymerization is moderate. A weak nucleophile such as chloride anion can attack the less hindered methylene carbon of the monomer and initiate the polymerization. Otherwise, porphynatoaluminum bound alkoxide or chloride, only partially polarized, would not possibly attack the coordinated monomer due to a strong steric hindrance. Nucleophilic substitution between coordinated monomer and growing anionic species is also substantiated by the exclusive cleavage

of methylene-oxygen bond in the asymmetric epoxide. A proposed reaction scheme is shown in Fig. 8.

CONCLUSIONS

In the polymerization of propylene oxide using TPPAl-Cl catalyst system, it can be concluded that propagation rate is proportional to the first order of monomer and initiator concentrations with an activation energy of 9.7-11.1 kcal/mole. The ring cleavage took place exclusively at the less hindered methylene-oxygen bond as in the anionic mechanism. These observations along with ^{27}Al-NMR study afford the systematic verification of the coordination polymerization mechanism of propylene oxide over Aluminum-porphyrin catalyst.

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