

Studies of the Cyclopolymerization in the Presence of Alkylaluminum Chlorides. III. Cyclopolymerizations of *o*-Allylphenyl Acrylate and 2-(*o*-Allylphenoxy)ethyl Acrylate with *p*-Chlorostyrene

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ABSTRACT: The cyclopolymerizations of *o*-allylphenyl acrylate (APA) and 2-(*o*-allylphenoxy)ethyl acrylate (2-AOEA) with a donor monomer, *p*-chlorostyrene (*p*-CIS), in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ have shown that the electron-withdrawing double bonds are consumed in an equal proportion to the electron-releasing double bonds, irrespective of the initial composition of monomer feed. The copolymer composition tended to a limiting value with 50-mol % *p*-CIS units as the *p*-CIS mole fraction in the monomer feed increased. The extent of cyclization for the APA and the 2-AOEA units sharply decreased with an increase in the *p*-CIS unit fraction. The fraction of acrylic double bonds in the consumed double bonds always amounted to about 50-mol %; this indicates that the cyclopolymerizations are composed by alternating participation of the electron-withdrawing and the electron-releasing double bonds. On the other hand, the following values of k_p/k_c , the ratio of the rate constants for linear propagation and for cyclization, were obtained for APA at 40°C: 0.20 l mol⁻¹ in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ and 0.045 l mol⁻¹ in the presence of AlEtCl_2 . These values imply that the intramolecular interaction between the two double bonds plays an important role in the cyclopolymerization. The results have indicated that the mechanism being proposed for the alternating copolymerization would be applicable also to the cyclopolymerization. The character of cyclopolymerization was explained by the molecular complex mechanism rather than by the complexed radical mechanism.

KEY WORDS Cyclopolymerization / Alkylaluminum Chloride / *o*-Allylphenyl Acrylate / 2-(*o*-Allylphenoxy)ethyl Acrylate / *p*-Chlorostyrene / Cyclization Constant / Intramolecular Interaction / Molecular Complex / Complexed Radical /

The cyclopolymerization of nonconjugated dienes, which is composed of alternating intramolecular—intermolecular reactions, is analogous to the alternating copolymerization. Therefore, the technique for producing alternating copolymers may be employed to improve on the cyclopolymerization tendency of the monomers.

The authors have reported that alkylaluminum chlorides, which are used as complexing agents for the preparation of alternating copolymers, increased the cyclopolymerization tendency of *o*-allylphenyl acrylate (APA)¹, 2-(*o*-allylphenoxy)ethyl acrylate (2-AOEA)², and 4-(*o*-allyl-

phenoxy)butyl acrylate (4-AOBA)². In general, the cyclopolymerization tendency falls sharply for rings of more than six atoms; nevertheless, in the presence of alkylaluminum chlorides highly cyclized polymers were obtained not only from APA in the form of eight-membered rings but also from 2-AOEA and 4-AOBA in the form of eleven- and thirteen-membered rings, respectively. These results suggested that there would be an intramolecular interaction between the acrylic and the allylic double bond; this seemed to be supported by the dependence of the extent of cyclization on the monomer con-

centration in the polymerizations of 2-AOEA and 4-AOBA.²

Therefore, it is the object of the present investigation to elucidate the nature of intramolecular cyclization by means of the cyclocopolymerizations of APA and 2-AOEA with *p*-chlorostyrene (*p*-CIS).

EXPERIMENTAL

Reagents

Monomers. *o*-Allylphenyl acrylate (APA) and 2-(*o*-allylphenoxy)ethyl acrylate (2-AOEA) were prepared by the methods described in the previous papers.^{1,2} *p*-Chlorostyrene (*p*-CIS) was prepared by the method given in the literature.^{3,4}

Alkylaluminum Chlorides. Ethylaluminum sesquichloride and ethylaluminum dichloride were kindly supplied by Mitsui Petrochemical Industries, Ltd.

Polymerization

The polymerizations were carried out as described in a previous paper.¹ In order to exclude the influence of monomer concentration from the intramolecular cyclization, the copolymerizations were carried out at constant APA and 2-AOEA concentration but increasing *p*-CIS concentration.

Analysis

Determination of the Composition in Copolymers. The *p*-CIS unit fractions in the copolymers were calculated from the halogen content determined by the Schöniger method.⁵

Determination of the Extent of Cyclization in Polymers and Copolymers. The extent of cyclization was determined by the procedure described in the previous papers.^{1,2}

RESULTS

Cyclocopolymerization of APA (M_1) with *p*-CIS (M_2)

p-CIS was selected as a comonomer to improve the accuracy of the analytical determination, though styrene was used in a previous investigation.¹ Figure 1 shows the composition data of the conventional radical copolymerization at constant APA concentration ($[M_1]$, 0.50 mol l^{-1}). The apparent copolymerization parameters r_1 and r_2 were determined on the basis of the

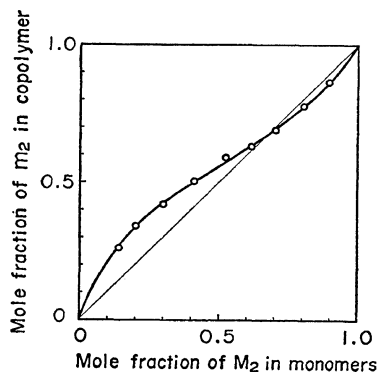


Figure 1. Variation of copolymer composition with monomer feeds in the system of *o*-allylphenyl acrylate (M_1)—*p*-chlorostyrene (M_2): $[M_1]$, 0.50 mol l^{-1} ; temp, 60°C.

Table I. Cyclocopolymerization of *o*-allylphenyl acrylate (M_1) with *p*-chlorostyrene (M_2) in the presence of $AlEt_{1.5}Cl_{1.5}$ ^a

M_2 , mole fraction in monomers	Time, min	Yield, %	Cyclohexane/ benzene-soluble fraction, ^b wt %	m_2 , mole fraction in copolymer	Extent of cyclization in m_1 units, %
0.119	180	23.0	0	0.268	64.0
0.206	150	20.8	0	0.303	52.0
0.382	120	25.8	0	0.377	39.0
0.512	90	27.8	0	0.400	34.0
0.700	60	12.2	13	0.446	20.0
0.760	60	21.5	—	0.475	20.0
0.796	10	3.9	19	0.489	—
0.898	3	4.9	84	0.501	—

^a Solvent, toluene; $[M_1]$, 0.46 mol l^{-1} ; Al/M_1 molar ratio, 1.0; temp, 40°C.

^b Cyclohexane(80)/benzene(20)-soluble fraction is poly(*p*-CIS).

Mayo—Lewis equation⁶ without consideration for the intramolecular cyclization. The Kelen—Tüdös plots^{7,8} of the results yielded a straight line, giving $r_1=0.32$ and $r_2=0.67$.

Table I shows the results of the copolymerization at constant APA concentration ($[\text{M}_1]$, 0.46 mol l^{-1}) in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$. A mixture of copolymer and poly(*p*-ClS) was obtained with the *p*-ClS mole fraction higher than about 0.7 in monomer feed, and so the products were extracted with cyclohexane(80)/benzene(20) mixture. The cyclohexane/benzene soluble fraction was the homopolymer of *p*-ClS, while the insoluble fraction was the copolymer of APA with *p*-ClS. The formation of a homopolymer can be explained as a phenomenon similar to the result in which the alternating copolymerization was accompanied by the cationic polymerization of the donor monomer.⁹ In Figure 2 the copolymer compositions and the extent of cyclization for the APA units are plotted against the monomer feed. The composition curve was quite different from that in Figure 1, indicating the effects of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ for the cyclopolymerization. The compositions tended to a limiting value with about 50-mol% *p*-ClS as the monomer feed increased. The extent of cyclization sharply decreased with an increase in the *p*-ClS unit fraction. The results indicate that the intramolecular cyclization of the electron-releasing

allylic double bond was suppressed by the incorporation of the donor monomer, *p*-ClS, into the polymerization.

Cyclopolymerization of 2-AOEA (M_1) with *p*-ClS (M_2)

Table II shows the results of the copolymerization at constant 2-AOEA concentration ($[\text{M}_1]$, 0.43 mol l^{-1}) in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$. The copolymer was not accompanied by poly(*p*-ClS). In Figure 3 the copolymer compositions and the extent of cyclization for the 2-AOEA units are plotted against the monomer feed. The com-

Table II. Cyclopolymerization of 2-(*o*-allylphenoxy)ethyl acrylate (M_1) with *p*-chlorostyrene (M_2) in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ ^a

M_2 , mole fraction in monomers	Time, min	Yield, %	m_2 , mole fraction in copolymer	Extent of cyclization in m_1 units, %
0.130	120	14.6	0.303	48.8
0.221	90	15.1	0.380	31.0
0.328	70	13.7	0.398	23.0
0.416	50	12.1	0.407	19.8
0.509	35	8.3	0.419	17.0
0.595	15	7.7	0.433	—
0.699	11	5.2	0.452	—
0.799	6	2.7	0.492	—

^a Solvent, toluene; $[\text{M}_1]$, 0.43 mol l^{-1} ; Al/M_1 molar ratio, 1.0; temp, 40°C .

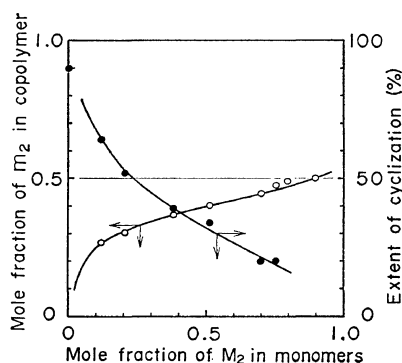


Figure 2. Variations of copolymer composition and the extent of cyclization with monomer feeds in the system of *o*-allylphenyl acrylate (M_1)—*p*-chlorostyrene (M_2) in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$: $[\text{M}_1]$, 0.46 mol l^{-1} ; Al/M_1 molar ratio, 1.0; temp, 40°C .

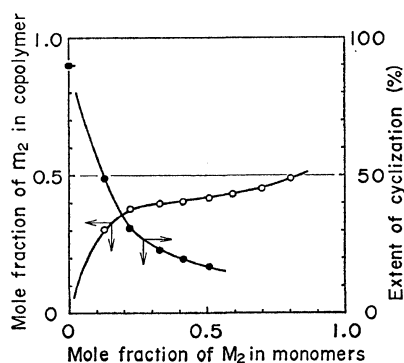


Figure 3. Variations of copolymer composition and the extent of cyclization with monomer feeds in the system of 2-(*o*-allylphenoxy)ethyl acrylate (M_1)—*p*-chlorostyrene (M_2) in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$: $[\text{M}_1]$, 0.43 mol l^{-1} ; Al/M_1 molar ratio, 1.0; temp, 40°C .

position curve showed a greater alternating tendency than that for APA. The higher the *p*-ClS unit fraction, the more strongly the extent of cyclization decreased. Thus the incorporation of *p*-ClS significantly retarded the intramolecular cyclization of 2-AOEA in this system as well.

Dependence of the Extent of Cyclization on the Monomer Concentration in the Polymerization of APA

In order to elucidate the nature of intramolecular cyclization, the dependence of the extent of cyclization on the monomer concentration was reexamined.¹ The experimental data are given in Table III. The following equation, which relates the fraction of cyclized units f_c to the monomer concentration $[M]$, has been derived by Roovers and Smets¹⁰

$$\frac{1}{f_c} = 1 + \frac{k_p}{k_c}[M] \quad (1)$$

where k_p and k_c are the rate constants for linear propagation and cyclization, respectively. Plots of $1/f_c$ vs. $[M]$ are indeed linear, as shown in Figure 4. For the polymerization in the presence of AlEtCl_2 the slope gives $k_p/k_c = 0.045 \text{ l mol}^{-1}$. In the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ the slope corresponds to $k_p/k_c = 0.20 \text{ l mol}^{-1}$, though the intercept does not quite pass through 1.0. The

Table III. Effect of monomer concentration on the polymerization of *o*-allylphenyl acrylate in the presence of alkylaluminum chlorides^a

M, mol l ⁻¹	Time, min	Conversion, %	Extent of cyclization, %
AlEt_{1.5}Cl_{1.5}			
1.99	15	12.0	68.5
1.52	30	15.1	73.0
0.95	45	18.2	79.0
0.49	75	20.3	86.0
0.25	90	20.9	90.0
AlEtCl₂			
2.00	10	8.8	92.5
1.52	20	9.8	93.0
0.98	40	16.2	97.0
0.49	60	20.8	97.0
0.25	80	14.5	99.0

^a Solvent, toluene; Al/M molar ratio, 1.0; AIBN/M molar ratio, 0.01; temp, 40°C.

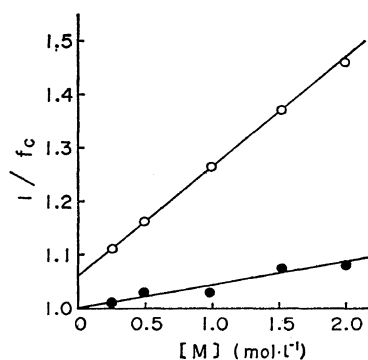


Figure 4. Variation of $1/f_c$ as a function of *o*-allylphenyl acrylate concentration: (○) in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$; (●) in the presence of AlEtCl_2 .

value of k_p/k_c obtained in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ is comparable to those for 2-AOEA and 4-AOBA.² The value obtained in the presence of AlEtCl_2 implies the formation of a strong intramolecular interaction in the polymerization process.

DISCUSSION

The copolymerization parameters to characterize the composition curves in Figures 2 and 3 could not be estimated by using the usual Mayo—Lewis equation.⁶ The Roovers—Smets equation¹⁰ for the cyclocopolymerization was also inapplicable to these systems. Thus the conventional copolymer composition equations did not adequately describe the cyclocopolymerization in the presence of alkylaluminum chlorides.

The results of the dependence of the extent of cyclization on the monomer concentration for the polymerizations of APA and 2-AOEA in the presence of $\text{AlEt}_{1.5}\text{Cl}_{1.5}$ and AlEtCl_2 indicated that there would be an intramolecular interaction between the electron-withdrawing and the electron-releasing double bond in the polymerization process. Therefore, it is assumed that such an interaction plays an important role in these cyclocopolymerizations as well.

The proportions among the three double bonds which were consumed by the cyclocopolymerization, *i.e.*, the acrylic and the allylic double bond in APA or 2-AOEA, and the vinylic double

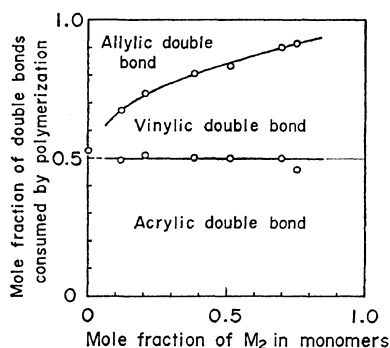


Figure 5. Variations of the mole fractions among three double bonds consumed by the polymerization against monomer feeds in the system of *o*-allylphenyl acrylate—*p*-chlorostyrene.

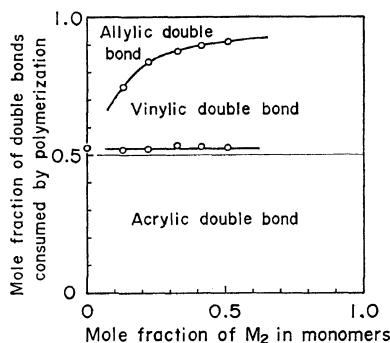


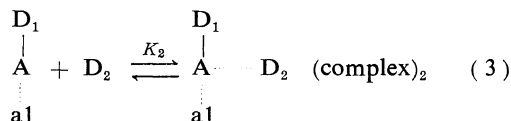
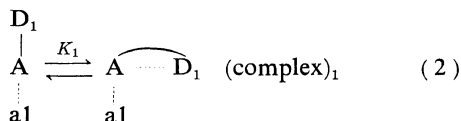
Figure 6. Variations of the mole fractions among three double bonds consumed by the polymerization against monomer feeds in the system of 2-(*o*-allylphenoxy)ethyl acrylate—*p*-chlorostyrene.

bond in *p*-CIS, were calculated from the copolymer composition and the extent of cyclization. The results are given in Figures 5 and 6. The fraction of acrylic double bonds always amounts to about 50 mol %, which is equal to the amounts of the electron-releasing double bonds, irrespective of the initial composition of monomer feed. The cyclopolymerizations are composed of the alternating participation of the electron-withdrawing and the electron-releasing double bonds; this process is therefore similar in character to alternating copolymerization.

Therefore, the application of the mechanisms being proposed to explain the character of alternating copolymerizations, the molecular complex mechanism¹¹⁻¹³ and the complexed radical mechanism,¹⁴ to the cyclopolymerization was ex-

amined.

According to the molecular complex mechanism, the intramolecular complex (complex)₁ and the intermolecular complex (complex)₂ may be formed in the cyclopolymerization process. The equilibria of their formation are shown as follows



where the subscript 1 indicates APA or 2-AOEA, and the subscript 2 *p*-CIS; A and D represent the electron-withdrawing and the electron-releasing double bond, respectively; al represents the alkylaluminum chloride; and K_1 and K_2 are the equilibrium constants of complex formation.

Since the cyclopolymerization is treated as a copolymerization between (complex)₁ and (complex)₂, the composition equation is derived according to the procedure similar to that used for the alternating copolymerization by Iwatsuki and Yamashita¹¹

$$\frac{m_{\text{D}_1}}{m_{\text{D}_2}} = \frac{1}{[\text{D}_2]} \frac{K r_1 + [\text{D}_2]}{1 + (r_2/K)[\text{D}_2]} \quad (4)$$

where K is K_1/K_2 , $[\text{D}_2]$ is the concentration of *p*-CIS, and r_1 and r_2 are the reactivity ratios. After introduction of $1/[\text{D}_2] = x$ and $m_{\text{D}_1}/m_{\text{D}_2} = y$, the composition equation is written as the Kelen—Tüdös equation⁷

$$\eta = \left\{ K r_1 + \frac{(r_2/K)}{\alpha} \right\} \xi - \frac{(r_2/K)}{\alpha} \quad (5)$$

where η , ξ , and α have their original meanings.⁷

In Figure 7 the experimental data of Tables I and II are plotted according to eq 5. The plots show satisfactory linearity for the system APA—*p*-CIS. The data fall approximately on a straight line for the system 2-AOEA—*p*-CIS, but a large deviation of the point corresponding to the *p*-CIS mole fraction of 0.13 in monomer feed was observed. This deviation can be attributed to experimental errors due to considerable variations

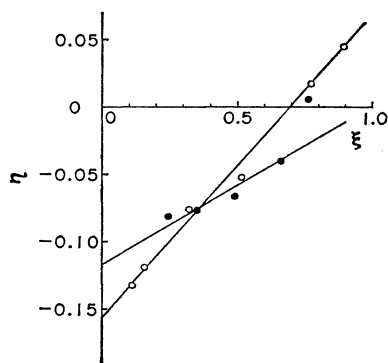
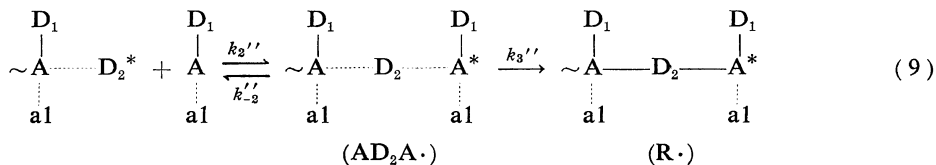
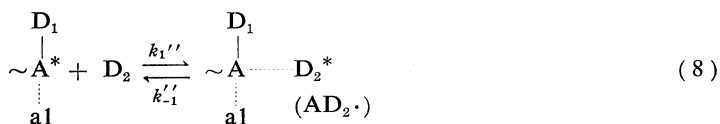
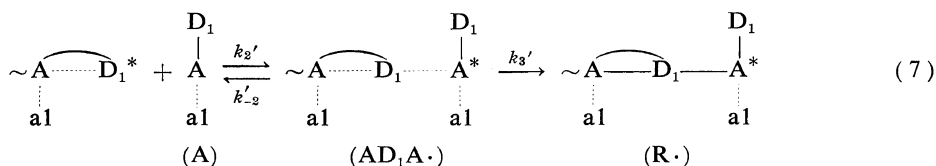
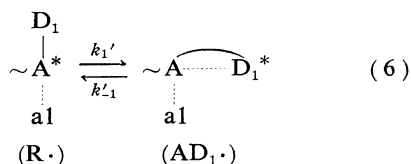


Figure 7. Kelen—Tüdös plots: (○) for the system of *o*-allylphenyl acrylate—*p*-chlorostyrene; (●) for the system of 2-(*o*-allylphenoxy)ethyl acrylate—*p*-chlorostyrene.

both in the copolymer composition and in the extent of cyclization in the region of *p*-ClS mole fractions of 0 to 0.2 as shown in Figure 3. Kr_1 and $(r_2/K)/\alpha$ were calculated from the intercepts at $\xi=1$ and $\xi=0$, respectively. The following values were obtained: $Kr_1=0.07$ and $(r_2/K)=2.9$ for the system APA—*p*-ClS, and $Kr_1 \approx 0$ and $(r_2/K)=7.9$ for the system 2-AOEA—*p*-ClS.

According to the complexed radical mechanism, the propagation steps are symbolized as follows, using both simple formulas and a shorter notation



where R· represents the growing polymer radical; AD₁· and AD₂· represent the intra- and the intermolecular radical complex, respectively; and AD₁A· and AD₂A· are the double complexed radicals. Under steady state conditions, the concentrations of complexes [AD₁A·] and [AD₂A·] are derived according to the procedure similar to those used for the alternating copolymerization by Furukawa¹⁵ and McKenna and Logothetis.¹⁶

$$[AD_1 A \cdot] = \frac{k_1' k_2' [R \cdot] [A]}{(k'_{-2} + k_3')(k'_{-1} + k_2' [A])} \quad (10)$$

$$[AD_2 A \cdot] = \frac{k_1'' k_2'' [R \cdot] [A] [D_2]}{(k''_{-2} + k_3'')(k'_{-1} + k_2'' [A])} \quad (11)$$

So the composition equation is given by

$$\frac{m_{D_1}}{m_{D_2}} = \frac{k_3' [AD_1 A \cdot]}{k_3'' [AD_2 A \cdot]} = \frac{k_1' k_2' k_3' (k'_{-2} + k_3') (k'_{-1} + k_2' [A])}{k_1'' k_2'' k_3'' (k''_{-2} + k_3'') (k'_{-1} + k_2'' [A])} \frac{1}{[D_2]} \quad (12)$$

Since the concentration of A, [A], is kept constant under the experimental conditions, eq 12

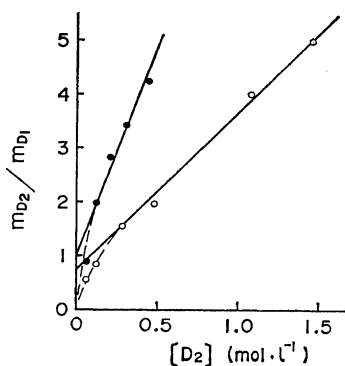


Figure 8. Plots of m_{D_2}/m_{D_1} against the D_2 concentration: (○) for the system of *o*-allylphenyl acrylate—*p*-chlorostyrene; (●) for the system of 2-(*o*-allylphenoxy)ethyl acrylate—*p*-chlorostyrene.

reduces to

$$\frac{m_{D_2}}{m_{D_1}} = K' [D_2] \quad (13)$$

where K' is a constant.

Plots of m_{D_2}/m_{D_1} vs. $[D_2]$ do not yield a straight line passing through the origin, as is shown in Figure 8.

On the other hand, if the term Kr_1 in eq 4 is negligible compared to the D_2 concentration, this gives

$$\frac{m_{D_2}}{m_{D_1}} = 1 + (r_2/K)[D_2] \quad (14)$$

In Figure 8 the linear relation between m_{D_2}/m_{D_1} and $[D_2]$ is obeyed at higher D_2 concentrations. The value of the intercept at the ordinate is found to be 0.75 for the system APA—*p*-ClS and 1.0 for the system 2-AOEA—*p*-ClS. Both systems are in better agreement with eq 14 than with eq 13.

Therefore, the results indicate that in the presence of alkylaluminum chlorides the character of cyclopolymerization is explained by the molecular complex mechanism rather than by the complexed radical mechanism and the nature of intramolecular cyclization is very similar to that of propagation in the alternating copolymerization.

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