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Polymerization of 2-Oxazolines. II. Kinetics of the Cationic Polymerization of 2-Phenyl-2-oxazoline Initiated by Oxazolinium Perchlorate in N,N-Dimethylacetamide Solution*

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SUMMARY

The solution polymerization of 2-phenyl-2-oxazoline in N,N-dimethylacetamide media was carried out at 120-150°C with the use of the oxazolinium salt of monomer and perchloric acid as an initiator. A marked acceleration in rate was observed in the early stage of polymerization. After the period of acceleration the polymerization rate and the moles of polymer chains were shown to remain constant, whereas the number-average degree of polymerization increased almost proportionally with an increase in the degree of conversion. The kinetic discussion, divided

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into two stages, gave the following results: an early stage of polymerization with slow initiation where the moles of the active propagating species increased, and a later stage with a stationary state where the moles of the active propagating species remained constant and the growth of polymer chains proceeded. The kinetics was reformulated as a function of the differential monomer concentration. The simulation of the kinetics with the use of the rate constants of initiation and propagation reactions obtained experimentally expressed the experimental facts.

INTRODUCTION

In the previous paper [1] the present authors reported the bulk polymerization of 2-phenyl-2-oxazoline with the use of various kinds of oxazolinium salts of Brönsted acids to give N-benzoyl polyethylenimine. Based on spectroscopic studies of the oxazolinium salts and the kinetic feature of the bulk polymerization, the mechanisms of initiation and propagation reactions were discussed.

In order to elucidate the detailed mechanism of the ring-opening polymerization of 2-oxazolines, the solution polymerization of 2-phenyl-2-oxazoline in N,N-dimethylacetamide with oxazolinium perchlorate is studied from a kinetic point of view. The characteristic feature of the solution polymerization was made clear, and the initiation and propagation rate constants were determined.

EXPERIMENTAL

Materials

The preparation of 2-phenyl-2-oxazoline from methyl benzoate with monoethanolamine and the purification were carried out according to the previous paper [1]: (bp 129°C/13 mm Hg; lit. [2]; 69°C/0.2 mm Hg).

The salt of 2-phenyl-2-oxazoline and perchloric acid (oxazolinium perchlorate) was prepared from 2-phenyl-2-oxazoline and perchloric acid (mp 150.5-151.0°C). Analysis: Calculated for $C_9H_{10}NO_5Cl$: C, 43.64; N, 5.71; Cl, 14.36. Found: C, 43.68; N, 5.65; Cl, 14.42.

N,N-Dimethylacetamide (G.R. Grade) was purified by several careful fractionations under reduced pressure [3].

Procedure

The homogeneous mixture of 2.00 ml of 2-phenyl-2-oxazoline (1.503×10^{-2} mole), 37.2 mg of oxazolinium perchlorate (molar ratio of catalyst to monomer = 1.00×10^{-2}), and 3.00 ml of N,N-dimethylacetamide was charged into a glass ampoule carefully dried before use. After several freeze-evacuate-thaw cycles, the ampoule was sealed under high vacuum (before 10^{-5} mm Hg). The polymerization was carried out in a similar method previously described.

In order to determine the monomer conversion in the early stage of polymerization, the reaction mixture was diluted to 100 ml in a volumetric flask with chloroform and then scanned in a fixed-KBr cell (0.020 cm) between 1000-900 cm^{-1} in an IR spectrum of the solution. The Lambert-Beer law held for the standard monomer solution. The conversion was obtained from the intensity change of the characteristic absorptions attributed to the ring skeletal vibrations in oxazoline heterocycle at 975 and 945 cm^{-1} in the IR spectrum of the above chloroform solution. In the later stage of polymerization, the white powdery polymer was precipitated from vigorously stirred n-hexane (about 800 ml) after the reaction mixture was diluted with a small quantity of chloroform (about 15 ml).

The sample provided for measurement of the molecular weight of the resultant polymer was reprecipitated three times in the above manner after the treatment with the sodium hydroxide-methanol-acetone solution. The molecular weight of polymer was measured by the same method described previously [1].

RESULTS AND DISCUSSION

Kinetic Feature of the Solution Polymerization

In the bulk polymerization of 2-phenyl-2-oxazoline initiated by the oxazolinium salt of monomer with perchloric acid (oxazolinium perchlorate) [1], the moles of polymer chains were found to be equal to the moles of the catalyst initially charged, and the polymerization rate was constant during the course of the polymerization. These results indicated that the polymerization belonged to a rapid initiation system and that the long-lived active propagating species existed without termination and transfer reactions.

The characteristic information on the polymerization of 2-phenyl-2-oxazoline with the use of ClO_4^- as a counterion was obtained by the solution polymerization in N,N-dimethylacetamide. The effects of reaction time and temperature on the polymerization are shown in Tables 1-3. In each reaction temperature, an S-shaped curve is obtained in the early stage of polymerization (Fig. 1). It is observed that there is a marked acceleration in rate (until 25% of conversion), while its period is shortened with rising temperature. Therefore, it is suggested that the solution polymerization is a slow initiation system [4] with the accumulation of active propagating species.

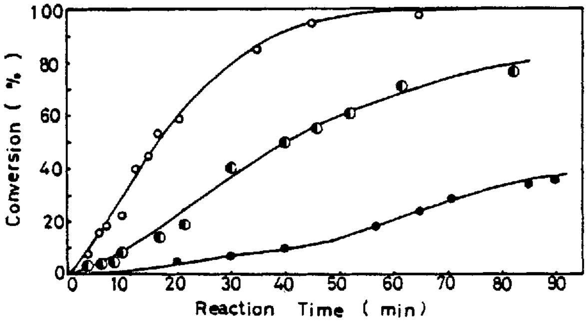


FIG. 1. The time-conversion curves of the solution polymerization of 2-phenyl-2-oxazoline initiated by oxazolinium perchlorate in N,N-dimethylacetamide. Reaction temperature: (O) 150°C, (◐) 135°C, (●) 120°C. The full lines denote the theoretical values calculated from Eqs. (20) and (21) with the use of k_i and k_p obtained experimentally.

On the other hand, the degree of polymerization of the polymer formed after the early stage increased almost proportionally with an increase in the polymer formed, as shown in Table 1. Furthermore, the moles of the polymer chains are shown to remain constant, as will be described below. From these observations it is considered

TABLE 1. Solution Polymerization of 2-Phenyl-2-oxazoline at 150°C Initiated by Oxazolinium Perchlorate in N,N-Dimethylacetamide

		Observed[a]		Calculated[b]		
Run No.	Reaction time (min)	Conversion of monomer (%)	$\overline{P}_n$	Conversion of monomer (%)	$\overline{P}_n$	Conversion of catalyst (%)
1	4.0	8.1	-	8.3	16.5	50.2
2	6.0	16.1	-	15.7	24.6	63.7
3	7.0	20.6	-	19.7	28.6	68.8
4	10.0	23.1	27.6	27.7	39.9	79.0
5	15.0	46.7	43.8	48.7	53.5	87.7
6	21.0	59.7	58.4	62.8	71.4	92.2
7	35.0	85.0	83.1	86.7	90.4	95.5
8	45.0	93.3	96.4	93.3	97.0	96.3
9	65.0	98.3	96.8	98.3	100.2	98.8

[a] The conversions of monomer in Runs No. 1-3 were obtained from the measurement of the IR spectra of the reaction mixture, and the others from the measurement of the weight of the resulting polymers.

[b] Calculated from Eqs. (19), (20), (21), and (22) with the use of $k_i = 0.061$ and $k_p = 2.39$.

TABLE 2. Solution Polymerization of 2-Phenyl-2-oxazoline at 135°C Initiated by Oxazolinium Perchlorate in N,N-Dimethylacetamide

		Observed[a]		Calculated[b]		
Run No.	Reaction time (min)	Conversion of monomer (%)	$\overline{P}_n$	Conversion of monomer (%)	$\overline{P}_n$	Conversion of catalyst (%)
1	4.0	1.6	-	1.3	5.5	24.1
2	6.0	3.1	-	2.6	7.6	33.6
3	8.0	5.7	-	4.1	9.9	41.9
4	10.0	8.6	-	6.0	12.2	49.5
5	16.0	14.0	-	12.6	19.5	65.0
6	21.0	18.3	-	24.7	27.8	80.1
7	31.0	39.0	42.1	40.2	41.4	92.3
8	40.0	51.0	-	49.2	49.9	97.5
9	46.0	54.9	-	55.0	55.6	98.1
10	52.0	60.7	59.1	60.3	60.7	98.7
11	62.0	69.4	-	67.7	68.0	99.1
12	82.0	78.6	81.3	79.1	79.2	99.5

[a] The conversions of monomer in Runs No. 1-5 were obtained from the measurement of the IR spectra of the reaction mixtures, and the others from the measurement of the weight of the resulting polymers.

[b] Calculated from Eqs. (19), (20), (21), and (22) with the use of $k_i = 0.0234$ and $k_p = 0.690$.

TABLE 3. Solution Polymerization of 2-Phenyl-2-oxazoline at 120°C Initiated by Oxazolinium Perchlorate in N,N-Dimethylacetamide

		Observed[a]		Calculated[b]		
Run No.	Reaction time (min)	Conversion of monomer (%)	$\overline{P}_n$	Conversion of monomer (%)	$\overline{P}_n$	Conversion of catalyst (%)
1	20.0	3.8	-	4.0	8.6	24.3
2	30.0	6.1	-	7.2	10.1	36.5
3	40.0	11.5	-	12.6	17.5	50.2
4	57.0	18.8	-	20.0	25.4	72.6
5	65.0	23.4	-	22.4	27.1	82.1
6	71.0	28.4	31.6	29.3	32.0	87.6
7	85.0	33.9	-	34.0	36.5	92.4
8	90.0	35.1	32.1	36.3	37.6	93.2

[a] The conversions of monomer in Runs No. 1-3 were obtained from the measurement of the IR spectra of the reaction mixture, and the others from the measurement of the weight of the resulting polymers.

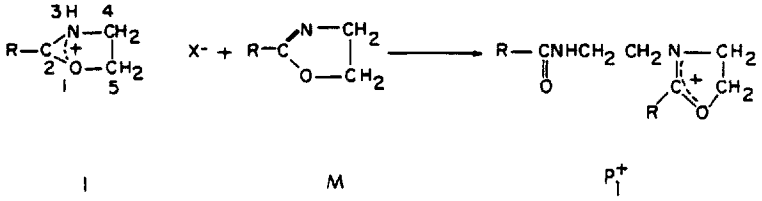
[b] Calculated from Eqs. (19), (20), (21), and (22) with the use of $k_i = 0.0070$ and $k_p = 0.250$.

that the polymerization system should be divided into two stages: an early stage with slow initiation where the moles of propagating species are increased, and a later stage with a stationary state where the moles of the active propagating species remain constant.

Evaluation of the Rate Constant of Initiation Reaction in the Early Stage of Polymerization

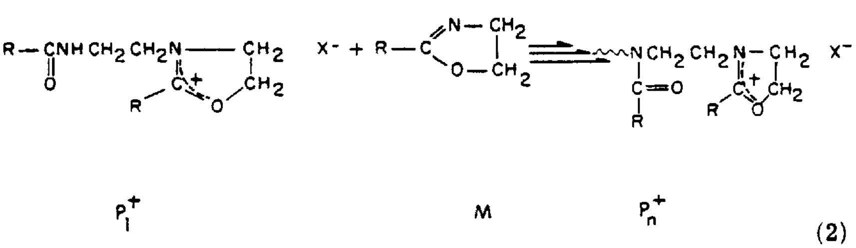
As described in Part I of this series [1], the initiation and propagation reactions in this solution polymerization are considered to proceed by the nucleophilic attack of monomer on the electron-deficient 5-position of the oxazolinium salt, and the quaternization of the incoming monomer may facilitate the nucleophilic attack of monomer due to the change of the bonding state in the incoming heterocycle. The oxazoline monomer is therefore assumed to be incorporated into the polymer chain according to the following reactions of monomer with the oxazolinium ion-pair as an active propagating end:

Initiation Reaction



(1)

Propagation Reaction



(2)

where I and M represent the catalyst and monomer, respectively, and $\overline{P}_n{}^+$ denotes the active propagating species composed of n monomer units.

In the early stage of the polymerization the rate of the consumption of the catalyst, R_i, and that of monomer, R_p, are derived from the elementary reactions represented schematically in Formulas (1) and (2) as

$$R_i = -\frac{d[I]}{dt} = k_i[I][M] \tag{3}$$

$$R_p = -\frac{d[M]}{dt} = k_i[I][M] + k_p[P^+][M] \tag{4}$$

where [I] and [M] represent the instantaneous concentration of oxazolinium perchlorate as catalyst and monomer, respectively, $[P^+]$ is the total concentration of the active propagating species, irrespective of size $\left(\sum_{n=1} [\overline{P}_n{}^+] = [P^+]\right)$, and k_i and k_p denote the rate constant of the initiation and propagation reactions, respectively.

Since the monomer consumption in the early stage of polymerization is small, the instantaneous concentration of the catalyst can be derived approximately from Eq. (3) as

$$[I] = [I]_0 \exp(-k_i[M]_0 t) \tag{5}$$

where $[I]_0$ and $[M]_0$ denote the initial concentration of catalyst and monomer, respectively.

At the stage with low conversion,

$$\exp(-k_i[M]_0 t) \simeq 1 - k_i[M]_0 t$$

Accordingly, Eq. (5) transforms approximately into

$$[I] = [I]_0(1 - k_i[M]_0 t) \tag{6}$$

Assuming that the polymerization at the early stage proceeds without termination reaction, the concentration of the active propagating species $[P^+]$ is expressed as a function of reaction time:

$$[P^+] = [I]_o - [I] = k_i[M]_o[I]_ot \qquad (7)$$

From the facts that $[M]_o$ is very much larger than $[I]_o$ and the polymerization belongs to a slow initiation system, the rate of monomer consumption represented by Eq. (4) can be written approximately into

$$-\frac{d[M]}{dt} \simeq k_p[P^+][M] = k_ik_p[I]_o[M]_o[M] \qquad (8)$$

Accordingly, integration of the above equation gives

$$\ln \frac{[M]_o}{[M]} = \frac{1}{2} k_ik_p[I]_o[M]_ot^2 \qquad (9)$$

By plotting ln $[M]_o/[M]$ against t^2, linear relations through the origin are obtained at the early stage of polymerization (Fig. 2). From the slope of this straight line and the value of the rate constant of propagation reaction (k_p), as has been evaluated below, the rate constant of initiation reaction (k_i) can be evaluated as shown in Table 4.

The period (t_f) which the initiation reaction is essentially completed is evaluated by substituting $[I] = 0$ for Eq. (6):

$$t_f = 1/k_i[M]_o \qquad (10)$$

The values at different temperatures are 6 min (150°C), 16 min (135°C), and 53 min (120°C). These values are almost equal to the observed period of rate acceleration.

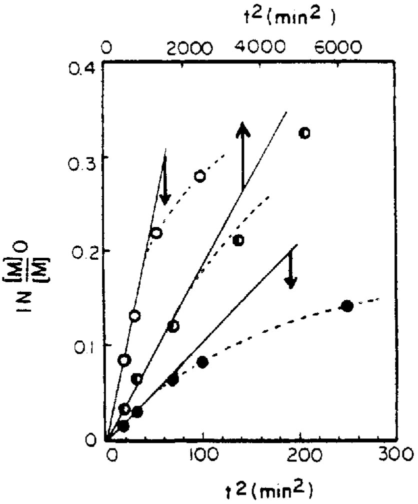


FIG. 2. The plot of ln $[M]_0/[M]$ vs. t^2 in the early stage of polymerization. Reaction temperature: (O) 150°C, (●) 135°C, (◐) 120°C).

Evaluation of the Rate Constant of Propagation Reaction in the Later Stage of Polymerization

The rate of monomer consumption (R_p) after the rate acceleration is given by

$$R_p = -d[M]/dt = k_p[P^+][M] \tag{11}$$

Integration of the Eq. (11) gives

$$\ln [M]_0/[M] = k_p \int [P^+]\, dt \tag{12}$$

As shown in Fig. 3, the first-order plot with respect to monomer concentration shows a fairly linear relationship up to almost complete conversion (98.3%). These observations indicate that

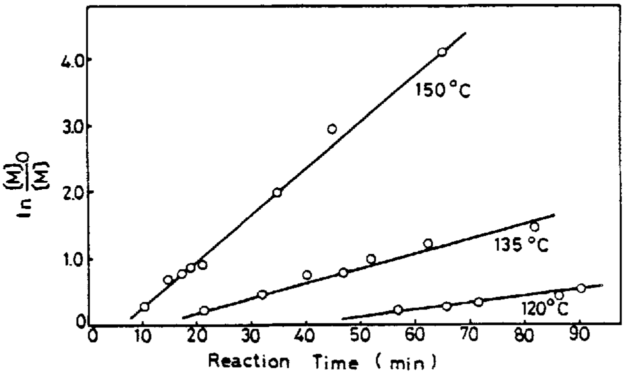


FIG. 3. The first-order plot with respect to [M] in the later stage of polymerization.

the concentration of the active propagating species remains constant during the course of polymerization except for the early stage of polymerization. Accordingly, the propagation rate is expressed as

$$\ln [M]_0/[M] = k_p[P^+]'(t - t') \tag{13}$$

where t' denotes the correction term resulting from neglecting the second term on the left-hand side of Eq. (4), and $[P^+]'$ denotes the concentration of the active propagating species in the later stage of polymerization.

On the other hand, the number-average degree of polymerization, $\overline{P}_n$, is expressed by the ratio of the moles of polymerized monomer to those of the polymer chain. On the basis of the assumption that the polymerization proceeds without transfer and bimolecular termination,

$$\overline{P}_n = \frac{[M]_0 - [M]}{[P^+]'} = \frac{[M]_0}{[P^+]'} \frac{[M]_0 - [M]}{[M]_0} \tag{14}$$

As shown in Fig. 4, the number-average degree of polymerization in the later stage of polymerization increases linearly with an increase in conversion. In addition, the number-average degree of polymerization of the resultant polymer at different reaction temperatures is found to ride on the same straight line. This result leads to the conclusion that the moles of polymer chain in the later stage of polymerization evaluated from the slope of the straight line in Fig. 4 remain constant and are almost equal to the moles of catalyst initially charged independently of the reaction temperature.

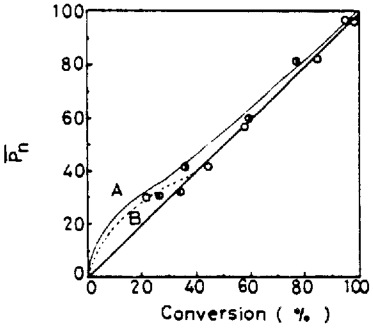


FIG. 4. The relation between $\overline{P}_n$ and conversion. Reaction temperature: (O) 150°C, (◑) 135°C, (◐) 120°C). Line A denotes the theoretical line calculated from Eqs. (20), (21), and (22) at 150°C with the use of $k_i = 0.061$ and $k_p = 2.39$, and Line B at 135°C with the use of $k_i = 0.0234$ and $k_p = 0.690$.

From the fact that the polymerization rate after the period of rate acceleration remains constant, it is concluded that the moles of active propagating species are essentially equal to the moles of catalyst initially charged, and the efficiency of the catalyst for initiation is unity ($[P^+] = [P^+]' = [I]_0$). The rate constants of propagation reaction (k_p) evaluated from Eq. (13) at different temperatures are summarized in Table 4.

TABLE 4. Evaluated Rate Constants of Initiation (k_i) and Propagation (k_p) Reactions

Reaction temperature (°C)	Initiation rate constant, k_i (liter/mole-min)	Propagation rate constant, k_p (liter/mole-min)
150	6.1×10^{-2}	2.39
135	2.34×10^{-2}	0.690
120	7.0×10^{-3}	0.250

In order to confirm the values of the propagation rate constant, the following two-stage polymerization with respect to reaction temperature was carried out. After the polymerization at 150°C for 17.0 min (Period I), the ampoule was immersed in a Dry Ice-methanol solution (-78°C) for 4 hr and then heated at 135 and 120°C (Period II). Figure 5 shows a first-order plot with respect to monomer concentration against reaction time. The rate constants of propagation reactions in Period II are obtained from the slope of the straight line at the first-order plot in Fig. 5, and those are identical with the values evaluated previously.

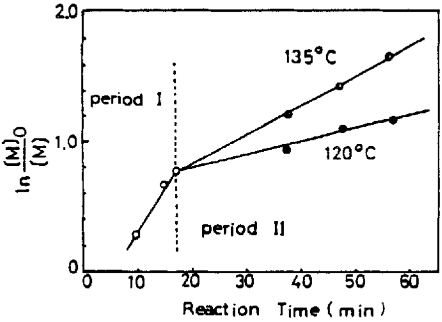


FIG. 5. The first-order plot with respect to [M] in the two-stage polymerization. Period I was carried out at 150°C, and Period II at 135°C and 120°C.

Reformulation of the Kinetics of the Solution Polymerization

Integration of Eq. (3) gives

$$\ln [I]_o/[I] = k_i \int [M]\, dt \tag{15}$$

Here, introducing the following variable,

$$\Phi = \int [M]\, dt \tag{16}$$

$$d\Phi/dt = [M] \tag{17}$$

Eq. (15) converts to

$$[I] = [I]_o \exp(-k_i\Phi) \tag{18}$$

Accordingly, assuming polymerization without termination reaction, the instantaneous total concentration of active propagating species $[P^+]$ is given as

$$[P^+] = [I]_o - [I] = [I]_o [1 - \exp(-k_i\Phi)] \tag{19}$$

By using Eqs. (18) and (19), and integrating Eq. (4) with respect to monomer concentration, gives

$$[M]_o - [M] = [I]_o \left\{ k_p\Phi - \frac{k_p - k_i}{k_i} [1 - \exp(-k_i\Phi)] \right\} \tag{20}$$

From Eqs. (20) and (17) the following differential equation as a function of Φ and t is obtained:

$$\frac{d\Phi}{dt} = [M]_o + \frac{k_p - k_i}{k_i} [I]_o [1 - \exp(-k_i\Phi)] - k_p[I]_o\Phi \tag{21}$$

Substituting the values of k_i and k_p obtained before in the above differential equation, the relation between $\Phi(t)$ and t is obtained from computation by the numerical integration method (Runge-Kutta-Gill method) under the initial condition ($t = 0$, $\Phi = 0$). The relation between reaction time and conversion calculated from Eqs. (20) and (21), as shown in Fig. 1 and Tables 1-3, is almost reformulated experimental data except for the very early stage of polymerization. The variation of conversion of catalyst to active propagating species ($[P^+]/[I]_0 = 1 - \exp(-k_i\Phi)$) with reaction time, as shown in Fig. 6, indicates that all the catalyst converts essentially to the active propagating species in the early stage of polymerization. The fact mentioned above is consistent with results obtained before.

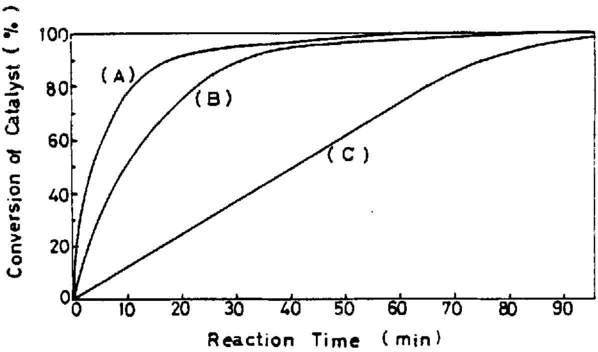


FIG. 6. Variation of the conversion of the catalyst $[1 - \exp(-k_i\Phi)]$ with the reaction time. The full lines were calculated from Eqs. (19), (20), and (21) with the use of k_i and k_p values obtained experimentally. (A) 150°C, (B) 135°C, (C) 120°C.

The number-average degree of polymerization, $\overline{P}_n$, is obtained from Eqs. (14), (19), and (20) as

$$\overline{P}_n = \frac{k_p\Phi}{1 - \exp(-k_i\Phi)} - \frac{k_p - k_i}{k_i} \tag{22}$$

The calculated relation between $\overline{P}_n$ and conversion, as shown in Fig. 4, which shows a slightly convex, upward curve in all experimental series, is nearly equal to the observed straight line. These facts indicate that the kinetic behavior of the present solution polymerization is expressed by Eqs. (20), (21), and (22) with the use of the values of k_i and k_p obtained experimentally.

The above results lead to the conclusion that the present solution polymerization belongs to the type of successive polymerization with slow initiation reaction without the termination and transfer reactions. A detailed discussion on the initiation and propagation reactions from the point of view of energetics will be described in a subsequent paper in connection with the role of the solvent in the incorporation reaction of monomer into polymer chains.

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