

Kinetics of the Anionic Ring-Opening Polymerization of Octamethylcyclotetrasiloxane Initiated by Potassium Isopropoxide

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ABSTRACT: Kinetics of the anionic ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) in bulk initiated by potassium isopropoxide was studied. Several promoters including *N*-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), and diglyme were used. It is indicated that the reactions are first-order in D_4 during the initial stage of polymerization. The polymerization rate of D_4 is influenced by a number of factors, such as the nature of promoters, the molar ratio of promoter to initiator (C_p/C_i ratio), and the reaction temperatures. With the use of NMP as promoter, the polymerization rate constant at 30°C is 10.482 h⁻¹

with the C_p/C_i ratio equal to 3.0. As the C_p/C_i ratio increases, the polymerization rate constant increases sharply and the cyclic oligomers content in polymer decreases evidently. The back-biting reaction that leads to the formation of decamethylcyclopentasiloxane (D_5) occurred in the polymerization of D_4 . The rate of the D_5 formation relatively to the rate of D_4 conversion increases with the conversion of D_4 . © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3510–3516, 2006

Key words: anionic polymerization; ring-opening polymerization; polysiloxanes; activation energy; kinetics

INTRODUCTION

The industrial synthesis of polydimethylsiloxane (PDMS) by anionic ring-opening polymerization of octamethylcyclotetrasiloxane (D_4) is well-known.^{1,2} But this method often suffers following drawbacks: the initiator such as KOH has poor solubility in apolar solvents or in D_4 , and high temperature (140°C) is needed for the polymerization, and the resulting polysiloxanes are equilibrium mixtures of linear and cyclic species. Recently, more attempts have been focused on the nonequilibrium polymerization of D_4 , especially on the development of new efficient initiation systems.^{3–7} Among variety of initiators, alkali metal alkoxide is of interest because of its high efficiency and low cost. The polymerization of D_4 can proceed successfully under this type of initiator without any promoter,⁸ while the high reaction temperature (above 150°C) greatly restricted its industrial application. So far, the polymerization of D_4 with this type of initiator under promoters has not been reported. In this work, to achieve the nonequilibrium polymerization of D_4 in bulk near room temperature, potassium isopropoxide is used as the

initiator because of its comparatively good solubility in apolar solvent or in D_4 . *N*-Methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), and diglyme were used as promoters, respectively.

EXPERIMENTAL

Materials

Isopropanol was distilled from 4 Å molecular sieves. Hexane was refluxed over sodium for 24 h and distilled under nitrogen. NMP, DMF, and diglyme were dried over sodium and collected by trap-to-trap distillation under reduced pressure. D_4 was dried over CaH₂ and distilled under nitrogen. Trimethylchlorosilane (Me₃SiCl) was distilled under nitrogen. After purification, all reagents were stored under a nitrogen atmosphere. Potassium is cut into small pieces in nitrogen prior to use.

Preparation of initiator

To a mixture of 4.2 g (0.11 mol) potassium and 36 mL hexane, a hexane (24 mL) solution of isopropanol (6 mL, 0.08 mol) was added dropwise over 1 h at room temperature under nitrogen. After being stirred for another 2 h, the unreacted potassium and insoluble white precipitate were removed. The titration of the resulted solution with HCl gave the concentration of 0.312M.

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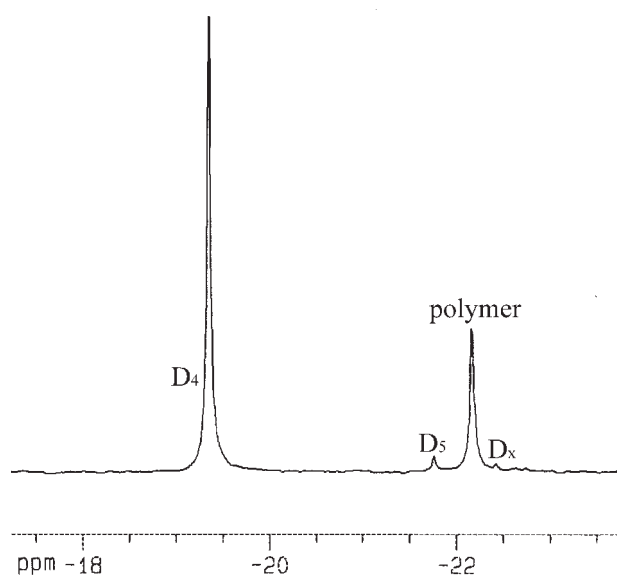


Figure 1 ²⁹Si-NMR spectrum of the sample from the polymerization system of D₄ initiated by potassium isopropoxide.

Polymerizations

To the flask charged with D₄ (6.5 mL, 0.02 mol), the solution of initiator (1 mL, 3.12×10^{-4} mol) was added. As a designed amount of promoter was injected into the mixture via a microsyringe, the initiation then the propagation immediately started. After designed time, the reaction mixture was quenched with an excess amount of trimethylchlorosilane.

Measurements

Gel permeation chromatography

Gel permeation chromatography (GPC) measurements in toluene were performed with a Waters system

including a 515 high-pressure liquid chromatography (HPLC) pump, a 2410 differential refractive-index detector, and Styragel columns (HR) at 40°C at a rate of 0.35 mL/min with linear polystyrene standards.

²⁹Si-NMR

²⁹Si-NMR spectra were recorded on a Bruker DPX400 instrument operating at 79.5 MHz for ²⁹Si.

Kinetic experiments

For all polymerizations, the reaction mixtures were sampled in designed time with a dry syringe and quenched with trimethylchlorosilane. After neutralized with an aqueous solution of sodium bicarbonate, the organic layer was dried over sodium sulfate and submitted to ²⁹Si-NMR and GPC measurement.

RESULTS AND DISCUSSION

Potassium isopropoxide was prepared by reacting isopropanol with potassium. Then the kinetics of the polymerization of D₄ initiated by potassium isopropoxide under several promoters was investigated. Kinetics of the formation of D₅ was also estimated.

Kinetics of the polymerization of D₄

Kinetics of the anionic ring-opening polymerization of hexamethylcyclotrisiloxane (D₃) has been studied thoroughly under various conditions, however only a limited attention has been paid on that of D₄. To elucidate the kinetic law of the polymerization of D₄, a number of kinetic experiments were performed.

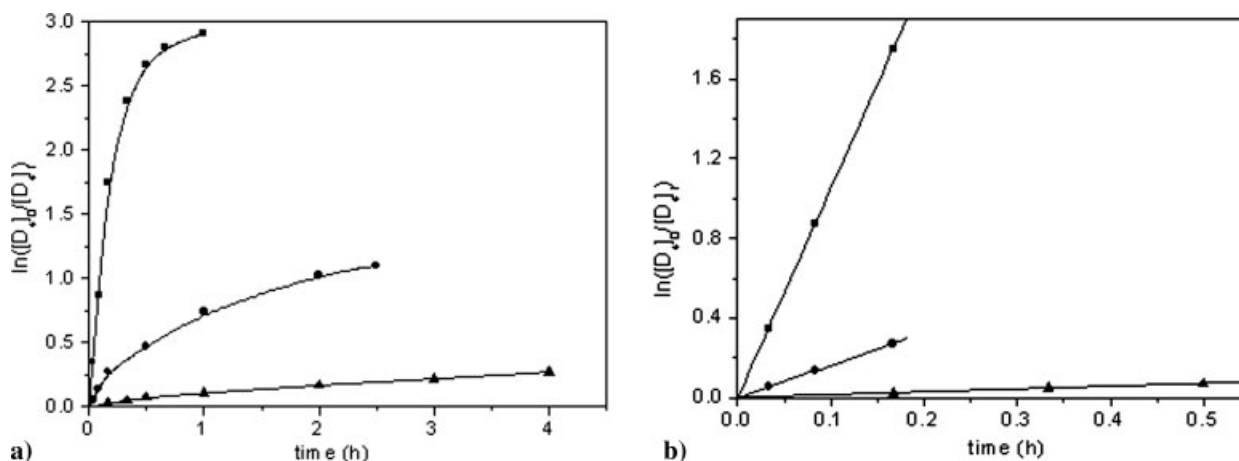


Figure 2 (a) Comparison of kinetics on the polymerization of D₄ promoted by different promoters [(■), NMP; (●), DMF; (▲), diglyme] with the same C_p/C_i ratio equal to 3.0 at 30°C. (b) Enlarged time dependence at the beginning of the polymerization.

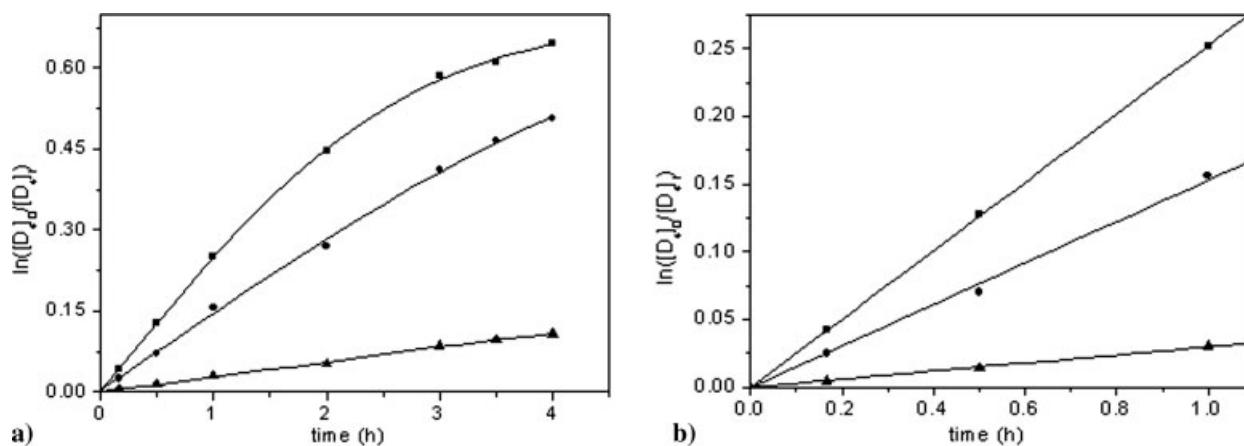


Figure 3 (a) Comparison of kinetics on the polymerization of D_4 promoted by different promoters [■, NMP; ●, DMF; ▲, diglyme] with the same C_p/C_i ratio equal to 1.0 at 30°C. (b) Enlarged time dependence at the beginning of the polymerization.

The values as below can be calculated according to ^{29}Si -NMR spectrum (Fig. 1):

$$[D_4]_0/[D_4]_t = (S_{D_4} + S_{D_5} + S_P + S_{D_x})/S_{D_4}$$

$$[D_5]_t = (4/5) [D_4]_0 S_{D_5}/(S_{D_4} + S_{D_5} + S_P + S_{D_x})$$

$$\begin{aligned} \text{Conversion of } D_4 &= ([D_4]_0 - [D_4]_t)/[D_4]_0 \text{ 100\%} \\ &= (S_{D_5} + S_P + S_{D_x})/(S_{D_4} + S_{D_5} + S_P + S_{D_x}) \text{ 100\%} \end{aligned}$$

where $[D_4]_0 = 2.80 \text{ mol/L}$, S_{D_4} , S_{D_5} , S_P , and S_{D_x} represents for the integration area marked in ^{29}Si -NMR spectrum for D_4 , D_5 , Polymer and D_x ($x > 5$), respectively.

The relation between $\ln([D_4]_0/[D_4]_t)$ and the reaction time (Figs. 2–5) shows linearity during the initial stage of polymerization of D_4 indicating that the

reaction is first order in D_4 at the beginning. The polymerization rate constant “ k ” (i.e., the slope of the linear part of each curve) was obtained then the activation energy “ E_a ” of the polymerization was calculated as follows: According to Arrhenius formula ($k = A \exp(-E_a/RT)$), for the same reaction at two different reaction temperatures, it can be deduced that: $\ln(k_2/k_1) = (E_a/R) \cdot (1/T_1 - 1/T_2)$ (supposing that “ E_a ” is independent on “ T ”).

Both “ k ” and “ E_a ” were listed in Table I. Evidently, the polymerization rate constant “ k ” is influenced remarkably by the nature of promoters, the C_p/C_i ratio, and the reaction temperature. It decreases in the order: NMP > DMF > diglyme and increases with the C_p/C_i ratio or the temperature. It is noteworthy that using NMP as the promoter with the C_p/C_i ratio equal to 3.0, the polymerization rate constant at 30°C is 10.482 h^{-1} , much larger than the other “ k ”

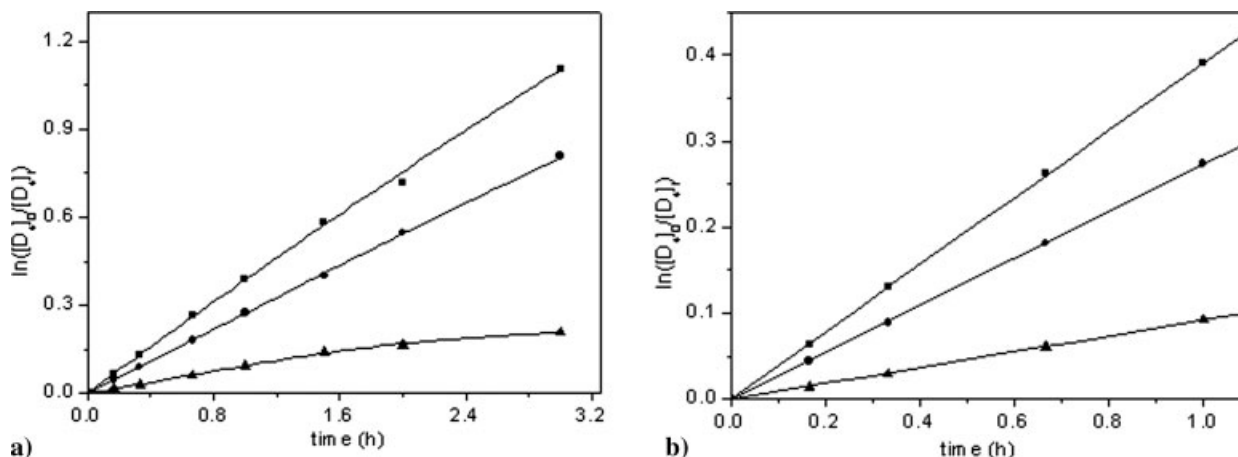


Figure 4 (a) Comparison of kinetics on the polymerization of D_4 promoted by different promoters [■, NMP; ●, DMF; ▲, diglyme] with the same C_p/C_i ratio equal to 1.0 at 50°C. (b) Enlarged time dependence at the beginning of the polymerization.

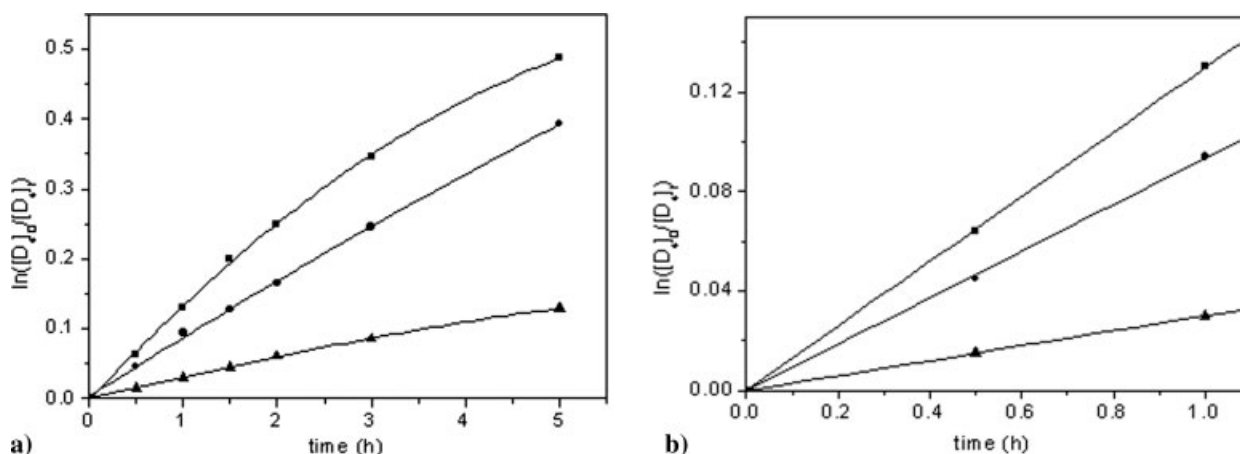


Figure 5 (a) Comparison of kinetics on the polymerization of D₄ promoted by different promoters [■], NMP; ●, DMF; ▲, diglyme] with the same C_p/C_i ratio equal to 0.33 at 50°C. (b) Enlarged time dependence at the beginning of the polymerization.

listed in Table I. The polymerizations accelerated by promoters show large reaction rates at room temperature, which benefits its potential industrial applications. Another two valuable points were also obtained from Table I: One is that “E_a” of the reaction promoted by NMP with C_p/C_i = 1.0 is only 17.3 kJ mol⁻¹, which is considerably low for the anionic ring-opening polymerization of D₄. The activation energy of the anionic polymerization of D₄ initiated by potassium siloxanolate without any promoter is 81.5 kJ mol⁻¹.^{9,10} The other is when the C_p/C_i ratio is not more than 1.0, the difference of “k” between the reaction with C_p/C_i = 1.0 and that with C_p/C_i = 0.33, with the value of 3.0 (k₁/k₂), is identical for each promoter.

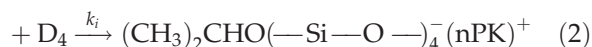
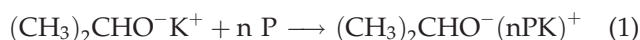
Considering all the above, a possible mechanism for the reaction could be summarized as follows:

TABLE I
Polymerization Rate Constants and Activation Energies of the Polymerization of D₄ Initiated by Potassium Isopropoxide^a

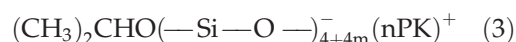
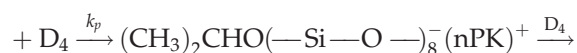
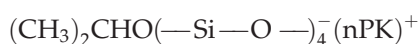
Promoter	[P]/[I]	T (°C)	k (h ⁻¹)	E _a (kJ mol ⁻¹)
NMP	3.0	30	10.482	–
NMP	1.0	30	0.252	17.3
NMP	1.0	50	0.385	17.3
NMP	0.33	50	0.130	–
DMF	3.0	30	1.632	–
DMF	1.0	30	0.137	29.1
DMF	1.0	50	0.280	29.1
DMF	0.33	50	0.094	–
Diglyme	3.0	30	0.144	–
Diglyme	1.0	30	0.028	43.3
Diglyme	1.0	50	0.082	43.3
Diglyme	0.33	50	0.028	–

^a For all polymerizations, the initial concentration of D₄ is 2.80 mol/L and the molar ratio of monomer to initiator is 67.

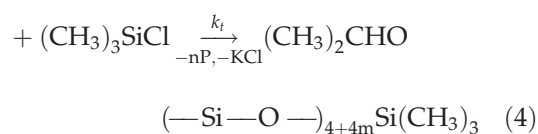
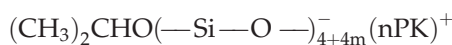
1. Initiation:



2. Propagation:



3. Termination:



In eqs. (1)–(4) P is the promoter molecule and n is the complexing number. k_i, k_p, and k_t is the reaction rate constant for the initiation, propagation, and termination process, respectively.

The cation “K⁺” of the initiator is firstly complexed with promoters [eq. (1)]. Then a loosely bonded potassium siloxanolate ion pair, which is the true active propagation center, is formed [eq. (2)].

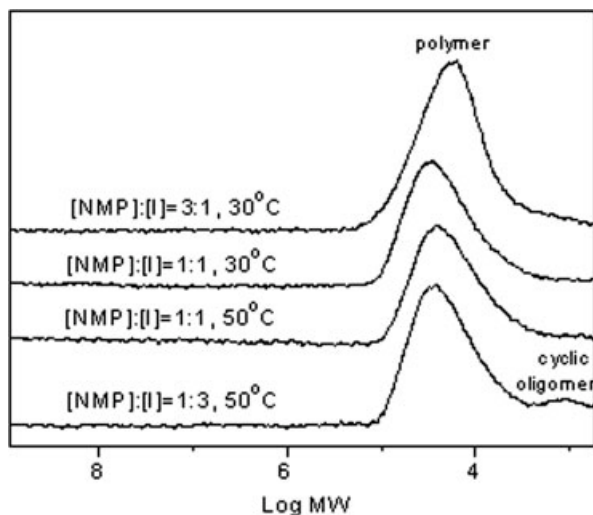


Figure 6 GPC curves of samples from the polymerization systems of D_4 promoted by NMP with various C_p/C_i ratios and temperatures at monomer conversion of 58%.

The kinetics at the initial stage of polymerization are given by eq. (5):

$$-\frac{d[D_4]}{dt} = k_p[-\text{SiO}^-(\text{nPK})^+][D_4] \quad (5)$$

where $[-\text{SiO}^-(\text{nPK})^+]$ represents the total concentration of the propagation center. Thus, eq. (5) can be changed into eq. (6):

$$-\frac{d[D_4]}{dt} = k[D_4] \quad (6)$$

Here, there are two instances about “ k ” given by eqs. (7) and (8):

$$k = k_p[-\text{SiO}^-(\text{nPK})^+] = k_p[I]_0 \quad (C_p/C_i \geq 1.0) \quad (7)$$

$$k = k_p[-\text{SiO}^-(\text{nPK})^+] = k_p[I]_0 C_p/C_i = k_p[P]_0 \quad (C_p/C_i < 1.0) \quad (8)$$

In eqs. (7) and (8), $[I]_0$ and $[P]_0$ refer to the initial concentrations of the initiator and promoter, respectively. Since “ k ” is a constant for each reaction, the polymerization of D_4 proceeds with first order kinetics to the concentration of D_4 from eq. (6), which is in agreement with the results from Figures 2–5. The reaction rate constant “ k ” with $C_p/C_i = 1.0$ and $C_p/C_i = 0.33$ is given by eqs. (7) and (8), respectively. In the two instances, the constant “ k_p ” is identical due to the same value of “ n ” equal to 1. Thus the former “ k ” is three times as large as the latter one, in agreement with the results from Table I.

Figures 6–8 show the GPC results of various samples at monomer conversion of 58%, 52%, and 47%, respectively. For each of the promoters, the cyclic

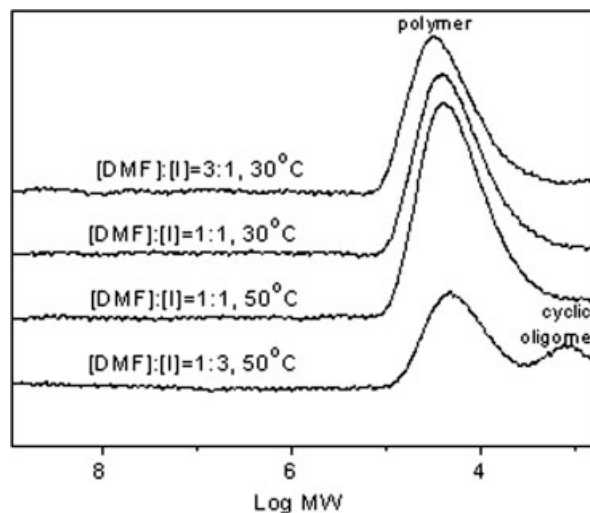


Figure 7 GPC curves of samples from the polymerization systems of D_4 promoted by DMF with various C_p/C_i ratios and temperatures at monomer conversion of 52%.

oligomers content in polymer increases with the decreasing C_p/C_i ratio. Especially when the C_p/C_i ratio is lower than 1.0, the cyclic oligomers in polymer become distinct. It reveals that the addition of promoters leads to the reduction of the cyclic oligomers content in polymer, which is one of the most important contributions of promoters in the anionic ring-opening polymerization of D_4 . On the other hand, at the same C_p/C_i ratio and similar monomer conversion, the cyclic oligomers content in polymer decreases in the order: diglyme > DMF > NMP, indicating that NMP is the best one among the three promoters.

Kinetics of the anionic ring-opening polymerization of D_4 is determined only by the C_p/C_i ratio at the

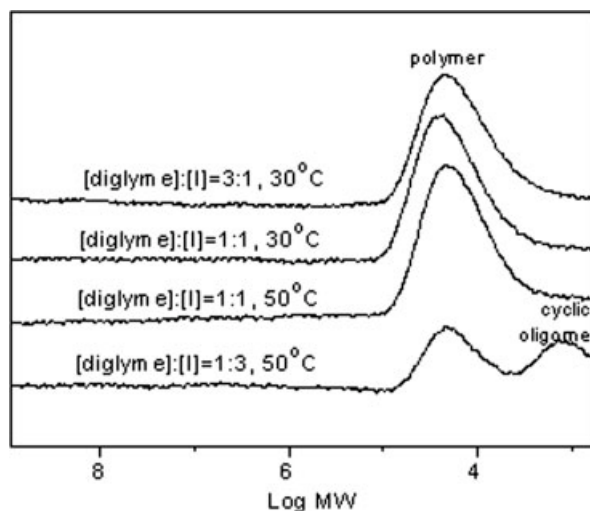


Figure 8 GPC curves of samples from the polymerization systems of D_4 promoted by diglyme with various C_p/C_i ratios and temperatures at monomer conversion of 47%.

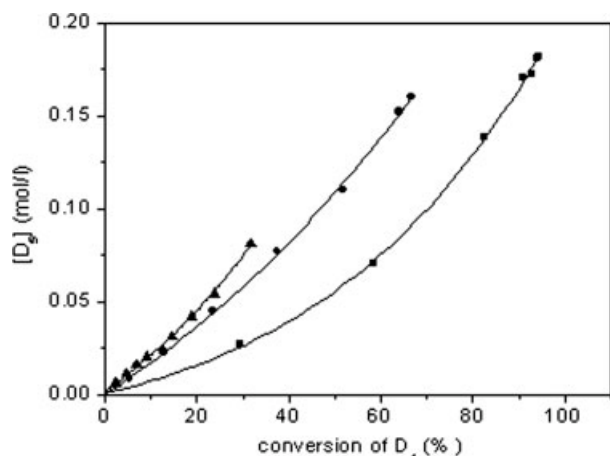


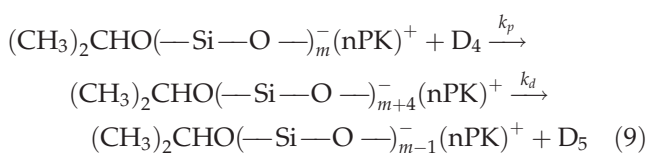
Figure 9 Relation between the concentration of D₅ and the conversion of D₄ in the polymerization process promoted by [(■), NMP; (●), DMF; (▲), diglyme] with the same C_p/C_i ratio equal to 3.0 at 30°C.

same promoter and temperature. As the C_p/C_i ratio increases, the identical active center coordinated with increasing promoters occurs thus the polymerization rate constant increases sharply and the cyclic oligomers content in polymer decreases evidently, which both suggest the realization of the nonequilibrium polymerization of D₄.

Kinetics of the formation of D₅

Another interesting consequence during the polymerization of D₄ is the kinetics of the formation of D₅ (Fig. 9). The rate of the D₅ formation relatively to the rate of D₄ conversion increases with the conversion of D₄. Similar result was also obtained when using a superbase as the initiator.¹¹

In other C_p/C_i ratios and reaction temperatures, the formation of D₅ shows the similar kinetic law. A possible mechanism is as below:



The kinetics is given by eqs. (10) and (11).

$$\frac{d[\text{D}_5]}{dt} = k_d[I] \quad (10)$$

$$-\frac{d[\text{D}_4]}{dt} = k_p[I][\text{D}_4] \quad (11)$$

It can be further deduced that:

$$[\text{D}_5] = \frac{k_d}{k_p} \ln\left(\frac{[\text{D}_4]_0}{[\text{D}_4]}\right) \quad (12)$$

The slope of the curve in Figure 9 is given by eq. (13).

$$\frac{d[\text{D}_5]}{d\left(\frac{[\text{D}_4]_0 - [\text{D}_4]}{[\text{D}_4]_0}\right)} = [\text{D}_4]_0 \left(-\frac{d[\text{D}_5]}{d[\text{D}_4]}\right) = \frac{k_d}{k_p} \frac{[\text{D}_4]_0}{[\text{D}_4]} \quad (13)$$

Since the concentration of D₄ decreases with the conversion of D₄, the ratio between the concentration of D₅ and the conversion of D₄ becomes larger as the polymerization proceeds [eq. (13)]. Then an upward curve is shown in Figure 9. On the other hand, at a certain conversion of D₄, the slope of the curve is only determined by the ratio k_d/k_p, which is a characteristic of the reaction accelerated by the promoters. From Figure 9, the slope of the curve at the same conversion of D₄ decreases in the order: diglyme > DMF > NMP, indicating that the promoters improve "k_p" greater than "k_d" thus reduce the cyclic oligomers content in polymer, which is also evidenced by the foregoing GPC results. The formation of D₅ during the polymerization of D₄ is in agreement with the result that mixed cyclosiloxanes, also resulted from the back-biting reaction of polysiloxane chain, occurs at the final stage of the nonequilibrium polymerization of D₃.

CONCLUSIONS

The anionic ring-opening polymerization of D₄ in bulk initiated by potassium isopropoxide is first order in D₄ at the beginning. The active propagation center is a loosely bonded potassium siloxanolate ion pair separated by the promoter. A number of factors including the nature of promoters, the C_p/C_i ratio, and the reaction temperature affect the polymerization remarkably. Among the variety of promoters, NMP is the best promoter for the polymerization of D₄ initiated by potassium isopropoxide. As the C_p/C_i ratio increases, the polymerization rate constant increases sharply and the cyclic oligomers content in polymer decreases evidently, which both suggest the realization of the nonequilibrium polymerization of D₄. The back-biting reaction of the propagation center produces D₅. The rate of the D₅ formation relatively to the rate of D₄ conversion increases with the conversion of D₄.

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