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Cationic Copolymerization with Depropagation. The Copolymerization of α-Methylstyrene and Styrene

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ABSTRACT

To evaluate the existence of the depropagation reaction in the copolymerization of vinyl monomers, the cationic copolymerization of α-methylstyrene with styrene was studied. The copolymer composition exhibited an extensive dependency on the temperature of polymerization and the monomer concentration, this fact not being explained by the Mayo-Lewis equation. Treatment of the copolymerization in terms of the depropagation reaction led to an estimate of the monomer reactivity ratio and the equilibrium constant between the polymer and the monomer of α-methylstyrene. A comparison of the equilibrium constants thus obtained with those reported in the literature indicates that the magnitude of the equilibrium constants depends on the sequence length of α-methylstyrene units. By extrapolation to

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long sequence length, the equilibrium constants approach the values which are reported for high molecular weight poly(α-methylstyrene).

INTRODUCTION

The anionic polymerization of α-methylstyrene is known to involve a depropagation reaction [1], leading to the following thermodynamic equilibrium between the polymer and monomer.

$$(m)_n + M \rightleftharpoons (m)_{n+1}$$

This phenomenon is believed to originate from the steric interference of the substituents in the product polymer [2]. There are a few monomers, such as methyl methacrylate and α-methylstyrene, which exhibit some depropagation at the usual temperatures of polymerization by anionic or radical mechanisms [1, 3]. However, the existence of the depropagation reaction in the cationic vinyl polymerization has not been observed.

In the present investigation the cationic copolymerization of α-methylstyrene with styrene was investigated in order to study the possibility of the depropagation reaction in cationic polymerization.

The kinetics of the cationic polymerization of α-methylstyrene was investigated by Bywater and Worsfold [4] in order to make certain of the existence of the depropagation reaction, but the depropagation reaction was not observed. It was concluded that the depropagation step is too slow to be important for low molecular weight chains at normal concentrations of the monomer.

The copolymer composition can usually be related to the monomer feed by the Mayo-Lewis equation, which contains the assumption of no reversibility of the propagation. A theoretical treatment for the copolymerization with depropagation has been given by Lowry [5]. Three different cases of depropagation are considered: (I) the terminal m_1 group has an appreciable tendency to depolymerize whenever it is attached to another m_1 unit, (II) the terminal m_1 unit has an appreciable tendency to depolymerize whenever it is attached to a sequence of two or more m_1 units, (III) either monomer has an appreciable tendency to depolymerize whenever it is attached to a sequence of two or more m_1 units.

The experimental investigations of these cases are reported in several papers. O'Driscoll et al. [6] and Ivin et al. [7] concluded that the experimental results are in accord with Mechanism II for the copolymerizations containing α-methylstyrene as a monomer. Wittmer [8] analyzed the radical copolymerization of α-methylstyrene, using Mechanism I. Monomer reactivity ratios were evaluated by the use of an equilibrium constant K known in an anionic polymerization.

In the present paper we wish to report the results of the cationic copolymerization of α-methylstyrene with styrene and to confirm the existence of the depropagation reaction. A further attempt was made to determine the equilibrium constant.

EXPERIMENTALS

Materials

Styrene and α-methylstyrene were obtained commercially. After distilling twice under a reduced pressure of nitrogen, these monomers were treated with lithium aluminum hydride overnight in order to remove impurities, and then redistilled twice under a high vacuum immediately before use [9]. Methylene chloride was purified by distillation and dried with a molecular sieve. Stannic chloride and trichloroacetic acid were distilled. A catalyst solution was prepared as a n-hexane solution (0.05 mole/liter) of $SnCl_4$-trichloroacetic acid (1:0.5 mole).

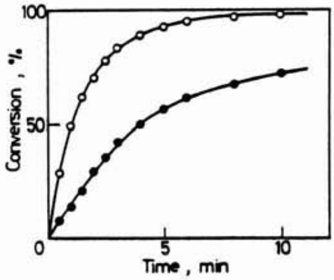
Polymerization

Methylene chloride (18 ml) and monomers (about 2 ml) were charged into a 100-ml ampoule equipped with a thermometer and a magnetic stirrer through a self-sealing rubber cap. The mixture was brought to the desired polymerization temperature in a thermostat (±0.1°C) under a slight positive pressure of dry nitrogen. The polymerization was started by adding the catalyst (0.2 ml) through the rubber cap. At an initial stage of the polymerization, elevation of temperature was observed by +0.2° at 0°C and +0.7° at -75°C. The amount of residual monomer was determined by programmed temperature gas chromatography (column; silicone DC 550 on

Celite 225 cm; temperature, 100-170°C). Toluene (0.5 ml) was previously added to the reaction system as an internal standard. A small amount of solution was withdrawn intermittently from the reaction system by a hypodermic syringe. The polymerization was stopped by a small amount of triethylamine previously added to the receivers.

RESULTS

The copolymerization of α-methylstyrene (M_1) with styrene (M_2) apparently shows a temperature dependency. In Figs. 1-4 are shown the time-conversion curves for the copolymerization at 0, -25, -50, and -75°C, respectively. As seen in the figures, the difference of the reactivities of these monomers was reduced with an increase in the polymerization temperature. Neither of the copolymerization systems had an induction period. From these curves we obtained correlation curves between M_1 and M_2, and a tangent on the curve gives dM_1/dM_2 at a given M_1/M_2.



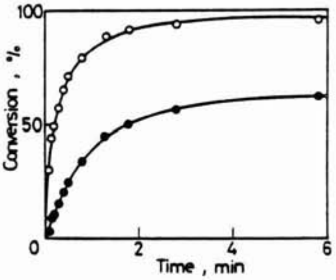
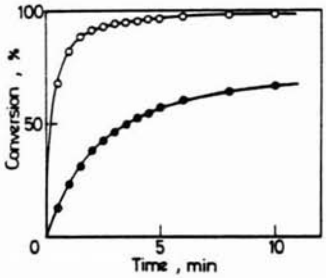


FIG. 1. Time-conversion curves for the copolymerization of α-methylstyrene and styrene in methylene chloride at 0°C. (○) α-Methylstyrene. (●) Styrene. [α-MeSt] = 0.080 mole/l, [St] = 0.350 mole/l, [Cat] = 0.13 mmole/l.

FIG. 2. Time-conversion curves for the copolymerization of α-methylstyrene and styrene in methylene chloride at -25°C. (○) α-Methylstyrene. (●) Styrene. [α-MeSt] = 0.080 mole/l, [St] = 0.350 mole/l, [Cat] = 0.25 mmole/l.



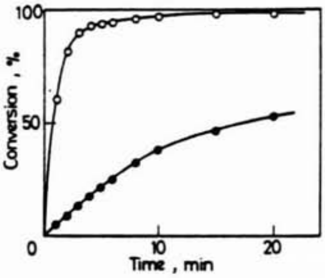


FIG. 3. Time-conversion curves for the copolymerization of α-methylstyrene and styrene in methylene chloride at -50°C. (O) α-Methylstyrene. (●) Styrene. [α-MeSt] = 0.080 mole/l, [St] = 0.350 mole/l, [Cat] = 0.58 mmole/l.

FIG. 4. Time-conversion curves for the copolymerization of α-methylstyrene and styrene in methylene chloride at -75°C. (O) α-Methylstyrene. (●) Styrene. [α-MeSt] = 0.080 mole/l, [St] = 0.350 mole/l, [Cat] = 0.37 mmole/l.

Data at -50°C are plotted according to Fineman-Ross Eq. (1) in Fig. 5:

$$\frac{F}{f}(f - 1) = r_1\left(\frac{F^2}{f}\right) + r_2 \tag{1}$$

where F and f are the monomer ratio in the feed ($F = M_1/M_2$) and the copolymer ($f = dM_1/dM_2$). The straight line in Fig. 5 indicates a theoretical line obtained from the values $r_1 = 40$, $r_2 = 0.42$, which will be mentioned later. The points at the extreme right correspond to copolymerization at the initial stage. The plots deviate from the theoretical straight line with polymerization and with a decrease in the concentration of α-methylstyrene. An apparent value of r_1 is zero at the final stage of copolymerization.

This abnormal deviation from Eq. (1) appears to show an effect of the concentration of α-methylstyrene. Figure 6 shows the relationship between the two monomer concentrations as the polymerization process proceeds, indicating that at lower monomer concentrations parallel straight lines were obtained. A break of the line was

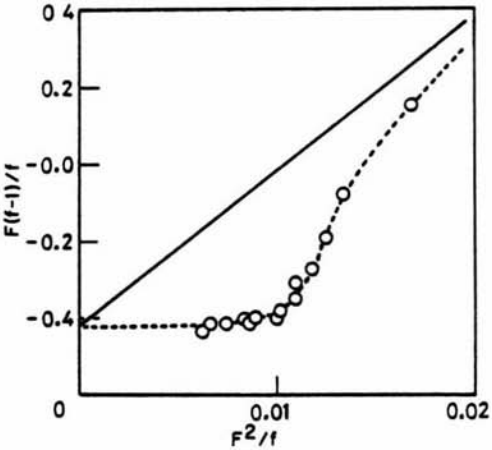


FIG. 5. Fineman-Ross plots for the copolymerization of α-methylstyrene (M_1) and styrene (M_2) at -50°C. The straight line is a theoretical line for $r_1 = 40$ and $r_2 = 0.42$. Reaction conditions are the same as in Fig. 3.

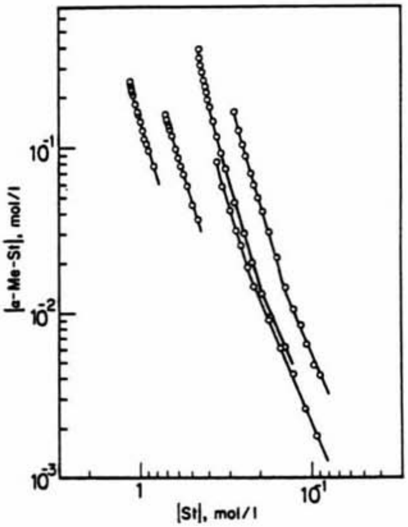


FIG. 6. Residual monomer concentrations in the copolymerization at 0°C. Reaction conditions are the same as in Fig. 1.

observed at 0.03, 0.02, 0.009, and 0.002 mole/liter of the α-methylstyrene concentration in the polymerizations at 0, -25, -50, and -75°C, respectively. The break point is not dependent on the styrene concentration. This fact has been confirmed by copolymerization experiments with varying initial monomer ratios and by varying the initial concentrations of α-methylstyrene. These data show that the break point is located at the same α-methylstyrene concentration independent of the initial molar ratio.

Figure 7 shows the first-order plot of the monomers for the copolymerization at 0°C. The data show straight lines during the initial stage of the polymerization, and there is a break at the point where the α-methylstyrene concentration is around 0.01 mole/liter. This phenomenon was observed in other experiments with varying initial molar ratios.

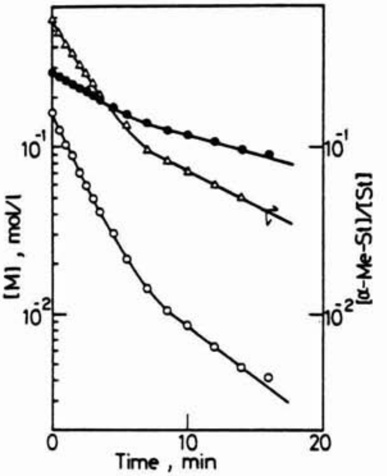


FIG. 7. First-order plot for the copolymerization at 0°C. (O) α-Methylstyrene. (●) Styrene. (△) α-Methylstyrene/styrene.

DISCUSSION

The results of the copolymerization can not be interpreted in terms of four propagation rate constants. Deviations from the Mayo-Lewis equation have sometimes been interpreted in terms of failure of the underlying assumption. α-Methylstyrene is known to exhibit depropagation in anionic polymerization. In the following analyses of the copolymerization data, the depropagation reaction was taken into consideration. Lowry's Case I [5] was applied to the present copolymerization as the simplest mechanism of depropagation. In this case, m_1 has an appreciable tendency to depropagate whenever it is attached to another m_1 unit. There are four propagating steps in the copolymerization reaction:

$$\sim\!\sim m_1 + M_1 \underset{k_{\overline{11}}}{\overset{k_{11}}{\rightleftharpoons}} \sim\!\sim m_1m_1 \tag{2a}$$

$$\sim\!\sim m_1 + M_2 \xrightarrow{k_{12}} \sim\!\sim m_1m_2 \tag{2b}$$

$$\sim\!\sim m_2 + M_1 \xrightarrow{k_{21}} \sim\!\sim m_2m_1 \tag{2c}$$

$$\sim\!\sim m_2 + M_2 \xrightarrow{k_{22}} \sim\!\sim m_2m_2 \tag{2d}$$

The rates of consumption of monomers are given by Eqs. (3) and (4).

$$-\frac{dM_1}{dt} = k_{11}M_1 \sum_{n=1}^{\infty} (m_1)_n - k_{\overline{11}} \sum_{n=2}^{\infty} (m_1)_n + k_{21}M_1m_2 \tag{3}$$

$$-\frac{dM_2}{dt} = k_{22}M_2m_2 + k_{12}M_2 \sum_{n=1}^{\infty} (m_1)_n \tag{4}$$

where the symbol $(m_1)_n$ denotes the concentration of an active end containing consecutive n units of monomer 1, k_{ij} is the rate constant for the addition of monomer j to a chain end m_i, and $k_{\overline{ij}}$ is the rate constant for the reverse reaction.

The steady-state assumption of Eq. (5) induces the copolymer composition Eq. (6).

$$k_{12}M_2 \sum_{n=1}^{\infty} (m_1)_n = k_{21}M_1m_2 \tag{5}$$

$$\frac{dM_1}{dM_2} = \frac{1 + r_1 \dfrac{M_1}{M_2} - K \dfrac{r_1}{M_2} \dfrac{\sum_{n=2}^{\infty} (m_1)_n}{\sum_{n=1}^{\infty} (m_1)_n}}{1 + r_2 \dfrac{M_2}{M_1}} \tag{6}$$

$r_1 = k_{11}/k_{12}$, $r_2 = k_{22},/k_{21}$, $K = k_{\overline{11}}/k_{11}$

If symbol α is defined as follows and assumed to be a constant, Eq. (6) is transformed into Eq. (7):

$$\alpha = (m_1)_{n+1}/(m_1)_n$$

It follows that:

$$\alpha = \sum_{n=2}^{\infty} (m_1)_n / \sum_{n=1}^{\infty} (m_1)_n$$

and

$$\frac{dM_1}{dM_2} = \frac{1 + r_1 \dfrac{M_1}{M_2} - r_1K \dfrac{\alpha}{M_2}}{1 + r_2 \dfrac{M_2}{M_1}} \tag{7}$$

This equation is simplified as

$$\frac{dM_1}{dM_2} = \frac{1 + r_1' \frac{M_1}{M_2}}{1 + r_1 \frac{M_1}{M_2}} \tag{8}$$

$$r_1' = r_1(1 - \frac{K\alpha}{M_1})$$

Equation (8) is an analogous form of the Mayo-Lewis equation. A Fineman-Ross-type equation of Eq. (8) is

$$\frac{F}{f}(f - 1) = r_1'(\frac{F^2}{f}) + r_2 \tag{9}$$

where F and f are M_1/M_2 and dM_1/dM_2, respectively.

Integration of Eqs. (3) and (4) gives Eqs. (10) and (11):

$$\log \frac{M_1}{(M_1)_0} = k_{11}\int(1 - \frac{K\alpha}{M_1})m_1dt + k_{21}m_2t \tag{10}$$

$$\log \frac{M_2}{(M_2)_0} = k_{22}m_2t + k_{12}m_1t \tag{11}$$

Deviation from the normal Fineman-Ross equation, as shown in Fig. 5, is explained qualitatively by the monomer dependency of r_1' values in Eq. (9). During the initial stage of polymerization and high monomer concentration, term $K\alpha/M_1$ is negligible as compared with 1, and r_1' is nearly equal to r_1. As the polymerization proceeds, the concentration of α-methylstyrene approaches an equilibrium monomer concentration (i.e., M_1 approaches $K\alpha$) and r_1' approaches zero. Equation (10) also contains a term which depends on the concentration of α-methylstyrene. This equation explains the break phenomena in Figs. 6 and 7. First-order plots of styrene in Fig. 7 also show a dependency on the monomer concentration. This fact can not be explained by Eq. (11), which does not contain the monomer dependent term. The reason may be the decrease of the m_1 end near the equilibrium concentration.

The symbol α defined above is equal to the probability, P_{11}, of the addition of M_1 to the m_1 end in the normal copolymerization:

$$\alpha = \frac{(m_1)_{n+1}}{(m_1)_n} = P_{11} \tag{12}$$

If the copolymerization reaction involves significant depropagation as follows,

$$\begin{tikzcd}
{} \arrow[r, rightleftharpoons] & (m_1)_n \arrow[r, rightleftharpoons, "k_{11}", "k_{\overline{11}}"'] \arrow[d, "k_{12}"] & (m_1)_{n+1} \arrow[r, rightleftharpoons] \arrow[d, "k_{12}"] & {} \\
 & (m_2) & (m_2) &
\end{tikzcd}$$

the probability P_{11} is represented by Eq. (13), which is then rearranged to Eq. (14):

$$\alpha = (P_{11}) = \frac{k_{11}M_1 - \alpha k_{\overline{11}}}{k_{11}M_1 - \alpha k_{\overline{11}} + k_{12}M_2} \tag{13}$$

$$\frac{1}{1 - \alpha} = 1 + r_1 \frac{M_1}{M_2} - r_1 K \frac{\alpha}{M_2} \tag{14}$$

The right side of Eq. (14) is equal to the numerator of the right side of Eq. (7). Substitution of Eq. (14) into Eq. (7) yields Eq. (15):

$$\frac{dM_2}{dM_1} = \left(1 + r_2 \frac{M_2}{M_1}\right)(1 - \alpha) \tag{15}$$

To use this equation for the calculation of α, it is necessary to know r_2. The value of r_2 was reasonably estimated in the following way. As mentioned before, Fig. 6 shows that at the final stage of polymerization and at low concentrations of α-methylstyrene, straight lines with the same slope were observed. At this period, α-methylstyrene may have a negligible tendency to undergo self-propagation. The concentration of m_1 may be much smaller than that of m_2. This assumption leads to Eq. (16) by dividing Eq. (11) by Eq. (10).

$$\log M_1 = \frac{k_{21}}{k_{22}} \log M_2 + \text{const} \tag{16}$$

The straight lines in Fig. 6 may be expressed by Eq. (16) and the reactivity ratio $r_2 = 0.42$ was obtained from the slopes of these lines. The slope was not dependent on the polymerization temperature, and hence we may reasonably assume r_2 is 0.42 at 0 to -75°C. Thus we can calculate α for a given M_2/M_1 value, but α thus obtained is not a constant value.

Once α is known from Eq. (15), it is possible to estimate r_1 and K using Eq. (14). Transposition of Eq. (14) yields Eq. (17):

$$\frac{M_1}{\alpha} = \frac{1}{r_1} \left(\frac{M_2}{1 - \alpha}\right) + K \tag{17}$$

A linear plots of (M_1/α) against $M_2/(1 - \alpha)$ will give $1/r_1$ and K from the slope and intercept, respectively. Plots of Eq. (17) are shown in Figs. 8 and 9. Figure 9 for the copolymerization at -75°C shows a straight line, giving the reactivity ratio $r_1 = 70$, and the equilibrium constant K = 0.002 mole/liter. Figure 8 for the polymerization at 0°C with varying initial molar ratio and the monomer concentration indicates that the experimental points may be best represented by a full line ($r_1 = 14$, K = 0.1 mole/liter). However, plots of the initial stage and the final stage of the polymerization did not fall on the line. The equilibrium constant K thus obtained is much smaller than the literature value. The deviation from the literature value becomes larger the higher the polymerization temperature. This seems to be interpreted in terms of a defect of the initial assumptions: the equilibrium constant is independent of the degree of polymerization. The equilibrium between low molecular weight anionic living polymers and α-methylstyrene was investigated by Szwarc [10]. It was found that the equilibrium constant is dependent on chain length and becomes larger with an increase in the chain length. Also, in our case a K value for high polymer may be obtained by extrapolation to $\alpha = 1$, i.e., the homopolymerization

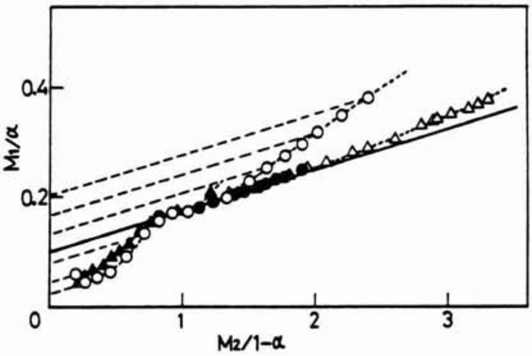


FIG. 8. Evaluation of equilibrium constant from Eq. (17) for the copolymerization at 0°C. Initial concentration, [St], [α-MeSt] mole/l: (▲) 0.280, 0.160; (○) 0.448, 0.393; (●) 0.706, 0.157; (△) 1.12, 0.248. The full line indicates K = 0.1 mole/l and r_1 = 14.

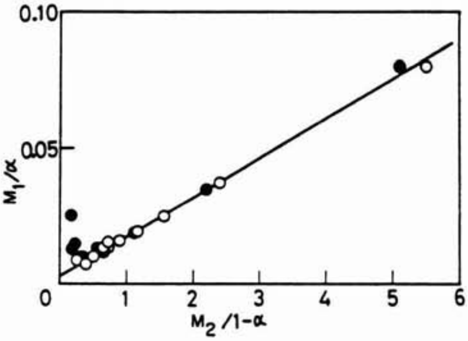
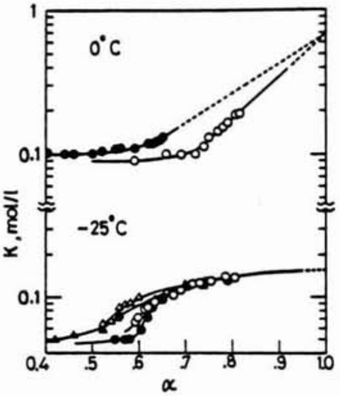


FIG. 9. Evaluation of equilibrium constant from Eq. (17) for the copolymerization at -75°C. Initial concentration, [St], [α-MeSt] mole/l: (○) 0.340, 0.0753; (●) 0.341, 0.0749. The full line indicates K = 0.002 mole/l and r_1 = 70.

of α-methylstyrene. As shown in Fig. 8, a series of parallel lines with a constant r_1 value gave apparent K values corresponding to the experimental points. The K values obtained by this way are plotted against α in Fig. 10. Here, extrapolation to α = 1 seems to give K values which nearly agree with those reported for the equilibrium involving high molecular weight polymer in the anionic polymerization (Fig. 11).



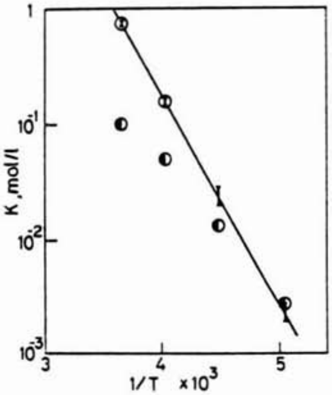


FIG. 10. Equilibrium constants of α-methylstyrene in the copolymerization. Initial concentration, [St], [α-MeSt] mole/l: At 0°C, (O) 0.457, 0.393; (●) 1.12, 0.248: At -25°C, (O) 0.550, 0.309; (●) 0.635, 0.237; (△) 0.794, 0.169; (▲) 0.720, 0.159.

FIG. 11. Equilibrium constants of α-methylstyrene. (◐) The present study. Obtained as in Figs. 8 and 9. (O) Extrapolated values obtained from Fig. 10. (I) Anionic polymerization [1c].

The kinetic investigation of the cationic polymerization of α-methylstyrene, studied by Worsfold and Bywater [4], reveals that the self-termination reaction may be neglected for the polymerization at low temperatures or at high monomer concentrations. However, for the polymerization at high temperatures or at low monomer concentrations, this term must be taken into consideration in Eq. (13), leading to Eq. (18). Deviation from a straight line in Fig. 8 seems to be partially explained by this.

$$\alpha = \frac{k_{11}M_1 - \alpha k_{\bar{1}\bar{1}}}{k_{11}M_1 - \alpha k_{\bar{1}\bar{1}} + k_{12}M_2 + k_t} \qquad (18)$$

where k_t is a rate constant for the self-termination.

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