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Registry No. P3HT, 108568-44-1; $NO^+PF_6^-$, 16921-91-8; tetrabutylammonium perchlorate, 1923-70-2.

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Graphical Method for Polymerization Kinetics. 3.[†] Living Polymerization with Nonequal Propagation Rate Constants

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ABSTRACT: According to Schulz et al., the propagation rate constants depend upon the degree of polymerization in the initial stage of the anionic polymerization of methyl methacrylate in tetrahydrofuran at −46 °C. This work deals with the non-steady-state kinetics for the living polymerizations with nonequal propagation rate constants, using the graphical technique. Several cases have been taken into account, and expressions for the number- and weight-average degrees of polymerization, the heterogeneity index, and the molecular weight distribution function are derived. The relationships between the reaction conditions and the molecular parameters of the resultant polymer have also been established.

Introduction

Terminationless polymerization was first described by Ziegler[1-3] and later by Mark.[4] For living polymerization with the initiation rate constant equal to the propagation constant, Flory[5] has given the Poisson distribution for the polymer formed. However, it was Szwarc[6,7] who actually discovered living polymerization in 1956 on the basis of highly convincing experiments. Two years later, Gold[8] took account of the fact that the rate constant of initiation is different from that of propagation and obtained the improved Poisson distribution. It is of interest that several authors[9-12] have estimated the individual propagation rate constants from their own experimental data. Maget[13] have studied theoretically the molecular weight distribution for living polymerization with n reaction steps and nonequal rate constants. However, the other important molecular parameters, such as the number- and weight-average degrees of polymerization and the heterogeneity index, have not yet been reported. Mita[14] has dealt with this problem with the assumptions of instantaneous initiation and m propagation steps, but little improvement has been made. Recently, Schulz and co-workers[12] have reported that the propagation rate constants vary with the degree of polymerization in the initial stage of the anionic polymerization of MMA in THF at −46 °C and compared the experimental results with numerical solutions of the related kinetic equations. Obviously, it is necessary to treat comprehensively living polymerization with nonequal propagation rate constants. Using the graphical method[15-17] and Laplace transformation, all the molecular parameters for the resulting living polymer are derived in this paper.

1. General Treatment

The differential equations for the formation and disappearance of the living n-mer N_1, N_2, ..., N_n, as well as for the consumption of initiator N_0, are given by the following equations:

[†] Part 2: cf. ref 17.

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$$\mathrm{d}N_0/\mathrm{d}t = -k_0MN_0 \qquad (1)$$

$$\mathrm{d}N_n/\mathrm{d}t = k_{n-1}MN_{n-1} - k_nMN_n, \quad n = 1, 2, 3, ... \qquad (2)$$

where M is the concentration of monomer. The initial conditions of eq 1 and 2 are

$$N_0(t{=}0) = I \qquad N_{n\geqslant 1}(t{=}0) = 0 \qquad M(t{=}0) = M_0$$

I and M_0 are the initial concentrations of initiator and monomer, respectively. For the convenience of derivation, the following variable transformation is introduced:

$$x = \int_0^t M\,\mathrm{d}t \qquad (3)$$

Hence

$$\mathrm{d}N_0/\mathrm{d}x = -k_0N_0 \qquad (4)$$

$$\mathrm{d}N_n/\mathrm{d}x = k_{n-1}N_{n-1} - k_nN_n \qquad (5)$$

Furthermore, in terms of definitions of the Laplace transformation, we have

$$R_n = \int_0^\infty e^{-\lambda x}N_n\,\mathrm{d}x, \quad n = 0, 1, 2, ...$$

$$\lambda R_0 - I = \int_0^\infty e^{-\lambda x}\frac{\mathrm{d}N_0}{\mathrm{d}x}\,\mathrm{d}x$$

$$\lambda R_n = \int_0^\infty e^{-\lambda x}\frac{\mathrm{d}N_n}{\mathrm{d}x}\,\mathrm{d}x \quad n = 1, 2, 3, ...$$

Then

$$\frac{\lambda + k_0}{I}R_0 = 1 \qquad (6)$$

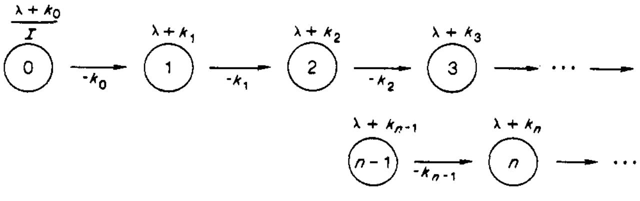
$$(\lambda + k_n)R_n - k_{n-1}R_{n-1} = 0 \qquad (7)$$

The set of algebraic equations can also be expressed thus

$$\begin{bmatrix} (\lambda + k_0)/I & & & & & & 0 \\ -k_0 & (\lambda + k_1) & & & & & \\ & -k_1 \ddots & (\lambda + k_2) \ddots & & & & \\ & & \ddots -k_{n-2} & (\lambda + k_{n-1}) & & & \\ & & & -k_{n-1} & (\lambda + k_n) & & \\ & 0 & & & -k_n \ddots & (\lambda + k_{n+1}) \ddots & \end{bmatrix} \times \begin{bmatrix} R_0 \\ R_1 \\ R_2 \\ \vdots \\ R_{n-1} \\ R_n \\ R_{n+1} \\ \vdots \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ \vdots \\ \vdots \\ \vdots \\ 0 \end{bmatrix} \qquad (8)$$

The coefficient matrix of eq 8 relates to the topology of the algebraic set which can be denoted by Graph G$_1$.

Graph G$_1$



In Graph G$_1$, a vertex corresponds to a diagonal element of the triangle matrix, and an edge diverting from a vertex to the next is associated with one of the nondiagonal elements. The initial vertex possesses a weight of $(\lambda + k_0)/I$, and vertex n (n = 1, 2, 3, ...) has a weight of $(\lambda + k_n)$. The weight of the edge between vertex $n - 1$ and n is $-k_{n-1}$. According to the graphical rule,[15] the expression of image function R_n is a fraction with a factor $(-1)^n$, of which the numerator is a product composed of weights of all edges in Graph G$_1$, and the denominator is also a product of weights of all vertices in the same graph. For vertex zero, the numerator is defined to be unity. Then we have

$$R_0 = \frac{I}{\lambda + k_0}$$

$$R_n = I\frac{\prod\limits_{i=0}^{n-1}k_i}{\prod\limits_{i=0}^{n}(\lambda + k_i)}, \quad n \geqslant 1 \qquad (9)$$

Equation 9 is corroborated in Appendix A. In accordance with the Riemann-Melin integral, the reverse Laplace transformation is

$$N_n = \frac{1}{2\pi i}\int_L R_ne^{\lambda x}\,\mathrm{d}x = \sum_j \mathrm{res}\,[R_ne^{\lambda x}]_{\lambda=\lambda_j} \qquad (10)$$

where "res" symbolizes the residue and L is an arbitrary line parallel to the imaginary axes in the complex plane, at the right hand of which there is no pole of image function R_n. Equation 9 shows that there are $n + 1$ poles in R_n, i.e., $\lambda_0 = -k_0$, $\lambda_1 = -k_1$, $\lambda_2 = -\mathrm{k}_2$, ..., $\lambda_n = -k_n$. All of them are the first-order poles, so that it is easy to perform the reverse Laplace transformation:

$$N_0 = \mathrm{res}\,[R_0e^{\lambda x}]_{\lambda=-k_0} = \lim_{\lambda\to -k_0}\{Ie^{\lambda x}\} = Ie^{-k_0x} \qquad (11)$$

$$\mathrm{res}\,[R_ne^{\lambda x}]_{\lambda_j} = \lim_{\lambda\to -k_j}\{I\prod_{i=0}^{n-1}k_ie^{\lambda x}/\prod_{i=0}^{n}{}'(\lambda + k_i)\} = I\prod_{i=0}^{n-1}k_ie^{-k_jx}/\prod_{i=0}^{n}{}'(k_{\mathrm{i}} - k_j), \quad n \geqslant 1 \qquad (12)$$

where $\prod_{i=0}^{n}{}'$ denotes $i \neq j$ in the product of the terms indicated. Finally we obtain

$$N_n = \sum_{j=0}^{n}\mathrm{res}\,[R_ne^{\lambda x}]_{\lambda_j} = I\sum_{j=0}^{n}\{\prod_{i=0}^{n-1}k_ie^{-k_jx}/\prod_{i=0}^{n}{}'(k_i - k_j)\}, \quad n \geqslant 1 \qquad (13)$$

This is the general expression for the molecular weight distribution function of a living polymer. The statistical moments are respectively adapted to the following equations, which are derived from eq 4 and 5.

$$\frac{\mathrm{d}\sum\limits_{n=1}^{\infty}N_n}{\mathrm{d}x} = k_0N_0 \qquad (14)$$

$$\frac{\mathrm{d}\sum\limits_{n=1}^{\infty}nN_n}{\mathrm{d}x} = \sum_{n=0}^{\infty}k_nN_n \qquad (15)$$

$$\frac{\mathrm{d}\sum\limits_{n=1}^{\infty}n^2N_n}{\mathrm{d}x} = 2\sum_{n=1}^{\infty}nk_nN_n + \sum_{n=0}^{\infty}k_nN_n \qquad (16)$$

Equations 15 and 16 result in

$$\sum_{n=1}^{\infty}N_n = I(1 - e^{-k_0x}) \qquad (17)$$

$$\sum_{n=1}^{\infty} nN_n = I\sum_{n=0}^{\infty}\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x}) \tag{18}$$

$$\sum_{n=1}^{\infty} n^2 N_n = I\sum_{n=0}^{\infty}(2n + 1)\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x}) \tag{19}$$

Hence, the number- and weight-average degrees of polymerization are respectively

$$\bar{P}_n = \frac{\sum_{n=0}^{\infty}\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x})}{1 - e^{-k_0 x}} \tag{20}$$

$$\bar{P}_w = \frac{\sum_{n=0}^{\infty}(2n + 1)\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x})}{\sum_{n=0}^{\infty}\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x})} \tag{21}$$

Provided M_0 and M are the initial and residual concentrations of monomer and Y and t represent the monomer conversion and reaction time, one obtains

$$M = M_0 - I\sum_{n=0}^{\infty}\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x}) \tag{22}$$

$$Y = \frac{I}{M_0}\sum_{n=0}^{\infty}\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x}) \tag{23}$$

and

$$t = \int_0^x \frac{\mathrm{d}x}{M_0 - I\sum_{n=0}^{\infty}\sum_{j=0}^{n}\prod_{i=0}^{n}{}'\frac{k_i}{k_i - k_j}(1 - e^{-k_j x})} \tag{24}$$

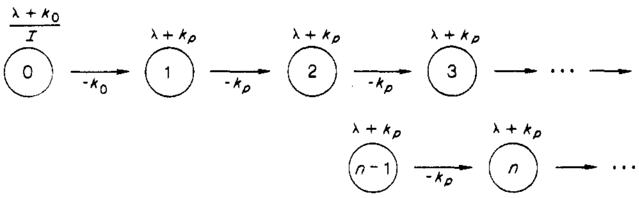
The value of x can be calculated from eq 23 or 24. Then all the molecular parameters of the living polymer can be evaluated according to the polymerization conditions.

Equation 13 is the so-called Bateman equation,[19] which is frequently used in nuclear chemistry but seldom met in polymerization kinetics. Several more realistic cases are discussed below.

2. $\boldsymbol{k_0 \neq k_p}$, $\boldsymbol{k_{n\geqslant 1} = k_p}$

In case of $k_0 \neq k_p$ and $k_1 = k_2 = k_3 = ... = k_p$, the topological graph of the related algebraic set becomes Graph G_2. In accordance with the graphical rule, the image function for N_n is

Graph G_2



$$R_n = \frac{Ik_0{k_p}^{n-1}}{(\lambda + k_0)(\lambda + k_p)^n} \tag{25}$$

It is evident that the expression for N_0 is the same as in eq 11. In eq 25, there are two poles, one of which is the first-order pole, $\lambda_0 = -k_0$, and the other is the nth-order pole, $\lambda_1 = -k_p$. Subsequently, the respective residues are

$$\text{res}\,[R_n e^{\lambda x}]_{\lambda_0} = \frac{Ik_0{k_p}^{n-1}e^{-k_0 x}}{(k_p - k_0)^n} \tag{26}$$

$$\text{res}\,[R_n e^{x}]_{\lambda_1} = \frac{I}{(n-1)!}\frac{\mathrm{d}^{n-1}}{\mathrm{d}\lambda^{n-1}}\left\{\frac{k_0{k_p}^{n-1}e^{\lambda x}}{\lambda + k_0}\right\}_{\lambda = -k_p} = -\frac{Ik_0{k_p}^{n-1}}{(k_p - k_0)^n}\sum_{j=0}^{n-1}\frac{[(k_p - k_0)x]^j e^{-k_p x}}{j!} \tag{27}$$

Hence

$$N_n = \text{res}\,[R_n e^{\lambda x}]_{\lambda_0} + \text{res}\,[R_n e^{\lambda x}]_{\lambda_1} = I\frac{ae^{-a\alpha}}{(1 - a)^n}\left\{1 - \sum_{j=0}^{n-1}\frac{[(1 - a)\alpha]^j}{j!}e^{-(1-a)\alpha}\right\} \tag{28}$$

where $a = k_0/k_p$, $\alpha = k_p x$. Equation 28 is the improved Poisson distribution, which is identical with that reported by Gold,[8] if some necessary substitutions are made. Equation 28 can also be expressed as follows (see Appendix B):

$$N_n = I\frac{ae^{-a\alpha}}{(1 - a)^n(n - 1)!}\Gamma_{(1-a)\alpha}(n) \tag{29}$$

where

$$\Gamma_{(1-a)\alpha}(n) = \int_0^{(1-a)\alpha}[(1 - a)\alpha]^{n-1}e^{-(1-a)\alpha}\,\mathrm{d}[(1 - a)\alpha] \tag{30}$$

and $\Gamma_{(1-a)\alpha}(n)$ is an incomplete gamma function. It is easy to calculate the statistical moments by way of eq 29.

$$\sum_{n=1}^{\infty} n^s N_n = Iae^{-a\alpha}\int_0^{\alpha} e^{-(1-a)\alpha}\sum_{n=1}^{\infty}\frac{\alpha^{n-1}n^s}{(n - 1)!}\,\mathrm{d}\alpha \qquad s = 0, 1, 2 \tag{31}$$

It follows that

$$\sum_n N_n = I(1 - e^{-a\alpha}) \tag{32}$$

$$\sum_n nN_n = I\left\{\alpha - \frac{1 - a}{a}(1 - e^{-a\alpha})\right\} \tag{33}$$

$$\sum_n n^2 N_n = I\left\{\alpha^2 + \left(3 - \frac{2}{a}\right)\alpha + \left(1 - \frac{3}{a} + \frac{2}{a^2}\right)(1 - e^{-a\alpha})\right\} \tag{34}$$

Therefore

$$\bar{P}_n = \frac{\alpha - \frac{1 - a}{a}(1 - e^{-a\alpha})}{1 - e^{-a\alpha}} \tag{35}$$

$$\bar{P}_w = \frac{\alpha^2 + \left(3 - \frac{2}{a}\right)\alpha + \left(1 - \frac{3}{a} + \frac{2}{a^2}\right)(1 - e^{-a\alpha})}{\alpha - \frac{1 - a}{a}(1 - e^{-a\alpha})} \tag{36}$$

$$\frac{\bar{P}_w}{\bar{P}_n} = \frac{(1 - e^{-a\alpha})\left\{\alpha^2 + \left(3 - \frac{2}{a}\right)\alpha + \left(1 - \frac{3}{a} + \frac{2}{a^2}\right)(1 - e^{-a\alpha})\right\}}{\left[\alpha - \frac{1 - a}{a}(1 - e^{-a\alpha})\right]^2} \tag{37}$$

Gold[8] has not related his result to the polymerization conditions, so that there has been a gap between the theoretical and experimental studies. A simple method is established below, by which the molecular parameters

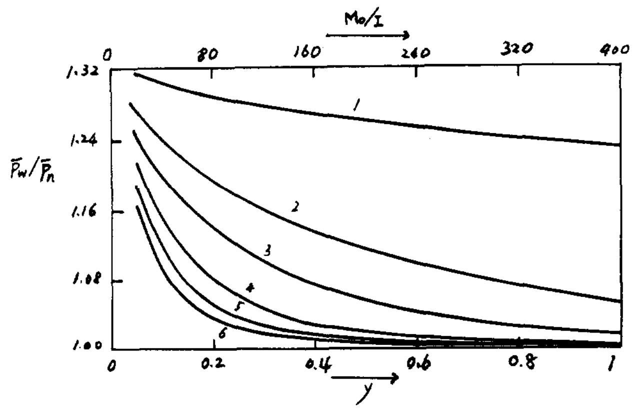


Figure 1. Relationship between the heterogeneity index and the monomer conversion or the ratio of initial concentration of monomer to that of initiator, $I/M_0 = 2.5 \times 10^{-3}$ for $P_w/P_n \sim Y$, $Y = 1$ for $P_w/P_n \sim M_0/I$: (1) $a = 1 \times 10^{-3}$; (2) $a = 1 \times 10^{-2}$; (3) $a = 2 \times 10^{-2}$; (4) $a = 4 \times 10^{-2}$; (5) $a = 6 \times 10^{-2}$; (6) $a = 8 \times 10^{-2}$.

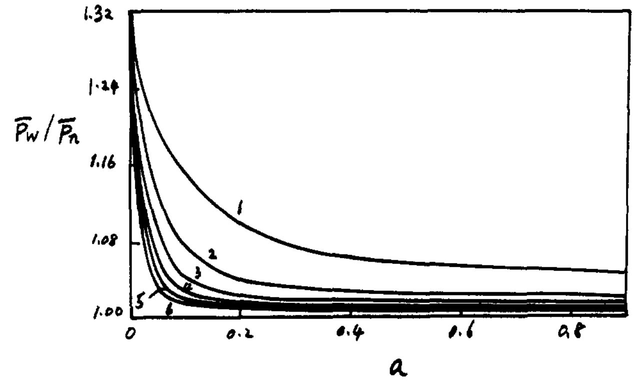


Figure 2. Relationship between the heterogeneity index and the value of constant a, $I/M_0 = 1/400$: (1) $Y = 0.05$; (2) $Y = 0.10$; (3) $Y = 0.15$; (4) $Y = 0.20$; (5) $Y = 0.25$; (6) $Y = 0.30$.

of living polymer are connected with the corresponding reaction parameters. From the definition of monomer conversion and eq 3, we have

$$Y = \frac{I}{M_0}\left\{\alpha - \frac{1-a}{a}(1 - e^{-a\alpha})\right\} \tag{38}$$

and

$$t = \frac{1}{k_p}\int_0^{\alpha} \frac{d\alpha}{M_0 - I\left\{\alpha - \dfrac{1-a}{a}(1 - e^{-a\alpha})\right\}} \tag{39}$$

According to eq 38, the magnitude of parameter α is determined in terms of the Newton-Raphson method,[18] as is the molecular weight distribution curve and the average degrees of polymerization. Figure 1 shows the relation between the heterogeneity index and monomer conversion at certain magnitudes of kinetic ratio a and $I/M_0 = 2.5 \times 10^{-3}$. The same figure also presents the relation between the heterogeneity index and initiator level at $Y = 1$ and various values of a. Figure 2 indicates that the resulting living polymer becomes more homogeneous with the increasing of ratio a. The molecular weight distribution curves computed from the polymerization conditions are displayed in Figure 3.

Now, we consider a few more special cases, i.e., $k_i = k_p$ and $k_i \to \infty$. When $a = 1$, eq 28 is rearranged to

$$N_n = \frac{Ia}{(1-a)^n}\left\{e^{-a\alpha} - e^{-\alpha}\sum_{j=0}^{n-1}\frac{[(1-a)\alpha]^j}{j!}\right\}$$

Then

$$N_n = I\left\{a\frac{\dfrac{\partial^n}{\partial a^n}\left[e^{-a\alpha} - e^{-\alpha}\displaystyle\sum_{j=0}^{n-1}\frac{[(1-a)\alpha]^j}{j!}\right]}{\dfrac{\partial^n}{\partial a^n}[(1-a)^n]}\right\}_{a=1} = I\frac{\alpha^n e^{-\alpha}}{n!} \tag{40}$$

If $a \to \infty$, eq 28 must be rearranged in another form:

$$N_n = I\frac{ae^{-\alpha}}{1-a}\left\{\frac{e^{(1-a)\alpha}}{(1-a)^{n-1}} - \sum_{j=0}^{n-1}\frac{\alpha^j}{j!(1-a)^{n-1-j}}\right\}$$

Because $a/(1-a) \doteq 1$, $e^{(1-a)\alpha}/(1-a)^{n-1} \doteq 0$, and

$$\sum_{j=0}^{n-2}\frac{\alpha^j}{j!(1-a)^{n-1-j}} \doteq 0$$

hence

$$N_n = I\frac{\alpha^{n-1}e^{-\alpha}}{(n-1)!} \tag{41}$$

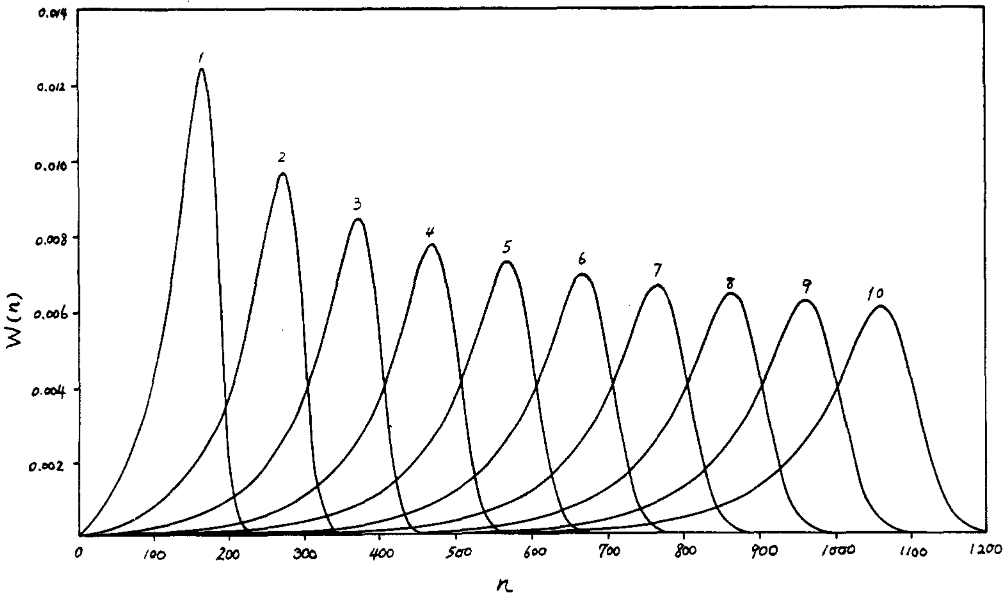


Figure 3. Differential molecular weight distributions at various monomer conversions, $W(n) = nN_n/\sum_n nN_n$, $a = 1 \times 10^{-2}$, $I/M_0 = 1 \times 10^{-3}$: (1) $Y = 0.10$; (2) $Y = 0.20$; (3) $Y = 0.30$; (4) $Y = 0.40$; (5) $Y = 0.50$; (6) $Y = 0.60$; (7) $Y = 0.70$; (8) $Y = 0.80$; (9) $Y = 0.90$; (10) $Y = 1.00$.

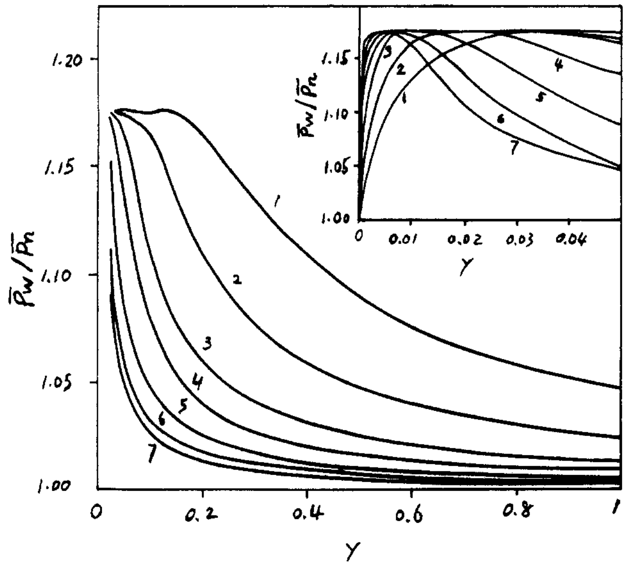


Figure 4. Relationship between the heterogeneity index and the monomer conversion, $a = 1.1$, $b = 3.1$ (from Schulz et al.[12]): (1) $I/M_0 = 0.05$; (2) $I/M_0 = 0.025$; (3) $I/M_0 = 0.0125$; (4) $I/M_0 = 1/120$; (5) $I/M_0 = 0.005$; (6) $I/M_0 = 1/300$; (7) $I/M_0 = 0.0025$.

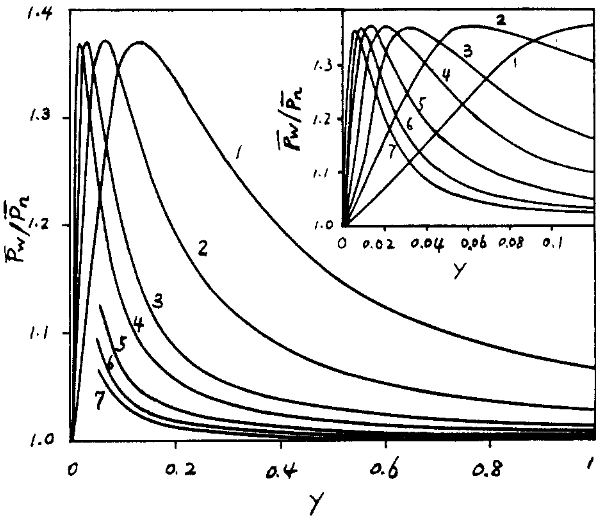


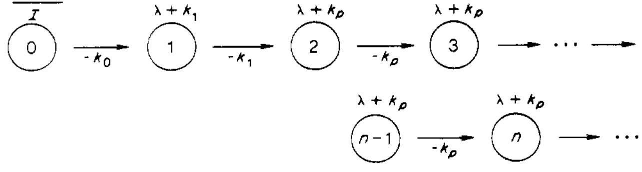
Figure 5. Relationship between the heterogeneity index and the monomer conversion, $a_0 = 11/7$, $a_1 = 16/35$, $a_2 = 4/7$, $a_3 = 5/7$: (1) $I/M_0 = 0.05$; (2) $I/M_0 = 0.025$; (3) $I/M_0 = 0.0125$; (4) $I/M_0 = 1/120$; (5) $I/M_0 = 0.005$; (6) $I/M_0 = 1/300$; (7) $I/M_0 = 0.0025$.

In both cases of $k_i = k_p$ and $k_i \to \infty$, the Poisson distribution is obtained.

3. $k_{n\geq 2} = k_p$

According to Schulz et al.,[12] the anionic oligomerization of MMA using MIB-Na as the initiator in THF at −46 °C is free from side reactions and falls within the type of the polymerization treated in this section. When $k_2 = k_3 = \ldots = k_p$, the weights of the vertices and edges are shown in Graph G3. Apparently

Graph G3



$$R_1 = \frac{Ik_0}{(\lambda + k_0)(\lambda + k_1)} \tag{42}$$

$$R_n = \frac{Ik_0k_1{k_p}^{n-2}}{(\lambda + k_0)(\lambda + k_1)(\lambda + k_p)^{n-1}}, \quad n = 2, 3, \ldots \tag{43}$$

Equation 11 is still valid for this case, and

$$N_1 = I\left\{\frac{b}{b-a}e^{-a\alpha} - \frac{a}{b-a}e^{-b\alpha}\right\} \tag{44}$$

where $b = k_1/k_p$, and symbols a and α have the same meanings as before. There are three poles in eq 43, namely, the first-order poles $\lambda_0 = -k_0$ and $\lambda_1 = -k_1$ and the $(n-1)$th pole $\lambda_2 = -k_p$. It follows that

$$\text{res }[R_ne^{\lambda x}]_{\lambda_0} = \frac{Ik_0k_1{k_p}^{n-2}}{(k_1 - k_0)(k_p - k_0)^{n-1}}e^{-k_0x} \tag{45}$$

$$\text{res }[R_ne^{\lambda x}]_{\lambda_1} = \frac{Ik_0k_1{k_p}^{n-2}}{(k_0 - k_1)(k_p - k_1)^{n-1}}e^{-k_1x} \tag{46}$$

$$\begin{aligned}\text{res }[R_ne^{\lambda x}]_{\lambda_2} &= \frac{I}{(n-2)!}\,\frac{\mathrm{d}^{n-2}}{\mathrm{d}\lambda^{n-2}}\left\{\frac{k_0k_1{k_p}^{n-2}}{(\lambda + k_0)(\lambda + k_1)}e^{\lambda x}\right\}_{\lambda=-k_p} \\ &= \frac{Ik_0k_1{k_p}^{n-2}}{(n-2)!}\left\{\sum_{j=0}^{n-2}\sum_{m=0}^{n-2-j}\frac{(n-2)!}{j!m!(n-2-j-m)!}\,\frac{\mathrm{d}^j}{\mathrm{d}\lambda^j} \times\right. \\ &\qquad \left.(e^{\lambda x})\frac{\mathrm{d}^m}{\mathrm{d}\lambda^m}\left(\frac{1}{\lambda + k_0}\right)\frac{\mathrm{d}^{n-2-j-m}}{\mathrm{d}\lambda^{n-2-j-m}}\left(\frac{1}{\lambda + k_1}\right)\right\}_{\lambda=-k_p} = \\ &\frac{Ik_0k_1{k_p}^{n-2}}{(k_p - k_0)(k_p - k_1)}\sum_{j=0}^{n-2}\frac{x^je^{-k_px}}{j!}\;\frac{1}{(k_p - k_1)^{n-2-j}}\sum_{m=0}^{n-2-j}\left\{\frac{k_p - k_1}{k_p - k_0}\right\}^m \\ &= Ik_0k_1{k_p}^{n-2}\frac{e^{-k_px}}{(k_1 - k_0)(k_p - k_1)^{n-1}}\sum_{j=0}^{n-2}\frac{[(k_p - k_1)x]^j}{j!} + \\ &\qquad \frac{e^{-k_px}}{(k_0 - k_1)(k_p - k_0)^{n-1}}\sum_{j=0}^{n-2}\frac{[(k_p - k_0)x]^j}{j!}\end{aligned} \tag{47}$$

Finally we obtain

$$N_n = \frac{Iab}{(n-2)!}\left\{\frac{e^{-a\alpha}}{(b-a)(1-a)^{n-1}}\Gamma_{(1-a)\alpha}(n-1) + \frac{e^{-b\alpha}}{(a-b)(1-b)^{n-1}}\Gamma_{(1-b)\alpha}(n-1)\right\} \tag{48}$$

For derivation of various moments, it is convenient to utilize the following equation:

$$\sum_{n=1}^{\infty}n^sN_n = N_1 + Iab\left\{\frac{e^{-a\alpha}}{b-a}\int_0^{\alpha}e^{-(1-a)\alpha}\sum_{n=2}^{\infty}\frac{n^s\alpha^{n-2}}{(n-2)!}\,\mathrm{d}\alpha + \frac{e^{-b\alpha}}{a-b}\int_0^{\alpha}e^{-(1-b)\alpha}\sum_{n=2}^{\infty}\frac{n^s\alpha^{n-2}}{(n-2)!}\,\mathrm{d}\alpha\right\}, \quad s = 0, 1, 2 \tag{49}$$

This results in expressions for the average degrees of polymerization etc.

$$\bar{P}_\mathrm{n} = \left\{b\left[\alpha + \left(2 - \frac{1}{a}\right) - \left(2 - \frac{1}{a} - \frac{a}{b}\right)e^{-a\alpha}\right] - a\left[\alpha + \left(2 - \frac{1}{b}\right) - \left(1 - \frac{1}{b}\right)e^{-b\alpha}\right]\right\}\Big/ (b-a)(1 - e^{-a\alpha}) \tag{50}$$

$$\bar{P}_{\mathrm{w}} = \left\{b\left[\alpha^2 + \left(5 - \frac{2}{a}\right)\alpha + \left(4 - \frac{5}{a} + \frac{2}{a^2}\right) - \left(4 - \frac{5}{a} + \frac{2}{a^2} - \frac{a}{b}\right)e^{-a\alpha}\right] - a\left[\alpha^2 + \left(5 - \frac{2}{b}\right)\alpha + \left(4 - \frac{5}{b} + \frac{2}{b^2}\right) - \left(3 - \frac{5}{b} + \frac{2}{b^2}\right)e^{-b\alpha}\right]\right\} \Big/ \left\{b\left[\alpha + \left(2 - \frac{1}{a}\right) - \left(2 - \frac{1}{a} - \frac{a}{b}\right)e^{-a\alpha}\right] - a\left[\alpha + \left(2 - \frac{1}{b}\right) - \left(1 - \frac{1}{b}\right)e^{-b\alpha}\right]\right\} \quad (51)$$

$$Y = \frac{I}{M_0}\left\{\frac{b}{b-a}\left[\alpha + \left(2 - \frac{1}{a}\right) - \left(2 - \frac{1}{a} - \frac{a}{b}\right)e^{-a\alpha}\right] + \frac{a}{a-b}\left[\alpha + \left(2 - \frac{1}{b}\right) - \left(1 - \frac{1}{b}\right)e^{-b\alpha}\right]\right\} \quad (52)$$

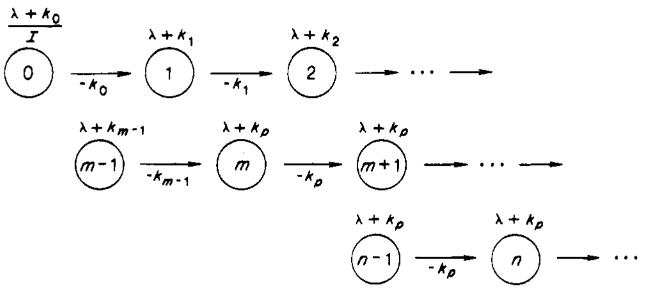
$$t = \frac{1}{k_p}\int_0^{\alpha}[(b-a)\,\mathrm{d}\alpha] \Big/ \left\{M_0 - I\left\{b\left[\alpha + \left(2 - \frac{1}{a}\right) - \left(2 - \frac{1}{a} - \frac{a}{b}\right)e^{-a\alpha}\right] - a\left[\alpha + \left(2 - \frac{1}{b}\right) - \left(1 - \frac{1}{b}\right)e^{-b\alpha}\right]\right\}\right\} \quad (53)$$

Then the molecular weight distribution curve and the average degrees of polymerization of the resulting polymer can be calculated from the reaction conditions, such as the initial molar ratio of the initiator to monomer and the monomer conversion. For instance, the relationship between the heterogeneity index and monomer conversion is given in Figure 4.

4. $\boldsymbol{k_{n\geqslant m} = k_p}$

For the case under consideration here, the topological graph of the correspondent algebraic set is Graph G_4.

Graph G_4



$N_{n<m}$ can be derived simply. By cutting away all the vertices on the right hand of vertex $(m-1)$ from Graph G_4 and comparing the residual graph with Graph G_1, we immediately obtain

$$N_{n<m} = I\sum_{j=0}^{n}\frac{\prod_{i=0}^{n-1}a_i e^{-a_j\alpha}}{\prod_{i=0}^{n}{}'(a_i - a_j)} \quad (54)$$

where $a_i = k_i/k_p$. For $N_{n\geqslant m}$, the image function is

$$R_n = I\prod_{i=0}^{m-1}\frac{k_i k_p^{\,n-m}}{(\lambda + k_i)(\lambda + k_p)^{n-m+1}} \quad (55)$$

In eq 55, there are $(m+1)$ poles, one of which is the $(n-m+1)$th-order pole, $\lambda_m = -k_p$, and the others are the first-order poles ($\lambda_j = -k_j$, $j = 0, 1, 2, ..., m-1$). Subsequently

$$\operatorname{res}\,[R_n e^{\lambda x}]_{\lambda_j} = \frac{I\prod_{i=0}^{m-1}k_i k_p^{\,n-m}e^{-k_j x}}{\prod_{i=0}^{m-1}{}'(k_i - k_j)(k_p - k_j)^{n-m+1}} \quad (56)$$

and

$$\operatorname{res}\,[R_n e^{\lambda x}]_{\lambda_m} = \frac{I}{(n-m)!}\,\frac{\mathrm{d}^{n-m}}{\mathrm{d}\lambda^{n-m}}\left\{\prod_{i=0}^{m-1}\frac{k_i k_p^{\,n-m}e^{\lambda x}}{(\lambda + k_i)}\right\}_{\lambda=-k_p} = \frac{I\prod_{i=0}^{m-1}k_i k_p^{\,n-m}}{(n-m)!}\left\{\sum_{k=0}^{n-m}\sum_{\sum_{t=0}^{m-1}S_t = n-m-k}\frac{(n-m)!}{k!\prod_{t=0}^{m-1}S_t!}\,\frac{\mathrm{d}^k}{\mathrm{d}\lambda^k}\times (e^{\lambda x})\prod_{t=0}^{m-1}\frac{\mathrm{d}^{S_t}}{\mathrm{d}\lambda^{S_t}}\left(\frac{1}{\lambda + k_t}\right)\right\}_{\lambda=-k_p} = -I\sum_{j=0}^{m-1}\frac{\prod_{i=0}^{m-1}k_i k_p^{\,n-m}e^{-k_p x}}{\prod_{i=0}^{m-1}{}'(k_i - k_j)(k_p - k_j)^{n-m+1}}\sum_{k=0}^{n-m}\frac{[(k_p - k_j)x]^k}{k!} \quad (57)$$

Finally, the following equation is derived:

$$N_{n\geqslant m} = \frac{I\sum_{j=0}^{m-1}\dfrac{\prod_{i=0}^{m-1}a_i e^{-a_j\alpha}}{\prod_{i=0}^{m-1}{}'(a_i - a_j)(1 - a_j)^{n-m+1}}\,\Gamma_{(1-a_j)\alpha}(n - m + 1)}{(n-m)!} \quad (58)$$

where $\Gamma_{(1-a_j)\alpha}(n - m + 1)$ is an incomplete gamma function, $a_j = k_j/k_p$, and α is equal to $k_p x$. It is easy to derive the statistical moments, and the results are

$$\sum_{n=1}^{\infty}N_n = I(1 - e^{-a_0\alpha}) \quad (59)$$

$$\sum_{n=1}nN_n = I\left\{\sum_{n=1}^{m-1}n\sum_{j=0}^{n}\frac{\prod_{i=0}^{n-1}a_i e^{-a_j\alpha}}{\prod_{i=0}^{n}{}'(a_i - a_j)} + \sum_{j=0}^{m-1}\prod_{i=0}^{m-1}{}'\frac{a_i}{a_i - a_j}\left[\left(m - \frac{1}{a_j}\right)(1 - e^{-a_j\alpha}) + \alpha\right]\right\} \quad (60)$$

$$\sum_{n=1}n^2N_n = I\left\{\sum_{n=1}^{m-1}n^2\sum_{j=0}^{n}\frac{\prod_{i=0}^{n-1}a_i e^{-a_j\alpha}}{\prod_{j=0}^{n}{}'(a_i - a_j)} + \sum_{j=0}^{m-1}\prod_{i=0}^{m=1}{}'\frac{a_i}{a_i - a_j}\left\{\alpha^2 + \left(2m + 1 - \frac{2}{a_j}\right)\alpha + \left(m^2 - \frac{2m+1}{a_j} + \frac{2}{a_j^{\,2}}\right)(1 - e^{-a_j\alpha})\right\}\right\} \quad (61)$$

In accordance with the definitions of the number- and weight-average degrees of polymerization, the related expressions are obtained from eq 59–61. The representations for the monomer conversion and reaction time are as follows:

$$Y = \frac{I}{M_0}\left\{\sum_{n=1}^{m-1}n\sum_{j=0}^{n}\frac{\prod_{i=0}^{n-1}a_i e^{-a_j\alpha}}{\prod_{i=0}^{n}{}'(a_i - a_j)} + \sum_{j=0}^{m-1}\prod_{i=0}^{m-1}{}'\frac{a_i}{a_i - a_j}\left[\alpha + \left(m - \frac{1}{a_j}\right)(1 - e^{-a_j\alpha})\right]\right\} \quad (62)$$

and

$$t = \frac{1}{k_p}\int_0^{\alpha} \frac{\mathrm{d}\alpha}{M_0 - \sum\limits_{n=1}^{\infty} nN_n} \tag{63}$$

Equations 58–63 are the universal expressions for the molecular parameters of the living polymer. Recently, Schulz et al. have reported that for the anionic polymerization of MMA using MIB-Li as the initiator in THF at −46 °C, side reactions are absent, and $k_0 = 100$, $k_1 = 32$, $k_2 = 40$, $k_3 = 50$, $k_4 = k_5 = ... = k_p = 70$. For this oligomerization system, the visualized expressions of the molecular weight distribution, the number- and weight-average degrees of polymerization, and the monomer conversion can easily be obtained from eq 54 and 58–62. As an example, we find the heterogeneity index for the oligomer from the reaction conditions, and the results are shown in Figure 5.

It is necessary to point out that the molecular weight of the initiator fragment must be taken into account for the oligomer with very short chains. A little revision may be introduced into the definitions of number- and weight-average molecular weights from Schulz et al.:

$$\bar{M}_{\mathrm{n}} = \frac{N_0W_0 + \sum\limits_{n=1}^{\infty}(W_0 + nW)N_n}{I} \tag{64}$$

$$\bar{M}_{\mathrm{w}} = \frac{N_0W_0^2 + \sum\limits_{n=1}^{\infty}(W_0 + nW)^2N_n}{N_0W_0 + \sum\limits_{n=1}^{\infty}(W_0 + nW)N_n} \tag{65}$$

The differential molecular weight distribution is

$$W(n) = \frac{(W_0 + nW)N_n}{N_0W_0 + \sum\limits_{n=1}^{\infty}(W_0 + nW)N_n}, \quad n = 0, 1, 2, ... \tag{66}$$

where W_0 and W are the respective molecular weights of the initiator fragment and monomer. Schulz et al.[12] have recently given the numerical solutions of eq 1 and 2 for the oligomerization of MMA in THF at −46 °C initiated by MIB-Li or MIB-Na, which conform with the experimental data. We have calculated the molecular weight distribution curves for the same oligomerization systems by eq 66 combined with eq 58 and 60 or eq 48 and its first-order moment; the results are identical with those of Schulz and co-workers. It seems worth mentioning that Szymański[20] has utilized some of the equations of this work to treat successfully his experimental data.

Appendix A

Due to the Cramer rule, eq 8 results in

$$R_n = D_n/D \tag{A1}$$

where

$$D = \begin{vmatrix}
(\lambda + k_0)/I & & & & & & \\
-k_0 & (\lambda + k_1) & & & & 0 & \\
 & -k_1 & (\lambda + k_2) & & & & \\
 & & \ddots & \ddots & & & \\
 & & & -k_{n-2} & (\lambda + k_{n-1}) & & \\
 & & & & -k_{n-1} & (\lambda + k_n) & \\
 & 0 & & & & -k_n & (\lambda + k_{n-1}) \\
 & & & & & \ddots & \ddots
\end{vmatrix} = \frac{1}{I}\prod_{i=0}^{\infty}(\lambda + k_i) \tag{A2}$$

and

$$D_n = \begin{vmatrix}
(\lambda + k_0)/I & & & & & 1 & & \\
-k_0 & (\lambda + k_1) & & & & 0 & & \\
 & -k_1 & (\lambda + k_2) & & & 0 & & \\
 & & \ddots & \ddots & & \vdots & & \\
 & & & -k_{n-2} & (\lambda + k_{n-1}) & \vdots & & \\
 & & & & -k_{n-1} & 0 & & \\
 & & 0 & & & 0 & (\lambda + k_{n+1}) & \\
 & & & & & & -k_{n+1} & (\lambda + k_{n+2}) \\
 & & & & & & \ddots & \ddots
\end{vmatrix} =$$

$$\begin{vmatrix}
(\lambda + k_0)/I & & & & & 1 \\
-k_0 & (\lambda + k_1) & & & & 0 \\
 & -k_1 & (\lambda + k_2) & & & 0 \\
 & & \ddots & \ddots & & \vdots \\
 & & & -k_{n-2} & (\lambda + k_{n-1}) & 0 \\
 & 0 & & & -k_{n-1} & 0
\end{vmatrix} \times$$

$$\begin{vmatrix}
(\lambda + k_{n+1}) & & & 0 \\
-k_{n+1} & (\lambda + k_{n+2}) & & \\
 & -k_{n+2} & (\lambda + k_{n+3}) & \\
 & & \ddots & \ddots \\
0 & & &
\end{vmatrix} = \prod_{i=0}^{n-1} k_i \prod_{i=n+1}^{\infty}(\lambda + k_i) \tag{A3}$$

Therefore

$$R_n = I\frac{\prod\limits_{i=0}^{n-1} k_i}{\prod\limits_{i=0}^{n}(\lambda + k_i)}$$

Appendix B

Let

$$y = 1 - \sum_{i=0}^{n-1}\frac{x^ie^{-x}}{i!} = \sum_{i=n}^{\infty}\frac{x^ie^{-x}}{i!} \tag{B1}$$

$$\frac{\mathrm{d}y}{\mathrm{d}x} = \sum_{i=n}^{\infty}\frac{x^{i-1}e^{-x}}{(i-1)!} - \sum_{i=n}^{\infty}\frac{x^ie^{-x}}{i!} = \frac{x^{n-1}e^{-x}}{(n-1)!} \tag{B2}$$

then

$$y = \int_0^x \frac{x^{n-1}e^{-x}}{(n-1)!}\,\mathrm{d}x = \frac{1}{(n-1)!}\Gamma_x(n) \tag{B3}$$

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Syntheses of Polysilanes with Functional Groups. 2. Polysilanes with Carboxylic Acids

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ABSTRACT: Polysilanes with carboxylic acids were synthesized by the reaction of phenol-linked polysilanes with carboxylic acid anhydrides. Saturated carboxylic acid and the unconjugated double bond were easy to introduce, but the introduction of allyl and conjugated double bonds was not achieved satisfactorily. The introduction of carboxylic acid drastically increased the solubility of the polysilanes to an aqueous basic solution. The unsaturated double bond in the carboxylic moiety reacted when polysilanes were photodecomposed. In this case, molecular scission surpassed the cross-linking which was brought by the reaction of the unsaturated bond. However, the double bond reacted thermally at 170 °C to cause cross-linking. An exothermic reaction occurred drastically at 250 °C. The base solubility depended on the content of carboxylic acid moieties and the molecular weight. The base solubility of the polysilanes increased rapidly under $M_w = 5 \times 10^{-4}$. Lines (0.3 μm) and spaces were fabricated.

Introduction

Various polysilanes which are soluble in organic solvents have been synthesized.[1-10] Most of them have hydrophobic moieties like alkyl or aromatic groups. The authors have been interested in polysilanes with hydrophilic moieties, especially phenol moieties, because (1) there have been no reports on the polymer syntheses and the polymer properties and (2) various functional groups may be substituted by reacting the phenol moieties with other functional molecules. For example, the reaction of the phenol moieties with acid anhydrides, acid chlorides, isocyanates, and alkyl halides produces carboxylic acids, esters, urethanes, and ethers, rather mildly. It was considered an important point whether polysilanes with phenol moieties could be prepared or not, because, usually, polysilanes are synthesized under a vigorous reaction condition, such as in Na dispersion at around 110 °C, and it was thought that the organic functional group may be damaged and/or may inhibit the Wurtz reaction between SiCl and SiCl. Syntheses of chlorosilanes with phenol moieties (monomer) were another important area. Simple silanes substituted with phenol moieties, such as *p*-(triphenylsilyl)phenol and *p*-(trimethylsilyl)phenol, were synthesized from bromophenol, lithium, and triphenylchlorosilane[11] or from [(trimethylsilyl)oxy]chlorobenzene and trimethylsilyl chloride in dispersed Na.[12]

The latter method is probably suitable for the preparation of polysilanes, since the hydrolysis of (trimethylsilyl)oxy groups is rather easy. However, the reaction of phenyltrichlorosilane with [(trimethylsilyl)oxy]phenyl chloride in dispersed Na did not produce [[(trimethylsilyl)oxy]phenyl]phenyldichlorosilane, because the Wultz reaction between phenyltrichlorosilane and another phenyltrichlorosilane is much faster than the reaction between phenyltrichlorosilane and [(trimethylsilyl)oxy]phenyl chloride. The authors found a new route for synthesizing silane monomers substituted with both chloro- and [(trimethylsilyl)oxy]phenyl moieties.[13] The reaction used was the hydrosilylation of methyldichlorosilane and isopropenylphenols, by which the desired silane monomer could be synthesized easily. Polysilanes substituted with phenol moieties could be obtained by using the Wurtz reaction, followed by hydrolysis of the trimethylsilyl group. The (trimethylsilyl)oxy group was a suitable protector for the phenolic moiety. These results have been reported previously.[13]

Our next goal was to synthesize polysilanes containing carboxylic acid groups. Silane monomers substituted with both chloride and $COOSiMe_3$ were difficult or impossible to synthesize by this route, because the hydrosilylation of unsaturated double bonds containing $COOSiMe_3$ with methyldichlorosilane was unsuccessful. The reason was that the Pt catalyst could not effectively coordinate with the unsaturated double bond, presumably due to complexation of the carbonyl group. Furthermore, it seemed likely that even if the monomer could have been synthesized, the polysilane would not have been obtained, because the COO group was labile under polymerization conditions. Therefore, the introduction of carboxylic acid was carried out by the polymer reaction of the phenolic-substituted polysilanes with acid anhydrides.

This paper describes (i) the yield of polysilanes substituted with carboxylic acids, (ii) the dependence of the former on the acid anhydride structure, (iii) the relative photodecomposition rates, and (iv) the dependence of solubility in organic alkaline solutions on molecular weight.

Experimental Section

All experiments were carried out in an argon atmosphere. The solvents were purified and dried by CaH_2 before use.

Synthesis of Methyl[2-[3-[(trimethylsilyl)oxy]phenyl]-propyl]dichlorosilane (M-1). Methyldichlorosilane (200 g) was mixed with trimethylsilylated *m*-isopropenylphenol (200 g), which was prepared by the reaction of *m*-isopropenylphenol with hexamethyldisilazane at room temperature followed by distillation. *m*-Isopropenylphenol was purchased from Mitsui Petroleum Chemical Co. Then 1 g of a Pt complex catalyst, purchased from Toshiba Silicone Co. (not commercially available), was added slowly. A conventional catalyst, H_2PtCl_6, can also be used in this reaction. However, because of the strong acidity of the catalyst,

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