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Effects of Chain Length Dependence of Termination Rate Constant on the Kinetics of Free-Radical Polymerization. 1. Evaluation of an Analytical Expression Relating the Apparent Rate Constant of Termination to the Number-Average Degree of Polymerization

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ABSTRACT: The nonclassical kinetics of low-conversion, free-radical polymerization have been studied. The models adopted assume a termination rate constant for radicals of size m and n given by $k_{t(n,m)} = k_{t0}(nm)^{-a}$. Using the expression for radical population and the rate of production of polymer, a relationship between apparent rate constant of termination $\bar{k}_t$ and average degree of polymerization, $\bar{X}_n$, is found to be $\bar{k}_t$ = (constant)$(\bar{X}_n)^{-2a}$. This relationship is in good agreement with the experimental data obtained in the polymerization of styrene and methyl methacrylate.

Introduction

Deviations of polymerization kinetics from simple systems of rules of free-radical polymerization have mostly been discussed in terms of primary radical termination,[1,2] portion of disproportionation in the termination,[3] variation in the efficiency of initiation,[4] etc. On the other hand, several workers[5–17] remarked that the rate of termination between polymer radicals is not always independent of their chain length; e.g., in a recent series of papers[10–15] it has been pointed out that the termination rate constant in free-radical polymerization, k_t, is a decreasing function of the size of reacting radicals (k_t is a decreasing function of the chain length and the linear expansion coefficient). The polymerization kinetics may also be influenced by the chain length dependence of termination rates between polymer radicals. Conventional methods for the kinetic study of radical polymerization are shown to lead to erroneous conclusions if the effect of the chain length dependence of termination rate constants is not taken into account.[16,18,19]

These studies clearly show that a command of the complete solution of a "nonclassical" kinetic scheme, i.e., a kinetic scheme which involves a chain length dependent termination rate constant, would be a very useful idea. To much greater accuracy, the above-mentioned effects could be analyzed. In addition, all further predictions of this scheme could be easily put to test by comparison with the appropriate basic experimental data.

The complete solution to a nonclassical kinetic scheme requires not only an appropriate analytical function relating the chain length of two reacting radical chains to the termination rate constant, but also a procedure which provides the solution of the system of equations resulting from the introduction of this analytical function so that finally the desired relationships between the various characteristic quantities of the kinetics are obtained.

A number of models exist which give a functional dependence of termination rate constant, k_t, on the chain length of two reacting radical chains.[9–11,17,20] These models can be simplified to the relationship

$$k_{t(n,m)} = k_{t0}(nm)^{-a} \tag{1}$$

where $k_{t(n,m)}$ is the specific rate constant of termination between two radicals of size n and m and k_{t0} is a constant. In this work an attempt to solve the nonclassical kinetic scheme was made by using eq 1. A relationship between the apparent rate constant of termination and the average degree of polymerization was found. In a subsequent communication the analytical relationships between other characteristic quantities of the kinetic scheme will be presented.

Kinetic Analysis

The mechanism of polymerization to be considered consists of chemical initiation by first-order decomposition of initiator to produce radical with chain length unity, first-order propagation with respect to monomer, and chain transfer to produce a dead polymer. Second-order terminations by disproportionation and/or combination are taken into account. The kinetic mechanism may be represented as

initiation $\quad I \xrightarrow{k_d} 2R^\circ$

$$R^\circ + M \xrightarrow{k_i} P_1^\circ$$

propagation $\quad P_n^\circ + M \xrightarrow{k_p} P_{n+1}^\circ$

chain transfer $\quad P_n^\circ + Y \xrightarrow{k_{tr,y}} P_n + Y^\circ$

termination

by disproportionation $\quad P_n^\circ + P_m^\circ \xrightarrow{k_{td(n,m)}} P_n + P_m$

by combination $\quad P_n^\circ + P_m^\circ \xrightarrow{k_{tc(n,m)}} P_{n+m}$

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where R° is a primary radical, and $P_n°$ and P_n represent a growing radical and a dead polymer molecule having n monomeric units, respectively. Y is a chain-transfer agent such as monomer (M), initiator (I), or other deliberately added materials. k_p, $k_{tr,y}$, and k_d are respectively the rate constants of propagation, chain transfer, and initiator decomposition. They are assumed to be independent of chain size, while $k_{tc(n,m)}$ and $k_{td(n,m)}$, the termination rate constant of combination and disproportionation, are chain length dependent.

From material balance, the following set of equations is obtained

$$d[M]/dt = -k_p[M][P^0] \quad (2)$$

$$d[I]/dt = -k_d[I] \quad (3)$$

$$d[R^0]/dt = 2fk_d[I] - k_i[M][R^0] \quad (4)$$

$$d[P_1°]/dt = k_i[R°][M] - k_p[M](1 + 1/\nu_1)[P_1°] \quad (5)$$

$$d[P_n°]/dt = k_p[M][P_{n-1}°] - k_p[M](1 + 1/\nu_n)[P_n°] \quad (6)$$

$$d[P_n]/dt = k_{tr,y}[P_n°][Y] + \frac{\epsilon}{1+\epsilon}\sum_{m=1}^{\infty} k_{t(n,m)}[P_n°][P_m°] + \frac{1}{2+2\epsilon}\sum_{m=1}^{n-1} k_{t(m,n-m)}[P_m°][P_{n-m}°] \quad (7)$$

where

$$\frac{1}{\nu_n} = \sum_{m=1}^{\infty} k_{t(n,m)}\frac{[P_m°]}{k_p[M]} + C_y\frac{[Y]}{[M]} \quad (8)$$

$$C_y = k_{tr,y}/k_p \quad (9)$$

$$\epsilon = k_{td}/k_{tc} \quad (10)$$

Applying stationary-state kinetics to this scheme for individual radicals yields

$$[R°] = 2fk_d[I]/k_i[M] \quad (11)$$

$$[P_1°] = \xi_1 k_1[R°]/k_p \quad (12)$$

$$[P_n°] = \xi_n[P_{n-1}°] \quad (13)$$

where

$$\xi_n = 1/(1 + 1/\nu_n) \quad (13a)$$

The solution to the difference equation (13) with respect to the initial conditions (11) and (12) is (the detailed calculations are given in the Appendix)

$$[P_n°] = \frac{2fk_d[I]}{k_p[M]}\exp\left(\frac{-r_t}{1-a}n^{1-a} - r_{tr}n\right) \quad (14)$$

where r_t and r_{tr} (eq 6a and 7a) can be considered as the contributions of polymer–polymer termination and that of chain-transfer reaction to the kinetic chain length, respectively.

If one substitutes $[P_n°]$ from eq 14 to eq 7, the rate of production of dead polymer with size n can be written as (the detailed calculations are given in the Appendix)

$$\Delta_{(n)} = d[P_n]/dt = (2fk_d[I])\frac{r_{tr} + \frac{\epsilon}{1+\epsilon}r_t n^{-a} + \frac{1.733(1-a)k_{t0}(2kf_d[I])n^{1-2a}}{(2+2\epsilon)k_p^2[M]^2}}{\exp\left(\frac{r_t n^{1-a}}{1-a} + r_{tr}n\right)} \quad (15)$$

Equations 14 and 15 can be used to obtain relationships between characteristic quantities of the nonclassic kinetic scheme. However, the aim of this work is the calculation of the relationship between the apparent rate constant of termination, $\bar{k}_t$, and the number-average degree of polymerization, $\bar{X}_n$.

The apparent rate constant of termination, which is the average rate constant for reaction between all possible pairs of radicals existing in the radical population, can be expressed by

$$\bar{k}_t = \sum_n\sum_m k_{t(n,m)}[P_n°][P_m°]/[P°]^2 \quad (16)$$

where

$$[P°] = \sum_n [P_n°]$$

Substituting for $[P_n°]$ from eq 14 yields

$$\bar{k}_t = k_{t0}\theta^2 \quad (17)$$

where

$$\theta = \int_0^{\infty} n^{-a}\frac{[P_n°]}{[P°]}\,dn$$

The number-average degree of polymerization at low conversion can be written as

$$\bar{X}_n = \frac{\int_0^{\infty} n\Delta_{(n)}\,dn}{\int_0^{\infty}\Delta_{(n)}\,dn} \quad (18)$$

Equations 17 and 18 are solved for the following cases.

1. Predominance of Transfer: $r_{tr} \gg r_t$. When the production of polymer is mainly by transfer, i.e., $r_{tr} \gg r_t$, the term r_t in eq 14 and 15 can be neglected

$$[P_n°] = \frac{2fk_d[I]}{k_p[M]}\exp(-r_{tr}n) \quad (19)$$

$$\Delta_{(n)} = 2fk_d[I][r_{tr}\exp(-r_{tr}n)] \quad (20)$$

and eq 17 and 18 can be simplified to the following equations:

$$\bar{k}_t = k_{t0}[r_{tr}{}^a\Gamma(1-a)]^2 \quad (21)$$

$$\bar{X}_n = \frac{1}{r_{tr}} \qquad r_{tr} = C_y\frac{[Y]}{[M]} \quad (22)$$

or

$$\bar{k}_t = k_{t0}\Gamma^2(1-a)\bar{X}_n^{-2a} \quad (23)$$

Equation 23 gives the relationship between the apparent rate constant of termination and the average degree of polymerization in the case of predominance of transfer.

2. Nontransfer: $r_t \gg r_{tr}$. When the production of polymer is mainly by polymer–polymer termination, i.e., $r_t \gg r_{tr}$, the effect of transfer reactions can be neglected ($r_{tr} \simeq 0.0$). Then eq 14 and 15 can be simplified to the following equations:

$$[P_n°] = \frac{2fk_d[I]}{k_p[M]}\exp\left(\frac{-r_t}{1-a}n^{1-a}\right) \quad (24)$$

$$\Delta_{(n)} = 2fk_d[I]\left[\frac{\epsilon r_t}{1+\epsilon} + \frac{1.733(1-a)k_{t0}(2fk_d[I])n^{1-a}}{(2+2\epsilon)k_p^2[M]^2}\right]n^{-a}\exp\left(\frac{-r_t}{1-a}n^{1-a}\right) \quad (25)$$

Then eq 17 and 18 can be represented as

$$\bar{k}_t = k_{t0}\left[\frac{(r_t/(1-a))^{a/(1-a)}}{\Gamma\left(\frac{1}{1-a}\right)}\right]^2 \tag{26}$$

$$\bar{X}_n = \left(\frac{r_t}{1-a}\right)^{-1/(1-a)} \times \left[\frac{2\epsilon\Gamma\left(\frac{2-a}{1-a}\right) + 1.733(1-a)^2\Gamma\left(\frac{3-2a}{1-a}\right)}{2\epsilon + 1.733(1-a)^2}\right] \tag{27}$$

where r_t is given by

$$r_t = [(2fk_d[I])k_{t0}]^{1/2}/k_p[M] \tag{28}$$

Equations 27 and 26 can be written as

$$\bar{k}_t = k_{t0}\left[\Gamma\left(\frac{1}{1-a}\right)\right]^{2a-2}\left[\frac{2\epsilon + 3.466(1-a)^2}{2\epsilon + 1.733(1-a)^2}\right]^{2a}[\bar{X}_n]^{-2a} \tag{29}$$

When termination is only by disproportionation ($\epsilon = \infty$), eq 29 can be written as

$$\bar{k}_t = k_{t0}\left[\Gamma\left(\frac{1}{1-a}\right)^{2a-2}\right][\bar{X}_n]^{-2a} \tag{29a}$$

If termination is only by combination ($\epsilon = 0.0$), then eq 29 can be simplified to

$$\bar{k}_t = k_{t0}\left[4^a\Gamma\left(\frac{1}{1-a}\right)^{2a-2}\right][\bar{X}_n]^{-2a} \tag{29b}$$

Equation 29 gives the relationship between $\bar{k}_t$ and $\bar{X}_n$ in the case of negligible chain-transfer reaction.

3. Termination and Transfer Competition: $r_t \simeq r_{tr}$. To find the relationship between $\bar{k}_t$ and $\bar{X}_n$ in a case in which termination and chain-transfer reactions were in competition, i.e., $r_t \simeq r_{tr}$, eq 14–18 were solved numerically by using required kinetic constants and parameters. It was found that, independent of kinetic rate constants and parameters, the functional dependency of $\bar{k}_t$ on $\bar{X}_n$ can be written as

$$\bar{k}_t = k_{t0}\gamma_{(a)}(\bar{X}_n)^{-2a} \tag{30}$$

where $\gamma_{(a)}$ is a parameter depending on a.

Figure 1 shows the result of numerical solution of eq 17 and 18 for bulk polymerization of styrene at 60 °C. In this case, chain transfer to monomer was competing with termination. It is clear that the log–log plot of $\bar{k}_t$ vs. $\bar{X}_n$ is linear with a slope of $-2a$. $\gamma(a)$ increases from 1 to 1.2 when a is raised from 0.0 to 0.15. Equations 23, 29, and 30 give the relationship between $\bar{k}_t$ and $\bar{X}_n$ for the nonclassical scheme of low-conversion, free-radical polymerization. This relationship can be represented in the general form

$$\bar{k}_t/k_{t0} = \gamma_{(a)}(\bar{X}_n)^{-2a} \tag{31}$$

where $\gamma_{(a)}$ for a given polymerization system is only a function of a. $\gamma_{(a)}$ for different polymerization conditions and various values of a are given in Table I. It is clear that for $a < 0.2$ the values of γ are less than 1.5.

The chain length dependence of the termination reaction can be represented by eq 1 or 31. The advantage of eq 31 is that both $\bar{k}_t$ and $\bar{X}_n$ can be obtained experimentally and therefore the chain length dependence of k_t could be easily put to test utilizing this equation. $\bar{k}_t$ can be obtained by using the rotating sector technique or the SIP (spacial intermittent polymerization) reactor.[14,15] As an example the experimental data obtained by using the SIP reactor[14,15] for styrene and methyl methacrylate (MMA) polymerization are used. Log–log plots of $(\bar{k}_t)_{exptl}$ vs. $(\bar{X}_n)_{exptl}$ for styrene and MMA are shown in Figures 2 and 3. It is clear that log $(\bar{k}_t)_{exptl}$ vs. log $(\bar{X}_n)_{exptl}$ for both monomers are linear. The least-squares analysis of these data yields

$$\bar{k}_t = 1.31 \times 10^8(\bar{X}_n)^{-0.15} \quad \text{MMA/25 °C}$$

$$\bar{k}_t = 2.6 \times 10^8(\bar{X}_n)^{-0.24} \quad \text{styrene/30 °C}$$

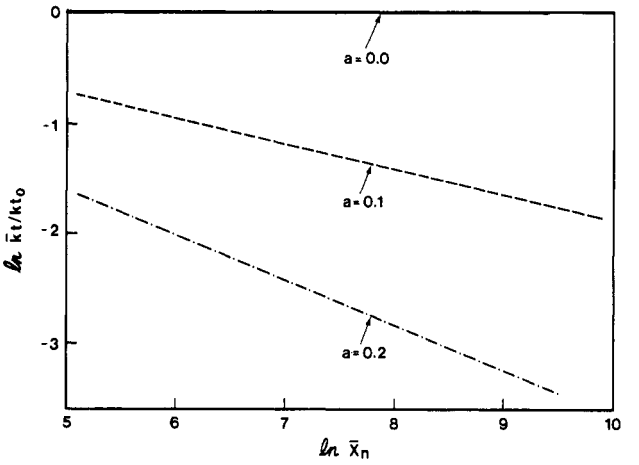

Figure 1. $\ln \bar{k}_t/k_{t0}$ vs. $\ln \bar{X}_n$ for bulk polymerization of styrene at 60 °C. Lines: numerical solution of eq 17 and 18 with $10^{-5} \le r_t \le 10^{-2}$ and $10^{-5} \le r_{tr} \le 10^{-3}$.

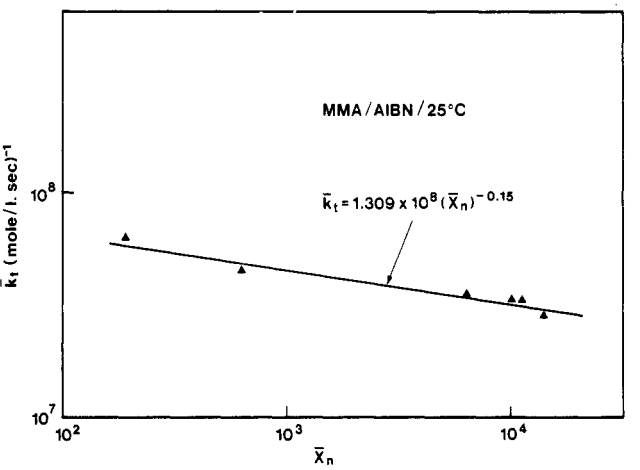

Figure 2. $\bar{k}_t$ vs. $\bar{X}_n$ for bulk polymerization of MMA at 25 °C.

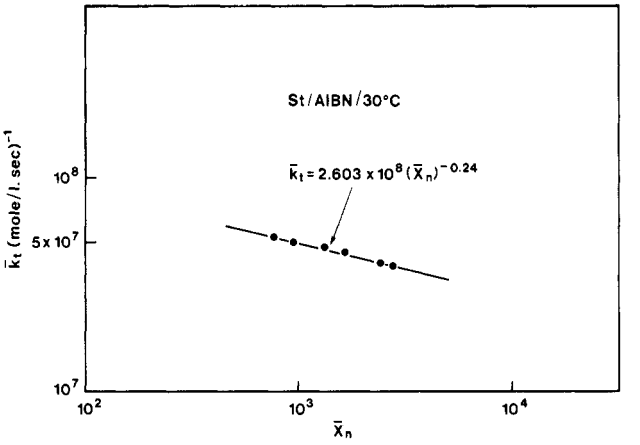

Figure 3. $\bar{k}_t$ vs. $\bar{X}_n$ for bulk polymerization of styrene at 30 °C.

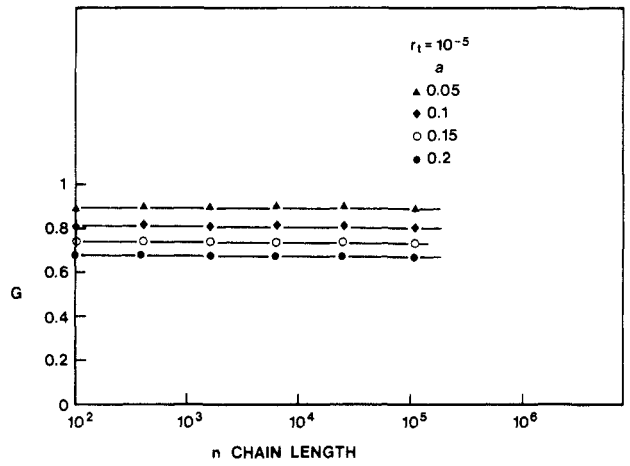

Figure 4. G vs. n for $r_t = 10^{-5}$.

These relationships can be compared with eq 31 to estimate a and k_{t0}. It was assumed that termination is by disproportionation to MMA polymerization and by combination for styrene polymerization. Chain transfer to monomer was neglected for bulk polymerization of both monomers at such a low temperature. Considering these conditions and using Table I, $\gamma_{(a)}$ and then k_{t0} were estimated. Substitution of the estimated k_{t0} and a in eq 1 yields

$$k_{t(n,m)} = 1.22 \times 10^8 (nm)^{-0.075} \qquad \text{MMA/25 °C}$$

$$k_{t(n,m)} = 1.97 \times 10^8 (nm)^{-0.12} \qquad \text{styrene/30 °C}$$

Equation 31 can also be used to predict the effect of chain length dependence of k_t on the rate of polymerization and average molecular weight of polymer. This can be done by substituting eq 31 for k_t in the classical expressions for rate and average degree of polymerization.[21,22]

Conclusion

The complete solution of the nonclassical kinetic scheme of low-conversion, free-radical polymerization, recognizing the chain length dependence of k_t, has been carried out. A relationship between apparent rate constant of termination and average degree of polymerization was found. This relationship was tested against experimental data for styrene and methyl methacrylate polymerizations.

Appendix

Difference equation (13) can be written as

$$[P_n^\circ] = (2fk_d[I]/k_p[M])\prod_{i=1}^{n}\xi_i \tag{1A}$$

or

$$\ln [P_n^\circ] = \ln (2fk_d[I]/k_p[M]) + \sum_{i=1}^{n} \ln \xi_i \tag{2A}$$

Since ξ_i is close to, but less than, unity, $\ln \xi_i$ may be approximated by $1-\xi_i/\xi_e = -1/\nu_i$ and then eq 2A can be replaced by

$$\ln [P_n^\circ] = \ln (2fk_d[I]/k_p[M]) - \sum_{i=1}^{n}(1/\nu_i) \tag{3A}$$

Substituting $1/\nu_i$ from eq 8 and assuming long-chain approximation, eq 3A can be written as

$$\ln [P_n^\circ] = \ln (2fk_d[I]/k_p[M]) - \left(\int_0^n r_t n^{-a}\, dn + \int_0^n r_{tr}\, dn\right) \tag{4A}$$

or

$$[P_n^\circ] = \frac{2fk_d[I]}{k_p[M]} \exp\left(\frac{-r_t}{1-a}n^{1-a} - r_{tr}n\right) \tag{5A}$$

where

$$r_t = (k_{t0}[P^\circ]/k_p[M])\theta \tag{6A}$$

$$r_{tr} = C_y[Y]/[M] \tag{7A}$$

and θ is a parameter independent of n given by

$$\theta = \frac{\int_0^\infty n^{-a}[P_n^\circ]\, dn}{[P^\circ]} = \frac{\int_0^\infty n^{-a} \exp\left(\frac{-r_t}{1-a}n^{1-a} - r_{tr}n\right) dn}{\int_0^\infty \exp\left(\frac{-r_t}{1-a}n^{1-a} - r_{tr}n\right) dn} \tag{6A^1}$$

Using long-chain approximation, eq 7 can be written as

$$\frac{d[P_n]}{dt} = k_p[M][P_n^\circ] \times \left\{C_y\frac{[Y]}{[M]} + \frac{\epsilon}{1+\epsilon}\int_0^\infty \frac{k_{t0}n^{-a}m^{-a}[P_m^\circ]}{k_p[M]}\, dm + \frac{1}{2+2\epsilon}\int_1^{n-1} \frac{k_{t0}m^{-a}(n-m)^{-a}[P_m^\circ][P_{n-m}^\circ]}{k_p[M][P_n^\circ]}\, dm\right\} \tag{8A}$$

or

$$\frac{d[P_n]}{dt} = k_p[M][P_n^\circ]\left\{r_{tr} + \frac{\epsilon}{1+\epsilon}\frac{k_{t0}n^{-a}}{k_p[M]}\int_0^\infty m^{-a}[P_m^\circ]\, dm + \frac{1}{2+2\epsilon}\frac{k_{t0}}{k_p[M][P_n^\circ]}\int_1^{n-1} m^{-a}(n-m)^{-a}[P_m^\circ][P_{n-m}^\circ]\, dm\right\} \tag{9A}$$

Substituting $[P_m^\circ]$ and $[P_{n-m}^\circ]$ from eq 5A yields

$$\frac{d[P_n]}{dt} = k_p[M][P_n^\circ]\left\{r_{tr} + \frac{\epsilon}{1+\epsilon}r_t n^{-a} + \frac{1}{2+2\epsilon}\frac{k_{t0}(2fk_d[I])}{\exp\left(\frac{-r_t}{1-a}n^{1-a}\right)k_p^2[M]}\int_1^{n-1} m^{-a}(n-m)^{-a}\exp\left(\frac{-r_t}{1-a}[(m)^{1-a} + (n-m)^{1-a}]\right) dm\right\} \tag{10A}$$

Assuming

$$\phi_n = \int_1^{n-1} m^{-a}(n-m)^{-a}\exp\left(\frac{-r_t}{1-a}[(m)^{1-a} + (n-m)^{1-a}]\right) dm \tag{11A}$$

and substituting $m = ny$[11]

$$\phi_n = n^{1-2a}\int_{1/n}^{1-(1/n)} y^{-a}(1-y)^{-a} \times \exp\left(\frac{-r_t}{1-a}n^{1-a}[y^{1-a} + (1-y)^{1-a}]\right) dy \tag{12A}$$

Table I
Functional Dependence of γ on a

polymerization	γ	$\gamma_{a=0.0}$	$\gamma_{a=0.1}$	$\gamma_{a=0.2}$
predominance of transfer	$\Gamma^2(1-a)$	1	1.14	1.35
nontransfer	$\left[\Gamma\left(\frac{1}{1-a}\right)\right]^{2a-2}\left[\frac{2\epsilon + 3.466(1-a)^2}{2\epsilon + 1.733(1-a)^2}\right]^{2a}$	1		
termination by combination ($\epsilon = 0.0$)	$\left[\Gamma\left(\frac{1}{1-a}\right)\right]^{2a-2}(4)^{a}$	1	1.26	1.55
50% termination by combination ($\epsilon = 1.0$)	$\left[\Gamma\left(\frac{1}{1-a}\right)\right]^{2a-2}\left[\frac{2 + 3.466(1-a)^2}{2 + 1.733(1-a)^2}\right]^{2a}$	1	1.18	1.32
termination by disproportionation ($\epsilon = \infty$)	$\left[\Gamma\left(\frac{1}{1-a}\right)\right]^{2a-2}$	1	1.10	1.17

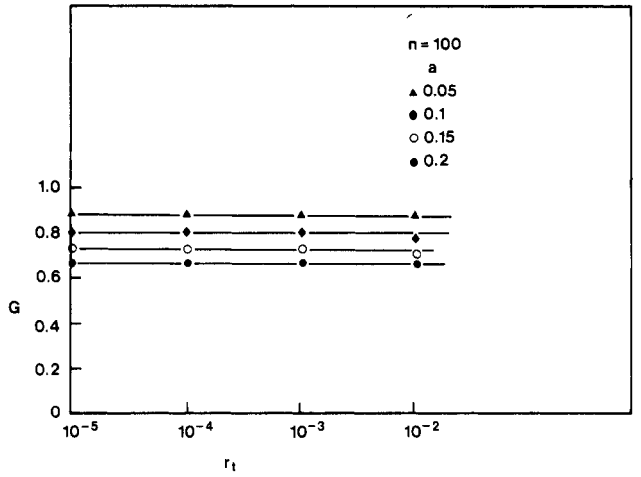

Figure 5. G vs. r_1 for $n = 100$.

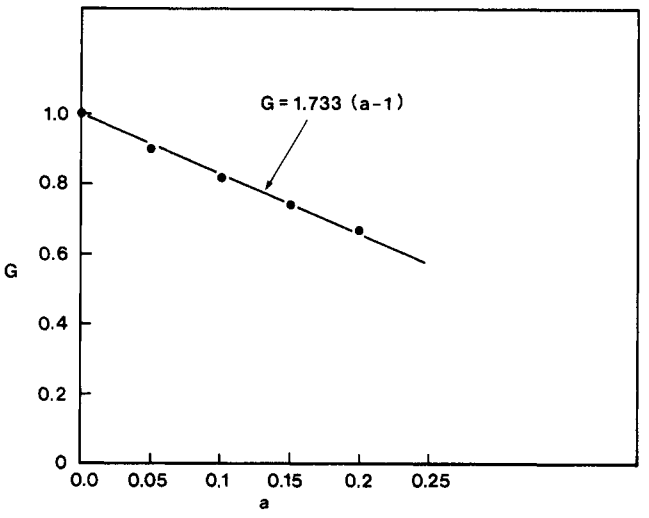

Figure 6. G vs. a: (●) calculated, (solid line) best fit.

Numerical integration of eq 12A was carried out by using $10^{-5} \leq r_t \leq 10^{-2}$ and $10^2 \leq n \leq 10^5$. It was found that eq 12A can be simplified to

$$\phi_n = Gn^{1-2a}\exp\left(\frac{-r_t}{1-a}n^{1-a}\right) \qquad (13A)$$

where G is a parameter depending on a. The parameter G was calculated by comparing the results of numerical integration of eq 12A with eq 13A. The results are reported in Figures 4 and 5. It is clear that G is independent of n and r_t and that G is a decreasing function of a.

The dependency of G on a as shown in Figure 6 can be written as

$$G = 1.733(a-1) \qquad (14A)$$

Substituting eq 13A to eq 10A yields

$$\frac{d[P_n]}{dt} = (2fk_d[I])\left[\exp\left(\frac{-r_t}{1-a}n^{1-a} - r_{tr}n\right)\right] \times \left[r_{tr} + \frac{\epsilon}{1+\epsilon}r_t n^{-a} + \frac{1.733(a-1)k_{t0}(2kf_d[I])}{(2+2\epsilon)(k_p^2[M]^2)}n^{1-2a}\right] \qquad (15A)$$

Registry No. MMA, 80-62-6; styrene, 100-42-5.

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Stereocontrolled Polymerization of Acrylic Monomers within a Tris(*o*-phenylenedioxy)cyclotriphosphazene Tunnel Clathrate

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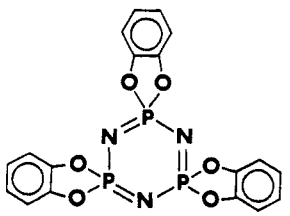
ABSTRACT: The ^{60}Co γ-ray-initiated polymerization of acrylic monomers (acrylic acid, acrylic anhydride, acrylonitrile, methyl acrylate, methyl methacrylate, methyl vinyl ketone) within the tunnel-clathrate system formed by tris(*o*-phenylenedioxy)cyclotriphosphazene (I) provides a general route to the synthesis of enhanced stereoregular polymers. A feature of the clathrate-mediated polymerization is that no radiation cross-linking of multifunctional monomers occurs, in contrast to some of the bulk polymerizations. For example, the clathrate polymerization of acrylic anhydride yielded a new linear polymer, whereas the analogous bulk polymerization gave a cross-linked matrix. The molecular weights of the clathrate-synthesized polymers were similar to those of polymers prepared in the bulk phase. Copolymers were also prepared within host I, and these were found to have a random sequence distribution, in contrast to copolymers prepared in the bulk phase.

Introduction

The synthesis of polymers with precisely controlled structures is one of the main challenges confronting modern chemists. Ziegler–Natta, other coordination systems, anionic, or group-transfer methods are appropriate for the controlled synthesis of a few polymers, but a wide variety of unsaturated monomers have not yet been converted to polymers that have a precisely defined structure and stereo character. Acrylic and other polar monomers are often the most difficult to polymerize in a stereospecific manner.[1-9]. Di- or multifunctional unsaturated monomers present special problems because of the possibilities for cross-linking.

Our objective was to develop a method by which acrylic monomers could be polymerized in a stereoregular fashion. We have previously reported the inclusion of a variety of molecules within the tunnels of a clathrate system derived from tris(*o*-phenylenedioxy)cyclotriphosphazene (I).[10-17]

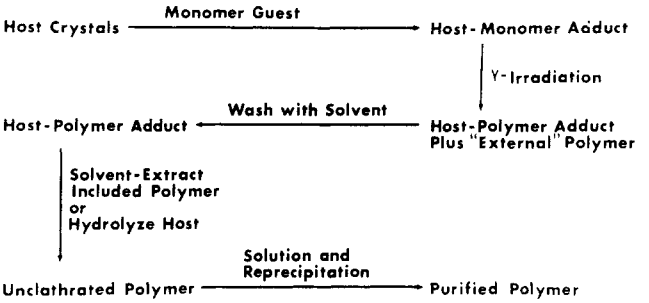


I

In this system the guest molecules are packed in 5 Å diameter tunnels that penetrate the host crystal structure (Figure 1). The constraints of the tunnel shape and dimensions allow a regular stacking of some guest molecules within the tunnels in a manner appropriate for ^{60}Co γ-radiation-induced polymerization.[16,18]

Spirocyclotriphosphazene clathrates have a distinct advantage over other inclusion systems in the sense that the tunnel diameter can be varied by alterations in the size of the spiro side groups.[10] This permits an unusually wide range of guest molecules to be incorporated into the clathrate. Other host systems, such as urea or thiourea, are much less versatile and are appropriate for the clathrate polymerization of fewer guests.[19] Perhydrotriphenylene clathrates a variety of acrylic monomers, but the tendency for stereoregular polymerization is low.[20]

Scheme I



In this paper we describe the stereospecific polymerization of acrylic acid, acrylic anhydride, acrylonitrile, methyl acrylate, methyl methacrylate, and methyl vinyl ketone, as well as some copolymerizations using combinations of those monomers. All these reactions make use of host system I as a solid-state template.

Experimental Section

Overall Experimental Approach. The methodology followed in the present work is summarized in Scheme I. First, the monomer molecules were absorbed by direct imbibition of the liquid guest into the crystal framework of the pure host. After saturation of the host tunnel system, excess monomer was removed in vacuo. Polymerization of the clathrated guest molecules was then induced by ^{60}Co γ-irradiation. Low temperatures were used when possible in order to favor stereoregular propagation. After irradiation, unreacted monomer was removed in vacuo, and any polymer present on the outer crystal surfaces was removed by washing. Finally, the included polymer was solvent extracted from the host in a one- or two-phase solvent system, or the host molecules were decomposed by hydrolysis. The resultant polymers were characterized by ^{13}C NMR spectroscopy. Elemental microanalysis data were also obtained for the copolymers. Molecular weights were estimated by solution viscometry. The exact yields for the clathrate-mediated polymerizations were difficult to estimate because the degree of occupancy of monomer within the host framework was variable from experiment to experiment. However, yields of 20–50% were typical.

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