Effect of Chain-Length Dependence of Termination Rate Constant on the Kinetics of Free-Radical Polymerization. 2. Evaluation of an Analytical Expression for the Rate of Polymerization

Hadi-Khan Mahabadi

Xerox Research Centre of Canada, 2660 Speakman Drive,
Mississauga, Ontario, L5K 2L1 Canada

Received April 18, 1990; Revised Manuscript Received July 10, 1990

ABSTRACT: The nonclassical kinetics of low-conversion, free-radical polymerization have been studied. The model adopted assumes a termination rate constant for radicals of size m and n given by $k_{t(n,m)} = k_{t_0}(nm)^{-a}$. When this chain-length dependency for the termination rate constant was used, a simple analytical expression for the rate of nonclassical free-radical polymerization, R_p, is found to be R_p = (Constant)[M][I]$^{0.5}(\bar{X}_n)^a\eta^{0.5}$, where [M] and [I] are monomer and initiator concentrations, $\bar{X}_n$ is the number-average degree of polymerization, and η is the viscosity of medium. This expression was compared and found to be in good agreement with experimental data obtained in the polymerization of several monomers.

Introduction

Deviation of polymerization rate from the simple rate expression of free-radical polymerization

$$R_p = (2fk_dk_p^2/k_t)^{0.5}[\mathrm{M}][\mathrm{I}]^{0.5} \tag{1}$$

have mostly been discussed in terms of primary radical termination,[1,3] a portion of combination or disproportionation in the termination,[4,5] variation in the efficiency of initiation,[6] etc. On the other hand, several workers[7-19] remarked that the rate of termination between polymer radicals, k_t, is not always independent of their chain length. In a recent series of papers,[12-17] a theoretical treatment of k_t has been presented and tested against experimental data. It has been shown that k_t can be written as a product of two functions

$$k_{t(n,m)} = F_1(\zeta,T)\,F_2(n,m) \tag{2}$$

where F_1 is a function only of temperature and the segmental friction coefficient, ζ, and is given by

$$F_1 = \frac{10^{-2}T}{3N_0r\eta} \tag{3}$$

where r is the hydrodynamic radius of a monomeric unit in a segment, η is solvent viscosity, and N_0 is the number of monomeric units in a segment. F_2 is a complex function of n and m, the sizes of reacting radicals, and can be approximated to[11-14,19-22]

$$F_2 = C(nm)^{-a} \tag{4}$$

where C is a constant.

Substitution of eqs 3 and 4 in eq 2 yields

$$k_{t(n,m)} = k_{t_0}(nm)^{-a} \tag{5}$$

$$k_{t_0} = \frac{10^{-2}CT}{rN_0\eta} \tag{5a}$$

where $k_{t(n,m)}$ is the specific rate constant of termination between two radicals of size n and m.

The polymerization rate may also be influenced by the chain-length dependence of k_t as given by eq 5. Conventional methods for kinetic study of free-radical polymerization are shown to lead the erroneous conclusion if the effect of the chain-length dependence of termination on the rate of polymerization is not taken into account.[3,18,23] These studies clearly show that there is a need for the complete solution of a kinetic scheme including chain-length dependence of k_t, which leads to a simple analytical expression for rate of polymerization. Such an expression can be used to analyze the above-mentioned effects with greater accuracy. In addition, the rate of polymerization predicted by this scheme could be easily put to the test by comparison with the appropriate basic experimental data. It is the purpose of this work to provide a simple and utilitarian expression for the rate of nonclassical free-radical polymerization.

Kinetic Analysis

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

initiation

$$\mathrm{I} \xrightarrow{k_d} 2\mathrm{R}^0$$

$$\mathrm{R}^0 + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1{}^0$$

propagation

$$\mathrm{P}_n{}^0 + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}{}^0$$

chain transfer

$$\mathrm{P}_n{}^0 + \mathrm{Y} \xrightarrow{k_{tr,y}} \mathrm{P}_n + \mathrm{Y}^0$$

termination by disproportionation

$$\mathrm{P}_n{}^0 + \mathrm{P}_m{}^0 \xrightarrow{k_{td(n,m)}} \mathrm{P}_n + \mathrm{P}_n$$

termination by combination

$$\mathrm{P}_n{}^0 + \mathrm{P}_m{}^0 \xrightarrow{k_{tc(n,m)}} \mathrm{P}_{n+m}$$

where R^0 is a primary radical and $\mathrm{P}_n{}^0$ 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 constant of propagation, chain transfer, and initiator

0024-9297/91/2224-0606$02.50/0

Table I
Functional Dependence of γ on a

polymerizn	$\gamma(a)$	γ for $a = 0.1$	γ for $a = 0.2$
(1) predominance of transfer	$r^2(1-a)$	1.14	1.36
(2) nontransfer	$\left[r\left(\frac{1}{1-a}\right)\right]^{2a-2}\left[\left(\frac{2\epsilon + 1.733(2-a)(1-a)}{2\epsilon + 1.733(1-a)^2}\right)\left(\frac{1}{1-a}\right)\right]^{2a}$		
termn by combination ($\epsilon = 0.0$)	$\left[r\left(\frac{1}{1-a}\right)\right]^{2a-2}\left[\frac{2-a}{(1-a)^2}\right]^{2a}$	1.31	1.66
termn by disproportion ($\epsilon = \infty$)	$\left[r\left(\frac{1}{1-a}\right)\right]^{2a-2}\left[\frac{1}{1-a}\right]^{2a}$	1.12	1.20

decomposition. They are assumed to be independent of chain size, while $k_{\mathrm{tc}(n,m)}$ and $k_{\mathrm{td}(n,m)}$, the termination rate constant of combination and disproportionation, are chain-length dependent.

When stationary-state kinetics are applied to this scheme for individual radicals, the concentration of the growing radical of size n can be expressed by[25]

$$[\mathrm{P}_n{}^0] = \frac{2fk_\mathrm{d}[\mathrm{I}]}{k_\mathrm{p}[\mathrm{M}]}\exp\left(\frac{-r_\mathrm{t}}{1-a}n^{1-a} - r_\mathrm{tr}n\right)$$

$$r_\mathrm{t} = k_{\mathrm{t}_0}[\mathrm{P}^0]^2/(k_\mathrm{p}[\mathrm{M}]) \int_0^\infty z^{-a}[\mathrm{P}_z{}^0]\,\mathrm{d}z \text{ and } r_\mathrm{tr} = C_\mathrm{y}[\mathrm{Y}]/[\mathrm{M}] \quad (6)$$

where r_t and r_tr can be considered as the contributions of polymer–polymer termination and of chain-transfer reaction to the overall termination reaction, respectively.[25] Equation 6 can be used to obtain an expression for the rate of nonclassical free-radical polymerization

$$R_\mathrm{p} = k_\mathrm{p}[\mathrm{M}]\sum_{n=1}^{\infty}[\mathrm{P}_n{}^0] = 2fk_\mathrm{d}[\mathrm{I}]\sum_{n=1}^{\infty}\exp\left(\frac{-r_\mathrm{t}}{1-a}n^{1-a} - r_\mathrm{tr}n\right) \quad (7\mathrm{a})$$

Assuming long-chain approximation, eq 7a can be written as

$$R_\mathrm{p} = 2fk_\mathrm{d}[\mathrm{I}]\sum_{0}^{\infty}\exp\left(\frac{-r_\mathrm{t}}{1-a}z^{1-a} - r_\mathrm{tr}z\right)\mathrm{d}z \quad (7\mathrm{b})$$

To find the relationship between R_p and kinetic parameters and rate constants, eq 7b should be solved numerically. However, the aim of this work is to obtain a simple analytical rate expression, which can be achieved by using the apparent rate constant of termination, $\bar{k}_\mathrm{t}$.

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

$$\bar{k}_\mathrm{t} = \sum_n\sum_m k_{\mathrm{t}(n,m)}[\mathrm{P}_n{}^0][\mathrm{P}_m{}^0]/[\mathrm{P}^0]^2 \quad (8)$$

where

$$[\mathrm{P}^0] = \sum_n[\mathrm{P}_n{}^0]$$

Substitution for $k_{\mathrm{t}(n,m)}$ from eq 5 and for $[\mathrm{P}_n{}^0]$ from eq 6 results in a relationship between $\bar{k}_\mathrm{t}$ and kinetic parameters. In a recent paper[25] it has been pointed out that, independent of kinetic rate constants and parameters, this relationship can be written as

$$\bar{k}_\mathrm{t} = k_{\mathrm{t}(0)}\gamma(a)(\bar{X}_\mathrm{n})^{-2a} \quad (9)$$

where $\bar{X}_\mathrm{n}$ is the number-average degree of polymerization and $\gamma(a)$ for a given polymerization system is only a function of "a". Since the functional dependency of $\gamma(a)$ as reported in a previous paper[25] contained an error, the corrected version is given here in Table I.

Considering the dependency of k_{t_0} on medium viscosity (eq 5), eq 9 can be rearranged to

$$\bar{k}_\mathrm{t} = \frac{k_\mathrm{t}{}^*}{\eta}(\bar{X}_\mathrm{n})^{-2a} \quad (9\mathrm{a})$$

where $k_\mathrm{t}{}^* = k_{\mathrm{t}_0}\eta\gamma(a)$ is a constant.

Substituting eq 9a in the equation for the rate of free-radical polymerization yields

$$R_\mathrm{p} = \left(\frac{2fk_\mathrm{d}k_\mathrm{p}{}^2}{k_\mathrm{t}{}^*}\right)^{0.5}\eta^{0.5}[\mathrm{M}][\mathrm{I}]^{0.5}(\bar{X}_\mathrm{n})^a \quad (10)$$

or

$$\ln\left(\frac{R_\mathrm{p}}{\eta^{0.5}[\mathrm{M}][\mathrm{I}]^{0.5}}\right) = \text{Constant} + a\ln\bar{X}_\mathrm{n} \quad (10\mathrm{a})$$

Parameter a is bounded as $0 < a < 0.25$.[27] A lower value of a translates to a weaker chain-length dependence of k_t, and for $a = 0$ k_t is independent of chain length (classical kinetic). Properties such as solvent–radical interaction will have an effect on a. a decreases as the polymerization medium becomes a thermodynamically poorer solvent for terminating radicals.

Equations 10 or 10a predict the effect of chain-length dependence of k_t on the rate of free-radical polymerization at low conversion. The advantages of this nonclassical rate expression compare to eq 7b, and those reported in the literature are its simplicity. R_p, [M], [I], $\bar{X}_\mathrm{n}$, and if needed η can be obtained experimentally, and therefore the chain-length dependence of k_t could be easily put to the test by utilizing this equation.

Effect of Chain-Length Dependence of k_t on the Rate of Free-Radical Polymerization at Low Conversion. When eq 10 is utilized, the effect of chain-length dependence of k_t on the rate of free-radical polymerization was studied for the following cases.

1. **Predominance of Transfer.**

$$r_\mathrm{tr} \gg r_\mathrm{t}$$

When the production of polymer is mainly by transfer,

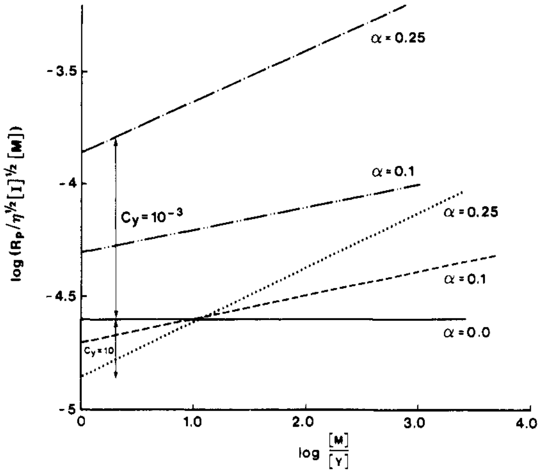

Figure 1. Effect of [M]/[Y] on the rate of free-radical polymerization: (—) $a = 0.0$ (classical kinetics); (- - -) $a = 0.1$, $C_y = 10$; (· · ·) $a = 0.25$, $C_y = 10$; (– · · –) $a = 0.1$, $C_y = 10^{-3}$; (– · –) $a = 0.25$, $C_y = 10^{-3}$.

the average number degree of polymerization can be written as[25]

$$\bar{X}_n = 1/(C_y[Y]/[M]) \tag{11}$$

Substitution of $\bar{X}_n$ from eq 11 into eq 10 results in

$$R_p = \left(\frac{2fk_dk_p{}^2}{k_tC_y{}^{2a}}\right)^{0.5}\eta^{0.5}[Y]^{-a}[M]^{1+a}[I]^{0.5} \tag{12}$$

This expression predicts a monomer exponent greater than 1 and also dependency of R_p on the concentration of transfer agent. Figure 1 shows the effect of [M]/[Y] on the $R_p/[M][I]^{0.5}\eta^{0.5}$ for different values of a and C_y. It is clear that both slope and interception of the lines calculated assuming chain-length dependence of k_t deviate substantially from those obtained assuming classical kinetics.

2. Nontransfer.

$$r_t \gg r_{tr}$$

When the production of polymer is mainly by polymer–polymer termination, then the average degree of polymerization can be written as[25]

$$\bar{X}_n = \beta(\epsilon,a)((2fk_dk_{to}/k_p{}^2)^{0.5}[I]^{0.5}/[M])^{-1/(1-a)} \tag{13}$$

where β is constant depending on a and termination mode (ϵ). Substitution of $\bar{X}_n$ from eq 13 into eq 10 yields

$$R_p = (\text{Constant})\eta^{0.5}[I]^{0.5[(1-2a)/(1-a)]}[M]^{1/(1-a)} \tag{14}$$

This expression predicts an exponent higher than 1 for monomer and less than 0.5 for initiator. For the highest value of $a = 0.25$, i.e., strong chain-length dependence of k_t at low-conversion polymerization, the exponents for monomer and initiator are $^4/_3$ and $^1/_3$, respectively. It is clear that the deviations of monomer and initiator exponents from classical values for a low-conversion polymerization system with strong chain-length dependence of k_t are $+^1/_3$ and $-^1/_6$, respectively.

The effects of monomer and initiator concentration on the rate of polymerization in this case are shown in Figures 2 and 3. It is obvious that use of classical rate expression when chain-length dependence of k_t is strong can lead to a large error in kinetic parameter estimation.

3. Termination and Transfer Competition.

$$r_t \simeq r_{tr}$$

Since eq 10 was derived based on the kinetic scheme in which termination and transfer were in competition, this equation can be used, without any further simplification, for studying the effect of chain-length dependence of k_t on the rate of polymerization in this case. Figure 4 shows the effect of $\bar{X}_n$ on the rate of free-radical polymerization for $a = 0$ and 0.25. It is clear that the rate of polymerization increases with $\bar{X}_n$ and that the deviation of the rate with strong chain-length dependence of k_t from classical rate is significant and cannot be neglected. Equation 10 was also tested against experimental data reported by Ito[26] for styrene and methyl methacrylate polymerization in various solvents at 50 °C.

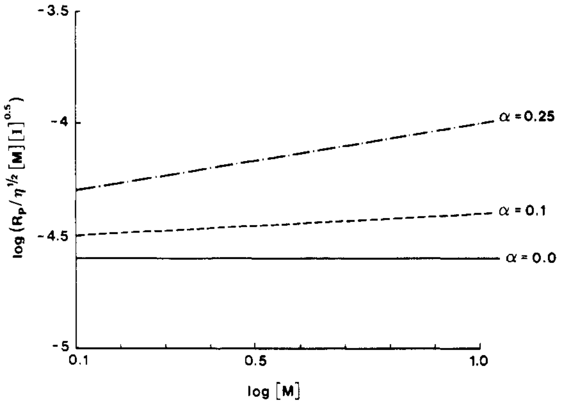

Figure 2. Effect of monomer concentration on the rate of free-radical polymerization: (—) $a = 0.0$ (classical kinetics); (- - -) $a = 0.1$, mild chain-length dependence of k_t; (– · –) $a = 0.25$, strong chain-length dependence of k_t.

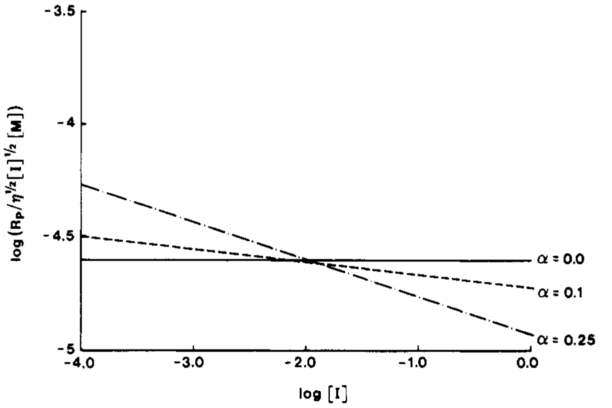

Figure 3. Effect of initiator concentration on the rate of free-radical polymerization: (—) $a = 0.0$ (classical kinetics); (- - -) $a = 0.1$, mild chain-length dependence of k_t; (– · –) $a = 0.25$, strong chain-length dependence of k_t.

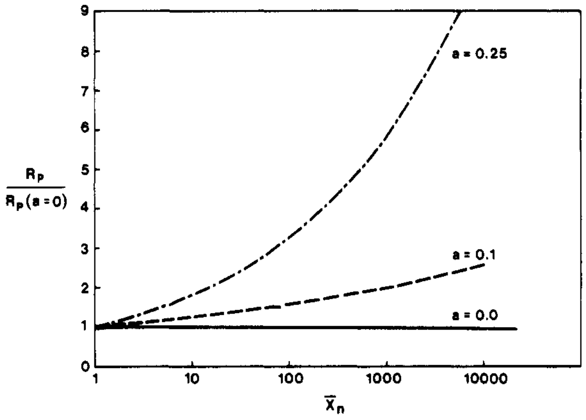

Figure 4. Effect of $\bar{X}_n$ on R_p: (—) $a = 0.0$; (- - -) $a = 0.1$; (– · –) $a = 0.25$.

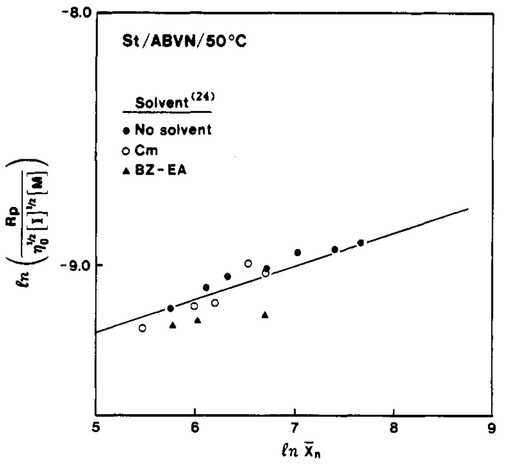

Figure 5. log-log plot of $R_p/\eta^{1/2}[I]^{1/2}[M]$ vs $\bar{X}_n$ for low-conversion polymerization of styrene in a good solvent, initiator ABVN, temperature 50 °C. Solvent:[26] (●) styrene (bulk polymerization), (○) Cm, (▲) BZ-EA, (—) eq 10a.

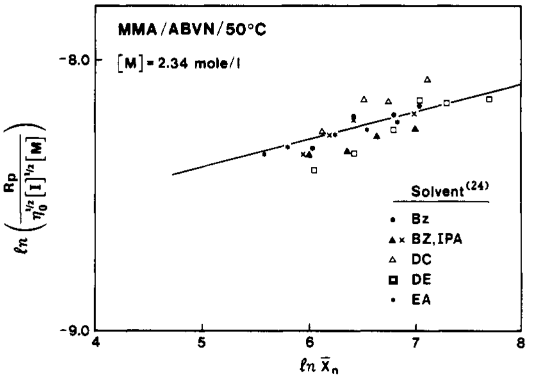

Figure 6. log-log plot of $R_p/\eta^{1/2}[I]^{1/2}[M]$ vs $\bar{X}_n$ for low-conversion polymerization of methyl methacrylate in a good solvent, initiator[24] ABVN, temperature 50 °C, [M] = 2.34 mol/L. Solvent: (●) BZ, (▲,X) BZ-IPA, (△) DC, (□) DE, (*) EA, (—) eq 10a.

Log-log plots of $(R_p/(\eta^{0.5}[M](I]^{0.5}))$ vs $\bar{X}_n$ for styrene and MMA are shown in Figures 5 and 6, respectively. As expected log $(R_p/(\eta^{0.5}[M](I]^{0.5}))$ vs $\bar{X}_n$ for both monomers are linear. The least-squares analysis of these data and comparison with eq 10a yield

$$\frac{2fk_dk_p^2}{k_t^*} = 1.70 \times 10^{-4}\ \mathrm{L/mol/s^2} \quad \mathrm{MMA/good\ solvent/50\ ^\circ C}$$

$$a = 0.0995$$

$$\frac{2fk_dk_p^2}{k_t^*} = 8.27 \times 10^{-5}\ \mathrm{L/mol/s^2} \quad \mathrm{styrene/good\ solvent/50\ ^\circ C}$$

$$a = 0.1306$$

The estimated values of a in this work are in good agreement with 0.075 for MMA at 25 °C and 0.12 for styrene at 30 °C reported earlier[25] by using experimental data obtained from SIP reactor.[16,17]

Equation 10a also applied to experimental data of MMA polymerization in a poor solvent (Figure 7). As expected, a linear relationship between log $(R_p/(\eta^{0.5}[I]^{0.5}[M])$ and log $\bar{X}_n$ was found. The least-squares analysis of this data yields a lower value of a = 0.036 as compared to that obtained from Figure 6. This indicates that the chain-length dependence of k_t for MMA polymerization in a poor solvent is weak. This was expected since the excluded-volume effects contribute to the chain-length dependence of k_t and since this effect is minimum in a poor solvent.[14]

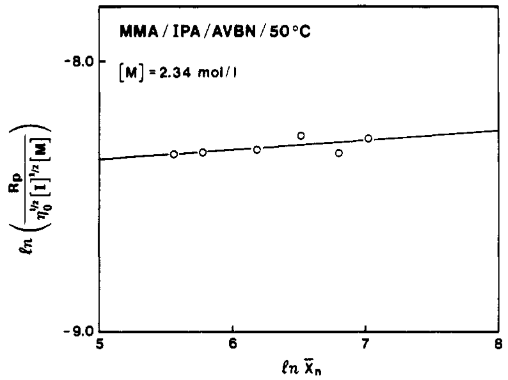

Figure 7. log-log plot of $R_p/\eta^{1/2}[I]^{1/2}[M]$ vs $\bar{X}_n$ for low-conversion polymerization of methyl methacrylate in a poor solvent, solvent[24] IPA, [M] = 2.34 mol/L, initiator AVBN, temperature 50 °C.

Conclusion

The solution of the nonclassical kinetic scheme of low-conversion, free-radical polymerization recognizing the chain-length dependence of k_t has been carried out, and a simple expression for the rate of polymerization was found. When this rate expression was used, the chain-length dependence of k_t could be easily verified. The nonclassical rate expression, obtained here, was tested against experimental data for styrene and methyl methacrylate polymerization.

References and Notes

(1) Bamford, C. H.; Jenkins, A. D.; Johnson, R. *Trans. Faraday Soc.* **1959**, *55*, 1451.
(2) Deb. P. C.; Meyerhoff, G. *Eur. Polym. J.* **1974**, *10*, 709.
(3) Mahabadi, H.-Kh.; Meyerhoff, G. *Eur. Polym. J.* **1979**, *15*, 607.
(4) Berger, K. C.; Meyerhoff, G. *Makromol. Chem.* **1975**, *176*, 1983.
(5) Berger, K. C. *Makromal. Chem.* **1975**, *176*, 3575.
(6) Pallen, R. H.; Siverts, C. *Can. J. Chem.* **1957**, *35*, 723.
(7) Benson, S. W.; North, A. M. *J. Am. Chem. Soc.* **1959**, *81*, 1339; **1962**, *84*, 935.
(8) Allen, P. E.; Patrick, C. R. *Makromol Chem.* **1961**, *47*, 154; **1964**, *72*, 106.
(9) Schultz, G. V.; Fischer, J. P. *Makromol. Chem.* **1969**, *127*, 176.
(10) Olaj, O. F. *Makromol. Chem.* **1973**, *147*, 235.
(11) Horie, K.; Mita, I.; Kambe, H. *Polym. J.* **1973**, *4*, 341.
(12) Yasukawa, T.; Takahashi, T.; Murakami, K. *Makromol. Chem.* **1973**, *174*, 235.
(13) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 701.
(14) Mahabadi, H.-Kh.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 283.
(15) Mahabadi, H.-Kh.; O'Driscoll, K. F. *Macromolecules* **1977**, *10*, 55.
(16) O'Driscoll, K. F.; Mahabadi, H.-Kh. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 869.
(17) Mahabadi, H.-Kh.; O'Driscoll, K. F. *J. Makromol. Sci., Chem.* **1977**, *11*, 967.
(18) Yasukawa, T.; Murakami, K. *Polymer* **1980**, *21*, 1423.
(19) Olaj, O. F.; Zifferer, G. *Makromol. Chem., Rapid Commun.* **1982**, *3*, 549.
(20) Olaj, O. F.; Zifferer, G.; Gleixner, G.; Stickler, M. *Eur. Polym. J.* **1986**, *22*, 585.
(21) Olaj, O. F.; Zifferer, G.; Gleixner, G. *Makromol. Chem.* **1986**, *187*, 977.
(22) Olaj, O. F.; Zifferer, G. *Macromolecules* **1987**, *20*, 850.
(23) Mahadadi, H.-Kh.; O'Driscoll, K. F. *Makromol. Chem.* **1977**, *178*, 2629.
(24) Olaj, P. F.; Zifferer, G. *Makromol. Chem. Symp.* **1987**, *10/11*, 165.
(25) Mahabadi, H.-Kh. *Macromolecules* **1985**, *18*, 1319.
(26) Ito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 258.
(27) Mahabadi, H.-Kh. *Makromol, Chem., Symp.* **1987**, *10/11*, 127.

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