Hydrogen Transfer Reactions of Nitroxides in Free Radical Polymerizations†

Alexei A. Gridnev

Central Research and Development, Experimental Station, DuPont, Wilmington, Delaware 19880-0328

Received January 13, 1997; Revised Manuscript Received September 12, 1997⊗

ABSTRACT: The kinetics of radical polymerization of styrene with nitroxide stable radicals and the corresponding hydroxylamines and secondary amine were investigated at 90 °C. The amine derivative was found to be inert. The hydroxylamine causes retardation of polymerization. The rate constant of termination of the styrene propagating radicals by hydroxylamines, C_x, was found to be 0.18−0.43, depending on the structure of the nitroxyl. Nitroxide caused an induction period and retarded the rate after the induction period ended. Both retardations are ascribed to hydrogen transfer. In the case of hydroxylamines it is the result of hydrogen abstraction from the hydroxyl group of the hydroxylamine by the polystyryl radical. In the case of nitroxides, it is suggested that retardation is caused by hydroxylamine formed as a byproduct during the induction period when the nitroxide reacts with the propagating radical. This is generally a minor side reaction of the propagating radical scavenging by nitroxyl radicals, but this reaction may become important at elevated temperatures when the adduct of the styrene radical with nitroxide is unstable and a reversible reaction prevails. When these two reactions of retardation occur simultaneously, it makes termination of the propagating radicals by nitroxides a catalytic reaction.

Introduction

The mechanism of cobalt-catalyzed chain transfer in free radical polymerization is relatively well studied.[1] Under some conditions, the catalytic chain transfer is accompanied by catalytic termination of free radical chains in the polymerization.[2] Chain transfer catalysis is exemplified by reactions 1 and 2, where M is monomer, R_1 is the monomeric radical, R_n is the polymeric radical, $P_=$ is the corresponding polymer terminated with a double bond, Co is a cobalt(II) chelate, and CoH is the corresponding hydride of cobalt(III) chelate. The mechanism of catalytic termination is not clear.[3] One possible scheme suggests hydrogen abstraction from the intermediate CoH by a propagating radical:

$$R_n + Co \xrightarrow{k_{Co}} P_= + CoH \quad (1)$$

$$CoH + M \xrightarrow{K_r} Co + R_1 \quad (2)$$

$$CoH + R_n \xrightarrow{K_a} Co + PH \quad (3)$$

where PH stands for a terminally-saturated polymer molecule. The very high rate constant of reaction 1, $k_{Co} = 10^6-10^8$ L·mol^{-1}·s^{-1}, indicates the free radical character of the cobalt chelate—it is essentially a stable radical. The hydride, CoH, is extremely unstable,[4] making its isolation difficult[4,5] and quantification in solution unreliable. Minor modification of the cobalt chelate and switching from methacrylates to acrylates convert the system from catalytic chain transfer to metal-mediated living radical polymerization.[6] We were interested in exploring the similarities of these reactions to potential reactions in nitroxide-mediated living radical polymerizations.

This work involves the evaluation of nitroxyl radicals, another class of stable radicals, under conditions under which they can act as catalytic terminators. Though the descriptor "stable" is often added to nitroxyl radicals, it is understood that the term "stable" is relative and that there are conditions under which their reactivity is noninnocent. Several good reviews on the chemistry of nitroxides are available.[7] For the purpose of the current work it is necessary to mention that nitroxyl radicals are known to abstract hydrogen atoms from a variety of substrates, including other nitroxides, especially at elevated temperatures[7b,c,8] forming the corresponding hydroxylamine, XH. In contrast to CoH, many XH are stable enough to be isolated and handled without difficulty. In reactions where they are formed, appreciable concentrations can develop. If the substrate has labile hydrogen atoms, hydrogen abstraction by nitroxyl radical is very efficient.[9]

Nitroxides are potential catalysts for chain termination only if XH is converted back to X under polymerization conditions. When peroxides such as benzoyl peroxide (BPO) are used as initiators, formation of hydroxylamines should not be a problem because BPO is known to oxidize hydroxylamines to nitroxyl radicals.[10] Though BPO can oxidize nitroxyl radicals further to a nitron, this reaction, which would lead to nitroxide destruction, is suppressed in the presence of a monomer.[11]

Azo-initiators do not oxidize nitroxides.[12] When AIBN was used to initiate polymerization of MMA in presence of nitroxides,[13] the stoichiometric coefficient of inhibition, μ, was found to be greater than 1. Other authors[14] found $\mu = 2.8 - 6.5$ for radical polymerization of partially fluorinated methacrylates in the presence of different nitroxides at 60 °C. To explain this and some other observed effects, the following scheme was proposed:[13,14]

$$X + R \xrightarrow{k_X} XH + P_= \quad (4)$$

$$XH + R \xrightarrow{k_{XH}} X + PH \quad (5)$$

† Contribution No. 7501 from Central Research and Development.

⊗ Abstract published in *Advance ACS Abstracts,* November 15, 1997.

S0024-9297(97)00021-1 CCC: $14.00

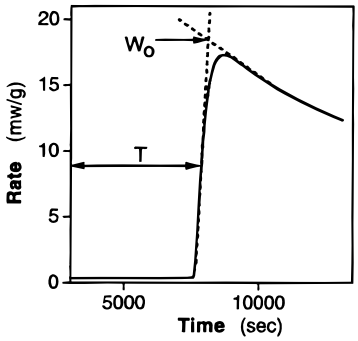


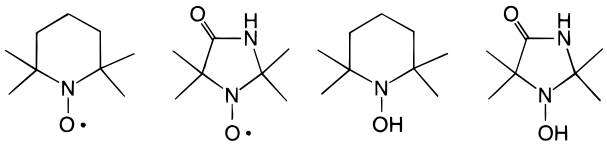
Figure 1. Thermogram of styrene polymerization. styrene: DMAC = 4:1 v/v, [VAZO-88] = 0.05 mol/L, T = 90 °C, and [TEMIO] = 0.018 mol/L.

Reaction 4 is a disproportionation, and reaction 5 is a hydrogen atom transfer. The experimental objective of this work was to evaluate ability of polystyryl radicals to abstract hydrogen by pathway 5.

Experimental Section

Materials. All solvents, monomers and 2,2,6,6-tetramethylpiperidine (TEMPH) (Aldrich) were vacuum distilled immediately prior to each experiment. 1,1-Azo(bis(cyclohexanecarbonitrile (VAZO-88, DuPont), 2,2,6,6-tetramethyl-1-piperidineoxyl (TEMPO, Aldrich), and 4-oxo-2,2,5,5-tetramethylimidazolidin-1-oxyl (TEMIO, a gift of Dr. A. Anderson, DuPont) were used as received. 2,2,6,6-Tetramethyl-1-piperidinol (TEMPOH) and 1-hydroxy-2,2,5,5-tetramethyl-4-imidazolidinone (TEMIOH) were synthesized by reduction of the corresponding radicals by treatment with sodium dithionite according to reference.[15]

TEMIOH was recrystallized from acetone at 50 °C by cooling to dry ice temperature to give a white powder (mp 252−253 °C). Its purity was confirmed by TLC and proton NMR (300 MHz, DMSO): δ 1.099 (3H, s, CH_3); δ 1.240 (3H, s, CH_3); δ 1.099 (3H, s, CH_3); δ 7.829 (1H, s, OH); δ 8.255 (1H, s, NH). It was difficult to purify TEMPOH because its physical properties are too close to the starting material. We found that TEMPOH is not stable enough in air to give an initial free radical. For this reason, the unpurified TEMPOH used in kinetic experiments contained about 10% of the corresponding free radical as estimated by NMR and the duration of the induction period in the polymerization.



Procedure. All polymerization experiments were conducted at 90 °C. This temperature was chosen to minimize thermal initiation of the styrene polymerization. Bulk styrene was used when TEMPO or TEMPOH were applied. The poor solubility of TEMIO and TEMIOH in organic solvents required the addition of minor quantities of dimethylacetamide (DMAC) into the styrene to solubilize both imidazolinones. After all ingredients were mixed, the polymerization mixture was then transferred to a Pyrex tube (8−40 mm) adapted to a high vacuum line. The tubes were evacuated by three freeze−pump−thaw cycles and sealed under vacuum (while frozen). Then the tubes were placed into a Setaram C-80 isothermal calorimeter at 90 °C. The voltage signal of the calorimeter was converted into the rate of polymerization applying the heat of polymerization, $\Delta H_p = -0.6702$ kJ/g.[16] The resulting kinetic curve was used to determine the induction period and the initial rate of polymerization, W_o, shown in Figure 1.

TEMPH and TEMIOH showed no induction period. Some induction period was observed in polymerizations containing TEMPOH due to the presence of residual TEMPO. TEMPO and TEMIO gave very similar induction periods on the basis of molar concentration, indicating that the addition of DMAC into the styrene did not significantly change the rate of free radical production by VAZO-88 decomposition under the conditions utilized. Separate blank experiments without nitroxyl radicals added showed no retardation with DMAC added versus the bulk polymerization (concentration of monomer was adjusted). Hence, DMAC does not react with radicals under the conditions employed, and all radicals produced by thermal decomposition of the initiator were trapped exclusively by nitroxyl radicals. One may then calculate the rate of free radical formation by VAZO-88. It was found that 0.05 mol/L of VAZO-88 at 90 °C gave $(1.9 \pm 0.1) \times 10^{-6}$ L·mol^{-1}·s^{-1} with TEMPO as a trapping agent and $(2.1 \pm 0.1) \times 10^{-6}$ L·mol^{-1}·s^{-1} with TEMIO.

Method. To minimize the difficulties associated with conversion, the initial rate of polymerization was used throughout the work. To determine the radical loss due to irreversible scavenging, the calculations employed a retardation coefficient, γ

$$\gamma = \frac{W_o}{W_{oo}} = \frac{k_p[M][R]_o}{k_p[M][R]_{oo}} = \frac{[R]_o}{[R]_{oo}} \tag{6}$$

where W_{oo} is the initial rate of polymerization without nitroxide or its derivatives, and W_o is the initial rate of polymerization with an additive. $[R]_{oo}$ and $[R]_o$ are the corresponding concentrations of the propagating radicals. In the case where nitroxides were added, the polymerizations exhibited induction periods while the nitroxyl radical was consumed and then exhibited normal polymerization kinetics (Figure 1). In this case, W_o was measured after the induction period as indicated in Figure 1.

Since propagation is negligible during the induction period, the concentration of monomer, [M], stays the same until all of the scavenger is consumed. In contrast to the monomer, the concentration of the azo-initiator changes during the induction period, thus affecting the rate of radical production. Therefore, W_{oo} must be adjusted to account for the consumption of the initiator using the coefficient, α

$$W_\alpha = W_{oo}\alpha \quad [R]_\alpha = \alpha \tag{7}$$

For polymerization initiated by initiator I at steady state, the rate of polymerization is determined by eq 8, where R is the

$$W = k_p[M][R] = k_p[M]\sqrt{\frac{k_f[I]}{2k_t}} \tag{8}$$

propagating radical, k_f is the effective rate constant of radical production by decomposition of the initiator, and k_t is the rate constant of the bimolecular termination of two propagating radicals. Therefore, the coefficient α in eq 7 is

$$\alpha = \sqrt{\frac{[I]_{t=0}}{[I]_{t=T}}} \tag{9}$$

where $[I]_{t=0}$ is the concentration of the initiator (VAZO-88 in this case) before polymerization and $[I]_{t=T}$ is the concentration of initiator when the induction period ended. Time T can be determined on the kinetic curves as an inflection point. The concentration of VAZO-88 for $t = T$ was obtained from published data on azo-initiators decomposition (at 90 °C, $k_d = 3.89 \times 10^{-5}$).[17]

Results and Discussion

Both stable free radicals, TEMPO and TEMIO, showed a slight reduction in the rate of polymerization after the induction period (Figures 2 and 3). The observation cannot be attributed to an error in the calculation of $[\text{VAZO-88}]_{t=T}$ because the reduction in rate with TEMPO

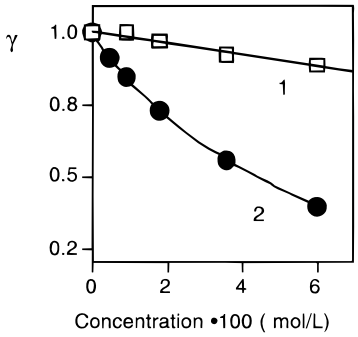


Figure 2. Dependence of the relative rate of styrene polymerization in the presence of different additives. Styrene:DMAC = 4:1 v/v, [VAZO-88] = 0.05 mol/L, and T = 90 °C. Key: **1**, TEMIO; **2**, TEMIOH.

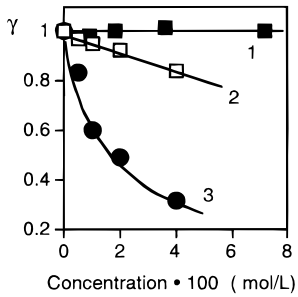


Figure 3. Dependence of the relative rate of styrene polymerization in the presence of different additives. Neat styrene was used [VAZO-88] = 0.05 mol/L, and T = 90 °C. Key: **1**, TEMPH; **2**, TEMPO; **3**, TEMPOH.

was almost twice that observed for TEMIO while the periods of inhibition were the same.

The corresponding hydroxylamines, TEMPOH and TEMIOH, showed more pronounced retardations in the rate of polymerization. The retardation might be related to the OH-group, because the amino-derivative, TEMPH, had no influence on the rate of styrene polymerization at 90 °C (Figure 3). Hence, it is likely that in the presence of added XH, the retardation originates by abstraction of a hydrogen atom from the OH-group by the propagating radical of styrene to yield the nitroxide (reaction 5). The nitroxide, X, then reacts with another radical by pathway 4 or any other pathway. At the beginning of the polymerization, the concentration of RX is negligible, so that

$$\frac{d[R]}{dt} = k_f[I] - 2k_t[R]_0^2 - k_{XH}[XH][R]_o - k_{12}[X][R]_o - k_X[X][R]_o \approx 0 \quad (10)$$

$$\frac{d[X]}{dt} = k_{XH}[XH][R]_o - k_{12}[X][R]_o - k_X[X][R]_o \approx 0 \quad (11)$$

Subtracting eq 11 from 10 and replacing $k_f[I] = 2k_t[R]_{oo}^2$ and $[R]_o = \gamma[R]_{oo}$, we have

$$\frac{d[R]}{dt} = 2k_t[R]_{oo}^2 - 2k_t\gamma^2[R]_{oo}^2 - 2k_{XH}[XH]\gamma[R]_{oo} \approx 0$$

or

$$\frac{1-\gamma^2}{\gamma} = \frac{2k_{XH}k_p[M]}{2k_tW_{oo}}[XH] \quad (12)$$

The data in Figure 4 fit eq 12 well. Taking k_p = 815 $mol^{-1}\cdot L\cdot s^{-1}$ [18] and $2k_t = 1 \times 10^8$ $mol^{-1}\cdot L\cdot s^{-1}$,[19] we obtain

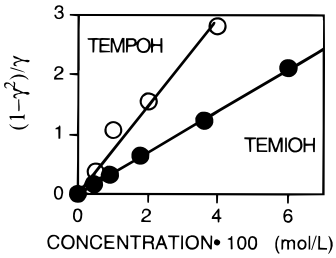


Figure 4. Dependence of $(1 - \gamma^2)\gamma^{-1}$ (see explanation in the text) on the concentration of TEMIOH or TEMPOH hydroxylamine. Data are taken from Figures 2 and 3.

$k_{XH}/k_p = 0.18$ (k_{XH} = 15 $mol^{-1}\cdot L\cdot s^{-1}$) for TEMIOH and $k_{XH}/k_p = 0.43$ (k_{XH} = 35 $mol^{-1}\cdot L\cdot s^{-1}$) for TEMPOH. These values indicate that the hydroxylamine derivatives of nitroxyl radicals are an order of magnitude more active in chain transfer than, for example, carbon tetrachloride.[20]

Polymerizations in the presence of added nitroxide must now be considered. The polymerization begins with inhibition (Figure 1) during which time practically all of the nitroxide is converted into RX or XH. In this case, the reversible termination (13) should be considered:[21]

$$R + X \underset{k_{12}}{\overset{k_{11}}{\rightleftharpoons}} RX \quad (13)$$

When the induction period ends (Figure 1) and the concentrations of residual X and the propagating radical become quasi-stationary we have

$$\frac{d[X]}{dt} = k_{12}[RX] + k_{XH}[XH][R]_o - k_X[X][R]_o - k_{11}[X][R]_o \approx 0 \quad (14)$$

$$\frac{d[R]}{dt} = k_f[I] - 2k_t[R]_o^2 + k_{12}[RX] - k_{XH}[XH][R]_o - k_X[X][R]_o - k_{11}[X][R]_o \approx 0 \quad (15)$$

Repeating the modification of eqs 10 and 11 on eqs 14 and 15, we again obtain eq 12. The only difference is that W_a should be used instead of W_o (see Experimental Section). It indicates that reversible termination does not affect the concentration of radicals when all of the added nitroxide is consumed. Therefore, reaction 5 is solely responsible for the reduction in W_o.

Hence, we can calculate the concentration of hydroxylamine XH formed during the induction period by measuring the reduction of the rate of polymerization. The most simple way to do that is to draw a horizontal line on Figure 2. The points of intersection of this line with lines 1 and 2 gives the concentration of added hydroxylamine in the first case, $[X]_{oo}$, and concentration of XH after the induction period, $[XH]_o$, in the second case. The ratio between the rate constants of hydrogen abstraction vs recombination when X reacts with R during the induction period is given by

$$\frac{[XH]_o}{[X]_{oo} - [XH]_o} = \frac{[XH]_o}{[XR]_o} = \frac{\int_{t=0}^{t=T}(k_X[X]_t[R]_t)}{\int_{t=0}^{t=T}(k_{11}[X]_t[R]_t)} = \frac{k_X}{k_{11}} \quad (16)$$

According to eq 16 and the data in Figure 2, $k_X/k_{11} \approx 0.1$ for the TEMIO radical. The same approach gives $k_X/k_{11} \approx 0.3$ for the TEMPO radical.

During the induction period, the nitroxyl radicals effectively scavenge any radicals in the reaction medium. There is a question as to the nature of these radicals. The possibility of the initiating cyanocyclohexyl radical, obtained from decomposition of VAZO-88 reacting with the nitroxide rather than with styrene must be considered. The ratio between rates of these two reactions is given by

$$\frac{W_1}{W_2} = \frac{k_1[\mathrm{M}][\mathrm{R}^*]}{k_2[\mathrm{X}][\mathrm{R}^*]} = \frac{k_1[\mathrm{M}]}{k_2[\mathrm{X}]} \qquad (17)$$

where R* is the initiating radical. We could not find values either for k_1, the rate constant for addition of the cyanocyclohexyl to styrene, or for k_2, the rate constant of coupling of this radical with nitroxides. Some data are available for the dimethylcyanomethyl radical which has a comparable reactivity in the abstraction reaction.[22] The rate of addition of the dimethylcyanomethyl radical to methacrylonitrile is about 500 $L \cdot mol^{-1} \cdot s^{-1}$ at 60 °C.[23] At 90 °C it should be ≈2000 $L \cdot mol^{-1} \cdot s^{-1}$. The copolymerization rate constant of methacrylonitrile with styrene is ≈0.2,[24] indicating that the dimethylcyanomethyl radical reacts five times faster with styrene than with methacrylonitrile. Hence, we may expect k_1 to be 10^4 $L \cdot mol^{-1} \cdot s^{-1}$.

The rate constant for reaction of nitroxyl radicals with polystyryl radicals is $k_2 = 1 \times 10^5$ $L \cdot mol^{-1} \cdot s^{-1}$.[13,14e] Taking [M] = 9 $mol \cdot L^{-1}$ and the average concentration of nitroxyl radical utilized in this work, [X] = 10^{-2} $mol \cdot L^{-1}$, we obtain $W_1/W_2 \approx 10$. Therefore, during the induction period, nitroxyl radicals react with styrene propagating radicals in preference to the initiating cyanocyclohexyl radical.

Conclusions

We have demonstrated that under selected conditions, it is possible to effect catalytic chain termination in the polymerization of styrene mediated with nitroxides. The mechanism of this reaction is in accord with observation made for the catalytic chain termination in methacrylate polymerizations containing cobalt macrocycles. Obviously, for successful "living radical polymerizations", these reactions must be minimized. However, it may also be possible to utilize these reactions for the preparation of macromonomers, utilizing nitroxides or other stable radicals rather than cobalt complexes at less than the stoichiometric concentrations required for living systems and high temperatures.

Acknowledgment. The author thanks S. D. Ittel and D. Paquet for helpful discussion and A. G. Anderson for a gift of TEMIO stable radical.

References and Notes

(1) (a) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis*; Wiley: New York, 1992; p 85. (b) Davis, T. P.; Haddleton, D. M.; Richards, S. N. *J. Macromol. Sci.—Rev. Macromol. Chem. Phys.* **1994**, *C23*, 243.

(2) (a) Gridnev, A. A. *Polym. Sci. (Engl. Transl.)* **1989**, *31*, 2369; (b) Gridnev, A. A.; Lampeka, Y. D.; Smirnov, B. R.; Yatsimirskii, K. B. *Theor. Exp. Chem. (Engl. Transl.)* **1987**, *23*, 293. (c) Smirnov, B. R.; Puschaeva, L. M.; Plotnikov, V. D. *Polym. Sci. (Engl. Transl.)* **1989**, *31*, 2607. (d) Suddaby, K. G.; O'Driscoll, K. F.; Rudin, A. *J. Polym. Sci.* **1992**, *A30*, 643.

(3) Smirnov, B. R.; Il'in, A. A. *Polymer Sci. (Engl. Transl.)* **1989**, *31*, 2369.

(4) (a) Schrauzer, G. N.; Holland, R. J. *J. Am. Chem. Soc.* **1971**, *93*, 1505. (b) Chao, T. H.; Espenson, J. *J. Am. Chem. Soc.* **1978**, *100*, 129. (c) Simandi, L. I.; Budo-Zahonyi, E.; Szeverenyi, Z.; Nemeth, S. *J. Chem. Soc., Dalton Trans.* **1980**, 276.

(5) The author's attempt to isolate hydridocobaloxime gave negative result. Several researchers admitted failure in isolation of hydridocobaloximes when this issue was discussed with the author.

(6) Wayland, B. B.; Poszmik, G.; Mukerjee, S.; Fryd, M. *J. Am. Chem. Soc.* **1994**, *116*, 7943.

(7) (a) Volodarsky, L. B.; Reznikov, V. A.; Ovcharenko, V. I. *Synthetic Chemistry of Stable Nitroxides*; CRC Press: Boca Raton, FL, 1994. (b) Rozantsev, E. G. *Free Nitoxyl Radicals*: Plenum Press: New York, 1970. (c) Buchachenko, A. L.; Vasserman, A. M. *Stable Radicals. Electronic Structure, and Use*; Chimia: Moscow, 1973 (Russian: *Chem. Abstr.* **1974**, *80*, 113018).

(8) (a) Yoshioka, T.; Higashida, S.; Morimura, S.; Murayama, K. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2207. (b) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.* **1981**, *103*, 3094. (c) Banks, R. E.; Haszeldine, R. N.; Stevenson, M. J. *J. Chem. Soc. C* **1966**, 901. (d) Keana, J. F. W.; Dinerstein, R. J.; Baitis, F. *J. Org. Chem.* **1971**, *36*, 209. Bowman, D. F.; Gillan, I.; Ingold, K. U. *J. Am. Chem. Soc.* **1971**, *93*, 6555.

(9) Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon: New York, 1995.

(10) (a) Rykov, S. V.; Sholle, V. D. *Bull. Russ. Acad. Sci., Div. Chem. (Eng. Transl.)* **1971**, *23*, 2351. (b) Scott, A. C.; Tedder, J. M.; Walton, J. C. *J. Chem. Soc., Perkin 2* **1980**, 260. (c) Low, H., Paterson, I.; Tedder, J. M.; Walton, J. C. *J. Chem. Soc., Chem. Commun.* **1977**, 177. (d)

(11) Moad, G.; Rizzardo, E.; Solomon, D. H. *Tetrahedron Lett.* **1981**, *22*, 1165.

(12) Ruban, L. V.; Buchachenko, A. L.; Neiman, M. B.; Kokhanov, Y. V. *Polym. Sci. (Engl. Transl.)* **1966**, *8*, 1812.

(13) (a) (a) Goldfein, M. D.; Rafikov, E. A.; Stepukovich, A. D.; Skipko, L. A. *Polym. Sci. (Engl. Transl.)* **1974**, *16*, 779. (b) Goldfein, M. D.; Rafikov, E. A.; Kozhevnikov, V. N.; Stepukovich, A. D.; Trubnikov, A. V. *Polym. Sci. (Engl. Transl.)* **1975**, *17*, 1919.

(14) (a) Il'in, A. A.; Smirnov, B. R.; Golikov, I. V.; Mogilevich, M. M. *Polym. Sci., Ser A (Engl. Transl.)* **1993**, *35*, 728. (b) Il'in, A. A.; Smirnov, B. R.; Rybin, N. V.; Golikov, I. V.; Mogilevich, M. M.; No, V. B. *Polym. Sci., Ser. B (Engl. Transl.)* **1993**, *35*, 728. (c) Kovtun, G. A.; Alexandrov, A. L.; Golubev, V. A. *Bull. Acad. Sci. USSR, Div. Chem. (Engl. Transl.)* **1974**, 2197. (d) Il'in, A. A.; Smirnov, B. R. *Polymer Sci. (Engl. Transl.)* **1992**, *34*, 53. (e) Lagunov, V. M.; Golikov, I. V.; Smirnov, B. R.; Korolev, G. V. *Polym. Sci. (Engl. Transl.)* **1987**, *29*, 1584.

(15) Ozinskas, A. J.; Bobst, A. M. *Helv. Chim. Acta* **1980**, *63*, 1407.

(16) *Encyclopedia of Polymer Science and Engineering*; Wiley: New York, 1989; Vol. 16, p 1.

(17) Overberger, C. G.; Biletch, H.; Finestone, A. B.; Lilker, J.; Herbert, J. *J. Am. Chem. Soc.* **1953**, *75*, 2078.

(18) Hutchinson, R. A.; Aronson, M. T.; Richards, J. R. *Macromolecules* **1993**, *26*, 6410.

(19) Berger, K. C.; Meyerhoff, G. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1898; p II-67.

(20) Reference 19, p II-118.

(21) (a) Solomon, D. H.; Rizzardo, E.; Cacioli, P. US Pat. 4,581,-429, 1985, to CSIRO. (b) Hawker, C. J.; Hedrick, J. L. *Macromolecules* **1995**, *28*, 2993. (c) Moad, G.; Rizzardo, E. *Macromolecules* **1995**, *28*, 8722. (d) Veregin, R. P. N.; Odell, P. G.; Michalak, L. M.; Georges, M. K. *Macromolecules* **1996**, *29*, 3346. (e) Matyjaszewski, K.; Shigemoto, T.; Frechet, J. M. J.; Leduc, M. *Macromolecules* **1996**, *29*, 1995;

(22) Keck, G. E.; Burnett, D. A. *J. Org. Chem.* **1987**, *52*, 2958.

(23) (a) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864. (b) Shipp, D. A.; Smith, T. A.; Solomon, D. H. *Macromol. Rapid Commun.* **1995**, *16*, 837.

(24) Greenley, R. Z. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1898; p II-206.

MA970021M