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KINETIC STUDIES ON THE CATIONIC POLYMERIZATION

OF TETRAHYDROFURAN UNDER HIGH PRESSURE

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The cationic polymerization of tetrahydrofuran initiated by triethyloxonium tetrafluoroborate has been studied kinetically at 0°C up to 2000 kg/cm². * The course of the reaction was followed by the thermal method, and the rate constants for the elementary reactions were determined. The volumes of activation for the initiation and propagation reaction were -5.0 ± 1.9 and -10.5 ± 2 cm³/mol in the region from 40 to 1000 kg/cm², respectively. The volume change for the polymerization was -7.9 cm³/mol, and the volume of activation for the depropagation reaction was calculated to be -2.6 ± 2 cm³/mol.

Introduction

The cationic polymerization of tetrahydrofuran (THF) has been well studied thermodynamically[1] and kinetically[2-4]. The reaction initiated by triethyloxonium tetrafluoroborate ($Et_3O^+BF_4^-$) is characterized as a living polymerization in a dry system at not too high temperature[2,4]. The initiation reaction is so fast that the polymerization under high pressure can not be followed by a conventional method. This fact is an essential problem in studies on the ionic polymerization under high pressure. A high pressure technique for the kinetic study of moderately fast reactions in solution was devised previously by the present authors[5]. It was made possible to initiate the reaction after thermal equilibration at desired pressure and temperature and to follow thermally the reaction having half life longer than a few minutes.

This paper deals with the effect of pressure on the elementary reactions of the cationic polymerization of THF initiated by $Et_3O^+BF_4^-$ in dichloromethane.

 1) D. Sims, *J. Chem. Soc.*, 1964, 864 ; M. P. Dreyfuss and P. Dreyfuss, *J. Polymer Sci.*, A1, 4, 2179 (1966) ; B. A. Rozenberg, O. M. Chekhuta, E. B. Lyudrig, A. R. Gantmakher and S. S. Medvedv, *J. Polymer Sci.*, C16, 1917 (1967) ; J. Leonard and D. Maheux, *J. Macromol. Sci.*, A7, 1421 (1973)
 2) D. Vofsi and A. V. Tobolsky, *J. Polymer Sci.*, A 3, 3261 (1965)
 3) T. Saegusa and S. Matsumoto, *J. Macromol. Sci.*, A 4, 873 (1970)
 4) M. Sangster and D. J. Worsfold, *Macromolecules*, 5, 229 (1972)
 5) M. Sasaki, M. Okamoto, H. Tsuzuki and J. Osugi, *Chem. Lett.*, 1289 (1976)

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Experimentals

Reagents

Dichloromethane was refluxed over and fractionated from calcium hydride. THF was also purified according to the similar procedure but under nitrogen atmosphere. Both were stored on calcium hydride on a vacuum line.

Epichlorohydrin was dried and distilled by the usual method. Boron trifluoride etherate was distilled under reduced pressure of nitrogen. Triethyloxonium tetrafluoroborate was prepared by the method of Meerwein[6]. The product was washed several times with dry ether under nitrogen atmosphere and stored at low temperature $(< -10°C)$. It was purified with dichloromethane and ether immediately before use.

High pressure apparatus

The general lay-out of the high pressure apparatus is shown in Fig. 1. Temperatures were kept constant within $\pm 1/500°C$. Pressures were determined from the resistance of a manganin wire whose pressure coefficient was determined with the Bourdon gauge calibrated by the free piston gauge in Kobe Steel Ltd.
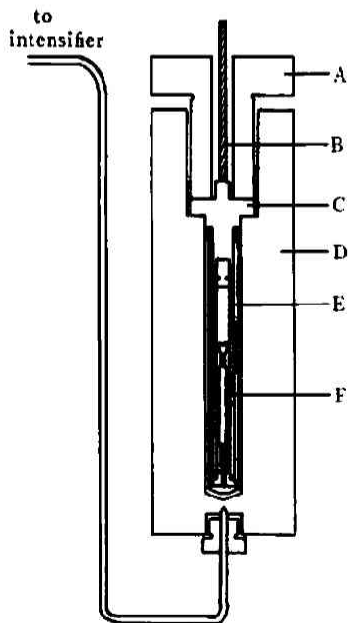

Fig. 1   Schematic diagram of high pressure apparatus
    A : Nut
    B : Lead wire
    C : High pressure plug
    D : High pressure vessel
    E : Holder of reaction cell
    F : Reaction cell

6) H. Meerwein, E. Battenberg, H. Gold, E. Pfeil and G. Willfang, *J. Prakt. Chem.*, **154**, 83 (1939)

Mixing technique and operation

The mixing technique and operation under high pressure were described in the previous paper[5]. The reaction was followed by measuring the differential temperature between the reaction solution and the thermostat, due to the heat of polymerization.

Polymerization procedure

The monomer solution (THF in dichloromethane) was prepared on a vacuum line. and the initiator solution in a dry box under nitrogen atmosphere by dissolving the known weight of the initiator in dichloromethane.

The reaction was initiated by the addition of an aliquot of the initiator according to the method described in the previous paper[5], and the differential temperature was recorded just after the time of mixing. After the desired time, the polymerization was stopped short by adding the reaction mixture to a methanolic sodium methoxide. The polymer was isolated by liquid extraction. The solution stopped short was poured into a separatory funnel. diluted with dichloromethane and extracted with water to remove all water-soluble components. The final solution was transferred to a preweighed beaker, evaporated and dried in vacuum at room temperature. The conversion was gravimetrically determined.

Measurement of the molar volumes

Compressibilities were measured in a mercury displacement piezometer[7] up to 2000 kg/cm² at 0°C. The compressibility of THF was measured directly. That of the polymer was measured by comparing the compressibility of dichloromethane alone with that of the polymer solution in dichloromethane. The molar volumes were determined by the densities at 1atm and the compressibilities.

Result and Discussion

Volume change of the polymerization

The volume change of the polymerization (ΔV) was determined from the molar volumes of the polymer and the monomer at 0°C. The results are shown in Fig. 2. As stated in the later section, the ΔV values are necessary in order to determine the equilibrium conversion under high pressure.

Determination of the rate constants from the differential temperature measurement

The cationic polymerization of THF initiated by $Et_3O^+BF_4^-$ in dichloromethane can be characterized as a living system[2,4]. and proceeds simply as follows;

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7) D. M. Newitt and K. E. Weale, *J. Chem. Soc.*. 1951, 3092

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$$Et_3O^+BF_4^- \quad + \quad \text{(ring)} \quad \xrightarrow{k_1} \quad [EtO^+ \text{(ring)}] BF_4^- \quad + \quad Et_2O$$

$$[\sim\sim O^+ \text{(ring)}] BF_4^- \quad + \quad \text{(ring)} \quad \underset{k_d}{\overset{k_p}{\rightleftharpoons}} \quad [\sim\sim O(CH_2)_4 O^+ \text{(ring)}] BF_4^-$$
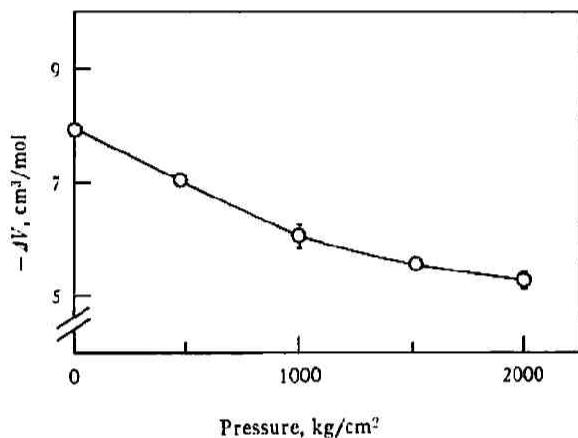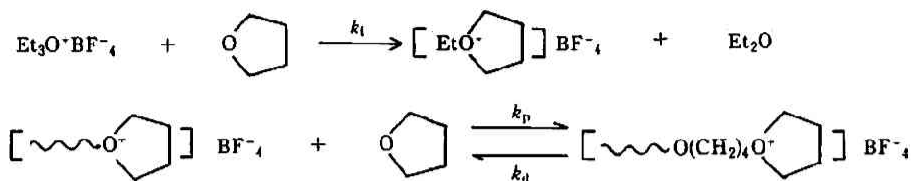

Fig. 2 The relationship between $-\Delta V$ and pressure

The chain propagation step is known to occur *via* not only an ion pair but a free ion. The reactivity of a free ion is thought to be about seven times higher, although its concentration to be much lower[4]. The net effect of free ion on the rate of polymerization is uncertain but small. So in the present treatment the propagation chain is assumed to be in an ion pair.

The temperature of the reaction system changes according to equation (1)[8].

$$\frac{d\Delta T}{dt} = -k\Delta T + \alpha_p R_p, \tag{1}$$

where k, R_p and α_p are the overall cooling constant, the rate of the polymerization and proportionality constant which is a function of the heat capacity of the system and the heat of the reaction. The rate of the polymerization can be given by equation (2).

$$R_p = -\frac{d[M]}{dt} = k_p[I]_0[M]_0(y_\infty - y)[1 - \exp\{-k_1[M]_0\int_0^t(1-y)dt\}], \tag{2}$$

where $[I]_0$, $[M]_0$, y and y_∞ are the initial concentration of the initiator, the initial concentration of monomer, the conversion at the reaction time t and its equilibrium value. The integration of equation (1) gives equation (3).

$$\int_0^t\left(\frac{d\Delta T}{dt} + k\Delta T\right)dt = \alpha_p\{[M]_0 - [M]\} = \alpha_p[M]_0 y. \tag{3}$$

Combining equation (1) with (2), equation (4) is derived.

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8) M. Okamoto, *This Journal*, **44**, 77 (1974)

$$ln\left\{\alpha_p k_p[I]_0[M]_0 - \frac{1}{y_\infty - y}\left(\frac{d\varDelta T}{dt} + k\varDelta T\right)\right\}$$

$$= ln\alpha_p k_p[I]_0[M]_0 - k_i[M]_0\int_0^t (1-y)dt \qquad (4)$$

The value of k can be experimentally determined from the cooling process of the compression heat just before initiating the reaction[8]. The relaxation of the compression heat is plotted as in Fig. 3. The good linearity was obtained and overall cooling constant k was determined from the slopes. In Fig. 4 are shown the typical examples of the differential temperature ($\varDelta T$) in the course of the polymerization reaction. On the base of Figs. 3 and 4, the values of the term, $(d\varDelta T/dt)+k\varDelta T$. can be calculated which are plotted as a function of time in Figs. 5, 6 and 7. And since one knows the conversion quenched at a known time and the values of the left hand side of equation (3) at that time, α_p can be determined. The value of equilibrium conversion y_∞ at 1 atm was cited from literature[2,4] and that at high pressure was calculated using $\varDelta V$ in Fig. 2 according to the following equation ;

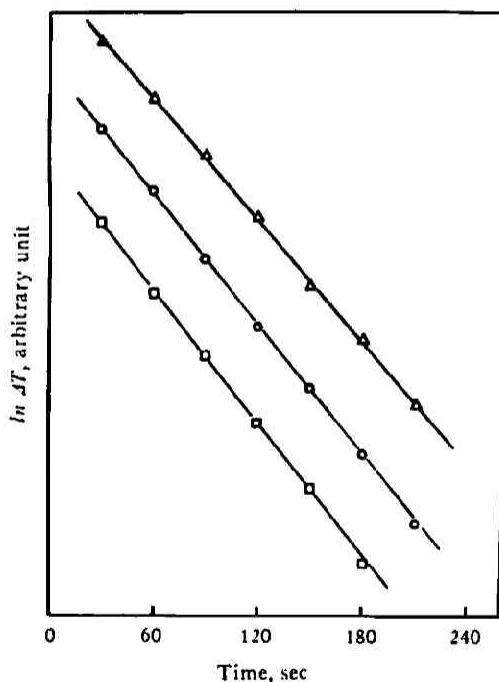$$ln\frac{(1-y_\infty)_{P=1}}{(1-y_\infty)_{P=P}} = -1/RT\int_1^P \varDelta V dP.$$

Fig. 3 The relationship between $ln\varDelta T$ and cooling time
△ : 40 kg/cm²,
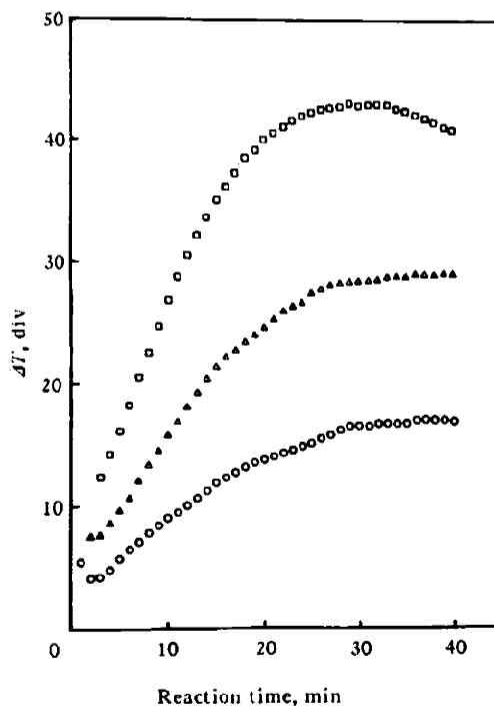○ : 1000 kg/cm²,
□ : 2000 kg/cm²

Fig. 4 Time-course in $\varDelta T$ of the cationic polymerization of THF at various pressures
○ : 40kg/cm², $[M]_0 = 5.37$mol/kg, $[I]_0 = 5.87\times10^{-2}$mol/kg. △ : 1000kg/cm², $[M]_0 = 5.23$ mol/kg, $[I]_0 = 4.84\times10^{-2}$ mol/kg, □ : 2000kg/cm², $[M]_0 = 5.43$mol/kg, $[I]_0 = 4.23\times10^{-2}$mol/kg

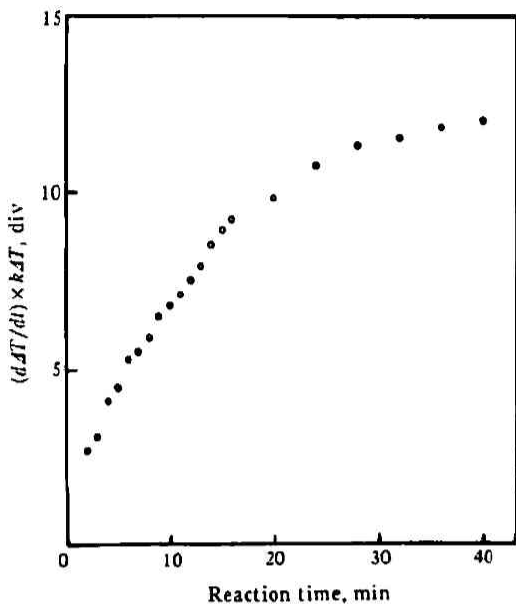38   M. Okamoto, M. Sasaki and Osugi

Fig. 5   Change of $(d\varDelta T/dt)+k\varDelta T$ with time at
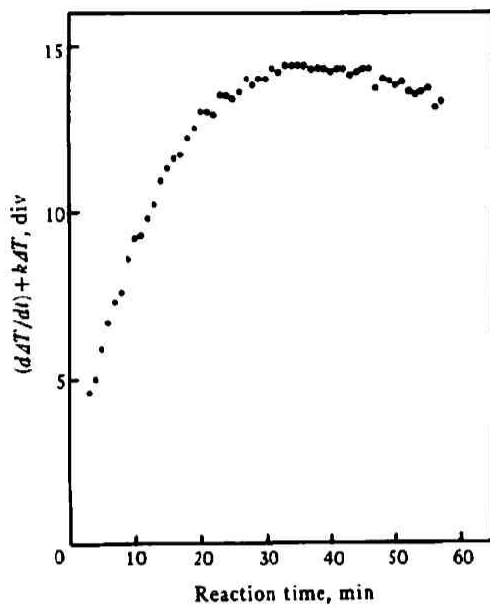0° C, 40 kg/cm²
[I]₀ = 5.87 × 10⁻² mol/kg,
[M]₀ = 5.37 mol/kg

Fig. 6   Change of $(d\varDelta T/dt)+k\varDelta T$ with time at
0° C, 1000 kg/cm²
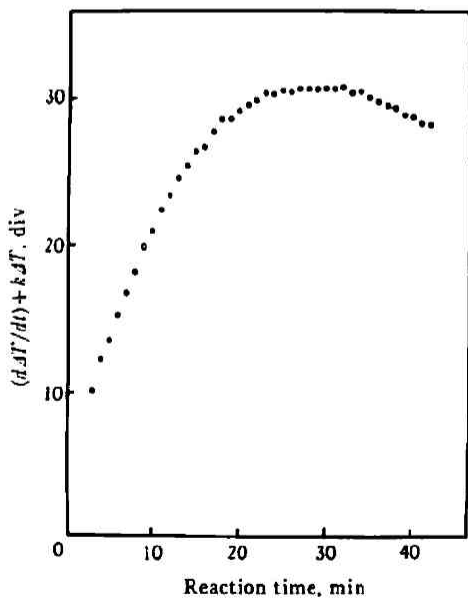[I]₀ = 3.28 × 10⁻² mol/kg,
[M]₀ = 5.05 mol/kg

Fig. 7   Change of $(d\varDelta T/dt)+k\varDelta T$ with time at
0° C, 2000 kg/cm²
[I]₀ = 4.23 × 10⁻² mol/kg,
[M]₀ = 5.43 mol/kg

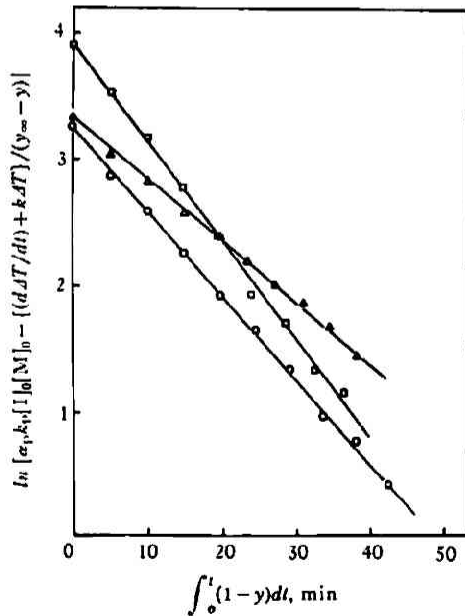

Fig. 8   Plots of equation (4) at various pressures
△: 40 kg/cm², ○: 1000 kg/cm², □:
2000 kg/cm²

Table 1   Numerical values of k_i and k_p for the cationic polymerization of THF initiated by $EtO^+BF_4^-$ in CH_2Cl_2 at high pressure (0° C)

Pressure, kg/cm²	k_i, kg/mol min[a]	k_p, kg/mol min
1 atm	9.2×10^{-3}[3]	0.23[3]
		0.097 (for ion pair)[4]
		0.69 (for free ion)[4]
40	9.60×10^{-3}	0.148
1000	1.18×10^{-2}	0.228
2000	1.29×10^{-2}	0.299

$[M]_0 = 5.05 - 5.49$ mol/kg, $[I]_0 = 2.83 \times 10^{-2} - 5.87 \times 10^{-2}$ mol/kg

a) $k_i = ln\{[I]_0/[I]\}\{\int_0^t [M]dt\}^{-1}$

Once k_p is determined, the left hand side of equation (4) can be plotted against $\int_0^t (1-y)dt$.

The value of k_p giving a good linearlity of the plot, and consistent with the calculated value from the intercept was found by the trial and error. The value of k_i was determined from the slope. The plots thus obtained at 40, 1000 and 2000 kg/cm² are shown in Fig. 8. The values of the rate constants are given in Table 1. The rate constants at 40 kg/cm² were close to the values reported by other workers at 1 atm[2-4].

Effect of pressure

The kinetic studies of cationic polymerization at high pressure are, to the authors' knowledge.
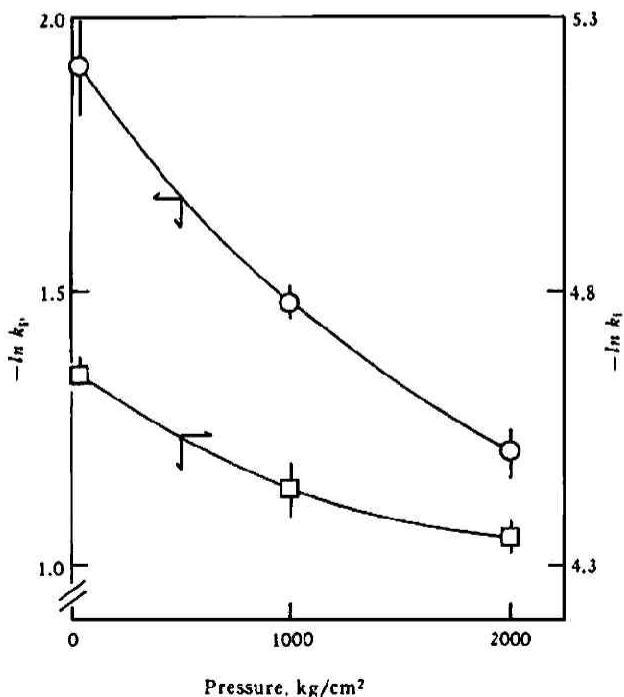

Fig. 9   The effect of pressure on k_i and k_p.

only on the systems of styrene initiated by perchloric acid[9] and isoamyl vinyl ether by iodine[10], where the activation volume is -20 to -25 cm²/mol and -22 to -25 cm³/mol, respectively. Those large negative volumes of activation were considered to arise from the strong electrostriction around the highly polar transition state compared with the initial one.

The activation volumes which were calculated based on the pressure dependences of k_i and k_p which were shown in Fig. 9, were -5.0 ± 1.9 and -10.5 ± 2 cm³/mol for the initiation and propagation steps, respectively, in the region from 40 to 1000 kg/cm³, and -2.1 ± 2 and -6.4 ± 1.5 cm³/mol in the region from 1000 to 2000 kg/cm². Those values are considerably more positive than those of vinyl compounds.

The volume of activation for the initiation reaction seems to be reasonably understood, taking into account that the initiaton is a type of ionic exchange reaction, because the values so far reported for the ionic exchange reactions are in the range $-5\sim-13$ cm³/mol[11].

The propagation of polymerization of THF can be regarded to proceed by a S_N2 mechanism in which THF acts as a nucleophile attacking the α-carbon atoms of propagating oxonium ion. Matyjaszewski et al. studied the rate of polymerization of THF as a function of dielectric constant D in THF/CCl₄ mixtures and obtained the following relationship[12];

$$k_p=1.78\times10^{-2}\exp\{4.9/D\}.$$

The contribution of electrostriction term ΔV_{el}^{*} to the activation volume can be estimated from the equation,

$$\Delta V_{el}^{*}=(RT/D^2)\{\partial ln k_p/\partial(1/D)\}_{P,T}(\partial D/\partial P)_{T,\text{Comp}}.$$

Using Eckert's value for $\partial D/\partial P$[13], we found $\Delta V_{el}^{*}=+1.5$ cm³/mol which is unimportant for this reaction as usually pointed out for S_N2 reactions[11]. Therefore, the volume loss -10.5 ± 2 cm³/mol may arise mainly from the structural term.

The volume change for the polymerization (Fig. 2) was -7.9 cm³/mol at 0° C and 1 atm, and so the activation volume for the depropagation reaction was calculated to be -2.6 ± 2 cm³/mol. The depropagation reaction occurs by a nucleophilic attack by the penultimate oxygen atom followed by the expulsion of monomer. Therefore, we should expect a greater decrease in volume than this. It seems likely that the formation of empty space in the middle of the ring in the transition state partly compensates the decrease of volume that occurs when the transition state is formed, as discussed in the acid-catalyzed lactonization of γ-hydroxybutyric acid[14].
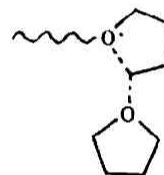
9) A. A. Zharov, A. A. Bellin and N. S. Enikolopyan, *J. Polymer Sci.*, C16, 2313 (1967)

10) S. D. Hamann and D. R. Teplitzky, *J. Phys. Chem.*, 65. 1654 (1961); S. D. Hamann, A. J. Murphy. D. H. Solomon and R. I. Willing, *J. Macromol. Sci.*, A6, 771 (1972)

11) R. S. Bradley, High Pressure Physics and Chemistry, vol. 2, Academic Press, 1963, Chap. 8.

12) K. Matyjaszewski, P. Kubisa and S. Penczek. *J. Polymer Sci., Polymer Chem.*, 13, 763 (1975)

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