2912 *Macromolecules* **1986**, *19*, 2912–2915

Kinetic and Electron Spin Resonance Studies on Radical Polymerization of Isopropenyl Acetate

Yoko Kuwae, Mikiharu Kamachi,* and Shun-ichi Nozakura

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan. *Received April 18, 1986*

ABSTRACT: An electron spin resonance (ESR) spectrum of the propagating radical in the photopolymerization of isopropenyl acetate (IpAc) in bulk at 32.5 °C was observed. The propagation rate constant k_p for the bulk polymerization of IpAc at 32.5 °C was determined to be 280 M^{-1} s^{-1} by ESR, comparable to that of methyl methacrylate (MMA). The cross propagation rate constants for the copolymerization of IpAc with MMA and with vinyl acetate (VAc) were estimated from k_p's for each monomer and the monomer reactivity ratios. The rate constants suggest that reactivities of IpAc and its propagating radical are large enough to give high-molecular-weight polymers in the homopolymerization. The chain-transfer constants to monomer (C_m's) for IpAc at three temperatures were determined by a Mayo plot to be 2 orders larger than that of VAc. The temperature dependence of C_m shows that the activation energy for the chain-transfer reaction is smaller than that for the propagation reaction, which was supported by ESR observation of allylic radical in the photoinitiated polymerization at −160 °C. The difficulty in preparing high-molecular-weight polymers from IpAc was concluded to be due to considerable chain-transfer reaction to monomer as compared with those of monomers which provide high-molecular-weight polymers. In addition, the temperature dependence of the ESR spectrum shows that the propagating radical has two stable conformations which rapidly interchange at room temperature.

Introduction

Several studies[1-4] have been published on the radical polymerization of isopropenyl acetate (IpAc), and most of them[1-3] have reported that high-molecular-weight polymer is not obtained under nitrogen. This phenomenon was explained by degradative chain transfer due to hydrogen abstraction of the propagating radical from the α-methyl group of the monomer. Bywater et al.,[4] however, reported high-molecular-weight polymer in the polymerization under high pressure, suggesting that the difficulty in forming high-molecular-weight polymer at atmospheric pressure is not due to degradative chain transfer but to a low propagation rate coupled with an effective depropagation. In order to make clear which factor is predominant, estimation of the propagation rate constant for IpAc and ESR observation of radicals should be attempted in the polymerization system.

We succeeded in observing ESR spectra of propagating radicals in the polymerization of some monomers at room temperature[5,6] and in estimating their rate constants by using an ESR spectrometer equipped with a TM_{110} cavity modified for photoreaction.[5] This ESR technique was applied to the polymerization of IpAc.

In this paper, we determine rate constants for the polymerization of IpAc, the chain-transfer constant to monomer, and monomer reactivity ratios in the copolymerization with VAc and with MMA and discuss the origin of the difficulty in the formation of high polymer. In addition, the ESR study on the polymerization system showed that the propagating radical has two stable conformations.

Experimental Section

IpAc was polymerized in bulk with benzoyl peroxide (BPO) or 2,2′-azobis(isobutyronitrile) (AIBN) under UV irradiation in an ESR spectrometer (Japan Electron Optics Laboratory Model JES-FE1X) with an ES-VT variable-temperature accessory, and ESR spectra were recorded. A TE_{011} mode cavity with a UV irradiation window was used for the measurement at −160 °C, and a TM_{110} mode cavity was employed for the measurements at various temperatures. A Spectrosil sample tube (5-mm i.d.) was used in the frozen state.

Specimens for the measurement were degassed by repeated melting and freezing under vacuum and sealed. The measurement with the TM_{110} cavity was carried out under nitrogen in a flat cell (35 mm × 30 mm, 1.0-mm thickness). The light source for photoinitiated polymerization was a 500-W, high-pressure mercury lamp (Ushio 500). The simulation spectrum was obtained with an EC-6 computer, where JEOL ESR simulation program 0398 was used. The radical concentration for estimating the propagation rate constant k_p was determined from the area under the integrated ESR spectrum by the use of the relation calibrated with the spectra for 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl of known concentrations dissolved in either the monomer or the mixture of the monomer and solvent. The polymerization rate R_p was estimated from the weight of the polymer isolated by removing monomer under vacuum after a given time of polymerization. Polymerizations for the Mayo plot were performed with AIBN at 50.3, 70.7, and 90.5 °C.

Table I
Bond Lengths and Bond Angles for the Poly(IpAc) Radical Model

bond	length, Å	bond angle	angle, deg
C–C	1.54	C–C–C	109.5
C–C·	1.37	C–$\dot{\mathrm{C}}$–C	120
C–H	1.10	O=C–CH_3	126
C=O	1.21	O–C–CH_3	111
·C–O	1.35	C–O–C	123
C–O	1.40		
C–OCH_3	1.49		

The degree of polymerization P_n was estimated from GPC measurement in THF with a Toyo Soda HLC-801A high-speed liquid chromatograph and was calibrated with polystyrene standards.

Copolymerizations of IpAc with MMA or VAc were performed with AIBN at 60 °C. Copolymer compositions were estimated by ^1H NMR analysis. In poly(IpAc-*co*-VAc), the relative ratio of the peak at 4.9–5.1 ppm, due to the methine proton of the VAc unit,[7] to that at 2.5 ppm, due to methylene proptons,[8] was used, and in poly(IpAc-*co*-MMA), the relative ratio of the area under the peak at 3.6 ppm, due to methoxy protons of the MMA unit,[9] to that at 1.2–2.5 ppm, due to the sum of methylene, acetoxy, and methyl protons, was used.

The monomer reactivity ratios were evaluated according to the Fineman–Ross method.

Isopropenyl acetate was purified by the conventional method.[10] MMA,[5] vinyl acetate,[11] AIBN,[7] and BPO[5] were purified as shown previously. Commercially available di-*tert*-butyl peroxide was purified by distillation, bp 50 °C (90 mmHg).

Calculation. The conformational energy calculation was carried out by taking into consideration the internal rotation, the nonbonded atomic interaction, and the electrostatic interaction.[12,13] The last two monomer units were adopted as a model of the propagating radical as shown in Figure 1. In the estimation of conformational angles, the planar zigzag trans conformation was defined as 180°. Table I shows the bond angles and bond lengths

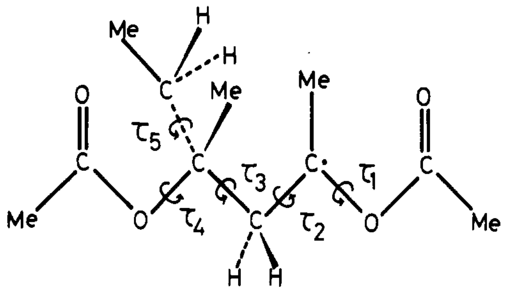

Figure 1. Schematic diagram of poly(IpAc) radical.

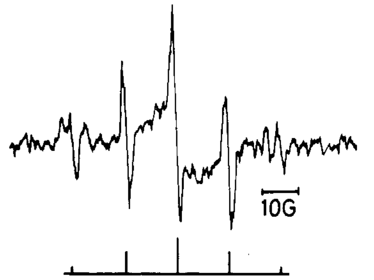

Figure 2. ESR spectrum of the bulk polymerization of IpAc at −160 °C. [Di-*tert*-butyl peroxide] = 1 × 10^{-1} M.

used for the calculation. The conformational energies were calculated by varying the parameters of five internal rotational angles at 5° intervals of τ_2 and 30° intervals of τ_1, τ_3, τ_4, and τ_5.

Results and Discussion

ESR Study on Polymerization Systems. Figure 2 shows the ESR spectrum obtained in the reaction of IpAc with di-*tert*-butyl peroxide at −160 °C. The ESR spectrum is composed of five lines with an equal spacing of 14.5 G. The intensity distribution is 1:4:6:4:1 and indicates that the radical has four equal protons and is attributed to the allylic radical ($CH_2{=\!=}\dot{C}(OCOCH_3){=\!=}CH_2$) obtained by hydrogen abstraction from the α-methyl group of IpAc. The spectrum due to the addition reaction of the *tert*-butoxy radical to IpAc was hardly observed. This fact might be ascribed to the high preference of the *tert*-butoxy radical for hydrogen abstraction to the addition reaction at −160 °C.

BPO, which is known to be less selective in hydrogen abstraction than di-*tert*-butyl peroxide,[14] was used as an initiator in the bulk polymerization system. The five-line spectrum was also observed. This result suggests that even the benzoyloxy radical reacts by hydrogen abstraction rather than by addition to the C=C bond of IpAc at −160 °C and that the double bond of IpAc is less reactive to radicals than that of methacrylic esters since only the propagating radical of methacrylic esters was observed under similar conditions.[15]

The ESR spectrum shown in Figure 3A was observed in the polymerization of IpAc at 32.5 °C with the TM_{110} cavity, which was specially designed for photoreactions.[5] This is the first example of an ESR spectrum obtained from photoinitiated polymerization of IPAc with di-*tert*-butyl peroxide in bulk at room temperature. Initiator concentration higher than 0.1 M was necessary for the detection of the ESR spectrum, because the molecular extinction coefficient of di-*tert*-butyl peroxide is less than 0.5 at 365 nm.[16] When the initiator concentration was less than 3 × 10^{-1} M, the ESR spectrum of the initiator radical was concealed in this spectrum. A similar spectrum was computer simulated as a doublet of doublets, due to magnetically inequivalent β-methylene protons, and a doublet of quartets, due to α-methyl protons, where the coupling constants are a_H = 15 G, a_H = 13.6 G, and $a_H^{CH_3}$ = 23 G, as shown in Figure 3B. Chiral radicals of the structures $X{-}CH_2{-}\dot{C}(Y)Z$, where X has an asymmetric center, would be expected in general to show magnetically β-methylene protons even if there were rapid rotation about the C_α–C_β bond.[17] Inequivalent hyperfine splitting constants of β-methylene protons has also been found in the ESR spectrum of poly(MMA) radical.[5,18] Therefore, the spectrum is reasonably attributed to the propagating radical of IpAc.[19] However, the intensity of the inner four lines, which are shown by arrows in Figure 3, of the observed spectrum (A) becomes weaker and broader as temperature decreases. The temperature dependence of the ESR spectrum was investigated to obtain information on the difference in the intensity distribution. The ESR spectra obtained at −20, −50, and −60 °C are shown in Figure 4. The relative intensity of the four lines decreases and becomes broader as temperature decreases. Other lines scarcely change with temperature. This phenomenon is ascribed to exchange broadening caused by dynamical interchange of β-methylene protons. The origin of the dynamical interchange of β-methylene protons is considered to be due to the presence of two stable conformations that can be interconverted by free rotation of the C_α–C_β bond, as discussed later.

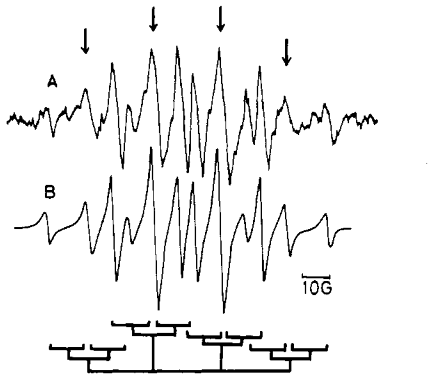

Figure 3. ESR spectra of the propagating radical of IpAc at 32.5 °C: (A) observed ESR spectrum; (B) simulated ESR spectrum. [Di-*tert*-butyl peroxide] = 1 × 10^{-1} M.

Table II
Temperature Dependence of P_n, R_p, and C_m for the Bulk Polymerization Initiated with AIBN

T, °C	10^2[initiator], M	10^4R_p, M s^{-1}	P_n	10^2C_m
90.5	2.0	1.4	17.3	3.7
	6.0	2.3	14.0	
	10	3.0	12.3	
70.7	2.0	0.46	18.8	4.6
	6.0	0.93	16.2	
	10	1.3	15.1	
50.3	2.0	0.12	15.0	5.7
	6.0	0.19	13.7	
	10	0.30	12.2	

Table III
Temperature Dependence of P_n for the Bulk Polymerization of IpAc Initiated with Benzoyl Peroxide[a]

polym temp, °C	P_n	polym temp, °C	P_n
90.5	9.4	50.3	8.1
70.7	9.3	30.0	7.4

[a] [Initiator] = 0.104 M.

Chain-Transfer Reaction. Polymerizations of IpAc were performed with AIBN or BPO at various temperatures. The results with AIBN are shown in Table II, indicating that polymerization rates increase with increasing temperature. The degree of polymerization P_n was not so sensitive to polymerization temperature, as shown in Ta-

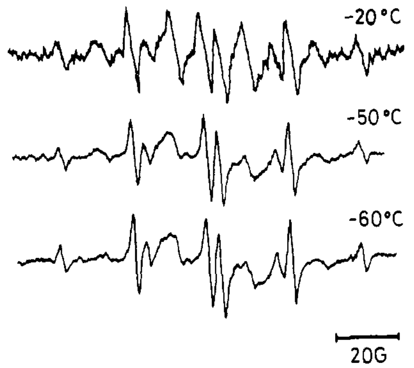

Figure 4. Temperature dependence of the ESR spectrum of poly(IpAc) radical. [Di-*tert*-butyl peroxide] = 1 × 10^{-1} M.

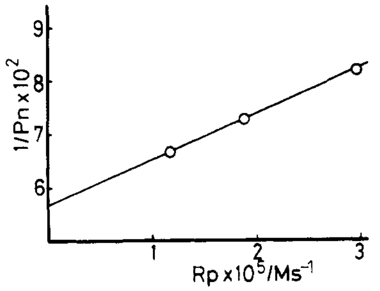

Figure 5. Mayo plot of IpAc at 50.3 °C. [AIBN] = 2 × 10^{-2}, 6 × 10^{-2}, and 1 × 10^{-1} M.

bles II and III. The chain-transfer constant C_m was determined in the bulk polymerization of IpAc with AIBN, because the chain-transfer constant to AIBN is known to be small enough to be neglected in the Mayo equation.[20] Figure 5 shows the Mayo plot at 50.3 °C, and similar linear relations were obtained at other temperatures. Usually, k_t depends considerably on the chain length of propagating radicals in the oligomer region, and hence it is probably difficult to obtain a straight line in the Mayo plot if P_n is varied over a wide range. The straight line shown in Figure 5 might be ascribed to the fact that P_n's of the oligomers obtained are of the same order. The intercept of the straight line provides C_m. C_m's at three temperatures are shown in Table II. The difference in activation energy between the chain-transfer and propagation reactions (E_{trm} and E_p) was estimated to be 2.6 kcal/mol by an Arrhenius plot. Since the reliability of P_n of the poly(IpAc) estimated from the GPC measurement on the basis of polystyrene standards is yet to be investigated, discussion on the absolute value of the activation energy is meaningless. However, since estimation of the order of magnitude of C_m is possible from the Mayo plot, the temperature dependence of C_m qualitatively shows that E_{trm} is smaller than E_p. Accordingly, the fraction of allylic radical is considered to increase as temperature decreases. This explains the ESR observation of allylic radical at −160 °C, because hydrogen abstraction reaction of free radicals from the α-methyl group of IpAc is preferred to the addition reaction at low temperature. As a result, it is concluded that the chain transfer to the monomer prevents formation of high-molecular-weight polymer.

Reactivity of Propagating Radicals. The ESR spectrum of the propagating radical of IpAc was observed at 32.5 °C by the ESR spectrometer equipped with the TM_{110}. k_p was approximately evaluated by the equation

$$R_p = -d[M]/dt = k_p[M\cdot][M] \qquad (1)$$

where [M] and [M·] are the concentrations of monomer and radical, respectively. When monomer chain transfer takes place to a considerable extent, k_p obtained by eq 1 includes a transfer term. However, since C_m for IpAc is of the order of 10^{-2}, k_p thus obtained can be reasonably regarded as k_p for IpAc. k_p for IpAc is shown in Table IV along with those for MMA and VAc estimated from the ESR technique.[5,6] k_p for IpAc is almost the same as that for MMA and about one-fifth that for VAc and is considered to be large enough to give high-molecular-weight polymers if the chain-transfer reaction does not take place. These facts seem to be in conflict with Bywater's proposal that a low propagation rate constant for IpAc limits the degree of polymerization.

Table IV
Propagation and Cross Propagation Rate Constants for Radical Polymerization and Copolymerizations of IpAc (M^{-1} s^{-1})

	monomer		
propagating radical	MMA	IpAc	VAc
MMA	190[a]	7.0	
IpAc	4700	280	380
VAc		420	1600[b]

[a] From ESR method.[5] [b] From ESR method.[6]

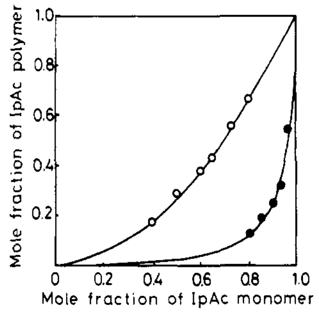

Figure 6. Copolymer composition curves of poly(MMA-*co*-IpAc) and poly(VAc-*co*-IpAc): (●) poly(MMA-*co*-IpAc); (○) poly(VAc-*co*-IpAc); (—) theoretical curve based on monomer reactivity ratios obtained by the Fineman–Ross plot.

To understand the radical reactivity of IpAc, we attempted to estimate the cross propagation rate constants for the copolymerizations of IpAc with VAc and MMA. Monomer reactivity ratios r_1 and r_2 have been previously estimated by selective saponification of the VAc unit in poly(VAc-*co*-IpAc) and of the IpAc unit in poly(MMA-*co*-IpAc).[1] However, large experimental errors are considered to be included in the ratios, because selective saponification is difficult in the copolymers. Alternatively, we estimated the ratios by NMR analysis of the copolymrs. Figure 6 shows the copolymer composition curves. The ratios for the copolymerization of IpAc (M_1) with VAc (M_2) were $r_1 = 0.74 \pm 0.042$ and $r_2 = 3.8 \pm 0.17$, and the ratios with MMA (M_2) were $r_1 = 0.059 \pm 0.013$ and $r_2 = 27.3 \pm 0.20$.

The cross propagation rate constants were estimated from r_1, r_2, and k_p for each monomer. Results are shown in Table IV, indicating that the poly(IpAc) radical is much more reactive than the poly(MMA) radical, and monomer reactivity of IpAc with free radical is almost the same as that of VAc. Therefore, the propagation of IpAc is considered to be large enough to yield high-molecular-weight polymers.

Conformation of the Propagating Radical. The ESR spectrum at 32.5 °C was reasonably simulated except for the relative intensity of the inner four lines as shown in Figure 3B. The discrepancy in the intensity of the four lines from the simulated spectrum was explained by exchange broadening due to interchange of β-methylene protons caused by interconversion of the propagating ends

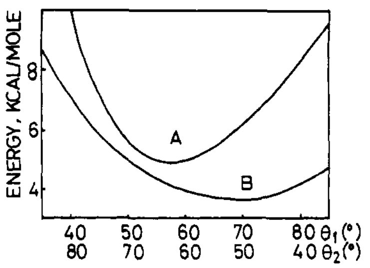

Figure 7. Conformational energy of the poly(IpAc) radical as a function of dihedral angle of the β-methylene protons.

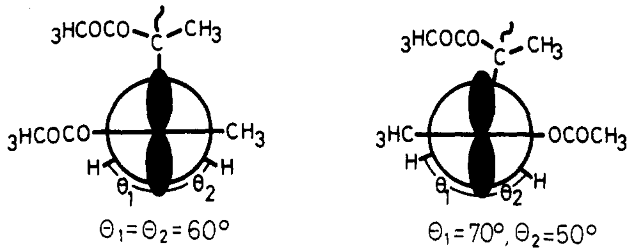

Figure 8. Two stable conformations of the poly(IpAc) radical.

between two conformations.[21]

To understand the conformation of the propagating radical, we carried out conformational energy calculations by the method previously reported for poly(MMA) radical.[13] The calculations supported the presence of two conformations, A ($\tau_1 = 60°$, $\tau_2 = 90°$, $\tau_3 = 60°$, $\tau_4 = 60°$, and $\tau_5 = 170°$) and B ($\tau_1 = 290°$, $\tau_2 = 280°$, $\tau_3 = 305°$, $\tau_4 = 180°$, and $\tau_5 = 70°$), shown in Figure 7. The dihedral angles of β-methylene protons with a p-orbital of unpaired electrons estimated from the value of τ_2 were $\theta_1 = 60°$ and $\theta_2 = 60°$ for conformation A and $\theta_1 = 70°$ and $\theta_2 = 50°$ for conformation B, as shown in Figure 8. Since conformation B is more stable than conformation A (Figure 7), the weighted mean of the two conformations is considered to be closer to conformation B than conformation A. However, angles estimated from the splitting constant of the β-methylene protons by using

$$a_H = 58.6 \cos^2 \theta \qquad (2)^{22}$$

are $\theta_1 = 61°$ and $\theta_2 = 59°$, closer to conformation A than conformation B. This discrepancy between observed and calculated values is probably due to the fact that the choice of bond lengths and bond angles for the conformational analysis may not be best because of a lack of a detailed study on the bond angles and bond lengths of poly(IpAc) and that no intermolecular interaction between the radical and solvents is taken into account in the conformational analysis. Consequently, the conformational analysis qualitatively shows that there are two stable conformations in which the dihedral angles of β-methylene protons with a p-orbital of unpaired electrons are different. The temperature dependence of the ESR spectra shown in Figure 4 can be reasonably explained by taking the two conformations into account: the rate of the interconversion due to the free rotation of the C_α–C_β bond between the two conformations decreases as temperature decreases, and hence the reciprocals of the lifetimes of the two conformations become closer to the difference in the hyperfine splitting constants of each β-methylene proton as temperature decreases from 32.5 to −60 °C.

In conclusion, kinetic study and ESR measurement of the polymerization of IpAc show that the difficulty in forming high polymers is not due to small k_p but to large C_m as compared with those of conventional monomers such as MMA and VAc. The temperature dependence of the ESR spectrum of the propagating radical of IpAc indicates that the propagating radical has two stable conformations which can interchange at room temperature. The presence of two conformations was supported by conformational analysis.

Registry No. IpAc, 108-22-5; MMA, 80-62-6; VAc, 108-05-4.

References and Notes

(1) Hart, R.; Smets, G. *J. Polym. Sci.* **1950**, *5*, 55.
(2) Gaylord, N. G.; Einrich, F. R. *J. Polym. Sci.* **1950**, *5*, 74.
(3) Gaylord, N. G.; Einrich, F. R. *J. Am. Chem. Soc.* **1952**, *74*, 337.
(4) Bywater, S.; Whalley, E. *ACS Symp. Ser.* **1960**, *10*, 22.
(5) Kamachi, M.; Kohno, M.; Kuwae, Y.; Nozakura, S. *Polym. J. (Tokyo)* **1982**, *14*, 749.
(6) Kamachi, M. *Adv. Polym. Sci.*, in press.
(7) Hatada, K.; Terawaki, Y.; Kitayama, T.; Kamachi, M.; Tamaki, M. *Polym. Bull. (Berlin)* **1981**, *4*, 451.
(8) Matsuzaki, K.; Kawamura, T.; saito, K. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 253.
(9) Braun, D.; Herner, M.; Johnsen, U.; Kern, W. *Makromol. Chem.* **1962**, *51*, 15.
(10) Ibonai, M.; Kato, T.; Yamashita, Y. *Kogyo Kagaku Zasshi* **1964**, *67*, 1068.
(11) Kamachi, M.; Liaw, D. J.; Nozakura, S. *Polym. J. (Tokyo)* **1979**, *11*, 921.
(12) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley: New York, 1979; pp 323–353.
(13) Kamachi, M.; Kuwae, Y.; Nozakura, S.; Hatada, K.; Yuki, H. *Polym. J. (Tokyo)* **1981**, *13*, 919.
(14) Hefter, H. J.; Hecht, T. A.; Hammond, G. S. *J. Am. Chem. Soc.* **1972**, *94*, 2793.
(15) Kamachi, M.; Kohno, M.; Liaw, D. J.; Katsuki, S. *Polym. J. (Tokyo)* **1978**, *10*, 69.
(16) Calvert, J. G.; Pitt, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; pp 447, 449.
(17) (a) Gilbert, B. C.; Larkin, J. P.; Norman, R. P. O. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1272. (b) Henderson, W. *Chem. Soc. Rev.* **1973**, *2*, 397.
(18) Smith, P.; Stevens, D. *J. Phys. Chem.* **1972**, *76*, 3141.
(19) Takahura, K.; Ranby, B. *J. Polym. Sci., Part A-1*, **1970**, *8*, 77.
(20) Brandrup, J.; Immergut, E. H., Eds.; *Polymer Handbook*, 2nd ed.; Wiley: New York, 1975; p II-98.
(21) Wertz, J. E.; Bolton, J. *Electron Spin Resonance: Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972; pp 192–222.
(22) (a) Fischer, H. *Z. Naturforsch., A* **1964**, *19a*, 866. (b) Fessenden, R. W.; Schuler, R. H. *J. Chem. Phys.* **1963**, *39*, 2147.