made possible the determination of the rate constants of the elementary steps.

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Determination of Rate Constants of Free-Ion and Paired-Ion Propagations in the Cationic Polymerization of Styrene by Trifluoromethanesulfonic Acid[1]

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ABSTRACT: The propagation step of the cationic polymerization of styrene was studied in detail with the CF_3SO_3H initiator in dichloroethane at −1 to 30 °C. The apparent rate constant of propagation $k_{p,app}$ was estimated from the time course of the carbocation (P^+) formation and monomer consumption by the combination of stopped-flow spectroscopy and the rapid quenching technique. Then $k_{p,app}$ was separated into the rate constants of the free-ion and paired-ion propagations ($k_p{}^+$ and $k_p{}^\pm$) on the basis of the dependence of $k_{p,app}$ on $[P^+]$ and of the effect of a common ion salt. The values of $k_p{}^+$ and $k_p{}^\pm$ were (2–30) × 10^5 M^{-1} s^{-1} and (0.4–1.2) × 10^5 M^{-1} s^{-1}, respectively, in the temperature range studied. The ratio $k_p{}^+/k_p{}^\pm$ was 6–24, which is much smaller than those observed for the anionic polymerization.

The propagating species in the cationic vinyl polymerization may be composed of the free and paired carbocations. Although the exact nature of the propagating species has been established in the living anionic polymerization of vinyl monomers,[2] similar analyses were almost impossible in the cationic polymerization, because direct determination of the propagating carbocation could not be done. In recent years, however, direct analyses of the propagating cation were rendered possible in the polymerization of styrenes by stopped-flow/rapid-scan spectroscopy.[3-10] We described in the preceding paper[10] the determination of the rate constant of the elementary steps (initiation, propagation, chain transfer, and termination) in the cationic polymerization of styrene by trifluoromethanesulfonic acid as studied by stopped-flow/rapid-scan spectroscopy and by the rapid quenching (flow) technique.

As a next step, we conducted a detailed analysis of the propagating process and report the results in this paper. The rate constant of propagation for the free and paired cations could be separated on the basis of the effect of a common ion salt and of the rate dependence on the concentration of the propagating species.

Experimental Section

Materials and the polymerization procedure are described in the accompanying paper in detail.[10] The reaction was followed by a stopped-flow/rapid-scan spectrophotometer (Union Giken Co., Model RA 1300). The stopped-flow and flow (quenching) studies were carried out in the same apparatus by using a special attachment RA 416.

Results and Discussion

Determination of the Apparent Rate Constant of Propagation. It is established in the cationic polymeri-

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Table I
Apparent Rate Constant of Propagation

polym temp, °C	$[CF_3SO_3H]$, mM	[styrene], M	$10^5[P^+]_{max}$, M	$10^5[P^+]_{const}$,[a] M	$10^{-5}k_{p,app}$,[b] $M^{-1}\ s^{-1}$	$10^{-5}k_{p,app}$,[c] $M^{-1}\ s^{-1}$
−1	2.9	0.397	11.1	9.0	0.52	0.57
10	2.4	0.391	6.72	6.3	0.89	1.1
20	5.4	0.305	19.9	20	1.4	1.7
30	5.3	0.397	6.61	6.6	2.0	2.2

[a] $[P^+]$ value as averaged over a period where $[P^+]$ is fairly invariable (in the region of $[P^+]_{max}$) and used for determination of $k_{p,app}$ from eq 4. [b] Determined by eq 3. [c] Determined by eq 4.

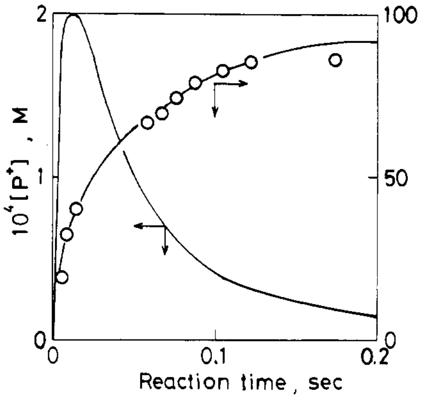

Figure 1. Time course of the formation of styryl cation and conversion. Polymerization conditions: 20 °C; dichloroethane solvent; $[CF_3SO_3H]$ = 5.4 mM; [styrene] = 0.305 M.

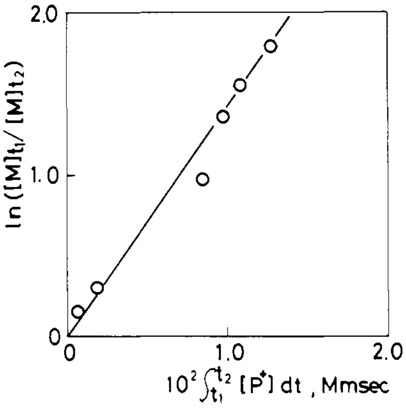

Figure 2. Plots of the data of Figure 1 according to eq 8.

zation of styrene by the CF_3SO_3H initiator that the initiation and propagation steps can be represented simply as follows:[7] initiation

$$CF_3SO_3H + CH_2{=}C(Ph)H \xrightarrow{k_i} CH_3C(Ph)H^+\ CF_3SO_3^- \quad (1)$$

propagation

$$\sim CH_2C(Ph)H^+\ CF_3SO_3^- + CH_2{=}C(Ph)H \xrightarrow{k_{p,app}} \sim CH_2C(Ph)HCH_2C(Ph)H^+\ CF_3SO_3^- \quad (2)$$

The $k_{p,app}$ value can be readily estimated from the concentration of the propagating cation $[P^+]$ and the monomer consumption from either of the following equations.

$$\ln([M]_{t_1}/[M]_{t_2}) = k_{p,app}\int_{t_1}^{t_2}[P^+]\,dt \quad (3)$$

$$\ln([M]_{t_1}/[M]_{t_2}) = k_{p,app}[P^+]\Delta t \quad (4)$$

where $\Delta t = t_2 - t_1$.

Equation 4 was applied to the steady polymerization where the absorbance at 340 nm ($[P^+]$) is constant with that in stopped-flow spectra. Equation 3 was used instead when $[P^+]$ was not constant. The molar extinction coefficient of the polystyryl cation has been assumed to be $1 \times 10^4\ M^{-1}\ cm^{-1}$.[7] It is assumed in this paper that the molar extinction coefficient is constant irrespective of whether the propagating cation is free or paired, in the absence of evidence to the contrary.

The procedures for the determination of $k_{p,app}$ are as follows. Figure 1 shows an example of the variations of the propagating species and the conversion with time. $[P^+]$ was graphically integrated between a given starting time (t_1) and the quenching time (t_2), and eq 3 was applied to these data to give a fairly satisfactory linear relation which passes through the origin, as shown in Figure 2. $k_{p,app}$ was determined from the slope to be $1.4 \times 10^{+5}\ M^{-1}\ s^{-1}$. On the other hand, there is a region of $[P^+]$ = constant near its maximal value (t_1 = 10 ms and t_2 = 15 ms), and eq 4 can be used in this region. $k_{p,app}$ thus determined from the data of Figure 1 is $1.7 \times 10^{+5}\ M^{-1}\ s^{-1}$. These two values are quite close. Table I compares the $k_{p,app}$ values determined by these two methods at four different temperatures at given concentrations of initiator and monomer.

Free-Ion and Paired-Ion Propagations. The propagating species may be a free ion or an ion pair in the cationic polymerization of styrene

$$\begin{array}{ll} P^+\ CF_3SO_3^- \xrightarrow[\text{monomer}]{k_p^{\pm}} & \\ \text{ion pair} & \\ \quad \Big\uparrow\!\Big\downarrow K_d & (5) \\ P^+ + CF_3SO_3^- \xrightarrow[\text{monomer}]{k_p^{+}} & \\ \text{free ion} & \end{array}$$

where K_d is the dissociation constant of the propagating ion pair, and k_p^+ and $k_p^{\pm}$ denote the rate constant of the free-ion and paired-ion propagations, respectively.

The ion-pair species may be further divided into the contact and solvent-separated varieties. However, the detailed characterization of the paired polystyryl cation is not yet possible, and these two species, if present, are not discriminated in this study. The kinetic treatment of the free-ion and paired-ion propagations has been established in the anionic polymerization. Thus, the same procedure was used in the present system. The apparent rate constant of propagation is then given by

$$k_{p,app} = (1 - x)k_p^{\pm} + xk_p^{+} \quad (6)$$

where x is the fraction of the free cation. Then

$$K_d = \frac{[P^+]_{free}[CF_3SO_3^-]_{free}}{[P^+CF_3SO_3^-]} = \frac{[P^+]^2_{free}}{[P^+CF_3SO_3^-]} = \frac{x^2[P^+]}{(1-x)} \quad (7)$$

If $x \ll 1$,

$$K_d = x^2[P^+] \quad (8)$$

$$\therefore\ x = (K_d/[P^+])^{1/2} \quad (9)$$

Substitution of eq 9 from eq 6 gives

$$k_{p,app} = k_p^{\pm} + k_p^{+}K_d^{1/2}/[P^+]^{1/2} \quad (10)$$

Table II
Dependence of $k_{p,app}$ on $[P^+]_{const}$

polym temp, °C	no. of runs	range of $[CF_3SO_3H]_0$, mM	range of $[styrene]_0$, M	$10^5[P^+]_{const}$, M	$10^{-5}k_p^{\pm}$, $M^{-1}\ s^{-1}$	$k_p^+K_d^{1/2}$
−1	4	2.9-9.8	0.305-0.397	9.0-9.5	0.40	160
10	3	2.4-12	0.305-0.397	1.2-5.9	0.73	124
20	4	3.8-7.1	0.266-0.397	0.12-0.25	0.6-0.8	600-800
30	4	2.8-5.8	0.315-0.397	0.062-0.17	1.1	1040

Table III
Effect of a Common Ion Salt on $k_{p,app}$[a]

$10^4[Bu_4N^+CF_3SO_3^-]$, M	10^4cz, M	$10^{-5}k_{p,app}$, $M^{-1}\ s^{-1}$
0.50	0.34	0.55
0.69	0.43	0.51
1.12	0.60	0.50
4.98	1.2	0.47

[a] Polymerization conditions: −1 °C, dichloroethane solvent, $[CF_3SO_3H]_0 = 5.5$ mM, $[styrene]_0 = 0.397$ M.

The stopped-flow study was then carried out with varying concentrations of CF_3SO_3H and styrene. The $k_{p,app}$ value decreased with increasing $[P^+]$.

Figure 3 shows the relation of $k_{p,app}$ and $[P^+]$ plotted according to eq 10. Linear relations were obtained for the data at all temperatures, and the $k_p^{\pm}$ and $k_p^+K_d^{1/2}$ values were estimated from the intercept and the slope, respectively. The results are summarized in Table II.

The k_p^+ and $K_d^{1/2}$ terms cannot be separated from these data alone. Therefore, the effect of a common ion salt was investigated in the subsequent experiments. Tetra-*n*-butylammonium trifluoromethanesulfonate was used as the common ion salt.

The dissociation constant K_B of the ammonium salt is estimated to be (5–7) × 10^{-5} M in the temperature range of 0–30 °C in dichloroethane solvent.[11]

$$n\text{-}Bu_4N^+\ CF_3SO_3^- \overset{K_B}{\rightleftharpoons} n\text{-}Bu_4N^+ + CF_3SO_3^- \quad (11)$$

$$K_B = \frac{[n\text{-}Bu_4N^+][CF_3SO_3^-]}{[n\text{-}Bu_4N^+CF_3SO_3^-]} \quad (12)$$

$$K_B = cz^2/(1 - z) \quad (13)$$

where c is the total concentration of the common ion salt and $z = [CF_3SO_3^-]/[Bu_4N^+CF_3SO_3^-]$.

Since $z > 0$, the following equation obtains

$$cz = \tfrac{1}{2}\{(K_B^2 + 4K_Bc)^{1/2} - K_B\} \quad (14)$$

Then the cz value can be estimated using K_B and c.

When the common ion salt is added to the polymerization system, two equilibria (eq 5 and 11) hold at the same time. If $x \ll 1$ in eq 6 and 8 and $K_B \gg K_d$, the total concentration of the propagating cation is nearly equal to the concentration of the paired propagating ion (i.e., $[P^+] \simeq [P^+CF_3SO_3^-]$), and the concentration of the free trifluoromethanesulfonate is nearly equal to cz. Using eq 7,

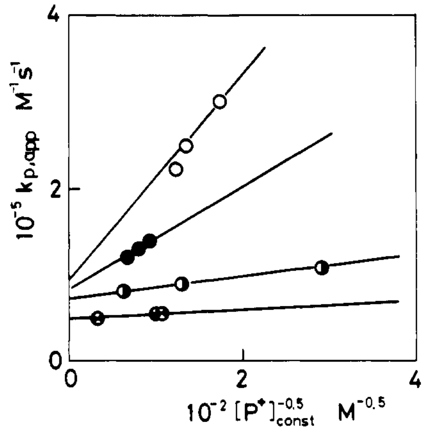

Figure 3. Dependence of $k_{p,app}$ on $[P^+]$. Plotted according to eq 10: ○, 30 °C; ●, 20 °C; ◑, 10 °C; ⊖, -1 °C.

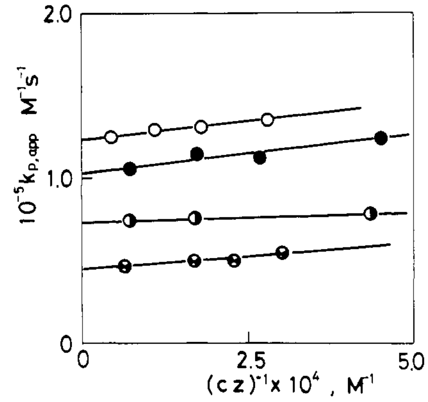

Figure 4. Effect of common ion salt on $k_{p,app}$. Plotted according to eq 16: ○, 30 °C; ●, 20 °C; ◑, 10 °C; ⊖, -1 °C.

$$x = \frac{[P^+]_{free}}{[P^+CF_3SO_3^-]} = \frac{K_d}{[CF_3SO_3^-]_{free}} = \frac{K_d}{cz} \quad (15)$$

From eq 6 and 15,

$$k_{p,app} = k_p^{\pm} + k_p^+(K_d/cz) \quad (16)$$

Table III shows the effect of addition of the common ion salt on $k_{p,app}$ at the polymerization temperature of −1

Table IV
Rate Constants Obtained from the Effect of a Common Ion Salt[a]

polym temp, °C	no. of runs	$[CF_3SO_3H]$, mM	[styrene], M	$10^{-5}k_p^{\pm}$, $M^{-1}\ s^{-1}$	$k_p^+K_d$, s^{-1}	10^5K_B, M
−1	3	5.5	0.397	0.47	0.25	7.0
10	3	3.8	0.397	0.75	0.081	6.0
20	3	4.5	0.397	1.0	0.44	5.5
30	3	5.3	0.315	1.2	0.57	5.0

[a] Common ion salt added, 0.017-1.2 mM.

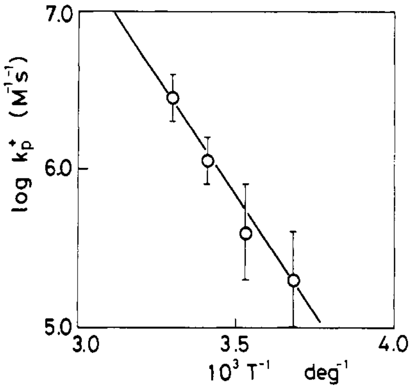

Figure 5. Arrhenius plots for the free-ion propagation.

Table V
Kinetic Constants of Propagation

polym temp, °C	$10^{-5}k_p^{\pm}$, $M^{-1}\ s^{-1}$	$10^{-5}k_p^{+}$, $M^{-1}\ s^{-1}$	10^7K_d, M	$k_p^+/k_p^{\pm}$
−1	0.43 ± 0.04	2.5 ± 1.5	16 ± 7	6
10	0.74 ± 0.05	5.1 ± 3.2	2.8 ± 1.7	7
20	1.0 ± 0.2	12 ± 4	4.2 ± 1.3	12
30	1.2 ± 0.2	29 ± 7	2.1 ± 0.5	24

°C. The *cz* value increases, and $k_{p,app}$ decreases with increasing amounts of the common ion salt added. These data are plotted according to eq 16 as shown in Figure 4 to give a linear relation. Similar plots are given for the data at other temperatures. The $k_p^{\pm}$ and $k_p^+K_d$ values are obtained from the intercept and the slope, respectively, and the results are summarized in Table IV. The $k_p^{\pm}$ values obtained by the use of the common ion salt effect (Table IV) are generally in good agreement with those obtained from the variation of the concentration of the propagating cation (Table II); e.g., 4.7×10^4 $M^{-1}\ s^{-1}$ vs. 4.0×10^4 $M^{-1}\ s^{-1}$ at −1 °C.

The k_p^+ and K_d values were then separated by using the $k_p^+K_d^{1/2}$ and $k_p^+K_d$ values given in Tables II and IV. Table V contains the k_p^+ and $k_p^{\pm}$ values thus determined. The $k_p^{\pm}$ value is given as averages of those obtained by the two different methods. The experimental error for $k_p^{\pm}$ is estimated to be less than 20%, but that for k_p^+ is much larger (50–100%) because the fraction of free ion is small under the polymerization conditions used.

Activation Parameters. The Arrhenius plots for k_p^+ and $k_p^{\pm}$ data are shown in Figures 5 and 6, respectively. Since the experimental errors for the rate constants of propagation are large, the Arrhenius plots can give only crude estimations of the activation parameter. The results are given in Table VI. It is curious that the activation energy for the free-ion propagation is much larger than that for the ion-pair propagation. The free-ion propagation is faster than the ion-pair propagation because of the greater frequency factor in the former. Lorimer and Pepper[5] reported that the activation energies for the free-ion and ion-pair propagations ($HClO_4$ initiator) are 1 and 4 kcal/mol, respectively. These values are much smaller than those obtained in the present study. We do not have an appropriate explanation for this discrepancy at the moment.

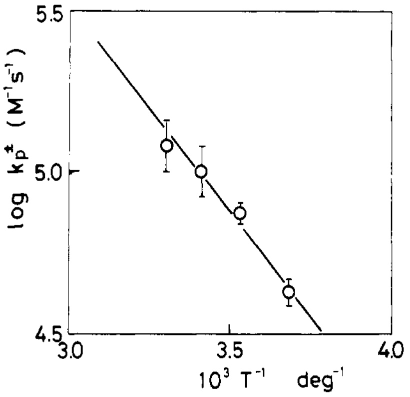

Figure 6. Arrhenius plots for the paired-ion propagation.

Comparisons of Rate Constants of Propagation. In Table VI are compared the rate constants of styrene propagation obtained in various polymerization systems. First of all, the k_p^+ value obtained at 30 °C in the present system is quite close to the k_p value obtained in the radiation polymerization of bulk styrene at 25 °C,[13] 3×10^6 vs. 2.4×10^6 $M^{-1}\ s^{-1}$. These values are larger than that of the free anion propagation. Previously, the propagation rate of the styryl cation was estimated to be rather small under similar conditions. For example, Pepper and coworkers reported in their classical papers[14,15] that the overall rate constant was 500–1000 $M^{-1}\ s^{-1}$ at 25 °C in dichloroethane with H_2SO_4 or $HClO_4$ initiators. Apparently, these small values arise from the overestimation of the concentration of the propagating species. More recently, Lorimer and Pepper[5] gave a k_p^+ value of 2×10^4 $M^{-1}\ s^{-1}$ at −80 °C in the $HClO_4$–CH_2Cl_2 system based on the stopped-flow study. Thus, we conclude that the propagation rate of styrene is truly large.

The $k_p^{\pm}$ value obtained in this study (1.0×10^5 $M^{-1}\ s^{-1}$ at 20 °C) is close to that (2.6×10^4 $M^{-1}\ s^{-1}$ at 20 °C) which was estimated by extrapolation of the data of Lorimer and Pepper obtained at −60 to −80 °C.[5]

It is interesting that the ratio of rate constants of the free-ion and paired-ion propagation $k_p^+/k_p^{\pm}$ is in the range of 6–24. Although these ratios are close to those obtained by Pepper ($k_p^+/k_p^{\pm}$ = 10–20) with the $HClO_4$ initiator, they are much smaller than those (200–10 000) estimated in the anionic polymerization.[16] In general, the counterion is larger and less specifically solvated in the cationic polymerization than in the anionic polymerization, hence there is less influence of the counterion on the reactivity of the propagating ion in the former.

Table VI
Rate Constants of Styrene Propagation

propagating species	counterion	solvent	temp, °C	k_p, $M^{-1}\ s^{-1}$	E_p, kcal/mol	log A_p	ref
paired cation	$CF_3SO_3^-$	$(CH_2Cl)_2$	30	1×10^5	5	9	this work
free cation	(CF_3SO_3H)	$(CH_2Cl)_2$	30	3×10^6	14	16	this work
free cation	$(HClO_4)$	CH_2Cl_2	−80	2×10^4	ca. 1		5
paired cation	ClO_4^-	CH_2Cl_2	20	2.6×10^4	2.7		5
paired cation	ClO_4^-	CH_2Cl_2	−80	2×10^3	ca. 4		5
free cation	(radiation)	bulk	25	2.4×10^6	2.2 ± 1.1	8.0 ± 1.1	13
paired anion	Cs^+	THF	25	21	5.35	5.7	16
free anion		THF	25	6.4×10^4	5.9	9.1	16

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(11) According to Sherrington,[12] the ion-pair dissociation constant K_B of quaternary ammonium hexachloroantimonates is virtually independent of the chain length of the alkyl substituent: K_B(average) = 7.3×10^{-5} M at 0 °C in CH_2Cl_2. The change of the anion also affects little the K_B value: $K_B = 4.1 \times 10^{-5}$ M for trimethylanilinium perchlorate at 25 °C in dichloroethane. Thus K_B for $(n\text{-Bu})_4N^+CF_3SO_3^-$ was estimated to be 7×10^{-5} M (0 °C, dichloroethane). Somewhat smaller K_B values were assumed at higher temperatures (10–30 °C), as given in Table IV. However, the K_B variation of this extent does not significantly alter $k_p^{\pm}$ and $k_p^{+}K_d$ values.
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Polypropylene Oxidation: The Apparent Rate Constant for Peroxy Radical Termination and the Photoinitiation Efficiency[‡]

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ABSTRACT: The decay of peroxy radicals in a series of photooxidizing polypropylene films upon cessation of irradiation has been examined, using electron spin resonance spectroscopy. Rate constants for peroxy radical termination of 1–8 $M^{-1}\ s^{-1}$ have been observed. The efficiency of the initiation process has been found to be $\sim 10^{-3}$ by using these data and a knowledge of the rate of radical generation during irradiation. The significance of these very low termination constants and initiation efficiencies is discussed in terms of the low mobility of polymeric peroxy radicals in a polymer matrix.

There is considerable interest in the values of the rate constants associated with the autoxidation of solid polypropylene (PPH).[1-7] A recent critical review by Mayo[1] has rationalized much of the published literature on the rate constants k_p and $2k_t$ for the propagation and termination of polymeric tertiary peroxy radicals ($PPO_2\cdot$) (reactions 1 and 2). However, the work reviewed depends upon the

$$PPO_2\cdot + PPH \xrightarrow{k_p} PPOOH + PP\cdot \qquad (1)$$

$$PPO_2\cdot + PPO_2\cdot \xrightarrow{2k_t} \text{nonradical products} \qquad (2)$$

use of appreciable concentrations of thermal initiators (with their associated compatibility and plasticization problems) and/or free-radical scavengers which may not give a valid estimation of the important propagating radicals.[8] We report here some observations concerning the decay in peroxy radical concentration that occurs in a photooxidizing PPH film sample upon cessation of irradiation, essentially as described by Roginskii et al.[3,5] The rate of decay gives $2k_t$ directly, and when this is combined with a knowledge of the radical concentration and the rate of radical generation during irradiation it also gives the efficiency of macroperoxy radical production during the initiation step. The advantage of this method of determining kinetic parameters is that as well as being experimentally simple and direct it also allows rate constants to be determined under near normal photooxidation conditions without the use of additional initiators or radical scavengers.

Isotactic polypropylene film (Enjay, chill-roll cast, 25 μm thick, Soxhlet extracted with acetone and vacuum dried) was irradiated in a xenon arc Weather-Ometer.[9] Samples (~100 mg) were removed at chosen irradiation times and inserted, tightly rolled, into electron spin resonance (ESR) tubes. In this way ESR spectra could be obtained from uniformly irradiated film samples within 5 min of the end of irradiation. Radical concentrations were estimated by double integration of the ESR signals and comparison with a standard (4-oxo-2,2,6,6-tetramethylpiperidine-*N*-oxyl). A typical ESR spectrum is shown in Figure 1 and corresponds well to that of a peroxy radical in a polymer matrix.[3,6,7] The decay of the ESR signal was then followed for several hours at 25 °C in the cavity of the spectrometer. Hydroperoxide concentrations were measured by infrared spectroscopy.[9]

From a comparison of the spectral intensity distribution of the output of the Weather-Ometer under our operating conditions with the absorption spectrum of the hydroperoxide chromophore, we have previously determined that the rate of radical production by hydroperoxide photolysis (the dominant photoinitiation process[10]) is given by eq 3.

$$PPOOH \xrightarrow{h\nu} PPO\cdot + \cdot OH \xrightarrow{PPH/O_2} 2PPO_2\cdot \qquad (3a)$$

$$d[PPO_2\cdot]/dt = 0.6 \times 10^{-5} f[PPOOH] \qquad (3b)$$

[PPOOH] is the molar hydroperoxide concentration and f is the efficiency of generating propagating peroxy radicals from the hydroperoxide cleavage. For 50% crystalline isotactic PPH, only the amorphous phase is assumed to oxidize so that all concentrations quoted are twice those determined experimentally for the film as a whole. A primary quantum yield of 2 for radical production from

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