Radiation-Induced Polymerization of Tetrahydrofuran by Diphenyliodonium and Triphenylsulfonium Hexafluorophosphates

Xiao-Hua Ma, Yukio Yamamoto,* and Koichiro Hayashi

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan. *Received April 24, 1987*

ABSTRACT: Cationic polymerization of tetrahydrofuran (THF) is initiated when dilute THF solutions of Ph_2IPF_6 and Ph_3SPF_6 are irradiated with γ-rays. A study of pulse radiolysis revealed that the salts scavenge the solvated electron ($k = 9.5 \times 10^{11}$ M^{-1} s^{-1}) to prevent the neutralization reaction of the radiolytically produced cation, THF(H^+), which initiates the polymerization of THF. The rate of polymerization with Ph_2IPF_6 is much higher than that with Ph_3SPF_6 when irradiated with the same dose. This is attributed to the decomposition of Ph_2IPF_6 by chain reactions providing the initiating cation.

Introduction

Diaryliodonium and triarylsulfonium salts with complex metal halide anions are known as photoinitiators for cationic polymerization.[1-15] Upon irradiation with UV light, the salts undergo photodecomposition to yield Brønsted acids capable of initiating cationic polymerization.[1-9] We have studied the radiolysis of solutions containing Ph_2IPF_6 and Ph_3SPF_6. When irradiated with γ-rays, the reactions of the salts depend on solvent. In dichloromethane, which is an electron scavenger, the decomposition of the salts is not important. As reported earlier,[16-19] the salts promote the radiation-induced cationic polymerization of styrenes in dichloromethane. Results of the pulse radiolysis suggested that the effect of the salts is due to the stabilization of the monomer and dimer radical cations toward neutralization through the ion-pair formation with PF_6^-. An additional effect observed for Ph_2IPF_6 is an enhancement of the formation of the initiating cations. It has been proposed that radiolytically produced free radicals are responsible for the effect of Ph_2IPF_6. On the other hand, in tetrahydrofuran (THF), which is a cation scavenger, the salts decompose by capturing the solvated electron. The present study is concerned with the cationic polymerization of THF irradiated with γ-rays in the presence of the salts.

There are several reports on the cationic polymerization of THF by using various kinds of photoinitiators.[1,2,4,11,20-22] When pure THF is irradiated with ionizing radiation, the cationic polymerization is initiated by no means because of the occurrence of the fast neutralization reaction between the radiolytically produced cation and the solvated electron.[23] This is the first report of the radiation-induced cationic polymerization of THF, which is a result of the electron scavenging of Ph_2IPF_6 and Ph_3SPF_6. The difference in the initiation steps between the Ph_2IPF_6 and Ph_3SPF_6 systems, which are essentially similar in the photoinduced polymerization, is described.

Experimental Section

THF (Wako Chemicals) was distilled over calcium hydride, and the middle fraction was stored under vacuum over calcium hydride. Ph_2IPF_6 and Ph_3SPF_6 were prepared according to the literature.[2,4] The salts were twice recrystallized from ethanol–water mixtures.

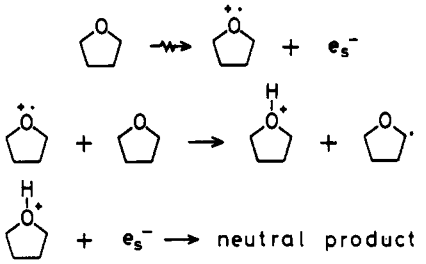
The polymerization samples were prepared in a high-vacuum operation. THF, whose volume was measured in a calibrated tube, was introduced into Pyrex ampules containing the salts by trap-to-trap distillations. The samples for the pulse radiolysis experiments were prepared in a similar manner and sealed into Pyrex ampules fitted with Suprasil cells of 10-mm optical path length.

The samples for polymerization were irradiated with γ-rays from a ^{60}Co source at 0 °C. The solutions became viscous by keeping them at 0 °C after the irradiation. The polymerization was terminated by adding an excess amount of methanol containing NH_4OH. The isolated polymer was dried under vacuum and weighed. The molecular weight distribution was measured by a gel permeation chromatograph (Toyo Soda HLC-801) in THF. Two 2-ft TSK-Gel G2000H8 and G4000H8 columns connected in series were used for the measurement. The yields of PhI from Ph_2IPF_6 and of Ph_2S from Ph_3SPF_6 were determined by a gas chromatograph (Shimadzu GC 7A) on a 2-m Silicone OV-17 column. Runs were programmed from 100 to 230 °C at a heating rate of 16 °C/min.

An L-band linear accelerator operating at 28 MeV was used for the pulse radiolysis. The pulse width was 8 ns. The optical measuring and signal processing systems consist of a 450-W xenon pulse lamp (OPG-450, Osram), a monochromator (Nikon G-250), a photomultiplier (Hamamatsu-TV R928), and a programmable digitizer (Textronix 7912 AD). The experiments were carried out at room temperature, kept at ca. 22 °C.

Results and Discussion

Irradiation of THF with ionizing radiation results in the formation of an oxonium ion capable of initiating the cationic polymerization of THF. In pure THF, the cation is rapidly neutralized with the solvated electron simultaneously produced.[23] The rate constant for the neutralization reaction, determined by pulse radiolysis at room temperature, is 2.0×10^{12} M^{-1} s^{-1}.[24] On the other hand, the propagation rate constant is 4.19×10^{-3} M^{-1} s^{-1} when the counterion is PF_6^- and at 0 °C.[25] Although the propagation rate constant for the free ion may be somewhat higher than the reported value, the cationic polymerization does not occur in irradiated pure THF because of the fast neutralization reaction.



(1)

(2)

(3)

The pulse radiolysis of dilute solutions of Ph_2IPF_6 and Ph_3SPF_6 in THF revealed that the solvated electron, which has absorption above 800 nm (λ_{max} = 2120 nm),[24] is scavenged by the salts. This means the occurrence of one-electron reductions of the salts as reported earlier.[26,27] The

$$Ph_2IPF_6 + e_s^- \longrightarrow PhI + Ph\cdot + PF_6^- \quad (4)$$

$$Ph_3SPF_6 + e_s^- \longrightarrow Ph_2S + Ph\cdot + PF_6^- \quad (5)$$

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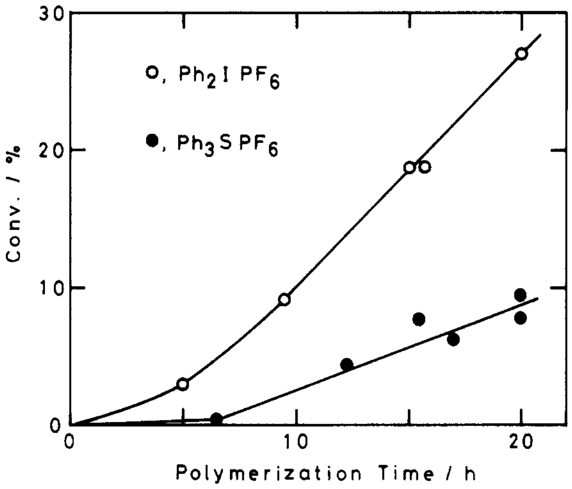
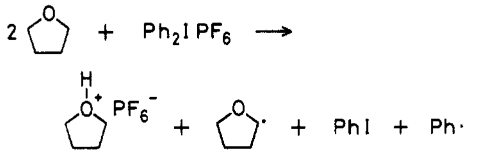


Figure 1. Postpolymerization of THF irradiated in the presence of 1×10^{-2} M Ph_2IPF_6 and Ph_3SPF_6 at 0 °C. The irradiation times are 30 min for the Ph_2IPF_6 samples and 120 min for the Ph_3SPF_6 samples: dose rate, 5×10^3 Gy h^{-1}.

net results of the primary steps when irradiated in the presence of the salts are as follows.



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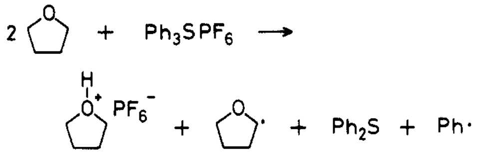

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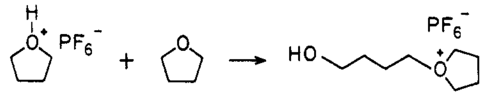
These are similar to the net results of the photoinduced primary steps.[1-9] The pulse irradiated solutions became gradually viscous, suggesting that the polymerization of THF is initiated by $THF(H^+)PF_6^-$.

The radiation-induced polymerization of THF in the presence of Ph_2IPF_6 and Ph_3SPF_6 was investigated in detail by using a ^{60}Co γ source. When the solutions of 1×10^{-2} M Ph_2IPF_6 and Ph_3SPF_6 were irradiated, in sealed ampules, for 120 min at a dose rate of 5×10^3 Gy h^{-1}, the polymer yields immediately after the irradiation were negligibly small. The formation of poly(tetrahydrofuran) is due exclusively to the postpolymerization. The rate of polymerization with Ph_2IPF_6 was much higher than that with Ph_3SPF_6.

Figure 1 shows the time-conversion curves for the postpolymerization at the irradiation times of 30 and 120 min for the Ph_2IPF_6 and Ph_3SPF_6 solutions, respectively. The polymer yields increase linearly with the polymerization time after inhibition periods. The inhibition periods in the postpolymerization may be explained in terms of the slow rate of the initiation reaction



(8)

compared with that of the propagation reaction, similarly to the case of the polymerization of THF initiated by 2-methyl-1,3-dioxolenium perchlorate.[25]

The weight-average molecular weight of poly(tetrahydrofuran) was determined by the viscosity measurement in ethyl acetate at 30 °C according to the equation $[\eta] = 4.22 \times 10^{-4} \bar{M}_w^{0.65}$ presented in the literature.[28] The molecular weight increases with the polymerization time as shown in Figure 2, suggesting the occurrence of living polymerization as reported earlier.[25] There is no difference in the molecular weight between the Ph_2IPF_6 and Ph_3SPF_6 systems. That is to say, the propagation step is not responsible for the difference in the rate of polymerization

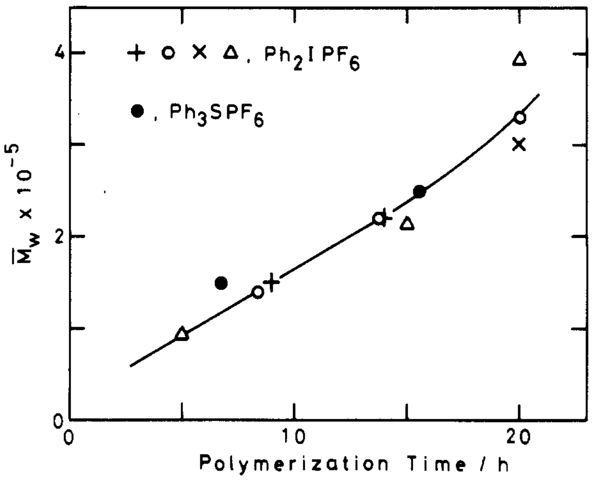


Figure 2. Weight-average molecular weights of poly(tetrahydrofuran) as a function of postpolymerization time. The irradiation times are (+) 10 min, (O) 30 min, (×) 60 min, and (Δ,●) 120 min.

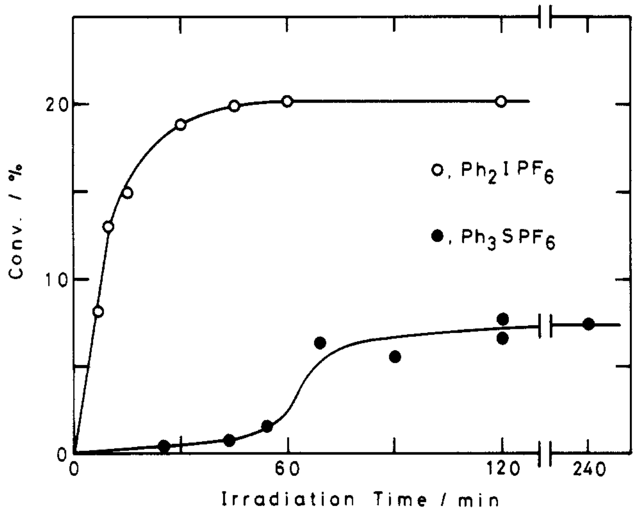


Figure 3. Polymer yields at a postpolymerization time of 15.5 h as a function of irradiation time: salt concentration, 1×10^{-2} M.

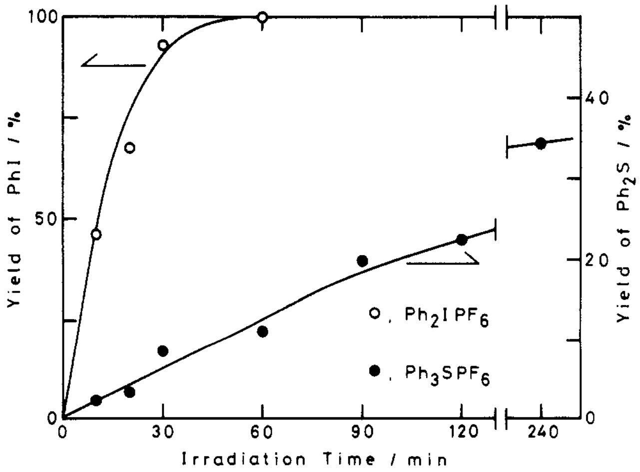


Figure 4. Yields of radiolysis products as a function of irradiation time: salt concentration, 1×10^{-2} M.

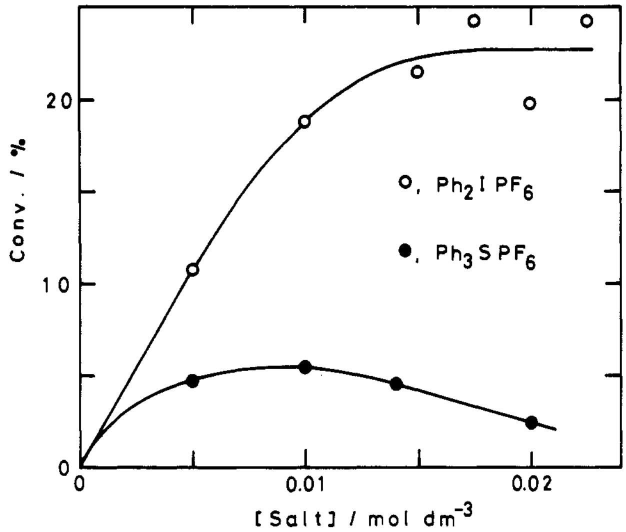


Figure 5. Polymer yields at a postpolymerization time of 15.5 h as a function of salt concentration. The irradiation times are 30 min for the Ph_2IPF_6 samples and 120 min for the Ph_3SPF_6 samples.

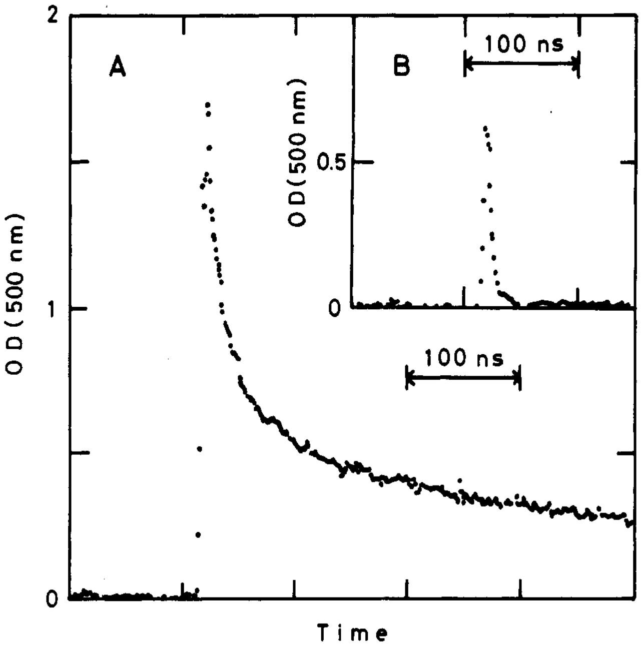


Figure 6. Formation and decay behaviors of $St^{\bullet-}$ in the pulse radiolysis of 5 × 10^{-2} M St in THF: (A) alone; (B) with 1 × 10^{-2} M Ph_2IPF_6.

between these systems (Figure 1). It is also demonstrated that the molecular weight is independent of the irradiation time. The $\bar{M}_w/\bar{M}_n$ ratios for these polymers, calculated from the gel permeation chromatograms, are in the range from 1.2 to 1.5. The $\bar{M}_w$ values are converted into the $\bar{M}_n$ values by using these ratios. If the rate of the increase in $\bar{M}_n$ is taken to be 1.2 × 10^4 h^{-1} as an average, the propagation rate constant is calculated to be 3.8 × 10^{-3} M^{-1} s^{-1}. This is close to the literature value, 4.19 × 10^{-3} M^{-1} s^{-1}.[25]

Figure 3 shows the dependence of the polymer yields on the irradiation time at a postpolymerization time of 15.5 h. The polymer yields are correlated to the concentration of the initiating cation, $THF(H^+)$, at the end of the irradiation. Figure 4 shows the time-conversion curves for the decomposition of the salts followed by the measurement of the yields of PhI and Ph_2S. For the Ph_2IPF_6 system, the curve for the polymer yield (Figure 3) is similar to that for the yield of PhI (Figure 4), which demonstrates that the salt is fully consumed until 60 min. The G value of PhI, determined from the initial slope of the plot, is 74. This means that the decomposition of Ph_2IPF_6 is due to chain reactions. For the Ph_3SPF_6 system, an inhibition period is observed for the polymerization (Figure 3) but not for the decomposition of the salt (Figure 4). Therefore, the inhibition period may be attributed to the capture of the initiating cation, $THF(H^+)$, by basic impurities contained in the solution. The G value of Ph_2S, determined from the straight line in the early stage, is 2.7. This value is the same as the maximum electron yield reported,[29] suggesting that the decomposition of Ph_3SPF_6 is due largely to reaction 5. When the irradiation is prolonged, the polymer yield with Ph_3SPF_6 becomes constant, whereas the yield of Ph_2S continues to increase. This can be explained if we assume that the initiation of the polymerization is inhibited by any byproducts of the radiolysis. The rate of the formation of Ph_2S decreases at the prolonged irradiation times. This is attributed to the contribution of reaction 3 because the concentration of $THF(H^+)$ increases with increasing irradiation time. For the both systems, the polymer yields were independent of the dose rate in the range from 5 × 10^3 to 2 × 10^4 Gy h^{-1}.

Figure 5 shows the dependence of the polymer yields on the salt concentration at a postpolymerization time of 15.5 h. Above 1 × 10^{-2} M, the polymer yield is almost constant (for the Ph_2IPF_6 system) or decreases with increasing salt concentration (for the Ph_3SPF_6 system). The result may be explained in terms of the capture of the initiating cation by basic impurities contained in the salts and/or basic byproducts from the salts. The yields of polymer chains, calculated on the basis of the $\bar{M}_n$ values, are 1 order of magnitude smaller than those of PhI and Ph_2S. This also demonstrates the low efficiency of the initiation of the polymerization.

The γ-radiolysis experiments were also carried out with dichloromethane solutions of 1 × 10^{-2} M Ph_2IPF_6 and Ph_3SPF_6 at a dose rate of 5 × 10^3 Gy h^{-1} at 0 °C. The yields of the decomposition products, PhI and Ph_2S, were much smaller than those in THF; the G values of PhI and Ph_2S were 0.96 and 0.18, respectively. It is suggested that the decomposition of the salts is not important in dichloromethane which is an electron scavenger.

Pulse radiolysis of an aromatic compound in THF results in the formation of the solute radical anion by attachment of the solvated electron. The decay of the radical anion is due to neutralization with $THF(H^+)$. The effects of Ph_2IPF_6 and Ph_3SPF_6 on the formation of the radical anion were investigated in order to obtain information about the electron attachment to the salts. *trans*-Stilbene (St) was used as the solute. The rate constant for the electron attachment to St, presented in the literature, is 1.16 × 10^{11} M^{-1} s^{-1}.[23]

$$e_s + St \rightarrow St^{\bullet-} \qquad (9)$$

The transient light absorption observed for the THF solutions of St, irradiated in the absence and presence of the salts, was attributed to $St^{\bullet-}$. The absorption spectrum is characterized by a sharp peak at 500 nm.[23] Figure 6 shows the formation and decay behaviors of $St^{\bullet-}$, monitored at 500 nm, in the absence and presence of 1 × 10^{-2} M Ph_2IPF_6. The yield of $St^{\bullet-}$ is remarkably decreased by the addition of the salt. In the absence of the salt, the solvated electron is completely scavenged by St at the St concentration 5 × 10^{-2} M.[30] Therefore, the result is explained in terms of the competition between reactions 4 and 9. The decay of $St^{\bullet-}$ is also accelerated by the addition of the salt, suggesting the occurrence of the electron transfer from $St^{\bullet-}$ to the salt. Similar results were obtained for the solution containing Ph_3SPF_6.

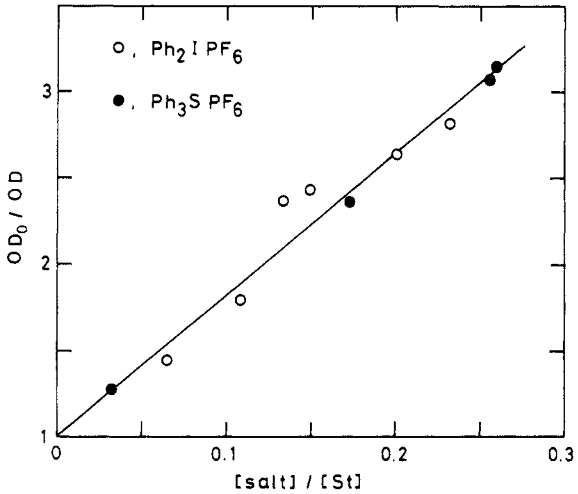


Figure 7. Competition kinetics plot for the formation of $St^{\bullet -}$.

For the competition between reactions 4 and 9, the experimental optical-density ratio is given by

$$OD_0/OD = 1 + k_4[\text{salt}]/k_9[\text{St}] \qquad (10)$$

where OD_0 and OD are the optical densities in the absence and presence of the salt. The equation is based on the assumption that all of the salt is in the ion-paired state. The plot of OD_0/OD against [salt]/[St] gives a straight line as shown in Figure 7, which includes the results for the Ph_3SPF_6 system. It is demonstrated that the rate constants for reactions 4 and 5 are similar. By using the literature value for k_9, the value of k_4 ($=k_5$) is determined to be 9.5×10^{11} M^{-1} s^{-1} from the slope of the plot. The rate constants for the reactions of the solvated electron are in the order $k_3 > k_4 = k_5 > k_9$. This order may be correlated to the extent of the electrostatic interaction between the reacting species. That is, reaction 3 and reactions 4 and 5 are accelerated by the ion–ion and ion–dipole interactions, respectively.

We have previously studied the effects of quaternary ammonium salts in the pulse radiolysis of THF solutions of St.[30] It should be noted that the effects of quaternary ammonium salts are quite different from those of the present salts capable of initiating the polymerization of THF. The addition of Bu_4NPF_6 results in the retardation of the decay of $St^{\bullet -}$ without change in its yield. The spectral shift of $St^{\bullet -}$ observed in the presence of the salt suggests that $St^{\bullet -}$ forms a contact ion pair with Bu_4N^+; the neutralization reaction occurs between the ion pairs, $Bu_4N^+St^{\bullet -}$ and $THF(H^+)PF_6^-$.

On the basis of the results of the pulse radiolysis, it seems reasonable to consider that the chain reactions of Ph_2IPF_6 providing the initiating cation are initiated by the solvated electron and the chain carrier is $Ph^\bullet$ produced by reaction 4. However, no simple mechanism can explain the result that the chain reactions do not occur in dichloromethane. Clearly further investigation is required to reveal the precise mechanism.

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Registry No. THF, 109-99-9; THF (homopolymer), 24979-97-3; THF (SRU), 25190-06-1; Ph_2IPF_6, 58109-40-3; Ph_3SPF_6, 57835-99-1; PhI, 591-50-4; Ph_2S, 139-66-2.

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