Photoinduced and Radiation-Induced Cationic Polymerizations of Tetrahydrofuran by Various Sulfonium Hexafluorophosphate Salts

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Introduction

Diaryliodonium and triarylsulfonium salts with complex metal halide anions are known as photoinitiators for cationic polymerization.[1] We have recently reported that cationic polymerization of tetrahydrofuran (THF) is initiated when dilute THF solutions of Ph_2IPF_6 and Ph_3SPF_6 (Ph, phenyl) are irradiated with γ-rays.[2] In the present investigation, various sulfonium hexafluorophosphate salts having phenyl, benzyl (Bz), butyl (Bu), and methyl (Me) S-substituents have been examined as initiators for the photoinduced and radiation-induced cationic polymerizations of THF. The effect of the substituents of the salts on the initiation efficiency for the polymerization is described. A comparison is made with the polymerization by Ph_2IPF_6.

Experimental Section

The sulfonium salts were prepared by the same method as described in the literature.[3,4] THF, Ph_2IPF_6, and Ph_3SPF_6 were the same as those used previously.[2] Zone-refined anthracene (Tokyo Kasei) was used as a photosensitizer without further purification. Details of sample preparation and procedures of the radiation-induced polymerization have been given in our preceding paper.[2] The photopolymerization was carried out with a super-high-pressure mercury lamp (USHIO, 1 kW). The samples were irradiated in sealed quartz cells through appropriate cut-off filters. Absorption spectra of the salts were recorded on a Shimadzu MPS-2000 spectrophotometer.

Results and Discussion

The sulfonium salts examined are Ph_2BzSPF_6, Bz_2PhSPF_6, Ph_2BuSPF_6, $PhBzMeSPF_6$, Ph_2MeSPF_6, Bu_2PhSPF_6, Bz_2MeSPF_6, Bu_2BzSPF_6, and Ph_3SPF_6. Figure 1 shows the UV absorption spectra of the salts. The polymerization experiments were carried out with THF solutions of the salts at a concentration of 1×10^{-2} mol dm^{-3} and at 0 °C. The polymer yields just after the UV and γ-irradiation were negligibly small because of the small propagation rate constant of THF, 4.19×10^{-3} dm^3 mol^{-1} s^{-1}.[5] The polymer is produced exclusively by the postpolymerization. The molecular weight of polymer increases with the postpolymerization time because of the occurrence of living polymerization.[2] The yields of the photoinduced and radiation-induced polymerizations at a postpolymerization time of 20 h are listed in Table I. The data for Ph_2IPF_6 are shown for the sake of comparison. Among the salts prepared, Ph_2BzSPF_6, having large absorption at the longer wavelengths (Figure 1A, curve e), decomposed during the sample preparation by daylight, and the polymerization set in as soon as the sample was prepared. Results for this salt are not presented in Table I.

The UV irradiation at wavelengths above 270 nm leads to the polymerization with all the salts except Bu_3SPF_6 of which absorption at these wavelengths is negligibly small (Figure 1A, curve f). These salts are considered to undergo photodecomposition to yield Brønsted acids by the mechanism reported for Ph_3SPF_6:[1]

$$Ph_3SPF_6 \xrightarrow[SH]{h\nu} H^+PF_6^- + Ph_2S + Ph^\bullet \qquad (1)$$

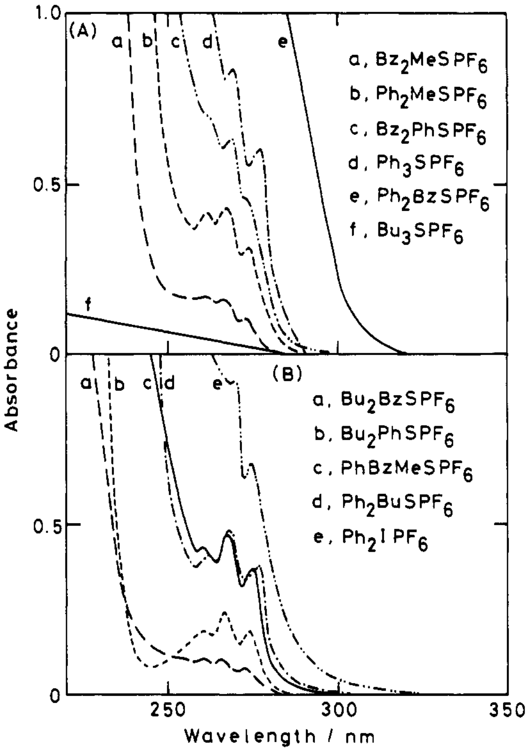

Figure 1. UV absorption spectra for the salts in THF at a concentration of 2×10^{-4} mol dm^{-3}.

Table I
Postpolymerization in the THF Solutions of Various Salts Irradiated with UV Light and γ-Rays at 0 °C[a]

		polymer yields, %		
		UV light		
salt	mp, °C	270 nm	350 nm[b]	γ-rays
Ph_3SPF_6	203.2–205.3	7.5	17.9	7.8
Bz_2PhSPF_6	133.9–135.0	31.1	19.5	9.5
$PhBzMeSPF_6$	141.7–143.7	16.2	11.3	5.1
Ph_2MeSPF_6	90.4–91.5	9.6	3.1	4.7
Ph_2BuSPF_6	111.6–113.5	2.3	2.4	5.0
Bu_2PhSPF_6	36.9–40.0	3.1	0	3.0
Bu_2BzSPF_6	112.0–113.0	4.0	0	0
Bz_2MeSPF_6	135.9–137.7	2.9	0	0
Bu_3SPF_6	65.3–65.8	0	0	0
Ph_2IPF_6	142.7–144.9	23.7	59.2	32.5

[a] The THF solutions of 1×10^{-2} mol dm^{-3} salts were irradiated for 10 min with UV light and for 2 h with γ-rays at a dose rate of 5×10^3 Gy h^{-1}. The postpolymerization time was 20 h. [b] The solutions contained 1×10^{-3} mol dm^{-3} anthracene as a photosensitizer.

where SH is a solvent or monomer from which hydrogen is abstracted to form $H^+PF_6^-$. Bz_2PhSPF_6 and $PhBzMeSPF_6$ give much higher yields than Ph_3SPF_6. The result can be ascribed in part to the difference in the extinction coefficients of the salts. Bz_2PhSPF_6 and $PhBzMeSPF_6$ have absorption tails up to 300 nm, in contrast to Ph_3SPF_6, which has much smaller absorption above 290 nm. The difference in the extinction coefficients at wavelengths above 290 nm is important when the salt concentration is as high as 1×10^{-2} mol dm^{-3}. A leaving group propensity of Bz > Ph may also be responsible for the larger polymer yields with the salts having Bz substituents. The leaving group propensity of Bz > alkyl > Ph has been reported for one-electron reduction of sulfonium salts.[3] Similar results were obtained in the present photolysis experiments; the sulfide products (relative yields) detected were PhBzS (100%) from Bz_2PhSPF_6 and PhMeS (96.4%) and PhBzS (3.6%) from $PhBzMeSPF_6$.

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Table II
Yields of Sulfide Products in the Radiolysis of Sulfonium Salts[a]

salt	product (rel yield, %)	conv, %	G^b
Bz_2PhSPF_6	PhBzS	76	8.3
$PhBzMeSPF_6$	PhMeS (97), PhBzS (3)	44	4.8
Ph_2BuSPF_6	Ph_2S (63), PhBuS (37)	41	4.5
Ph_2MeSPF_6	Ph_2S	61	6.6
Bu_2BzSPF_6	Bu_2S (97), BzBuS (3)	18	1.9
Bz_2MeSPF_6	BzMeS (91), Bz_2S (9)	17	1.9

[a] The THF solutions of 1×10^{-2} mol dm^{-3} salts were irradiated for 2 h at a dose rate of 5×10^3 Gy h^{-1} at 0 °C. [b] Number of molecules of a product for a 100-eV energy absorbed by the medium.

The photosensitized polymerization was carried out with solutions containing 1×10^{-3} mol dm^{-3} anthracene as a sensitizer. The solutions were irradiated at wavelengths above 350 nm, where the salts have no absorption. The highly effective initiators for the photosensitized polymerization are Ph_3SPF_6, Bz_2PhSPF_6, and $PhBzMeSPF_6$, similar to the case of direct photoexcitation. On the other hand, Bu_2PhSPF_6, Bz_2MeSPF_6, and Bu_2BzSPF_6 are ineffective, whereas they initiate polymerization by direct photoexcitation. This result should be explained in terms of the sensitization efficiencies for the salts.

When the solutions of the salts were irradiated with γ-rays, the polymerization of THF was initiated with the salts having Ph substituents. As previously reported for Ph_3SPF_6, the salts decompose through one-electron reduction by the solvated electron:[2]

$$Ph_3SPF_6 + e_s^- \rightarrow Ph_2S + Ph^\bullet + PF_6^- \qquad (2)$$

The electron scavenging by the salts results in prevention of neutralization of the radiolytically produced cation, THF(H^+), which initiates the polymerization. This is confirmed by the pulse radiolysis experiments similar to the case of Ph_3SPF_6.[2] Pulse radiolysis of THF solutions of an aromatic compound results in the formation of the radical anion of the solute via the attachment of the solvated electron. The effect of the salts on the yield of the radical anion was examined by using *trans*-stilbene as the aromatic solute. The yield of the *trans*-stilbene radical anion was extremely decreased by the addition of the salts, suggesting the occurrence of the competitive electron scavenging by the salts. The yields of the radiation-induced polymerization are in the range from 3.0% to 9.5%. The range is narrow compared with that of the photoinduced polymerization. This may be attributed to the fact that the salts react with the solvated electron, a strongly reducing species, and the reaction is less selective. The results of the pulse radiolysis experiments demonstrated that Bz_2MeSPF_6, Bu_2BzSPF_6, and Bu_3SPF_6 also scavenge the solvated electron, whereas they did not initiate the polymerization. At the present time, no explanation is given for the ineffectiveness of these salts in the radiation-induced polymerization.

The product analysis data for the radiolysis of some sulfonium salts are presented in Table II. The relative yields of the sulfide products demonstrate the leaving group propensity of Bz > methyl ≃ butyl > phenyl. The decomposition yields for Bu_2BzSPF_6 and Bu_2MeSPF_6, not initiating the polymerization, are small compared with those for the other salts. The *G* values for the salts initiating the polymerization are higher than that for Ph_3SPF_6, which was 1.8 for the 2-h irradiation, in spite of the high polymer yield for Ph_3SPF_6. The high *G* values suggest the contribution of decomposition processes other than the one-electron reduction by the solvated electron. A radical-initiated decomposition might occur for these sulfonium salts as well as the one-electron reduction. The yields of the photoinduced and radiation-induced polymerization by Ph_2IPF_6 are much larger than those by the sulfonium salts. This has been attributed to the decomposition of Ph_2IPF_6 by a chain reaction initiated by the radical derived from THF.[2,6]

As described above, the reaction of the salts in the radiation-induced polymerization differs from that in the photopolymerization. When irradiated with γ-rays, the salts act as an electron scavenger, whereas they decompose via the excited states upon irradiation with UV light. The difference in the initiation mechanism was evidenced by the effect of the added chlorinated compounds which scavenge electron to give the nucleophilic chloride anion. The radiation-induced polymerization by Ph_3SPF_6 was inhibited by the addition of 10 vol % dichloromethane or carbon tetrachloride, whereas the photopolymerization was not affected by the additives. On the other hand, there was no difference in molecular weight between the polymers produced by the photoinduced and radiation-induced polymerizations, when compared at the same post-polymerization time. The result of the GPC measurements agrees with the fact that living polymerization occurs in both systems.

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Registry No. THF (homopolymer), 24979-97-3; THF (SRU), 25190-06-1; Ph_3SPF_6, 57835-99-1; Bz_2PhSPF_6, 119071-32-8; $PhBzMeSPF_6$, 112406-12-9; Ph_2MeSPF_6, 23686-31-9; Ph_2BuSPF_6, 116737-91-8; Bu_2PhSPF_6, 119108-51-9; Bu_2BzSPF_6, 119071-33-9; Bz_2MeSPF_6, 119071-34-0.

References and Notes

(1) For a review, see: Crivello, J. V. *Adv. Polym. Sci.* **1984**, *62*, 1–48.
(2) Ma, X.-H.; Yamamoto, Y.; Hayashi, K. *Macromolecules* **1987**, *20*, 2703–2706.
(3) Beak, P.; Sullivan, T. A. *J. Am. Chem. Soc.* **1982**, *104*, 4450–4457.
(4) Saeva, F. D.; Morgan, B. P. *J. Am. Chem. Soc.* **1984**, *106*, 4121–4125.
(5) Yamashita, Y.; Kozawa, S.; Hirota, M.; Chiba, K.; Matsui, H.; Hirota, A.; Kodama, M.; Ito, K. *Makromol. Chem.* **1971**, *142*, 171–181.
(6) For radical-initiated chain reactions of iodonium salts, see: (a) Beringer, F. M.; Gindler, E. M.; Rapoport, M.; Taylor, R. J. *J. Am. Chem. Soc.* **1959**, *81*, 351–361. (b) Knapczyk, J. W.; Lubinkowski, J. J.; McEwen, W. E. *Tetrahedron Lett.* **1972**, *35*, 3739–3742. (c) Pappas, S. P.; Gatechair, L. R.; Jilek, J. H. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 77–84. (d) Ma, X.-H.; Yamamoto, Y.; Hayashi, K. *J. Org. Chem.* **1988**, *53*, 5443–5445.

Self-Consistent Approximation to Fluorescence Decay in Macromolecules with Energy Migration and Dissociating Traps

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1. Introduction

The phenomenon of excitation transport and trapping in fluid and solid solutions of polymers that contain aro-

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