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Radiation-Induced Polymerization of Isobutyl Vinyl Ether by Diphenyliodonium Hexafluorophosphate. Contribution of Free Radicals to Cationic Polymerization

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Synopsis. The radiation-induced cationic polymerization of isobutyl vinyl ether by Ph_2IPF_6 was investigated in dichloromethane solution. The polymerization occurs in the aerated solution containing the salt and is extremely accelerated when the solution is degassed. Contribution of radiolytically produced radicals to the cationic initiation is described. Results for the polymerization by Ph_3SPF_6 are also presented for the sake of comparison.

UV- and radiation-curing has been the subject of recent industrial interest. Numerous studies have been done on the application of diaryliodonium and triarylsulfonium salts having complex metal halide anions as photoinitiators for cationic polymerization since it was first developed by Crivello and Lam.[1] Upon irradiation with UV light the salts undergo photodecomposition to yield Brönsted acids capable of initiating cationic polymerization. We have investigated the radiation-induced cationic polymerization by Ph_2IPF_6 and Ph_3SPF_6.[2–6] When dilute solutions of the salts are irradiated with ionizing radiation such as γ-rays, the radiation energy is absorbed mainly by solvents. The salts react with the reactive species produced from the solvents. This facilitates a quantitative comparison of the initiation efficiencies of Ph_2IPF_6 and Ph_3SPF_6 based on the absorbed energy.

The reactions of the salts in irradiated solutions depend on solvents.[7] In alcohols, ethers, acetonitrile, and acetone, the salts decompose through one-electron reduction by the solvated electrons or the solvent anions, the latter of which is the case of acetonitrile and acetone. The one-electron reduction is inhibited in dichloromethane, because the solvent itself is an electron scavenger. In alcohols and ethers having α-hydrogen, the α-alkoxyalkyl radicals produced from the solvents are oxidized by Ph_2IPF_6 to the corresponding cations, but not by Ph_3SPF_6, as reported for the photochemical reactions.[1] The radical-induced decomposition of Ph_2IPF_6 is a chain reaction of which chain carrier is the phenyl radical produced from the salt.

The present study is concerned with the radiation-induced cationic polymerization of isobutyl vinyl ether (IBVE) by Ph_2IPF_6 in dichloromethane solution, where the contribution of radiolytically produced radicals to the cationic initiation is expected to be important. Similar experiments were carried out for Ph_3SPF_6 for the sake of comparison.

Experimental

IBVE (Tokyo Kasei) and dichloromethane (Wako Chemicals) were successively washed three times with 10% aqueous sodium hydroxide solution and with water and then distilled over calcium hydride. Ph_2IPF_6 and Ph_3SPF_6 were the same as those used in the previous study.[5] The radiation-induced polymerization was carried out at room temperature for aerated and degassed solutions by using a ^{60}Co source. The monomer and salt concentrations were 1.9 and 0.01 mol dm^{-3}, respectively. The degassed samples were prepared by the freeze-thraw method and were sealed under vacuum. Polymer was precipitated by an excess of aqueous methanolic ammonia, dried under vacuum, and then weighed.

Results and Discussion

The major primary species produced by γ-irradiation of the dichloromethane solution of IBVE containing a small amount of the salts are the solvent radical cation and electron. The electron is scavenged by the solvent to give a chloromethyl radical, which is expected to give the 2-methyl-1-(ethenyloxy)propyl radical through hydrogen abstraction from IBVE.

$$CH_2Cl_2 \rightsquigarrow CH_2Cl_2^{+\cdot} + e^- \quad (1)$$

$$e^- + CH_2Cl_2 \longrightarrow Cl^- + CH_2Cl\cdot \quad (2)$$

$$CH_2Cl\cdot + IBVE \longrightarrow CH_3Cl + IBVE(-H)\cdot \quad (3)$$

where $IBVE(-H)\cdot$ is $(CH_3)_2CH\dot{C}HOCH{=}CH_2$. If the radical is oxidized by Ph_2IPF_6 to the corresponding cation, the initiation efficiency of the polymerization by Ph_2IPF_6 becomes much larger than that by

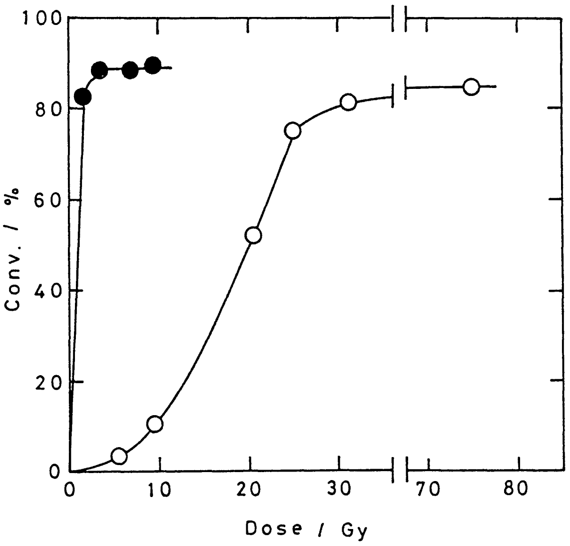

Fig. 1. Dose-conversion curves for the radiation-induced polymerization by Ph_2IPF_6 in the aerated (○) and degassed (●) solutions: [IBVE]=1.9 mol dm^{-3}, [Ph_2IPF_6]=0.01 mol dm^{-3}.

Ph_3SPF_6. It is also expected that the radical-induced decomposition is more important in the radiation-induced polymerization than in the photoinduced polymerization because of the higher radical yield by the radiolysis of the solvent.

No polymer was obtained when the aerated solution of IBVE was irradiated with γ rays in the absence of the salts. The addition of the salts to the solution enables the cationic polymerization even in the aerated solution. The polymer yields by Ph_2IPF_6 were much larger than those by Ph_3SPF_6 when compared at the same absorbed dose.

Figure 1 shows the polymer yields plotted against the absorbed dose for the aerated and degassed dichloromethane solutions of IBVE containing Ph_2IPF_6. The dose rates were 11 and 41 Gy h^{-1} for the aerated and degassed solutions, respectively. The extremely high polymer yields for the degassed solution, compared with those for the aerated solution, demonstrate the contribution of free radicals to the cationic initiation of polymerization. The initiating cations are considered to be generated from the IBVE(−H)· radical by the chain reaction.

$$\mathrm{IBVE(-H)\cdot + Ph_2IPF_6 \longrightarrow IBVE(-H)^+ + PF_6^- + PhI + Ph\cdot} \quad (4)$$

$$\mathrm{Ph\cdot + IBVE \longrightarrow PhH + IBVE(-H)\cdot} \quad (5)$$

The G value of monomer consumption for the degassed solution, determined from the straight line in the early stage of the polymerization, was 7.3×10^6, whereas the maximum G value determined from the polymer yield in the aerated solution was 4.7×10^5.

Figure 2 shows the similar plots for the Ph_3SPF_6 systems. The dose rate was 3.4×10^3 Gy h^{-1}. It can be seen that the polymerization by Ph_3SPF_6 is scarcely affected by the presence of oxygen. The absorbed dose required for the polymerization by Ph_3SPF_6 is about 200 times that by Ph_2IPF_6 in the aerated system.

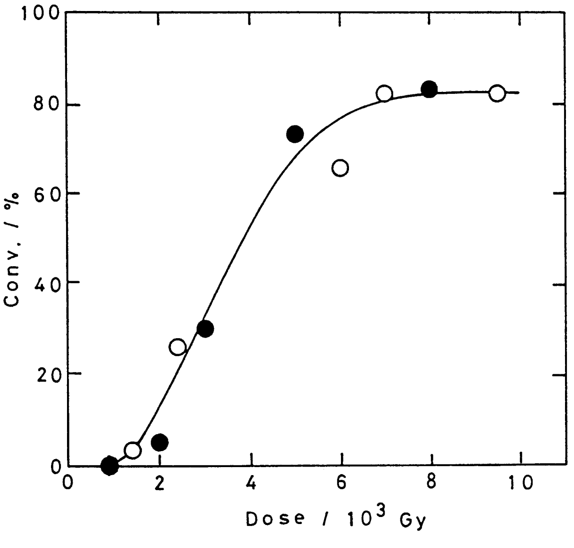

Fig. 2. Dose-conversion curves for the radiation-induced polymerization by Ph_3SPF_6 in the aerated (○) and degassed (●) solutions: [IBVE]=1.9 mol dm^{-3}, [Ph_3SPF_6]=0.01 mol dm^{-3}.

It has been reported that the photoinduced cationic polymerization of N-vinylcarbazole by Ph_3SAsF_6 is suppressed in oxygen-saturated dichloromethane solution.[8] This was interpreted in terms of the photodecomposition of the salt via the triplet excited state giving the Brönsted acid. The absence of the oxygen effect in the present Ph_3SPF_6 system suggests that the decomposition of the salt via the excited state is not important in the γ-irradiated dichloromethane solution.

The initiation of the polymerization in the Ph_3SPF_6 system may be due to the monomer radical cation produced via charge transfer from the solvent radical cation. The promotion of the polymerization by the salt is attributed to the non-nucleophilic anion, PF_6^-, which forms ion pairs with the initiating and propagating cations. The ion-pair formation results in the stabilization of the cations toward neutralization with Cl^-, a product of reaction 2. In the absence of the salt, the cations are rapidly neutralized with Cl^- not to yield detectable amounts of polymer. Such an effect of the ion-pair formation has previously been reported for the radiation-induced cationic polymerization of styrene and α-methylstyrene by Ph_2IPF_6 and Ph_3SPF_6 in dichloromethane.[2-4] We have also reported the effect of quaternary ammonium salts having non-nucleophilic anions on the photoinduced cationic polymerization of IBVE by butyl iodide.[9] The ion-pair formation of the propagating cation with the anions such as AsF_6^-, ClO_4^-, PF_6^- and BF_4^- results in the acceleration of the polymerization, initiated by the photochemically produced I_2, depending on the sizes of the anions. The effect of the ion-pair formation may also be important for the Ph_2IPF_6 system, although the initiation of the polymerization is due largely to IBVE(−H)$^+$ produced by the chain reaction.

Contribution of a radical, produced from the monomer, other than IBVE(−H)· cannot be ruled out for the Ph_2IPF_6 system. An α-alkoxyalkyl radical may be produced by the radical-addition reaction.

$$\mathrm{R\cdot + IBVE \longrightarrow IBVE(R)\cdot} \quad (6)$$

where R· is Ph· or CH_2Cl· and IBVE(R)·, $(CH_3)_2CHCH_2O\dot{C}HCH_2R$. The contribution of IBVE(−H)$^+$ and IBVE(R)$^+$ depends on the relative magnitudes of the rate constants for the hydrogen abstraction and addition reactions, which give IBVE(−H)· and IBVE(R)·, respectively. Unfortunately, we have no datum on the accurate rate constants for these reactions.

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