Photochemistry of Triphenylsulfonium Salts in Poly[4-[(*tert*-butoxycarbonyl)oxy]styrene]: Evidence for a Dual Photoinitiation Process

Triarylsulfonium salts are widely used as photoinitiators for acid-catalyzed processes in polymer films.[1] Early work on onium salt photolysis led to the proposal that acid was produced by reaction of the initially formed intermediates with solvent.[1,2] However, recent mechanistic studies have found that onium salt photolysis produces acid by in-cage fragmentation–recombination reactions, in addition to cage–escape reactions with the solvent.[3-7] We have recently reported that photolysis of acetonitrile solutions of triphenylsulfonium salts produces 2-, 3-, and 4-phenylthiobiphenyls, diphenyl sulfide, acetanilide, benzene, and acid (Scheme I).[3a-c] The excited state of the sulfonium salt cleaves by heterolysis of the carbon–sulfur bond to give the phenyl cation and diphenyl sulfide, in a solvent cage, which can subsequently form the in-cage pair of a phenyl radical and a diphenylsulfinyl radical cation by an electron-transfer reaction. Both pairs of in-cage intermediates can react with solvent or recombine, at one of the phenyl rings of the sulfur containing intermediate, to generate acid. In contrast, sensitization, by electron transfer or by triplet energy transfer, gives diphenyl sulfide, from triphenyl sulfur radical or the phenyl radical–diphenylsulfinyl radical cation triplet radical pair, respectively.[4]

In light of these new photochemical decomposition pathways, relatively few mechanistic studies on the photochemistry of onium salts in polymer films have been reported. We have recently examined the photolysis of sulfonium salts in poly(methyl methacrylate) and poly(vinyl acetate),[3b] and McKean has studied acid production by sulfonium salts in a number of polymeric systems.[8] In view of the importance of analogues of poly[4-[(*tert*-butoxycarbonyl)oxy]styrene] (TBOC) and photoacid initiators in the electronics industry,[1,9] an investigation into the photochemistry of triphenylsulfonium salts in TBOC films is appropriate. We report here the photochemistry of TBOC/sulfonium salt mixtures as films and in solution, UV emission studies on these films, and present evidence for a novel dual photoinitiation process in which the sulfonium salt decomposes via sensitization from the excited state of the polymer, in addition to a direct photodecomposition pathway.

Irradiation (λ = 254 nm) of polymer films of TBOC containing 0.1%, 1.0%, and 10.0% triphenylsulfonium hexafluoroantimonate (TPS·SbF_6) gave 2-, 3-, and 4-phenylthiobiphenyls and diphenyl sulfide (Scheme I).[10] While the film with 0.1% salt gave only traces of photoproduct, the films with 1.0% and 10% loadings gave detectable amounts of sulfides (Table I, entries 1–3). The ratios of the sum of the three phenylthiobiphenyl isomers to diphenyl sulfide, the cage/escape ratio (C/E), were 2.04 and 1.70 for 1% and 10% salt loadings, respectively. These C/E values seem remarkably low for viscous media; for example, irradiation of PMMA films containing similar loadings of TPS·SbF_6 under identical conditions gives C/E values of 2.81–3.51 (Table I, entries 6–8). To determine if sensitization of TPS·SbF_6 was the reason for the increase in diphenyl sulfide formation, the films were irradiated at 300 nm where the polymer absorbs but where the salt has only a very weak absorbance ($\epsilon < 1$). Under these conditions, at 1% and 10% loading, the cage/escape ratio decreases to 0.78 and 0.86, respectively (Table I, entries 4 and 5). However, when the TBOC/TPS·SbF_6 films are dissolved in acetonitrile and irradiated under identical conditions, the C/E values are 0.71–0.79 at 254 nm and 0.04 at 300 nm (Table I, entries 9–13). The normal C/E values for direct photolysis under these conditions in acetonitrile are 1.1 at λ = 254 nm and 0.35 at λ = 300 nm.

Scheme I
Photoproducts from Irradiation of Triphenylsulfonium Salts

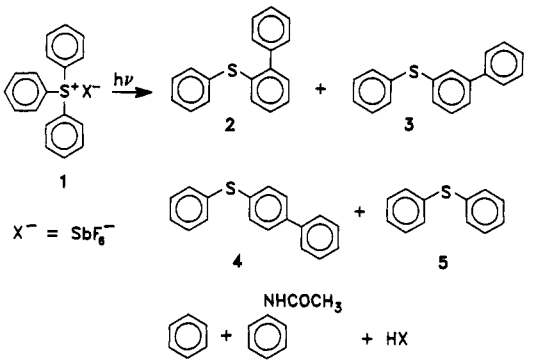

Table I
Photoproduct Distribution from Irradiation of Triphenylsulfonium Salts (Concentration ×10⁵ M)

entry	% loading TPS·SbF_6	Ph_2S	Ph–PhSPh	cage/escape
1	0.1%, TBOC, film, λ = 254 nm	ND	trace	
2	1.0%, TBOC, film, λ = 254 nm	0.95	1.95	2.04
3	10.0%, TBOC, film, λ = 254 nm	3.96	6.74	1.70
4	1.0%, TBOC, film, λ = 300 nm	0.70	0.55	0.78
5	10.0%, TBOC, film, λ = 300 nm	5.95	5.07	0.86
6	0.1%, PMMA, film, λ = 254 nm	0.71	2.49	3.50
7	1.0%, PMMA, film, λ = 254 nm	1.92	6.75	3.51
8	10.0%, PMMA, film, λ = 254 nm	6.57	18.46	2.81
9	0.1%, TBOC, CH_3CN, λ = 254 nm	1.72	1.21	0.70
10	1.0%, TBOC, CH_3CN, λ = 254 nm	13.24	10.42	0.79
11	10.0%, TBOC, CH_3CN, λ = 254 nm	110.9	82.8	0.75
12	1.0%, TBOC, CH_3CN, λ = 300 nm	1.28	trace	
13	10.0%, TBOC, CH_3CN, λ = 300 nm	8.96	0.37	0.04
14	0.01 M, CH_3CN, λ = 254 nm	121.5	137.3	1.13
15	0.01 M, CH_3CN, λ = 300 nm	3.70	1.29	0.35
16	0.01 M CH_3CN + 0.1 M anisole, λ = 254 nm	221.4	75.0	0.34
17	0.01 M CH_3CN + 0.1 M anisole, λ = 300 nm	14.43	0.79	0.06

Cage/escape ratios are very sensitive to the rigidity of the environment. For example, the C/E for TPS·triflate in glycerol is 5.63,[3c] and in PMMA it is 2.40,[3b] whereas for TPS·SbF_6 it is 4.10 in the solid state,[3f] and in PMMA it is 2.81–3.51. Thus environments with limited diffusion favor the recombination reaction to yield in-cage products. TBOC films are such an environment, yet there are less in-cage products than expected. One explanation for the observation of more diphenyl sulfide than expected might be reaction of the excited state, or the initially formed decomposition fragments, with a suitable nucleophile. However, it has been demonstrated that photosolvolysis of the excited state of triarylsulfonium salts does not occur.[3c] Also, hexafluoroantimonate is a nonnucleophilic anion and is unlikely to react with the initially formed decomposition fragments. Reactions that do favor the formation of escape products, however, are sensitization reactions. Triplet energy transfer occurs from sensitizers with $E_T > 74$ kcal mol^{-1} to give 100% escape reaction, via the triplet phenyl radical–diphenylsulfinyl radical cation

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Scheme II
Dual Photoinitiation Mechanism for Photolysis of Triphenylsulfonium Salts in Poly[4-[(*tert*-butoxycarbonyl)oxy]styrene]

$$P + Ph_3S^+ X^- \xrightarrow{h\nu} [P]^* + Ph_3S^+ X^- + [Ph_3S^+ X^-]^* + P$$

$$[Ph_3S^+ X^-]^* \longrightarrow 2 + 3 + 4 + 5 + HX$$

$$[P]^* + Ph_3S^+ X^- \longrightarrow P^{+\cdot} + Ph_3S^{\cdot} + X^-$$

$$P^{+\cdot} + Ph_3S^{\cdot} + X^- \longrightarrow P^{+\cdot} + Ph^{\cdot} + Ph_2S + X^-$$

$$P^{+\cdot} + Ph^{\cdot} + X^- \longrightarrow \text{P-Ph} + HX$$

where P = (poly(4-*tert*-butoxycarbonyloxystyrene)

pair.[4a] If anisole (E_T = 80.8 kcal mol^{-1}) is used as a model for TBOC, the triplet excited state is high enough for energy transfer to occur.[11] Sensitization of triarylsulfonium salts with anthracene occurs by electron transfer via the triphenyl sulfur radical and also gives a 100% escape reaction.[4b] Again, if anisole is used as a model, electron transfer is exothermic by 44 and 22 kcal mol^{-1} from both singlet and triplet excited states, respectively.[12] Indeed, irradiation of TPS·SbF_6 with anisole in acetonitrile does appear to undergo a sensitization reaction, resulting in a higher yield of sulfides than from direct photolysis and giving a C/E of 0.34 at λ = 254 nm, where both anisole and TPS·SbF_6 compete for the incident light, and a C/E of 0.06 at λ = 300 nm, where anisole absorbs >90% of the incident light (Table I, entries 16 and 17). Anisole parallels the behavior of TBOC very well. More escape products are observed at λ = 254 nm than at λ = 300 nm from irradiation of the TBOC/TPS·SbF_6 films and solutions, regardless of the loading of onium salt.

A particularly interesting observation is the fact that substantially more escape reactivity is observed in solution than in the film for TBOC/TPS·SbF_6 at both λ = 254 and 300 nm. This suggests that sensitization is more efficient in solution than in the polymer film, even though the polymer absorbs 85% of the incident light at 254 nm for 1% loading[8] and absorbs >90% at 300 nm for all loadings. Thus for 1% loading of TPS·SbF_6 at λ = 254 nm, assuming equal efficiencies for direct and sensitized photolysis, the C/E should be less than 0.18, yet in the polymer film it is 2.04 and in solution it is 0.79. Even for anisole in acetonitrile the C/E is 0.34, which suggests that sensitization is not 100% efficient. An explanation for the reduced efficiency for sensitization in the film versus solution is that some of the TPS·SbF_6 is aggregated in the film, making less TPS·SbF_6 available to quench the excited-state polymer.[15] Regardless of the cause of the inefficiency for the sensitization process, the observation of phenylthiobiphenyls in the polymer film indicates that TPS·SbF_6 also decomposes by a direct photolysis mechanism, in addition to sensitized photolysis; i.e., a dual photoinitiation process operates. The mechanism for this process is summarized in Scheme II. Irradiation of TBOC/TPS·SbF_6 gives a mixture of the excited states of both the polymer and TPS·SbF_6, in addition to the ground states of these components. The excited state of TPS·SbF_6 gives phenylthiobiphenyls, diphenyl sulfide, and acid by the direct photolysis route previously described for solution reactions,[3c] whereas the polymer excited state undergoes electron transfer with the ground state of TPS·SbF_6 to produce diphenyl sulfide and acid by a mechanism similar to that reported for anthracene sensitization.[1,4b]

To gain more insight into the sensitization mechanism, the fluorescence spectrum of a TBOC film was measured and the effects of TPS·SbF_6 on this fluorescence were examined. The polymer film (approximately 1.0 μm) in the absence of sulfonium salt exhibits an emission maximum at 310 nm. This maximum does not shift when TPS·SbF_6 is added to the film; however, a marked decrease in luminescence intensity is observed. While we use an interrogation wavelength of 295 nm and monitor the emission at 320 nm, the intensity is decreased by greater than a factor of 3 when the concentration of TPS·SbF_6 is increased from 0 to 0.12 mol/L, corresponding to a loading of approximately 7% by weight of TPS·SbF_6 in TBOC. At this loading, the fraction of excited states quenched is approximately 68%.

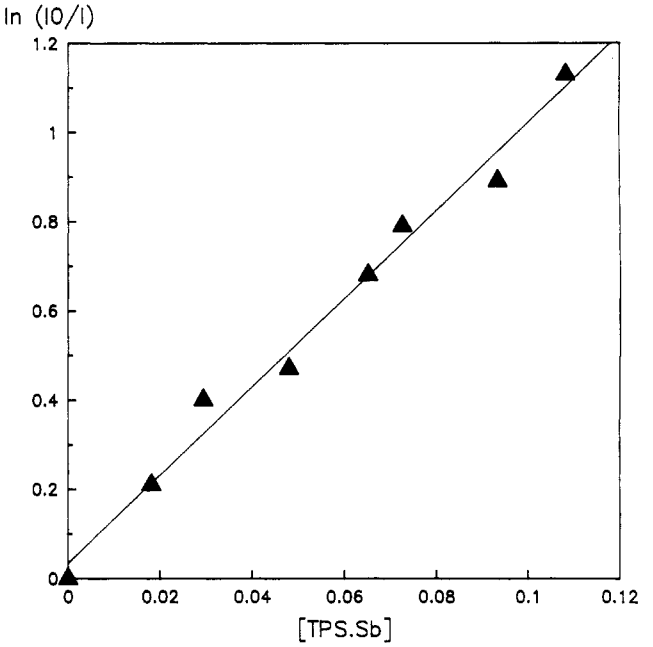

Figure 1. Plot of ln I_0/I vs molar concentration for poly[4-[(*tert*-butoxycarbonyl)oxy]styrene] emission at λ = 320 nm in the presence triphenylsulfonium hexafluroantimonate (excitation at λ = 295 nm).

The data presented in Figure 1 show that the observed luminescence quenching can be approximated by the Perrin model for static quenching,[16,17] eq 1, where I_0 is the

$$\ln (I_0/I) = VN[Q] \quad (1)$$

intensity of luminescence in the absence of quencher, I is the intensity in the presence of quencher, V is the volume of the active sphere, N is Avogadro's number, and [Q] is the concentration of the quencher in the solid matrix. From this equation the radius of the active sphere is found to be approximately 16 Å. Although, triplet energy transfer from the excited-state polymer to the TPS·SbF_6 is energetically feasible,[4a,12] it is unlikely that it is the mechanism for the photosensitized decomposition of TPS·SbF_6, especially when the observed fluorescence quenching described above is taken into consideration.[18] These results and the model photochemistry described above are, however, consistent with electron-transfer sensitization. In such a mechanism, the triphenylsulfonium cation is reduced to the corresponding triphenyl sulfur radical by the excited-state polymer as outlined in Scheme II.

These results demonstrate not only that is the absorbance of the incident light by the photoinitiator important but also that the polymer can play an important role.[19] The classic approach for improving the photosensitivity of the polymer resist system is to use a polymer with minimal absorbance at the irradiation wavelength and to increase the photoinitiator concentration, both of which increase the relative amount of incident light absorbed by

the initiator. While this may have some effect on photosensitivity improvement, a major effect in the TBOC system is due to more efficient quenching of the polymer fluorescence at higher concentrations of TPS·SbF_6, thus improving the sensitization process. This also explains why improvements in photosensitivity reach a maximum with increasing photoinitiator concentration. Once the maximum fluorescence quenching of the polymer is attained, adding more photoinitiator will not increase the sensitization efficiency. Indeed, one way to improve the photoinitiation process would be to increase the absorbance of the incident light by the polymer rather than the photoinitiator, thus taking full advantage of the photosensitization component for initiation.

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(10) Triphenylsulfonium salt polymer films were prepared by dissolving the appropriate amounts of polymer and salt in a suitable solvent (PMA or dichloromethane), allowing the solvent to evaporate for 16 h, and finally drying overnight in a vacuum oven at 70 °C. Pieces of the films (0.1 g) were placed in quartz or Pyrex tubes, which were purged with nitrogen for 20 min and irradiated for 30 min in a Rayonet reactor (Southern New England Ultraviolet Co.) equipped with four bulbs, RPR2537A or RPR3000A, for $\lambda = 254$ or 300 nm, respectively. The reaction mixtures were mixed with acetonitrile (4 mL), sonicated, quenched with brine (10 mL), and extracted with hexanes (1 mL) containing *n*-tetradecane internal standard. The photoproducts were identified by retention times compared with known concentrations of authentic samples in acetonitrile, which were subjected to the same work-up procedure, to compensate for extraction efficiencies and response ratios (see ref 3c).

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