The Photodecomposition of Triphenylsulphonium Hexafluoroantimonate sensitized by *N*-Vinylcarbazole

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N-Vinylcarbazole is shown to photosensitize the decomposition of triphenylsulphonium hexafluoroantimonate at wavelengths beyond those of the absorption bands of the onium salt; rapid polymerization of the monomer ensues both in solution, and in a resist-formulation.

The demand for new resist-formulations for application in high resolution microlithography has in recent years prompted a search for new photoinitiators of addition polymerizations. Prominent amongst the classes of compounds that offer promise, the aryl-diazonium, -iodonium, -sulphonium, and -selenonium salts are themselves stable, short wavelength sensitizers of cationic polymerization[1] (typically Scheme 1). For the most part these materials display absorption maxima in the range 240—280 nm so they cannot be used directly to carry out visible or near u.v. light-induced polymerizations. Perylene, however, has been reported to act as a sensitizer of the decomposition of onium salts using light of wavelength up to 475 nm.[2] It must therefore be concluded that the triplet state energies of onium salts are lower than that of perylene, *viz.* 35 kcal mol^{-1}.† It follows that any monomer (M) which is susceptible to cationic polymerization, which absorbs at longer wavelengths than an onium salt, and which readily undergoes intersystem crossing to a triplet state of energy higher than that of the onium salt, should itself act as a sensitizer of the decomposition, and hence of its own polymerization (Scheme 2). *N*-Vinylcarbazole (VCZ) fulfils these requirements having an electron-rich vinyl group, absorption bands extending to 360 nm, a $S_1 \rightarrow T_1$ intersystem crossing (ISC) efficiency of about 35%, and E_T *ca.* 70 kcal mol^{-1}.

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† 1 cal = 4.18 J.

$$\mathrm{Ar_3S^+\,X^-} \xrightarrow{h\nu} [\mathrm{Ar_3S^+\,X^-}]^* \qquad (1)$$

$$[\mathrm{Ar_3S^+\,X^-}]^* \longrightarrow \mathrm{Ar_2S^{+\cdot}} + \mathrm{Ar^{\cdot}} + \mathrm{X^-} \qquad (2)$$

$$\mathrm{Ar_2S^{+\cdot}} + \mathrm{R{-}H} \longrightarrow \mathrm{Ar_2S^{+}{-}H} + \mathrm{R\cdot} \qquad (3)$$

$$\mathrm{Ar_2S^{+}{-}H} \longrightarrow \mathrm{Ar_2S} + \mathrm{H^+} \qquad (4)$$

$$\mathrm{H^+} + n\mathrm{M} \longrightarrow \text{Polymer} \qquad (5)$$

Scheme 1

$$\mathrm{M} \xrightarrow{h\nu} {}^1\mathrm{M}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{M}^* \qquad (6)$$

$${}^3\mathrm{M}^* + \mathrm{Ar_3S^+\,X^-} \longrightarrow \mathrm{M} + {}^3[\mathrm{Ar_3S^+\,X^-}]^* \qquad (7)$$

. . . thence reactions (2)—(5) of Scheme 1.

Scheme 2

Figure 1 shows the conversion against time plots for VCZ/triphenylsulphonium hexafluoroantimonate systems in dichloromethane solution irradiated with light of wavelength 334 nm at room temperature. Under anaerobic conditions, polymerization is rapid and virtually complete after 10 minutes, whilst in the dark or in the absence of the onium salt, polymer formation is barely observable after an hour. In the presence of diphenylamine the polymerization is almost completely suppressed indicating that the dominant chain carrier is indeed cationic. In addition it is reasonable to assume that a triplet state, that of VCZ, is involved in the forward reaction path since polymer formation is also suppressed in oxygen saturated solution.

In order to demonstrate that the reduced mobilities encountered in the almost solid matrix of a resist application do not markedly affect the photosensitization of polymerization, a resist containing 0.6% triphenylsulphonium hexafluoroantimonate, 20% VCZ in poly(methyl methacrylate-co-1,2-dichloropropyl acrylate) was exposed to a mercury arc lamp through a 313 nm filter; a wavelength that affords the least attenuation of the incident beam by the resist layer. Though polymerization was not complete, the marked reduction in the absorption bands at 240 and 275 nm (associated with the vinyl group of VCZ and its conjugation to the aromatic π-system) indicated conversions of approximately 30 and 60% after 1 and 6 minutes respectively.

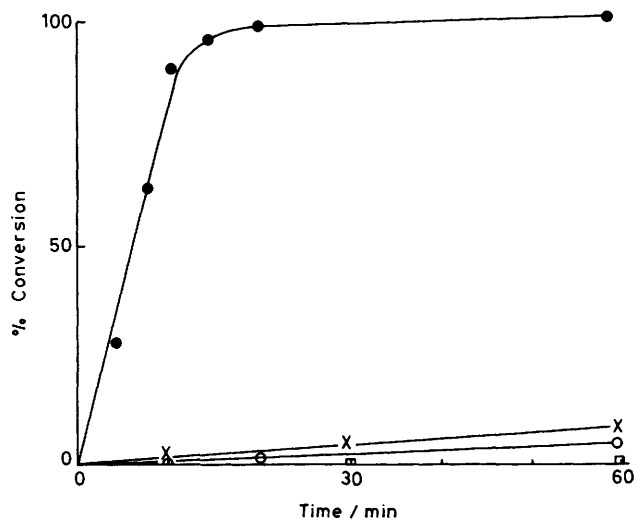

Figure 1. Conversion plots for the photopolymerization of *N*-vinylcarbazole (1 mol dm^{-3}) in the presence of triphenylsulphonium hexafluoroantimonate (TPS) at 298 K. [TPS] = 10^{-2} mol dm^{-3}: ●, deaerated; ×, oxygen saturated; ○, deaerated, $\mathrm{Ph_2NH}$ included; □, [TPS] = 0, deaerated.

This capability of monomers with readily accessible ππ*-triplet states to sensitize the photoinitiators of their own polymerization, offers a new approach to the formulation of resists based on onium salts, in which longer wavelength sensitivity can be achieved without recourse either to structural variation of the onium salt, or the inclusion of a third component.

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References

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