# Photopolymerization of vinyl ether by hydroxy- and methylthio-alkylphosphonium salts as novel photocationic initiators

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2-Hydroxy-3-chloropropyl- and 2-methylthio-1-phenylethyltriphenylphosphonium salts have been used as novel photoinitiators for cationic polymerization of vinyl ethers.

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Recently, there has been great interest in the photopolymerization of cationically polymerizable monomers such as epoxides, styrene, α-methylstyrene, *N*-vinylcarbazole and alkyl vinyl ethers catalysed by iodonium and sulfonium salt-type initiators: $R_2I^+$ $X^-$, $R_3S^+$ $X^-$; R = Ph, Tol, etc., $X^- = SbF_6^-$, $PF_6^-$, etc.[1-3]. Numerous attempts have also been made to obtain a photodecomposition mechanism for these initiators[4-8]. More recently, much attention has been focused on alkyl vinyl ethers in the cationic monomers owing to their higher reactivities[9-12]. However, the exploration of cationic initiators in these photopolymerization studies has been very limited. Therefore, it is important to develop photopolymerization systems of vinyl ethers by using novel cationic photoinitiators. There have been reports of the synthesis of a series of hydroxy- and methylthio-alkylphosphonium salts by reactions of cyclic ethers with triphenylphosphine in the presence of strong acid[13], and of olefins with dimethyl(methylthio)sulfonium salts in the presence of triphenylphosphine[14]. Obviously, it is of considerable interest to investigate photopolymerization by using these phosphonium salts. In the course of this study we tried to apply these phosphonium salts as photopolymerizable cationic catalysts of cyclohexyl vinyl ether (CHVE), and these catalysts have been found to indicate a quite different photodecomposition behaviour from the sulfonium salts previously reported by Crivello *et al.*[1-3]. The results are described in this communication.

In a typical experiment, the photoinitiated cationic polymerization of CHVE (2.5 g) was carried out with 2-hydroxy-3-chloropropyltriphenylphosphonium salt ($Ph_3P^+$-$CH_2CH(OH)CH_2Cl$ $BF_4^-$; u.v. $\lambda_{max}$ 266 nm), or 2-methylthio-1-phenylethyltriphenylphosphonium salt ($Ph_3P^+$-$CHPhCH_2SMe$ $CF_3SO_3^-$; u.v. $\lambda_{max}$ 268 nm), each of 6 $\mu$M in MeCN. The conditions were 1 mol% CHVE, at 20°C for 10 min under irradiation with a 500 W high-pressure mercury lamp. The conversion of CHVE was measured by gas–liquid chromatography, and the average molecular weights of the obtained polymers were determined by gel permeation chromatography calibrated with standard polystyrenes. The cationic photopolymerization of CHVE catalysed by a phosphonium salt without a hydroxyl or methylthio group (1-propenyltriphenylphosphonium salt: $Ph_3P^+$–$CH{=}CHMe$ $BF_4^-$: u.v. $\lambda_{max}$ 268 nm; 6 $\mu$M in MeCN), by triphenylphosphine, and the control system (no catalyst), were also examined under similar conditions for comparison, and these results are shown in *Table 1*.

No polymerization took place in the dark, but the polymerization of CHVE was observed when irradiation was started. As *Table 1* shows, both hydroxy- and methylthio-containing phosphonium salts are very active initiators for CHVE. However, 1-propenyltriphenylphosphonium salt and triphenylphosphine did not show any catalytic effect. It is known that for 1-propenyltriphenylphosphonium salt and triphenylphosphine, photolysis of the hydroxy- and methylthio-containing phosphonium salts could easily abstract a proton from them to generate a strong acid ($HBF_4$ or $CF_3SO_3H$), which would be an initiating species of the cationic polymerization of CHVE. No catalytic activity of 1-propenyltriphenylphosphonium salt or triphenylphosphine in this system would result, because no proton could be abstracted from these salts owing to their possessing neither hydroxyl nor methylthio

**Table 1** Cationic bulk photopolymerization of CHVE catalysed by hydroxy- and methylthio-alkylphosphonium salts

| Catalyst | Conversion of CHVE (%) | $\bar{M}_n(\bar{M}_w/\bar{M}_n)$ |
|---|---|---|
| $Ph_3P^+$-$CH_2CH(OH)CH_2Cl$ $BF_4^-$ | 100 | 19 000 (1.67) |
| $Ph_3P^+$-$CHPhCH_2SMe$ $CF_3SO_3^-$ | 100 | 13 000 (1.71) |
| $Ph_3P^+$–$CH{=}CHMe$ $BF_4^-$ | 7 | – |
| $PPh_3$ | 7 | – |
| No catalyst | 6 | – |

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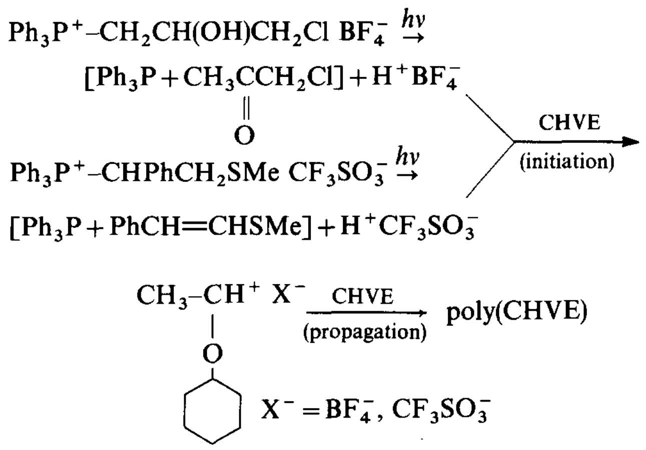
group. In contrast, the iodonium or sulfonium salt-type initiators ($R_2I^+$ $X^-$ or $R_3S^+$ $X^-$) are known to generate *in situ* a strong acid (HX), produced by proton abstraction from a solvent upon irradiation by light, which initiates cationic polymerization[4–8]. Our present results are likely to be accounted for in terms of the following cationic polymerization mechanism:



Comprehensive studies on the scope and limitation of the photopolymerization with hydroxy- and methylthioalkylphosphonium salts are in progress.

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