

**Cationic photopolymerization by Polymeric Triphenyl Phosphonium Salts****ABSTRACT**

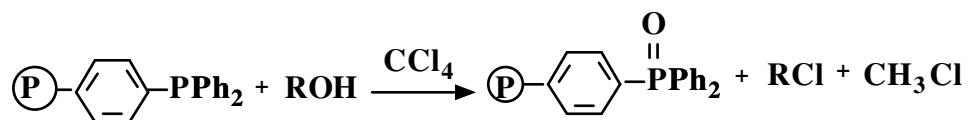
Phenacyl triphenylphosphonium and p-nitrobenzyl triphenylphosphonium polymer bound salts with  $\text{SbF}_6^-$  counter ions, have been synthesized and examined as polymeric photoinitiators for the cationic photopolymerization of epoxide monomers such as cyclohexene oxide and vinyl monomers such as N-vinyl carbazole and p-methyl styrene. These polymeric phosphonium salt catalysts were found to be easy to handle and stable when stored in the dark. Reaction of the nonpolymerizable compound trans-stilbene oxide with the phosphonium gives the isomerization product diphenyl acetaldehyde as major product.

keywords: Polymeric triphenylphosphonium salts, cationic photoinitiators, cyclohexene oxide, N-vinylcarbazole, p-methylstyrene, trans-Stilbene oxide isomerization.

**INTRODUCTION**

Polymer supported reagents has many applications in biochemistry, organic synthesis, specific separation and analysis, the crosslinked polymer is easily cleaned of soluble reactants and products, this permits the polymeric reagent to be used in either columns or batch processes, and it may be regenerated several times.

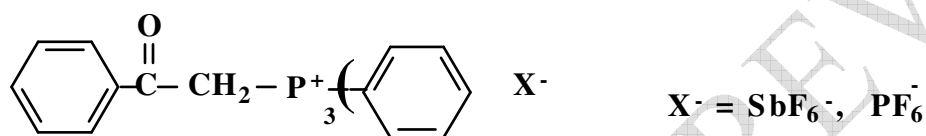
Polymeric triphenylphosphine reacted with alcohols in presence of carbon tetrachloride (equation 1) to give the corresponding alkyl chlorides [1].



(equation 1)

30 Soluble polymeric phosphonium salts have been used as photoinitiators for free radical  
 31 polymerization of styrene and methylmethacrylate [2], Polymeric photoinitiators are attracting a  
 32 great deal of interest in many applications such as printing and UV-curable lacquers for surface  
 33 coatings, inks and microelectronics, for example, Bronsted acids produced from photolysis of  
 34 triphenylsulfonium salts find increasing utility in polymerization reactions [3], crosslinking of  
 35 polymer films [4], or deprotection of chemical functionality [5].

36 Recently we reported that photodecomposition of phenacyl triphenyl phosphonium and  
 37 arsonium salts (1) having  $\text{SbF}_6^-$  anions produces a Bronsted acid which initiates the  
 38 polymerization of cyclohexene oxide [6.7], styrene [8] and p-methyl styrene [9].

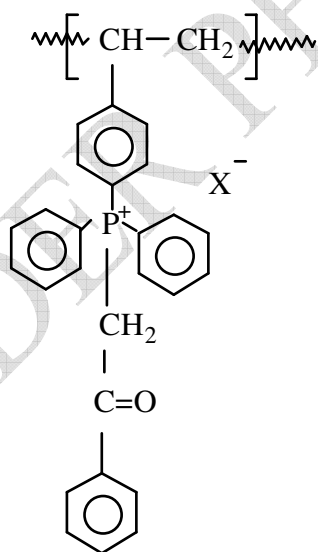


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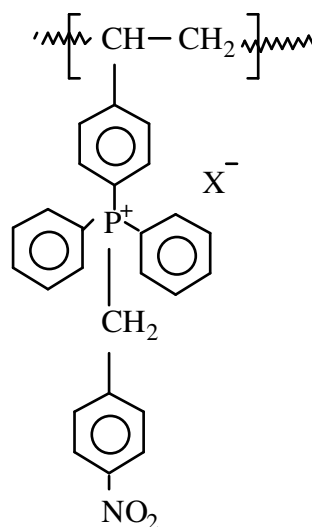
41 In this paper the synthesis of the polymeric phenacyltriphenylphosphonium (2) and p-nitrobenzyl  
 42 triphenylphosphonium (3) salts with  $\text{SbF}_6^-$  anion are reported.



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46 These polymeric salts are easy to handle, store and sensitive toward UV light. Therefore, they can  
47 be used as photocatalysts in polymerization or curing reactions at room temperature. Also, in the  
48 present paper the uses of these polymeric reagents in acid catalyzed reactions is demonstrated by  
49 the reaction of salt **2** with the non-polymerizable oxirane namely trans-Stilbene oxide (**4**).

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## 51 **Experimental**

52 Photopolymerization was carried out as described before<sup>6</sup>. Swelling of the resin in  
53 dichloromethane was done by stirring the required salt for 20 mins in dichloromethane for the  
54 monomer to penetrate to all of the catalyst sites. Monomer was added before exposure to light.  
55 Irradiation was carried out using a Xenon ARC Lamp, ILC Technology, Inc., Model PS-150-8  
56 with power supply adjusted to 12 ampere constant current; the light intensity was  $11.24 \times 10^{18}$   
57 photon  $\text{sec}^{-1}\text{cm}^{-2}$ . Methanol was added to the reaction product in order to precipitate the polymer.  
58 Monomers and solvents (Fluka) were dried over calcium hydride and distilled before use. Infrared  
59 spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer.

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## 61 **Preparation of polymeric triphenyl phosphonium salts (2 and 3)**

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63 The polymeric phosphonium salts used were prepared by reaction of polymer bound  
64 triphenylphosphine obtained from Flucka chemical company with phenacyl bromide or 4-  
65 nitrobenzyl bromide in acetone as described below:

66 2.0 gram of phenacyl bromide (0.05 mol) or 4-nitrobenzyl bromide (0.05 mol) were added slowly  
67 to a stirred suspension of 10.0 g of polymer bound triphenylphosphine (~ mmol  
68 triphenylphosphine/gram polymer, 200-400 mesh) in 500 ml acetone, and the reaction mixture  
69 was stirred under reflux for about 6 hours. The product was filtered off and the residue was  
70 washed with acetone several times, then dichloromethane, and finally dried under vacuum at room  
71 temperature overnight. The bromide ion was replaced by the  $\text{SbF}_6^-$  anion by treating the polymeric  
72 salt with  $\text{KSbF}_6$  in acetone and stirring the reaction mixture at room temperature for 3 hours,  
73 washing with acetone three times, after that with methanol then acetone, and finally with  
74 dichloromethane.

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## RESULTS AND DISCUSSION

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83 Salts having chloride or bromide anion did not initiate the cationic polymerization, Table 1 shows  
84 that the yield of the polymer depend on the structure of salt used (anion =  $\text{SbF}_6^-$ ), salt 2  
85 polymerize the vinyl type monomers and did not polymerize cyclohexene oxide, this is could be  
86 due to interaction between the nitro group and the propagated oxonium cation which can  
87 terminate the polymerization at early stage.

88 These results suggest that polymeric salt **3** having anion  $\text{SbF}_6^-$  is apparently much better at  
89 stabilizing the oxonium ion and is good initiators for cationic polymerization of epoxide and vinyl  
90 monomers

91 Photopolymerization of selected monomers (cyclohexene oxide = CHO, N-vinylcarbazole =  
92 NVC, p-methylstyrene = pmethst.) was examined using salts **2** and **3**, and the results are shown in  
93 table 1.

94 **Table 1** Photopolymerization of selected monomers by salts 2 and 3, polymerization Time = 30  
95 minutes. Monomer concentration 50/50 by volume. Solvent dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), Initiator  
96 concentration  $3.5 \times 10^{-3}$ .

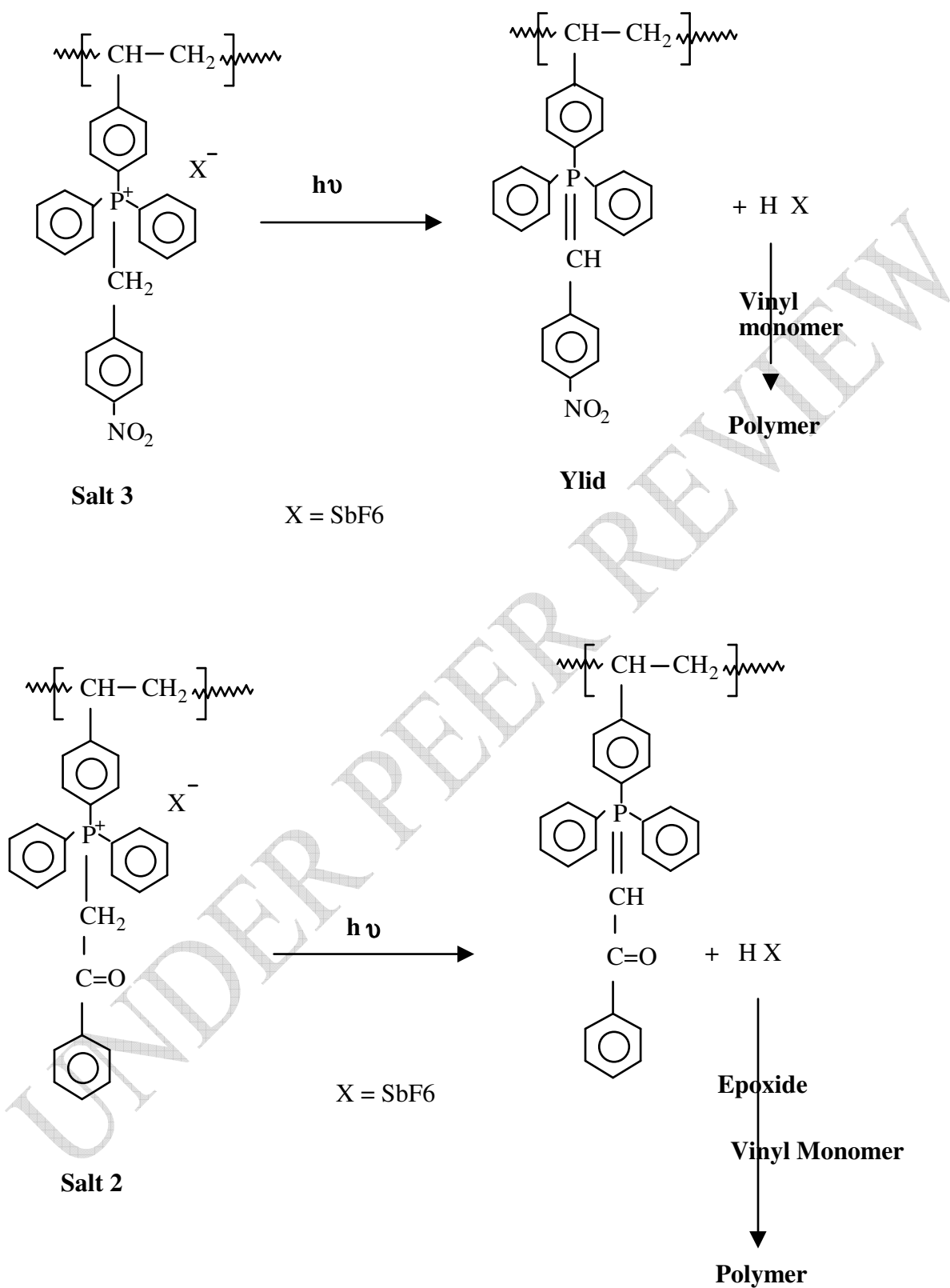
| Monomer          | Salt structure | % conversion to polymer |
|------------------|----------------|-------------------------|
| CHO              | 2              | 21.4                    |
| CHO              | 3              | 7.6                     |
| NVC              | 2              | 100                     |
| NVC              | 3              | 100                     |
| p-methyl styrene | 2              | 16.6                    |
| p-methyl styrene | 3              | 14.2                    |

105 Scheme1 shows the photolysis of the triphenyl phosphonium salt 2 and 3 produce the Bronsted  
106 acid and the yield following the established mechanism for the model compounds [4.6]. The  
107 Bronsted acid can initiated the cationic polymerization.

108 Chemical treatment of the isolated yields obtained from photolysis of **2** or **3** with HCl solution  
109 gives the corresponding salt with the chloride counter ion.

110 The Infra-red analysis of the polymeric salts 2 shows  $(\text{C}=\text{O}) = 1678 \text{ cm}^{-1}$ , Also for salt 3 nitro  
111 group at  $1524$  and  $1348 \text{ cm}^{-1}$  when the spectra are compared to the starting polymer.

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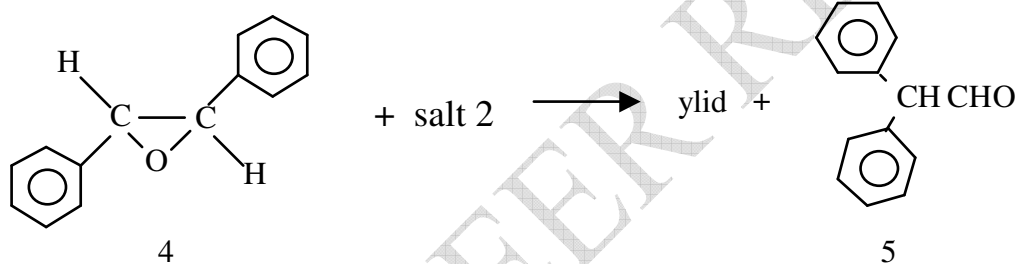
(Scheme 2) Photolysis of salt 2 and 3

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**116 Reactions of (Polystyryl) diphenyl phosphonium salts with trans stilbene oxide (4).**

117 Diphenylacetaldehyde (5) was obtained from trans-stilbene oxide (4) by the action of boron  
118 trifluoride in ether.<sup>10</sup> We have examined the reaction of (4) with the polymeric salt 2. In these  
119 reactions salt (2) reacts photochemically with trans-stilbene oxide in dichloromethane, the  
120 reaction product was isolated by filtration and solvent evaporation gives the reaction product  
121 which was isolated as viscous liquid. IR analysis of the reaction product showed that the epoxy  
122 group at  $1285\text{ cm}^{-1}$  has disappeared and is replaced by the aldehyde carbonyl group at  $1708\text{ cm}^{-1}$   
123 and the aldehydic CH at  $2840$  and  $2730\text{ cm}^{-1}$ , the by-product polymer gives slightly red color  
124 beads.

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**CONCLUSION**

131 Polymer-bound phenacyl and benzyl triphenyl phosphonium salts can initiate the  
132 photopolymerization of epoxide and vinyl monomers, and can be used in acid catalyzed reactions  
133 of nonpolymerizable organic compounds.

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