

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

Phenacyl triphenylphosphonium and p-nitrobenzyl triphenylphosphonium polymer bound salts with 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. The polymeric phosphonium salts utilized as photocatalysts and were found to be easy to handle and stable when stored far from normal light. Reaction of the nonpolymerizable epoxide compound trans-stilbene oxide with the polymeric phenacyl phosphonium was investigated in dichloromethane solvent and found to give diphenyl acetaldehyde.

keywords: Polymeric triphenyl phosphonium salts, cationic photo initiators, cyclohexene oxide, N-vinyl carbazole, p-methyl styrene, trans-Stilbene oxide acid isomerization.

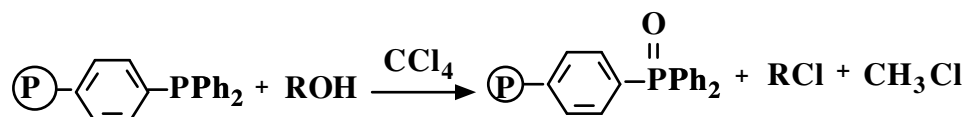
INTRODUCTION

Phosphonium compounds offer a vast and attractive field of research for the chemists and biologists, and polymeric materials containing quaternary ammonium and/or phosphonium salts have been extensively studied and applied to a variety of antimicrobial-relevant areas. [1]

Various polymeric phosphonium salts and the corresponding low molecular weight model compounds were prepared and their antibacterial activities were explored. Antibacterial activity of the polymers was found to be higher than that of the corresponding model compounds [2,3].

The process of heterogenization of homogeneous catalysts defined as the modification of homogeneous catalyst permits the polymeric reagent or catalyst to be used in either columns or batch processes, and it may be regenerated several times, or activated in a very attractive economical way and the product(s) can be easily separated. Polymeric triphenylphosphine reacted

32 with alcohols in presence of carbon tetrachloride (equation 1) to give the corresponding alkyl
33 chlorides equation (1) [4].



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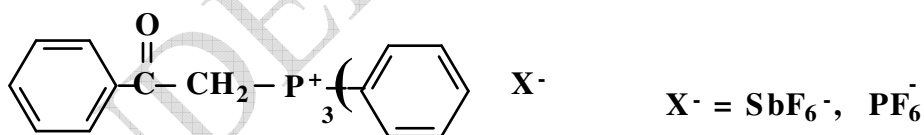
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(equation 1)

36 Soluble polymeric phosphonium salts have been used as photoinitiators for free radical
37 polymerization of styrene and methyl methacrylate when irradiated with 365 nm and cationic
38 photoinitiated cyclohexene oxide when irradiated by 300 nm wave length light. [5]

39 Polymeric photoinitiators are attracting a great deal of interest in many applications such as
40 printing and UV-curable lacquers for surface coatings, inks and microelectronics; for example,
41 Bronsted acids produced from photolysis of triphenylsulfonium salts find increasing utility in
42 polymerization reactions [6,7], crosslinking of polymer films [8,9], or deprotection of chemical
43 functionality [10,11].

44 Photodecomposition of phenacyl triphenyl phosphonium and arsonium salts (1) having SbF_6^-
45 anions can give a Bronsted acid H^+SbF_6^- , and this can initiate the cationic polymerization
46 cyclohexene oxide [12,13], styrene [14] and p-methyl styrene [15]. The counterion structure (X^-) is
47 very important to initiation process efficiency, and will decide on the termination process of the
48 propagated chain; and generally in polymerization the reactivity of the counter ion depends on the
49 propagated chain type and mode of polymerization [5].



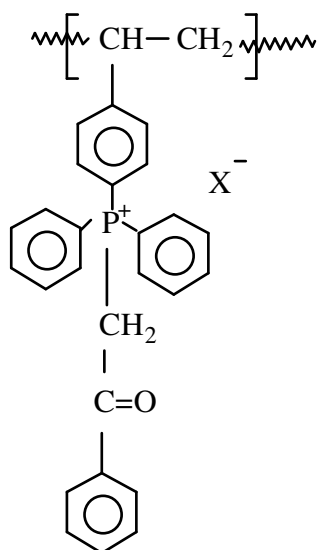
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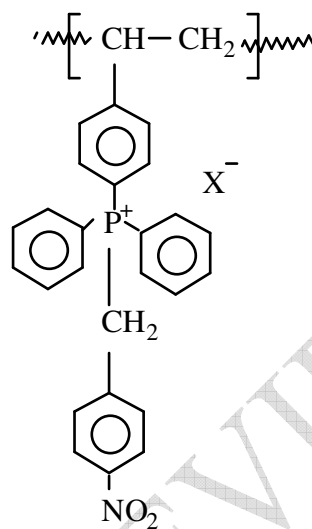
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52 The heterogenization of the phenacyl and benzyl phosphonium was carried out to extend the shelf
53 life and storage of the salt, working conditions stability, reactivity and product separation of the
54 simple nonpolymeric salt. In this paper we report on the synthesis of the polymeric

55 phenacyltriphenylphosphonium (2) and p-nitrobenzyl triphenylphosphonium (3) salts with SbF_6^-
56 anion and examine the reactivity in polymerization of selected epoxide and vinyl monomers.



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60 These polymeric salts are easy to handle, store and sensitive toward photolysis. Therefore, they
61 can be used as photocatalysts in polymerization or curing reactions at room temperature. The
62 reaction of the synthesized polymeric salts for acid catalyzed reactions is demonstrated here by the
63 reaction of salt 2 with the non-polymerizable epoxide namely trans-Stilbene oxide (**4**) where the
64 product obtained is diphenyl acetaldehyde (**16**).

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Experimental

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Chemicals:

68 Cyclohexeneoxide, p-methylstyrene and N-vinylcarbazole monomers, dichloromethane and
69 methanol, acetone solvents were obtained from Fluka chemical company were dried over calcium
70 hydride and distilled before use. phenacyl bromide or 4-nitrobenzyl bromide obtained from
71 Aldrich.

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73 Infrared spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer.

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Photopolymerization:

76 Photopolymerization was carried out by swelling of the polymeric phosphonium resin (salt 2 or
77 salt 3) in dichloromethane was done by stirring 2 grams from the polymeric resin in 50 mL
78 dichloromethane, the loaded in small column after 20 minutes from mixing. Monomer was added

79 to resin and left to penetrate through, then irradiation was carried out using a Xenon ARC Lamp,
80 ILC Technology, Inc., Model PS-150-8 with power supply adjusted to 12 ampere constant current;
81 the light intensity was 11.24×10^{18} photon $\text{sec}^{-1} \text{cm}^{-2}$. After the selected time period the reaction
82 product obtained by opening the column into four-fold excess methanol, double washing with 5
83 mL dichloromethane was carried out in order to extract all monomer/ polymer. Cyclohexeneoxide,
84 p-methylstyrene and N-vinylcarbazole monomers, dichloromethane and methanol, acetone
85 solvents were obtained from Fluka chemical company were dried over calcium hydride and
86 distilled before use. phenacyl bromide or 4-nitrobenzyl bromide obtained from Aldrich. Infrared
87 spectra were recorded on a Nicolet 5 DXB FT-IR spectrophotometer.

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89 **Polymeric salts synthesis**

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91 Preparation of polymeric triphenyl phosphonium salts (2 and 3):

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93 The polymeric phosphonium salts 2 and 3 used in this work were prepared by reaction of polymer
94 bound triphenylphosphine with phenacyl bromide to prepare salt (2) or 4-nitrobenzyl bromide to
95 prepare salt (3) in acetone as described below:

96 2.0 gram of phenacyl bromide (0.05 mol) or 4-nitrobenzyl bromide (0.05 mol) were added slowly
97 to a stirred suspension of 10.0 g of polymer bound triphenylphosphine (~ mmol
98 triphenylphosphine/gram polymer, 200-400 mesh) in 500 ml acetone, and the reaction mixture
99 was stirred under reflux for about 6 hours. The reaction product was filtered off and the residue
100 was washed three times with acetone, then two times dichloromethane, and finally dried under
101 vacuum at room temperature overnight. The bromide ion was replaced by the SbF_6^- anion by
102 treating the polymeric salt with KSbF_6 in acetone by stirring the reaction mixture at room
103 temperature for 3 hours, then washed with acetone three times, and finally with dichloromethane
104 and dried at room temperature to be ready for utilization in further reactions.

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110 **RESULTS AND DISCUSSION**

111 Salts having bromide anion did not initiate the cationic polymerization due to the termination
112 process resulting from the bromide ion to the propagated cation. Table 1 shows that the product of
113 the polymer depend on the structure of the onium salt used (anion = SbF_6^-), 4-nitrobenzyl
polymeric phosphonium hexafluoro antimonate (salt 2) polymerize the vinyl monomers (p-

114 methylstyren and N-vinylcarbazole), and did not initiate the cationic polymerization of
 115 cyclohexene oxide, this could be due to interaction between the polar nitro group and the
 116 propagated oxonium cation which can terminate the polymerization at early stage.

117 The Polymeric phenacyltriphenyl phosphonium (salt 3) having anion SbF_6^- is apparently much
 118 better compared to salt 2 in stabilizing the propagated oxonium ion of cyclohexene oxide and is
 119 good initiators for cationic polymerization of both epoxide and vinyl monomers under the
 120 conditions reported. Photopolymerization of selected monomers (cyclohexene oxide = CHO, N-
 121 vinylcarbazole = NVC, p-methylstyrene = pmethst.) was examined using salts 2 and 3, under the
 122 same conditions, the obtained results of conversion monomer to polymer for each monomer are
 123 shown in table 1 below.

124 **Table 1.** Photopolymerization of the selected monomers by salts 2 and 3. Polymerization Time =
 125 30 minutes. Monomer concentration is 50/50 by volume in dichloromethane. Initiator
 126 concentration 3.5×10^{-3} , solvent used dichloromethane.

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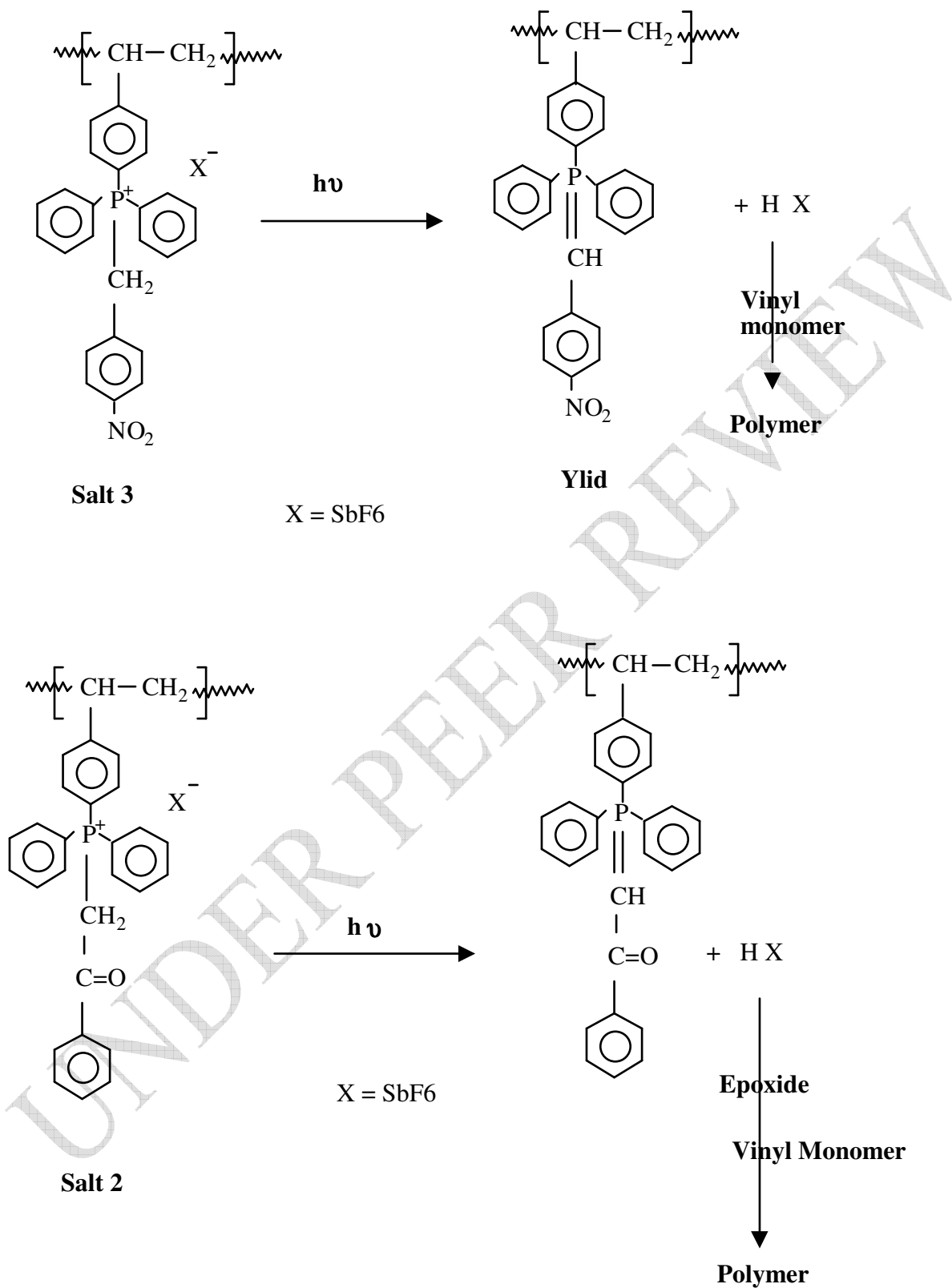
Monomer	Salt structure	% conversion to polymer
CHO	2	21.4
CHO	3	7.6
NVC	2	100
NVC	3	100
p-methyl styrene	2	16.6
p-methyl styrene	3	14.2

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136 Scheme1 below shows the photolysis of triphenyl phosphonium salt 2 and 3 which gives the
 137 Bronsted acid HSbF_6 when counter ion of thee used salt is SbF_6^- and the neutral phosphonium
 138 yield (P=C). Following the established mechanism for the phosphonium salt (1) reported in our
 139 early work [7,12,13]. The Bronsted acid can initiated the cationic polymerization.

140 In another experiment, chemical treatment of the isolated yield obtained from photolysis of salt 2
 141 or salt 3, with 2.0 M HCl solution gives the corresponding salt with chloride (Cl^-) counter ion.

142 The was proven from the Infra-red analysis of the polymeric salts 2 shows (C=P) at 1678 cm^{-1} ,
 143 and salt 3 the P=C group at 1524 and 1348 cm^{-1} , corresponding to yield produced compared to
 144 the starting polymer salt in each case. These characterized group were disappeared after the
 145 addition of HCl to the yield (P=C).



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(Scheme 2) Photolysis of salt 2 and 3

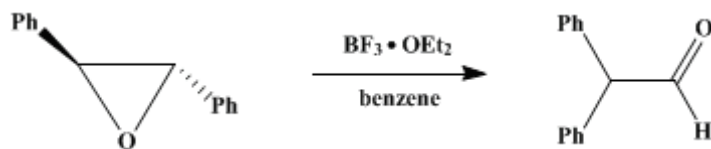
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149 **REACTION OF SALT 2 WITH TRANS-STILBENE OXIDE (4)**

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151 Reif and House [16] report on the formation of diphenyl acetaldehyde (5) from trans stilbene
152 oxide (4) in the presence of boron trifluoride etherate in benzene as shown in scheme (3) below.

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155 Scheme (3): Formation of diphenyl acetaldehyde from trans stilbene oxide in the presence of
156 boron trifluoride etherate.

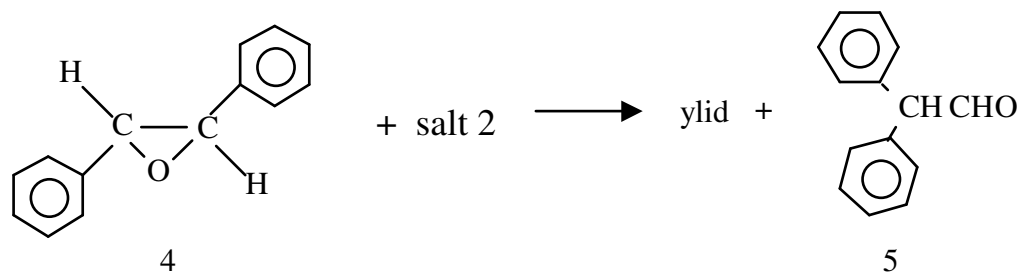
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158 Epoxides are one of the most versatile functional groups in organic chemistry due to their ready
159 availability and ease of transformation into a wide variety of functional groups, and several
160 reagents have been utilized for this purpose [17-19].

161 Rearrangement of epoxides to carbonyl compounds in the presence of reusable acidic zeolite
162 catalysts under mild conditions [20-22].

163 We investigated the photochemical reaction of trans -stilbene oxide (4) with the polymeric (salt 2)
164 in dichloromethane, reaction was found to be fast, efficient and the product was isolated by
165 filtration from the solid phase resin in column process. After solvent evaporation the reaction
166 product was isolated, and the IR analysis showed the epoxy group at 1285 cm⁻¹ has disappeared
167 and replaced by the aldehyde group at 1708 cm⁻¹ and the aldehydic (CH) at 2840 and 2730 cm⁻¹.
168 As shown in scheme (4).

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170 .
 171 Scheme (4): Formation of diphenyl acetaldehyde from trans stilbene oxide by photolysis of (salt
 172 2).
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174 Thus, our effort directed towards finding environmentally friendly processes for the
 175 photopolymerization of epoxides and vinyl monomers; and the chemical rearrangement of
 176 nonpolymerizable epoxides is achieved in the presence of reusable polymeric phosphonium salt
 177 under mild conditions.
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CONCLUSION

181 Polymer-bound phenacyl and benzyl triphenyl phosphonium salts can initiate the
 182 photopolymerization of epoxide and vinyl monomers, the rate of polymerization depends on
 183 phosphonium salt, monomer structure and counter ion (X^-), salt (2) is more efficient towards
 184 cyclohexene oxide monomer and salt 3 is more efficient towards vinyl group monomers such as
 185 N-vinyl carbazole and P-Methyl styrene. Other aspects of super acids were utilized here by
 186 applying the reaction of salt 2 with trans - stilbene oxide which is a nonpolymerizable epoxide
 187 conversion of trans stilbene oxide to diphenyl acetaldehyde was achieved in a quantitative
 188 measure.
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