



Cationic Photopolymerization by Polymeric Triphenyl Phosphonium Salts

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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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.

1. 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

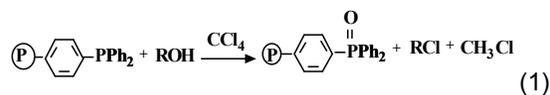
have been extensively studied and applied to a variety of antimicrobial-relevant areas [1].

Various polymeric phosphonium salts and the corresponding low-molecular-weight model compounds were prepared and their antibacterial

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

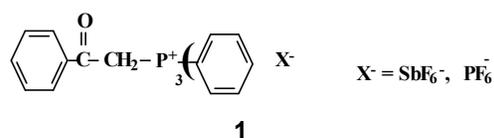


Soluble polymeric phosphonium salts have been used as photoinitiators for free radical polymerization of styrene and methyl methacrylate when irradiated with 365 nm and cationic photoinitiated cyclohexene oxide when irradiated by 300 nm wave length light [5].

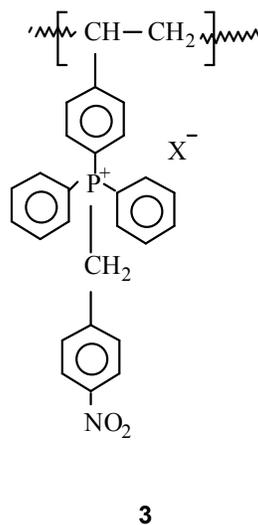
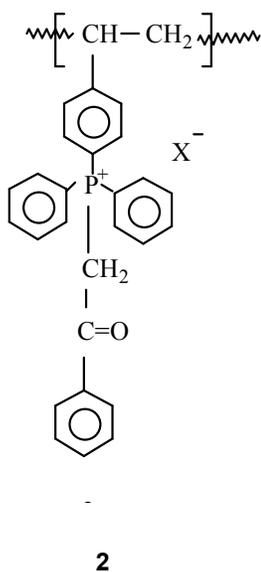
Polymeric photoinitiators are attracting a great deal of interest in many applications such as printing and UV-curable lacquers for surface coatings, inks and microelectronics; for example, Bronsted acids produced from photolysis of triphenylsulfonium salts find increasing utility in polymerization reactions [6,7], crosslinking of

polymer films [8,9], or deprotection of chemical functionality [10,11].

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



The heterogenization of the phenacyl and benzyl phosphonium was carried out to extend the shelf life and storage of the salt, working conditions stability, reactivity and product separation of the simple nonpolymeric salt. In this paper we report on the synthesis of the polymeric phenacyltriphenylphosphonium (2) and p-nitrobenzyl triphenylphosphonium (3) salts with SbF_6^- anion and examine the reactivity in polymerization of selected epoxide and vinyl monomers.



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

2. EXPERIMENTAL

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

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

Photopolymerization: Photopolymerization was carried out by swelling of the polymeric phosphonium resin (salt 2 or salt 3) in dichloromethane was done by stirring 2 grams from the polymeric resin in 50 mL dichloromethane, the loaded in small column after 20 minutes from mixing. Monomer was added to resin and left to penetrate through, then irradiation was carried out using a Xenon ARC Lamp, ILC Technology, Inc., Model PS-150-8 with power supply adjusted to 12 ampere constant current; the light intensity was 11.24×10^{18} photon $\text{sec}^{-1} \text{cm}^{-2}$. After the selected time period the reaction product obtained by opening the column into four-fold excess methanol, double washing with 5 mL dichloromethane was carried out in order to extract all monomer/ polymer.

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

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

2.0 gram of phenacyl bromide (0.05 mol) or 4-nitrobenzyl bromide (0.05 mol) were added slowly to a stirred suspension of 10.0 g of polymer bound triphenylphosphine (~ mmol triphenylphosphine/gram polymer, 200-400

mesh) in 500 ml acetone, and the reaction mixture was stirred under reflux for about 6 hours. The reaction product was filtered off and the residue was washed three times with acetone, then two times dichloromethane, and finally dried under vacuum at room temperature overnight. The bromide ion was replaced by the SbF_6^- anion by treating the polymeric salt with KSbF_6 in acetone by stirring the reaction mixture at room temperature for 3 hours, then washed with acetone three times, and finally with dichloromethane and dried at room temperature to be ready for utilization in further reactions.

3. RESULTS AND DISCUSSION

Salts having bromide anion did not initiate the cationic polymerization due to the termination process resulting from the bromide ion to the propagated cation. Table 1 shows that the product of 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-methylstyren and N-vinylcarbazole), and did not initiate the cationic polymerization of cyclohexene oxide, this could be due to interaction between the polar nitro group and the propagated oxonium cation which can terminate the polymerization at early stage.

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

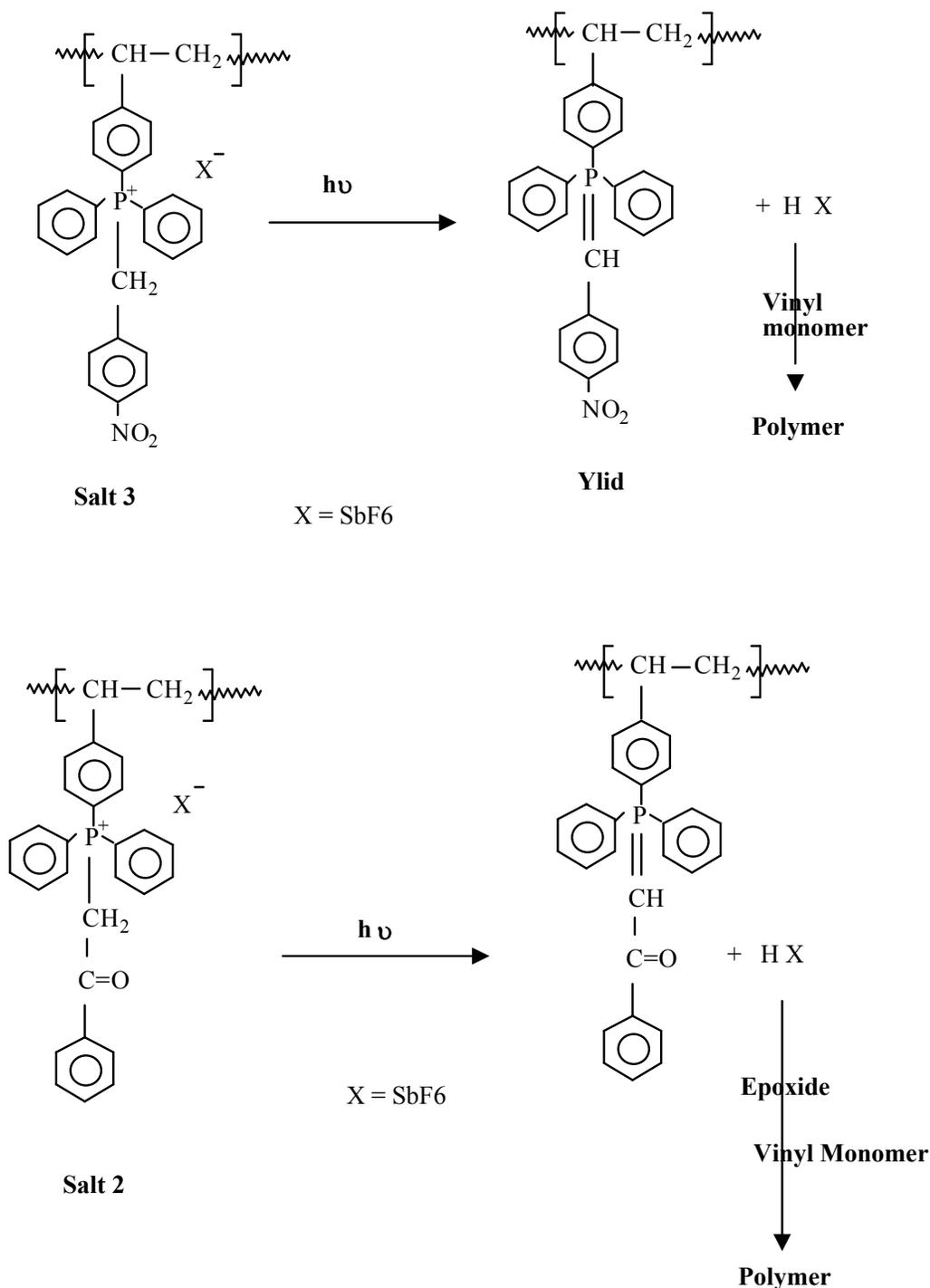
Scheme1 below shows the photolysis of triphenyl phosphonium salt 2 and 3 which gives the Bronsted acid HSbF_6 when counter ion of the used salt is SbF_6^- and the neutral phosphonium yield ($\text{P}=\text{C}$). Following the established mechanism for the phosphonium salt (1) reported in our early work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

In another experiment, chemical treatment of the isolated yield obtained from photolysis of salt 2 or

salt 3, with 2.0 M HCl solution gives the corresponding salt with chloride (Cl⁻) counter ion.

This was proven from the Infra-red analysis of the polymeric salts 2 shows (C=P) at 1678 cm⁻¹,

and salt 3 the P=C group at 1524 and 1348 cm⁻¹, corresponding to yield produced compared to the starting polymer salt in each case. These characterized group were disappeared after the addition of HCl to the yield (P=C).



Scheme 1. Photolysis of salt 2 and 3

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

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

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

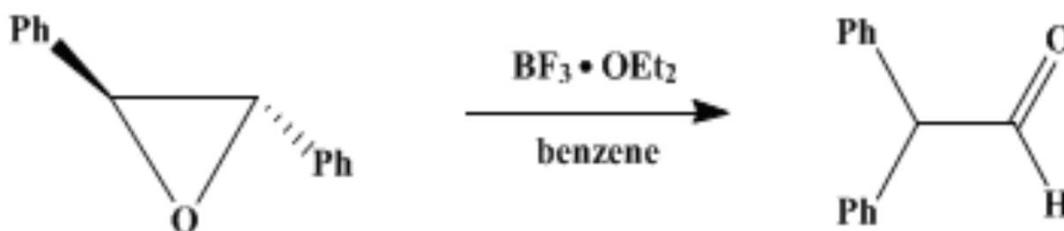
Reif and House [16] reported on the formation of diphenyl acetaldehyde (5) from trans stilbene oxide (4) in the presence of boron trifluoride etherate in benzene as shown in scheme (2).

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

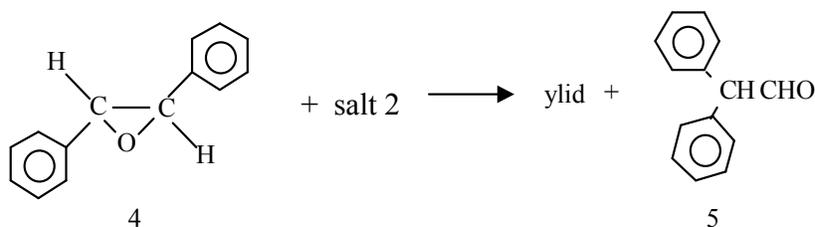
Rearrangement of epoxides to carbonyl compounds in the presence of reusable acidic zeolite catalysts under mild conditions [20-22].

We investigated the photochemical reaction of trans -stilbene oxide (4) with the polymeric (salt 2) in dichloromethane, reaction was found to be fast, efficient and the product was isolated by filtration from the solid phase resin in column process. After solvent evaporation the reaction product was isolated, and the IR analysis showed the epoxy group at 1285 cm^{-1} has disappeared and replaced by the aldehyde group at 1708 cm^{-1} and the aldehydic (CH) at 2840 and 2730 cm^{-1} . As shown in scheme (3).

Thus, our effort directed towards finding environmentally friendly processes for the photopolymerization of epoxides and vinyl monomers; and the chemical rearrangement of nonpolymerizable epoxides is achieved in the presence of reusable polymeric phosphonium salt under mild conditions.



Scheme 2. Formation of diphenyl acetaldehyde from trans stilbene oxide in the presence of boron trifluoride etherate



Scheme 3. Formation of diphenyl acetaldehyde from trans stilbene oxide by photolysis of (salt 2)

5. CONCLUSION

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

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COMPETING INTERESTS

Author has declared that no competing interests exist.

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