

## STUDIES ON THE PROMOTED POLYMERIZATION OF 4-VINYLCYCLOHEXENDIOXIDE

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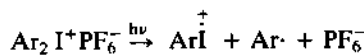
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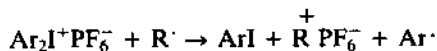
**Abstract**—Promoted polymerization of 4-vinylcyclohexendioxide (4-VCHD), using a radical source or sensitizer and a cationic salt such as diphenyliodonium hexafluorophosphate, has been studied. The effects of phenylazotriphenylmethane on both thermal and photochemical induced polymerizations were examined. Several other activators were used.

### INTRODUCTION

Currently, there is interest in initiation systems which produce Lewis acids suitable for polymerization of epoxides [1]. Arylonium salts have been found suitable for this purpose [2,3]. Photodecomposition of arylonium salts and subsequent reaction of the arylonium radical cation with solvent leads to the formation of Brønsted acid,  $H^+$ , which is responsible for further initiation, thus



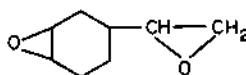
The decomposition may also be accomplished by electron free radicals or suitable sensitizers [4].



$R\cdot$  = electron donor free radical

Efficient activation requires matching of redox potentials for the promoting free radical and onium salts. On the other hand, several potential mechanisms for the photosensitization have been proposed [5-8].

This paper describes some approaches to the activated polymerization of 4-vinylcyclohexendioxide (4-VCHD).



(4-VCHD)  
 Scheme 1

### EXPERIMENTAL

4-VCHD was distilled over  $CaH_2$  and the middle fraction was collected. Bulk monomer containing known amount of initiator was contained in a reaction vessel which was placed in a thermostat at  $80^\circ$ . At the end of the

reaction time, polymer was recovered by reprecipitating in methanol containing a small amount of base. Cross-linked polymers were separated from polymers which are filtered as benzene solubles. Photochemically induced polymerizations were carried out as for the thermal reactions except that the reaction vessels were irradiated by a 250 W medium pressure Hg lamp while in a water bath at  $25^\circ$ . Absorption by the iodonium salt was excluded by using glass vessels.

### RESULTS AND DISCUSSION

Using phenylazotriphenylmethane (PAT) and  $Ph_2I^+PF_6^-$  as radical source and cationic salt respectively, the rates of polymerization and cross-linking were examined as a function of the reaction time. Figure 1 shows that in the early stages the polymerization proceeds at an appreciable rate while very little cross-linked polymer is formed. The

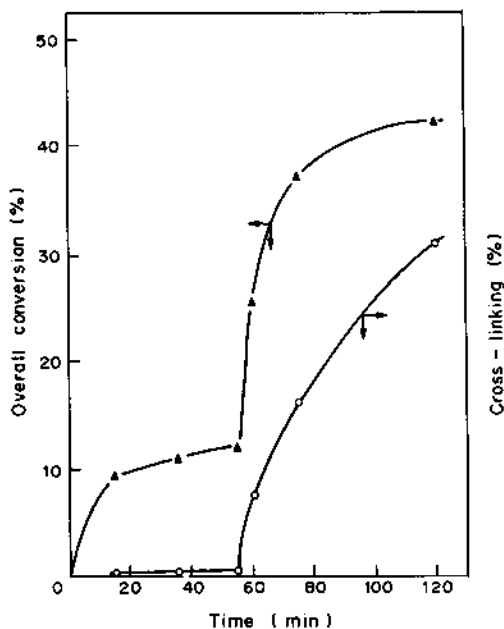


Fig. 1. Thermal polymerization of 4-VCHD at  $80^\circ$  in the presence of  $PhN=NCPPh_3$  at  $10^{-2}$  M and  $Ph_2I^+PF_6^-$  at  $3 \times 10^{-2}$  M.