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A Novel Initiation System for the Cationic Polymerization of Glycidyl Phenyl Ether: Triphenylcyclopropenium Tetrakis(pentafluorophenyl)gallate/ Cyclohexanone

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With the development of rapid, efficient photoinitiators for UV-induced cationic polymerization, such photopolymerizations are now widely employed in applications ranging from coatings and adhesives to printing inks. In the generic onium salt photoinitiator used for this, a strongly oxidizing cation is generally paired with nonnucleophilic anions, such as BF_4^-, PF_6^-, SbF_6^-, $B(C_6F_5)_4^-$, or $Ga(C_6F_5)_4^-$.[2−4] These onium salt/nonnucleophilic anion combinations often have high photosensitivity but excellent thermal stability in the absence of light. The compounds release superacids like $HSbF_6$ upon UV irradiation. These superacids are the primary species responsible for the initiation of cationic polymerization because they are thought to directly protonate the monomer.

Triphenylcyclopropenium (TPCP) ion is the smallest Hückel aromatic compound.[5] The reduction potential of the TPCP cation, measured in acetonitrile, is −0.75 V vs SCE.[6] We thought it therefore a potentially interesting cation with which the cascade of nonnucleophilic anions might be paired for investigation as photochemical superacid sources. Photolysis of TPCP salts in sulfuric acid solvent had previously been reported to produce hexaphenylbenzene.[7]

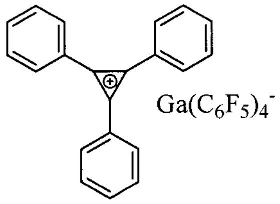

Figure 1. Structure of TPCP gallate.

A series of TPCP salts containing different counterions [SbF_6^-, PF_6^-, and $B(C_6F_5)_4^-$] were thus synthesized as potential photoinitiators. The compounds were rather insoluble in epoxy monomers, and preliminary results showed them to be inefficient in the photopolymerization of epoxides. Surprisingly these compounds were good thermal initiators when employed along with specific carbonyl group containing solvents.[8] The least nucleophilic anion, tetrakis(pentafluorophenyl)gallate, $Ga(C_6F_5)_4^-$ (gallate), when paired with TPCP (Figure 1) was chosen for study.[4]

Even though it is somewhat more soluble in monomers than the other salts, there is also limited photopolymerization of a standard epoxy monomer when TPCP gallate is used. However, when a solution of TPCP gallate dissolved in cyclohexanone was added to a standard epoxide, polymerization took place rapidly at room temperature without UV light. This was evaluated quantitatively using the polymerization of glycidyl phenyl ether (GPE). Conversion of GPE was greatly influenced by changing the ratio of GPE/TPCP gallate/cyclohexanone, with the optimum catalytic activity at a ratio of 100:3:30 (by weight) GPE/TPCP gallate/cyclohexanone.

TPCP gallate is a white crystal (mp 208−209 °C) stable in air at room temperature. It was synthesized from TPCP SbF_6 (prepared by metathesis of TPCP chloride[9] with $NaSbF_6$) by anion exchange using $LiGa(C_6F_5)_4$. The structure was confirmed by ^1H NMR, ^{13}C NMR, ^{19}F NMR, and elemental analysis. TPCP gallate

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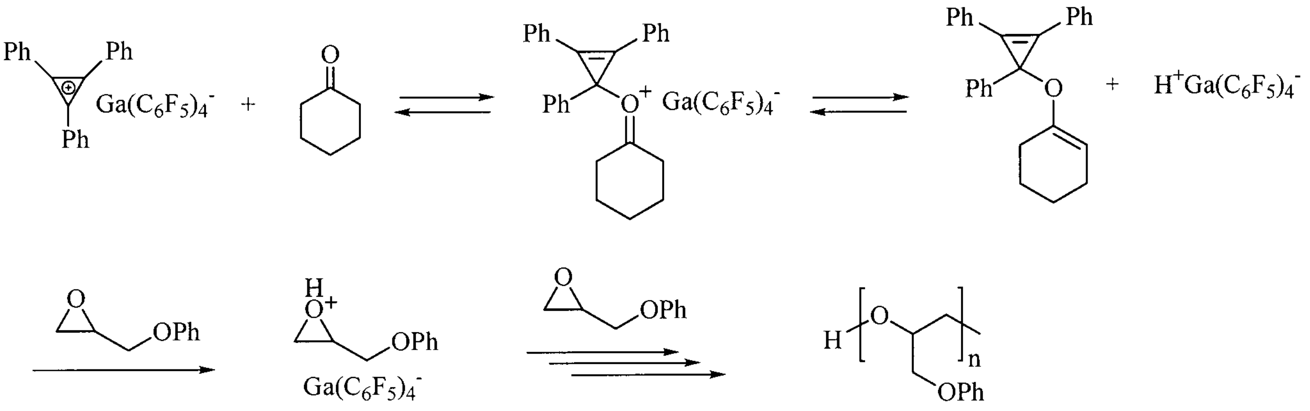
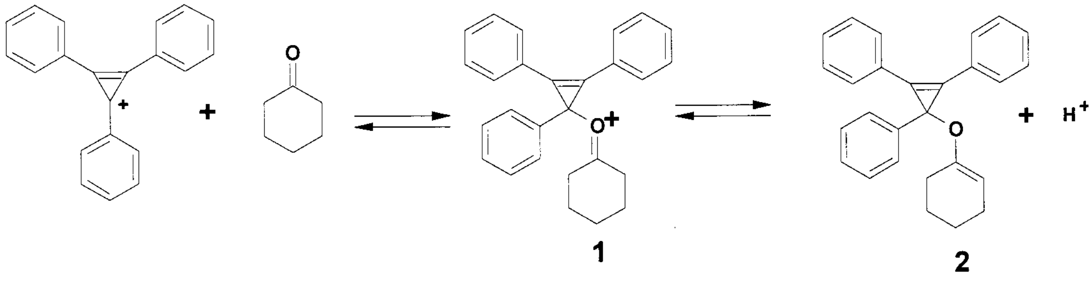
Scheme 1



Scheme 2



exhibits two strong UV absorption bands in acetonitrile at 306 nm ($\epsilon_{max} = 3.56 \times 10^4$ cm^{-1} M^{-1}) and 320 nm ($\epsilon_{max} = 3.18 \times 10^4$ cm^{-1} M^{-1}).

Polymerization of GPE with TPCP gallate/cyclohexanone was carried out at room temperature, and the conversion of GPE was estimated by ^{1}H NMR spectroscopy. The signals at 2.76−2.93 ppm due to hydrogens on the unsubstituted carbon atom of the epoxide were monitored and integrated with time. The signals at 6.90−7.33 ppm were used as an internal standard, and conversion was calculated from the following equation:

$$\text{conversion} = 1 - \frac{(I_{2.76-2.93}/I_{6.90-7.33})_t}{(I_{2.76-2.93}/I_{6.90-7.33})_0} \qquad (1)$$

TPCP gallate alone possesses little activity as a catalyst for the thermal polymerization of GPE (Figure 2). However, in the presence of cyclohexanone, activity increased significantly. When the ratio of GPE/TPCP gallate is held constant, and the ratio of cyclohexanone to TPCP gallate increased, the conversion of GPE increases dramatically. If the ratio of GPE to cyclohexanone is held constant, as in Figure 3, and the ratio of TPCP gallate to GPE increased, conversion of GPE does not increase significantly in comparison with the results of the previous case.

When TPCP gallate/cyclohexanone is held constant (Figure 4), conversion of GPE reaches a maximum at a ratio of 100:3:30 for GPE/TPCP gallate/cyclohexanone.

The results reveal that the polymerization rate of GPE is greatly dependent on the ratio of GPE/TPCP gallate/cyclohexanone. With an increase in the ratio between TPCP gallate and cyclohexanone, the conversion of GPE was increased significantly, especially in the first hour. Consequently, the initiating species in this polymerization is not the TPCP cation, but a

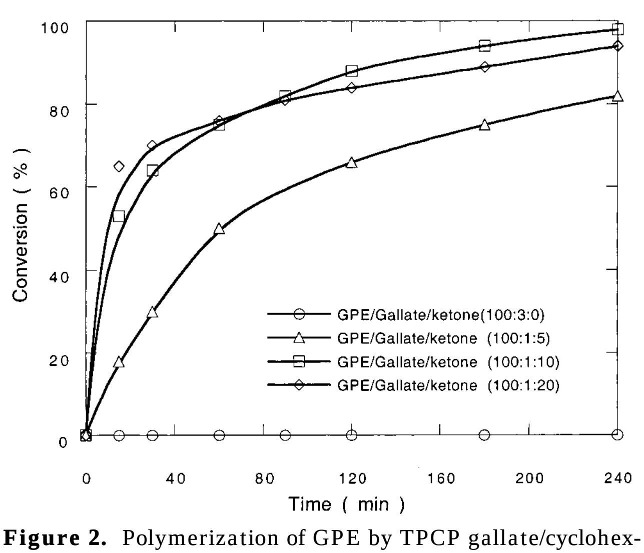


Figure 2. Polymerization of GPE by TPCP gallate/cyclohexanone: ratio of GPE/TPCP gallate = 100:1 (by weight).

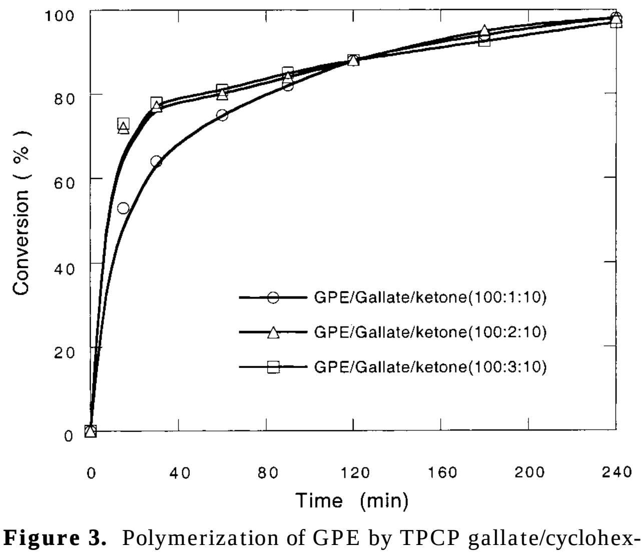


Figure 3. Polymerization of GPE by TPCP gallate/cyclohexanone: ratio of GPE/cyclohexanone = 100:10 (by weight).

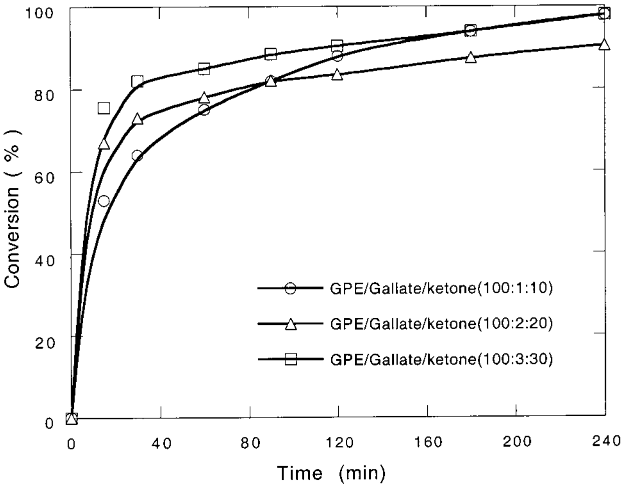


Figure 4. Polymerization of GPE by TPCP gallate/cyclohexanone: ratio of TPCP gallate/cyclohexanone = 1:10 (by weight).

reactive species that is dependent on both the TPCP gallate and cyclohexanone. This is most likely a proton. The concentration of initiating species increases with an increased ratio between TPCP gallate and cyclohexanone as evidenced by the increased rate of polymerization. We postulate the reactions in Scheme 1.

We propose the mechanism for the generation of proton in Scheme 2. This mechanism is strongly supported by the observation of triphenylcyclopropenyl cyclohexenyl ether (**2**). In the GC/MS analysis of the reaction mixture of TPCP gallate with cyclohexanone, its peak exhibited strong signals at 364 (M+), 267 (M−C_6H_9O), and 178 ($PhC{\equiv}CPh$). Additionally, the proton was trapped using triethylamine as a base to give triethylammonium gallate. The formation of this product was confirmed by ^{1}H NMR and ^{19}F NMR spectroscopy.

In addition, ^{1}H NMR spectroscopy of the polymer obtained from the polymerization of propylene oxide by this initiator system showed neither a TPCP nor a cyclohexanone moiety in the polymer, providing additional evidence that a proton was the actual initiating species.

In summary, our work reveals that TPCP gallate, along with cyclohexanone, serves as a thermal initiator for the cationic polymerization of epoxide. The α-H of cyclohexanone forms the actual initiation species.

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