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Unconventional Methods of Initiating Cationic Polymerization Using Onium Salts

James V. Crivello

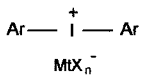
Department of Chemistry, Rensselaer Polytechnic Institute, Troy, New York 12180, USA

Summary: Onium salts are latent sources of cationic species that can be released on demand to initiate cationic polymerizations by the application of various external physical and chemical stimuli. This paper will report on the use of several different types of stimuli to provide interesting and useful unconventional methods for initiating cationic polymerizations.

Introduction

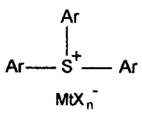
Many different initiators for cationic polymerization are known and have been used over the years. Among such initiators are Lewis and Bronsted acids, esters and anhydrides of fluorinated alkyl sulfonic acids and stable carbocationic salts such as trityl and tropylium ion salts. While these initiators are well suited for the homogeneous preparation of linear polymers from monofunctional monomers, they are not suitable for the polymerization of multifunctional monomers to produce network polymers. Attempts to use the traditional initiators for this purpose usually results in inhomogeneous reaction leading to similarly inhomogeneous products. For this reason, cationic addition polymerizations have not found applications involving the formation of thermosets. The successful polymerization of multifunctional monomers requires initiators with sufficient latency to allow them to be dissolved without substantial reaction. Then, the initiator should smoothly induce polymerization on demand by the application of an external stimulus.

These requirements are met by onium salts having the generalized structures **I-III**. Such onium salts are room temperature stable, well-characterized organic salts that can be easily handled and purified by conventional techniques. In this article is briefly reported the response of these onium salt initiators to such stimuli as light, heat, redox conditions, electrolysis and exposure to electron-beam and γ-ray irradiation.



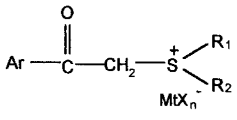
$\mathrm{Ar}-\overset{+}{\mathrm{I}}-\mathrm{Ar}\quad \mathrm{MtX}_n^-$

I



$\mathrm{Ar}-\overset{\overset{\mathrm{Ar}}{|}}{\mathrm{S}^+}-\mathrm{Ar}\quad \mathrm{MtX}_n^-$

II



III

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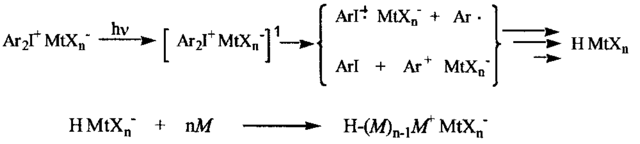
Photoinduced Cationic Polymerizations

Over the past two decades, the use of UV and visible light to induce the efficient cationic photopolymerizations with onium salts **I-III** in which MtX_n^- represents a weakly nucleophilic counterion such as PF_6^- or SbF_6^- has been well documented by work in this and other laboratories.[1] In Scheme 1 is shown a proposed abbreviated mechanism for the photolysis of diaryliodonium salts.



$$Ar_2I^+MtX_n^- \xrightarrow{h\nu} \left[Ar_2I^+MtX_n^-\right]^1 \longrightarrow \left\{\begin{array}{c} ArI^{+\cdot}\ MtX_n^- + Ar\cdot \\ ArI + Ar^+\ MtX_n^- \end{array}\right\} \longrightarrow HMtX_n \qquad (1)$$

$$HMtX_n^- + nM \longrightarrow H\text{-}(M)_{n-1}M^+\ MtX_n^- \qquad (2)$$

Scheme 1

As illustrated in Scheme 1, during the photolysis of a diaryliodonium salt (eq. 1), cations, radicals and cation-radicals are efficiently produced with a high quantum yield. Further reactions of the highly reactive positively charged species result in the formation of a strong protonic acid, $HMtX_n$. This latter acid directly initiates the polymerization of a wide variety of vinyl and heterocyclic monomers (*M*) (eq. 2).

Continued research in this area has resulted in the development of photosensitizers that not only allow the tailoring of the spectral sensitivity of the photoinitiators, but also increase the overall efficiency of the response of the onium salt photoinitiators to broad band light. As a result, cationic photopolymerizations can now be carried out using visible light with the aid of a photosensitizer. While the photopolymerization of virtually any cationically polymerizable monomer can be effected in the presence of onium salts, most of our interest has focused on multifunctional epoxides and on the corresponding vinyl ethers. Additional novel monomers of these two types have been designed expressly for high reactivity in cationic photopolymerizations.[2]

Commercial interest in the field of cationic photopolymerizations is very high. Cationic photocrosslinking polymerization of epoxide monomers using diaryliodonium and triarylsulfonium salt photoinitiators is widely employed for both protective and decorative coatings on metals, plastics and wood. Other applications include printing inks and adhesives. Stereolithography, photolithography and electronic encapsulations are additional areas where this chemistry has found application. Most research efforts in this laboratory currently focus on enhancing the efficiency of the cationic photocrosslinking process through the development of novel photoinitiators, photosensitizers and monomers.

Activation of Onium Salt Polymerizations with Ionizing Radiation

The “free” cationic polymerization of monomers induced by electron-beam and γ-ray irradiation is well known. Such polymerizations, however, are known to be highly sensitive to the presence of oxygen and other impurities. In this laboratory, it has been found that the irradiation of monomers with ionizing radiation in the presence of onium salts induces highly efficient cationic polymerization.[31] The mechanism shown in Scheme 2 has been proposed.

$$M\text{—H} \xrightarrow[\text{or } \gamma\text{-rays}]{\text{e-beam}} \left[M\text{—H} \right]^{+\bullet} \tag{3}$$

$$\left[M\text{—H} \right]^{+\bullet} \longrightarrow M\bullet + H^{+} \tag{4}$$

$$Ar_2I^{+}\,MtX_n^{-} + M\bullet \longrightarrow Ar_2I\bullet + M^{+}\,MtX_n^{-} \tag{5}$$

$$M^{+}\,MtX_n^{-} + mM \longrightarrow (M)_mM^{+}\,MtX_n^{-} \tag{6}$$

$$Ar_2I\bullet \longrightarrow ArI + Ar\bullet \tag{7}$$

Scheme 2

Irradiation with electron-beam or ^{60}Co γ-rays results in the ionization of the monomer, M-H, (eq. 3) with the formation of a cation-radical. Further fragmentation (eq. 4) results in the formation of cation and radical species. The cation can initiate polymerization by the “free” cationic process mentioned above. Simultaneously, the radical, M•, can be oxidized to the corresponding cation as illustrated in equation 5 by an iodonium salt. Polymerization (eq. 6) ensues by attack of this latter cation on monomer. The entire process is made irreversible by the fragmentation of the diaryliodine radical to give an aryl radical and an aryliodide (eq. 7). Aryl radicals produced in eq. 7 can abstract protons from the monomer to continue the cycle. The entire sequence shown in Scheme 2 is best described as an efficient ionizing radiation stimulated chain decomposition of the photoinitiator that leads to polymerization induced by the formation of the resulting cations.

Employing either electron-beam or ^{60}Co γ-rays, we have demonstrated that it is possible to conduct very rapid crosslinking reactions of multifunctional epoxide and vinyl ether monomers for the fabrication of thin films and thick carbon-fiber reinforced composites.

Thermally Induced Cationic Polymerizations

When diaryliodonium salts are heated in the presence of epoxide monomers at temperatures from 170-200 °C, cationic polymerization ensues. Analysis of the polymers that are formed showed that they contain aryl end groups derived from the onium salt by arylation of the monomer. While this is an interesting result, the temperatures required for themal activation are too high to be useful. It was subsequently observed that the activation temperature can be markedly reduced by the addition of a copper(II) complex.[4] Typically, organic soluble copper complexes such as copper acetylacetoneate or copper benzoate are used. Investigation into this reaction has led to the mechanism proposed in Scheme 3.

$$\mathrm{Cu(II)L_2} \xrightarrow[100\text{-}120^{\circ}\mathrm{C}]{\text{Red-H}} \mathrm{Cu(I)L} \qquad (8)$$

$$\mathrm{Ar_2I^+\,MtX_n^-} + \mathrm{Cu(I)L} \xrightarrow{25^{\circ}\mathrm{C}} \mathrm{ArI} + \mathrm{ArCu(I)L^+\,MtX_n^-} \qquad (9)$$

$$\mathrm{ArCu(I)L^+\,MtX_n^-} + \mathrm{n}M \xrightarrow{25^{\circ}\mathrm{C}} \mathrm{Ar}(M)_{\mathrm{m}}^{+}\,\mathrm{MtX_n^-} + \mathrm{Cu(I)L} \qquad (10)$$

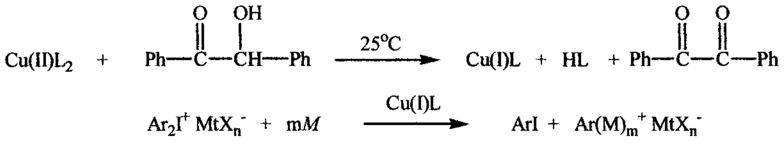
Scheme 3

The slowest and temperature dependent step involves the reduction of the copper(II) complex (eq. 8). In the polymerization of epoxide monomers traces of primary and secondary alcohols serve as the reducing agent, Red-H. Once the copper(I) complex is formed, it reacts spontaneously with the diaryliodonium salt (eq. 9) to form an arylcopper species. This latter species is a powerful arylating agent and the formal transfer of an aryl cation to the monomer takes place to intiate polymerization (eq. 10). In support of this mechanism, we have shown that a wide variety of other nucleophiles including phenoxide, thiophenoxide, arylsulfides, pyridines and quinolines can be quantitatively arylated by heating at 125°C for one hour in the presence of a diarylidonium salt.

The above chemistry provides convenient methodology for the development of shelf stable, yet rapid processing thermosets based on multifunctional epoxide resins. Such thermosets can be compression, transfer or injection molded. The incorporation of reinforcements provides composites processed by pultrusion, filament winding and traditional lay-up techniques.

Redox Initiation of Cationic Polymerization

As shown in Scheme 3, the temperature of the copper(II) catalyzed thermally activated polymerizations using diaryliodonium salt depends on the type of agent employed to reduce the copper complex. When more powerful reducing agents are employed, polymerizations can be carried out at essentially room temperature. An example is shown in Scheme 4 in which benzoin undergoes facile oxididation to benzil.[5]



$$\mathrm{Cu(II)L_2} + \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{OH}{|}}{C}H{-}Ph} \xrightarrow{25^{\circ}\mathrm{C}} \mathrm{Cu(I)L} + \mathrm{HL} + \mathrm{Ph{-}\overset{\overset{O}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}Ph} \qquad (11)$$

$$\mathrm{Ar_2I^+\,MtX_n^-} + \mathrm{m}M \xrightarrow{\mathrm{Cu(I)L}} \mathrm{ArI} + \mathrm{Ar(M)_m^+\,MtX_n^-} \qquad (12)$$

Scheme 4

Since polymerizations carried out under the above conditions are spontaneous, systems based on this chemistry are necessarily composed of two components. Typically, one component contains the monomer, a diaryliodonium salt and the copper(II) complex. The second component contains the monomer and the reducing agent. Polymerization ensues when these two components are mixed together. At room temperature, the redox reaction proceeds sufficiently slowly that it is possible to achieve homogeneous conditions before appreciable polymerization sets in. However, once the exothermic ring-opening polymerization begins, the temperature rises dramatically and an autoacceleration process takes place.

A practical demonstration of this chemistry was its use in reaction injection molding (RIM). In this process, the above two liquid components were pumped into an intensive mixing chamber and then, directly into a mold containing a glass fiber mat where polymerization took place. Using this process, a one meter diameter radar receiver dish was produced.

Electroinitiated Cationic Polymerizations

Since onium salts contain positively charged oxidized heteroatoms, they can be reduced as described above by chemical agents. It was also of interest to determine if these onium salts could be directly reduced by electrons under electrolytic conditions and whether such reductions could be employed to trigger cationic polymerizations.

Indeed, it was observed that the electrolysis of a wide variety of cationically polymerizable monomers in bulk or solution in the presence of onium salts as supporting electrolytes results in facile polymerization that takes place at low voltages (1.5~2.0 V).[6] Detailed investigations to determine the mechanism of the electroinitiated cationic polymerization resulted in the proposed sequence of reactions shown in Scheme 5.

$$H_2O \xrightarrow[> +1.00\ V]{e^-} \begin{array}{l} 2H^+ + [O] + e^- \\ H^+ + \bullet OH + e^- \end{array} \qquad (13)$$

$$M\text{-}H + \bullet OH \text{ (or } [O]) \longrightarrow M\bullet + H_2O \qquad (14)$$

Scheme 5

At potentials above 1.0 V, trace amounts of water present in the monomer undergo anodic electrolysis to form unstable metal oxides, [O], and hydroxyl radicals. These latter two species abstract hydrogen atoms or add to the double bonds of vinyl and heterocyclic monomers to generate monomer bound radicals. These latter monomer radicals are oxidized to cations by onium salts as depicted previously in equations 5-7 of Scheme 2.

Electroinitiated cationic polymerizations in the presence of onium salts are extraordinarily efficient requiring only the passage of a catalytic amount of electric current. The polymerizations can be carried out using multifunctional monomers in an undivided electrochemical cell to afford pinhole-free films exclusively at the anode.

Conclusion

Onium salts are latent initiators of cationic polymerization that can be triggered by various external stimuli including; light, ionizing radiation, heat, reducing agents and electrolysis.

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