

## Recent aspects in the sensitized decomposition of cationic photoinitiators

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### ABSTRACT

This review concentrates on the recent aspects in the sensitized (indirect) decomposition of cationic photoinitiators, namely onium salts. There are three general methods where various additives play an indirect role to decompose onium salts. The first method involves electron transfer reaction of electronically excited sensitizers with onium salts to yield sensitizer radical cations. In the second method electron donor compounds in charge transfer complexes undergo similar electron transfer reactions. In this case the radical cations of the electron donor compounds are formed. Finally, photochemically formed radicals can induce the initiation of cationic polymerization via electron transfer or addition-fragmentation mechanisms.

### 1. INTRODUCTION

During the past decade photoinitiated polymerization have received considerable attention and practically applied in variety of areas, including printing inks, adhesives, surface coating, microelectronics and printing plates [1-6]. The advantages of photoinitiated polymerization over conventional thermal polymerization lie in the high speed reaction at ambient temperature, low energy consumption and solvent free formulation. Photoinitiated polymerization is typically a process that transforms a monomer into polymer by a chain reaction initiated by reactive species (free radicals or ions) which are generated by UV irradiation.

Much effort have been devoted to free radical systems [2, 5] mainly due to the availability of a wide

range of photoinitiators and the great reactivity of acrylate-based monomers. Despite the most popular industrial application based on the photoinitiated free radical photopolymerization there are some drawbacks associated with this type polymerization such as the inhibition effect of oxygen and post-cure limitations which may affect the properties of the final product. UV initiated cationic polymerization holds considerable promise in future, particularly as a means of overcoming volatile emission, toxicity and molecular oxygen inhibition limitations.

Although the cationic polymerization exhibits several advantages it has not as yet achieved the commercial significance of radical polymerization in UV curing applications. This was mainly because of the limited choice of the cationic photoinitiators and monomers that were commercially available until recently. This situation changed with two significant improvements. First, cationically polymerizable important classes of monomers such as vinyl ethers and epoxides became commercially available. Second, a new class of cationic photoinitiators with non-nucleophilic counter ions such as  $SbF_6^-$  and  $AsF_6^-$  has been utilized [7].

Since the photoinitiator is one of the most important part of a UV initiated polymerization, many research efforts have been devoted to understand what type of photoinitiators is applicable to generate cations. Among the various type of photoinitiators that can lead to the formation of cation as a result of UV light induced fragmentation, onium salts have found considerable application in UV curing and photorezist technology. The photochemistry of these novel classes of photoinitiators is well documented [1, 6]. Upon photolysis, these thermally and hygroscopically stable