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# Vinyl epoxide accelerators for the photoinitiated cationic polymerization of oxetane monomers

James V. Crivello\*

Department of Chemistry and Chemical Biology, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY, 12180, USA

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## ABSTRACT

Epoxides bearing vinyl groups bonded to one of the carbon atoms of the three-membered ring, exhibit the ability to dramatically increase the rate of the photoinitiated cationic polymerization of 3-mono- and 3,3-disubstituted oxetanes by eliminating or sharply reducing the length of the induction periods. This effect, termed by us as “kick-starting”, results from the ability of the aforementioned epoxides to undergo ring-opening on protonation to yield resonance stabilized allylic carbocations. Several examples are given of “kick-starting” epoxides together with their use in the photopolymerization of various oxetane monomers.

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## 1. Introduction

It would be difficult to overstate the present and growing importance of crosslinking photopolymerization technology, encompassed under the term “UV-curing”, with respect to the present and future technological impact of this field. A simple recitation of a few of the many examples of applications will serve to illustrate how pervasive this technology has become. Without a doubt, the electronic and microelectronic revolution that has profoundly changed and now pervades our current lives would not have been possible without the use of photopolymerizations. Additional applications of UV-curing chemistry are the rapid curing printing inks used in magazines and packaging materials, in the floor coatings and wallpaper used in our homes and the simulated wood that is used in furniture, cabinetry and paneling. UV-curable dental composites, dental coatings and orthodontic retainers are other areas where this technology is being applied to improve human health and welfare. Employing computer-aided design and using such 3-dimensional imaging techniques as digital imaging, stereolithography and ink-jet printing together with photopolymerization chemistry has revolutionized the way in which design, engineering and manufacturing processes are conducted in many industries. As an added bonus, this technology has provided these and a myriad of similar items at lower cost, with less

environmental impact and reduced energy consumption than obtainable by traditional means used in their manufacture.

Historically, the first and still most widely applied classes of reactive monomers employed for free-radical UV-curing were multifunctional acrylates and methacrylates [1]. Later, the development of photocurable unsaturated polyester-styrene systems were developed mainly for wood coating applications. The UV-cure of these two systems is markedly inhibited by oxygen and requires that the photopolymerizations be conducted in the absence of air. Under these conditions, the UV-cures are rapid and this is their main attractive feature. While the mechanical and thermal properties of acrylate-based thermosets are adequate for such applications as printing inks and adhesives, they are not sufficient for use in areas such as composite matrix resins and high performance coatings. Beginning in the mid-1970's, the discovery in this laboratory that diaryliodonium and triarylsulfonium salts are highly photosensitive and can be used as photoacid generators made it possible to conduct the photoinitiated cationic ring-opening UV-cure of epoxy resins. Cationic UV-cured epoxy resin systems have considerably better thermal and mechanical properties than acrylates and unsaturated polyester-styrene systems and do not display oxygen inhibition effects. On the other hand, their photopolymerization rates are considerably slower than the former free radical systems. Oftentimes, a thermal postcure is conducted after the UV irradiation to complete their polymerizations and to reach their ultimate mechanical properties.

\* Tel: +1 (518) 276 6825.

E-mail address: [crivej@rpi.edu](mailto:crivej@rpi.edu).

In an effort to address some of the deficiencies of cationically UV-cured epoxy resins, we have been investigating alternative monomer systems. The present communication reports the development of a novel cationic UV-curable oxetane system that possesses the reactivity comparable to systems based on acrylate and methacrylate monomers while retaining the better mechanical and thermal performance characteristics of cationically UV-cured epoxy resins.

## 2. Experimental

### 2.1. Materials

3-Ethyl-3(2-ethylhexyloxymethyl)oxetane (EHOXT), 3-ethyl-3-phenoxyethyl oxetane (POX) and bis{[(1-ethyl(3-oxetanyl)methyl) ether (DOX), were gratefully received as gifts from the Toagosei Chemical Company, Nagoya, Japan. POX and DOX were purified prior to use by fractional vacuum distillation. 3-Benzyloxymethyl-3-ethyloxetane (BzOXT), was kindly supplied as a sample from Tronly Chemical Co. LTD, Changzhou, China. 3-Allyloxymethyl-3-ethyloxetane (AIOXT) was prepared as previously described [3] and purified by distillation. 3,4-Epoxy-1-butene (EB) was kindly provided as a gift from the Eastman Chemical Co, Knoxville, TN. 2-Methyl-2-vinylloxirane (MVO), 1,4-epoxy-1,4-dihydronaphthalene and 1,4-epoxy-1,2,3,4-tetrahydronaphthalene were purchased from the Aldrich Chemical Company, Milwaukee, WI, and used as received without further purification. The diaryliodonium salt [4] and triarylsulfonium [5] salt and dialkylphenacylsulfonium salt [6] photoinitiators were prepared as described previously. In this article, three of these photoinitiators were employed and we have developed shorthand designations for these compounds. For example, IOC-8 SbF<sub>6</sub> refers to (4-*n*-octyloxyphenyl)phenyliodonium hexafluoroantimonate, having the structure shown below in which an *n*-octyloxy group is attached to one of the phenyl groups in the 4-position, while SbF<sub>6</sub> denotes the hexafluoroantimonate anion. In a similar manner, SOC-10 SbF<sub>6</sub> refers to S(4-*n*-decyloxyphenyl)-S,S-diphenylsulfonium hexafluoroantimonate. DAPS-C1C8 SbF<sub>6</sub> is a shorthand notation for S-methyl-S-*n*-octyl-S-phenacylsulfonium hexafluoroantimonate.



### 2.2. Optical pyrometry characterization of “kick-started” oxetane photopolymerizations

We have previously described the analytical techniques and apparatus used in this laboratory for optical pyrometry (OP) [7,8]. Samples for OP kinetic analysis were prepared by sandwiching a liquid monomer containing the designated photoinitiator between two thin (12.5 μm) films of fluorinated poly(ethylene-cocopolypropylene) (DuPont FEP thermoplastic film) using a thin, open polyester mesh as a spacer. The samples were mounted in plastic 2 cm × 2 cm slide frames and then inserted into the sample holder

for analysis. The average thickness of the samples was 0.912 mm. Irradiation with UV light was accomplished using a UVEXS Model SCU-110 mercury arc lamp (Sunnyvale, CA) equipped with a liquid optic cable. The liquid optic cable served as a light filter passing UV light of wavelengths greater than 300 nm, but blocks both shorter wavelengths as well as wavelengths in the infrared region. UV irradiation intensities were measured using a Control Cure Radiometer (UV Process Supply, Chicago, IL). Several kinetic runs were performed for each photopolymerizable system and the results reported in this article were the average of at least three kinetic runs. Typically, the reproducibility of the kinetic data was ±5%. All kinetic studies were conducted at ambient laboratory temperature (25–28 °C) unless otherwise noted. Photoinitiator concentrations are given in either or both mol% and weight% depending on the given experiment.

### 2.3. Thin film crosslinking photopolymerization studies

Thin film photopolymerizations of an 8:1 M mixture of DOX and MVO containing 3.0 wt% of IOC-8 SbF<sub>6</sub> were carried out on a Fusion Systems Model MC 6R microwave-activated 300 W electrodeless lamp system equipped with a UV D bulb mounted above a variable speed conveyor. Exposure intensities were measured using a Control Cure Radiometer, UV Process Supply, Chicago, IL. Line speeds were calculated using a stopwatch. The length of the conveyor belt is 120 cm. Uniform 3 mil (75 μm) liquid monomer-photoinitiator films were coated onto aluminum Q-panels using a drawknife and transferred to the conveyor for curing. Tack-free times were determined by immediately testing the films for tackiness on exiting from the UV cure zone. The UV cured samples were colorless, transparent, glossy and hard.

## 3. Results and discussion

In several papers from this laboratory, [3,9,10] we have described the synthesis and photoinitiated cationic polymerizations of a number of novel 3-mono- and 3,3-difunctional oxetane monomers. Several other groups have also been active in this field. [11,12,13] Several of these oxetane monomers are now being offered commercially. While the synthesis and mechanical properties of the UV-cured oxetanes were interesting, their photopolymerization

rates were much too slow to be of interest for most of the major uses that were described in the introduction portion of this communication. Recent mechanistic investigations [14,15] revealed that this problem is due to a slow initiation step in the multistep mechanism of the ring-opening polymerization. This is evidenced by a long induction period during which the sample is subjected to UV irradiation, but polymerization does not proceed or takes place very slowly. More recently, in a publication from this laboratory [16] it was reported that the addition of small amounts of certain alkyl-substituted epoxides to oxetane monomers results in a dramatic reduction in the induction periods of their cationic ring-opening

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