

**REACTIVITY STUDIES OF  
OXIRANE AND OXETANE MONOMERS  
IN PHOTOINITIATED CATIONIC POLYMERIZATIONS**

By

Umut Bulut

An Abstract of a Thesis Submitted to the Graduate

Faculty of Rensselaer Polytechnic Institute

in Partial Fulfillment of the

Requirements for the degree of

DOCTOR OF PHILOSOPHY

Major Subject: Chemistry

The original of the complete thesis is on file  
In the Rensselaer Polytechnic Institute Library

Examining Committee:

James V. Crivello, Thesis Adviser

James A. Moore, Member

Leonard Interrante, Member

Brian Benicewicz, Member

Glenn Eisman, Member

Rensselaer Polytechnic Institute  
Troy, New York

April, 2007  
(For Graduation May 2007)

The photoinitiated cationic ring-opening polymerizations (PCROP) of various epoxide and 3,3-disubstituted oxetane monomers display a marked induction period which renders these monomers of limited value for many applications. Three general methods were found effective in distinctly shortening or eliminating the induction period: (1) carrying out the photopolymerizations at higher temperatures, (2) copolymerization or simultaneous polymerization with more reactive monomers, and (3) the use of free radical photoinitiators. Studies of the onium salt photoinitiated cationic ring-opening polymerizations have been conducted with real-time infrared spectroscopy and optical pyrometry (OP).

The characteristic induction period of 3,3-disubstituted oxetanes in PCROP is followed by very rapid thermally accelerated polymerization. When a thin-film sample of such a monomer is irradiated for a time within the induction period and then allowed to stand at room temperature, no appreciable further conversion of monomer to polymer takes place. However, when heat is applied to a small portion of the films rapid polymerization takes place as a front, which propagates rapidly throughout the entire reaction mass. OP was employed to characterize these frontal polymerizations.

The absorption characteristics of the diaryliodonium salt photoinitiators can be adapted for particular applications requiring activation at wavelengths above 300 nm by utilization of photosensitizers. Curcumin, a naturally occurring, intensely yellow dye extracted from the spice, turmeric, is employed as an efficient photosensitizer for diaryliodonium salt photoinitiators to carry out the cationic photopolymerization of a wide variety of epoxide, oxetane and vinyl monomers as well as naturally derived monomers using long wavelength UV and visible light.

Selective inhibition of the PCROP of epoxides by dialkyl sulfides has provided dual systems that can be activated by UV irradiation and then subsequently be polymerized by the application of heat. It is proposed that dialkyl sulfides terminate the initial or growing polyether chains at an early stage to form stable trialkylsulfonium salts. These systems are dormant at room temperature but on thermolysis, the sulfonium salts are capable of reinitiating ring-opening polymerization. These dual photo- and

thermal cure systems have potential applications in adhesives, potting resins, and composites.