

# “Kick-started” oxetanes in photoinitiated cationic polymerization: scale-up synthesis and structure-property studies

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## Abstract

A new class of UV/electron beam (EB) curable oxetane monomers has been identified for kick-started cationic polymerization with an aim to have a transformative impact on the radiation curing industry. These materials have the potential to replace acrylic monomers and reactive oligomers in many existing applications. However, the availability of oxetane monomers has been limited in small quantities in a laboratory scale, and the development of scale-up synthesis has been the technical barriers for the immediate scalable manufacturing impacts in industry. Among oxetane monomers, 3,3'-(oxybis(methylene))bis(3-ethyloxetane), DOX, is potentially one of the most inexpensive, highly reactive multifunctional oxetane monomers that can be cross-linked by UV and EB. In this study, the scale-up synthesis of DOX monomer in melt without using solvents was accomplished. A series of different functional epoxy monomers was employed as co-monomers for targeting specific end-use applications. A fundamental understanding of structure-processing-property relationship was established to evaluate the effect of different co-monomer compositions on the viscosity, conversion, network formation and thermo-mechanical properties.

## Introduction

Photo-curing technology represent state-of-the-art technology, which have found myriad of applications in the areas of printing inks, graphic arts, adhesives and photo-lithography. High-energy efficiency, low VOC, high productivity, and cost-effectiveness are the major highlights of photo curing technology.<sup>1,2,3</sup> Free radical and cationic polymerizations represent two of the major areas of focus with each possessing different mode of polymerization, reaction kinetics and final material properties.

Advantages of photo-cationic polymerizations include low volumetric shrinkage stress, high reactivity, and uninhibited by the presence of oxygen.<sup>4,5</sup> Different photo-cationic monomers including epoxides<sup>6,7</sup>, oxetanes<sup>8,9,10</sup> and vinyl ethers<sup>11,12</sup> have been studied in literature. In recent times, oxetanes have received much attention, while an extensive amount of research is based on epoxides in both academia and industry. Compared to epoxides, oxetanes possess similar ring strain and higher basicity; yet have been shown to exhibit longer induction period and low overall polymerization rates.<sup>13</sup> Very recently, it was discovered that the use of certain highly substituted epoxides such as limonene dioxide (LDO) in oxetane systems led to faster rate of initiation, thereby significantly lowering the induction time (also referred to as “kick-start effect”), and increasing the overall polymerization kinetics of oxetanes.<sup>14,15</sup>

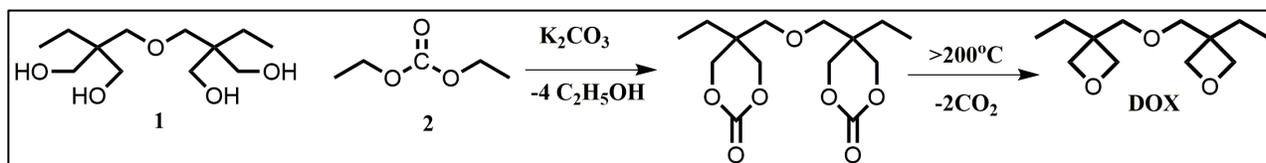
Despite the advantageous characteristics of oxetanes and advancements made so far, the development of oxetanes in scalable and sustainable manufacturing is majorly impeded by the limited commercial availability of oxetane monomers and oligomers, and there exists a lack of fundamental understanding of formulation-property relationship in this area of research.

The motivation of this study stemmed from addressing the aforementioned shortcomings of oxetane systems with an aim to expand the scope of research and applications. Among oxetane monomers, 3,3'-(oxybis(methylene))bis(3-ethyloxetane), DOX, is potentially one of the most inexpensive, highly reactive multifunctional oxetane monomers that can be cross-linked by UV and EB. DOX monomer is a colorless, odorless liquid with high boiling (119 °C, 5 mmHg) and low viscosity with almost no detectable odor, which renders ease of handling and good processability characteristics. DOX can be synthesized from a simple, synthetic procedure using inexpensive raw materials, and the use of solvent-free synthesis facilitates green chemistry and sustainable manufacturing. Additionally, simple purification by fractional distillation of the liquid monomer makes it favorable for scale-up synthesis.

For this study, scale-up synthesis of DOX has been accomplished. The synthesized DOX was mixed with LDO in a 4:1 molar ratio and was blended separately with different functional epoxy monomers at varying molar concentrations using a sulfonium-based photoinitiator. The goal of this study was aimed at establishing structure-processing-property relationship by evaluating the effect of different co-monomer compositions on conversion, network formation and thermo-mechanical properties.

## Experimental

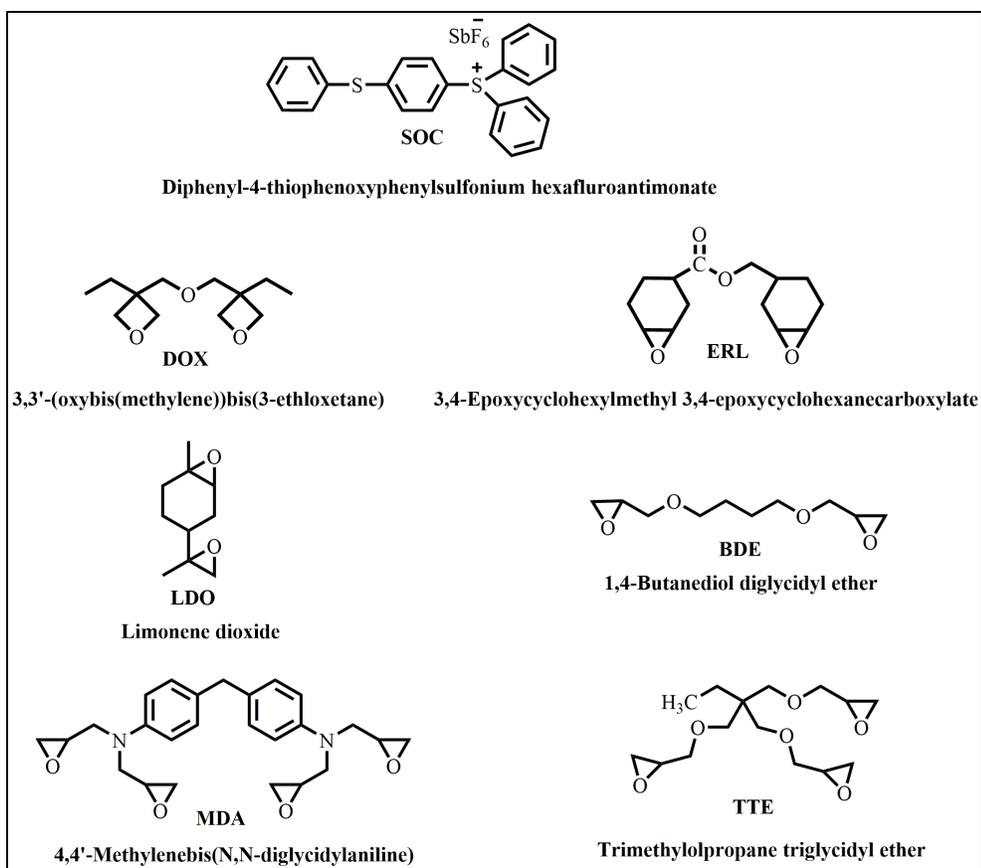
The one-pot synthesis of DOX consisting of two mechanistic stages was carried out using the modified literature procedure<sup>16,17</sup>, as shown in Scheme 1. In the first step, a mixture of ditrimethylolpropane (0.02 mol), diethyl carbonate (0.04 mol) and potassium carbonate (0.05 wt %) was kept in a heating mantle, pre-heated at 110 °C and refluxed for 3 h with rapid stirring. The ethanol was distilled out continuously while keeping the head temperature at 70-75 °C. The temperature was further raised to 150 °C to remove the residual ethanol and unreacted diethyl carbonate, wherein the pressure was gradually reduced to 15 mmHg. Starting from 180 °C-220 °C, the crude monomer began to distill out (120-170 °C) with the elimination of CO<sub>2</sub>. Purification of crude DOX was carried out using fractional distillation (Yield = 42%).



**Scheme 1.** Schematic representation of DOX synthesis.

## Film preparation and characterization

The chemical structures and abbreviations of the materials used in this study are shown in Figure 1. A 4:1 mixture of DOX/LDO was blended with different amounts of epoxy co-monomers at concentrations ranging from 0 mol% to 50 mol%. The mixture was homogeneously mixed using a vortex stirrer, before and after the addition of 2 wt% sulfonium-based photo-cationic initiator (SOC). The photo-curable mixture was drawn on a glass substrate and exposed to UV light using the Fusion system (mercury bulb). The resultant UV cured films were transparent and tack-free, and were post-baked to cure the residual epoxy and oxetane moieties. The fully cured films were used for TGA analysis to study the thermal stability, and DMA analysis was used for evaluating thermo-mechanical properties.



**Figure 1.** Chemical structures and abbreviations of monomers and photo-initiator used in this study.

$^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  measurements were performed using a Bruker 600 MHz NMR spectrometer in deuterated chloroform.

In-situ monitoring of the progress of the UV cure was performed using Real-time FTIR spectroscopy. FTIR studies were conducted using a Nicolet iS50 FTIR spectrometer with a KBr beam splitter and an MCT/A detector with a 320-500 nm filtered ultraviolet light source. The monomer resin was sandwiched between two NaCl plates using a Teflon spacer for thickness control and exposed to UV light for 60s. Series scans were recorded, taking spectra at the rate of approximately 4 scans per second, each with a resolution of  $4\text{ cm}^{-1}$ . All experiments were done under ambient conditions.

A thermogravimetric analyzer, TA Instruments TGA Q50 was used with a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  from  $40\text{ }^\circ\text{C}$  to  $600\text{ }^\circ\text{C}$  in a nitrogen atmosphere.

Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 DMA in tension film mode with a heating rate of  $2\text{ }^\circ\text{C}/\text{min}$  at 1Hz from  $-40\text{ }^\circ\text{C}$  to  $150\text{ }^\circ\text{C}$  for the cured films. Thin polymer films were prepared by casting a thin layer of photo-curable on a glass substrate.

## Results and Discussion

DOX used in this study was synthesized using the modified literature procedure.<sup>16,17</sup> The first step is the trans-esterification reaction between the ditrimethylolpropane and diethyl carbonate ester to form a six-membered bis(cyclic carbonate) intermediate, with the elimination of ethanol. The formation of the intermediate was accompanied with a sudden increase in viscosity of the reaction mixture. Each one of the parameters - temperature, reflux time, pressure and stirring speed were optimized to ensure

homogenous mixing, and to favor the formation of desired intermediate and product. The second step involves the thermal elimination of carbon dioxide, resulting in the oxetane formation. The crude monomer was simply purified by fractional distillation process. The use of inexpensive starting materials, simplistic synthetic methodology and purification, and solvent-free synthesis promoting green chemistry, facilitated the scale-up synthesis of DOX.

The progress of UV cure was evaluated by the decrease in the absorbance intensities of the characteristic epoxy peak at  $780\text{ cm}^{-1}$  and oxetane peak at  $980\text{ cm}^{-1}$  as a function of irradiation time. Diphenyl-4-thiophenoxyphenylsulfonium hexafluoroantimonate (SOC) was chosen for this study, as it possesses two characteristic UV absorption bands at 225 nm and  $300\text{ nm}^{18}$ , making them operable in the mid-UV range (320-500 nm). The completion of UV cure was confirmed by examining the residual cure exotherm using DSC cure studies.

The thermal stability and char yield of the co-monomer compositions were evaluated using TGA analysis. Thermo-mechanical studies using DMA analysis of the cured co-polymer networks demonstrated a broad range of tailorable material properties.

## Conclusions

We have described the combination of “kick start effect” of DOX/LDO system with different functional epoxy co-monomers targeting a range of material properties. The scale-up synthesis, and the fundamental information gained in the field of oxetanes would provide a platform to develop tailor made solutions for specific end-use applications in the areas of coatings, adhesives, sealants and high performance composites.

## Acknowledgements

The authors gratefully acknowledge financial support from New York State Energy Research and Development Authority (NYSERDA) grant.

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