

# Influence of Acrylate Secondary Functionalities on Epoxide Reactivity During Acrylate/Epoxide Hybrid Photopolymerizations

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## ABSTRACT

Epoxide cationic photopolymerizations were suppressed by urethane acrylate oligomers. Thus, acrylates with various secondary groups were examined in hybrid systems containing diepoxides. The epoxide polymerization rate and final conversion were affected significantly by acrylate structures and concentration. Acrylates containing ether or urethane groups negatively affected the epoxide kinetics at higher molar ratios due to fixation or abstraction of protons generated from photoinitiator photolysis by ether or urethane groups.

## I. INTRODUCTION

Epoxide-acrylate hybrid systems mitigate atmospheric sensitivity of free-radical and cationic photopolymerizations. Control of networks produced by chemically independent free-radical and cationic polymerizations allows tuning of polymer properties. Yet, little is known about interactions between acrylate and epoxide during hybrid polymerization. Thus, the effect of acrylate structure and molar ratio on the kinetics of epoxide photopolymerizations was examined using a series of acrylates with diepoxide.

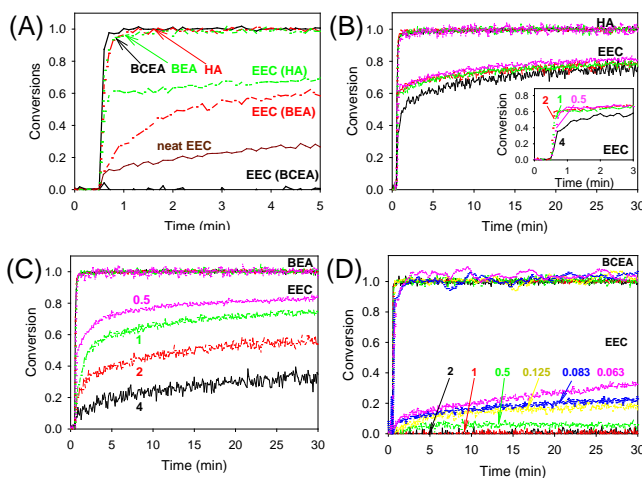
## II. MATERIALS AND METHODS

Three acrylates (Sigma-Aldrich) were free-radically polymerized: HA (hydrocarbon), BEA (ether), and BCEA (urethane). Diepoxide (EEC, Union-Carbide) was cationically polymerized. 2,2-Dimethoxy-2-phenyl-acetophenone (DMPA, Aldrich) and diaryliodonium hexafluoroantimonate (IHA, Sartomer) initiated the C=C and epoxide ring reactions, respectively. Formulations were photopolymerized with an Acticure® Spot Cure System (EFOS); Raman spectra were collected using a 785-nm laser and a Mark II probe head attached to a HoloLab 5000R spectrograph (KOSI).

## III. RESULTS AND DISCUSSION

Acrylate photopolymerization proceeded much quicker than EEC photopolymerization (Fig. 1A).

Reactivity of epoxide increased in the presence of equimolar HA or BEA due to their dilution effect (Fig. 1A). The epoxide reactivity was lower for ether-containing BEA and even further decreased with higher molar ratios of BEA to EEC (Fig. 1B & C). This decrease is caused by the fixation of protons by 1,2 position ether oxygen acting as crown ether-like structure in growing acrylate chains<sup>1</sup>. Urethane groups of BCEA completely inhibited the EEC cationic photopolymerization (Fig 1D). This detrimental effect was caused by high nucleophilicity and basicity of amine and carbonyl ester groups in the urethane structure.



**Figure 1.** Conversion profiles of acrylate and epoxide during hybrid photopolymerizations: (A) systems of 1:1 ratio; (B) HA-EEC, (C) BEA-EEC, and (D) BCEA-EEC at various [acrylate]/[diepoxide]. [DMPA] = 32mM, [IHA] = 32mM, room temperature, effective irradiance = 100mW/cm<sup>2</sup>.

## REFERENCES

1. A. Hartwig, K. Koschek, A. Lühring, O. Schorsch, "Cationic polymerization of a cycloaliphatic diepoxide with latent initiators in the presence of structurally different diols", *Polymer*, Vol. 44, pp.2853-2858, 2003.