CATIONIC PHOTOPOLYMERIZATION OF BIOBASED OXETANE MONOMERS FROM ADIPIC, ITACONIC AND CITRIC ACID FUNCTIONALIZATION

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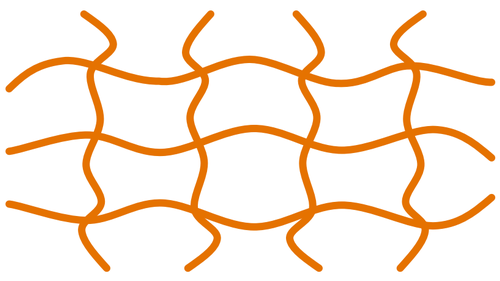
Introduction

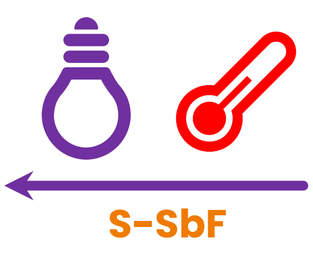
In the context of sustainable materials development, **biobased monomers** are essential for reducing reliance on fossil-based chemicals. This study reports the **synthesis of three novel oxetane monomers**, derived from the esters of adipic, itaconic, and citric acids (**BOA, BOI, and TOC**), via a one-pot transesterification reaction with 3-ethyl-3-oxetanemethanol.

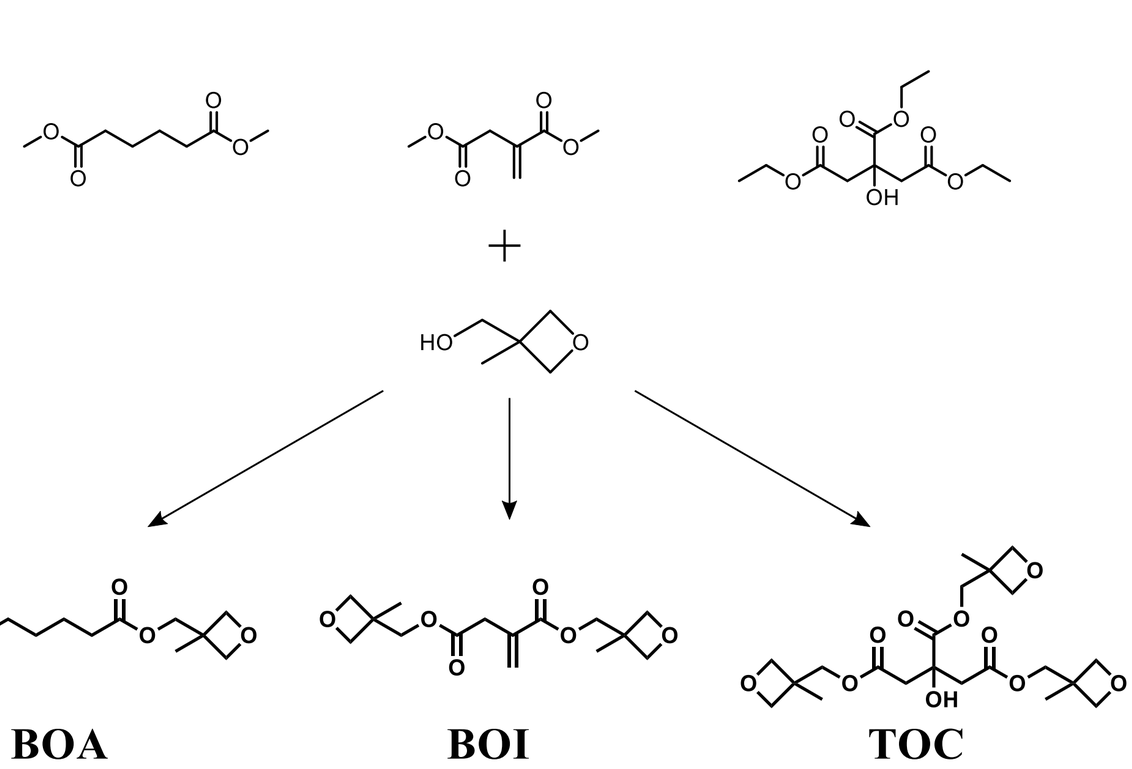
Cationic ring-opening photopolymerization (CROP) was employed to produce crosslinked materials. Characterization by FTIR, photo-DSC, DSC, and DMTA demonstrated effective curing kinetics and promising thermomechanical properties, particularly at irradiation temperatures above 85 °C. This work contributes to the development of sustainable, high-performance materials.

Synthesis and Photopolymerization

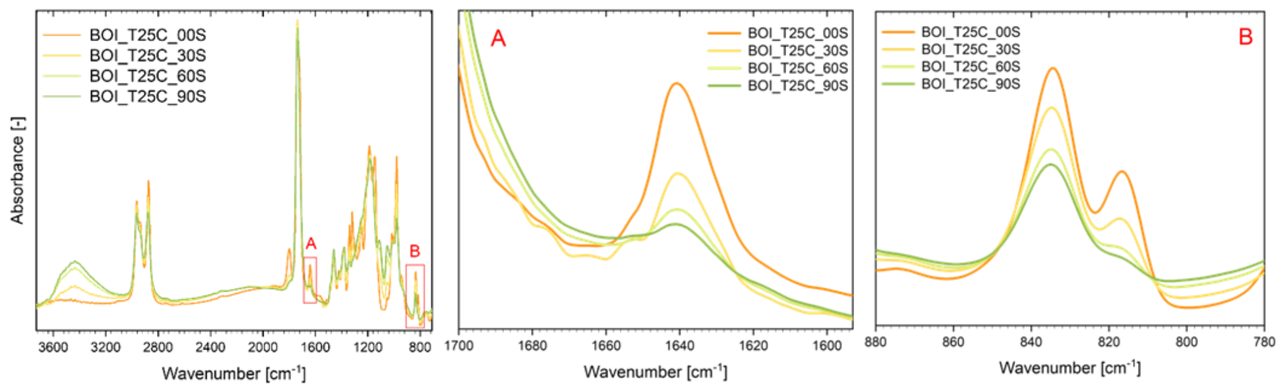
- **Transesterification** reaction using 3-ethyl-3-oxetane methanol with di-/tri-carboxylic esters (DMA, DMI, TEC), catalysed by DBTO.
- **Photoinitiator**: triarylsulfonium hexafluoroantimonate salts (S-SbF)



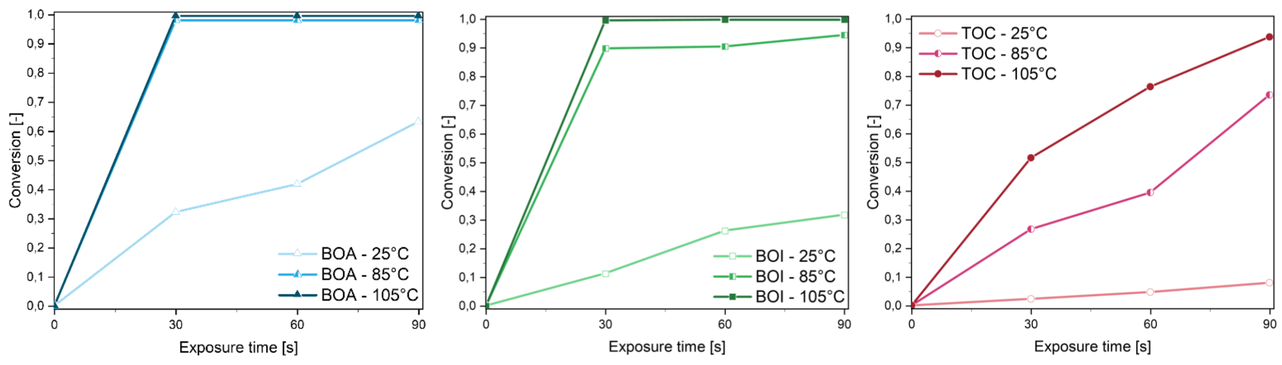


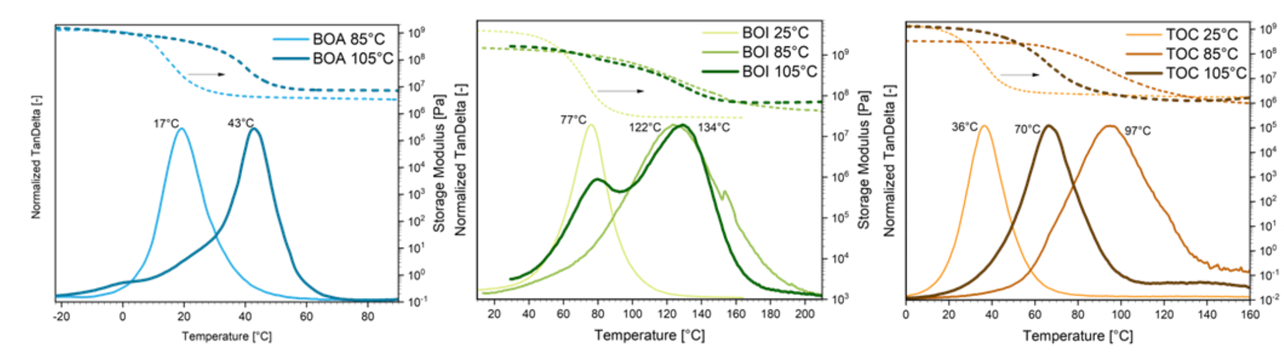


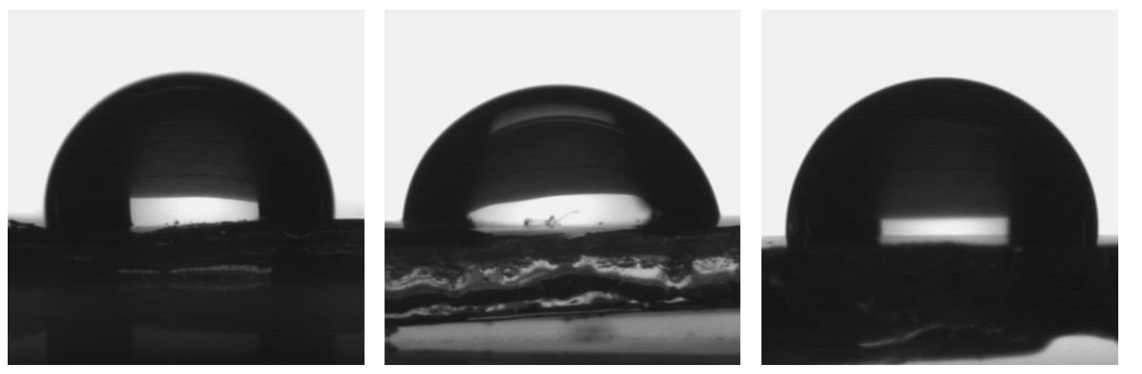
Results



Curing Temperature		DMTA Tg [°C]	Modulus [Pa]	Contact angle [°]	Gel content [%]
BOA	25 °C	N/A	N/A	NA	NA
	85 °C	17	$3{,}69 \times 10^6$	93±4	89
	105 °C	43	$7{,}03 \times 10^6$	95±6	89
BOI	25 °C	77	$2{,}99 \times 10^7$	NA	NA
	85 °C	80/122	$5{,}68 \times 10^7$	72±4	100
	105 °C	134	$7{,}10 \times 10^7$	73±5	100
TOC	25 °C	36	$1{,}47 \times 10^6$	NA	NA
	85 °C	97	$1{,}24 \times 10^6$	92±3	100
	105 °C	70	$1{,}41 \times 10^6$	94±2	100







Conclusions

- Bio-based oxetane monomers show promising reactivity in UV curing, especially BOI with dual reactivity.
- High oxetane group conversion (>85 °C curing).
- BOI exhibits highest Tg and crosslink density, suggesting best performance for applications demanding rigidity.
- TOC's hydroxyl groups lead to ether linkages, lowering crosslinking density, and Tg.

Acknowledgments

EU Horizon 2020 Marie Skłodowska-Curie grant #101085759 (SURE-Poly).