Advanced Kinetic Modeling of Photocurable Polymer Systems: Acrylate vs Thiol-ene Chemistry

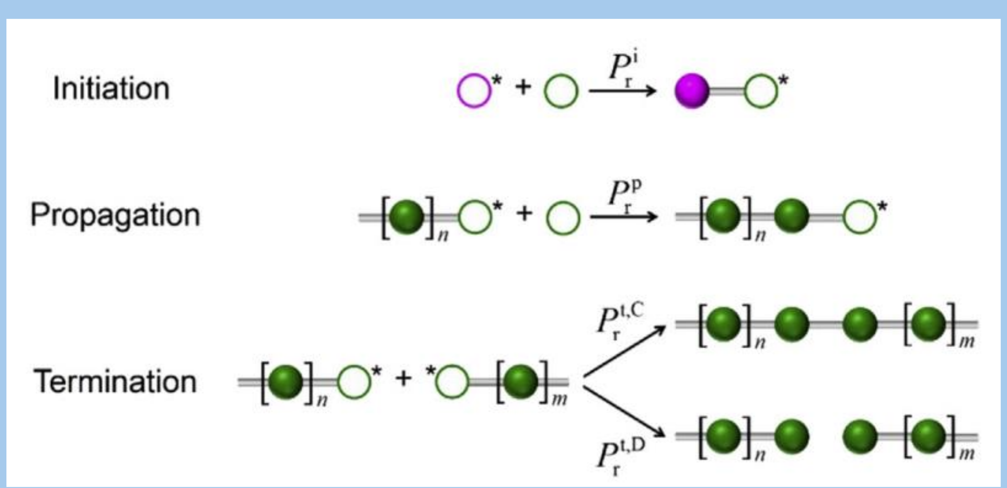
Kivanc Kacmaz [1,*], Ke Wang[1], Astrid Quaak[2], Guy Van Assche[1], Sandra Van Vlierberghe[2], Joost Brancart[1]

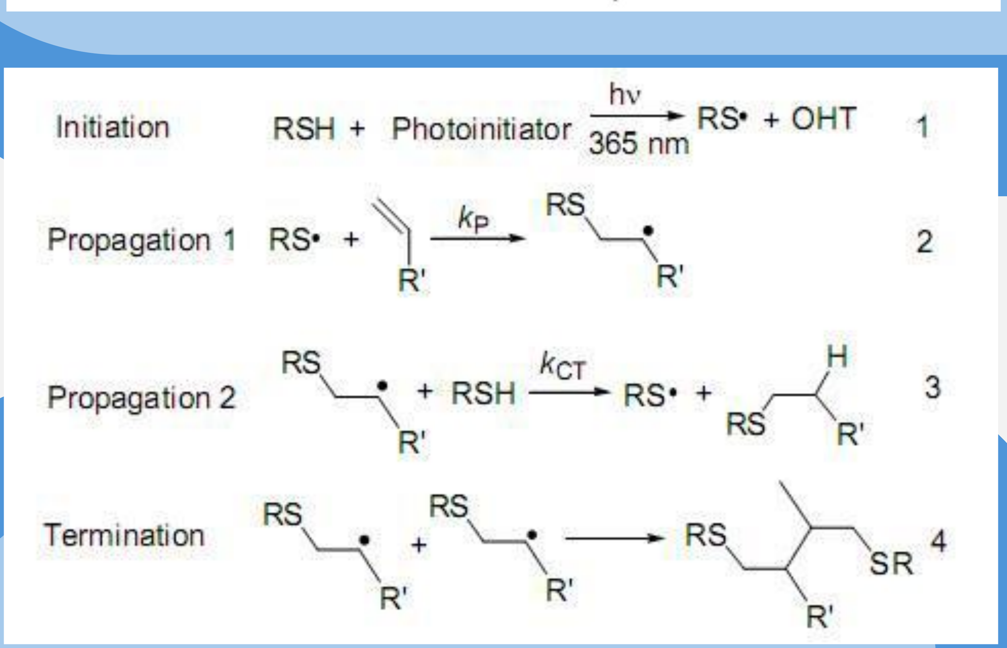
[1]Research Group of Physical Chemistry and Polymer Science, Vrije Universiteit Brussel, Brussels, Belgium

[2]Research Group of Polymer Chemistry and Biomaterials Group, Ghent University, Ghent, Belgium

BACKGROUND & AIM

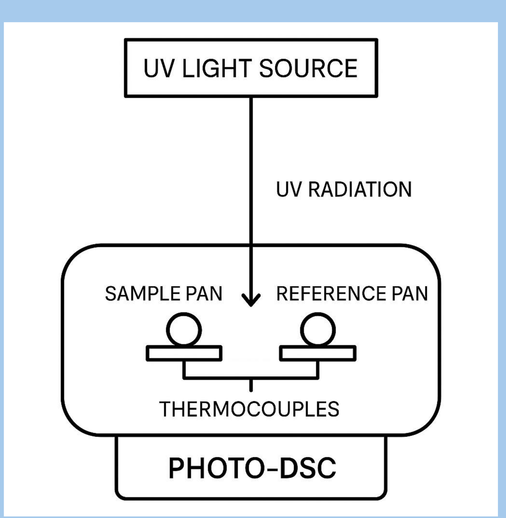
- Photocurable polymers are key in coatings, 3D printing, and biomedical devices. Fast curing and tunable chemistry make them ideal for industry and research.
- Standard kinetic models oversimplify the curing process and lack accuracy. This work compares PCL-based acrylate and thiol-ene systems.
- Acrylates: chain-growth, fast but oxygen-sensitive, form irregular networks.
- Thiol-enes: step-growth, oxygen-tolerant, form uniform networks.
- Goal: build detailed kinetic models using MATKIN software.

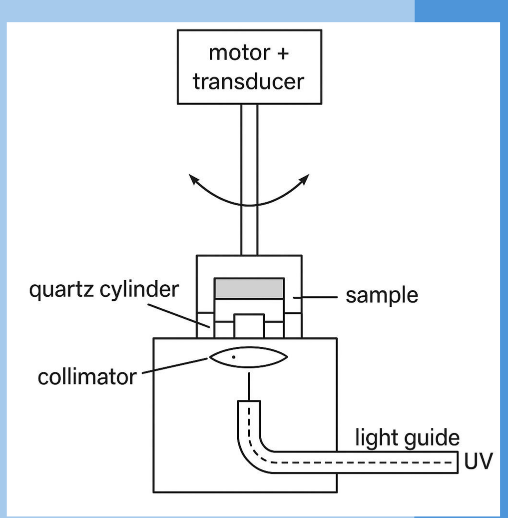




CHARACTERIZATION

- Photo-DSC for real-time curing kinetics under varied UV intensity, initiator concentration, and temperature.
- Kinetic modeling via MATKIN to fit and optimize across conditions.
- Photo-rheology to correlate viscoelastic build-up with network structure formation.





WHAT'S NEXT?

We aim to expand the kinetic model to study structure–property relationships through network formation dynamics. For both systems, we will explore different chemical environments to identify the most suitable kinetic expressions.

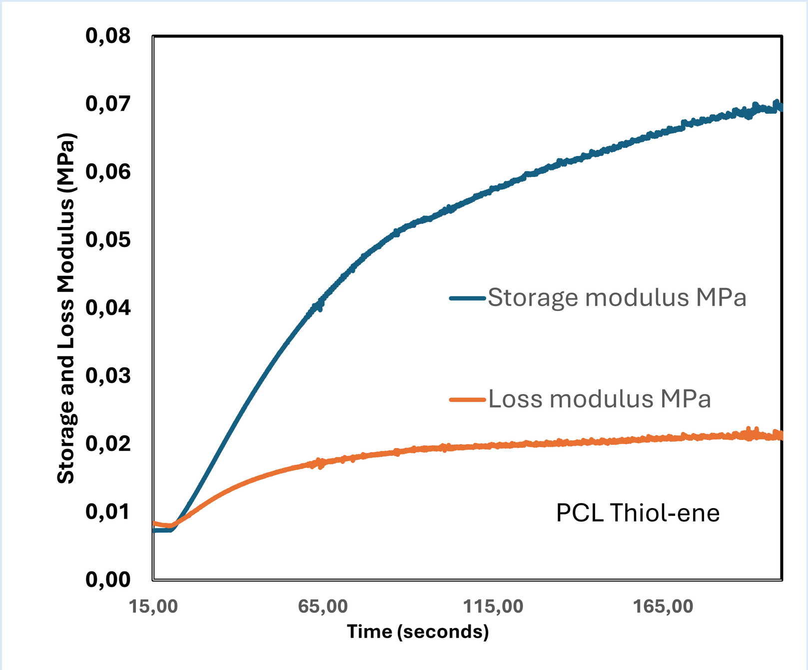
OUTCOME

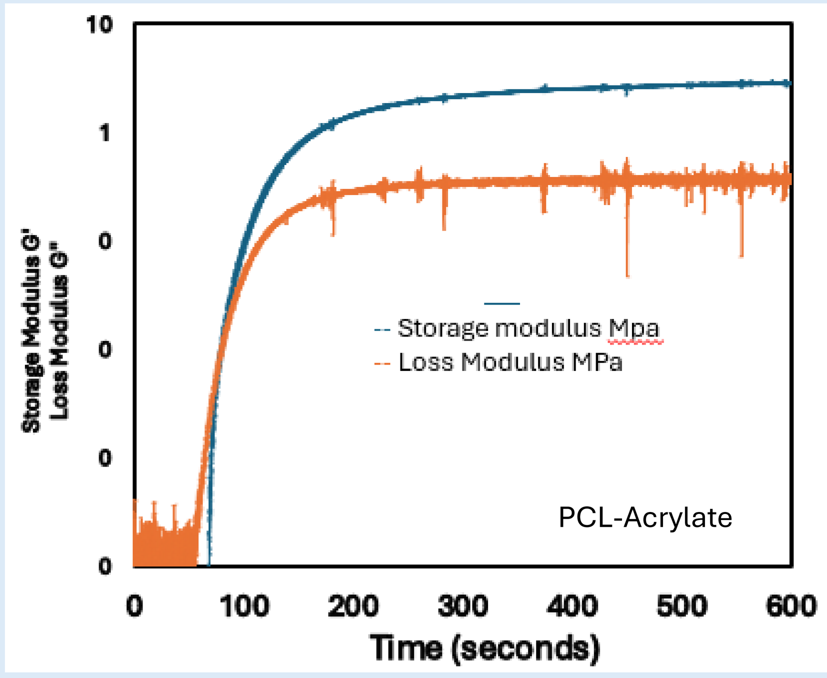
- Constructed accurate kinetic models for acrylate and thiol-ene systems using MATKIN.
- Captured real-time curing behavior across varying UV intensity, temperature, and initiator levels.
- Demonstrated improved model accuracy by incorporating distinct polymerization mechanisms.

RESULTS

Simulation accuracy improves with **diffusion-limited kinetics,** aligning with experimental photo-DSC and rheology validation.

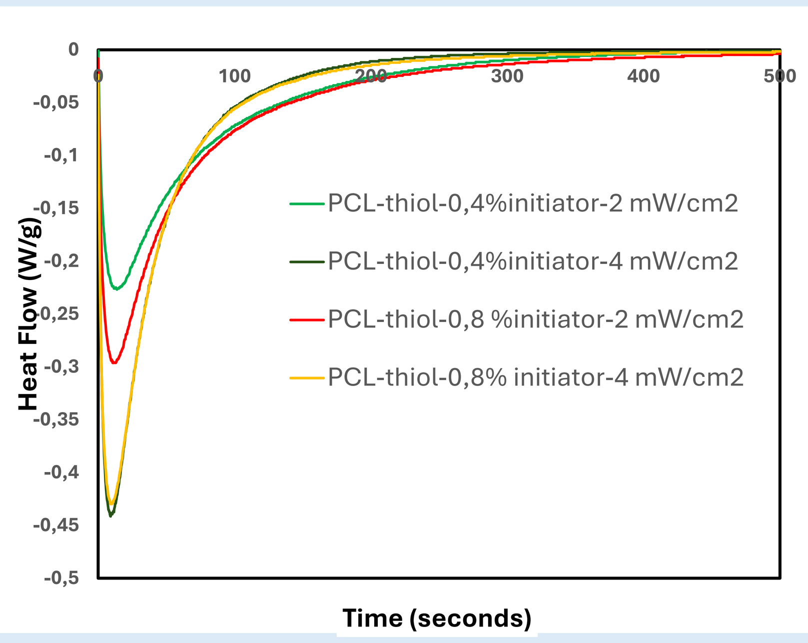
Photorheology – G' and G'' evolution

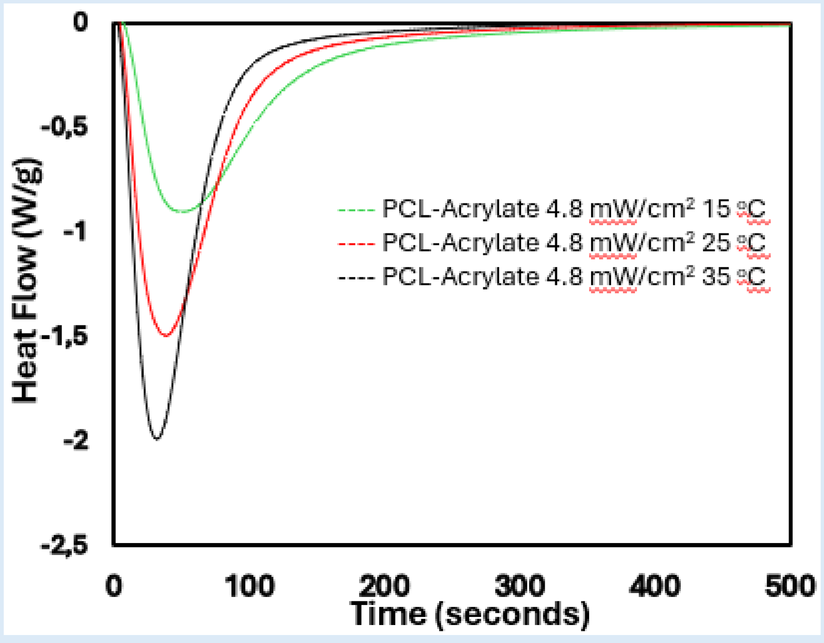




Supports the presence of diffusion limitation, showing modulus buildup at higher conversions.

Photo-DSC Heat Flow Curves



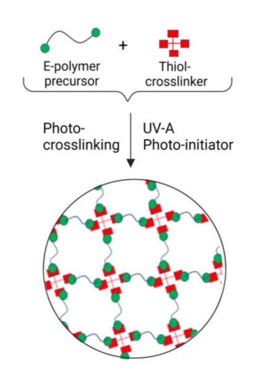


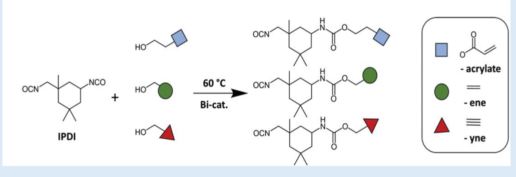
Experimental heat flow data under varying temperatures, used to calibrate and validate the kinetic model.

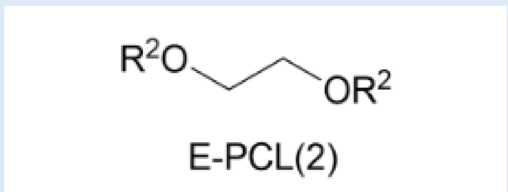
VARIED PARAMETERS

- UV intensity
- Initiator concentration
- Temperature

For the kinetic modelling, all the varying parameters optimized at once.

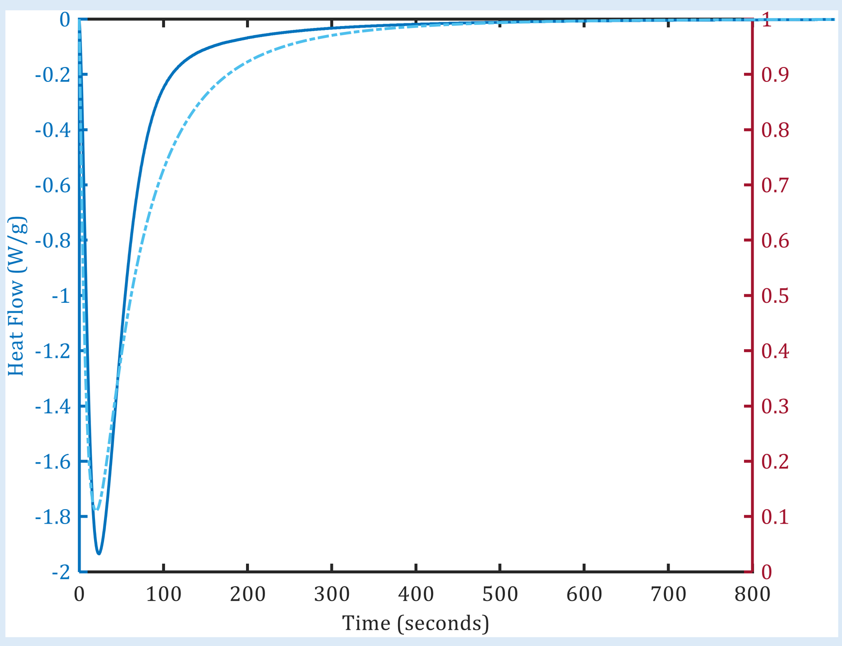




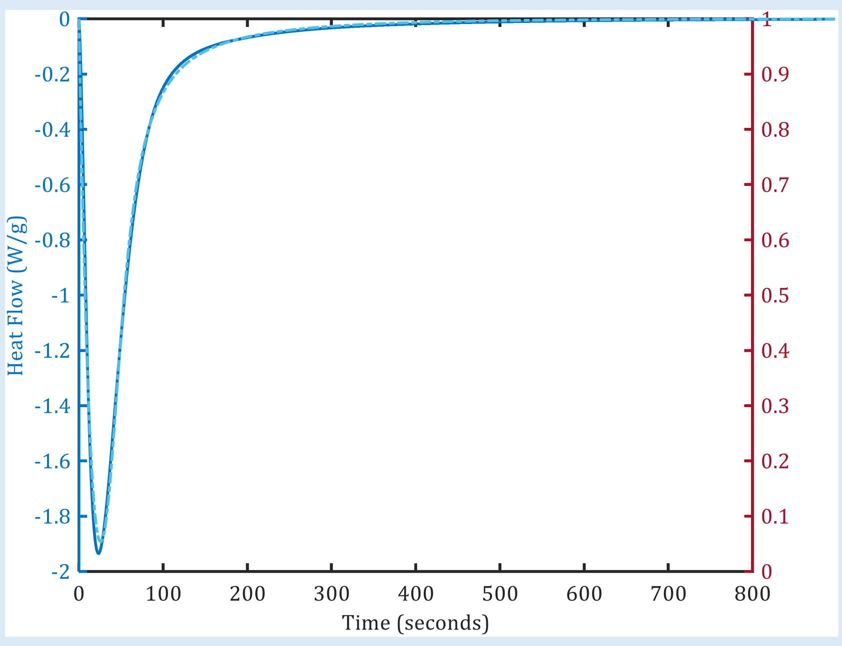


PCL Acrylate

Model Prediction Before Diffusion Correction

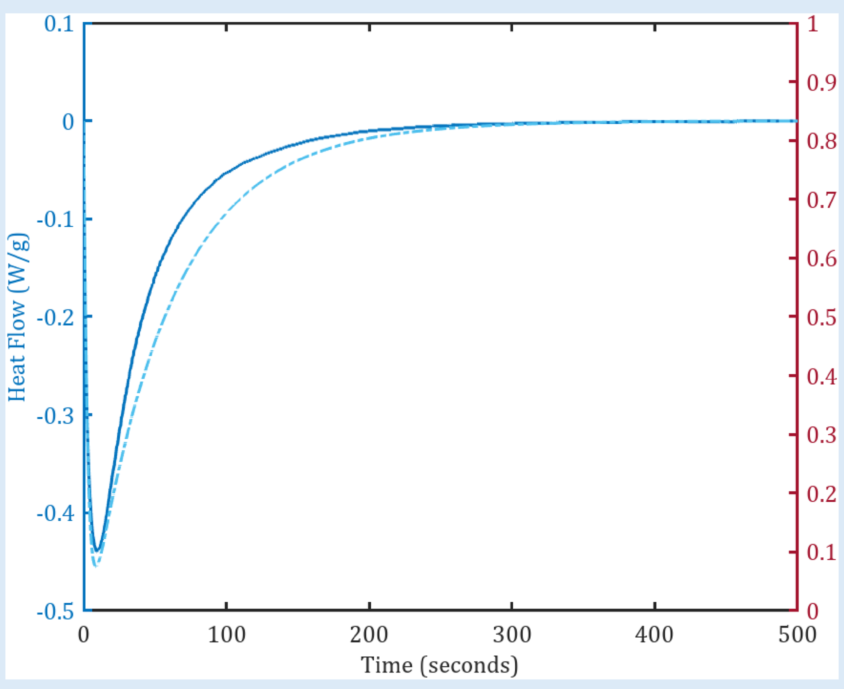


Model Prediction After Diffusion Correction

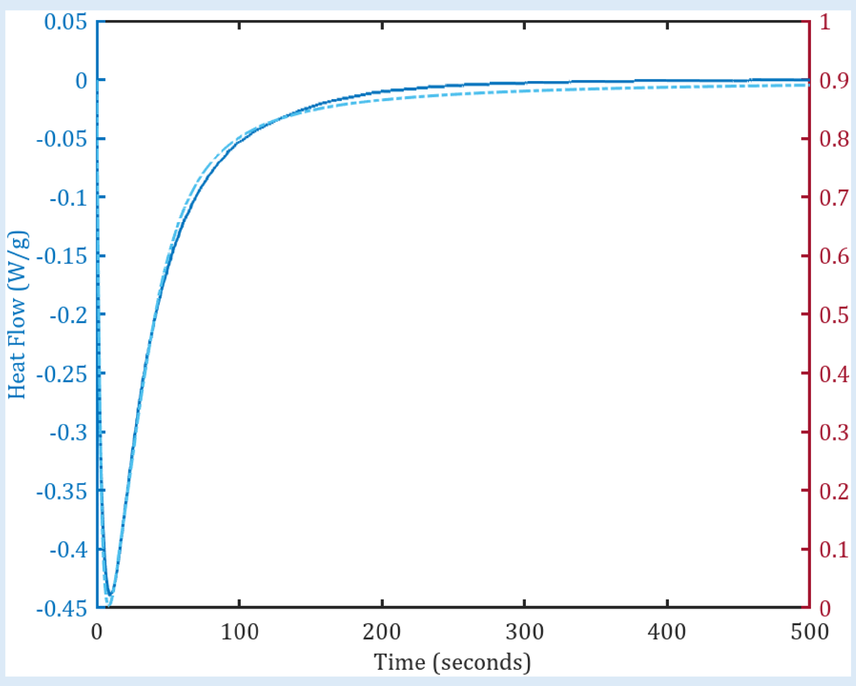


PCL Thiol-ene

Model Prediction Before Diffusion Correction



Model Prediction After Diffusion Correction



***Improved model accurately captures both early and late curing behaviour by incorporating diffusion limitation.**

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