

INVESTIGATION INTO RADICAL COPOLYMERIZATIONS OF ITACONATES WITH ACRYLATES

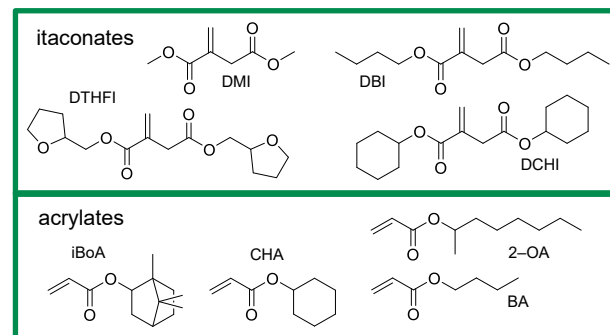
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Introduction

- itaconic acid and its esters are available from bio-based resources and offer access to bio-based polymers^[1,2]
- low radical polymerization rates and depropagation of itaconates are challenging
→ copolymerizations with acrylates appear attractive to enhance reaction rate and achieve high molar masses
- to allow for tailored copolymer compositions reactivity ratios were derived from kinetic Monte Carlo simulations based on experimental composition data from ¹H-NMR and SEC analyses
- propagation kinetics of itaconates were investigated using PLP-SEC tailored for monomers with low k_p and k_t



Experimental methods

Copolymerizations

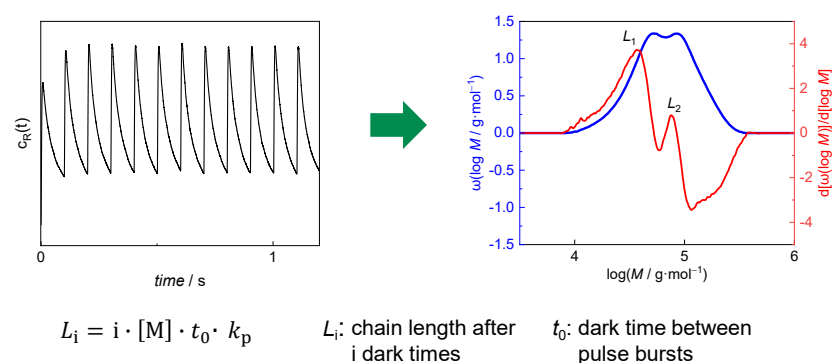
- copolymerizations in dioxane carried out at 80 °C for different reaction times
- in-line ¹H-NMR (600 MHz): DBI–BA copolymerizations in an NMR tube, dioxane-*d*₈, 60 °C, 4 h
- off-line ¹H-NMR (80 MHz or 400 MHz): itaconate–acrylate copolymerizations in dioxane at 60 to 80 °C
- SEC**: monomer conversions derived from elution curves of the reaction mixture

Propagation kinetics

- PLP–SEC with modified pulse profiles in a temperature range of 5–60 °C to be able to neglect depropagation

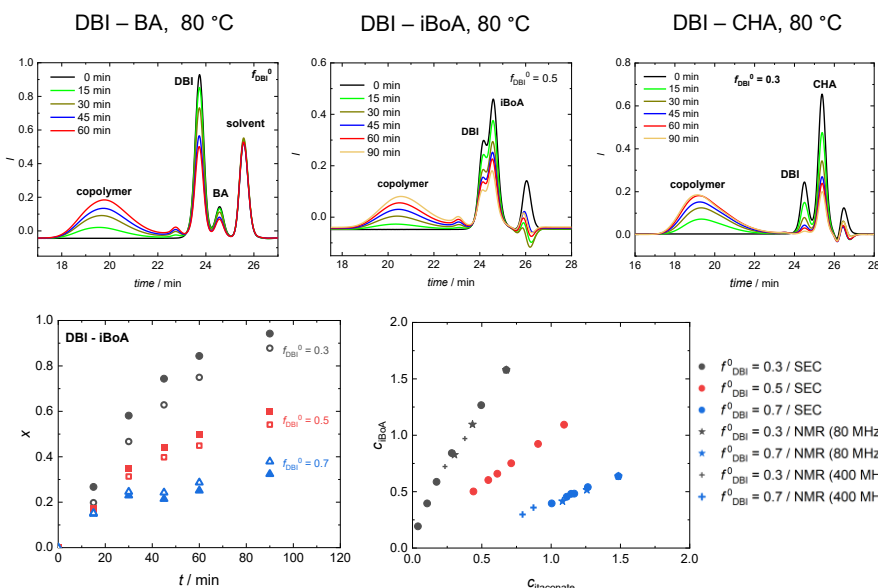
Pulsed-laser polymerization (PLP)

- periodically changing radical concentration due to irradiation with UV laser pulses
- IUPAC recommended method of choice for determination of k_p



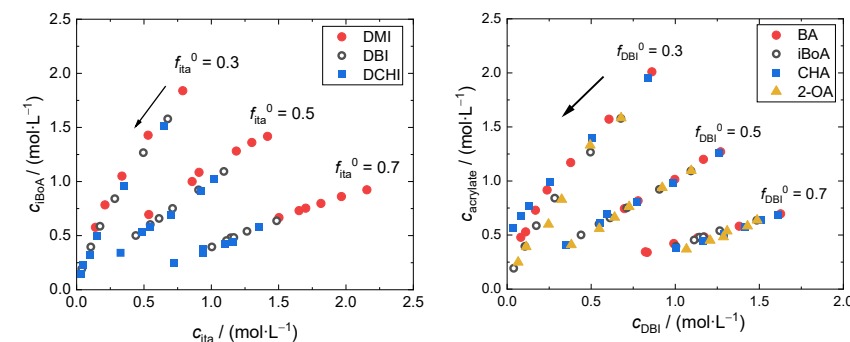
Copolymer composition data

SEC elution curves measured directly from the copolymerization reaction mixture



preferential incorporation of DBI at f_{DBI}^0 of 0.3 and 0.5

excellent agreement of data derived from three independent types of analyses



minor impact of itaconate ester group on copolymerizations with iBoA

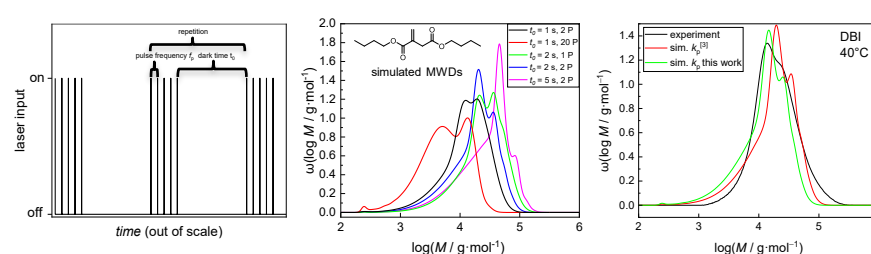
noticeable impact of acrylate ester group on copolymerizations with DBI for $f_{DBI}^0=0.3$

Reactivity ratios derived from the variation of both monomer concentrations throughout the copolymerization up to high conversions applying Monte Carlo simulations^[4]

M ₁	M ₂	r ₁	r ₂	M ₂	r ₁	r ₂	M ₂	r ₁	r ₂	M ₂	R ₁	r ₂
DMI				iBoA	1.96	0.52	2-OA	1.61	0.57	CHA	2.22	0.52
DBI	BA ^[4]	1.26	0.50					0.94	0.39		1.29	0.61
DCHI												

Propagation kinetics

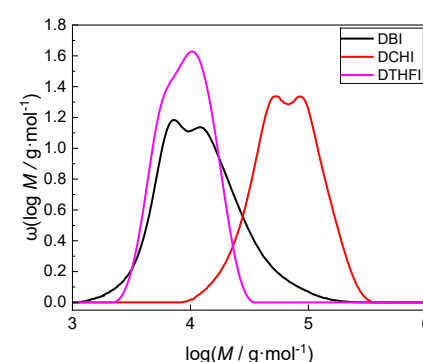
Pulse profiles determined via kinetic Monte Carlo simulations



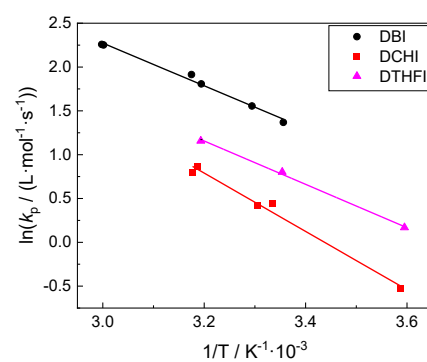
monomer	dark time t_0 [s]	pulses per burst
DBI	2	2
DCHI	20	40
DTHFI	10	2

good agreement of MWDs from simulations and experiment for DBI

experimental MWDs at 25 °C



Arrhenius diagram



monomer	activation energy E_A [kJ·mol ⁻¹]	pre-exponential factor A_0 [L·mol ⁻¹ ·s ⁻¹]	k_p at 25 °C [L·mol ⁻¹ ·s ⁻¹]	R ²
DMI ^[3]	27.8	7.29·10 ⁵	9.8	-
DBI	20.3	1.45·10 ⁴	4.1	0.990
DCHI	27.7	9.26·10 ⁴	1.5	0.987
DTHFI*	20.6	8.64·10 ³	2.2	0.998

*calibrated as polystyrene

sterically more demanding ester groups lead to a decrease in k_p

Conclusion

- r values derived from Monte Carlo simulation with consideration of itaconate depropagation
- preferential incorporation of itaconates
- activation energy and pre-exponential factors successfully determined via PLP employing special pulse profiles

outlook

- reactivity ratios for itaconate monomers with functional ester groups
- PLP-SEC investigation into depropagation kinetics of itaconates

Acknowledgments

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References

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