Copolymerisation of active esters and epoxides – model studies and catalyst screening

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Introduction

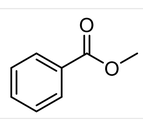
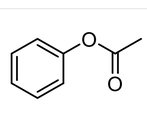
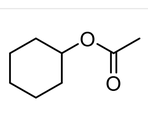
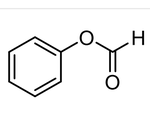
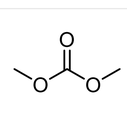
Epoxy resins are of high interest for coating and anchoring applications.[1] To improve hydrophobicity and dielectric properties epoxides can be cured with ester monomers to achieve hydroxyl-free epoxy resins.[2] We decided to test different esters as curing agents in a model reaction and subsequently use the best curing agent in a catalyst screening with widely used organocatalysts.

Model reaction

Different esters were used in the model reaction with phenyl glycidyl ether (PGE) at 80 °C for 24 hours with 5 mol% DMAP as catalyst. The epoxide conversion was determined by following the epoxide peak at 3.36 ppm via ^{1}H-NMR spectroscopy.

Fig 1.: Model reaction of PGE with different esters.

As seen in the spectrum in Fig. 2, the reaction of PGE and phenyl acetate leads to a single product. Phenyl formate as curing agent led to a high epoxide conversion, but due to side reactions the desired product was not obtained. All other tested esters showed poor epoxide conversion, as seen in the table below.

					
	Epoxide conversion in %				
1h	0	29	0	38	0
24h	11	>99	9	97*	0

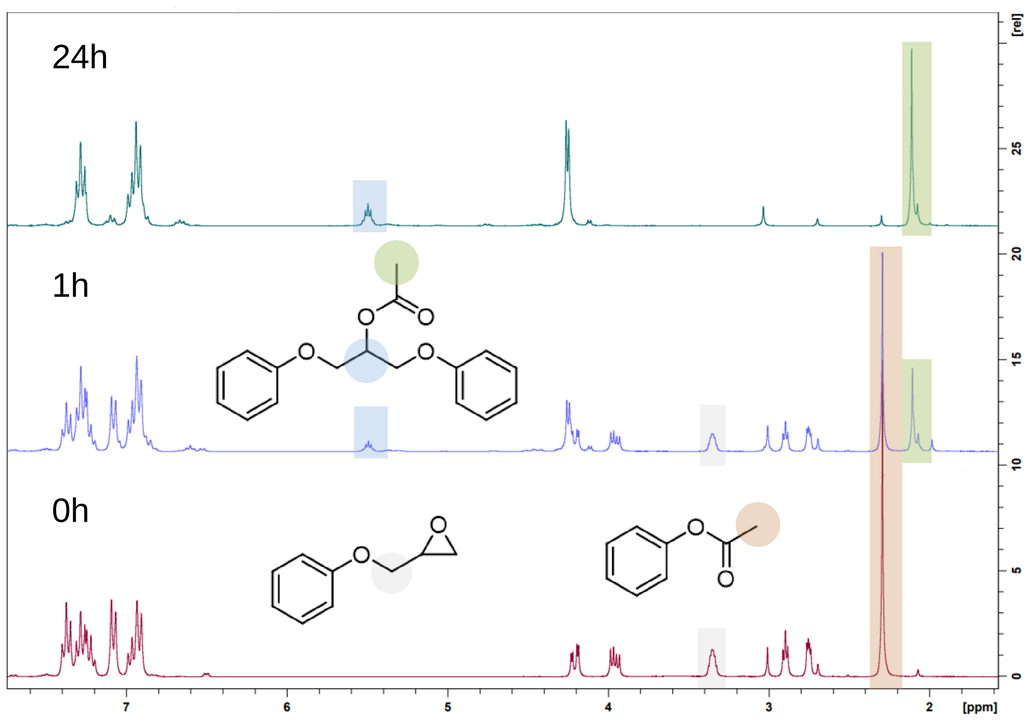


Fig. 2: ^{1}H-NMR spectra of the reaction of phenyl glycidyl ether and phenyl acetate.

Catalyst screening

The most reactive curing agent, phenyl acetate, was used with PGE in the catalyst screening. The screening was done at 80 °C and 120 °C to see the influence of temperature on the performance of different lewis base catalysts. The conversion of the epoxide-group was again monitored via ^{1}H-NMR spectroscopy.

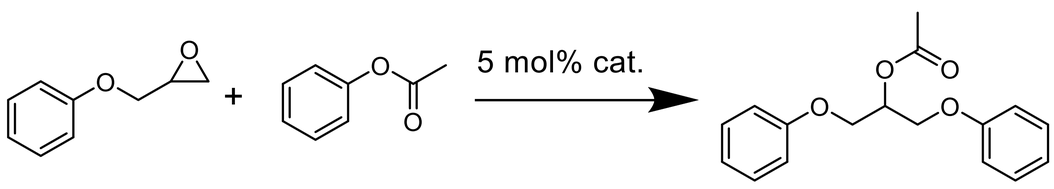
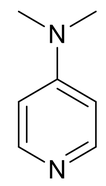
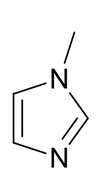
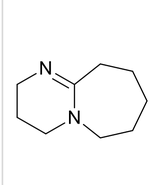
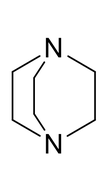
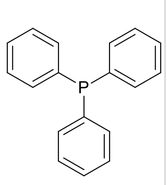
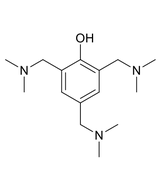


Fig. 3: Reaction for the catalyst screening.

As seen in the table on the right DMAP and 1-MI lead to full conversion even at 80 °C after 24 hours. Higher temperature enables faster conversion of the epoxide with all organic catalysts except DBU. Degradation reactions like hydrolysis are known for DBU and could explain the poor performance.[3]

The catalysts TPP, DABCO, and K54 produce up to 10 % PGE homopolymer as a side product at each temperature.

	 DMAP	 1-MI	 DBU	 DABCO	 TPP	 K54
80 °C	Epoxide conversion in %					
0.5 h	12.5	1	3	6	<1	<1
1 h	25	5	9	10	2	4
2 h	50	27	17	27	10	39
24 h	>99	>99	84	92	78	89
120 °C						
0.5 h	98	90	5	53	50	96
1 h	>99	97	5	66	70	97
2 h	>99	>99	5	81	92	>99
24 h	>99	>99	9	>99	>99	>99

Conclusion

- In the model reaction phenyl acetate led to the expected product with high epoxide conversion.
- DMAP and 1-MI lead to a full epoxide conversion even 80 °C.
- Not all catalysts are suitable for selective co-polymerisation

Acknowledgement

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References

[1]: H. Q. Pham and M. J. Marks, **2005**. Epoxy Resins. Ullmann's Encyclopedia of Industrial Chemistry. https://doi.org/10.1002/14356007.a09_547.pub2
[2]: C. H. Chen, Z. C. Gu, Y. L. Tsai, R. J. Jeng, C. H. Lin, *Polymer* **2018**, 140, 225-232. https://doi.org/10.1016/j.polymer.2018.02.045
[3]: A. M. Hyde, R. Calabria, R. Arvary, X. Wang, A. Klapars, *Org. Process Res. Dev.* **2019**, 23 (9), 1860-1871. https://doi.org/10.1021/acs.oprd.9b00187

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