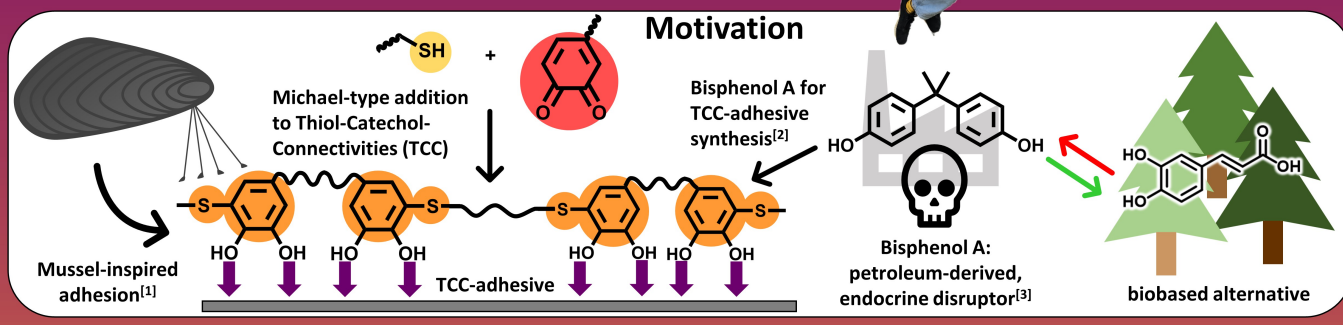
Caffeic Acid Based Adhesives: Thiol-Catechol Chemistry meets Photochemistry

Carla Hansen, Keven Walter, Dominik P. Hoch, Hans G. Börner

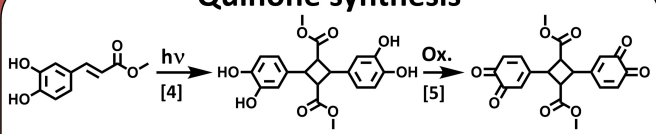
Laboratory for Organic Synthesis of Functional Systems
Institute for Chemistry, Humboldt-Universität zu Berlin

h.boerner@hu-berlin.de
carla.hansen@hu-berlin.de

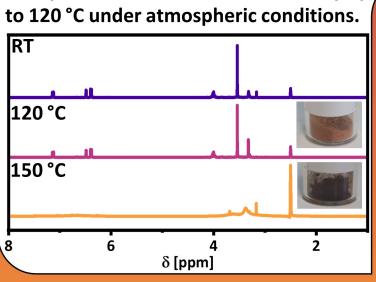
Motivation



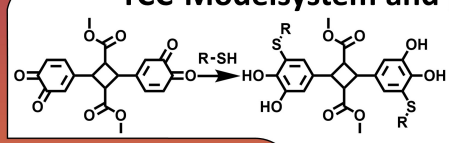
Quinone synthesis



The quinone showed thermal stability up to 120 °C under atmospheric conditions.

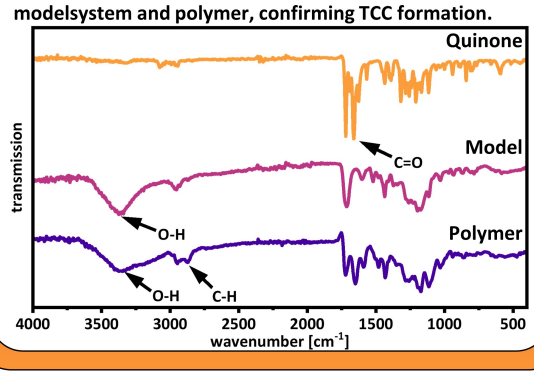


TCC-Modelsystem and polymer

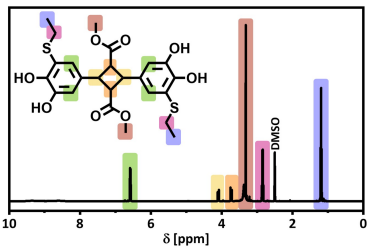


With SH for the TCC-Modelsystem and HS–O–O–SH for the Polymer.

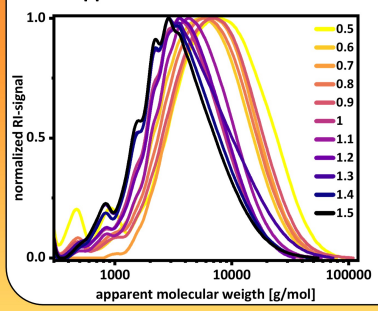
FTIR showed consumption of the conjugated C=O band of the quinone and formation of O-H vibrations in the modelsystem and polymer, confirming TCC formation.



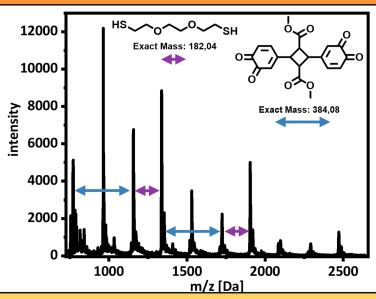
The sucessful TCC-formation was confirmed using 2D-NMR, FTIR and MALDI-ToF-MS.



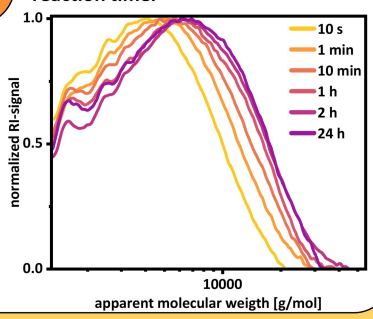
GPC showed formation of polymers with higher apparent molecular weight when an excess of quinone was applied.



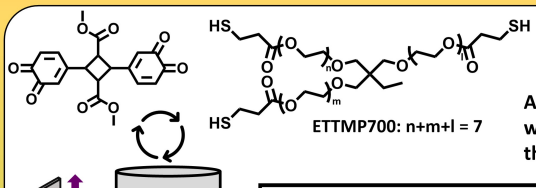
MALDI-ToF-MS showed alternating monomer fragments confirming the formation of the linear TCC-Polymer.



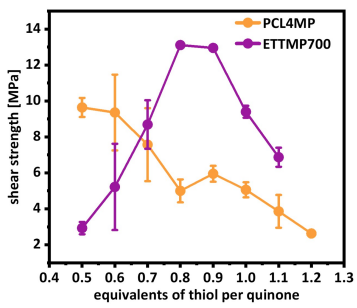
GPC analysis showed completion of the polymerization after 1 h of reaction time.

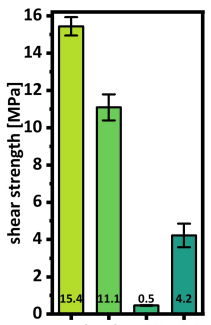


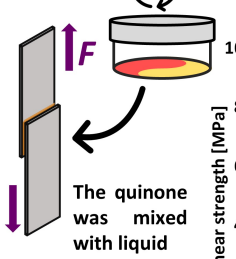
2K-Adhesives



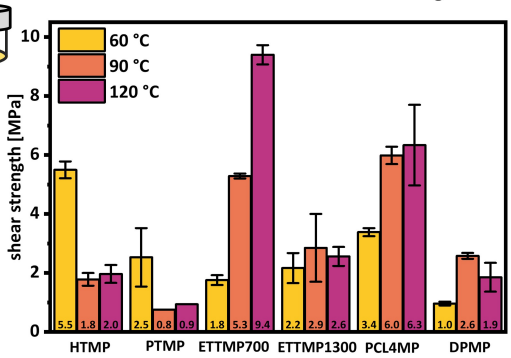
Adhesive strengths were determined after thermal curing for 17 h.







The quinone was mixed with liquid multithiols to determine shear strengths on aluminium.



3.7 MPa
granite

The adhesive strengths for the adhesive with ETTMP700 were investigated on different materials after curing at 120 °C.

Conclusion

The biobased caffeic acid was successfully converted into a bisquinone that was able to react via TCC-formation. The formation of polymers with dithiols was observed, showing further crosslinking with excess of quinone. With liquid multithiols the quinone was applied as 2K-adhesive, showing remarkable adhesive strength on aluminium, steel, wood and granite.

References:

[1] B. P. Lee, P. B. Messersmith, J. N. Israelachvili, J. H. Waite, *Annu. Rev. Mater. Res.* **2011**, 41, 99–132.
[2] J. M. Krüger, H. G. Börner, *Angew. Chem. Int. Ed.* **2021**, *60*, 6408-6413.
[3] S. A. Hafezi, W. M. Abdel-Rahman, *Curr. Mol. Pharmacol.* **2019**, *12*, 230–238.
[4] Z. Wang, Q. Flores, H. Guo, R. Trevizo, X. Zhang, S. Wang, *CrystEngComm* **2020**, 22, 7847-7857.
[5] A. Pelter, S. Elgendy, *Tetrahedron Lett.* **1988**, 29, 677-680.

Acknowledgements:

- Steffen Weidner (BAM) for MALDI-ToF-MS measurements

Gefördert durch
DFG Deutsche Forschungsgemeinschaft
project number: 536607484

BörnerLab