(De)Activating Bond Exchange Reactions in Dynamic Polymer Networks

D. Reisinger[1], S. Schlögl[1,2*]

[1]*Polymer Competence Center Leoben GmbH, Leoben, Austria*
[2]*Institute of Chemistry of Polymeric Materials, Technical University of Leoben, Leoben, Austria*
[*]*sandra.schloegl@pccl.at*

Latent catalysts are a versatile strategy to temporally and locally control the rate of bond exchange reactions (and the related material flow) in dynamic polymer networks.[1-4] Herein, we explored novel families of reversibly switchable catalysts, which undergo a distinctive shift in their pKa values due to an external trigger (either light or a change in temperature).

In a first step, the reversible activation/deactivation of a photoswitchable nitrogen superbase undergoing light-induced isomerization of dithienylethene groups was studied in thiol-ene photopolymers.[5] Depending on the color of light used (visible versus UV light), a substantial difference in the pKa value was observed, which was exploited to kinetically control the base-catalyzed bond exchange between thioester and thiol groups. The reversibility and local control of the isomerization reaction (and the related bond exchange kinetics) was demonstrated by stress relaxation, reshaping, micro imprint and tensile testing experiments.

In a further approach, photochromic merocyanine-based photoacids were synthetized and applied as reversibly switchable catalysts for acid-driven dynamic polymer networks.[6] Upon visible light exposure, the catalyst was activated by undergoing a spirocyclization, while the deactivation reaction took place under dark conditions at elevated temperature. The photoacid was placed in a thiol-ene photopolymer comprising ample -OH and ester moieties and a reversible control of the transesterification kinetics was demonstrated by stress relaxation studies. The fast isomerization kinetics and fatigue resistance were used to generate gradients of active photoacid in a spatially resolved manner at the micrometer level. The resulting gradient in relaxation properties was applied for mold-free reshaping of dynamic photopolymers.

Acknowledgments

The research work was carried out within the COMET-Module project "Repairtecture" (project-no.: 904927) at the Polymer Competence Center Leoben GmbH (PCCL, Austria) within the framework of the COMET-program of the Federal Ministry for Innovation, Mobility and Infrastructure and the Federal Ministry of Economy, Energy and Tourism. The COMET-Module is funded by the Austrian Government and the State Governments of Styria and Upper Austria.

A part of the research work has received funding from the European Union's Horizon2020 research and innovation program under the Marie Skłodowska-Curie grant agreement, No 101085759 (SURE-Poly).

References

[1] Reisinger, D., Kaiser, S., Rossegger, E., Alabiso, W., Rieger, B., Schlögl, S. Introduction of photolatent bases for locally controlling dynamic exchange reactions in thermo-activated vitrimers. *Angewandte Chemie* **2021**, *60*, 14302-14306.

[2] Dertnig, C., Guedes de la Cruz, G., Neshchadin, D., Schlögl, S., Griesser, T. Blocked Phosphates as Photolatent Catalysts for Dynamic Photopolymer Networks. *Angewandte Chemie* **2022**, *135*, e202215525.

[3] Rossegger, E., Shaukat, U., Moazzen, K., Fleisch, M., Berer, M., Schlögl, S. The role of photolatent catalysts on the exchange kinetics of dual-wavelength 3D printable and photopatternable thiol-click vitrimers. *Polymer Chemistry* **2023**, *14*, 2640-2651.

[4] Reisinger, D., Kriehuber, M. U., Bender, M., Bautista-Anguís, D., Rieger, B., Schlögl, S. Thermally Latent Bases in Dynamic Covalent Polymer Networks and their Emerging Applications. *Advanced Materials* **2023**, *35*, 2300830.

[5] Reisinger, D., Sietmann, A., Das, A., Plutzar, S., Korotkov, R., Rossegger, E., Walluch, M., Holler-Stangl, S., Hofer, T. S., Dielmann, F., Glorius, F., Schlögl, S. Light-Driven, Reversible Spatiotemporal Control of Dynamic Covalent Polymers. *Advanced Materials* **2024**, *36*, 2411307.

[6] Reisinger, D., Wimberger, L., Korotkov, R., Scott, T.F., Cameron, N.R., Boyer, C., Schlögl, S. Reversible On-Demand Activation of Acid-Catalyzed Dynamic Polymers for Gradient-Driven Reshaping. *Advanced Materials* **2025**, submitted.