

Real-Time Analysis of Anionic Polymerizations by Electrospray-Ionization Mass Spectrometry

K. Koszinowski,¹⁾ N. F. Eisele¹⁾, and F. Kreyenschmidt¹⁾

1) Universität Göttingen, Institut für Organische und Biomolekulare Chemie,
Tammannstr. 2, 37077 Göttingen, Germany

Anionic polymerizations are of enormous practical importance. Due to the high reactivity of the growing anionic polymer chains, in-situ measurements have been notoriously difficult. Here we show that electrospray-ionization mass spectrometry holds great promise for the real-time analysis of such reactions. Under carefully optimized conditions, the active anionic intermediates of the ring-opening polymerization of an acceptor-substituted cyclopropane as well as the organocobaltate anions formed in the coordinative anionic polymerization of isoprene can be detected [1,2]. The molar-mass distributions derived from the ESI mass spectra agree well with those of the isolated polymers determined independently by well-established methods, thus giving confidence in the quantitative accuracy of the ESI-mass spectrometric results. Besides simple mass distributions, the new approach affords individual rate constants and succeeds in the observation of side products. This wealth of mechanistic information improves our understanding of anionic polymerizations and should be instrumental for optimizing practical applications.

References

1. N. F. Eisele, M. Peters, K. Koszinowski; Chem. Eur. J., in press, doi: 10.1002/chem.202203762
2. F. Kreyenschmidt, N. F. Eisele, V. Hevelke, R. Rahrt, A.-K. Kreyenschmidt, K. Koszinowski; Angew. Chem. Int. Ed., **61**, e202210211 (2022)