

TAILORING POLYMER DISPERSITY IN PHOTOINDUCED IRON-CATALYZED ATRP

Manon Rolland, Nghia P. Truong, Richard Whitfield, and Athina Anastasaki*

Laboratory for Polymeric Materials, Department of Materials, ETH Zürich,
Vladimir-Prelog-Weg 5, 8093 Zürich, Switzerland

Although dispersity (\mathcal{D}) plays an important role in controlling polymer properties, there are very few chemical methods that can sufficiently tune it. Here we report a simple, batch, and environmentally benign photoinduced iron-catalyzed ATRP methodology that enables the efficient control of \mathcal{D} for both homopolymers and block copolymers. We show that by judiciously varying the concentration of the FeBr₃/TBABr catalyst, a range of dispersities can be obtained ($1.18 < \mathcal{D} < 1.80$) while maintaining monomodal molecular weight distributions. High end-group fidelity was confirmed by MALDI-ToF-MS and was further supported by the efficient synthesis of in situ block copolymers where the dispersity of the second block could be controlled upon demand. Importantly, through the use of low ppm amounts of the catalyst, perfect temporal control could be attained during intermittent “on/off” cycles. This work considerably expands the chemical toolbox for tuning \mathcal{D} of homo- and block copolymers.

