Tailoring Polymer Dispersity in Controlled Radical Polymerization

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Dispersity significantly affects the properties of polymers. However, current methods for controlling the polymer dispersity are limited to bimodal molecular weight distributions, adulterated polymer chains, or low end-group fidelity and rely on feeding reagents, flow-based, or multicomponent systems. To overcome these limitations, I will present a simple batch system whereby photoinduced atom transfer radical polymerisation is exploited as a convenient and versatile technique to control dispersity of both homopolymers and block copolymers. By varying the concentration of the copper complex, a wide range of monomodal molecular weight distributions can be obtained (Đ=1.05–1.75). In all cases, high end-group fidelity was confirmed by MALDI-ToF-MS and exemplified by efficient block copolymer formation (monomodal, Đ=1.1–1.5). Importantly, our approach utilises ppm levels of copper (as low as 4 ppm), can be tolerant to oxygen and exhibits perfect temporal control, representing a major step forward in tuning polymer dispersity for various applications.