THE INFLUENCE OF DEPROPAGATION ON PEGMA9 SOLUTION RADICAL HOMOPOLYMERIZATION AND COPOLYMERIZATION WITH DEAEMA

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While it is known that the synthesis of bottlebrush polymers is influenced by depropagation even at low temperatures, the effects of the monomer/polymer concentration and copolymer composition on this phenomenon have not been studied. Thus, free-radical homo and copolymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA9, Mn 500 g mol−1) with 2-(diethylamino)ethyl methacrylate (DEAEMA) at a low initial PEGMA9 concentration was investigated using in situ1H-NMR spectroscopy at 65 °C in CDCl3. Depropagation influences PEGMA9 homopolymerization kinetics at this low temperature due to the bottlebrush conformation of the polymer, with the equilibrium PEGMA9 concentration ([M]eq) dependent on the initial monomer concentration ([M]0). With [M]0 = 173 mM, an [M]eq value of 81.7 mM was estimated, corresponding to an equilibrium constant of Keq = 12.2 M−1. However, increasing [M]0 to 370 mM lowered [M]eq to 46 mM with an equilibrium constant of Keq = 21.7 M−1, an effect attributed to the influence of the poly(PEGMA9) concentration on the backbone chain flexibility that modifies the enthalpic and entropic properties of the reaction system. The copolymerization reactivity ratios of rDEAEMA = 1.66 ± 0.01 and rPEGMA9 = 0.68 ± 0.003 were estimated by fitting the variation in the comonomer composition with overall monomer conversion without considering the influence of depropagation. New dynamic models were formulated to represent composition drift with conversion in the presence of depropagation (Lowry Case I and Case II). However, these representations led to significant differences between experimental data and the model, indicating that PEGMA9 depropagation does not influence the copolymerization system, likely due to the disruption of the poly(PEGMA9) bottlebrush conformation by the insertion of DEAEMA units that generates more flexible copolymer backbone chains.

Keywords: PEGylated polymers, Depropagation, Smart materials

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