DESIGNING CONTROLLED RADICAL POLYMERIZATION: A SELECTION OF A TERMINAL OR PENULTIMATE MODEL FOR THE INTRINSIC REACTIVITIES

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In the past decades many efforts have been devoted to understand and design controlled radical polymerization (CRP) techniques such as atom transfer radical polymerization (ATRP) and nitroxide mediated polymerization (NMP). A crucial aspect is the use of detailed reaction schemes and the appropriate correction for diffusional limitations. Limited focus has however paid to the impact of penultimate monomer unit (PMU) effects, which can be explained by the complexity of the associated kinetic models with multiple reaction channels and the lack of data on reactivity ratios, in particular for NMP specific reactions. In the present contribution, it is demonstrated that depending on the comonomer pairs and the reaction conditions either a terminal [2] or penultimate model [3] is more suited. For copolymerizations with equimolar conditions for the comonomer amounts the PMU can be very pronounced even if based on the reactivity ratios as such this is not expected (Figure 1).

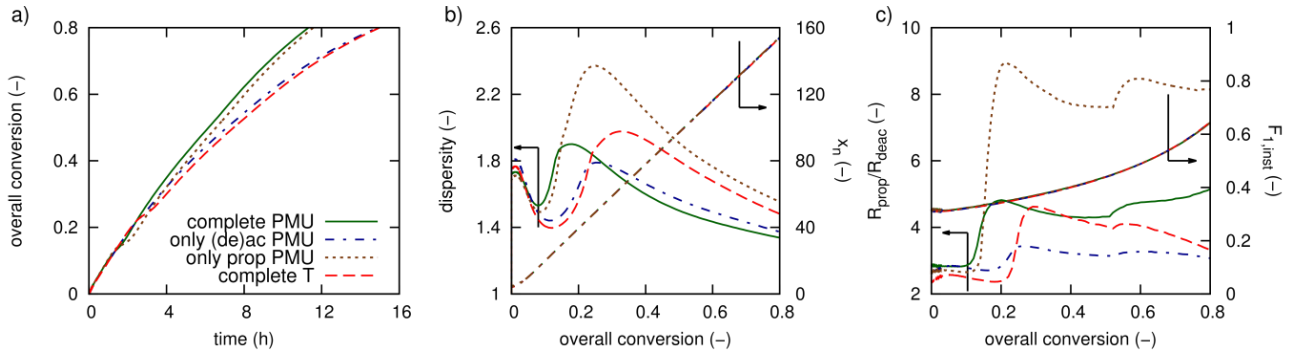

Figure 3 – Relevance of penultimate monomer unit effect in ICAR ATRP; comonomers: methyl methacrylate and n-butyl acrylate ([3]*); PMU: penultimate model; T: terminal model.*

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