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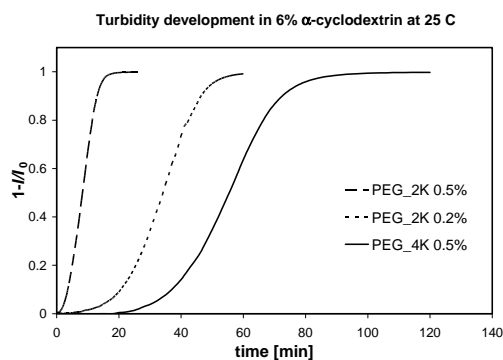
KINETICS OF POLYPSEUDOROTAXANE PRECIPITATION

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Formation of polypseudorotaxanes (PPR) in aqueous solutions of cyclodextrins (CD) and suitable water-soluble polymers (WSP) has been widely studied as an archetype of supramolecular self-assembling and as a potential source of components for a nanomachinery. A decade ago, turbidimetry on solutions of CDs and WSP was shown to provide useful information on PPRs formation. On the assumption that all WSP is converted to PPR with maximum number of CDs threaded before precipitation starts, the relation was derived between the PPRs stoichiometry and the time from mixing of CD and WSP solutions to turbidity appearance (lag time).[1] The equation has been frequently used but it predicts the lag time independent of WSP concentration and molecular weight and is thus clearly at variance with experimental results (see the figure). Therefore, reinterpretation of the kinetics of PPR precipitation is required. A model is presented in which the PPR formation is driven by its precipitation, and not the other way round. Furthermore, precipitation shows self-promoting effect, because the sigmoid shape, displayed by turbidity curves, is usually associated with autocatalysis. The model assumptions are implemented into the stochastic simulation of PPR formation in solution [2] in such a way that sufficiently long uninterrupted sequences of CDs on WSP chains are preserved. In order to explain the effect of WSP concentration, nucleation is taken into account, i.e., the number of sufficiently long sequences in the PPR set must exceed a certain value (“solubility”) for the sequence preservation to occur. The

simulation results also shows that high yields of solid PPR can be obtained without intraPPR cooperativity, i.e., without interaction of CDs adjacent on the chain.



[1] Ceccato M., Lo Nostro P., Baglioni P. *Langmuir* **1997**, *13*, 2436

[2] Horský J., *Macromol. Theory Simul.* **2000**, *9*, 759