Early Stage Kinetics in Polyelectrolyte Complexation Studied in a Stopped-Flow Configuration

XIAOQING LIU, MARIE HADDOU, JOANNA GIERMANSKA, Centre de Recherche Paul Pascal (CRPP), UPR CNRS 8641, Université Bordeaux, 33600 Pessac, France, CHRISTOPHE SCHATZ, Laboratoire de Chimie des Polymères Organiques, Ecole Nationale Supérieure de Chimie de Biologie et de Physique, 33600 Pessac, France, JEAN-PAUL CHAPEL, Centre de Recherche Paul Pascal (CRPP), UPR CNRS 8641, Université Bordeaux, 33600 Pessac, France — Polyelectrolyte complexes (PECs) are the association complexes formed between oppositely charged macromolecules. A large body of work has been devoted to the preparation and morphology characterizations of PECs. Much less attention was paid on formation kinetics of PECs, which often occurs under non-equilibrium conditions. Stopped-flow technique combined with light scattering was used to investigate the early stage complexation kinetics in the poly(acrylic acid) and poly(diallyldimethylammonium chloride) system. It was found that initial complexes form within a few ms. Depending on the PEs molar charge ratio \( z \), initial complexes followed different evolution pathways. For \( z > 0.7 \), a large complex aggregation ascribed to the onset of coacervation was identified by an increase of the scattered intensity while an unexpected decay was observed for \( z < 0.7 \) where small PECs are formed. The appearance of characteristic bell-shaped curves in the presence of different ionic strengths \( (I) \) highlighted the strong influence of the interaction intensity on the complexation/reorganization kinetics. The results revealed distinct assembly and ageing mechanisms as a function of \( z, I \) and molecular weights.

Xiaoqing Liu
Centre de Recherche Paul Pascal (CRPP), UPR CNRS 8641, Université Bordeaux, 33600 Pessac, France

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