Electrostatic assembly in non-stoichiometric mixtures of doublehydrophilic block copolymers. Computer study

Karel Procházka¹*, Karel Šindelka¹, Zuzana Limpouchová¹, Martin Lísal²

 ¹ Department of Physical and Macromolecular Chemistry, Charles University in Prague, Prague, Czech Republic
² Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic, Prague, Czech Republic

*kar.prochaz@centrum.cz

Dissipative particle dynamics (DPD) is a versatile coarse-grained simulation technique which (in its original variant) employs three types of forces: (i) soft coarse-grained repulsion, (ii) dissipative force (emulating friction) and (iii) random fluctuating force (emulating thermal collisions). Standard DPD enables studies of complex polymer systems and recently has been used also for simulations of polymer self-assembly. Although the electrostatic interactions have been included into DPD by Groot [1] some time ago, most authors studying the self-assembly of polyelectrolytes (PE) still use the so called "ion-free" approach. [2] In this variant, the electrostatic interactions are ignored at all and repulsion forces are described by effective pH-dependent or ionic strength-dependent parameters, which are recalculated from various dependences of macroscopic properties of the system on pH and ionic strength.

In contrast to the "ion-free" approach, we use DPD variant which includes explicit description of electrostatic forces between smeared charges localized on PE chains and on counterions for studies of self-assembling PE systems. [3, 4] The simulations are very computationally demanding and much slower than standard DPD runs, but we believe that the explicit electrostatics should be always used in DPD studies of systems with electric charges. The empowered model takes the entropy of counterions and electrostatic correlation effects directly into account (at least at the coarse-grained level of Kuhn segments) and enables detailed study aimed at the elucidation of principles of the behavior.

In this presentation, we discus new results concerning the electrostatic assembly in nonstoichiometric mixtures of two double-hydrophilic copolymers composed of one neutral water-soluble block and one (either positively or negatively charged polyelectrolyte block). The study confirms basic features of the behavior postulated by van der Burgh et al. [5], but it simultaneously shows that the behavior is more complex than that predicted by van der Burgh et al.

Acknowledgements The financial support of Czech Science Foundation(Grant GA ČR: P106-12-0143).

- [1] R. D. Groot, J. Chem. Phys., 2003, 118, 11265.
- [2] D. A. Pantano, P. B. Moore, M. L. Klein and D. E. Discher, Soft Matter, 2011, 7, 8182.
- [3] Z. Posel, Z. Limpouchova, K. Sindelka, M. Lisal and K. Prochazka, *Macromolecules*, 2014, 47, 2503.
- [4] K. Sindelka, Z. Limpouchova, M. Lisal and K. Prochazka, *Macromolecules*, 2014, 47, 6121.
- [5] S. van der Burgh, A. de Keizer, M. A. Cohen Stuart, *Langmuir*, 2004, **20**, 1073.