Molecular level insight into behavior of ternary polyelectrolyte complexes

Izabella Leszczyńska [1], Tamunoemi O. Braide [2], Maria Morga [1], Jodie Lutkenhaus [2] and Piotr Batys [1]

[1] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland
[2] Department of Materials Science and Engineering, Texas A&M University, College Station, Texas 77840, USA

izabella.leszczynska@ikifp.edu.pl

Polyelectrolyte complexes (PECs) are highly tunable soft materials formed by the association of oppositely charged polymers. Owing to their broad range of physicochemical properties and potential applications, PECs have attracted increasing attention in recent years. However, most studies have focused on binary systems, whereas ternary polyelectrolyte compositions remain comparatively underexplored. In this field, the lack of a molecular-level framework limits the reliable interpretation of experimental observations and hinders a comprehensive understanding of multicomponent polymer blends.
In this work, all atom molecular dynamics simulations and experimental characterization were used to investigate the ternary PECs composed of poly(styrenesulfonate) (PSS), poly(acrylic acid) (PAA), and poly(diallyldimethylammonium chloride) (PDADMAC). The results reveal a clear asymmetry between the two polyanions in ternary complexes. PSS forms preferential and comparatively salt-resistant ion pairs with PDADMAC, suggesting a more persistent contribution to the complex formation. In contrast, fully charged PAA interacts more strongly with PDADMAC at low ionic strength, whereas at higher salt concentration it becomes increasingly compensated by Na^+. As a result, PAA-rich complexes favor more hydrated, gel-like assemblies, whereas PSS-rich complexes form more compact, solid-like structures. These findings provide molecular level insight into the role of salt and composition in ternary PECs and suggest that ternary composition can be used as additional mean to tune the macroscopic properties of polyelectrolyte systems.

Keywords:
Ternary polyelectrolyte complexes, Polymer blends, Molecular dynamics simulation, PDADMAC, PSS, PAA

Acknowledgements:
This work is supported by the National Science Centre, Poland (grant no. 2023/50/O/ST5/00249)