Solvent controlled plasticization and thermal response of polyelectrolyte assemblies

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Polyelectrolyte (PE) complexes form spontaneously in solution with counterion release and ion-pair formation. PE complexes and multilayers are sensitive to pH, temperature, and ionic strength of the solution which makes PE assemblies highly responsive to external stimulus. Specifically interesting is their well-defined thermal transition that bears resemblance to a glass transition and is used widely in, e.g., thermo-responsive drug delivery and thermally adaptive polymer coatings. We have studied this transition, and its control via variation of the PE components, added salt, and most recently also the solvent environment by molecular modelling and theory approaches combined with experimental characterization of the corresponding materials.

Here, I discuss using solvent as a controlling means of the plasticization of polyelectrolyte assemblies, and in particular for the thermal transition at molecular level. We have combined molecular modelling and experimental characterization of PE assemblies to resolve the molecular level mechanisms and control means for various synthetic PE and solvent systems. Besides water as solvent, we have examined several different alcohol solvents and urea as solvent additives, extracting relation of the solvent quality and hydrogen bonding ability to the T_g and PE association response [1,2] but also connecting that the transition temperature T_g has a relation to the number of solvent molecules at the intrinsic ion pairs [3]. Our molecular simulations and experimental results together enable mapping the ionic strength and hydration, but also solvent composition dependencies of the intrinsic and extrinsic charge compensation of the PE assemblies and associating the transition specifically with the hydration of intrinsic PE-PE ion pairs and the solvent structure there [2-5]. In total, the findings rise attention to solvent and solvent partitioning as a control means to PE systems mechanical and structural characteristics.

Keywords:
polyelectrolyte complex, molecular modelling, layer-by-layer, LbL, multilayer, glass transition, thermal transition, thermal characterization, PE

References:

[1] H. Li, D. Tolmachev, P. Batys, M. Sammalkorpi, and J. L. Lutkenhaus. *Macromolecules* **58** , 292–303 (2025).
[2] M. Khavani, P. Batys, S. Lalwani, C. Eneh, A. Leino, J. L. Lutkenhaus, and M. Sammalkorpi, *Macromolecules* **55** *(8), 3140–3150 (2022).*
[3] Y. Zhang, P. Batys, J.T. O'Neal, F. Li, M. Sammalkorpi, and J. L. Lutkenhaus. *ACS Cent. Sci.* **4** (5), 638–644 (2018).
[4] P. Batys, S. Kivistö, S. M. Lalwani, J. L. Lutkenhaus, and M. Sammalkorpi, *Soft Matter* **15** (39), 7823–7831 (2019).
[5] T. Kastinen, P. Batys, T. Tolmachev, K. Laasonen, and M. Sammalkorpi, *ChemPhysChem* , e202400244 (2024).