Liquid-liquid Phase Separation of Polyether-based Polyguanidinium in Aqueous Solution: The Role of Strong π-stacking

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Simple coacervation is liquid-liquid phase separation (LLPS) of a polyelectrolyte solution induced by adding salts. Mostly, multivalent salts bridge the polyelectrolytes, resulting in LLPS as observed in arginine-rich protamine. In this work, we demonstrate that a monovalent salt cause LLPS of positively charged polyguanidinium. Well-defined guanidinium -functionalized poly(allyl glycidyl ether) (G-PAGE) was synthesized by anionic ring-opening polymerization and post-modification, producing ideal polymer system to investigate LLPS in aqueous media. Upper critical solution temperature (UCST) behavior of LLPS and the salt-concentration dependence of the transition temperature are observed. Also, the combination of the molecular dynamics (MD) simulation, infra-red (IR) spectroscopy, and the surface forces apparatus (SFA) confirms that the π-π interaction between guanidinium moieties plays a significant role to cause the LLPS with the help of salt molecules.