Self-assembly of thermoresponsive ion containing polymers into stable nanoparticles

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A novel approach to polymer self-assembly into nano-sized water soluble particles was recently introduced [1,2]. Nanoparticles were prepared by self-assembly of homopolymers (i.e. not copolymers) of one type only and without any assembly-triggering additives. Using partially charged thermoresponsive poly(ethylacrylic acid), stable tailor-sized nanoparticles were successfully formed on heating towards its lower critical solution temperature and subsequent cooling. Nanoparticles possess a mild acceptable degree of polydispersity, are stable over long periods of time and are stable in a broad range of salt concentrations including physiological.

This self-assembly mechanism is interesting from the point of view of applications (nanoparticle preparation, gelation) as well as from the point of view of basic research on solution properties, phase transitions, thermosensitive systems, gelation, etc. A deeper insight into the mechanism of the self-assembly is brought in this work by successful experiments on poly(propylacrylic acid), which is a more hydrophobic polymer. On the other hand we also present results on a less hydrophobic polymer from this series, poly(methacrylic acid), from which nanoparticles cannot be formed. Comparison of results on all three polymers supports the following molecular mechanism of the self-assembly: the solvent quality gradually worsens upon heating of a thermosensitive polymer solution and polymer-polymer contacts are preferred over polymer-solvent contacts, which leads to the formation of polymer assemblies. The presence of a significant amount of charge on chains prevents macroscopic phase separation. Upon subsequent cooling to laboratory temperature, the assemblies (particles) should eventually dissolve, however, this is not the case due to the fact that polymer chains brought to a close proximity at elevated temperatures become hydrogen-bonded. In addition, hydrogen bonds strengthen upon cooling. Mainly strong carboxylic-carboxylate hydrogen bonds (COOH….COO-) are responsible for the irreversibility of the process and the stability of nanoparticles. The situation is different in PMA solutions because the thermoresponsivity of PMA (close to the critical conditions) is achieved in a situation where ionization is almost completely suppressed in acidic environment and this is further reflected in two effects: (i) lower barrier in aggregation due to missing strong electrostatic repulsion between aggregating chains and (ii) absence of carboxylate groups capable of strong and irreversible hydrogen bonding with carboxylic groups. As a result, PMA undergoes macroscopic (not mesoscopic) phase separation and the process is reversible. In contrast, PEA and PPA achieve thermoresponsivity while relatively strongly charged (ionization 20% - 25%). A combination of static, dynamic, and electrophoretic light scattering, SAXS, calorimetry, FTIR spectroscopy, and quantum chemical calculations was used in this work.


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