

Thermo-responsive polymers

So-called stimuli-responsive polymers are capable of responding to small physical or chemical changes (stimulus) from the external surrounding and changes or even mutates in physical structure or chemical properties. As the strength of the stimulus-induced changes, the polymer can respond accordingly. Depending on the morphology of the polymer network, stimuli-responsive polymers can be studied in a polymer solution, in a cross-linked gel or fixed on the surface (grafted brush). In addition, thin films of stimuli-responsive polymers can be prepared with wet chemical deposition methods. According to the type of stimulus, the following groups of stimuli-responsive polymers can distinguished: thermo-responsive, pH-sensitive, photosensitive and magnetic/electric field responsive polymers (see Fig.1). ^[1]

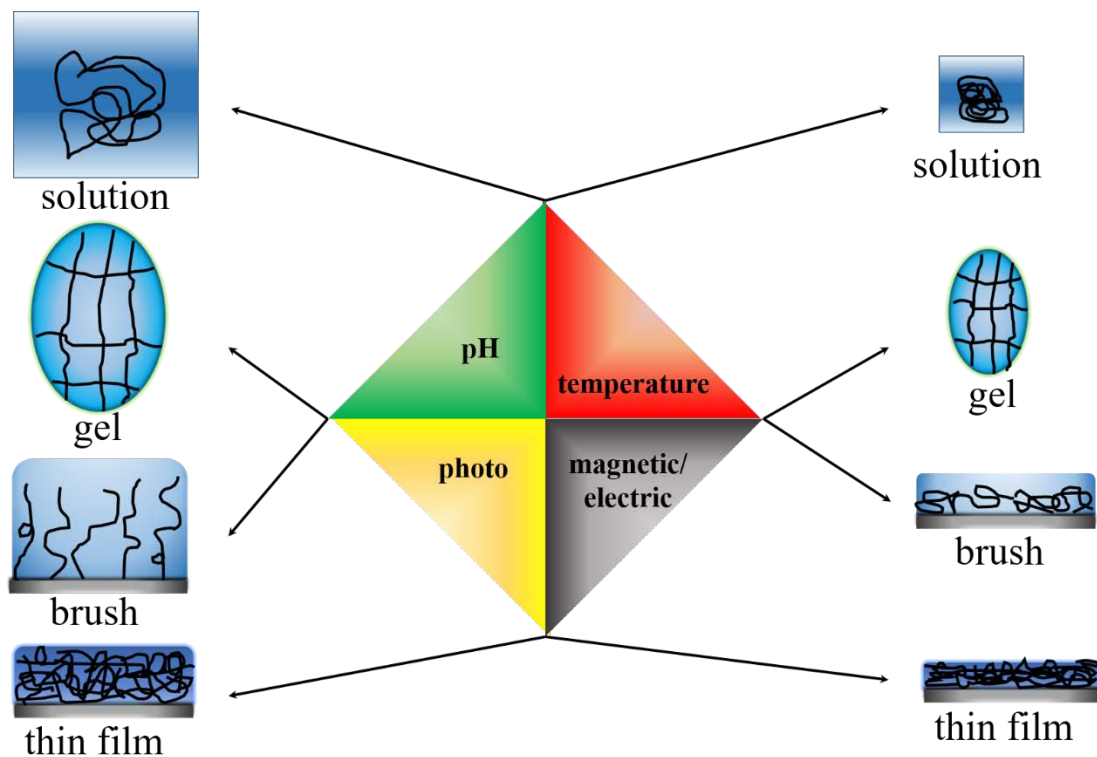


Figure 1: Sketch of phase transition of stimuli-responsive polymers in different configurations: solution, gel, brush and thin film.

Among them, thermo-responsive polymers have become the most widely and detailed studied stimulus-responsive polymers so far. This is mainly due to the facile control of temperature and its universality in many systems. The critical solution temperature is one of the most remarkable characteristics for thermo-responsive polymers. As shown in Fig. 2, in an lower critical solution temperature (LCST) scenario, the polymer undergoes a phase separation from the solvent when the temperature (T) raises beyond a transition temperature, and presents a homogeneous phase when the temperature is lower than this temperature. In the reversed scenario, it is an upper critical solution temperature (UCST) behavior.

At present, LCST-type thermo-responsive polymers are receiving strong attention. Typical examples are poly(N-isopropylacrylamide) (PNIPAM), polyoxyethylene (PEO) or poly(ethylene glycol) methyl ether methacrylate (POEGMA). Although intuitively, one would expect that polymers become more soluble in a solvent at higher temperatures, there are in fact few thermo-responsive polymers that exhibit a UCST-type phase separation in water, such as poly(sulfobetaine)s and poly(acrylic acid) (PAA), but only at high ionic strength. [1]

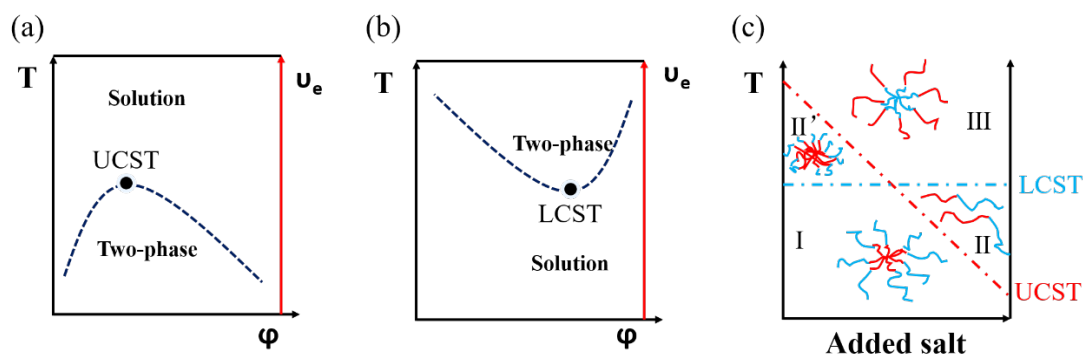


Figure 2: Sketch of possible phase diagrams for polymers exhibiting either (a) UCST-type or (b) LCST-type phase behavior. T is the temperature, ϕ is the polymer volume fraction. (c) Schematic phase behavior for electrolyte-modulated “schizophrenic” self-assembly. Figure adapted from reference [4].

PNIPAM is a typical temperature-sensitive polymer studied in our group, which shows an LCST around 32°C and is water soluble at when the temperature is lower than LCST. [2,3] The presence of hydrophilic amide groups and hydrophobic isopropyl groups assign to the polymer chain thermoresponsivity. The main driving force for the phase transition of PNIPAM in aqueous solution is the interplay between hydrogen bonding effect and the hydrophobic effect. At $T < \text{LCST}$ of PNIPAM, the polar amide groups on the molecular chain form strong hydrogen bonds with the surrounding water molecules: the PNIPAM solubility in water is high, and the vector nature of the hydrogen bonds allows the polymer molecular chain stretched, making the entire molecule appears hydrophilic. When $T > \text{LCST}$ of PNIPAM, the hydrogen bonding strength between the polymer and the water molecule weakens, and the hydrophobicity of the non-polar isopropyl group in the molecule dominates, thereby increasing the hydrophobicity of the entire molecule, resulting in a phase separation. Therefore, not only changes of the molecular weight and hydrophobic/hydrophilic balance in PNIPAM can alter the transition behavior but also the hydrophobic/hydrophilic position in PNIPAM chains. Moreover, the LCST of PNIPAM can also be altered when copolymerized with another polymer and its LCST can be tuned by varying the copolymer composition.

On the other hand, UCST behavior is mainly observed in organic and water/organic solvent mixtures, where interpolymer interactions are getting weaker upon heating. Polysulfobetaines have the ability to exhibit a UCST in solution due to ionic interactions, mutual inter/intra-molecular attraction of the zwitterionic groups, which dominate below

UCST. Above the UCST, these attractions weaken and a balance between attractive and repulsive interactions is generated, which promotes water-solubility due to the attractive water-polymer interactions^[1,4]. Besides the molar mass, the type and concentration of added low molar mass electrolytes can also strongly affect the UCST behavior of polysulfobetaines, as shown in Fig. 2(c).

At present, our group is mainly interested in multi-responsive polymer materials, spanning from aqueous solutions to three-dimensional hydrogel networks and supported thin films. Multi-functional blocks with a specific topology can simultaneously respond to changes in two or more external stimuli. These diblock copolymers have greatly expanded the application in different systems. The particularly designed orthogonally switchable diblock copolymers composed of nonionic and zwitterionic blocks featuring LCSTs and UCSTs allow the inversion of the micellar structure via either the molecularly dissolved state or via large aggregates by heating the solution provided the necessary salt content, which will be of strong benefit for many drug release applications.^[4] Copolymers composed of two thermoresponsive blocks with different LCST present a linear thickness shrinkage in a broad temperature region (25–55°C) onto Si substrates upon heating, with potential application as temperature sensors^[5]. An amphiphilic three-arm star-shaped thermo-responsive block copolymer thin film presents a special T-dependent phase transition behavior (turn out to be more hydrophobic at higher T's), which might be useful as thin film humidity sensors or water storage systems whose film thickness or water amount are desired to be modulated by the temperature^[6].

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