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Stimuli Responsive Polymers for Biophysical Applications

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Our quest to mimic biological functions using synthetic routes is an ongoing challenge that has shown immense potential in several biomedical applications. The potential of utilizing the smart behaviour of responsive polymers is wide open and has attracted the attentions of several leadingresearchers in the last two decades. Potential applications include and but limited are in drug delivery [1,2], biosensors [3], tissue engineering [4] and actuators [5]. The design of novel systems has to meet several criteria in order to become effective biomedical tools. They must be relativelysimple to synthesize and deliver in vivo, exhibit specific responses tuned to targeted event ofinterest, be biocompatible/ biodegradable and be cost effective.

Polymers that respond to specific stimuli by undergoing conformational or phase changes are ofparticular interest. The most widely studied synthetic smart responsive polymer is poly(N-isopropylacrylamide)(poly(NIPAAm)) which undergoes a reversible transition from a solublehydrophilic coil state to an insoluble hydrophobic globule state at approximately 32ºC in aqueous solutions [6-8]. The temperature at which the transition occurs is called the lower critical solutiontemperature (LCST), below which the polymer segments and solvent molecules co-exist as asingle homogeneous phase with favourable free energy of mixing (G<0). Above LCST, demixing occurs between the polymer segments and solvent molecules resulting in an increase in freeenergy (G>0) due to phase separation. Other thermoresponsive polymers include poly(diethylacrylamide) (poly(DEAAm)) [9], Poly(N-vinylcaprolactone) (Poly(VCL) [10] and poly(N-(dl)-(1-hydroxymethyl) propylmethacrylamide) (poly(dl)-HMPMA) [11], which all have a LCST in the range 32-37ºC. The close proximity of the transitions to physiological temperatures makes thesepolymers ideal for several biological applications.

Like temperature, pH is an important environmental stimuli for biomedical applications. Some ofthe common pH responsive polymers like poly(acrylic acid) (PAA), Chitosan, poly(L-lysine) (PL),and poly(ethylene imine) (PEI) [12-14]. There are drastic changes to the pH environment from thegastrointestinal tract (pH-1.3) to the stomach (pH 5-8). The presence of ionization groups likeamino or carboxyl groups offers pH sensitivity making them very desirable. Researcher's usually combine thermo and pH responsiveness in order to design multi-responsive polymer systems. For example, NIPAAm copolymerized with acrylic acid and spirobenzopyran, provides temperature, pH and photo responsiveness [15]. In another example, colloidal particles have beenused to design adhesion platforms for protein and specific cell types [16]. The possibilities of designing multi-responsive polymers are endless. There are however certain challenges owing tospatial restrictions that may occur especially at surfaces and interfaces of polymer gels or other similar systems. Another emerging area is to take advantage of biological compatibility with thesynthetic versatility by designing hybrid polymers. For instance, poly(ethylene glycol) (PEG)segments have been conjugated with proteins to enhance biological activity [17]. In another example, poly(NIPAAm) conjugated to streptavidin engineered to present a thiol functionality by introducing a cysteine residue near a Biotin site. It was seen that Biotin reacts strongly by binding with the polymer-streptavidin conjugate below the LCST (<32ºC) of NIPAAm. No evidence ofsuch strong binding was seen above the LCST, owing to the phase transition of the bioconjugate [18].

The design of stimuli responsive polymers in relatively a new and emerging area with infinite possibilities that need to be explored. The wide range of potential applications in biomedical fields such as in drug delivery, tissue engineering, surface activation, sensors, actuators etc. is only scratching the surface. Polymers that respond to single stimuli like temperature or pH alone are unlikely to find widespread applications. There is a need to fabricate materials that are truly smart with fine control over molecular weight, composition, and block architecture, incorporating multiple functionality within the polymer structures. The design of hybrid polymers that marry synthetic and biological features is the future of smart polymers for future biomedical applications. It is also imperative that researches focus on key areas like understanding the underlying molecular mechanism of designing better systems, improving mechanical robustness, improving specificity, and solving spatial constraints associated with confined systems.

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