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Review

Stimuli-responsive polymer nano-science: Shape anisotropy, responsiveness, applications

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ABSTRACT

Polymeric nanomaterials capable of altering volume, color, or shape have attracted significant scientific interests as these materials become increasingly critical in advancing unique technological developments. Design, synthesis, and assembly of nanomaterials with precisely controlled shapes and directional responsiveness are particularly critical in the development of new functional, near-device level materials. Spatial anisotropies are typically introduced by the placement of symmetrically or asymmetrically located responsive components enabling either interactions with the environment manifested by dimensional or color changes, energy storage and transfer, or diffusion. This review outlines recent advances in the synthesis, fabrication, and assembly of isotropic and anisotropic polymer-based nanomaterials in which dimensional, color, and morphological changes are induced by external stimuli. Specifically, core-shell, hollow, Janus, gibbous/inverse gibbous nanoparticles prepared with precisely controlled morphologies capable of spatially responding totemperature, pH, electromagnetic radiation or biological changes are discussed. Recent advances in the nanoparticle surface modifications which are introduced to guide nanomaterials to selectively interact and communicate with the environment are also highlighted. Since high aspect ratio nanomaterials, including polymeric nanowires or nanotubes containing responsive components, are particularly attractive in the development of 3D multi-functional objects, their manufacturing as well as applications are examined. Although many uses of stimuli-responsive nanomaterials in electronics, energy conversion, sensing, or biomedicine and other technologies are already in place, there are limitless opportunities for new applications as long as proper regulatory measures are exercised to elevate the impact of these materials on the environment. Polymeric stimuli-responsive nanomaterials offer a tremendous opportunity for the development of cognitive materials' systems, particularly when protein-like polymers containing amino acids joined by polypeptide bonds with enzymes or sugar-phosphate moieties as well as other sugar-containing interactions are utilized as building blocks and components of future materials.

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Nomenclature

AA	Acrylic acid
ATP	Adenosine triphosphate
ATRP	Atom transfer radical polymerization
AZO	N,N-dimethyl aminoazoaniline methacrylate
BD	Butadiene
BIEM	2-(2-Bromoisobutyryloxy)ethyl methacrylate
CdS	Cadmium sulfide
CRP	Controlled free radical polymerizations
CTA	Chain transfer agent
$DC_{8,9}PC$	1,2-bis(tricosa-10,12-diynoyl)-snglycero-3-phosphocholine diacetylenic phospholipid
DLS	Dynamic light scattering
DMAEMA	N,N'-dimethyl aminoethyl methacrylate
DOPA	L-3,4-dihydroxyphenylalanine
DTT	Dithiothreitol
DP	Degree of polymerization
EDDA	2,2′-(ethylenedioxy)diethylamine
HPMA	Hydroxypropyl methacrylate
HRP	Heterogeneous radical polymerization
ICAR ATRP	Initiators for continuous activator regeneration atom transfer radical polymerization
JB	Janus balance
LCST	Lower critical solution temperature
MAA	Methacrylic acid
ME	Mercaptoethanol
MMA	Methyl methacrylate
MRI	Magnetic resonance imaging
MSN	Mesoporous silica nanosphere
nBA	N-butyl acrylate
NIPAM	N-isopropylacrylamide
PADA	Poly((N-amidine)dodecylacrylamide)
PEG	Polyethylene glycol
PEO	Poly(ethylene oxide)
PFS	Pentafluorostyrene
PGMA	Poly(glycerol monomethacrylate)
PISA	Polymerization-induced self-assembly
PL	Phospholipid
PNT	Polymeric nanotube
PPO	Poly(propylene oxide)
PVCL	Poly(vinylcaprolactone)
P4VP	Poly(4-vinyl pyridine)
QD	Quantum dot
RAFT	Reversible addition-fragmentation transfer
SDS	Sodium dodecyl sulfate
St	Styrene
tBA	Tert-butyl acrylate
TEM	Transmission electron microscopy
THF	Tetrahydrofuran
TPMA	Tris(pyridin-2-ylmethyl)amine

1. Introduction; significance of stimuli-responsiveness at a nanoscale

Polymeric materials consist of repeating molecular units and their chemical composition, structure, and position along a polymer backbone determine the final properties. Typically, these materials are designed to serve specific functions. If molecular units are able to respond individually or collectively to external stimuli, a polymer backbone consisting of these units will respond. The responses at molecular level can be manifested by either conformational changes, reversible bonding, protonation-deprotonation, other rearrangements. When macromolecular chains are able to form higher nano- or microscale length constructs, their physical appearance may resemble biological systems, but no biological activity will be present unless stimuli-responsive components are present and other criteria, such as nutrient delivery is met. For comparison, basic structural components of living systems are cells. Although there are many types of cells which consist of several bioactive components serving multiple functions and interacting with each other, their common feature is cellular metabolism. These sequential chemical reactions facilitate the mechanisms for growth and reproduction, while maintaining living functions. Cell sizes may vary from 0.1–100 μm, and while most cells exhibit spherical or oval shapes, other morphologies also exist [1]. Their morphologies may change, depending upon external stimuli. For example, upon external disruptions, the red blood cells shown in Fig. 1A may transform to echinocytes of an abnormal shape with many small thorny projections sticking out of the membrane [2]. This is shown in Fig. 1B. On the other hand, the filamentous cells depicted in Fig. 1C usually exhibit long visible chains or filaments. One of the filamentous cells is the filamentous algae that intertwine to form a mat on a substrate in water. Another example are high aspect ratio Filoviruses cells with a diameter of 80 nm and a few microns in length [3]. In contrast to functional materials, to sustain living functions, cells require selectively tailored molecular structures and assemblies enabling the control of specific chemical and physical reactions in their environments. For example, phospholipids may control selective transport of proteins, but inhibit others [4]. These responsive biointerfacial boundaries have inspired numerous studies to develop stimuli-responsive nanomaterials with various shapes and responses. Although significant efforts will be necessary to achieve 'living' functions similar to biological systems, shape and shape changes combined with stimuli-responsiveness represent the first step in this direction. The first attempts towards this goal focused on the development of stimuli-responsive nanomaterials that may selectively release cargo at a targeted site [5]. For that purpose, various phospholipid vesicles and hollow nanoparticles were synthesized in order to increase the drug-loading capacity [6,7]. while avoiding renal clearance and cellular uptake (worm-like micelles, nanowires, or nanotubes) [8], or to achieve dual/multiple drug-delivery (Janus or multi-compartment particles) [9].

Among attractive nanomaterials that may potentially mimic biological cells are colloidal nanoparticles capable of responding to chemical/physical stimuli [10]. External stimuli may be applied to control particle structural changes, dimensions, morphologies, interactionsas well as self-assemblies. The striking resemblance between the shape of cells and synthetic colloidal assemblies is depicted in Fig. 1, A/A', B/B', and C/C'. Aside from the visual similarities, stimuli-responsive behavior stimulated many attempts to mimic biological systems. The significance of anisotropy and stimuli-responsiveness relies on the realization that unlike most of the existing macroscopic functional materials, the 1st generation of nano-materials dealt with passive metal, polymer, or ceramic nano-structures in a form of coatings, nanoparticles, or surface nanopattterning, and delivered new properties and selected tools. In contrast, the 2nd generation brought active nanostructures in a form of actuators with adaptive features, whereas hierarchical 3D architectures containing heterogeneous components represent the 3rd generation. It is anticipated that imbedded collective and cognitive behavior will lead to the 4th generation nanomaterials [11], and this review outlines recent advances in polymer nanoscience leading towards this goal.

The critical aspects in achieving stimuli-responsiveness is the placement of individual responsive building blocks into a polymer backbone. The ability to control their designated location will enable or disable their responsiveness. For that reason, atomic transfer radical polymerization (ATRP) [12,13], reversible addi-