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Stimulus-responsive polymer brushes on surfaces: Transduction mechanisms and applications

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ABSTRACT

Stimulus-responsive polymer brushes (SRPBs) exhibit a change in conformation and structure, often accompanied by a noticeable change in surface energy, due to an external stimulus such as a change in solvent composition, temperature, pH, ionic strength, light, or mechanical stress. SRPBs offer exciting and new possibilities to fabricate adaptive or responsive smart materials. This review summarizes selected, recent progress in SRPB applications in the field of surface wettability switching, mechanical actuation, and environmental sensing. Furthermore, we review selected papers from an emerging area in which SRPBs are used for nano- and microfabrication.

Contents

Abbreviations: AFM, atomic force microscopy; APBA, acrylamidophenylboronic acid; BTB, bromothymol blue; CA, contact angle; CRP, controlled radical polymerization; EMO, 3-ethyl-3-(methacryloyloxy) methyloxetane; LCST, lower critical solution temperature; MC, merocyanine; NCAM, nanocapillary array membrane; P2VP, poly(2-vinylpyridine); PEL, polyelectrolyte; PMAA, poly(methacrylic acid); PMEDSAH, poly[2-(methacryloyloxy)ethyl]-dimethyl(3-sulfopropyl)ammonium hydroxide; PMEP, poly(methacryloyl ethylene phosphate); PMETAC, poly[2-(methacryloyloxy)-ethyl-trimethylammonium chloride]; PMMA-b-PGMA, poly(methylmethacrylate-b-glycidylmethacrylate); PNIPAAM, poly(N-isopropylacrylamide); PNIPAAM-co-PVI, poly(N-isopropylacrylamide-co-N-vinylimidazole); PS, polystyrene; PS-b-(PMMA-co-PCdMA), polystyrene-b-(poly(methyl methacrylate)-co-poly(cadmium dimethacrylate); PSPM, poly(3-sulfopropyl methacrylate); PSPMA, poly(spiropyran methacrylate-co-methyl methacrylate); PS-b-4VP, poly(styrene-b-4-vinylpyridine); ROMP, ring-opening metathesis polymerization; SAMs, self-assembled monolayers; SI-ATRP, surface initiated atom transfer radical polymerization; SP, spiropyran; SPR, surface plasmon resonance; SRPB, stimuli-responsive polymer brushes; TEM, transmission electron microscopy; UCST, upper critical solution temperature; XPS, X-ray photoelectron spectroscopy.

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1. Introduction to stimulus-responsive polymer brushes

Polymer brushes are ensembles of sufficiently densely packed, surface-tethered polymer chains in which repulsive segment interactions can only be relieved by chain extension (swelling) normal to the substrate surface [1–3]. Polymer brushes are typically anchored to the substrate surface by physisorption or covalent chemical attachment [4–6]. The latter is often preferred as it overcomes some of the disadvantages of physisorption, including solvent and thermal instabilities. Two fundamentally different approaches are used to obtain polymer brushes. The grafting-to approach involves the experimentally simple process of tethering pre-synthesized, end-functionalized polymer chains to a suitable substrate. This technique, however, often leads to low grafting density and film thickness due to excluded volume effects imparted by previously adsorbed polymer chains. The grafting-from approach overcomes the shortcomings of the grafting-to approach, and yields densely packed polymer brushes through surface initiated polymerization (SIP). SIP is compatible with a wide range of polymerization chemistries, including anionic [7], cationic [8], plasma induced [9], condensation [10], photochemical [11], electrochemical [12], controlled radical polymerization (CRP) [13–15], and ring-opening metathesis polymerization (ROMP) [16]. The fabrication of patterned polymer brushes with controlled shape, feature dimension, grafting density and spacing has recently received considerable interest, and presents exciting opportunities for micro- and nanotechnology applications [17]. A wide range of patterning techniques such as photolithography [18–20], soft lithography [21–23], electron-beam (chemical) lithography [24–28], nano-shaving/grafting [29], anodization lithography [30], 'dip-pen' nanolithography [31], nanoimprinting lithography [32], capillary force lithography [33], and Langmuir–Blodgett lithography [34], have all been applied to fabricate patterned polymer brushes.

Stimulus-responsive polymer brushes (SRPBs) [35–38] are a category of polymer brushes that exhibit a change in their conformation, surface energy, or charge state, triggered by an external stimulus such as a change in solvent [24,39,40], temperature [41–43], pH [44–46], ionic strength [47,48], light [49–51], or mechanical stress [52]. The discovery of controllable, and reversible, polymer chain conformation and surface energy in SRPB has offered exciting and novel possibilities for the fabrication of adaptive or responsive surfaces and interfaces. As such, a range of unique properties can be exploited with a spectrum of applications in the areas of surface wettability [53], micro/nanofluidics and electronics [54–58], mechanical actuation and chemical sensing [52,59–67], biocompatibility and biotribology [22,68–72], controlled drug release, cell growth and separation [73–78], and micro/nanomaterials fabrication [79–84]. Applications of stimulus-responsive polymer brushes have received considerable attention in biomedical related fields and have recently been reviewed by several groups [38,85–87]. The articles selected for this review here, focus on recent, promising uses of SRPBs in the areas of surface wettability switching, sensing, actuation, and materials fabrication, and will provide the reader with an idea of the recent progress and breadth of applications in the field.

2. Switching surface wettability

Controlling the wettability of a surface is of considerable importance at biological interfaces, for industrial processes, and in agricultural applications [88–90]. For these applications, SRPBs offer unique properties as they often undergo large changes in surface energy when switching their conformation upon application of an external stimulus. SRPBs, particularly in combination with micro- or nanostructured surfaces, even allow switching between extremes of hydrophilicity and hydrophobicity.

2.1. Temperature-induced changes in wettability

Due to the relative ease of control, temperature is the most widely used external stimulus in synthetic and bio-inspired, stimulus-responsive systems. Many temperature-responsive polymers exhibit a critical solution temperature at which the polymer changes phase. If the polymer undergoes a phase transition from a soluble state to an insoluble state above the critical temperature, it is characterized as having a lower critical solution temperature (LCST), and conversely an upper critical solution temperature (UCST), if the brush transitions from an insoluble state to a soluble state with increasing temperature.

A well known temperature-responsive polymer is poly(N-isopropylacrylamide) (PNIPAAM) with a LCST of ~32 °C, which has been widely studied for its ability to switch surface wettability [41,91]. For example, PNIPAAM brush modified silica wafers exhibited thermally responsive switching of surface wettability, measured by contact angle (CA) changes between ~63° and ~93°, when the temperature increased from 25 °C to 40 °C (Fig. 1A). This effect