

Responsive brush layers: from tailored gradients to reversibly assembled nanoparticles

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We present a condensed overview of the recent developments of novel responsive thin polymer films from end-tethered chains (polymer brushes), which are different from conventional, uniform, and planar brush layers. For this discussion, we selected two types of recently introduced surface layers: binary brush layers with variable chemical composition forming a controllable gradient of composition and properties in a selected direction and brush layers either grafted directly to inorganic nanoparticles to form hybrid core-shell structures or combined with inorganic nanoparticles embedded into this layer. Unlike traditional brush layers, such a design brings a novel set of responsive surface properties allowing for capillary-driven microfluidic motion, combinatorial-like multiplexing response, reversible aggregation and dis-assembly of nanoparticles, fabrication of ultrahydrophobic coatings, and switchable mass transport across interfaces.

Introduction

Recent studies in the area of adaptive and/or responsive surfaces show their importance for prospective applications in micro- and nanofluidics, biocompatibility, controlled drug release, nano- and biotribology, controlled cell growth and proliferation, bio- and chemosensing, and bioelectronics focus on establishing firm relationships between bulk properties, composition, and microstructure of organic, polymeric, and hybrid materials and surfaces.^{1–5} Significant effort has been made to prepare, characterize, and understand the structure and properties of various responsive surface layers attached to or deposited on different surfaces. A lot of attention is paid to uniform and patterned

planar surfaces and mostly homogeneous chemical composition, as was reviewed in several recent publications.^{6–14} However, a recent spur of discoveries of novel responsive surface designs, which are highly non-traditional in the sense of their properties or substrates, are still awaiting summarization.

Therefore, herein we present a brief overview of the very recent developments of non-traditional responsive polymer brush surfaces, different from conventional, homogeneous, and planar ones. For this summary, we selected two novel types of brush layers that attracted recent attention: (i) binary brush layers with non-uniform chemical composition forming a directional gradient of composition and properties, and (ii) brush layers either grafted directly to inorganic nanoparticles to form core-shell structures, or brushes with embedded inorganic nanoparticles. Unlike traditional brush layers, such a design brings a novel dimension allowing *e.g.*, for capillary-driven microfluidic motion, combinatorial-like multiplexing response, or directional motion of nanoparticles.

Gradient surfaces considered in the first part of this review possess a directional continuous variation of, *e.g.* number of

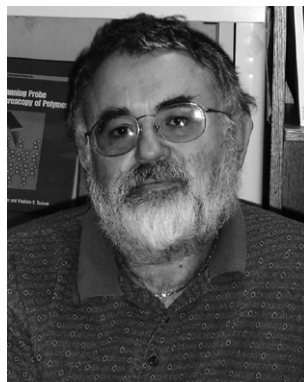
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functional groups,¹⁵ molecular weight,¹⁶ chemical composition,¹⁷ grafting density,^{18,19} or nanoparticle concentration.²⁰ A key advantage of the gradient surface is that a single sample can be used to investigate the variable surface properties in a combinatorial manner. Such a combinatorial/high-throughput method has been widely used for optimization of inorganic, semiconducting, and superconducting materials.²¹ Gradient substrates have also been successfully employed in combinatorial studies of biomaterials and synthetic polymers.^{22–30} The gradient surfaces have also found their own unique applications, such as substrates for transport of liquids,^{31,32} microfluidic motion,³³ direct movements of bacteria³⁴ and molecules.³⁵ Certain gradient-grafted layers were shown to be responsive to external stimuli (light, electric field, solvent, pH, temperature, ionic strength) and can therefore be classified as gradient-responsive polymer brushes. Since a typical gradient brush composition and properties change continuously, the responsive behavior is also not uniform along the surface coordinate.

On the other hand, a combination of nanoparticles and polymers is a traditional research area with numerous applications such as stabilization of colloids and regulation of their rheological properties, drug delivery, and sensors. It is well known that modified particles can regulate stability, structure and physical properties of different colloidal systems such as emulsions, suspensions, foams, and polymer blends. It is recognized that the surface modification of particles with specially tailored polymers can control their aggregation. Nanoparticle–polymers systems tailored as responsive nanomaterials will be a focus of the second part of this review. This approach is an important tool for directed self-assembly of functional particles into 3D, 2D, or 1D assemblies. A modern list of topic encounters includes, but is not limited to, microgel particles, dendrimers, core–shell block-copolymer micelles, mesoporous particles with grafted polymers, and particles introduced into tethered polymer layers.^{1,6,36,37}

Planar gradient-responsive surfaces

Gradient surfaces and polymer brushes

The gradient-responsive brush layers can generally be divided into three major categories:

- brushes consisting of inherently responsive macromolecules, where responsive behavior originates from a uniform response of the each polymer chain constituting the tethered layer;
- block copolymer (BC) brushes, where responsive behavior is originating from phase segregation of the different blocks in response to some stimuli;
- mixed polymer brushes, where responsive behavior is controlled by the balance of layered and lateral phase segregations for two or more different chains randomly grafted to the same substrate.

Recently, the synthesis of the gradient brush layers was reported in our work³⁸ and in that of others.^{16–19,39,40} In essence, the gradient brushes are tethered layers, where a directional continuous variation in brush parameters is generated as a result of a specifically developed synthetic procedure. Two major grafting techniques, namely, attachment of end-functionalized polymers (“grafting-to” method), and polymerization initiated from solid surfaces (“grafting-from” method) are utilized.

The “grafting-to” approach is employed to synthesize brush layers with variation in grafting density. There are two major approaches for the fabrication of gradient brushes by the grafting-to method. The density gradient can be induced by a gradient in the grafting temperature where the temperature dependence of grafting kinetics is used to create the gradient of grafting density.³⁸ The second approach is based on gradual controlled immersion of the sample into the reactor with liquid reactive polymer or solution of the polymer to regulate time of the contact of the substrate with the reagent and, consequently, time of the grafting reaction.⁴¹

The “grafting-from” approach, offering the possibility of synthesizing grafted polymer layers possessing higher grafting density are based on the formation of self-assembled monolayers (SAMs) of polymerization initiators. Two major approaches for the fabrication of gradient brushes by the grafting-from method are either (1) fabrication of the gradient of the polymerization initiator on the substrate surface, or (2) using a uniformly distributed initiator over the substrate surface and immersing the sample gradually in a monomer solution.

For instance, Genzer and co-workers^{16–19} developed two “grafting-from” methodologies that allow for the combinatorial variation of the grafting density and molecular weight of the grafted polymer layers. The first technique includes covering a substrate with a gradient of a polymerization initiator, followed by atom transfer radical polymerization (ATRP). Grafted macromolecules, with a gradual variation of molecular weight can also be prepared by ATRP employing an apparatus that controls the polymerization time with a micro-pump to change the level of monomer solution in the reactor with a vertically mounted sample with the polymerization initiator. Beers *et al.* employed a microfluidic system to vary the molecular weight and composition of the grafted polymer.⁴⁰ Zhao described the synthesis of gradient mixed PMMA/PS brushes from a binary gradient mixed initiator layer by combining ATRP and nitroxide-mediated radical polymerization.³⁹ In another work, a gradient in the density of ATRP initiator was created through the generation of a thickness gradient in a poly(glycidyl methacrylate) (PGMA) anchoring layer.⁴²

Wang and Bohn reported on gradient thickness of polyacrylic acid (PAA) grafted by electropolymerization in the presence of an in-plane electrochemical potential gradient.⁴³ This strategy, which is based on spatial gradient of electrochemical potential at ultrathin Au electrodes, was also employed for the generation of gradients of an immobilized ATRP initiator.⁴⁴ Polycondensation was employed to synthesize alternating copolymers based on ethylene oxide and ethylene.⁴⁵ A recent review by Genzer *et al.*⁴⁶ could provide an interested reader with additional information on the formation, characterization and applications of the surface-grafted polymer gradients.

Gradient-responsive polymer brushes from responsive macromolecules

Typical constituents of these gradient brushes are homopolymers or copolymers (*e.g.*, polyelectrolytes and thermoresponsive polymers) that demonstrate significant conformational changes as a function of temperature, solvent quality, pH, ionic

concentration, and electric or magnetic fields. The responsiveness of the macromolecules can be amplified or reduced appropriately.

For instance, Genzer *et al.* have reported on synthetic (“grafting-from”) procedure, which yields the formation of polyelectrolyte PAA brushes with a gradual variation of the grafting density.⁴⁷ The PAA brush gradients were obtained by first covering the substrate with a molecular gradient of the polymerization initiator, followed by the polymerization of *tert*-butyl acrylate (*t*BA), and finally the conversion of the *t*BA into PAA. It was found that at low grafting density, the wet thickness of the PAA brush remains relatively constant because the polymers are in the mushroom regime (separated grafted chains do not interact). Beyond a certain grafting density, the macromolecules enter the brush regime, where the thickness increases with increasing grafting density. In Fig. 1, the dependence of the PAA wet thickness on the solution ionic strength at different pH is presented. The data demonstrate that for a given density, the thickness exhibits a non-monotonic behavior as a function of the ionic strength of aqueous media. At large ionic strength, the thickness is small because the charges along PAA are completely screened by the excess of the external salt. As the ionic strength decreases, the PAA enters the so-called salt brush regime, where the height of the brush increases. At a certain ionic strength, the height reaches a maximum and then decreases again. A molecular theory was applied to predict the structural properties of the PAA brushes, in good agreement with the experimental observations.⁴⁸

Wang and Bohn reported on PAA thickness gradients, which have been mapped onto Au electrodes through electropolymerization.⁴³ These films represent gradient structures, in which the nominal composition is constant, while a physical property, *i.e.*, PAA film thickness, varies. According to the authors, one possible application of these PAA thickness gradients may involve the preparation of extra-cellular mimicking surfaces to study cellular adhesion.

Gradient brushes made from thermally responsive polymers exhibit measurable changes in their conformation as a function

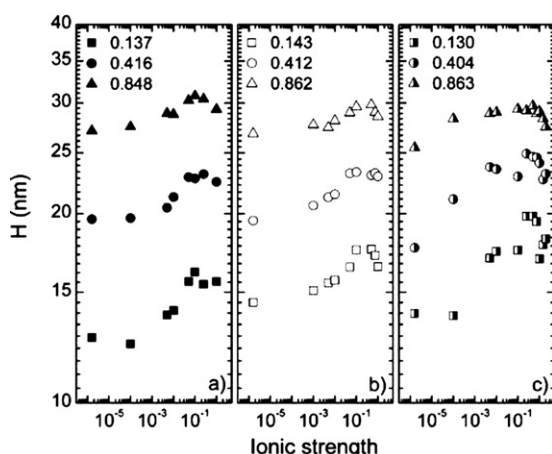


Fig. 1 Wet thickness of PAA (H) as a function of the solution ionic strength at (a) pH = 4, (b) pH = 5.8, and (c) pH = 10. The symbols represent different grafting densities of PAA in chains per nm². Reprinted with permission from ref. 47, Copyright (2007) American Chemical Society.

of grafting density and temperature.^{49,50} Poly(*N*-isopropylacrylamide) (PNIPAM) is the best known example.⁵¹ The polymer demonstrates lower critical solution temperature (LCST) behavior with phase-transition temperature in aqueous solution of 32 °C. While below this temperature PNIPAM is soluble in water, upon raising temperature above 32 °C the polymer phase-separates from the solution. Bohn *et al.* presented results on preparation of PNIPAM gradient polymer brushes.⁴⁹ The synthesis was achieved through ATRP utilizing surfaces on which the spatial profile of the initiator density was prepared by the reductive desorption using a electrochemical gradient. The temperature response of the uniform and gradient PNIPAM layers in water showed similar LCST transition temperatures (Fig. 2). Gradient PNIPAM layers with different grafting densities were also obtained by the “grafting-to” method.⁵⁰ The brushes were grown on a reactive anchoring layer made of PGMA, PGMA-*co*-poly(butyl methacrylate) (PGMA-*co*-PBMA), and PGMA-*co*-poly(oligoethylene glycol methacrylate) (PGMA-*co*-POEGMA) (Fig. 3). End-tethered copolymer

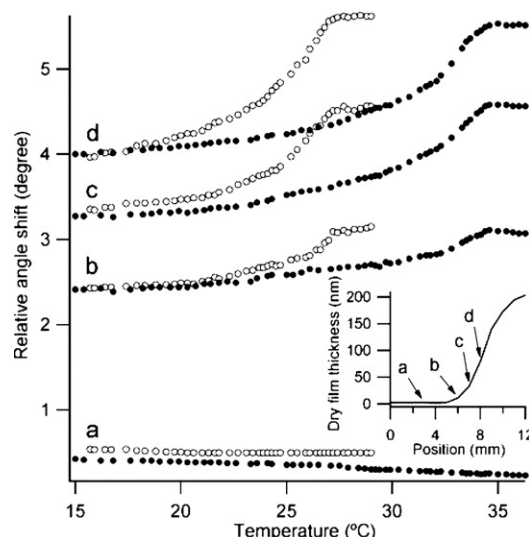


Fig. 2 Temperature response of a PNIPAAm gradient sample in water (solid circles) and 0.5 M NaCl (open circles) at positions with different PNIPAAm chain densities (positions a–d are taken from the ellipsometric film thickness gradient in the inset). Reprinted with permission from ref. 49, Copyright (2006) American Chemical Society.

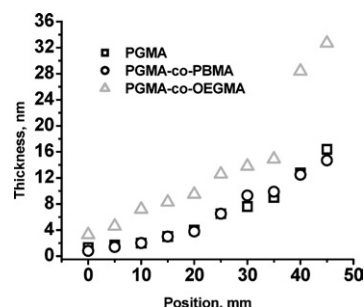


Fig. 3 Thickness of the PNIPAM layers grafted through anchoring polymer layers. Variation in thickness presented as function of the position along the wafer. Reprinted with permission from ref. 50, Copyright (2005) American Chemical Society.

brushes based on oligomers of ethylene oxide and ethylene were obtained with systematic grafting-density variation.⁴⁵ Their properties can be switched by the temperature variation across LCST, with all topography, adhesion, and contact angle changed.

Gradient-responsive polymer brushes from block-copolymers

Block copolymer (BC) brushes demonstrate a rich phase behavior, which is responsive to different external stimuli.^{7,52,53} The responsive behavior of BC brushes is based on the phase segregation, specifically if the solvent affinities to the different blocks are significantly different. Gradient BC brushes of poly(*n*-butyl methacrylate) (PBMA) and poly(2-(*N,N'*-dimethylamino)ethyl methacrylate) (PDMAEMA) *via* surface-initiated ATRP were obtained.^{54,55} The BC brush layers were examined to study the effect of relative block lengths on the response to solvent treatment. The gradient layers had uniform bottom PBMA blocks and molecular mass gradient of top PDMAEMA blocks. The rearrangement of the BC brushes upon exposure to water and hexane was assessed by contact angle measurements. The results demonstrated that the responsive behavior is greatly influenced by their relative block lengths. Three major regions of the responsive behavior have been observed (Fig. 4). After hexane treatment, the PBMA dominated the surface in the response region, where the PDMAEMA block was relatively short. In the partial-response region, PBMA and PDMAEMA coexisted at the air interface. Further increase of PDMAEMA thickness suppressed the rearrangement that allowed the PBMA segments to occupy the air interface after solvent treatment. In the non-response region, a thick PDMAEMA block suppressed the rearrangement of the PBMA and occupied the surface. Thus, while surface properties can be suppressed by a long top block, they can be enhanced by the extension of the bottom block.

Tomlinson and Genzer studied poly(2-hydroxyethyl methacrylate)-*b*-poly(methyl methacrylate) (PHEMA-*b*-PMMA) block

copolymer brushes with continuous composition gradient.^{17,56,57} The topography behavior of PHEMA-*b*-PMMA block was monitored as a function of the PHEMA and PMMA block lengths after selectively collapsing the top (PMMA) block. It was found that the surface morphology and wettability of the BC brushes at different locations are dependent on the sample history – treatment with different solvents.

Gradient-responsive polymer brushes composed of mixed polymer brushes

To obtain a mixed polymer brush, two or more different polymers have to be grafted to a surface.⁷ Their responsive behavior is controlled by phase segregation of two incompatible polymer chains. Upon external stimuli (solvent quality, temperature, pH) the phase segregation results in switching of spatial distribution of functional groups within the ultrathin film may be delivered to the brush exterior.^{58,59}

Zhao described synthesis and the surface behavior of gradient PMMA–PS brushes.³⁹ He studied the effect of relative grafting densities on solvent-induced assembly of the mixed brushes along the gradient substrate. The gradient brushes were synthesized from a gradient-mixed initiator-terminated monolayer by combining ATRP and nitroxide-mediated radical polymerization (NMRP) in a two-step process. The gradient initiator-terminated monolayer was fabricated by first forming a gradient in density of an ATRP initiator through vapor diffusion, followed by back-filling of an NMRP-initiator-terminated trichlorosilane. The advancing contact angle of water gradually changed from 74°, the value for PMMA to the value for a smooth PS surface after treatment with chloroform (Fig. 5a). After treatment of a gradient brush whose PS molecular weight was slightly lower than that of PMMA with glacial acetic acid, a selective solvent for PMMA, relatively ordered nanodomains were observed in the region where the ratio of PS to PMMA grafting density was in the range from 0.67 to 2.2. Contact angle hysteresis was high in this region and XPS studies confirmed that the PMMA chains were enriched at the outermost layer (Fig. 5b). The nanodomains were speculated to be of a micellar structure with PS chains forming the core shielded by PMMA chains.

A facile method to prepare mixed brush gradients using a grafting-from approach coupled with electrochemical-potential gradient⁴⁹ was extended by Wang and Bohn to generate gradient brushes of PNIPAM and PHEMA.⁶⁰ PNIPAAm and PHEMA were chosen because they represent two of the most thoroughly studied responsive materials. PNIPAM undergoes a LCST transition and PHEMA is a hydrophilic polymer that has been used in drug delivery. PHEMA also has been shown to exhibit voltage-induced free volume transitions. The authors have described a number of interesting potential applications for the as-formed mixed brush gradients. For example, one can modify the PHEMA to form chemical-composition gradients in the end functional group. Also, by adjusting the temperature below or above the LCST, these functional groups could be exposed (high-temperature collapsed PNIPAM) or hidden (low-temperature extended PNIPAM) inside the polymer matrix. Furthermore, the phase-segregation properties of PHEMA–PNIPAM could be exploited to tune morphology.

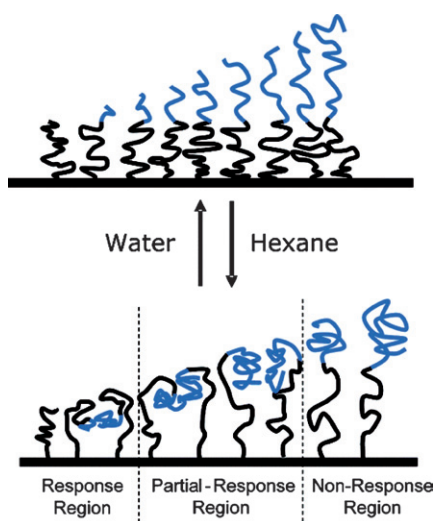


Fig. 4 Schematic illustration of three regions of the block copolymer brushes after hexane treatment. Black segments represent poly(*n*-butyl methacrylate). Blue segments represent poly(2-(*N,N'*-dimethylamino)ethyl methacrylate). Reprinted with permission from ref. 55, Copyright (2006) American Chemical Society.

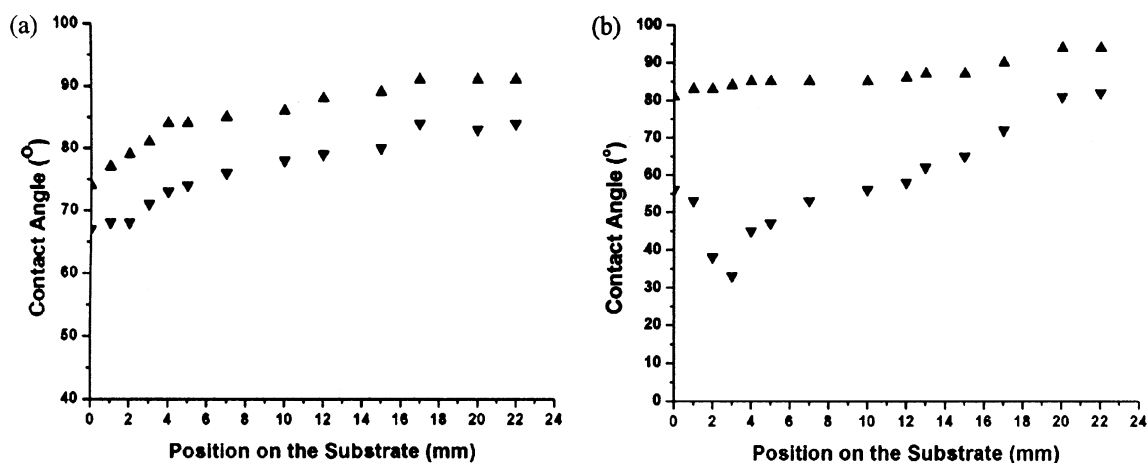


Fig. 5 Advancing ($\blacktriangle$) and receding ($\blacktriangledown$) contact angles of water on gradient-mixed PMMA-PS brushes after (a) treatment with CHCl_3 and (b) glacial acetic acid at 45°C for 1 h *versus* position on the substrate. Reprinted with permission from ref. 39, Copyright (2004) American Chemical Society.

Gradient mixed brush was prepared from PS and poly(2-vinyl pyridine) P2-VP (PS-*mix*-P2-VP) by the “grafting-to” approach using temperature gradient for the grafting of end-functionalized PS in the first step followed by the grafting of the end-functionalized P2-VP in the second step.^{61,62} The PS-*mix*-P2-VP mixed brush was successfully employed for the design of smart microfluidic channels, demonstrating new opportunities for manipulating the passage of liquids in the channels.³³ The gradual change of the brush composition was confirmed by ellipsometric and the contact angle measurements. The water contact angle increases almost linearly with the increase of the PS fraction (Fig. 6a). The composition of the top of the brush calculated using the Cassie equation was very close to the composition obtained from the ellipsometric data (Fig. 6b). However, the treatment of the brush with selective solvents (toluene and ethanol) revealed the unique switching behavior of the mixed brush. The gradient can be switched reversibly from the case when the wetting gradually increases from the left-hand side to the right-hand side to the case when the wetting is almost constant along the *x*-axis (Fig. 6).

The generalized schematics of the switching effects are shown in Fig. 7

- In selective solvent the favorite polymer is preferentially on the top for all compositions of the mixed brush. The gradient is “turned-off”.

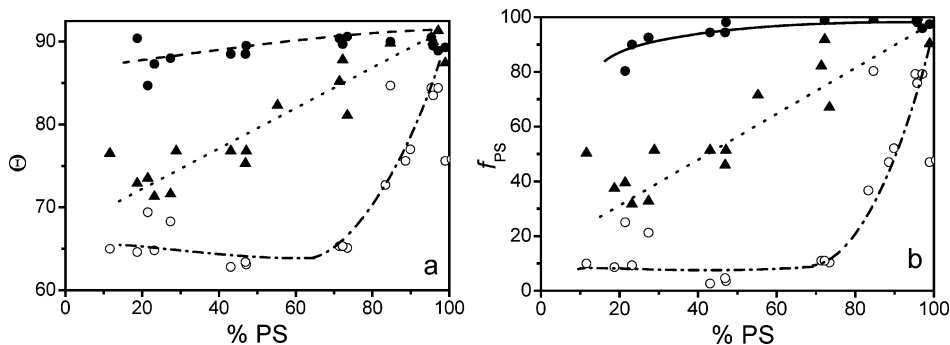


Fig. 6 Switching of water contact angle (θ) of the gradient PS-*mix*-P2-VP brush after exposure to different solvents (a) and the fraction of PS (f_{PS}) on the top of the brush estimated with Cassie equation (solid circles = toluene; solid triangles = chloroform; open circles = ethanol) (b) *vs.* the measurement location along *x*-axis expressed in terms of PS fraction. Reprinted with permission from ref. 62, Copyright (2005) American Chemical Society.

- In non-selective solvent both polymers are on the top and the composition of the gradient brush gradually changes along the *x*-axis. The gradient is “turned-on”.

The another example of gradient-responsive brush is represented by the mixed polyelectrolyte (PE) PAA-*mix*-P2-VP brush, which demonstrates a unique switching behavior in aqueous environment at different pH (Fig. 8).^{62,63} The mixed PE brush can be either hydrophilic or hydrophobic depending on pH and composition. The PAA-*mix*-P2-VP brushes (compositions ranging from 20 to 60% of PAA) were highly hydrophilic upon treatment with both low and high pH water. However, they were hydrophobic upon treatment with neutral water (see Fig. 8b–d). If the brush is strongly asymmetric, the switching behavior is dominated by a major component. For example if P2-VP is a major component, the mixed brush is hydrophilic at low pH, but hydrophobic at high pH (Fig. 8a). If PAA is a major component, the inverse wetting behavior was observed (Fig. 8e,f). The contact angle value increases at low and high pH with the increase of fraction of PAA and P2-VP, respectively.

Responsive brushes and nanoparticles

In this section, we break up our discussion into three parts based on the design of the nanoparticle-brush system (Fig. 9). In the first part, we review grafted polymer layers with incorporated

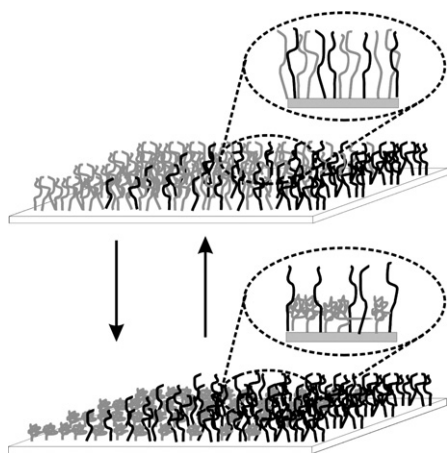


Fig. 7 Scheme of the gradient mixed brush morphology upon treatment with nonselective (top) and selective (bottom) solvents. In nonselective solvents both polymers are on top: the gradient is “turned on.” In selective solvent only a favorite polymer is on top: the gradient is “turned off”. Reprinted with permission from ref. 62, Copyright (2005) American Chemical Society.

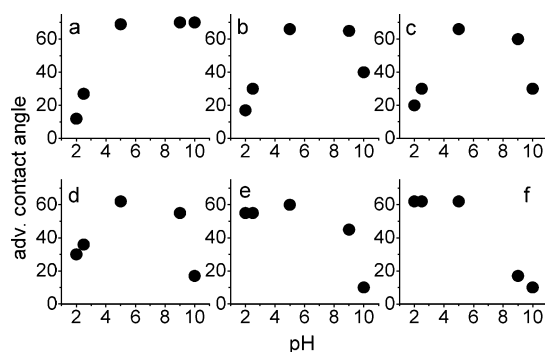


Fig. 8 Switching of water contact angle of the gradient PAA-*mix*-PVP brush at the locations with different fraction of PAA (a – 20%, b – 30%, c – 40%, d – 60%, e – 80%, f – 100%) vs. pH. Reprinted with permission from ref. 62, Copyright (2005) American Chemical Society.

nanoparticles. In the second part, we analyze reports on responsive behavior of particles with grafted polymer shells. Finally, particles-in tethered layer-on particle are discussed in the third part. Block-copolymer micelles and single-molecule spherical brushes (star-like copolymers) are excluded from the present review.^{64,65}

Nanoparticles embedded into polymer brushes

Polymer brushes with embedded nanoparticles represent an example of thin nanocomposite film where the particle’s environment can be regulated by molecular weight of tethered chains and their grafting density. Properties of such a composite film are tuned by controlled changes in the surrounding environment (solvent, temperature, pH) and switched in response to the abrupt phase transition in the polymer brush.⁶⁶ As known, the insertion of a nanoparticle into the polymer brush creates a repulsive pressure, which decays exponentially away from the region of insertion.^{67,68} If particles strongly interact with functional groups of tethered chains, the enthalpy of interaction can be

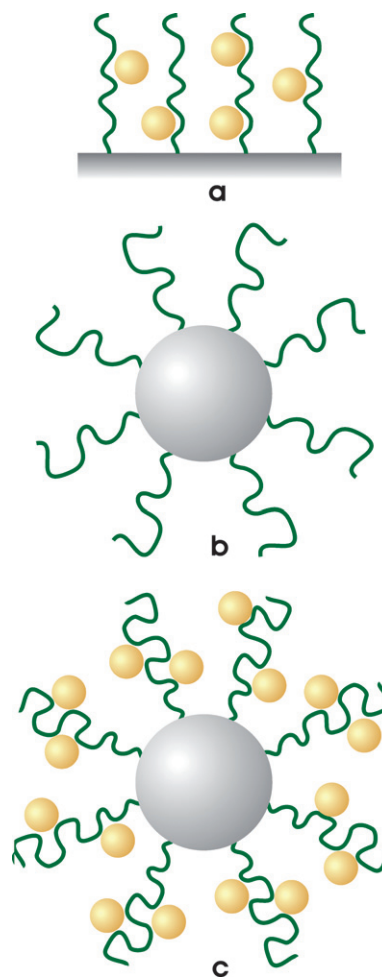


Fig. 9 Schematics of three different particle-tethered chain systems: nanoparticles embedded into polymer brush (a); spherical polymer brush (b); spherical brush with embedded nanoparticles (c).

large enough to overcome the repulsive term and nanoparticles are “dissolved” in the brush. Thus, tuning the interaction between tethered chain and nanoparticles can be used to regulate a fine balance between attractive and repulsive interactions of nanoparticles and polymer brushes.

Theoretical analysis has shown that strongly interacting with the polymer brush, small particles disperse freely within the polymer brush while polymer “insoluble” particles tend to aggregate in the brush.⁶⁹ It was shown experimentally that octanethiol-coated Au-nanoparticles form aggregates on top of polyolefin brush because of very poor interaction between the nanoparticles and the tethered polymer.⁷⁰ In contrast, PEO brush was loaded with silica particles due to strong interaction between the polymer and the nanoparticles.⁷¹

Reversible swelling/shrinking of responsive brushes results in exposing or hiding nanoparticles from/into the brush. It was reported that these structures can be used to regulate catalytic activity of nanoparticles, exploring the responsive properties of polyelectrolyte brushes to changes in pH and ionic strength⁷² where the brush was loaded with Pt,^{73,74} Ag^{75–77} or Au^{81,78} nanoparticles. Gold nanoparticles can be grown by reduction of Au-loaded (AuCl₄[–] ions) brushes with NaBH₄.^{79–81}

Genzer *et al.*⁸² explored orthogonal gradient polymer brushes to study the effect of molecular weight and grafting density on miscibility of PDMAEMA brush with gold nanoparticles and demonstrated that the increase of molecular weight and grafting density of polymer brush resulted in increase of particle uptake. This result was in some disagreement with theory predicting a relationship with maximum,^{71,83} and, thus, demonstrated a complex phase behavior of the system. In another twist, motion of nanoparticle adsorbed on the brush was induced by variation of the external conditions.⁸⁴

In a polymer system where noble metal or semiconductor nanoparticles are bound to the polymer, the stimuli-induced changes can be transformed into an optical signal.^{85,86} For noble metal nanoparticles (typically gold, silver, and platinum), optical signal originates from a localized plasmon resonance.^{87–89} This phenomenon, known as localized surface plasmon resonance (LSPR), can be observed as an absorption band in the UV-vis spectrum where the intensity and position of the band depend on the size^{90,91} and shape^{92,93} of nanoparticles, their size distribution and spatial organization,⁹⁴ surface modification (for the core-shell particles),^{95,96} and the dielectric constant of the surrounding medium.^{91,97}

Recently, LSPR spectroscopy was employed for detecting stimuli-induced changes in polymeric materials.^{98–105} In most cases, the conformational and chemical transitions in polymeric materials are accompanied by the modification of their dielectric function (ϵ), which can be detected using LSPR spectroscopy. In a typical configuration, metal nanoparticles are immobilized as a monolayer on a glass substrate, while a polymer material is either deposited on the top of the nanoparticles monolayer or between nanoparticles.^{98,102} A refractive index is sensitive to the distance between nanoparticles.^{95,96,106} The nanoparticles that are brought into close proximity to each other experience strong electromagnetic coupling resulting in a broadening and red-shift of the absorbance peak. Stimuli-induced conformational changes will alter the inter-particle distance and hence the strength of plasmon coupling.

Lee and Perez-Luna⁹⁹ reported the reversible aggregation of gold colloidal nanoparticles linked to the chains of the dextran brush in solvents of different polarity and the associated changes in the optical properties. In a P2-VP brush grafted to the surface-immobilized gold islands,^{104,105} the enhanced sensitivity to changes of pH and cholesterol concentration was observed. Stimuli-induced swelling/shrinkage of the polymer brush resulted in tuning the interaction between the gold islands localized at the grafting surface and gold nanoparticles on the top of the brush (Fig. 10). The changes in the nanoparticle–island distance are limited to 1–20 nm, which corresponds to the optimal distance between metal nanoparticles for electromagnetic coupling.

Responsive spherical brushes

Responsive brushes bring new interesting aspects and possibilities to tune and switch interactions between nanoparticles^{107–111} and organize those particles into various assemblies to obtain novel functional materials.^{112–114} Grafted polymer shells are effective for the regulation of interparticle distances and their interactions, allowing for the tuning of physical properties of the colloidal dispersion (Fig. 11).¹¹⁵ Besides inorganic particles,

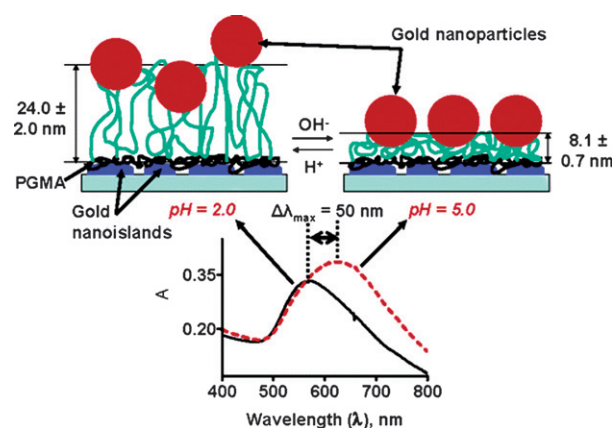


Fig. 10 Schematics of the reversible pH change-induced swelling of gold nanoparticle-coated poly(2-vinylpyridine) (P2-VP) polymer brushes. Bottom: T-SPR spectra of the brush upon changes in pH between pH 2.0 and 5.0. Reprinted with permission from ref. 104, Copyright (2004) American Chemical Society.

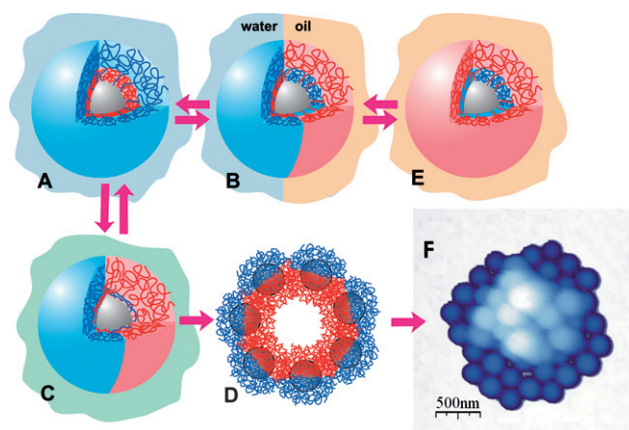


Fig. 11 The smart nanoparticles (hybrid structures from silica core and grafted block-copolymer shell) undergo reversible transitions between core-shell morphologies (A, B, C, and E) in selective solvents and at the “water–oil” interface. The particles have been used as building blocks of responsive colloidal dispersions (D and F) and for the fabrication of ultrahydrophobic coatings deposited from water-born suspensions. Reprinted with permission from ref. 118, Copyright (2007) Wiley.

various polymer latex particles were frequently used as carriers of spherical responsive brushes.

Significant advances have been made in the surface modification of the particles using anchoring of amphiphilic macromolecules or mixture of different polymers. Several processes have been developed to prepare polymer–inorganic hybrid nanoparticles with grafted mixed polymer brushes.^{116–120} Anisotropic thermoresponsive particles (Janus particles) were prepared with PNIPAM grafted to one hemisphere of spherical particles.^{121,122} Ballauff and co-workers developed synthesis of responsive polyelectrolyte brushes (PAA, PSS) on the surface of PS latex particles.^{72,109,123,124} Polyelectrolyte brushes were synthesized on the surface of gold nanoparticles¹²⁵ and pH-responsive magnetic particles were prepared using ATRP for grafting polyelectrolyte brushes on magnetic nanocrystals.¹²⁶ Thermally sensitive

spherical brushes were prepared from PNIPAM on metallic,¹²⁷ Fe₂O₃,^{128–130} silica,^{78,131} latex,¹³² and microgel¹³³ cores.

Behavior of spherical brushes in many aspects is similar to that for planar polymer brushes (Fig. 11). If radius of particle is much greater than the brush thickness, the brush has the same properties as planar brush. In this case the major advantage of the polymer brush–nanoparticle system is in its small size. Nanoparticle is a carrier of the brush and all properties associated with the brush and the nanoparticle. If radius of particle is comparable to or smaller than the brush thickness, behavior of the spherical brush is different as compared to planar brush. The major reason for this difference is the larger space available. The brush is more “relaxed” in periphery as compared to the grafting surface. The geometry affects radial concentration profile of polymer segments and, thus, properties of the brush. Spherical geometry of polymer brushes was considered in theoretical works^{134–147} and modeling.^{148–152} However, there were not many experimental studies yet reported^{111,153–155}

Literature analysis reveals several major directions exploring particles with responsive polymer brushes as carriers of biological molecules,^{156,157} drugs,¹⁵⁸ metal ions,^{125,159,160} and other chemicals where the responsive behavior is used for controlled uptake/release. They can be used for tunable stabilization of suspensions,^{161,162,163,164} emulsions^{165,166} and foams¹⁶⁷ with amphiphilic responsive particles located at the interface. Specifically, amphiphilic nanoparticles are used to populate the liquid–liquid interface and stabilize emulsions^{168,169} (often referred to as Pickering emulsions^{170,171}). Tunable amphiphilic properties can be easily approached with a responsive polymer brush grafted to nanoparticles.^{162,172} Tuning surface properties of particles is used to switch between w/o and o/w emulsions, adsorption and desorption,^{121,130,173} interaction with cell,¹⁷⁴ proteins,^{175–177} and to redirect transport of particles across liquid–liquid^{36,118,172,178} or liquid–solid¹³¹ interfaces. Finally, reversible aggregation of particles can be used to turn superstructures on and off.^{126,129,179,180,182}

Behavior of the mixed and block-copolymer brushes differs principally from the behavior of homopolymer brushes with thermo- or pH-responsive chains. In the latter case, changes in pH or temperature result in a change in hydrophilic properties of the amphiphiles. In contrast to that, mixed brushes switch the surface composition of the outer shell when either hydrophilic or hydrophobic (or their mixture) polymers occupy the surface of the particles (Fig. 11).¹¹⁸ Thus, not just the amphiphilic nature but the chemical composition of the interface is switched with the mixed brushes. It was demonstrated that switching between different segregated states in mixed and block-copolymer brushes is a powerful tool for the regulation of colloidal systems in a controlled environment.^{52,53,181,182} Indeed, recent studies of mixed polymer and block-copolymer brushes have shown possibilities of switching interfacial energy at the solid–liquid interface in a broad range (for example, between hydrophilic and ultrahydrophobic behavior¹⁸³). Binks *et al.*^{184,185} have demonstrated that stimuli responsive nanoparticles with grafted weak polyelectrolyte chains can be used for pH-induced inversion of o/w emulsions. Motornov *et al.*^{116,118} have shown that particles coated with mixed polymer brush undergo transformations at liquid–liquid, solid–liquid and solid–gas interfaces where the morphology of responsive particles can be switched

between Janus and stratified core–shell structure upon pH changes (Fig. 11).

Such a responsive behavior of the mixed brush–nanoparticle hybrids can be explored to fabricate material with unique combinations of sometimes contradicting properties. For example, mixed brush-coated particles can be dispersed in aqueous environment at pH range appropriate for ionization of a weak polyelectrolyte in the brush. The particle aggregation can be regulated by adjusting the pH value to the optimal size of the aggregates. Finally, the particles can be deposited on a solid substrate and switched into hydrophobic state (by pH change or upon water evaporation). Such rough coatings possess ultrahydrophobic properties without any application of organic solvents or surfactants.¹⁸⁶

An efficient method to produce well-defined amphiphilic gold nanoparticles with an equal number of hydrophobic and hydrophilic arms grafted onto a gold core in an alternating fashion was suggested by Zubarev *et al.*¹⁸⁷ The strategy involves direct coupling of V-shaped block copolymer with a carboxylic group at its junction point to mercaptophenol-terminated gold nanoparticles (Fig. 12). This strategy has been initially successfully developed for planar surfaces.¹⁸⁸ The reaction yields the high grafting density (2.9 chains per nm²) and extremely low polydispersity (1.07). The advantage of this system is the exact 1 : 1 molar ratio of hydrophilic PEG and hydrophobic PB chains attached to a given gold core (Fig. 12).^{189,190} This is due to the synthetic strategy used for the preparation of this material (Fig. 12).¹⁹¹

Such gold nanoparticles, functionalized with amphiphilic PB-PEG arms, formed stable Langmuir monolayers at the air–water and the air–solid interfaces with very different properties depending on conformational state of binary shells (Fig. 13).¹⁹² The binary arms vertically segregated into a dense polymer corona, which surrounded the gold nanoparticles keeping individual nanoparticles well-separated from each other and forming flattened nanostructures with 2 nm gold cores surrounded by the polymer shell with the diameter 11 nm (Fig. 13). Moreover, this design allows assembling and disassembling of the nanoparticles

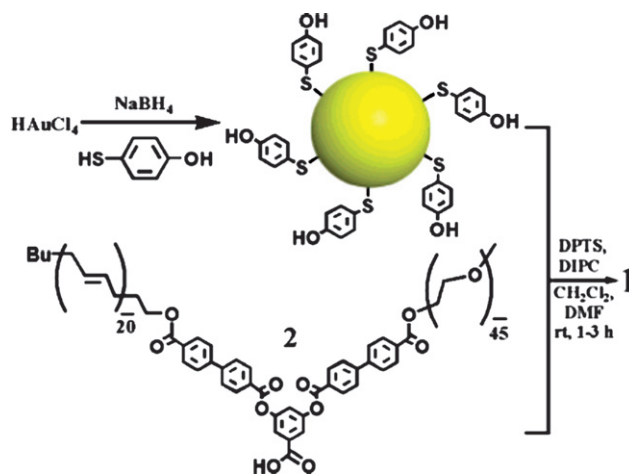


Fig. 12 Synthesis of gold nanoparticles with binary amphiphilic shells. Reprinted with permission from ref. 187, Copyright (2006) American Chemical Society.

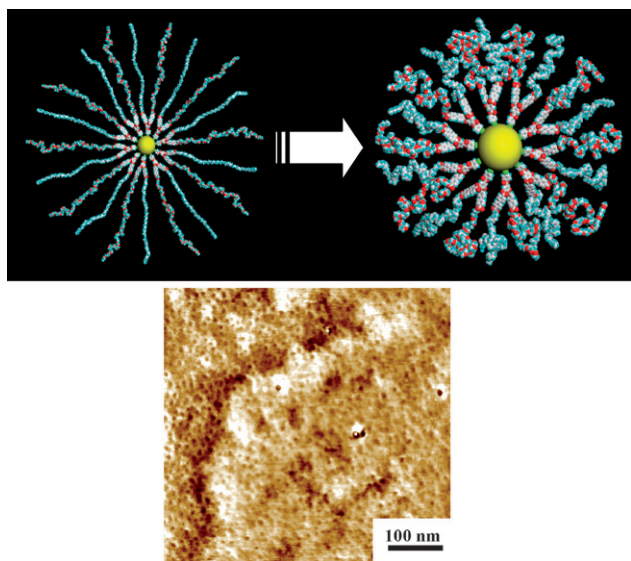


Fig. 13 Gold nanoparticles with binary amphiphilic shell in extended and collapsed states and AFM image of a monolayer of gold nanoparticles with binary shell. Reprinted with permission from ref. 192, Copyright (2006) American Chemical Society.

in a reversible manner, hence controlling the size and the morphology of the arrays by changing the preparation conditions. For instance, these amphiphilic nanoparticles in aqueous solution can form well-defined cylindrical micelles due to selective interactions of different blocks (Fig. 14).

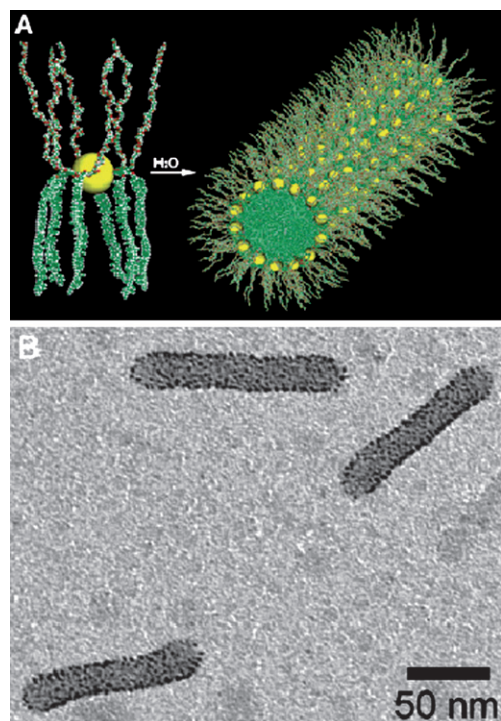


Fig. 14 Cylindrical micelles in solution assembled by gold nanoparticles with binary shell. Reprinted with permission from ref. 191, Copyright (2004) Wiley.

Multiresponsive spherical brushes

Multiresponsive block copolymers (concurrently responding to few stimuli) are well known.^{193,194} Several recent studies have reported novel hybrid multiresponsive tethered polymer systems that combined different responsive mechanisms in one particle.

For example, thermoresponsive brush was grafted to the surface of super-paramagnetic core.¹²⁸ Temperature change (increase above LCST) was used to accelerate particle aggregation. Because the aggregates are sensitive to external magnetic field the transport in microfluidic channels can be directly controlled by an external magnet. If the temperature dropped below LCST, the nanoparticles were re-dispersed in liquid, diminishing ability for magnetic field control. This scenario features dual response in such a way that magnetic response was dependent upon temperature since only aggregates of particles demonstrated response to magnetic field. A similar approach was reported by Wakamatsu *et al.*¹²⁹ and similar behavior was achieved by the combination of magnetic core and pH-responsive brushes.¹²⁶ Wu *et al.*^{133,195} have synthesized particles with different type of dual response: thermoresponsive microgel particles were used as a platform to graft PEO brushes¹⁹⁵ and PNIPAM brushes.¹³³ In the first example, temperature-induced swelling/shrinking of the core resulted in change of grafting density of PEO brush and, thus, in reversible stretching/shrinking of the PEO brush. In the second example both the core and the brush demonstrated temperature-dependent swelling/collapse. The number of such combined hybrid systems with multiple responses is limited yet by several examples. However, they clearly indicate the beginning of the development phase for a range of novel materials with a hierarchical architecture with coupled responsive mechanisms.

General conclusions

Here, we present an overview of recent results in the area of responsive surfaces and nanoparticles demonstrates a growing activity on this research front. Brush layers, grafted directly to inorganic particles and forming hybrid core-shell structures or brushes with embedded inorganic nanoparticles became more popular for designing responsive colloidal systems. We believe that the variety of designs presented in current literature bring intriguing responsive properties critical for prospective applications in a wide variety of fields, including capillary-driven microfluidic devices, plasmon-resonance based chemical and biological sensors, multiplexing response, and controlled/reversible aggregation/disassembly of nanoparticle assemblies, among others. We can speculate that multiresponsive nanoparticles and their aggregates as well as responsive gradient surfaces with complex 2D distributed response will be the next new intriguing developments in this field.

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References

- 1 T. P. Russel, *Science*, 2002, **297**, 964.
- 2 A. Lafuma and D. Quere, *Nat. Mater.*, 2003, **2**, 457.
- 3 V. V. Tsukruk, *Prog. Polym. Sci.*, 1997, **22**, 247.
- 4 H. G. Graighead, *Science*, 2000, **290**, 1532.
- 5 V. V. Tsukruk, *Adv. Mater.*, 2001, **13**, 95.
- 6 J. Yang, M. Yamato, T. Shimizu, H. Sekine, K. Ohashi, M. Kanzaki, T. Ohki, K. Nishida and T. Okano, *Biomaterials*, 2007, **28**, 5033.
- 7 I. Luzinov, S. Minko and V. V. Tsukruk, *Prog. Polym. Sci.*, 2004, **29**, 635.
- 8 N. Nath and A. Chilkoti, *Adv. Mater.*, 2002, **14**, 1243.
- 9 V. V. Tsukruk and V. N. Bliznyuk, *Prog. Polym. Sci.*, 1997, **22**, 1089.
- 10 I. Y. Galaev and B. Mattiasson, *Trends Biotechnol.*, 1999, **17**, 335.
- 11 J. A. Hubbell, *Curr. Opin. Biotechnol.*, 1999, **10**, 123.
- 12 Y. Ito, *Biomaterials*, 1999, **20**, 2333.
- 13 B. D. Ratner and S. J. Bryant, *Annu. Rev. Biomed. Eng.*, 2004, **6**, 41.
- 14 N. Nath and A. Chilkoti, *Adv. Mater.*, 2002, **14**, 1243.
- 15 J. H. Lee, H. W. Kim, P. K. Pak and H. B. Lee, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 1569.
- 16 M. R. Tomlinson and J. Genzer, *Macromolecules*, 2003, **36**, 3449.
- 17 M. R. Tomlinson and J. Genzer, *Chem. Commun.*, 2003, **12**, 1350.
- 18 T. Wu, K. Efimenko, P. Vlcek, V. Subr and J. Genzer, *Macromolecules*, 2003, **36**, 2448.
- 19 T. Wu, K. Efimenko and J. Genzer, *J. Am. Chem. Soc.*, 2002, **124**, 9394.
- 20 H. Cao, J. O. Tegenfeldt, R. H. Austin and S. Y. Chou, *Appl. Phys. Lett.*, 2002, **81**, 3058.
- 21 B. Jandeleit, D. J. Schaefer, T. S. Powers, H. W. Turner and W. H. Weinberg, *Angew. Chem., Int. Ed.*, 1999, **38**, 2495.
- 22 H. J. Busscher and H. Elwing, *Colloids Surf. B*, 1999, **15**, 1.
- 23 H. T. Spijker, R. Bos, W. V. Oeveren, J. Vries and H. J. Busscher, *Colloids Surf. B*, 1999, **15**, 89.
- 24 S. J. Lee, G. Khang, Y. M. Lee and H. B. Lee, *J. Colloid Interface Sci.*, 2003, **259**, 228.
- 25 I. Caelen, H. Gao and H. Sigris, *Langmuir*, 2002, **18**, 2463.
- 26 M. B. J. Wijesundara, E. Fuoco and L. Hanley, *Langmuir*, 2001, **17**, 5721.
- 27 J. C. Meredith, A. P. Smith, A. Karim and E. J. Amis, *Macromolecules*, 2000, **33**, 9747.
- 28 A. P. Smith, J. C. Meredith, J. F. Douglas, E. J. Amis and A. Karim, *Phys. Rev. Lett.*, 2001, **87**, 015503.
- 29 A. J. Crosby, A. Karim and E. J. Amis, *J. Polym. Sci., Part B: Polym. Phys.*, 2003, **41**, 883.
- 30 J. C. Meredith, A. Karim and E. J. Amis, *Macromolecules*, 2000, **33**, 5760.
- 31 M. K. Chaudhury and G. M. Whitesides, *Science*, 1992, **256**, 1539.
- 32 K. Ichimura, S. K. Oh and M. Nakagawa, *Science*, 2000, **288**, 1624.
- 33 L. Ionov, N. Houbenov, A. Sidorenko, M. Stamm and S. Minko, *Adv. Funct. Mater.*, 2006, **16**, 1153.
- 34 H. Baier and F. Bohnoeff, *Science*, 1992, **255**, 472.
- 35 T. Chang, D. I. Rozkiewicz, B. J. Ravoo, E. W. Meijer and D. N. Reinhoudt, *Nano Lett.*, 2007, **7**, 978.
- 36 Y. Lin, A. Boker, J. B. He, K. Sill, H. Q. Xiang, C. Abetz, X. F. Li, J. Wang, T. Emrick, S. Long, Q. Wang, A. Balazs and T. P. Russell, *Nature*, 2005, **434**, 55.
- 37 V. V. Tsukruk, *Adv. Mater.*, 1998, **10**, 253.
- 38 L. Ionov, B. Zdyrko, A. Sidorenko, S. Minko, V. Klep, I. Luzinov and M. Stamm, *Macromol. Rapid Commun.*, 2004, **25**, 360.
- 39 B. Zhao, *Langmuir*, 2004, **20**, 11748.
- 40 C. Xu, T. Wu, C. M. Drain, J. D. Batteas and K. L. Beers, *Macromolecules*, 2005, **38**, 6.
- 41 M. Motornov, R. Sheparovych, I. Tokarev, Y. Roiter and S. Minko, *Langmuir*, 2007, **23**, 13.
- 42 Y. Liu, V. Klep, B. Zdyrko and I. Luzinov, *Langmuir*, 2005, **21**, 11806.
- 43 X. Wang and P. W. Bohn, *J. Am. Chem. Soc.*, 2004, **126**, 6825.
- 44 X. Wang, H. Tu, P. V. Braun and P. W. Bohn, *Langmuir*, 2006, **22**, 817.
- 45 E. Manias, M. Rackaitis, T. M. D. Foley, K. Efimenko and J. Genzer, *Polym. Prepr.*, 2005, **46**, 11.
- 46 R. R. Bhat, M. R. Tomlinson, T. Wu and J. Genzer, *Adv. Polym. Sci.*, 2006, **198**, 51.
- 47 T. Wu, P. Gong, I. Szleifer, P. Vlcek, V. Subr and J. Genzer, *Macromolecules*, 2007, **40**, 8756.
- 48 P. Gong, T. Wu, J. Genzer and I. Szleifer, *Macromolecules*, 2007, **40**, 8765.
- 49 X. Wang, H. Tu, P. V. Braun and P. W. Bohn, *Langmuir*, 2006, **22**, 817.
- 50 V. Klep, B. Zdyrko and I. Luzinov, *PMSE Prepr.*, 2005, **93**, 462.
- 51 Y. K. Jhon, R. R. Bhat, C. Jeong, O. J. Rojas, I. Szleifer and J. Genzer, *Macromol. Rapid Commun.*, 2006, **27**, 697.
- 52 C. Singh, G. T. Pickett, E. Zhulina and A. C. Balazs, *J. Phys. Chem. B*, 1997, **101**, 10614.
- 53 S. S. Chem, E. B. Zhulina, G. T. Pickett and A. C. Balazs, *J. Chem. Phys.*, 1998, **108**, 5981.
- 54 C. Xu, T. Wu, J. D. Batteas, C. M. Drain, K. L. Beers and M. J. Fasolka, *Appl. Surf. Sci.*, 2006, **252**, 2529.
- 55 C. Xu, T. Wu, C. M. Drain, J. D. Batteas, M. J. Fasolka and K. L. Beers, *Macromolecules*, 2006, **39**, 3359.
- 56 R. R. Bhat, M. R. Tomlinson and J. Genzer, *J. Polym. Sci., Polym. Phys. Ed.*, 2005, **43**, 3384.
- 57 M. R. Tomlinson and J. Genzer, *Langmuir*, 2005, **21**, 11552.
- 58 J. Draper, I. Luzinov, S. Minko, I. Tokarev and M. Stamm, *Langmuir*, 2004, **20**, 4064.
- 59 M. Lemieux, D. Usov, S. Minko, M. Stamm, H. Shulha and V. V. Tsukruk, *Macromolecules*, 2003, **36**, 7244; D. Julthongpipit, Y.-H. Lin, J. Teng, E. Zubarev and V. V. Tsukruk, *J. Am. Chem. Soc.*, 2003, **125**, 15912; M. C. Lemieux, D. Julthongpipit, P. Duc Cuong, H.-S. Ahn, Y.-H. Lin and V. V. Tsukruk, *Langmuir*, 2004, **20**, 10046.
- 60 X. J. Wang and P. W. Bohn, *Adv. Mater.*, 2007, **19**, 515.
- 61 L. Ionov, A. Sidorenko, M. Stamm, S. Minko, B. Zdyrko, V. Klep and I. Luzinov, *Macromolecules*, 2004, **37**, 7421.
- 62 S. Minko, L. Ionov, A. Sydorenko, N. Houbenov, M. Stamm, B. Zdyrko, V. Klep, and I. Luzinov, in *Stimuli-responsive Polymeric Films and Coatings*, ed. M. W. Urban, American Chemical Society, Washington DC, ACS Symposium Series 912, 2005, p. 68.
- 63 L. Ionov, N. Houbenov, A. Sidorenko, M. Stamm, I. Luzinov and S. Minko, *Langmuir*, 2004, **20**, 9916.
- 64 W. J. Brittain and S. Minko, *J. Polym. Sci., Part A: Polym. Chem.*, 2007, **45**, 3505.
- 65 K. L. Genson, J. Hoffman, J. Teng, E. R. Zubarev, D. Vaknin and V. V. Tsukruk, *Langmuir*, 2004, **20**, 9044; S. Peleshanko and V. V. Tsukruk, *Prog. Polym. Sci.*, 2008, DOI: 10.1016/j.progpolymsci.2008.01.003.
- 66 S. Minko, *Polym. Rev.*, 2006, **46**, 397.
- 67 F. J. Solis and H. Tang, *Macromolecules*, 1996, **29**, 7953.
- 68 G. Subramanian, D. R. M. Williams and P. A. Pincus, *Macromolecules*, 1996, **29**, 4045.
- 69 J. U. Kim and B. O'Shaughnessy, *Phys. Rev. Lett.*, 2002, **89**, 238301.
- 70 Z. Liu, K. Pappacena, J. Cerise, J. Kim, C. J. Durning, B. O'Shaughnessy and R. Levicky, *Nano Lett.*, 2002, **2**, 219.
- 71 R. A. Gage, E. P. K. Currie and M. A. C. Stuart, *Macromolecules*, 2001, **34**, 5078.
- 72 M. Ballauff and Y. Lu, *Polymer*, 2007, **48**, 1815.
- 73 Y. Mei, G. Sharma, Y. Lu, M. Ballauff, M. Drechsler, T. Irrgang and R. Kempe, *Langmuir*, 2005, **21**, 12229.
- 74 G. Sharma, Y. Mei, Y. Lu, M. Ballauff, T. Irrgang, S. Proch and R. Kempe, *J. Catal.*, 2007, **246**, 10.
- 75 Y. Lu, Y. Mei, M. Schrunner, M. Ballauff and M. W. Moller, *J. Phys. Chem. C*, 2007, **111**, 7676.
- 76 Y. Lu, Y. Mei, R. Walker, M. Ballauff and M. Drechsler, *Polymer*, 2006, **47**, 4985.
- 77 Y. Lu, Y. Mei, M. Drechsler and M. Ballauff, *Angew. Chem., Int. Ed.*, 2006, **45**, 813.
- 78 K. Zhang, J. Ma, B. Zhang, S. Zhao, Y. P. Li, Y. X. Xu, W. Z. Yu and J. Y. Wang, *Mater. Lett.*, 2007, **61**, 949.
- 79 O. Azzaroni, A. A. Brown, N. Cheng, A. Wei, A. M. Jonas and W. T. S. Huck, *J. Mater. Chem.*, 2007, **17**, 3433.
- 80 M. M. Zhang, L. Liu, C. L. Wu, G. Q. Fu, H. Y. Zhao and B. L. He, *Polymer*, 2007, **48**, 1989.

- 81 M. Schrunner, F. Polzer, Y. Mei, Y. Lu, B. Haupt, M. Ballauff, A. Goldel, M. Drechsler, J. Preussner and U. Glatzel, *Macromol. Chem. Phys.*, 2007, **208**, 1542.
- 82 R. R. Bhat, M. R. Tomlinson and J. Genzer, *Macromol. Rapid Commun.*, 2004, **25**, 270.
- 83 E. P. K. Currie, J. Van der Gucht, O. V. Borisov and M. A. C. Stuart, *Pure Appl. Chem.*, 1999, **71**, 1227.
- 84 S. Santer and J. Ruhe, *Polymer*, 2004, **45**, 8279.
- 85 V. Maheshwari and R. F. Saraf, *Science*, 2006, **312**, 1501.
- 86 L. Ionov, S. Sapra, A. Synytska, A. L. Rogach, M. Stamm and S. Diez, *Adv. Mater.*, 2006, **18**, 1453.
- 87 E. Hutter and J. H. Fendler, *Adv. Mater.*, 2004, **16**, 1685.
- 88 K. A. Willets and R. P. Van Duyne, *Ann. Rev. Phys. Chem.*, 2007, **58**, 267.
- 89 A. Moores and F. Goettmann, *New J. Chem.*, 2006, **30**, 1121.
- 90 U. Kreibig and L. Genzel, *Surf. Sci.*, 1985, **156**, 678.
- 91 A. C. Templeton, J. J. Pietron, R. W. Murray and P. Mulvaney, *J. Phys. Chem. B*, 2000, **104**, 564.
- 92 R. C. Jin, Y. W. Cao, C. A. Mirkin, K. L. Kelly, G. C. Schatz and J. G. Zheng, *Science*, 2001, **294**, 1901.
- 93 C. J. Murphy and N. R. Jana, *Adv. Mater.*, 2002, **14**, 80.
- 94 C. L. Haynes, A. D. McFarland, L. L. Zhao, R. P. Van Duyne, G. C. Schatz, L. Gunnarsson, J. Prikulis, B. Kasemo and M. Kall, *J. Phys. Chem. B*, 2003, **107**, 7337.
- 95 R. A. Caruso and M. Antonietti, *Chem. Mater.*, 2001, **13**, 3272.
- 96 M. D. Malinsky, K. L. Kelly, G. C. Schatz and R. P. Van Duyne, *J. Am. Chem. Soc.*, 2001, **123**, 1471.
- 97 P. Mulvaney, *Langmuir*, 1996, **12**, 788.
- 98 O. Azzaroni, A. A. Brown, N. Cheng, A. Wei, A. M. Jonas and W. T. S. Huck, *J. Mater. Chem.*, 2007, **17**, 3433.
- 99 S. Lee and V. H. Perez-Luna, *Langmuir*, 2007, **23**, 5097.
- 100 Y. R. Leroux, J. C. Lacroix, K. I. Chane-Ching, C. Fave, N. Felidj, G. Levi, J. Aubard, J. R. Krenn and A. Hohenau, *J. Am. Chem. Soc.*, 2005, **127**, 16022.
- 101 N. H. Mack, J. W. Wackerly, V. Malyarchuk, J. A. Rogers, J. S. Moore and R. G. Nuzzo, *Nano Lett.*, 2007, **7**, 733.
- 102 M. Mitsuishi, Y. Koishikawa, H. Tanaka, E. Sato, T. Makayama, J. Matsui and T. Miyashita, *Langmuir*, 2007, **23**, 7472.
- 103 Z. M. Qi, M. Wei, I. Honma and H. Zhou, *ChemPhysChem*, 2007, **8**, 264.
- 104 I. Tokareva, S. Minko, J. H. Fendler and E. Hutter, *J. Am. Chem. Soc.*, 2004, **126**, 15950.
- 105 I. Tokareva, I. Tokarev, S. Minko, E. Hutter and J. H. Fendler, *Chem. Commun.*, 2006, 3343.
- 106 W. Rechberger, A. Hohenau, A. Leitner, J. R. Krenn, B. Lamprecht and F. R. Aussenegg, *Opt. Commun.*, 2003, **220**, 137.
- 107 G. S. Grest, K. Kremer and T. A. Witten, *Macromolecules*, 1987, **20**, 1376.
- 108 D. Richter, B. Stuhn, B. Ewen and D. Neger, *Phys. Rev. Lett.*, 1987, **58**, 2462.
- 109 X. Guo, A. Weiss and M. Ballauff, *Macromolecules*, 1999, **32**, 6043.
- 110 X. Guo and M. Ballauff, *Langmuir*, 2000, **16**, 8719.
- 111 X. Guo and M. Ballauff, *Phys. Rev. E*, 2001, **64**, 051406.
- 112 K. Ohno, K. Koh, Y. Tsujii and T. Fukuda, *Angew. Chem., Int. Ed.*, 2003, **42**, 2751.
- 113 F. Caruso, *Adv. Mater.*, 2001, **13**, 11.
- 114 *Colloids and Colloid Assemblies: Synthesis, Modification, Organization and Utilization of Colloid Particles*, ed. F. Caruso, Wiley-VCH, Weinheim, 2004.
- 115 N. B. Bowden, M. Weck, I. S. Choi and G. M. Whitesides, *Acc. Chem. Res.*, 2001, **34**, 231.
- 116 M. Motornov, R. Sheparovych, R. Lupitsky, E. MacWilliams and S. Minko, *J. Colloid Interface Sci.*, 2007, **310**, 481.
- 117 J. Shan, H. Chen, M. Nuopponen, T. Viitala, H. Jiang, J. Peltonen, E. Kauppinen and H. Tenhu, *Langmuir*, 2006, **22**, 794.
- 118 M. Motornov, R. Sheparovych, R. Lupitsky, E. MacWilliams, O. Hoy, I. Luzinov and S. Minko, *Adv. Funct. Mater.*, 2007, **17**, 2307.
- 119 Y. Guo and M. G. Moffitt, *Macromolecules*, 2007, **40**, 5868.
- 120 H. Yusuf, W. G. Kim, D. H. Lee, Y. Y. Guo and M. G. Moffitt, *Langmuir*, 2007, **23**, 868.
- 121 D. Suzuki, S. Tsuji and H. Kawaguchi, *Chem. Lett.*, 2005, **34**, 242.
- 122 L. Nie, W. Shen, D. Chen and M. Jiang, *Angew. Chem.*, 2007, **46**, 6321.
- 123 M. Ballauff, *Macromol. Chem. Phys.*, 2003, **204**, 220.
- 124 Y. Lu, A. Wittemann, M. Ballauff and M. Drechsler, *Macromol. Rapid Commun.*, 2006, **27**, 1137.
- 125 D. X. Li, Q. He, Y. Cui and J. B. Li, *Chem. Mater.*, 2007, **19**, 412.
- 126 M. Lattuada and T. A. Hatton, *Langmuir*, 2007, **23**, 2158.
- 127 J. R. Morones and W. Frey, *Langmuir*, 2007, **23**, 8180.
- 128 J. J. Lai, J. M. Hoffman, M. Ebara, A. S. Hoffman, C. Estournes, A. Wattiaux and P. S. Stayton, *Langmuir*, 2007, **23**, 7385.
- 129 H. Wakamatsu, K. Yamamoto, A. Nakao and T. Aoyagi, *J. Magn. Mater.*, 2006, **302**, 327.
- 130 R. Narain, M. Gonzales, A. S. Hoffman, P. S. Stayton and K. M. Krishnan, *Langmuir*, 2007, **23**, 6299.
- 131 H. L. Tu, L. Hong, S. M. Anthony, P. V. Braun and S. Granick, *Langmuir*, 2007, **23**, 2322.
- 132 J. N. Kizhakkedathu, R. Norris-Jones and D. E. Brooks, *Macromolecules*, 2004, **37**, 734.
- 133 T. J. Hu, Y. Z. You, C. Y. Pan and C. Wu, *J. Phys. Chem. B*, 2002, **106**, 6659.
- 134 E. K. Lin and A. P. Gast, *Macromolecules*, 1996, **29**, 390.
- 135 C. M. Wijmans and E. B. Zhulina, *Macromolecules*, 1993, **26**, 7214.
- 136 E. B. Zhulina and O. V. Borisov, *Macromolecules*, 1996, **29**, 2618.
- 137 E. B. Zhulina, T. M. Birshtein and O. V. Borisov, *Eur. Phys. J. E*, 2006, **20**, 243.
- 138 I. Borukhov and L. Leibler, *Phys. Rev. E*, 2000, **62**, R41.
- 139 R. Hariharan, C. Biver and W. B. Russel, *Macromolecules*, 1998, **31**, 7514.
- 140 R. Hariharan, C. Biver, J. Mays and W. B. Russel, *Macromolecules*, 1998, **31**, 7506.
- 141 I. Borukhov and L. Leibler, *Macromolecules*, 2002, **35**, 5171.
- 142 V. A. Belyi, *J. Chem. Phys.*, 2004, **121**, 6547.
- 143 H. Wang and A. R. Denton, *Phys. Rev. E*, 2004, **70**.
- 144 M. W. Matsen, *Macromolecules*, 2005, **38**, 4525.
- 145 A. Striolo and S. A. Egorov, *J. Chem. Phys.*, 2007, 126.
- 146 J. J. Xu, F. Qiu, H. D. Zhang and Y. L. Yang, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 2811.
- 147 R. Nap, P. Gong and I. Szeifer, *J. Polym. Sci., Part B: Polym. Phys.*, 2006, **44**, 2638.
- 148 K. Prochazka and Z. Limpouchova, *Coll. Czech. Chem. Commun.*, 1994, **59**, 2166.
- 149 S. Forster, E. Wenz and P. Lindner, *Phys. Rev. Lett.*, 1996, **77**, 95.
- 150 E. Lindberg and C. Elvingson, *J. Chem. Phys.*, 2001, **114**, 6343.
- 151 J. J. Cerda, T. Sintes and R. Toral, *Macromolecules*, 2003, **36**, 1407.
- 152 J. Klos and T. Pakula, *Macromolecules*, 2004, **37**, 8145.
- 153 F. Muller, P. Fontaine, M. Delsanti, L. Belloni, J. Yang, Y. J. Chen, J. W. Mays, P. Lesieur, M. Tirrell and P. Guenoun, *Eur. Phys. J. E*, 2001, **6**, 109.
- 154 N. Dingenouts, M. Patel, S. Rosenfeldt, D. Pontoni, T. Narayanan and M. Ballauff, *Macromolecules*, 2004, **37**, 8152.
- 155 A. Wittemann, M. Drechsler, Y. Talmon and M. Ballauff, *J. Am. Chem. Soc.*, 2005, **127**, 9688.
- 156 A. Wittemann and M. Ballauff, *Macromol. Biosci.*, 2005, **5**, 13.
- 157 K. Anik, C. Rucker, A. Wittemann, J. Wiedenmann, M. Ballauff and G. U. Nienhaus, *J. Phys. Chem. B*, 2005, **109**, 5418.
- 158 H. Devalapally, D. Shenoy, S. Little, R. Langer and M. Amiji, *Cancer Chemother. Pharmacol.*, 2007, **59**, 477.
- 159 H. B. Sonmez, B. F. Senkal and N. Bicak, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 3068.
- 160 Y. Mei, C. Abetz, O. Birkert, V. Schadler, R. J. Leyrer and M. Ballauff, *J. Appl. Polym. Sci.*, 2006, **102**, 233.
- 161 D. J. Li, X. Sheng and B. Zhao, *J. Am. Chem. Soc.*, 2005, **127**, 6428.
- 162 A. Kohut, S. Ranjan, A. Voronov, W. Peukert, V. Tokarev, O. Bednarska, O. Gevus and S. Voronov, *Langmuir*, 2006, **22**, 6498.
- 163 A. Kohut, A. Voronov and W. Peukert, *Langmuir*, 2007, **23**, 504.
- 164 A. Kohut, A. Voronov, V. Samaryk and W. Peukert, *Macromol. Rapid Commun.*, 2007, **28**, 1410.
- 165 B. P. Binks and S. O. Lumsdon, *Langmuir*, 2000, **16**, 8622.
- 166 B. P. Binks, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 21.
- 167 B. P. Binks, R. Murakami, S. P. Armes, S. Fujii and A. Schmid, *Langmuir*, 2007, **23**, 8691.
- 168 A. D. Dinsmore, M. F. Hsu, M. G. Nikolaides, M. Marquez, A. R. Bausch and D. A. Weitz, *Science*, 2002, **298**, 1006.
- 169 B. P. Binks and C. P. Whitby, *Langmuir*, 2004, **20**, 1130.
- 170 S. Pickering, *J. Chem. Soc.*, 1907, **91**, 2001.
- 171 P. Finkle, H. D. Draper and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1923, **45**, 2780.

- 172 E. W. Edwards, M. Chanana, D. Wang and H. Mohwald, *Angew. Chem.*, 2007, **46**, 1.
- 173 Y. Mei, A. Wittemann, G. Sharma, M. Ballauff, T. Koch, H. Gliemann, J. Horbach and T. Schimmel, *Macromolecules*, 2003, **36**, 3452.
- 174 H. Vihola, A. K. Marttila, J. S. Pakkanen, M. Andersson, A. Laukkanen, A. M. Kaukonen, H. Tenhu and J. Hirvonen, *Int. J. Pharm.*, 2007, **343**, 238.
- 175 A. Wittemann, B. Haupt, R. Merkle and M. Ballauff, *Macromol. Symp.*, 2003, **191**, 81.
- 176 C. Czeslik, G. Jackler, T. Hazlett, E. Gratton, R. Steitz, A. Wittemann and M. Ballauff, *Phys. Chem. Chem. Phys.*, 2004, **6**, 5557.
- 177 S. Rosenfeldt, A. Wittemann, M. Ballauff, E. Breininger, J. Bolze and N. Dingenouts, *Phys. Rev. E*, 2004, **70**.
- 178 Y. Lin, H. Skaff, T. Emrick, A. D. Dinsmore and T. P. Russell, *Science*, 2003, **299**, 226.
- 179 A. Striolo, *Small*, 2007, **3**, 628.
- 180 J. T. Russell, Y. Lin, A. Boker, L. Su, P. Carl, H. Zettl, J. B. He, K. Sill, R. Tangirala, T. Emrick, K. Littrell, P. Thiyagarajan, D. Cookson, A. Fery, Q. Wang and T. P. Russell, *Angew. Chem., Int. Ed.*, 2005, **44**, 2420.
- 181 A. Akinchina and P. Linse, *Langmuir*, 2007, **23**, 1465.
- 182 P. Linse, *J. Chem. Phys.*, 2007, 126.
- 183 S. Minko, M. Muller, M. Motornov, M. Nitschke, K. Grundke and M. Stamm, *J. Am. Chem. Soc.*, 2003, **125**, 3896.
- 184 S. Fujii, S. P. Armes, B. P. Binks and R. Murakami, *Langmuir*, 2006, **22**, 6818.
- 185 B. P. Binks, R. Murakami, S. P. Armes and S. Fujii, *Langmuir*, 2006, **22**, 2050.
- 186 M. Motornov, R. Sheparovych, R. Lupitsky, E. MacWilliams and S. Minko, *Adv. Mater.*, 2008, **20**, 200.
- 187 E. R. Zubarev, J. Xu, A. Sayyad and J. D. Gibson, *J. Am. Chem. Soc.*, 2006, **128**, 4958.
- 188 D. Julthongpiput, Y.-H. Lin, J. Teng, E. R. Zubarev and V. V. Tsukruk, *Langmuir*, 2003, **19**, 7832; D. Julthongpiput, Y.-H. Lin, J. Teng, E. R. Zubarev and V. V. Tsukruk, *J. Am. Chem. Soc.*, 2003, **125**, 15912; M. C. LeMieux, Y.-H. Lin, P. D. Cuong, H.-S. Ahn, E. R. Zubarev and V. V. Tsukruk, *Adv. Funct. Mater.*, 2005, **15**, 2529.
- 189 E. R. Zubarev, J. Xu, A. Sayyad and J. D. Gibson, *J. Am. Chem. Soc.*, 2006, **128**, 15098.
- 190 K. L. Genson, J. Hoffman, J. Teng, E. R. Zubarev, D. Vaknin and V. V. Tsukruk, *Langmuir*, 2004, **20**, 9044.
- 191 J. Xu and E. R. Zubarev, *Angew. Chem., Int. Ed.*, 2004, **43**, 5491.
- 192 K. L. Genson, J. Holzmueller, C. Jiang, J. Xu, J. D. Gibson, E. R. Zubarev and V. V. Tsukruk, *Langmuir*, 2006, **22**, 7011.
- 193 S. Peleshanko, K. D. Anderson, M. Goodman, M. D. Determan, S. K. Mallapragada and V. V. Tsukruk, *Langmuir*, 2007, **23**, 25.
- 194 C. Tsitsilianis, Y. Roiter, I. Katsampas and S. Minko, *Macromolecules*, 2008, **41**, 925.
- 195 T. J. Hu and C. Wu, *Macromolecules*, 2001, **34**, 6802.