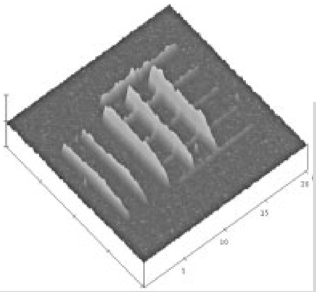
ADVANCED MATERIALS

Physicochemical Properties of Surface-Initiated Polymer Films in the Modification and Processing of Materials**

By *G. Kane Jennings** and *Eric L. Brantley*



This article reviews the physicochemical aspects of surface-initiated polymer films used to modify planar and non-planar surfaces and to produce micro- and nanoscale patterned features. Particular emphasis is placed on the molecular composition of the polymer and its effect on surface and bulk properties of ultrathin films. Recent advances in the use of responsive polymer films that exhibit dramatically altered properties upon changes in solvent, temperature, or ionic strength are reviewed. The uses of surface-initiated polymer films to modify materials' properties and impact applications in chromatography, nanoparticle-templated synthesis, and carbon nanotube dispersion are highlighted.

1. Introduction

Major advances in the solution-phase synthesis of polymers have yielded unprecedented control over macromolecular composition, molecular weight, and polydispersity, enabling the preparation of extremely well-defined polymeric materials.[1–3] Within the past few years, many of these advances have been extended to surfaces to construct polymer films by the continual addition of repeat units onto growing chains. This so-called surface-initiated polymerization strategy offers several advantages over traditional methods of preparing polymer films and coatings, including: 1) improved adhesion due to chemical coupling of the initiator/polymer chain to the substrate; 2) the ability to prepare uniform, conformal coatings on objects of any shape;[4] 3) excellent control over film thickness,[5] from a few nanometers up to the micrometer level[4,6] in some cases; 4) tunable grafting densities, based on the surface coverage of the initiator; 5) simplified separation issues, since the polymer is grown from a support; and 6) good control over depth-dependent composition by growing additional blocks to prepare copolymer films.[7–9] Due to these processing advantages, surface-initiated polymerizations have been utilized to functionalize or modify nanostructures and particles,[10–17] chromatography media,[18–23] and porous supports;[24–26] to prepare environmentally responsive brushes that alter their conformation upon exposure to a stimulus;[8,24,27–30] to provide a barrier against etching;[31,32] to serve as a dielectric layer in a device;[4] and to prevent or reduce biological adsorption.[33,34]

In general, surface-initiated polymerizations require the immobilization of appropriate initiator groups onto the surface prior to polymerization, typically achieved by preparing a self-assembled monolayer (SAM) from initiator-terminated adsorbates. These adsorbates are often synthesized to contain thiol[4,35,36] or disulfide[37,38] head groups to enable chemisorption at gold and other coinage metals, or chlorosilane[7,18,35,39] head groups for modification of oxide surfaces of silicon. In some cases, the simplest route is to chemically couple the initiator to an existing SAM, for example, by exposing a hydroxyl-terminated monolayer to a functionalized initiator.[40,41] In addition, initiator groups can often be anchored to polymers and other materials that present or are modified to present carboxylic acid-[10,42] or alcohol-rich[43] surfaces.

There are many different classes of surface-initiated polymerizations, as defined by the chemical mechanism for propagation, including anionic, cationic, ring-opening (ROP), radical, the more specific atom-transfer radical (ATRP), and ring-opening metathesis (ROMP). The general types of initiators and monomers used for each method and some key ad-

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vantages and disadvantages of each approach are summarized in Table 1. Living anionic routes[35,44–46] are highly controlled polymerizations that enable the preparation of chains with low polydispersity and films with complex polymer architectures. However, the growth rates for anionic polymerizations are rather slow, such that long exposure times (a few days) are commonly required to produce films with thicknesses of 10–20 nm at room temperature.[35] These polymerizations are also extremely sensitive to moisture and impurities.[35] Cationic polymerizations[1,47,48] exhibit many of the same advantages and disadvantages as anionic polymerizations but tend to propagate a bit faster and are generally not as controlled due to higher termination rates. Traditional radical polymerizations generally exhibit more rapid kinetics, often with significant loss of control, and are compatible with a wide variety of monomers, including those that contain polar or unprotected functional groups.[21,40] Unlike most other methods, traditional radical polymerizations do not allow the reactivation of chain ends to prepare block copolymer films. A specific class of controlled radical polymerizations, ATRP,[2,7] has become the most popular approach for preparing thin films, due in part to the wide variety of vinyl monomers that can be polymerized

Table 1. Commonly studied monomers and initiators for some different surface-initiated polymerization techniques and key advantages and disadvantages of each technique.

SIP Type	Initiators	Monomers	Advantages	Disadvantages	References
Anionic	Diphenyl-ethylene (activated by BuLi)	Vinyl	Low PDI, living (dienes and styrenes only)	Affected by moisture and impurities, slow kinetics	[35,44]
Cationic	Triflate, $-OCH_3$	Vinyl, propylene glycol	Greater propagation rate constants than anionic	Affected by moisture and impurities	[47,48]
Radical	Azo compounds	Vinyl	Allows monomers having polar functional groups	Cannot form block or graft copolymers	[21,40]
ATRP	Haloesters, halides	Vinyl	Rapid kinetics in water, can form multiple blocks, chemical diversity	Higher PDI than ionic, difficult with acidic monomers	[5,7,37]
ROP	Triflate, tin(II) octoate	Cyclic esters, oxazolines, glycidol	Preparation of biologically important polymers	Limited chemical diversity	[16,45,80]
ROMP	Ruthenium carbenes	Norbornenes	Mild reaction conditions, thick films	Limited chemical diversity	[4,13,50]
Surface-catalyzed/ Spontaneous	No initiator attachment required	Diazo compounds/ maleimides, vinyl	Rapid kinetics, mild conditions, no initiator, thick films	Lack of chemical diversity, mechanism unresolved	[6,52,55]

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and the ability to prepare films with different blocks by reactivating chain ends.[8,9,27] ATRP also tolerates moisture: in fact, for polar monomers, the kinetics of polymerization are greatly accelerated when water is used as solvent.[5,38] Polydispersity indices (PDIs) for ATRP chains are generally below 1.5,[2] lower than those for traditional radical polymerizations. Ring-opening polymerizations proceed by either cationic[16] or anionic[45] mechanisms and are used to produce linear polymers from cyclic monomers. Ring-opening metathesis polymerizations exhibit rapid kinetics under mild conditions but are somewhat limited compositionally.[4,19,49–51] The predominant ROMP monomer studied in surface-initiated cases has been norbornene and its functional derivatives.

In addition to general surface-initiated approaches, some polymers can be grown directly from an appropriate metal surface; these are termed either surface-catalyzed[6,52–54] or spontaneous[55–57] polymerizations, and are also summarized in Table 1. The surface-catalyzed decomposition of diazomethane at gold surfaces rapidly produces linear polymethylene (PM) films[52,53] via a proposed free-radical mechanism. Atomic-scale modification of gold with copper and silver (sub)monolayers greatly affects the kinetics of PM film growth and seems to alter the mechanism toward a controlled propagation.[6,54] Bell and co-workers have reported spontaneous polymerizations of thick (up to 50 μm) polyimide coatings upon exposure of copper,[55] steel,[56] and aluminum[57] to aqueous solutions of various donor and acceptor monomers that enable a proposed electrochemically initiated radical mechanism. These polymers effectively protect the underlying surfaces against corrosion.

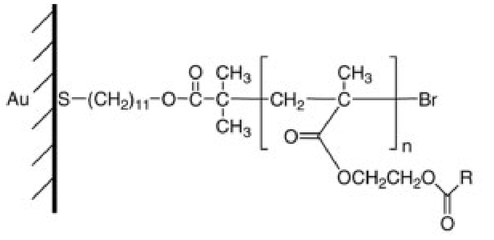
In this article, we review the use of surface-initiated polymerization strategies to impact the processing of advanced materials. We focus on physicochemical aspects of the films, which define their often unique properties and govern their applications. For example, we describe the use of specific polymer films to alter or modify material properties but do not focus on the details of the chemistry of polymer initiation/propagation, which is usually described in the cited works and has been addressed in other reviews.[1,58] We direct readers wishing to learn more about surface-initiated polymerizations to insightful and interesting reviews that focus on polymer brushes,[58–60] ATRP,[61] surface-initiated ATRP,[62] surface modification in microchip electrophoresis,[63] and polymerization from nanoparticle surfaces.[12] The remainder of the article is divided into three parts that focus on the use of surface-initiated polymerizations in the modification of planar surfaces, in microfabrication or nanofabrication, and in the modification of non-planar surfaces and particles.

2. Modification of Planar Surfaces

2.1. Effect on Surface Properties

The ability to modify and control the surface properties of materials has become increasingly important, which is due in part to the recent emergence of nanostructured materials where surface-area-to-volume ratios are high. Successful control over surface properties, such as wettability, adhesion, and adsorption, relies on engineering the composition and structure of the outer few angstroms of a material. Within the past 20 years, SAMs have been utilized widely to modify surface properties due to their ability to present a two-dimensional sheet of dense, homogeneous chemical functionality at a surface. Limitations of SAMs have included difficulty in producing films thicker than a few nanometers[64] and the finite stability of these molecular films.[65,66] Since the stability of tethered organic films generally improves with molecular weight (and thickness), due to increased interchain interactions,[67] surface-initiated polymerizations provide a controlled method for greatly amplifying the thickness and stability of molecular films. In addition, surface-initiated films can be synthesized and engineered to exhibit interesting dynamic behavior, such as stimuli-driven conformational changes that affect wettability or biological adhesion. To date, surface-initiated films have been used widely to alter surface wettability,[25,68–71] reduce protein adsorption,[34] and affect adhesion at a surface.[29,72] The remainder of this section highlights some recent uses of surface-initiated polymer films to influence surface properties.

The ability to readily prepare low-energy surfaces that are not wet by liquids and not easily contaminated is important in many applications, such as directed assembly,[73] selective dewetting,[74] and corrosion inhibition.[64] Low-energy surfaces are commonly generated by preparing thin films in which relatively non-polar groups such as $-CF_3$ or $-CH_3$ dominate the surface composition. We have recently used surface-initiated ATRP to grow poly(hydroxyethyl methacrylate) (PHEMA) films on gold that were subsequently modified by acylation with acid chlorides (RCOCl) of hydrocarbon ($R = C_pH_{2p+1}$)[71] or fluorocarbon ($R = C_mF_{2m+1}$; $R = C_6F_5$)[69,70] composition to produce ester-linked side groups (Scheme 1). The wettability of these films, also shown in Scheme 1 via advancing contact angles of water and hexadecane, depended on the composition and chain length of the side group. For $m = 7$,[69] the partially fluorinated film exhibited an advancing hexadecane contact angle of 79°, similar to that observed for SAMs containing densely packed, homogeneous CF_3 surfaces.[75] The critical surface energy of this partially fluorinated film is 9 mN m^{-1}, which is remarkably lower than that of polytetrafluoroethylene (18 mN m^{-1}), a pure fluorocarbon polymer. The low critical surface tension and high hexadecane contact angle for this film are consistent with a normal orientation of the fluorocarbon chains at the outer surface, such that the terminal CF_3 group dominates surface properties.[69] With hydrocarbon modification of PHEMA,[71] the advancing hexadecane contact angle increases with chain length and approaches the value for a densely packed methyl-terminated SAM (~50°).[76] The critical surface tension of these fluorocarbon- and hydrocarbon-modified films can be tuned from 9–27 mN m^{-1}, depending on the selection of R. These results demonstrate the importance of molecular engineering of polymer films to tailor



R	θ_A (H_2O)	θ_A (HD)	γ_C (mN/m)
CH_3	70	<10	
C_7H_{15}	104	<10	
$C_{11}H_{23}$	113	16	~27
$C_{13}H_{27}$	117	21	~26
$C_{15}H_{31}$	117	44	24
$C_{17}H_{35}$	115	47	23
CF_3	90	49	21
C_3F_7	110	67	15
C_7F_{15}	128	79	9
C_6F_5	90	<10	

Scheme 1. Schematic illustration of surface-initiated PHEMA films modified by reaction with acid chlorides (RCOCl). The effect of R on advancing contact angles (θ_A in degrees) for water and hexadecane (HD) and on critical surface energy (γ_c) is also shown.

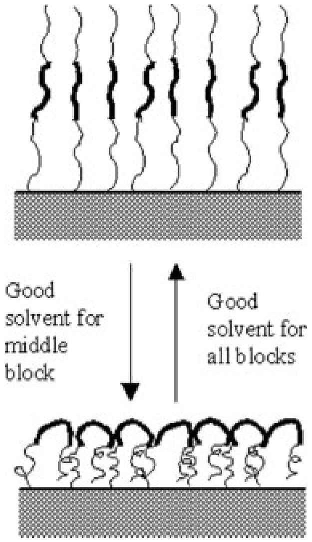
surface composition, and show that surface-initiated polymer films can present densely packed surfaces that approach the wettability behavior of monolayer films.

Park, Rühe, and co-workers[25] prepared ultrahydrophobic surfaces by polymerizing perfluoroalkylethyl acrylates via a radical mechanism onto the surface of porous silicon. The high values of roughness for the porous silicon support increase the contact angles of water on these partially fluorinated films to ~160°. The effect of surface roughness (r) on the measured contact angle (θ_{meas}) can be estimated via Wenzel's[77] relationship

$$\cos\theta_{\text{meas}} = r\cos\theta \tag{1}$$

where θ is the equilibrium contact angle on a compositionally identical flat surface. This work shows that surface-initiated films are compatible with rough substrates and that both chemical composition and morphological control of a substrate can be used to achieve extremely high contact angles that are appropriate for water-repellent surfaces.

An attractive feature of surface-initiated polymer films is the ability to prepare loosely packed, stimuli-responsive brushes that alter their conformation upon changes in the environment. This reversibility of conformation enables "switchable" surface properties, which could lead to applications in sensors as well as "smart" membranes and fabrics. ATRP enables the preparation of di- and triblock-copolymer films from a wide range of monomers where each block has a different interaction with a solvent to provide the framework for a solvent-sensitive film. Brittain and co-workers[8] have used ATRP to develop solvent-responsive films from ABA-type triblock-copolymer brushes where the middle block has different physicochemical properties from the end blocks. As shown schematically in Scheme 2, the film should adopt an extended brush configuration when exposed to a good solvent for all the blocks but adopt a folded brush conformation when exposed to a good solvent for only the middle block. Using a ~15 nm poly(methyl acrylate)-*block*-polystyrene-*block*-poly(methyl acrylate) (PMA-*block*-PS-*block*-PMA) film grown from silicon and initially exposed to dichloromethane (good solvent for all the blocks), the advancing water contact angle changes by ~20° upon exposure to cyclohexane (good solvent for PS). Brittain and co-workers have shown that this difference in wettability upon solvent exposure can be amplified to ~40° using diblock films with PMA as the lower block and poly(pentafluorostyrene) as the upper block on Si/SiO_2.[27]



Scheme 2. Reversible response of triblock-copolymer brushes to different solvents.

Another way of preparing responsive films is to utilize polymers that change conformation when temperature is changed. Poly(*N*-isopropylacrylamide) (PNIPAAm) exhibits a lower critical solution temperature (LCST) of about 32–33 °C. At temperatures below the LCST, the polymer displays an extended brush structure and a hydrophilic surface due to intermolecular H-bonding between PNIPAAm chains and water molecules.[68] At temperatures above the LCST, the polymer exhibits a collapsed structure and a hydrophobic surface due to intramolecular H-bonding between the PNIPAAm chains. At a smooth surface, the contact angles for PNIPAAm above and below the LCST are 93° and 63°, respectively.[68] Jiang and co-workers[68] have combined the thermoresponsiveness of PNIPAAm, prepared by surface-initiated ATRP, with a well-controlled rough surface, consisting of an array of squares fabricated by a laser cutter, to create films that switch between superhydrophobicity ($\theta \sim 150^\circ$) and superhydrophilicity ($\theta = 0^\circ$) upon a ~10 °C change in temperature (Fig. 1). The surface roughness dramatically enhances the contact angle on the hydrophobic surface but decreases the contact angle on the hydrophilic surface due to capillary effects, consistent with Equation 1. As the spacing between the squares decreases, the temperature-induced difference in contact angle increases (Fig. 1a), but no experiments were performed in which the spacing was reduced below 6 μm. More sophisticated patterning strategies, as discussed later in this review, should enable the preparation of thinner spacings that could further amplify this reversible difference in wettability. This demonstrated ability to dramatically alter wettability by small changes in temperature could affect the processing of thermally responsive drug-delivery vehicles and temperature-controlled gates or switches.

The thermoresponsive properties of surface-initiated PNIPAAm films have also been used to impact adhesion and biological adsorption. Lopez and co-workers[33] have shown that bacteria adsorb to hydrophobic PNIPAAm films (37 °C) but that rinsing with 4 °C artificial seawater effectively removes ~90 % of the cells, presumably due to an altered conformation within the film that reduces its adhesion with the bacteria. Jones et al.[29] have used atomic force microscopy (AFM) force measurements to show that PNIPAAm exhibits adhesion forces similar to a hydrophobic SAM above the LCST but no adhesion force could be measured below the LCST. Combined, these findings hold promise for "smart" surfaces that efficiently release biofilms and biological species upon changes in temperature.

2.2. Effect on Bulk Properties

While the surface composition of surface-initiated polymer films greatly affects wettability and biological adhesion, the bulk composition can have considerable impact on barrier properties and dielectric behavior. Many functional groups have been polymerized into these films or subsequently added by modification to affect ion-induced swelling,[78] alignment of liquid crystals,[79] biodegradability,[80,81] membrane separations,[26] impedance behavior,[69–71] and current–potential characteristics.[4] In addition, the responsive nature of some surface-initiated polymer films has led to altered film morphologies, thicknesses, and/or barrier properties upon changes in solvent,[8,27,30] ionic strength,[28] or temperature.[24,28] A notable example is the use of surface-initiated PNIPAAm to contract and open the pores of silica upon an increase in temperature.[24] In the remainder of this section, we highlight recent examples that illustrate the effect of polymer film composition on properties.

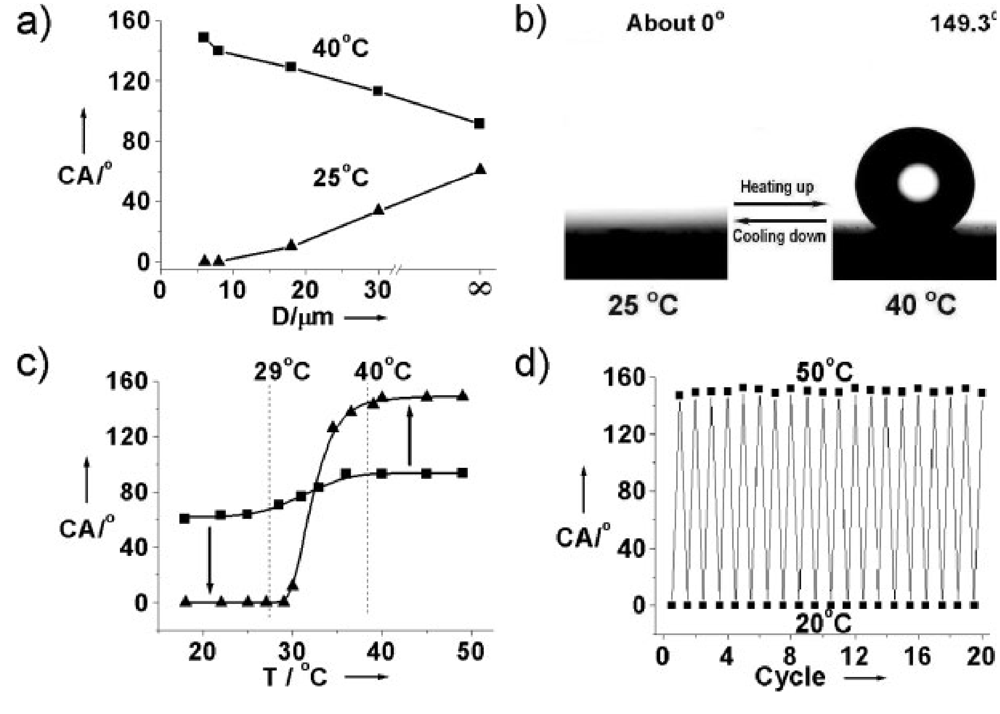


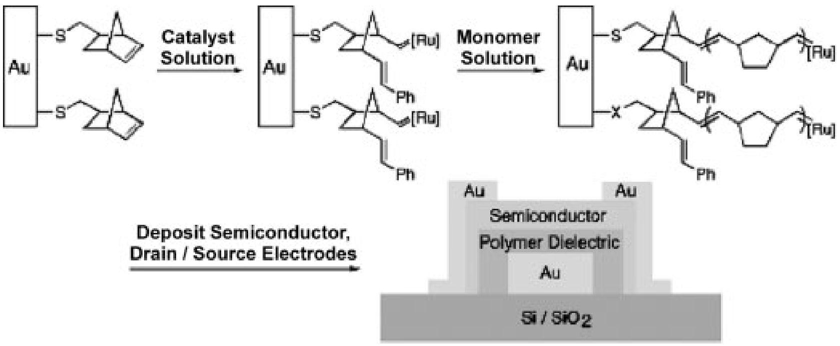
Figure 1. Surface-roughness-enhanced wettability of a PNIPAAm-modified surface. a) The relationships between groove spacing (*D*) of rough surfaces and the water contact angles (CAs) at low temperature (triangles, 25 °C) and at high temperature (squares, 40 °C). The groove spacing of ∞ represents a flat substrate. b) Water-drop profile for thermally responsive switching between superhydrophilicity and superhydrophobicity of a PNIPAAm-modified rough surface with groove spacing of ~6 μm, at 25 °C and 40 °C. c) Temperature (*T*) dependences of water CAs for PNIPAAm thin films on a rough substrate with groove spacing of ~6 μm (triangles) and on a flat substrate (squares). d) Water CAs at two different temperatures for a PNIPAAm-modified rough substrate with groove spacing of ~6 μm. Half cycles: 20 °C; and integral cycles: 50 °C. (Reprinted with permission from [68].)

Due to the ability to produce dense, conformal layers of controlled thickness and composition over any surface topology, surface-initiated polymer films have potential impact as dielectric layers in the preparation of low-cost, lightweight, organic thin-film transistors. Rutenberg et al.[4] have used ROMP to prepare polynorbornene dielectric layers atop a gold-strip gate electrode on silicon. The use of ROMP enables mild conditions and rapid access to sufficiently thick films (1.2 μm) that exhibit low capacitances (3 nF cm^{-2}) and are essentially pinhole free. The polynorbornene film provided a conformal coating over the electrode and was subsequently used to support a thin, vapor-deposited film of pentacene (semiconductor) before the entire structure was pressed against a PDMS substrate that contained two gold strips as drain and source electrodes (Scheme 3). The resulting field-effect transistor (FET) exhibited mobility ranges of 0.1–0.3 cm^2 V^{-1} s^{-1} and on/off ratios of 10–100. While polynorbornene films function well here, future investigation of other film compositions with even lower dielectric constants could lead to further improvements in dielectric properties at reduced film thicknesses. This work nicely illustrates a case where the characteristics of surface-initiated polymerizations match well with the needs of an emerging technology.

The molecular composition of a polymer thin film greatly affects its barrier properties and can be designed to impact applications in corrosion inhibition and etch resistance. Of particular importance is the penetration of water and ions into coatings, for which electrochemical impedance spectroscopy is an invaluable method of characterization. As shown in Scheme 1, we have modified ATRP, surface-initiated PHEMA films with fluorocarbon[69] and hydrocarbon[71] acid chlorides to investigate the effect of film composition on surface wettabilities (described above) and impedance properties, such as film resistance and capacitance (Table 2). In general, modification of a 250 nm thick PHEMA film leads to dramatic increases in film resistance by four to five orders of magnitude and reductions in film capacitance by two orders of magnitude. Upon analyzing the compositional effects on resistance and capacitance, we conclude that two important factors govern the barrier properties of these modified PHEMA films. The most important factor is the elimination of hydrophilic hydroxyl groups upon conversion to fluorocarbon or hydrocarbon esters to reduce water-diffusing pathways within the film. For example, modification of PHEMA with C_6F_5COCl results in higher conversions and superior resistance as compared with the fluoroalkyl-modified films, although the perfluoroaryl group is only a minor extension of the side chain and does not structure at the outer surface as the longer C_7F_{15} group does. Likewise, merely capping the hydroxyl groups of PHEMA with CH_3COCl provides a much higher conversion and resistance than those obtained by modifying with $C_{17}H_{35}COCl$, although the long hydrocarbon chains structure within the film and present a hydrophobic, oleophobic surface. Nonetheless, for films with similar conversion, structuring within the film and at the outer surface does provide a significant boost in film resistance, as evidenced by comparing C_7F_{15} to C_3F_7, where the longer group structures the film to a greater extent at the surface and in the bulk.[69] In addition, the resistance of the $C_{17}H_{35}$-modified PHEMA film can be improved greatly by exposure to CH_3COCl, which increases conversion from ~0.4 to ~0.8 (noted as $C_{17}H_{35}/CH_3$ in Table 2). The structuring of $C_{17}H_{35}$ chains within this hybrid film leads to enhanced barrier properties as compared with C_7H_{15}- or CH_3-modified PHEMA, which each exhibit high conversions. Thus, avoiding or eliminating hydrophilic groups and promoting film and interfacial structure through modification enables the preparation of highly blocking aqueous-phase barrier films.

Table 2. Film resistance (R_f) and capacitance (C_f) for 250 nm PHEMA films, unmodified and modified by acylation with RCOCl to achieve a % conversion (χ) of hydroxyls to esters.

R	log R_f [Ω·cm^2]	C_f [nF cm^{-2}]	χ [%]
unmodified PHEMA	3.0	640	
CH_3	6.7	19	93
C_7H_{15}	7.0	13	82
$C_{17}H_{35}$	4.2	25	37
$C_{17}H_{35}/CH_3$	7.7	11	80
C_3F_7	6.7	12	70
C_7F_{15}	7.4	9	67
C_6F_5	7.8	6	83



Scheme 3. Construction of a FET using a surface-initiated ROMP polymer dielectric layer. (Reprinted with permission from [4]. Copyright 2004, American Chemical Society.)

The ability to achieve both outstanding impedance properties and a densely packed, low-energy surface, as is accomplished with these modified PHEMA films, can produce more effective barrier films for applications in etch resistance and membrane separations. As a case in point, Bruening and co-workers[26] have used C_7F_{15}-modified PHEMA as an ultrathin (~50 nm) dense outer skin grown atop a gold-coated, porous-alumina membrane for application in the separation of gases. While unmodified PHEMA provides little or no selectivity, fluorinated PHEMA exhibits selectivities of 8–9 for CO_2/N_2 and

CO_2/CH_4. These results, combined with those shown in Table 2, demonstrate that appropriate modification of surface-initiated films is straightforward and can dramatically affect their barrier properties. Bruening and co-workers[26] also showed that crosslinked poly(ethylene glycol dimethacrylate) (PEGDMA) skins grown atop polyelectrolyte-coated alumina membranes exhibited an enhanced selectivity of ~ 20 for CO_2/N_2. As shown in Figure 2, the polymer layers were found to exist predominantly at the outer surface and did not clog inner pores of the membranes. The high level of control over thickness and composition of these surface-initiated films and the ability to initiate their growth from different surfaces—in this latter case, a polyelectrolyte layer atop porous alumina—is highly advantageous in the preparation of dense membrane skins.

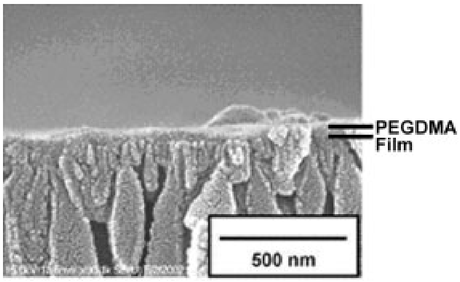
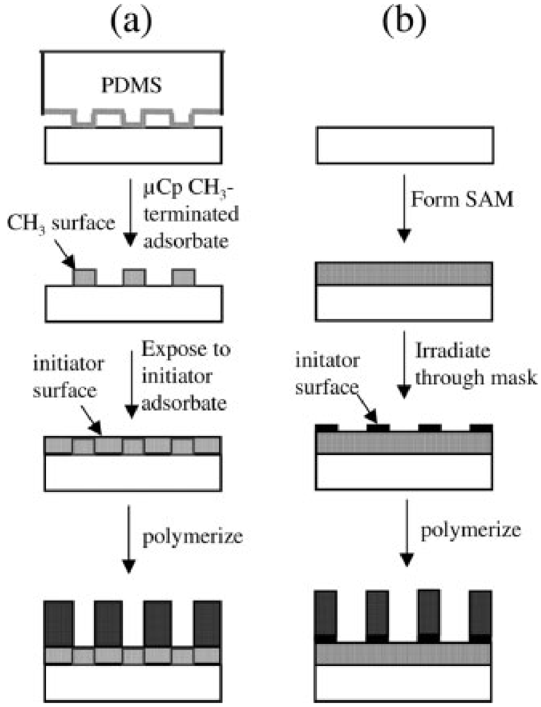


Figure 2. FESEM cross-sectional image of a porous alumina membrane (20 nm surface pore diameter) after depositing one bilayer of polyelectrolytes and growing PEGDMA from the surface. (Reprinted with permission from [26]. Copyright 2003 Elsevier.)



Scheme 4. Patterning surface-initiated polymer films by a) microcontact printing (μCp) or b) light-activation of an initiator.

3. Patterning and Microfabrication

The ability to pattern surface-initiated polymer films can lead to advances in surface-directed events and in microfabrication. The patterning of surface-initiated polymer films has been achieved by various methods that each succeed in localizing initiator-terminated groups on the surface. The most common method is to microcontact print an inert alkanethiol and subsequently backfill the pattern with an active thiol or disulfide to initiate polymerization locally (Scheme 4a).[31,37] Another method uses ultraviolet light through a mask to irradiate and activate an initiator layer for subsequent polymerization in selective regions (Scheme 4b).[82] These methods generally enable rapid patterning of fairly large surface areas (up to a few cm^2) but have not yet been reliably used to achieve submicrometer polymeric features. Irradiation with an electron beam (instead of UV light) has produced features as small as 70 nm with good throughput.[83] Methods based on the use of AFM tips can either remove and backfill (nanoshaving)[30] or deposit (dip-pen nanolithography)[51] molecular components and offer the capability to produce submicrometer features and control feature composition in a site-specific manner. Nonetheless, throughput is an issue with scanning-probe methods, and to be successful, these methods require the user to develop a significant expertise. In the remainder of this section, we highlight a few approaches that have been especially successful.

Hawker and co-workers[31,37] reported the first patterning of surface-initiated polymer films based on microcontact printing. Using the general method shown in Scheme 4a, they prepared patterned ultrathin films of poly(caprolactone) by ROP or poly(methyl methacrylate) (PMMA), PHEMA, and others by ATRP. The more hydrophobic polymers were observed to greatly resist the penetration of aqueous-phase etchants and reduced the rate of etching by two orders of magnitude over that of the initiator SAM. In this manner, the polymer greatly amplifies the etch resistance of the SAM.

To achieve a similar goal, Zhou et al.[32] exposed PMMA and PHEMA films prepared by surface-initiated ATRP to ultraviolet irradiation through a transmission electron microscopy (TEM) grid to completely remove the polymer brush and initiator in the irradiated regions. They then electrodeposited conducting polypyrrole microstructures in the bare regions of the surface or exposed the patterned films to etchants to create polymer-capped gold microstructures (Fig. 3). While hydrophobic PMMA films exhibited good etch resistance, hydrophilic PHEMA films did not, consistent with the poor barrier properties of PHEMA, as surmised from Table 2. Nonetheless, merely capping the hydroxyl groups of PHEMA by reaction with trimethylchlorosilane greatly improved the

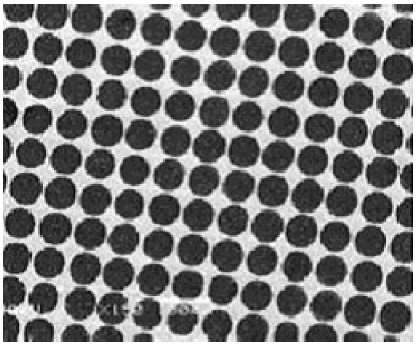


Figure 3. Optical micrograph of the positive gold pattern obtained by etching the trichlorosilane-modified PHEMA brush template using KI/I$_2$(aq). The brighter area is the unetched gold. Each feature is ~50 µm in diameter. (Reprinted with permission from [32].)

etch resistance of the films, again consistent with impedance results in Table 2, where capping hydroxyl groups of PHEMA with acetyl chloride produced a four order of magnitude improvement in film resistance.

Zauscher and co-workers[30] have developed a strategy to produce submicrometer features with surface-initiated PNIPAAm films on gold (Fig. 4). Briefly, they used an AFM tip to "nanoshave" away discrete lines of an inert octadecanethiolate monolayer and then backfilled the unmodified area with an initiator-terminated thiol. ATRP of NIPAAm resulted in polymer features with widths of 300–500 nm and heights of up to 60 nm. The actual feature height was dependent on the environment in which the patterned films were imaged. Figure 4 shows AFM images of the same patterned features in air, water, and methanol/water, where the numbers for the lines represent the nanoshaving time of each line in minutes prior to backfilling and polymerization.[30] The PNIPAAm chains are extended in water (Fig. 4b), a good solvent, but compressed in methanol/water (Fig. 4c), a poor solvent, and in air (Fig. 4a). This approach achieves environmental responsiveness for PNIPAAm without altering temperature. This visual display of the solvent responsiveness of PNIPAAm features demonstrates the potential for utilizing these films as a nanoscale valve that restricts flow through a channel or pore upon a change in liquid composition. Lopez and co-workers[24] have recently demonstrated that a temperature change can induce the constriction of pores within PNIPAAm-modified mesoporous silica.

Another approach to patterning polymer films relies on the atomic-level surface sensitivity of catalyzed reactions. An example of a surface-catalyzed polymerization is the decomposition of diazomethane (CH_2N_2) on gold surfaces in ether to grow polymethylene (PM) films.[52] This surface-catalyzed route to PM is important due to the poor solubility of polyethylene that limits its use in traditional thin-film processing. Our group[6,54] has shown that atomic-level modification of gold surfaces with underpotentially deposited metal submonolayers greatly affects the growth of PM, with a monolayer of silver completely preventing polymer formation while a submonolayer of copper greatly accelerates the growth of PM over that of an unmodified gold surface. We have used this surface sensitivity to direct the growth of PM films on gold surfaces containing patterned regions of copper and silver monolayers (Fig. 5).[6] The patterned surface was prepared by 1) underpotentially depositing (upd) copper over the entire surface; 2) microcontact printing a hexadecanethiolate SAM onto the surface in specific regions; 3) electrochemically removing copper in regions unprotected by the SAM; and 4) depositing a catalytically inactive silver monolayer to replace the removed copper.[6] The rapid growth of PM on the Cu-modified gold surface combined with the prevention of growth on Ag-modified gold enables the preparation of PM lines with ~900 nm height and widths that are governed by the feature size of the PDMS stamp used to prepare the patterned Ag/Cu surface. This ability to direct the growth of chemically stable PM through a surface-catalyzed synthesis at low temperatures (0 °C) under atmospheric conditions could be useful in commercial applications involving dielectrics and/or patterned barrier films.

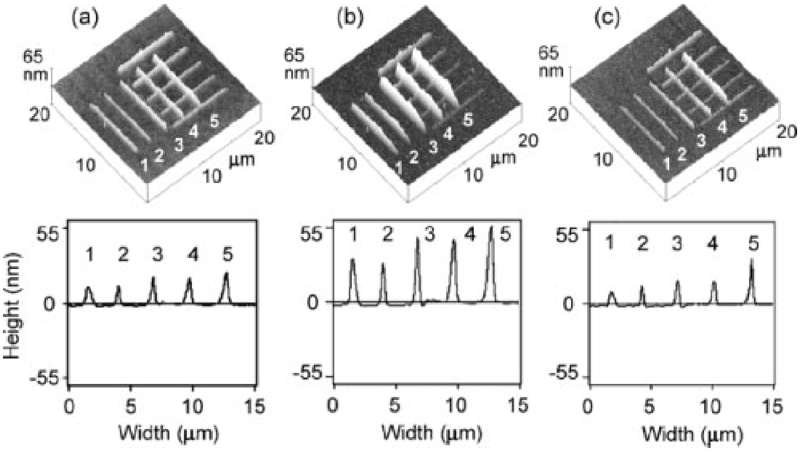


Figure 4. Contact-mode AFM height images (20 µm × 20 µm) and corresponding typical height profiles of a PNIPAAm brush line nanopattern imaged at room temperature in a) air, b) deionized water, and c) a mixture of methanol/water (1:1, v/v). The PNIPAAm line pattern was generated by first removing a thiol-resist through "nanoshaving" under large normal forces (~50 nN) using AFM, and subsequent surface-initiated polymerization of NIPAAm for 60 min using a backfilled, covalently attached thiol initiator. The labels 1–5 associated with the set of parallel PNIPAAm brush lines indicates the "nanoshaving" time of a line in minutes. (Reprinted with permission from [30]. Copyright 2004 American Chemical Society.)

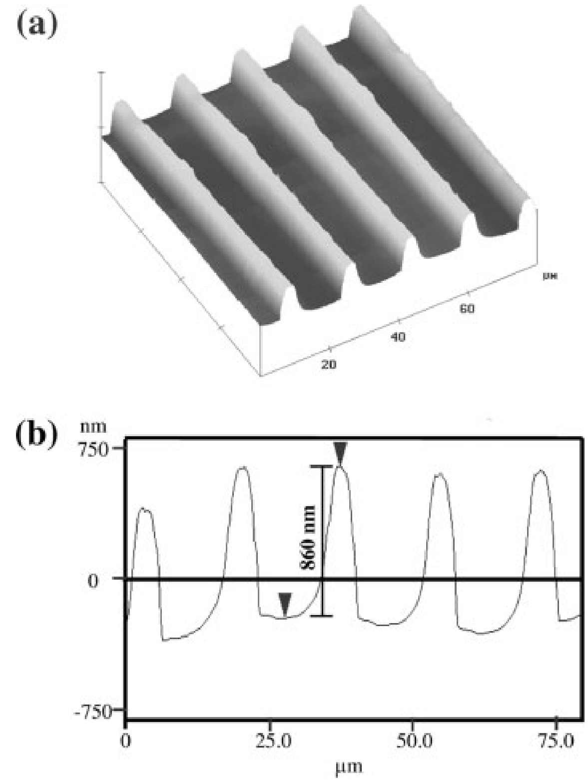


Figure 5. Tapping-mode AFM image and section analysis of a patterned PM film grown from a surface containing lines of Cu(upd)/Au (coverage = $\phi_{Cu} = 0.6$) and adjacent lines of Ag(upd)/Au ($\phi_{Ag} = 0.9$). a) Three-dimensional view that shows the morphology of the patterned lines and the uniformity of the pattern and b) section analysis that shows the patterned PM film with a thickness of ~860 nm and feature widths of ~8 µm. The substrate was prepared according to the procedure described in the text and then exposed to a 10 mM solution of diazomethane in ether at 0 °C for 20 h. (Reprinted with permission from [6].)

4. Modification of Non-planar Surfaces

As compared with traditional methods of applying polymer films, surface-initiated approaches provide a key advantage in their ability to uniformly coat non-planar surfaces. A variety of non-planar surfaces have been used as supports for polymerization, including gold,[13,16] silica,[15,18,19,21,22,24,84] clay,[85] latex,[14] dextran,[43] polystyrene,[86,87] and magnetite[88] particles, and carbon nanotubes.[10,11,89–92] This list is only a sampling of possible surfaces from which polymerization can be performed,[62] as any surface may be suitable if it can be functionalized with an initiator species. Furthermore, many surface-initiated polymerization techniques have been used to accomplish these modifications, including ROP,[16] ROMP,[13,19] free radical,[21,84,85,88,89] ATRP,[10,11,14,18,24,43,62,86,87,91,92] and anionic[90] routes.

With a focus on the ability to tailor properties at the molecular level, surface-initiated techniques are increasingly finding use in modification of non-planar substrates. The most common reason for modification of particles, nanotubes, and supports is to alter interactions of these materials with the surrounding environment, and thin polymer layers offer a straightforward way to accomplish this. Modification of a particle with an initiator allows subsequent controlled polymerization to occur equally across the entire surface area, allowing tremendous control over film growth and properties. Surface-initiated techniques enhance the dispersion or solvation of particles and nanotubes and alter composition for materials in separations processes.

A large volume of work has been devoted to non-planar surfaces in a few key research areas: chromatographic supports, nanoparticles, and nanotubes. Work in separations has focused on functionalization of materials to improve selectivity while nanotube and particle work has been concerned mainly with increasing the dispersion of these materials in solvents, constructing a polymer layer around a particle to protect from chemical or mechanical attack, or preparing well-defined nanoscale structures.

4.1. Chromatographic Supports

Modification of surfaces for separation processes has been widely used in recent years to improve selectivitity.[19,20,26] The tremendous control over uniformity, thickness, and composition offered by surface-initiated polymerization techniques is again the reason they have found use in these applications. Of particular interest in this area is work by Buchmeiser and co-workers centered on the use of ROMP to grow functionalized norbornenes from silica surfaces.[20,93,94] For the chromatographic separation of phenols, anilines, lutidines, and hydroxyquinolines, they have demonstrated the ability to grow poly(norborn-2-ene) (PNBE), poly(7-oxanorborn-2-ene-5,6 dicarboxylic acid) (PONDCA), or copolymers of these two compounds on silica supports.[20] As compared to supports created by coating solution polymers onto silica, which tends to clog pores and reduce surface area, the surface-initiated supports provided much improved separations. PNBE-modified silica serves as a non-polar stationary phase for separations and is ideal for reverse-phase liquid chromatography. In contrast, PONDCA-modified silica is hydrophilic and charged at higher pH and can be used for ion-exchange chromatography but is not suited to reverse-phase separations. The separation efficiency, particularly as related to the carboxylic acid groups of the PONDCA regions, was dependent on pH so that separations could be tailored based on the pK_a of analytes. Furthermore, Buchmeiser and co-workers have demonstrated a similar ability to separate biomolecules using reverse-phase chromatography with copolymers of NBE and 1,4,4a,5,8,8a-hexaydro-1,4,5,8-*exo*,*endo*-dimethanonaphthalene (DMN-H6) grafted onto borosilicate monoliths.[93] Separation of the various proteins was found to be dependent on physicochemical properties and microstructure of the grafted monoliths. These two examples show the usefulness of surface-initiated techniques for chromatographic separations. The ability to tune polymer properties by combining different monomers to achieve the desired effect is of utmost importance, particularly since the required properties will change depending upon the compounds to be separated.

4.2. Particles

A significant amount of interest has been shown in the surface-initiated modification of particles, both on the nanometer and micrometer size scales. For the most part, research on particles has focused on increasing their solubility or dispersibility in solutions by augmenting their interactions with solvents while some work has focused on materials synthesis. Of the considerable work in this latter area, Mandal et al.[95] and more recently Blomberg et al.[84] have utilized nanoscale particles as scaffolds to prepare hollow, polymeric capsules. Blomberg et al.[84] grafted poly(styrene-*co*-vinylbenzocyclobutene) or poly(styrene-*co*-maleic anhydride) onto silica nanoparticles (600 nm) via a free radical polymerization to create core–shell nanoparticles, as shown in the field-emission scanning electron microscopy (FESEM) image in Figure 6. Similar polymer modifications have been used on numerous particles to impart desirable surface interactions, such as to increase solubility or to protect the inner core material while maintaining its properties. However, since the desired application in these cases was not to improve particle–solvent interactions but to create hollow nanospheres, the choice of monomers was driven by one simple factor, the ability to exhibit crosslinking. To facilitate crosslinking in the polymer films surrounding the core, the benzocyclobutene group exhibits intermolecular coupling at elevated temperatures, or maleic anhydride may be reacted with a diamine compound. After polymerization and crosslinking, the inner silica core was chemically etched away with HF to reveal a nanocapsule. Only with the maleic anhydride polymer was the crosslinking sufficiently robust to withstand the conditions of core removal, enabling the nanocapsules to remain intact after processing. Control over the structural integrity of a system such as this allows for applications in drug and dye encapsulation upon infusion and other areas where protection or gradual release of an inner substance is desirable.

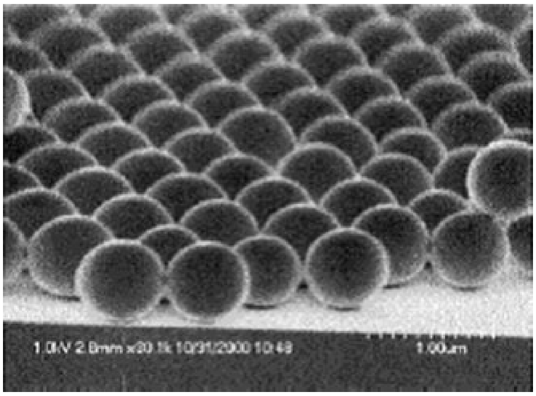


Figure 6. FESEM image of crosslinked poly(styrene-*co*-vinylbenzocyclobutene) grafted silica nanoparticles. (Reprinted with permission from [84].)

4.3. Carbon Nanotubes

Due to their extraordinary mechanical and electrical properties, carbon nanotubes have the potential to be used in a variety of applications (molecular wires, sensors, and composite materials) but are limited by poor solubility in most solvents that dramatically hinders their processability.[10,92] Covalent modifications of the nanotube surfaces tend to destroy the structure or properties of the nanotubes because a large number of sidewall carbons (at least one in ten) must be modified to achieve desirable solubility.[11] However, surface-initiated techniques can achieve good solubility while minimally altering nanotube structure by growing polymer from 1 in ~250 sidewall carbons.[11] Only a handful of examples of surface-initiated polymerization from carbon nanotubes exist in the literature.[10,11,89–92] From this small number, we highlight the work of Qin et al.[10] along with that of Kong et al.[91] Qin et al.[10] grew PS from carbon nanotubes using ATRP and found, as have other groups that perform surface-initiated polymerization from carbon nanotubes, that the starting carbon-nanotube bundles tend to separate into smaller bundles or even individual tubes during modification (Fig. 7). Furthermore, the PS exterior resulted in good dissolution of the nanotubes into common organic solvents.[10] Kong et al.[91] took this general approach (using PMMA instead of PS) one step further. As has often been achieved on planar surfaces using ATRP (since chain ends may be reactivated by addition of a transition-metal species), they grew a second polymer layer atop the PMMA layer. They chose a functional polymer (PHEMA) for this second layer, thus yielding a nanotube surrounded by a non-polar PMMA layer which itself was surrounded by a more polar PHEMA layer. The resulting solubility of the block-copolymer-grafted nanotube was dependent on solvent, with good solvents for PHEMA providing effective solvation. This methodology, adapted from work on simpler planar surfaces, may find use in creating novel devices and materials from functionalized carbon nanotubes.

5. Outlook and Summary

In this article, we have reviewed recent advances in the use of surface-initiated polymer films to modify the surface properties of materials, to provide an ultrathin medium (dielectric, barrier, etc.) that regulates transport, to prepare well-defined patterned surfaces, and to coat nanostructures and particles of various shape and dimension. We have focused on how the molecular constituency of the films affects physicochemical properties and applications. Particularly interesting for future

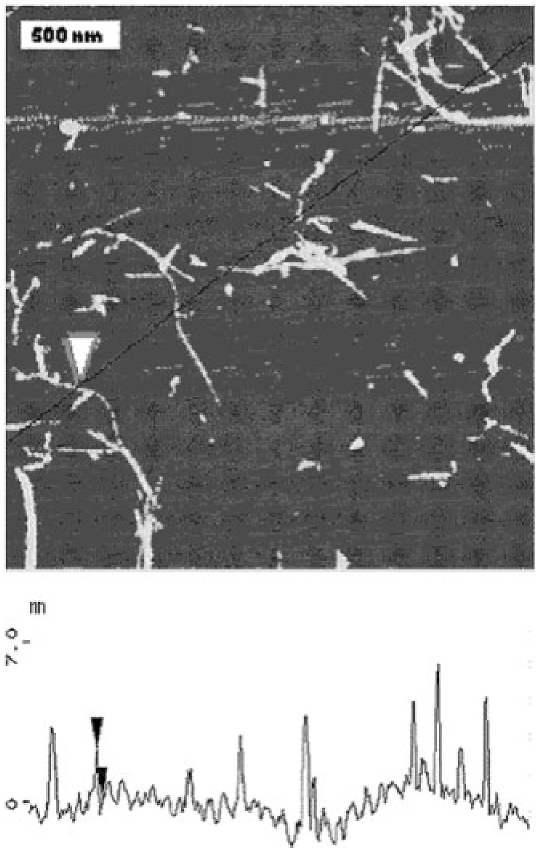


Figure 7. AFM image of PS-grafted single-walled carbon nanotubes, indicating the existence of individual nanotubes after surface-initiated modification. The height shown by the arrows is 2.1 nm. (Reprinted with permission from [10]. Copyright 2004 American Chemical Society.)

research are films that respond to changes in environmental conditions. Rather than relying solely on a known responsive polymer (PNIPAAm), we recommend further study in the use of molecular engineering and synthesis to design films in which the onset of the response is tuned to different ranges of temperatures, pH, ionic strength, species concentration, etc. Rather than synthesizing many different films, this objective may be accomplished more easily by modification of an existing film with different functional groups to (slightly) adjust film properties and the onset of the response. In addition, a stronger fundamental understanding of the factors affecting the magnitude of the range (i.e., ΔT) to accomplish the switching of film properties is needed. Finally, methods to rapidly transduce the film response to a measurable signal will become important as sensor applications are investigated. We feel these responsive films will become increasingly incorporated into nanoscale-patterned and microfabricated systems, to provide a sensitive and responsive coating on particles and other nanostructures, and to function as "smart" valves and sensors.

We have highlighted recent examples where surface-initiated polymer films are used as dielectric layers in organic thin-film transistors and as dense outer layers for membrane separations. The abilities to prepare robust, conformal coatings on various supports with nanometer-scale control over film thickness and precise control over polymer architecture and composition should enable surface-initiated polymer films to become more widely utilized in these applications. Methods to incorporate well-defined porosity into surface-initiated polymer films could reduce dielectric constants for applications in transistors. Future advances of surface-initiated films in membranes and chromatographic separations may rely on the incorporation of biological species (such as enzymes) into thin films to remove targeted components and improve efficiency.

Continued improvements in throughput and resolution of patterning approaches should enable many of the recent advances reviewed here to have far-reaching impact. Soft lithography and traditional photopatterning are extremely useful when micrometer-scale features will suffice. Techniques such as nanoshaving and dip-pen nanolithography are capable of fabricating site-specific features far thinner than the extended length of a polymer chain, thus providing unique experimental systems that enable the preparation of novel materials and the testing of physical models. Combining these techniques with the rapid kinetics and surface sensitivity of catalyzed polymer film growth could result in features with truly impressive aspect ratios. Future research in surface-catalyzed polymerizations should uncover additional systems (precursors and surfaces) to enable the rapid and directed generation of functionalized films as well as promoting a more comprehensive understanding of the catalyzed mechanism.

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