Polymer brushes and self-assembled monolayers (SAMs) are used as solid-state, 2-dimensional transport media to confine molecular diffusion. Microcontact printing and photolithography combined with surface-initiated atom transfer radical polymerization (ATRP) are the major techniques to construct patterned polymer brushes. Fluorescence recovery after photobleaching (FRAP) is used to determine diffusion coefficients of fluorescent dye, Prodan, in the polymer brushes and SAMs.

Similar diffusion coefficients of Prodan are found for the SAMs formed by chlorotrimethyl silane (CTS) and silanated poly(ethylene glycol) (PEG). No fluorescence recovery is observed on the octadecyltrichlorosilane (OTS) SAM or on the clean silica surface.

Patterned poly(N-isopropylacrylamide) (PNIPAAm) brushes were fabricated on silica substrates by surface-initiated ATRP of N-isopropylacrylamide from a micropatterned initiator. Variable temperature ellipsometry indicated that the lower critical solution temperature (LCST) of the hydrated PNIPAAm brush was broad, occurring over the range of 20-35 °C. FRAP results of Prodan in PNIPAAm layers indicate that bulk translational diffusion is very slow relative to other diffusion mechanisms.

Poly(oligoethylene glycol acrylate) (POEGA) chains are grafted onto silica substrates by surface-initiated ATRP. The diffusion of Prodan in dry POEGA is very fast, which is attributable to the low glass transition temperature of POEGA. The diffusion of Prodan in POEGA under variable humidity can be described reasonably well using WLF equation. Patterned POEGA brushes are not able to confine Prodan to diffuse exclusively inside the
polymer regions, and possible explanations are rotational diffusion and a combination of fast surface diffusion and slow bulk diffusion.

PNIPAAm chains are tethered onto silica particles via surface-initiated polymerization. Thermal annealing slightly improved the crystallinity of the colloidal assembly. Video microscopy of the two-dimensional diffusion of these colloids suggested that PNIPAAm brushes greatly improve the stability of the colloidal system. A three-fold increase in diffusion coefficient is observed when the temperature is increased from 22 ºC to 39 ºC. The LCST transition of PNIPAAm plays an important role in the diffusion of the colloids, and the interdigitation between PNIPAAm chains may have slowed down the colloidal diffusion at room temperature.
POLYMER BRUSHES FOR MOLECULAR TRANSPORT

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This thesis studies 2-dimensional transport of a fluorescent molecule, Prodan, in various polymer brushes and self-assembled monolayers (SAMs). Microcontact printing and photolithography combined with surface-initiated atom transfer radical polymerization are the major techniques to construct patterned polymer brushes; extensive surface characterizations, including atomic force microscopy (AFM), ellipsometry, Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectrometry (XPS), X-ray reflectometry (XRR) and etc., are used to confirm chemical identities and physical properties of the polymer brushes; fluorescence recovery after photobleaching (FRAP) is used to determine diffusion coefficients of Prodan.

Similar diffusion coefficients of Prodan, ~ 20 µm²/s, are found for the SAMs formed by chlorotrimethyl silane (CTS) and silanated poly(ethylene glycol) (PEG). No fluorescence recovery is observed on the octadecyltrichlorosilane (OTS) SAM or on the clean silica surface. Our hypothesis is that Prodan may partially intercalate in CTS and PEG layers whereas Prodan may aggregate on the OTS SAM, and form hydrogen bonds with the silanol groups on the clean silica surface.

Patterned poly(N-isopropylacrylamide) (PNIPAAm) brushes were fabricated on silica substrates by surface-initiated atom transfer radical polymerization (ATRP) of N-isopropylacrylamide from a micropatterned initiator. Variable temperature ellipsometry indicated that the lower critical solution temperature (LCST) of the hydrated PNIPAAm brush was broad, occurring over the range of 20-35 °C. FRAP results of Prodan in PNIPAAm layers indicate that bulk translational diffusion is very slow relative to other diffusion mechanisms.
Poly(oligoethylene glycol acrylate) (POEGA) chains are grafted onto silica substrates by surface-initiated ATRP. FRAP shows that the diffusion of Prodan in dry POEGA is very fast, which is attributable to the low glass transition temperature of POEGA. The diffusion of Prodan in POEGA under different humidity can be described reasonably well using WLF equation. Patterned POEGA brushes are prepared using two methods: (1) microcontact printing and surface-initiated polymerization of OEGA; (2) photolithography and RIE. So far the patterned POEGA brushes are not able to confine Prodan molecules to diffuse exclusively inside the polymer regions. Possible explanations for the fluorescence recovery observed are rotational diffusion and a combination of fast surface diffusion and slow bulk diffusion.

PNIPAAm chains are tethered onto monodisperse silica particles via surface initiated polymerization. Thermal annealing slightly improved the crystallinity of the colloidal assembly formed by these colloids. Video microscopy of the two-dimensional diffusion of the PNIPAAm/SiO₂ particles suggested that PNIPAAm brushes greatly improve the stability of the colloidal system. The diffusion kinetics is sensitive to the temperature change, and a three-fold increase in diffusion coefficient is observed when the temperature is increased from 22 ºC to 39 ºC. The LCST transition of PNIPAAm may have played an important role in determining the diffusion of the colloids, and our speculation is that interdigitation between PNIPAAm chains may have slowed down the colloidal diffusion at room temperature.
For my family
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LIST OF ABBREVIATIONS

FRAP  fluorescence recovery after photobleaching
SAM  self-assembled monolayer
$T_g$  glass transition temperature
PEG  poly(ethylene glycol)
CTS  chlorotrimethylsilane
OTS  octadecyltrichlorosilane
CSLM  confocal scanning laser microscope
EOM  electro-optical modulator
ROI  region of interest
PMT  photomultiplier tube
SIP  surface initiated polymerization
PNIPAAm  poly($N$-isopropylacrylamide)
LCST  lower critical solution temperature
ATRP  atom transfer radical polymerization
APS  (aminopropyl)triethoxysilane
PDMS  poly(dimethylsiloxane)
RIE  reactive ion etching
POEGA  poly(oligoethylene glycol acrylate)
DLS  dynamic light scattering
CHAPTER 1
INTRODUCTION

1.1 Objectives and General Experimental Approaches

1.1.1 Objectives

The primary goal of this thesis is to construct quasi two-dimensional “smart” molecular structures, using end-grafted polymer brushes as building blocks, which confine and regulate the transport of organic molecules, inorganic ions and nanoparticles (Figure 1.1). These well-defined, surface-bound polymer films act as a unique bridge that links the underlining surface, which can often be a solid inorganic or organic substrate, with the external environment, which can be a wide range of matters including vapors, fluids, solids and any combination of them, and more interestingly and more importantly, biomacromolecules such as proteins and DNA, and complex living organisms. It is scientifically and technologically intriguing to probe the molecular transport process mediated by the polymer brush pathways. By tuning different parameters in a model system consisting of diffusing species and the bound polymer entity, we can have a better knowledge about the thermodynamics and kinetics involved in the molecular transport in polymer brushes. Patterned polymer brush pathways represent a new paradigm for molecular transport, and it is envisioned that by patterning the brushes one will be able to have surface-directed molecular or ionic transport, separation, and chemical and biomolecular sensing properties that are important for a number of applications.

A long term objective of this research is to build a full range of transporting media, for a wide variety of species, and gain advanced control on the architecture of the transport pathways. Surface treatments using polymer brushes have been demonstrated to be very efficient in
controlling surface properties.[1-8] In our study, surface-initiated polymerization, i.e. both homopolymerization and copolymerization, of a wide variety of monomers can be applied to fulfill an extensive spectrum of surface and bulk properties of the polymer brushes, and therefore achieve a full library of diffusion behaviors using these polymer brushes for molecular transport. As schematically demonstrated in Figure 1.1, patterned polymer brushes of different chemical structures can be used to direct the diffusion of different molecules and ions and thus accomplish the goal of surface-directed molecular separation.

![Figure 1.1](image.png)

**Figure 1.1.** Schematic representation of patterned polymer brushes for directing molecular and ionic diffusion.

As a starting point, it is interesting to study the 2-dimensional (2-D), solid-state diffusion of small organic fluorophores in surface-bound polymer brushes of homopolymers. Molecular diffusion in solid-state polymer thin films is closely relevant to the potential applications of end-grafted polymers as photoresists for micro- and nano-electronics, antifriction coatings, protection layers against oxidation or other chemical reactions, adhesion layers, and biocompatible surfaces for medical devices.[3, 9, 10] Since the polymer brushes are covalently attached to the substrate and they are in solid state, the probe diffusion is occurring in an immobile 2-D matrix, and this is
fundamentally different from most of the existing research on 2-D diffusion such as the diffusion of lipid molecules in fluid-like supported lipid membranes[11, 12] and the surface diffusion of adsorbed macromolecules on various surfaces.[13, 14] This work is the first to examine solid-state translational diffusion of small probe molecules in surface-grafted polymer brushes.

The second goal is to study surface interactions through analysis of the self-assembly (in a concentrated dispersion) and the diffusion kinetics (in a dilute dispersion) of monodisperse silica particles grafted with stimuli-sensitive polymer brushes (Figure 1.2). These systems are all in fluid phase, in contrast to those solid-state systems for our first research goal.

![Figure 1.2. Schematic of colloids tethered with polymers: (a) colloids forms self-assembly in a concentrated dispersion; (b) a colloid on a polymer brush surface in a dilute dispersion.](image)

There is a wide range of applicable external stimuli, for instances, temperature gradient, pH, ionic strength, solvent quality, electric field and etc. The presence of stimuli-responsive polymers on the colloidal surfaces can strongly influence the phase behavior and kinetics of a complex fluid system. Upon receiving the external triggers, the polymers undergo conformational changes which may induce changes in the assembly structure and the diffusion behavior of the colloids. From a technological point of view, it is crucial to understand how colloids interact with themselves and with different surfaces, and how colloid-colloid and
colloid-surface interactions affect the equilibrium configurations formed by the colloids so that it is possible to smartly control the interactions by applying external stimuli to achieve the desired colloidal structures for various specific applications. Polymer brushes may also enable the formation of an equilibrium structure of the lowest possible energy by allowing a colloidal system to explore all available states. This may be possible by modulating the polymer brush conformation using external stimuli, for example, cycling the polymer brush above and below its LCST, and annealing out any kinetically trapped high-energy states. It is thus critical to understand how the colloidal system evolves in response to the external perturbations, and how the colloid-colloid and colloid-surface interactions affect the dynamics of the colloids or whether they play any role at all.

Patterned polymer brushes (on a flat surface) will be very interesting to study since dramatically different polymer structures can be attached in a single patterned sample, which allows exploring different colloid-surface interaction profiles simultaneously. Also, polymer brushes with gradient in molecular weight, grafting density and surface energy[15] can be utilized to systematically investigate the colloid-surface interactions.

In summary, end-grafted polymer brushes offer versatile pathways for directing molecular transport, and for modulating colloidal self-assembly and diffusion kinetics. Through this thesis research, we hope to lay ground work towards comprehensive understanding about how the molecular interactions between small molecules and the polymer brush matrix influence ensemble-averaged, solid-state diffusion of probe molecules in polymer brushes, and how polymer brushes determine the interactions between colloids and surfaces in fluid phase.
1.1.2 General experimental approaches

We combine microcontact printing and conventional photolithography with surface-initiated atom transfer radical polymerization (ATRP) to create spatially defined molecular pathways from end-grafted polymer brushes. In this study, poly(N-isopropylacrylamide) (PNIPAAm) and poly(oligoethylene glycol acrylate) brushes are grafted, and the typical dry polymer brush thickness in this study ranges from a few nanometers to about 100 nm. The chemical structures and fundamental physical properties of the polymer brushes are studied using extensive surface characterizations. Diffusive transport of organic fluorophores in these polymer brushes and some self-assembled monolayers is monitored with fluorescence techniques such as fluorescence recovery after photobleaching (FRAP).

Surface-initiated ATRP is used to attach the thermo-responsive PNIPAAm brushes onto monodisperse silica particles. The configurations formed in dense colloidal dispersions are studied under thermal treatments, and the diffusion kinetics of the brushed particles is investigated using video microscopy under variable temperatures.

The rest of this chapter is organized as follows: first, the synthesis of end-grafted polymer thin films is introduced; second, the patterning techniques used in this thesis are briefly discussed; third, the method used to determine molecular diffusion coefficient in this study, fluorescence recovery after photobleaching (FRAP), is discussed.

1.2 Growth of End-grafted Polymer Thin Films

Thin polymer films formed by tethering long-chain polymers onto a surface at one end through covalent bond are called end-grafted polymer thin films. Compared to polymer films prepared with other coating techniques such as spin coating, dip coating, spray coating, doctor blading, etc,[16] the apparent advantage of end-grafted polymer thin films is directly related with
the strong covalent bonding at the surface. As the result of the strong polymer-interface interaction, end-grafted polymer films do not de-wet at the underlining substrates or delaminate from substrates, and they have an outstanding tolerance for harsh external conditions including temperature changes, chemical environments, sonication, and radiation. When the density of polymer chains assembled on a surface is high enough, the polymer chains begin to extend, adopting a brush like conformation.[1, 3] In my thesis research, we are primarily interested in this kind of end-grafted polymer brushes.

There are three major approaches to prepare surface-grafted polymer brushes (Figure 1.3): (1) “grafting to” approach; (2) “grafting from” approach; (3) grafting via surface-attached monomers.[16]

Figure 1.3. Approaches to graft polymers onto substrates.
1.2.1 “Grafting to” approach

“Grafting to” approach is similar to the growth of self-assembled monolayers: A preformed polymer with a reactive end-group is used as the precursor, and the reaction typically occur in liquid phase in order to attach the polymer onto substrates.[5] Common reactive functional groups include thiols, silanes and acid etc. One intrinsic drawback of “grafting to” approach is that it is often difficult to react the end group of a high molecular weight polymer chain with a surface with high yield, and thus the grafting density is usually small. In addition, due to chemical compatibility requirements, the available systems with a suitable reactive end-group and compatible function units in the polymer chain are limited in scope.

1.2.2 “Grafting from” approach

In the “grafting from” approach, polymer chains are synthesized from a surface through immobilization of a monolayer of surface-initiators followed by in-situ polymerization of selected monomers. The “grafting from” approach is often referred to as surface-initiated polymerization (SIP). “Grafting from” is significantly more versatile than “grafting to”, and it has been shown that, through SIP, it is possible to assemble densely packed polymer brushes with low polydispersities from a large variety of monomers in a controllable way.[3] If there is no free monomer in solution, polymerization occurs exclusively at the surface. Importantly, the grafting density of the polymer chains can be finely tuned by varying the grafting density of the surface initiator.[7, 15, 17] Because of its versatility, reliability, and controllability, “grafting from” is attracting significant scientific interest, and it can be utilized in application areas such as colloid stabilization, new adhesive materials, protein-resistant bio-mimetic surfaces, chromatographic separation of organic and biomaterials, and organic-inorganic nanocomposites.[3, 4, 16, 18]
Almost all available polymerization techniques have been applied to graft polymers from substrates. These includes, living ring opening polymerization, living anionic polymerization, living cationic polymerization, ring opening methathesis polymerization (ROMP), nitroxide-mediated polymerization, atom transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT) polymerization.[3, 16, 19]

We are particularly interested in surface-initiated ATRP due to the excellent features of ATRP:[20, 21] First, the polymerization can be carried out in mild conditions such as at room temperature and in aqueous solutions; second, a broad range of vinyl monomers can be polymerized through ATRP, including styrenes, acrylates and methacrylates, acrylonitriles, acrylamides and methacrylamides, acrylic acids and methacrylic acids; third, the polymerization is a controlled/“living” radical chain reaction, and thus the polymer film thickness is easily controllable by adjusting the polymerization time or changing the monomer concentrations.

1.2.3 Grafting via surface-attached monomers

In this approach, polymerizations are carried out at the presence of substrates onto which functionalized monomers have been attached. The surface-attached monomers are incorporated into growing polymer chains in the same way as the monomers in solution (the monomers in solution are usually different from the surface-attached ones).[16] At the initial stage of polymerization, the polymerization rate for both the surface-attached monomers and the “free” monomers in solution should be identical; at the later stage, the surface is crowded with permanently attached oligomers or polymers, and the concentration of “free” monomer becomes very small. The surface polymerization could occur through two routes: (1) a macroradical attacks the free radicals on the surface (“grafting to”), or (2) the “free” monomers attach to the free radicals (“grafting from”). It has been shown that the “grafting to” step is the attaching
mechanism at the later stage, and thus represents a bottle neck to the polymer immobilization[22, 23]. Therefore, very similar layers are obtained by using surface-attached monomers as in “grafting to” approach. The major drawbacks of this approach are: (1) the surface topography of polymer films is less smooth compared to those in “grafting from” approach, due to the combination of two growth mechanisms at different stages of the polymerization;[16] (2) the available end-functionalized monomers are limited. Therefore this approach is not often used comparing to the “grafting from” approach.

1.3 Patterning of Polymer Thin Films on Silica Substrates

Microscopically and nanoscopically patterned polymer brushes have shown promise as components in microelectronics, cell-growth regulation, biosensors, microreaction vessels, and drug delivery.[3, 9, 10] There are two major techniques to prepare patterned polymer brushes in literature: optical photolithography method and microcontact printing.

1.3.1 Optical lithography

The principle of optical lithography is simple. A light sensitive photoresist is spun onto a substrate forming a thin layer on the surface. The resist is exposed to light through a mask with the desired pattern. The resist is then developed in a solvent which contains reactive chemical reagents. Depending on the type of photoresist, different regions of the photoresist film will be removed after the development step as a result of different photochemistry involved in the exposure step. In general, the exposed region of a positive-type resist is removed, whereas the unexposed region of a negative-type resist is stripped away during development. The pattern is transferred from the photomask to the substrate. Although the principle of photolithography is
straightforward, the actual implementation can be very expensive and time consuming, due to the high demands on resolution, placement accuracy, throughput, and defect density.[24]

1.3.2 Microcontact printing on silica

With the microcontact printing technique developed in the Whitesides group,[25, 26] microscale patterning of end-grafted polymer brushes on gold and silica surfaces has been achieved.[9, 27-34] In general, microcontact printing is a cost-efficient method to create two-dimensional patterns of organic materials on both hard and flexible surfaces with spatial resolutions approaching 250 nm (and better in specific cases).[35] Recently there have been multiple publications reporting the synthesis and properties of patterned polymer brushes on gold substrates,[9, 29-32] but very few publications on patterned polymer brushes on silica surfaces.[27, 33, 34] This may be because the reproducible formation of organosilane monolayers on silica can be difficult, and the film quality is sensitive to the details of the reaction conditions including temperature, solvent, water content of the solvent, and deposition time.[36-38] But recent publications have demonstrated that by controlling the reaction conditions carefully, highly ordered alkyltrichlorosilane based SAMs can be reproducibly patterned.[27, 37, 39] Inherently, patterned polymer brushes on silica have many advantages over similar brushes on gold. The silane/silica interface is much stronger than the thiol/gold interface. The S-Au bond energy is 30-40 kcal/mol[30] while the Si-O bond dissociation energy is 96-133 kcal mol⁻¹ and the Si-C bond dissociation energy is 90-95 kcal/mol.[40] The stability of polymer brushes formed on silica surfaces can be further increased with the crosslinked polysiloxane structure formed on the substrate surface when multifunctional silanes are used as end grafting agents.[37] Silica substrates are low in cost, stable (high tolerance to UV, heat, sonication and oxidation), smooth, and easy to prepare, whereas gold films are prone to delamination (at least in our
laboratory), sometimes rough,[36] and require more effort to prepare and handle. Additionally, patterning on oxidized silicon wafers may be compatible with integrated circuit technology, and, silica substrates are transparent, which is a significant advantage for optical studies.

1.4 Fluorescence Recovery after Photobleaching (FRAP)

There is a rich amount of literature on the diffusion of small molecular probes in thin polymer films.[41-46] The scientific motivation has been to answer how the chain conformation, glass transition, crystallization, permeability, and relaxation dynamics of polymer thin films (typically tens of nm to a few micron thick) differ from bulk materials.[42] Fluorescence-based techniques including FRAP and fluorescence correlation spectroscopy (FCS) have been applied to quantitatively characterize the transport of fluorescent molecules in polymer thin films.[46]

FRAP is chosen as our principle method to study diffusive transport. FRAP is commonly used in biological science to measure the mobility of fluorescent species over micron and submicron length scale.[46-49] Briefly, a small area or volume of a fluorescent material is photobleached by a short exposure to an intense focused laser beam, using one-photon or two-photon excitation. The recovery of the fluorescence is then monitored. The recovery of fluorescence occurs due to the transport of unbleached fluorophore from surrounding regions to the photobleached region.[46, 49] From FRAP experiments, one can learn: (a) transport process type, for example, random diffusion, directed flow, or a mixed process; (b) diffusion coefficient; and (c) the fraction of mobile fluorescent dye molecules.[50]

The FRAP technique in this thesis utilize the region of interest (ROI) function on a confocal laser scanning microscope (CLSM) to bleach circular areas: the laser beam is modulated by an electric-optical modulator (EOM) which selectively blocks it during rastering to result in the user-defined bleach geometry. Subsequently observed fluorescence recovery
Figure 1.4 (a) is assumed to occur from molecular diffusion in the 2-dimensional plane of the bleached region. The resulting fluorescence intensity versus distance profiles (i.e. concentration files) are extracted after image analysis using a program written in C.\cite{51, 52} Simulated concentration profiles are generated following Fick’s law (Figure 1.4 (b), see derivations below), and compared with the experimental results to determine the diffusion coefficient.

We consider the diffusion in our system occurring in an infinitely thin sheet in a long circular cylinder in which the diffusion is uniform along the radial direction. The concentration of diffusing molecules is a function of radius \( r \) and time \( t \).\cite{53}

\[
\frac{\partial C}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C}{\partial r} \right) \tag{1.1}
\]

The initial concentration distribution is: \( C = 0, 0 < r < r_0 \); the boundary condition is: \( C = C_0 \ (r \to \infty, \ t) \). Define \( C_1 = C_0 - C \), Equation (1.1) is changed to:

\[
\frac{\partial C_1}{\partial t} = D \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_1}{\partial r} \right) \tag{1.2}
\]

Now the boundary condition is \( C_1 (r \to \infty, \ t) = 0 \). After separation of variables, \( C_1 (r,t) = U(r) T (t) \), we can get the following equation:\cite{51-53}

\[
\frac{1}{T} \frac{dT}{dt} = \frac{D}{U} \left( \frac{1}{r} \frac{dU}{dr} + \frac{d^2U}{dr^2} \right) = -\alpha^2 D \tag{1.3}
\]

The general solutions to Equation (1.3) can be written as

\[
C_1 (r,t) = \int_0^\infty \alpha \alpha A(\alpha) J_0(\alpha r) e^{-\alpha^2 Dt} \tag{1.4}
\]

in which \( J_0 \) is Bessel function of the first kind \( (0^{th} \text{ order}) \). After imposing the initial condition, the final solution is:

\[
C(r,t) = C_0 - C_0 r_0 \int_0^\infty \alpha \alpha A(\alpha) J_1(\alpha r) e^{-\alpha^2 Dt} \tag{1.5}
\]

The complete derivation can be found in Ref. \#53, and the full descriptions of FRAP procedure and data analysis in our studies have been published elsewhere. \cite{51, 52}
Figure 1.4. Schematic representations of (a) FRAP images and (b) simulated fluorescence intensity profiles.

1.5 References


CHAPTER 2

PRODAN DIFFUSION ON SELF-ASSEMBLED MONOLAYERS ON SILICA


2.1 Introduction

This chapter discusses the diffusion of 6-propionyl-2-dimethylaminonaphthalene (Prodan, Figure 2.1(a)), on three organic surfaces and a bare silica surface: silanated poly(ethylene glycol) (PEG, Figure 2.1(b)), chlorotrimethylsilane (CTS, Figure 2.1(c)), and octadecyltrichlorosilane (OTS, Figure 2.1(d)) grafted to silica, and clean (piranha-treated) silica. Due to the covalent bonding at the substrate surface, the SAMs are immobile, and diffusion of Prodan occurs in or on the SAMs (solvent free). Since these four different surfaces have distinctly different surface chemistry, we expect that SAM-Prodan interaction in these systems plays an important role in determining the transport dynamics of Prodan. [1, 2]

![Chemical structures of (a) Prodan, (b) silanated PEG2000, (c) chlorotrimethylsilane, and (d) octadecyltrichlorosilane.](image)

*Figure 2.1.* Chemical structures of (a) Prodan, (b) silanated PEG2000, (c) chlorotrimethylsilane, and (d) octadecyltrichlorosilane.
2.2 Experimental

2.2.1 Materials

Octadecyltrichlorosilane (98%) and chlorotrimethylsilane (97%) were purchased from Aldrich and used as received. Silanated PEG2000 is synthesized according to literature procedures.[3, 4] Poly(ethylene glycol) methyl ether (m-PEG, average Mₙ ca. 2000) and dibutyltin dilaurate were purchased from Aldrich. 3-Isocyanatopropyltriethoxysilane (IPTS) was purchased from Gelest. 6-Propionyl-2-dimethylaminonaphthalene (Prodan) was purchased from Molecular Probes.

2.2.2 Instrumentation

A 400 MHz NMR spectrometer (Unity 400, Varian) was used to collect the ¹H-NMR spectrum of the silanated PEG 2000. IR spectrum (512 scans at 4 cm⁻¹ resolution) of the silanated PEG 2000 was collected using a Nexus 670 FT-IR E.S.P. (Thermo Nicolet). The molecular weight and polydispersity of the silanated PEG 2000 were tested using Waters 2410 GPC (RI detector, three Waters Styragel columns HT2 + HT3 + HT4, polystyrene as standard and THF as eluant at a flow rate of 1.0 mL/min). A Gaertner Ellipsometer Model L116C (Gaertner Scientific Corp.) was used to measure the thickness of the SAMs. Contact angle data was collected using a Ramé-Hart Goniometer (Model 100-00). A spincoater (Speedline Technologies, Specialty Coating Systems, Inc., Model P6204) was used to deposit Prodan solution onto the SAM modified surfaces. A Leica confocal laser scanning microscope (Model TS SP2) equipped with Ti:Sapphire tunable wavelength laser (Tsunami, Spectra-Physics) was used to collect fluorescence recovery after photobleaching (FRAP) images, and samples were
tested under continuous flow of nitrogen or nitrogen with controlled relative humidity using a custom-made sample holder.[1, 2]

2.2.3 Synthesis of silane-functionalized PEG

The synthesis (Scheme 2.1) was adapted from published procedures.[3, 4] Briefly, m-PEG (20 g, 0.004 mol) was dissolved in 150 ml of toluene in a 250 mL round-bottomed flask. 120 mL of toluene and as much water as possible were distilled out of the mixture via azeotropic distillation. 100 ml of dry THF (distilled over CaH$_2$) was then added to the mixture. IPTS (2.5mL, 0.01 mol) and dibutyltin dilaurate (0.23 mL, 0.4 mmol), dissolved in 20 mL of dry THF, were added dropwise to the m-PEG solution while stirring with a magnetic stirrer. The reaction mixture was stirred continuously for 48 hours at room temperature under dry nitrogen. After the reaction, the silanated PEG 2000 (Figure 2.1) was precipitated twice with petroleum ether, and then dried in vacuo. A white powder was obtained after drying. $^1$H NMR (CDCl$_3$): $\delta$ 0.58-0.66 (t, 2H), 1.38-1.46 (t, 9H), 1.56-1.66 (m, 2H), 3.12-3.22 (q, 2H), 3.52-3.76 (m, 180H), 3.40-3.48 (q, 6H), 3.74-3.85 (q, 6H), 4.16-4.24 (t, 2H). IR (512 scans, 4cm$^{-1}$): 840-1540 cm$^{-1}$ (v: C-O, C-C, C-Si, O-Si; $\delta$: C-H), 1724 cm$^{-1}$ (C=O, $\nu$), 2890 cm$^{-1}$ (CH$_2$ and CH$_3$, $\nu_{as}$), 2950 cm$^{-1}$ (CH$_2$, $\nu_{as}$), 2974 cm$^{-1}$ (CH$_3$, $\nu_{as}$), and 3356 cm$^{-1}$ (N-H, $\nu$). FTIR (512 scans, 4cm$^{-1}$): 1112 cm$^{-1}$ (C-O, $\nu$), 1445 cm$^{-1}$ (C-H, $\delta$), 1735 cm$^{-1}$ (C=O, $\nu$), 2858 cm$^{-1}$ (CH$_2$, $\nu_{as}$), and 2935 cm$^{-1}$ (CH$_2$, $\nu_{as}$). GPC characterization confirmed that the average number of ethylene oxide unit in PEG 2000 silane is ~45 and the polydispersity is ~1.08.

Scheme 2.1
2.2.4 Self-assembled monolayers (SAMs) formation

Fisherbrand microscope coverslips (22 mm x 22 mm x 0.17 mm) and silicon (100) wafers (25 mm x 25 mm x 0.5 mm) were cleaned in boiling piranha solution (3:1 v/v mixture of concentrated H₂SO₄ and 30% aqueous H₂O₂ solution) (CAUTION: piranha solutions are strongly oxidizing and should not be allowed to contact organic solvents.) for 3 hours. They were subsequently rinsed with an excess of Millipore® water (18.2 MΩ·cm) and dried with nitrogen.

Monolayers were formed by submerging cleaned substrates in hexane solutions of OTS or CTS (2 mM) for one hour. Samples were then sonicated in hexane to remove excess material from the surface and subsequently rinsed in hexane, ethanol and finally deionized water before being dried with nitrogen.

PEG layers were formed using the following procedure. 100 mg of silanated PEG 2000 was dissolved in 20 mL of ethanol and 1 mL water; hydrochloric acid was added until a drop of the solution turns pH paper a color corresponding to a pH of 2. The substrates remained in solution for two days at room temperature and were subsequently rinsed with ethanol and deionized water and blown dry with nitrogen.

2.2.5 Characterization of SAMs on silica

Ellipsometry thickness data were collected on the SAMs grafted on silicon wafers. At 632.8 nm (wavelength of incident light), the refractive index and extinction coefficient of the substrate are 3.85 and -0.02 respectively, and those of the organic layer are assumed to be 1.46 and 0 respectively. The thickness of the native oxide was subtracted from the measured thickness of the deposited layer.
Water contact angle data were collected both on SAMs on silicon wafer and on silica coverslips.

2.2.6 Fluorescence recovery after photobleaching (FRAP) procedure

Solutions of Prodan in ethanol were spin-coated onto the SAM modified surfaces at 2000 rpm. The dye solution concentration is 10 µM, and the final aerial concentrations of Prodan is 0.02 nm⁻², which corresponds to surface coverage of 2.4%.

A detailed description of the FRAP procedure can be found elsewhere.[1, 2] Here it will be described briefly. A 63× oil immersion objective (NA=1.32) was used and the field of view is 238 µm×238 µm. The pulsed IR laser was tuned to 780 nm to excite Prodan and the pulse width was ~ 57 fs. An electro-optical modulator (EOM) was used to modulate the laser intensity in order to draw region-of-interest (ROI) features. A circular area with a diameter of 119 µm was bleached in the center of the field of view by rastering the laser beam and selectively blocking it with the EOM. Bleaching was performed until the observed fluorescence did not change. Subsequent fluorescence images were taken at time intervals relevant to the specific system. The resulting fluorescence intensity profiles of all the captured images were analyzed according to literature methods to extract diffusion constants.[1, 2, 5]

2.3 Results and Discussion

2.3.1 Contact angle and ellipsometry thickness

The water contact angle and ellipsometry data of the SAM modified surfaces are listed in Table 2.1. PEG grafted surfaces show a small water contact angle, indicating a fairly hydrophilic surface. The thickness of the PEG layer is 14 Å, and this is reasonable for a monolayer prepared
using “grafting to” approach. The contact angle data of OTS modified surface has confirmed the formation of highly hydrophobic surface. The CTS surface has an intermediate value of contact angle, and it is attributable to incomplete surface coverage of the CTS silane due to the steric hindrance of the trimethyl group in the molecule. The CTS modified surface is therefore a two-phase heterogeneous surface: one component is CTS silane (assuming pure CTS has the same contact angle as OTS) and the other is pure silica. Using a Cassie approximation,[6, 7] the CTS coverage can be calculated.

\[
\cos \theta_{\text{total}} = f_1 \cos \theta_{\text{CTS}} + f_2 \cos \theta_{\text{silica}}
\]  

In Equation 2.1, \( f_1 \) is the surface coverage of CTS silane and \( f_2 \) is the surface coverage of silica. Assuming \( \theta_{\text{CTS}} \approx \theta_{\text{OTS}} \), \( f_1 \) is estimated to be \( \sim 0.48 \), which means only half of the CTS silane treated surface is actually grafted with CTS.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Contact Angle (º)</th>
<th>Thickness(Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>33 ± 0.5</td>
<td>14 ± 1.5</td>
</tr>
<tr>
<td>CTS</td>
<td>70.5 ± 0.5</td>
<td>60.5 ± 0.5</td>
</tr>
<tr>
<td>OTS</td>
<td>109 ± 1</td>
<td>93 ± 4</td>
</tr>
<tr>
<td>Clean glass</td>
<td>14 ± 1.5</td>
<td>0</td>
</tr>
</tbody>
</table>

### 2.3.2 Diffusion coefficients

A typical set of FRAP images are presented in Figure 2.2(a), and the experimental data(symbols) and simulated data (lines) of fluorescence intensity profile versus radial position as a function of time are presented in Figure 2.2(b).

Diffusion coefficients of Prodan on various surfaces under dry nitrogen and wet nitrogen with controlled humidity are summarized in Table 2.2.
Figure 2.2. FRAP on PEG modified surface at a Prodan aerial concentration of 0.02 nm⁻². (a) 2-Photon imaging of fluorescence recovery; (b) experimental (symbols) and simulated (lines) intensity vs. radial position as a function of time for varying values of $D$; the solid lines are for $D = 30 \mu m^2/s$; the dotted and dashed lines which lie below and above each solid line are for 20 $\mu m^2/s$ and 40 $\mu m^2/s$, respectively.

Table 2.2. Diffusion coefficients of Prodan on SAMs under different humidity.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Relative Humidity (%)</th>
<th>Diffusion Coefficient (µm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>0</td>
<td>18-30</td>
</tr>
<tr>
<td>PEG</td>
<td>45</td>
<td>25-30</td>
</tr>
<tr>
<td>PEG</td>
<td>90</td>
<td>25</td>
</tr>
<tr>
<td>CTS</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>CTS</td>
<td>22</td>
<td>18-25</td>
</tr>
<tr>
<td>CTS</td>
<td>30</td>
<td>18</td>
</tr>
<tr>
<td>CTS</td>
<td>45</td>
<td>18</td>
</tr>
<tr>
<td>OTS</td>
<td>0</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>glass</td>
<td>0</td>
<td>&lt;0.05</td>
</tr>
</tbody>
</table>

Prodan diffusion on PEG in dry nitrogen is slightly faster than on CTS in dry nitrogen. Varying the level of relative humidity does not result in a significant difference in the measured diffusion on PEG. A slight increase of diffusion coefficient, from 10 to 18 $\mu m^2/s$, is observed on the CTS surface at relative humidity levels greater than zero. Although the difference is within the error of one experiment, the measured diffusion constant on the CTS surface was highly reproducible, and thus we believe the difference is real.
Our surfaces can be divided into two categories: surfaces on which Prodan diffuses noticeably during the time scale of the experiment and surfaces on which it does not. The PEG and CTS surfaces fall under the first category and the clean silica and OTS surfaces fall under the latter. If one assumes that diffusion takes place on, and not in and through, the layer, which may not be entirely true on the PEG surface, the surface free energy seems to be the most important variable to consider. Figure 2.3 illustrates the two diffusion mechanisms of Prodan: on or in the SAMs. It appears that the PEG and the CTS surfaces which have the intermediate surface free energies, with water contact angles of 33° and 68° respectively, are more conducive to Prodan diffusion than OTS surface which have very low surface free energy as shown by its water contact angle of 109°, or the clean silica surface which has the high surface free energy as indicated by a water contact angle of 14°.

![Figure 2.3. Schematic representations of the diffusion of an individual probe molecule. (a) on a surface; (b) in and through the layer.](image)

Prodan is about 5 times more soluble in methanol (~20 mM) than in the less polar solvent hexane (~4.4 mM). Thus, we expect that it is likely to aggregate on the hydrophobic OTS derived surface. The fluorescence intensity of samples from the same Prodan concentration on the OTS surface is significantly lower than on the PEG or CTS surface, which is a strong indication of aggregation since dye aggregates are commonly known to self-quench.[8, 9] We
also sometimes observe bright dots on the OTS surface at higher dye concentrations. These “aggregates” are not observed on the PEG surfaces. It seems likely that diffusion of dye aggregates would be slower than that of well-dispersed small molecules, thus aggregation may be the reason no diffusion is observed on OTS during the time scale of the experiment.

The reason that diffusion is not observed on the clean hydrophilic silica surface is less clear; possibilities include aggregation and hydrogen bonding. The solubility limit of Prodan in water is quite low (3.5x10^{-6} M) indicating that aggregation on a polar surface is possible. However, diffusion may be limited even if Prodan molecules are well-dispersed because the piranha-treated glass surface contains a high concentration of silanol groups with which Prodan can form hydrogen bonds, making the energy barrier for diffusion considerably higher than it is for the other surfaces. The low fluorescence intensity from the same concentration of Prodan on a glass surface, compared to a PEG or CTS surface, may be due to either aggregation or hydrogen bond related quenching, (as is thought to occur for the fluorescent amino acid tyrosine).[10]

CTS is a small, branched molecule and unlike OTS which can form three bonds with the substrate, CTS only forms one bond to the substrate. The three methyl units of an attached CTS molecule sterically inhibit attachment of additional CTS molecules so that there are still ~50% unreacted silanol groups on the substrate. Due to the lack of van der Waals interactions between the attached CTS molecules, the packing is not expected to be ordered.[11] The CTS molecules on the surface should be homogenously random and isolated, as opposed to forming inhomogeneous islands on the surface (it lacks enthalpic driving force for CTS molecules to form islands). As a result, the CTS derived layer has partially exposed hydrophilic sites, i.e. silanol groups, with which the Prodan molecules can interact to improve their dispersion; on the other hand, because
half of the surface area is still coated with CTS molecules, Prodan molecules are not as strongly bound as they are to the clean silica surface, and therefore diffusion is possible. Unlike CTS, OTS forms a highly ordered, crystalline layer that is measured to be ~28 Å thick, which corresponds closely to the extended chain length of the molecule.[12] Because the OTS layer is both thicker and more ordered than the CTS derived surface, unreacted and exposed silanol groups and pockets are much less likely.

Our hypothesis for diffusion on the CTS surface suggests that the Prodan molecules may be interacting with the surface, and thus are partially “in” the layer rather than strictly “on” it. Prodan molecules are roughly 17 Å long and 7 Å wide and the CTS SAM is about 3 Å thick so the diffusing species must still exist mainly above the layer, however the ability of Prodan to partially interact with the underlying substrate may lead to a better dispersion of dye molecules on this surface than on OTS, which may lead to the greatly increased observed diffusion. On the PEG layer, which is 14 Å thick and probably amorphous, the possibility for partial insertion of the diffusing species is greater. As one extends to thicker and thicker layers, of PEG or other polymers, this question of “in” or “on” becomes increasing relevant and interesting to study.

Our FRAP results on various surfaces lend some insight into the nature of the diffusion observed. The fact that there are surfaces on which Prodan does not diffuse, specifically OTS and the clean glass, indicates that the diffusion is indeed two-dimensional in nature, and not through the overlying gas phase. If the fluorescence recovery was primarily due to dye molecules subliming and recondensing on the bleached region of the substrate, fluorescence recovery would be observed on at least the OTS surface, and probably on the clean glass surface as well. Although hydrogen bonding between Prodan and the clean glass may be a barrier for sublimation as well as diffusion, hydrogen bonding can not be present between the OTS surface
and the dye, and thus recovery due to sublimation and recondensation would be expected to take place on that surface if possible on any of the surfaces studied. The fact that the fluorescence recovery on the OTS surface is insignificant compared to the CTS or PEG functionalized surfaces rules out sublimation as a major contributor to the fluorescence recovery.

The effect of relative humidity on the rate of diffusion was not substantial. On the PEG surface, the value of $D$ determined from FRAP images taken from different spots on the same sample at the same relative humidity had as much variation (18 to 30 $\mu m^2/s$) as the value of $D$ determined for different relative humidities, and so it is impossible to determine a trend from this data. On the CTS surface, the difference in $D$ between 0% and 25% relative humidity (and above) is small (10 vs. 18 $\mu m^2/s$), but $D$ at elevated relative humidity is consistently greater than under completely dry nitrogen. Possibly, water molecules are interacting with exposed silanol groups which may block the Prodan from hydrogen bonding with the substrate. Water could also decrease other barriers to Prodan diffusion of which we are not yet aware.

Finally, we would like to compare the diffusion rates we observe in our systems with diffusion rates reported in literature for similar systems. Poly(ethylene glycol) was found to diffuse on the surface of an OTS monolayer with $D$ decreasing from ~ 1 to 0.01 $\mu m^2/s$, as the molecular weight increased from 2,200-30,500 g/mol.[13, 14] This is at least an order of magnitude lower than the $D$ values we calculated for diffusion of Prodan on CTS and PEG surfaces, but this is for diffusion of a polymer molecule which is at least an order of magnitude larger than the dye molecule studied in our system. The lateral diffusion constant of fluorescence-labeled lipids on supported phospholipid membranes was found to be 3.5 $\mu m^2/s$.[15] Tracer (dye molecule) diffusion in a free-standing smectic liquid-crystal was found to have a diffusion constant of 8 $\mu m^2/s$ in films 4 molecules thick. [16] These systems are similar to ours
in that they are all two-dimensional small molecule systems. The diffusion rates reported for the lipid bilayer and liquid-crystal film are similar to the diffusion constants we found for Prodan diffusion on CTS and PEG surfaces. As mentioned above, the lipid experiments are fundamentally different from ours in that the diffusing molecules and the medium are the same, and both are mobile. The diffusing and medium molecules in the tracer-liquid crystal system are chemically different but, again, the medium molecules are able to diffuse. Apparently, the immobility of the medium in our system does not significantly limit the mobility of the diffusing species. This is another indication that the important parameters for our system are the interaction of the diffusing species with the medium, the free volume of the medium, and, perhaps for the grafted-polymer case, the mobility of the polymer segments.

2.4 Conclusions

FRAP is used to determine diffusion coefficients for the dye Prodan on clean silica substrate, SAMs on silica formed from CTS and OTS, and silanated PEG 2000. Similar diffusion coefficients are found for the CTS and PEG layers, which is speculated to be due in part to the ability of Prodan to partially intercalate in these layers enabling good dispersion and diffusion. No fluorescence recovery is observed on the OTS SAM or on the clean silica surface. Prodan is thought to aggregate on the former and form hydrogen bonds with and possibly aggregate on the latter. Importantly, in systems where diffusion is observed, Prodan diffusion is determined to take place on the various surfaces and not through the gas phase. There is no significant change in the rate of diffusion with relative humidity on the PEG layer, but there is a slight increase on the CTS SAM.
2.5 References


CHAPTER 3

PATTERNED POLY(N-ISOPROPYLACRYLAMIDE) BRUSHES ON SILICA SURFACES


3.1 Introduction

We are interested in building quasi two-dimensional “smart” and stable molecular devices which are able to confine and regulate molecular diffusion, generate and conduct molecular signals upon receiving external stimuli as well as provide templates for the growth of biological molecules. In this study, we present our results on the patterning of poly(N-isopropylacrylamide) (PNIPAAm), which was selected because it has the potential to be responsive in aqueous environments near room temperature.

PNIPAAm is particularly interesting because it is biocompatible and thermoresponsive, exhibiting a lower critical solution temperature (LCST) near room temperature.[1-6] Free PNIPAAm chains in pure water undergo a sharp LCST phase transition at 32 ± 1-2 °C.[1] In contrast, a broadened LCST transition was first predicted[7] and then observed for PNIPAAm brushes.[8, 9] The general LCST behavior of end-grafted PNIPAAm is thought to be dependent on the geometry of the substrate, the grafting density of the polymers, and the polydispersity of the polymer.[7, 9-13]

Unpatterned PNIPAAm brushes have been grafted onto polystyrene culture dishes,[14] latex or microgel particles,[8, 15] planar gold surfaces,[9, 13] gold nanoparticles,[10] planar silica substrates,[12, 16, 17] and silica particles.[18, 19] Patterned PNIPAAm brushes have been
formed on gold through microcontact printing or scanning-probe lithography followed by surface-initiated atom transfer radical polymerization (ATRP) of NIPAAm.[20, 21]

In this chapter we discuss the synthesis and patterning of end-grafted PNIPAAm brushes on oxide substrates (oxidized silicon wafers and glass) through SIP. We demonstrate the highly reproducible formation of both uniform and patterned PNIPAAm brushes with a high grafting density, a small surface roughness, and a defined thickness. We characterized the chemical composition, thickness, roughness, hydrophilicity, density, and LCST behavior of the PNIPAAm brushes and carried out AFM and fluorescence experiments to confirm the successful micropatterning of the PNIPAAm brushes.

3.2 Experimental

3.2.1 Materials

All chemicals were purchased from Acros unless otherwise noted. Aminopropyltriethoxysilane (APS, 99%), 2-bromo-2-methylpropionic acid (BriBuA, 98%), 4-dimethylaminopyridine (DMAP, 99%), N, N’-dicyclohexylcarbodiimde (DCC, 99%), and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99+%) were used as received. N-isopropylacrylamide (NIPAAm, 99%) was purified by passing through an inhibitor removal column using a mixture of dichloromethane and n-hexane (v/v ~ 3:1) as the solvent and then recrystallized. Octadecyltrichlorosilane (98%), copper (I) bromide (99.999%) and the inhibitor removal columns were purchased from Aldrich and used as received. 6-propionyl-2-dimethylaminonaphthalene (Prodan) was purchased from Molecular Probes.
3.2.2 Instrumentation

A Gaertner Ellipsometer Model L116C (Gaertner Scientific Corp.) with a HeNe laser ($\lambda=632.8$ nm) was used to measure the thickness of the SAMs and the polymer brushes. Contact angle data was collected under ambient conditions using a Ramé-Hart Goniometer (Model 100-00). XPS was collected using a Kratos Axis ULTRA Imaging X-ray Photoelectron Spectrometer (Kratos Analytical Ltd.). FTIR spectra, 512 scans at 4 cm$^{-1}$ resolution, were obtained using a Nexus 670 FT-IR E.S.P. (Thermo Nicolet). AFM was done using a tapping mode etched silicon probe (Digital Instruments) on a Dimension 3100 AFM (Digital Instruments). X-ray reflectometry (XRR) data was collected using an X’pert 2 (Philips) and data analysis was performed using the WinGixa Reflectivity software package (Philips). The fluorescence emission spectra of Prodan were collected using a Jobin-Yvon Spectrometer (Model FluoroMax-3). A Zeiss Axiovert 100 inverted light microscope (Carl Zeiss Inc.) equipped with a mercury excitation lamp, a CoolSnap fx CCD camera and a triple band filter (Chroma) was used to acquire the fluorescent microscopy data of Prodan in the patterned PNIPAAm brush. A Leica confocal laser scanning microscope (Model TS SP2) equipped with Ti:Sapphire tunable wavelength laser (Tsunami, Spectra-Physics) was used to collect fluorescence recovery after photobleaching (FRAP) images, and samples were tested under continuous flow of nitrogen or nitrogen with controlled relative humidity using a custom-made sample holder.

A custom-built environmental cell was used for the variable temperature ellipsometry experiments under water. The sample was heated and cooled at less than 0.5 °C/min.

3.2.3 PNIPAAm brush formation and patterning

Silicon (111) wafers were used as substrates after cleaning in boiling H$_2$SO$_4$:H$_2$O$_2$ (v/v: 3/1) (CAUTION: piranha solutions are strongly oxidizing and should not be allowed to contact
organic solvents.) for 30 minutes followed by rinsing with an excess of Millipore® water (18.2 MΩ·cm) and drying with a stream of nitrogen. Glass cover slips used as substrates for PNIPAAm brush samples for fluorescence microscopy and FRAP were cleaned using the same procedure.

The patterning procedure is illustrated in Figure 3.1. First, a SAM of OTS was microcontact printed following a published procedure.[22] A 10 mM solution of OTS in hexane was inked onto a PDMS stamp using a conventional spin coater at 2000 rpm for 30 s. The inked PDMS stamp was dried with a stream of nitrogen for 10 s, and then was brought into contact with a freshly cleaned silicon wafer for 30 s. The OTS-patterned samples were subsequently sonicated in hexane and then ethanol before drying with nitrogen.

APS was backfilled into the unprinted regions by immersing the OTS-patterned wafers in a 10 mM solution of APS in hexane for 2 hours. After rinsing with hexane and ethanol and drying with nitrogen, the surface initiating unit was attached to the patterned OTS/APS SAMs following a published procedure.[23] The samples were immersed in a solution of BriBuA (267 mg) and DMAP (48 mg) dissolved in 80 mL of dichloromethane. The solution was cooled to 0 °C, and a solution of DCC (413 mg) in 10 mL of dichloromethane was added. The reaction was allowed to warm to room temperature and proceed overnight. Then the wafers were rinsed with dichloromethane, hexane, and ethanol and dried with nitrogen.

The surface initiated polymerization of N-isopropylacrylamide was performed using a procedure modified from a literature reference.[20] NIPAAm (12.6 g, 110 mmol), CuBr (160 mg, 1.11 mmol) and PMDETA (700 µL, 3.34 mmol) were dissolved in 120 mL of MeOH/H₂O mixture (v/v: 1:1) and degassed by two freeze-thaw cycles. The monomer and catalyst solution was then transferred via a canula into the degassed Schlenk tubes containing the silicon wafers
patterned with OTS and the initiator SAMs. The polymerization was carried out at room temperature under a nitrogen atmosphere for 30 to 120 min. At the conclusion of the reaction, the Schlenk tubes were disconnected from the nitrogen line and the substrates were rinsed extensively with H₂O followed with sonication in EtOH and then H₂O. After drying with a nitrogen stream, the samples were stored in a nitrogen dry box.

Figure 3.1. Schematic procedure for micropatterning of PNIPAAm brushes on silica substrates.

Unpatterned PNIPAAm brushes were prepared following the same procedure as the patterned PNIPAAm samples except that the OTS patterning step was skipped. As a result, PNIPAAm chains were grafted over the entire surface of the silicon substrates. The chemical route of the PNIPAAm brush synthesis is shown in Scheme 3.1.
3.2.4 Characterization of the PNIPAAm brush

XPS, FT-IR, XRR, ellipsometry, contact angle goniometry, and fluorescence spectroscopy data was collected on unpatterned PNIPAAm brush samples. Specifically, for the fluorescence spectroscopy experiments, an ethanol solution of Prodan (1×10⁻⁴ M) was deposited onto unpatterned PNIPAAm brushes on silicon wafers; after waiting 5 minutes the samples were spin-coated at 900 rpm for 60 seconds. For ellipsometry, the refractive index of the dry PNIPAAm films is assumed to be 1.46 for films less than 50 nm thick. For thicker PNIPAAm films, ellipsometry yields a refractive index of 1.47 to 1.49.

For fluorescence microscopy, an ethanol solution of Prodan was deposited onto patterned PNIPAAm brushes grafted on silica cover slips; after 5 minutes the samples were spin-coated at 2000 rpm for 60 seconds. Fluorescence microscopy imaging was carried out immediately.

3.3 Results

Characterization of the unpatterned PNIPAAm brushes was performed through XPS, FTIR, XRR, ellipsometry, and contact angle goniometry prior to patterning studies to investigate the fundamental characteristics of the surface initiated polymerization on silica substrates.
3.3.1 XPS characterization

XPS was used to confirm both the formation of the surface initiator on the silicon substrate and the successful polymerization of PNIPAAm. XPS was collected from the freshly cleaned silicon wafer, the APS-treated silicon wafer, the surface initiator, and the PNIPAAm brushes. In the spectrum of the clean silicon wafer, there was only one weak C 1s peak, likely due to organic contamination. After treatment with APS, both C 1s and N 1s peaks were observed and the intensity of C 1s was greater than on the bare substrate. Subsequent to grafting the initiator to the APS-treated substrate, the C 1s peak was at 285 eV, the N 1s peak was at 400.1 eV and the Br 3d peak was at 68.8 eV. The N 1s and Br 3d peaks are presented in Figure 3.2.

After polymerization, the chemical composition of a 54 nm thick PNIPAAm brush was determined using XPS (Figure 3.3). The oxygen:nitrogen:carbon molar ratio was determined to be 11.3:12.0:76.4, which agrees with the expected value ratio of 12.5:12.5:75.0 for PNIPAAm (Figure 3.3(a)). The high resolution C 1s spectrum was fit with the 4 peaks expected for PNIPAAm, resulting in a very close match to the experimentally observed spectrum (Figure 3.3(b)). The sp² hybridized carbon atom in the carbonyl group, labeled IV in Figure 3.3(b), is at 287.9 eV and has an integrated molar ratio of 15%, which is very close to the expected value (16.7%). The sp³ hybridized carbon peak at 285.0 eV was divided into three components: peak I at 284.9 eV corresponding to the two CH₃- groups in the isopropyl group and the -CH₂- in the PNIPAAm backbone; peak II at 285.3 eV attributable to the -CH- unit in the PNIPAAm backbone; peak III at 286.2 eV corresponding to the -CH- unit adjacent to the -NH- group. A molar ratio of 3:1:1 for the three components, I:II:III, yielded a match to the overall shape of the
sp³ hybridized carbon peak confirming the chemical composition of the grafted PNIPAAm brushes.

**Figure 3.2.** XPS spectra of the surface initiator on a silicon substrate. (a) N 1s; (b) Br 3d.

**Figure 3.3.** XPS spectra of PNIPAAm brushes on an oxidized silicon wafer. (a) survey spectrum, (b) C 1s high resolution spectrum with peak fitting. The solid curve in (b) is the experimental data and dashed curves the curve fits. The peak maximum of the CC/CH component in (b) was referenced to 285.0 eV.

### 3.3.2 FTIR characterization of PNIPAAm brushes

Transmittance-mode FTIR data was collected from a 54 nm thick PNIPAAm brush grafted on a silicon wafer (Figure 3.4). The N-H stretch at 3314 cm⁻¹ and the C=O stretch at
1650 cm$^{-1}$ confirmed the presence of amide groups in the polymer layer, and the characteristic doublet at 1388 and 1370 cm$^{-1}$ indicated the presence of the isopropyl group.[24]

![FTIR spectrum](image)

**Figure 3.4.** Transmittance-mode FTIR spectrum of a 54 nm thick PNIPAAm brush grafted on both sides of a silicon wafer.

### 3.3.3 X-ray reflectometry of PNIPAAm brushes

The normalized x-ray reflectometry spectrum of a 54 nm thick (ellipsometry calculated thickness) PNIPAAm brush on a silicon wafer is shown in Figure 3.5. The data was fit using a three-layer model of PNIPAAm, the native oxide layer, and the underlying silicon substrate (Figure 3.5, inset). The native oxide is determined to have a density of 2.05 g/cm$^3$ (the density of bulk SiO$_2$ is between 2.00 and 2.65 g/cm$^3$)[25, 26] and a thickness of 1.7 nm which is the same as the thickness determined by ellipsometry. The thickness of the polymer is calculated to be 62.6 nm (which agrees closely with the ellipsometry data from this sample (54 nm)), and the density of the polymer is calculated to be 0.95 g/cm$^3$. 
3.3.4 AFM of patterned PNIPAAm brushes

Tapping mode AFM was used to characterize the surface topography of the patterned substrates at the various stages of growth of the patterned PNIPAAm. The first step in the formation of the patterned polymer brush is the formation of the OTS/APS functionalized surface. In Figure 3.6, the brighter area corresponds to the OTS SAM, and the darker areas correspond to the APS SAM. Small islands of OTS are observed at the edge of the stamped region, which may be due to the reactive spreading of OTS.[22] The OTS coated regions are 10 Å higher than the APS coated regions, which is slightly less than the expected height difference of ~18 Å.
Figure 3.6. Tapping mode AFM topography image of the OTS/APS patterned surface.

Figure 3.7. Tapping mode AFM images of patterned PNIPAAm brushes prepared by surface initiated ATRP. The AFM images were obtained in ambient conditions: (a) topography image; (b) section analysis; (c) surface plot. The PDMS stamp used for creating these patterned PNIPAAm brushes had feature sizes comparable to the resulting PNIPAAm brush.
The AFM images of the patterned PNIPAAm brush are presented in Figure 3.7. The darker region in Figure 3.7(a) is the OTS SAM (lower in topography), and the brighter area is the PNIPAAm brush (higher in topography). The observed height difference between the OTS SAM and the PNIPAAm brush is 32.8 nm. Since the OTS layer is 1.8 nm thicker than the APS layer, the total thickness of the polymer brush is calculated to be 34.6 nm. The RMS roughness of the PNIPAAm brush is 2-4 nm as determined from the AFM topography image.

3.3.5 Thickness and contact angle measurements

The thicknesses of the PNIPAAm brushes were measured with two techniques: ellipsometry and atomic force microscopy (Table 3.1). The contact angles of water on the PNIPAAm brushes are also listed in Table 1. The ellipsometry data was collected from a region on the substrate outside of the printed region. The substrates were completely immersed during polymerization, so the PNIPAAm brush should be similar within and outside the patterned region of the substrate.

Table 3.1. Thickness of and contact angles on PNIPAAm brushes polymerized for 30, 60, and 120 minutes.

<table>
<thead>
<tr>
<th>Polymerization Time (min)</th>
<th>Thickness (nm)</th>
<th>H₂O Contact Angle (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ellipsometry</td>
<td>AFM (patterned polymer)</td>
</tr>
<tr>
<td>30</td>
<td>25 ± 6</td>
<td>13 ± 2</td>
</tr>
<tr>
<td>60</td>
<td>33 ± 8</td>
<td>23 ± 2</td>
</tr>
<tr>
<td>120</td>
<td>48 ± 2</td>
<td>31 ± 3</td>
</tr>
</tbody>
</table>

At room temperature (25 °C) in ambient air, the advancing contact angle of all PNIPAAm samples is about 57°, and the receding angle is around 30°. The large hysteresis between the advancing and receding angles (27°) may result from the swelling of PNIPAAm brush upon contact with H₂O during the contact angle measurement. A few measurements were
taken under 100% relative humidity where the advancing and receding contact angles were reduced by 10-30°, however, there was significant scatter in the data.

### 3.3.6 Thermal response of PNIPAAm brushes

The thermal response of a PNIPAAm brush with a dry thickness of ~21 nm (24 °C under dry N₂) was probed by environmental ellipsometry. Well below the LCST, under water, the PNIPAAm brush is swollen. As the temperature is increased through the LCST, the PNIPAAm brush expels water and contracts, decreasing in thickness and increasing in refractive index. Figure 8(a) shows the PNIPAAm brush thickness as a function of temperature, and Figure 8(b) shows the refractive index of the brush as a function of temperature. The LCST transition appears to occur over the broad temperature range of 20-35 °C, with the majority of the transition between 28 and 35 °C.

![Figure 3.8](image)

Figure 3.8. Thermal response of the PNIPAAm brush under water as a function of temperature. (a) thickness and (b) refractive index, during heating (○) and cooling (▲).
3.3.7 Fluorescence studies

3.3.7.1 Fluorescence spectroscopy and fluorescence microscopy

We have used fluorescence spectroscopy and fluorescence microscopy to characterize the fluorescent properties of the organic dye, 6-propionyl-2-dimethylaminonaphthalene (Prodan), dissolved in the dry PNIPAAm brushes. Prodan is interesting because it has a large excited state dipole moment and thus the wavelength of the fluorescence emission of this molecule is sensitive to the polarity of its local environment. Its emission maximum is 380 nm in cyclohexane, 448 nm in DMF, and 530 nm in water.[27, 28] Through this solvatochromic effect it may be possible to probe the local PNIPAAm environment from the emission of dissolved Prodan. Additionally, if Prodan dissolves in the patterned PNIPAAm, it will be possible to use fluorescence optical microscopy to image the patterned substrates.

Figure 3.9. Fluorescence emission spectrum and fluorescence microscopy image of Prodan in PNIPAAm brushes. (a) Fluorescence emission spectra of Prodan in PNIPAAm brushes tethered on silicon wafers coated with a 100 nm thick thermal oxide, $\lambda_{ex} = 340$ nm. Solid line: Prodan in 108 nm thick PNIPAAm brush; dashed line: Prodan in 57 nm thick PNIPAAm brush; dotted line: 52 nm thick PNIPAAm brush (no Prodan); dash dot line: silicon wafer (no Prodan). (b) Fluorescence microscopy image of Prodan in patterned PNIPAAm brushes grafted on a silica cover slip, $\lambda_{ex} = 395$ nm. The brighter region corresponds to the region covered with the PNIPAAm brush, and the darker region corresponds to OTS.
As shown in Figure 3.9(a), the emission maximum of Prodan is 446 nm in the 108 nm thick PNIPAAm, and 450 nm in the 57 nm thick PNIPAAm brush. As expected, the control samples, the PNIPAAm brush and the bare silicon substrate, do not fluoresce. Fluorescence optical microscopy was performed on patterned PNIPAAm brushes (Figure 3.9(b)). The PNIPAAm region appears brighter and the contrast between the PNIPAAm and OTS regions is very good.

3.3.7.2 FRAP in unpatterned PNIPAAm brushes

FRAP experiments were performed on the unpatterned PNIPAAm brushes in a manner identical to that for the surfaces presented in Chapter 2.

![FRAP data of Prodan in an unpatterned PNIPAAm brush sample. (a) FRAP images; (b) fluorescence intensity profiles.](image)

**Figure 3.10.** FRAP data of Prodan in an unpatterned PNIPAAm brush sample. (a) FRAP images; (b) fluorescence intensity profiles.
FRAP images and corresponding fluorescence intensity verses distance curves are shown in Figures 3.10. In Figure 3.10 (a), the first image shows the region of interest right after bleaching under dry nitrogen; the middle two images show fluorescence recovery under dry nitrogen; the final image shows the fluorescence recovery that occurred in this same spot after the sample was flowed with humid N\textsubscript{2} with 90% relative humidity. In Figure 3.10 (b), fluorescence intensity profiles for these four images are plotted. As we can see, very little fluorescence recovery is observed in the case of bleaching and recovery in dry nitrogen; recovery is observed, however, under nitrogen with 90% relative humidity.

3.3.7.3 FRAP in patterned PNIPAAm brushes

FRAP images of Prodan in a patterned PNIPAAm brush sample (thickness = 50 nm) are shown in Figures 3.11. The brighter squares in the fluorescent image correspond to PNIPAAm brush regions into which more Prodan molecules segregate, as discussed in 3.3.7.1. Although the bleached, isolated PNIPAAm squares are surrounded by OTS lines, fluorescence still recovers.

![Figure 3.11](image)

**Figure 3.11.** FRAP images of Prodan in a patterned PNIPAAm brush sample. (a) right after bleaching; (b) after 40 minutes in dry N\textsubscript{2}; (c) after an additional 10 minutes under humid N\textsubscript{2} with 90% RH. The scale bar applies to all of the images.
3.4 Discussion

The XPS data (Figure 3.2) confirmed the presence of N and Br within the initiator SAM, indicating that the initiator formation was successful. The XPS spectra (Figure 3.3) and the FTIR data (Figure 3.4) confirmed the chemical structure of the PNIPAAm brush on the silicon wafer.

Through XRR, ellipsometry, and contact angle measurements, we have studied the basic physical properties of the PNIPAAm brushes formed on SiO$_2$ including density, thickness, and water contact angle. The literature values for the density of bulk PNIPAAm range from 1.07 g/cm$^3$ to 1.12 g/cm$^3$,[1] however XRR indicated the PNIPAAm brushes have a density of 0.95 g/cm$^3$, which is ~15% less than the bulk density. Previous reports have observed a decrease in density in polymers which extends over two to three statistical segment lengths near a solid substrate when the polymer interacts weakly with the substrate.[29] Similar substrate effects may contribute to some extend to the lower polymer density observed in our experiments. Also, the density near the surface may be reduced due to the random nature of surface attachment points on an oxide substrate.

The water contact angles in ambient conditions, shown in Table 3.1, of the PNIPAAm brushes with different thicknesses are almost identical, implying that the surface chemistry and roughness of these polymer brushes are independent of thickness. This is reasonable since the polymer brushes were prepared under identical conditions with the only difference being the polymerization time. The contact angle measurements on the PNIPAAm brushes showed a large hysteresis between the advancing and receding contact angles of water which may be caused by swelling of the polymer brush upon contact with H$_2$O. Although the results were not as uniform, the contact angles under 100% relative humidity were 10-30° less than in ambient. Published
advancing water contact angles for PNIPAAm films include 66 ± 1°,[9] 59.5° to 64.3°,[16] and 48°.[14] Our advancing contact angle of 58° falls within the reported data range, and the reported distribution may simply be a function of relative humidity and temperature.

As presented in Figure 3.6, the OTS monolayer can be printed with an edge resolution of better than 1 µm. While small OTS islands form near the printed line edge due to reactive spreading, these islands are still within 500 nm of the edge and thus will only be a problem if very high resolution patterning is required.[22, 30] Another potential drawback to the OTS monolayer is that OTS chains lack the long-range order commonly found in alkanethiolate SAMs.[22] However, these drawbacks are of little concern for this work, since the OTS serves simply to prevent the attachment of APS and thus growth of PNIPAAm in specific regions. As can be observed in Figure 3.7, the OTS monolayer has a sufficiently high density and adherence to the substrate to prevent the underlying SiO₂ from reacting with APS. Thus, PNIPAAm is only formed outside of the OTS printed regions.

The PNIPAAm thickness calculated from the AFM images of the patterned samples was less than the thickness measured by ellipsometry for all samples. Perhaps the polymer brush was compressed by the AFM tip, in which case, the measured topography underestimated the height of the polymer film. A recent paper[20] has reported similar observations from AFM in comparison to ellipsometry for PNIPAAm brushes tethered on gold substrates. They found that for an ellipsometrically measured thickness of ~100 nm, a thickness of 62 ± 4 nm was obtained from AFM imaging in air. The difference was attributed to compression of the layer by the AFM tip. Another possible contribution to the discrepancy between the ellipsometry and AFM data may be related to the difficulties in quantitative tapping mode AFM analysis.[31-33] If the polar polymer chains stick to the AFM tip,[33, 34] the adhesion between the polymer and AFM tip
may damp the amplitude of the tip oscillation and increase the hysteresis in the force-distance curve, making difficult a quantitative comparison of the topographic difference between the polymer and OTS region. We speculate such a polymer-tip adhesion may result in an underestimate of the polymer brush thickness.

The reversible contraction and expansion of the water-swelled PNIPAAm brush, shown in Figure 3.8, occurs over the broad temperature range of 20-35 °C, with the majority of the transition occurring between 28 and 35 °C, instead of within 1-2 °C of 32 °C as for the LCST transition of bulk PNIPAAm in pure water.[1] The broadening of the LCST transition agrees well with the theoretical prediction for the coil-to-globule transition of neutral polymer chains grafted on a planar substrate.[7] Due to strong interchain interactions within the densely grafted brush, the transition is not truly second-order. Experimentally, this prediction has been confirmed. Reports include a 20 °C range for the LCST transition of the PNIPAAm chains grafted on polystyrene latex particles,[8] and the SPR signal of a PNIPAAm brush prepared by surface-initiated ATRP on a gold substrate gradually changed over 15-35 °C.[9] Our PNIPAAm brush collapses from ~82 nm at 20 °C to ~50 nm at 35 °C as shown in Figure 3.8(a). The extent of collapse is comparable to the temperature-dependent neutron reflectivity data reported by Yim et al. for a densely grafted PNIPAAm brush on gold prepared by surface-initiated ATRP,[13] where a contraction from ~67 nm to ~42 nm was observed upon heating from 20 to 41 °C for a film with a grafting density of 0.26 chains/nm². We speculate that the grafting density and the polydispersity of the PNIPAAm chains in our system are similar to those reported by Yim et al., since the thermal properties and polymerization chemistries are similar.

Prodan is solvatochromic, and thus it may be possible to use it as a probe of the local chemical environment within the PNIPAAm film. The Prodan emission in the PNIPAAm
brushes was in the range of 446-450 nm, which is very close to the emission of Prodan in DMF (448 nm),[27] indicating that the local environment of PNIPAAm is at least superficially similar to DMF. This could be expected given the similarities in their chemical structures (both consist of amide groups with N-alkyl substituents).

It is shown in Figure 3.9(a) that the intensity of fluorescence was almost the same from PNIPAAm brushes of two different thicknesses. This was expected because both samples were spin coated with dye under identical conditions, and thus the quantity of dye deposited on the substrate should be the same. Under spin coating at 900 rpm, using ethanol as the solvent, the thickness of the solvent layer formed during spin coating is estimated to be 2.73 µm.[35, 36] The calculated aerial density of the dye molecules in both cases was 0.16 nm⁻² assuming the dye concentration was only a function of the thickness of the solvent layer formed during spin coating and the initial dye concentration in the solvent. As expected, the pure PNIPAAm brush and the silicon wafer did not fluoresce.

Figure 3.9(b) shows that Prodan has a much stronger emission in the PNIPAAm-grafted region than in the OTS grafted region. Most likely this was because any Prodan molecules that were initially deposited on the OTS monolayer are either aggregated, and thus not fluorescent, or diffused off the OTS and into the PNIPAAm brush before imaging.

The shape of the fluorescence recovery curves in Figure 3.10(b) is not a normal translational diffusion curve. One possible explanation is rotational diffusion. A detailed discussion on this can be found elsewhere.[37] In the case of recovery due to rotational diffusion, the supply of fluorescent molecules is evenly distributed over the region of interest and so recovery has no distance dependence. However, the rate of rotational diffusion of a probe molecule in a polymer matrix is strongly dependent on temperature, especially near the glass
transition temperature.[38, 39] Under dry nitrogen (0% water absorbed), rotational diffusion should be very slow and so fluorescence recovery due to rotational diffusion during the time scale of the experiment should be negligible. In 95% relative humidity at RT, the PNIPAAm brush thickness increases by 18.6% (measured with ellipsometry, the brush thickness increases from 21.5 nm in dry nitrogen to 25.5 nm in humid nitrogen). We estimate that the brush absorbs about 18.6% water which should result in a decreased glass transition temperature and faster rotational diffusion. Hence, we believe that the fluorescence recovery observed in a humid environment is due to rotational diffusion occurring on the time scale of the experiment. Finally, if rotational diffusion is the reason fluorescence recovers, isolating regions of PNIPAAm with lines of printed OTS should not limit this recovery. Even if printed lines of OTS limit all translation diffusion to within the independent regions of PNIPAAm brush, fluorescence recovery through rotational diffusion could still occur. Under this assumption (printed lines limit all translational diffusion), if all of the (orientations of) dye molecules within an isolated PNIPAAm region are bleached, there should be no fluorescence recovery. However, if only molecules of a particular orientation (parallel to the bleaching laser) are bleached, the dye molecules would simply need to rotate to an orientation excitable by the impinging, imaging light for fluorescence to recover. Isolated regions could recover independently. Therefore, rotational diffusion is a possible explanation for the experimentally observed recovery in the patterned samples.

The second explanation is a combination of fast surface diffusion and slow bulk diffusion. For this case surface diffusion is fast relative to bulk diffusion; thus we can assume a constant dye concentration on the surface. Fluorescence recovery, in this case, is dependent on the rate of bulk diffusion. Some recovery must be due to bulk diffusion from outside the region
of interest to inside, and so the edge of the region of interest, if this explanation is correct, should not be a perfectly sharp step. However, the resolution of the microscope is ~250 nm, so if the rate of bulk diffusion is slow enough, we will still observe an abrupt change in intensity at the edge of the region of interest. For this scenario, most of the observed recovery would be due to diffusion from the (saturated) surface of the region of interest into the bulk. Recovery due to this mechanism would be mostly uniform in the region of interest. This is what is observed experimentally.

FRAP results in Chapter 2 indicate that Prodan diffusion on an OTS surface is negligible. This fact, along with the FRAP results of the patterned PNIPAAm surface, suggests that a combination of fast surface diffusion and slow bulk diffusion is not the correct explanation for the fluorescence recovery we observe on PNIPAAm (patterned and unpatterned) samples. If this explanation was correct (for the unpatterned PNIPAAm samples), the OTS printed lines of the patterned PNIPAAm sample should have prevented translational dye diffusion and the isolated, bleached squares of PNIPAAm brush should not recover their fluorescence.

However, if the printed OTS surface does not completely prevent the initiation and growth of PNIPAAm chains, fast surface diffusion may still occur. Even if only a few chains are permitted to grow on the OTS lines, they may lie flat on the surface creating a very thin layer of PNIPAAm on top of the OTS. This layer could be thin enough to be undetectable to fluorescence microscopy; the fluorescence intensity from the dye dissolved within it could be negligible compared to the fluorescence intensity from the squares of thicker PNIPAAm brush. To test for this possibility, an entire surface was printed with OTS prior to a ~12 hour NIPAAm polymerization. With only printed OTS, the layer was 2.3 ± 0.3 nm thick; after polymerization, the layer was 3.8 ± 0.5 nm thick (measured with ellipsometry). This apparent layer of
PNIPAAm, though thin, may still allow for fast (relative to bulk) surface diffusion. Thus, fluorescence would recover in the seemingly isolated PNIPAAm squares just as easily as it recovered on unpatterned surfaces as is observed experimentally.

3.5 Conclusions

In conclusion, we have demonstrated a facile route for forming patterned PNIPAAm brushes on oxide surfaces by microcontact printing of a surface initiator followed by the surface initiated ATRP of NIPAAm. The patterning of the surface initiator was achieved by microcontact printing octadecyltrichlorosilane followed by backfilling aminopropyltriethoxysilane onto the unprinted region. The amino group was subsequently reacted with bromoisobutyric acid forming the surface-grafted initiator. The surface-initiated ATRP of NIPAAm was then carried out. The chemical structure of the PNIPAAm brushes was confirmed by XPS and FT-IR, and the physical properties were characterized with ellipsometry, contact angle measurements, and XRR. AFM confirmed successful micropatterning of the PNIPAAm brushes. Environmental ellipsometry measurements showed that the LCST transition of the PNIPAAm brush occurs over a broad temperature range of 20 to 35 °C. The fluorescence emission spectra of Prodan in PNIPAAm brushes indicated that the local chemical environment of the PNIPAAm is very similar to that of DMF. In addition, fluorescence microscopy suggested that Prodan is localized in the patterned PNIPAAm brushes and excluded from the OTS regions. The FRAP results of Prodan on PNIPAAm layers indicate that bulk translational diffusion, if any is taking place, is at best very slow relative to other diffusion mechanisms. Isolating squares of PNIPAAm brush with printed OTS lines does not eliminate the fluorescence recovery after photobleaching entire isolated squares. Possible explanations for the fluorescence recovery
observed are rotational diffusion and a combination of fast surface diffusion and slow bulk diffusion.

3.6 References


CHAPTER 4

DIFFUSION OF PRODAN IN POLY(OLIGOETHYLENE GLYCOL ACRYLATE) BRUSHES

4.1 Introduction

As discussed in Chapter 3, in order to observe significant transport of small molecules in polymer brushes, it is important that the diffusion coefficient of the probes in the polymer to be sufficiently high. To increase the diffusion coefficient of probe molecules in the grafted polymer layers, one major strategy is to use polymer materials with low glass transition temperature, \( T_g \), as the transport media. Oligoethylene glycol acrylate (OEGA), was chosen as a monomer for the polymer brush because the resulting side chain polymer, poly(oligoethylene glycol acrylate) (POEGA) forms continuous, amorphous phases at room temperature which may be ideal for molecular transport. Bulk oligoethylene glycol of a similar molecular weight as the oligoethylene oxide side chain of POEGA has a \( T_g \) in the range of 158-233 K.[1] Compared to PNIPAAm, whose \( T_g \) is around 110 ºC, the significantly lower \( T_g \) of POEGA may the diffusion rate of Prodan in POEGA brushes to be increased greatly. OEGA is also compatible with ATRP so polymer brushes can be grown in a controlled fashion using surface-initiated polymerization. One additional consideration is that PEG can solubilize polar dyes as well as many salts. Therefore POEGA can be used as a medium for transporting polar organic species as well as ionic species.

4.1.1 PEO used in ion transport applications

Poly(ethylene oxide), PEO, based composite materials have long been recognized as one of the important types of solid-state, ion-conducting polyelectrolytes for rechargeable, high-
energy-density battery applications.[2, 3] Pure PEO is a semi-crystalline material. It is reported for bulk PEO that at room temperature 60% exists in a crystalline phase and the remainder exists in an amorphous phase. The melting temperature, $T_{m}$, of the crystalline phase is around 65 ºC and the $T_g$ of the amorphous phase is about -60 ºC. PEO can form complexes with a wide variety of metal salts, and these include a number of alkali and alkaline earth metal salts as well as transition metal salts with mono and divalent cations such as Li$^+$, Na$^+$, K$^+$, Cs$^+$, Ag$^+$, Mg$^{2+}$, Ca$^{2+}$, Zn$^{2+}$ and etc.[2, 4] Typically, for smaller metal ions such as Li$^+$ and Na$^+$, the maximum stoichiometry of CH$_2$CH$_2$O:metal ion is 3:1; larger ions such as K$^+$ and NH$_4^+$ tend to form 4:1 complexes. Regardless of the structure of the PEO-salt complexes, it is well understood that the ionic transport occurs only in the amorphous phase.[2, 4] Much less information is available on the phase diagrams of PEO-salt complexes with other alkali and alkaline ions.

Although PEO is an excellent solid matrix for the solvation of alkali metal ions and high ionic conductivities have been achieved at high temperatures ($>10^{-4}$ S cm$^{-1}$ at 70 ºC),[5] polyelectrolytes derived from pure PEO-metal salt complexes do not show high ionic conductivity at ambient temperatures due to the partially crystalline nature of PEO.[3] There are many methods developed for improving the ionic conductivities of the PEO-salt complexes and therefore lowering the operation temperature. The most common approach is to add plasticizers such as small organic compounds, salts, or ceramic powders into the polymer electrolytes.[2, 3, 5-7] This approach suffers drawbacks including low mechanical and electrochemical stabilities, and phase separation for incompatible systems. Another approach is to modify the chemical structure of the polymer by copolymerization,[2, 3, 5] but this leads to limited ionic conductivities. At present, much research effort is focused on optimization of the polyelectrolyte composition for practical solid-state battery applications.
4.1.2 PEO for biomedical applications

It is often important to control protein adsorption and cell adhesion in biomedical materials. Deposition of protein on the surfaces of medical implants often promotes the attachment and growth of cells, and result in unpredicted perturbation on the function of the implanted devices. So far, the most effective method to prevent protein adsorption and cell adhesion is to modify the artificial surfaces by grafting, through physical adsorption or chemical attachment, biocompatible, water-soluble polymers such as PEO and PEG onto the solid surfaces.[8, 9] In aqueous solutions, these polymer chains are neutral, highly mobile and flexible; they resist protein adsorption and cell attachment by a mechanism of the combination of steric stabilization effects (entropic repulsion) and rapid motion of the hydrated chains.[9-12]

This non-fouling property of PEO/PEG is not very sensitive to molecular weight. Although long PEO chains have been applied most commonly for protein-resistant surface treatment,[11, 12] it was reported that both long-chain and short-chain PEOs are capable of protecting surfaces from biofouling as long as a complete coverage of ethylene oxide group is achieved on the surface.[9, 10, 13] It was shown that alkanethiol SAMs terminated with oligoethylene glycol segments with greater than one ethylene oxide unit can effectively block protein adsorption.[10, 14]

In addition, PEO is not toxic. It does not harm proteins or cells when in direct contact with them. It exhibits excellent immunogenicity and nonantigenicity. Combined with its protein and cell-resistance properties, PEO is an unusually good surface treatment candidate for biocompatible medical devices.[11-13]
4.1.3 Oligoethylene glycol containing polymer brushes

Recently, polymer brushes containing oligoethylene glycol side chains have been tethered onto various substrates via surface-initiated polymerization to prevent protein adsorption and cell adhesion.[15-20] Physical adsorption of polymer chains has also been used to generate polymer brushes with oligoethylene glycol constituents. Copolymers containing oligoethylene glycol pendant chains have been spin-coated onto different substrates, and it was found that the oligoethylene glycol groups usually expose themselves towards water and therefore fulfill the function of suppressing protein and cell adhesion.[21] There are several recent review papers discussing the bio-related aspect of oligoethylene glycol containing polymer brushes.[8, 22]

4.1.4 Poly(oligoethylene glycol acrylate) brushes for molecular transport

We are mainly interested in studying the diffusion of probe molecules in the surface-tethered poly(oligoethylene glycol acrylate) brushes. Since the oligoethylene oxide chain is very short, we expect that the high concentration of end groups may prevent the formation of crystalline PEO phases. And, because the $T_g$ of the amorphous phase formed by these oligoethylene glycol chains is very low, we believe that POEGA brush will be a suitable medium to transport Prodan and other probe species effectively.

Because of the significant effects of water on diffusion in POEGA, we equilibrate the POEGA brushes under variable humidity and study the diffusion of Prodan in water vapor saturated POEGA brushes.
4.2 Experimental

4.2.1 Materials

All chemicals were purchased from Acros unless otherwise noted. Aminopropyltriethoxysilane (APS, 99%), 2-bromo-2-methylpropionic acid (BriBuA, 98%), 4-Dimethylaminopyridine (DMAP, 99%), N, N’-Dicyclohexylcarbodiimide (DCC, 99%), and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99+%) were used as received. Oligoethylene glycol acrylate (OEGA, Aldrich, FW=375, 99%) was purified by passing through an inhibitor remover column using a mixture of dichloromethane and n-hexane (v/v ~ 1:3) as the solvent to remove the monomethyl ether hydroquinone, and then the solvent is removed. Octadecyltrichlorosilane (98%), copper (I) bromide (99.999%) and the inhibitor remover disposable columns were purchased from Aldrich and used as received. 6-propionyl-2-dimethylaminonaphthalene (Prodan) was purchased from Molecular Probes.

4.2.2 Instrumentation

A Kratos Axis ULTRA Imaging X-ray Photoelectron Spectrometer (Kratos Analytical Ltd.) was used to acquire XPS data of the surface initiator and the POEGA brushes on silicon wafers. A Nexus 670 FT-IR E.S.P. with a Smart Refractor attachment (Thermo Nicolet) was used to collect the reflectance-mode IR spectrum (512 scans at 4 cm⁻¹ resolution) of the POEGA brushes on silicon wafer. Contact angle data was collected using a Ramé-Hart Goniometer (Model 100-00). A Phi TRIFT III ToF SIMS was used to collected the secondary ion mass spectrometry data. A Gaertner Ellipsometer Model L116C (Gaertner Scientific Corp.) was used to measure the thickness of polymer brushes. The wet thickness was collected using a custom-built environmental cell. The same environmental cell flowed with N₂ at the desired humidity
was used to test the thickness change of a POEGA brush when exposed to water vapor, and the sample has been equilibrated for at least 5 minutes until the thickness reading is stable. A Dimension 3100 AFM (Digital Instruments) was used to characterize the patterned polymer brushes, using a tapping mode etched silicon probe (Digital Instrument). The fluorescence emission spectra of Prodan were collected using a Jobin-Yvon Spectrometer (Model FluoroMax-3). A Leica confocal laser scanning microscope (Model TS SP2) equipped with Ti:Sapphire tunable wavelength laser (Tsunami, Spectra-Physics) was used to collect fluorescence recovery after photobleaching (FRAP) images, and samples were tested under continuous flow of nitrogen or nitrogen with controlled relative humidity using a custom-made sample holder.

4.2.3 POEGA brush formation and patterning

4.2.3.1 Unpatterned POEGA brush formation

The procedure of substrate cleaning, and APS and surface initiator tethering is identical as the one presented in Chapter 3, and the surface initiated polymerization of Oligoethylene glycol acrylate (Scheme 4.1) was performed using a procedure modified from literature references.[23, 24] OEGA (20.8 g, 110 mmol), CuBr (160 mg, 1.11 mmol) and PMDETA (700 µL, 3.34 mmol) were dissolved in 120 mL of MeOH/H₂O mixture (v/v: 1:1) and degassed by two freeze-thaw cycles. The monomer and catalyst solution was then transferred via a canula into the degassed Schlenk tubes containing the substrates tethered with the initiator SAMs. The polymerization was carried out at room temperature under a nitrogen atmosphere for 0.5 h to 24 h. At the conclusion of the reaction, the Schlenk tubes were disconnected from the nitrogen line
and the substrates were rinsed extensively with H₂O followed with sonication in EtOH and then
H₂O. After drying with a nitrogen stream, the samples were stored in a nitrogen filled box.

Scheme 4.1

4.2.3.2 Patterning of POEGA brush

The first patterning procedure is microcontact printing followed by surface initiated
polymerization as discussed in Chapter 3. Substrates with patterned OTS/initiator SAMs were
used in the polymerization step to grow patterned POEGA brushes.

The second patterning method applied in this study is surface-initiated ATRP followed by
photolithography and reactive ion etching. The procedure is briefly discussed here. POEGA
grafted silicon wafers and silica substrates are spin-coated with Shipley 1805 at 3000 rpm for 30
seconds, and the photoresist thickness is ~500 nm. After baking the samples at 105 °C for 60
seconds, they are exposed to UV light (wavelength = 365 nm, constant power=274 mW) through
a photomask (ordered from www.photoplotstore.com) for 5 seconds. After exposure, the
samples are developed in MF 319 for 12 seconds, rinsed with DI water for 3 times and dried
using N₂ gun. The patterned samples are then etched in reactive ion etching chamber for 3
minutes under O₂ flow (flow rate=20 sccm, pressure=30 mtorr, DC 200V, and power=50 W).

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The samples are sonicated in acetone for 5 minutes twice and in ethanol for 5 min once, and dried under flowing N₂.

4.2.4 Characterization of POEGA brushes

XPS, FT-IR, XRR, ellipsometry, and contact angle goniometry, and fluorescence spectroscopy data was collected on unpatterned POEGA brush samples. For the fluorescence spectroscopy experiments, an ethanol solution of Prodan (1×10⁻⁴ M) was deposited onto unpatterned POEGA brushes on silica coverslips; after waiting 2 minutes the samples were spin-coated at 900 rpm for 60 seconds.

For FRAP experiments, an ethanol solution of Prodan (5×10⁻⁵ M) was deposited onto unpatterned and patterned POEGA brushes grafted on silica coverslips; after 2 minutes the samples were spin-coated at 2000 rpm for 60 seconds. FRAP imaging was carried out immediately. A flow meter and a hygrometer were used to regulate and monitor the relative humidity during the FRAP experiments.

4.3 Results and Discussion

4.3.1 XPS, FTIR and ToF SIMS characterizations

After polymerization, the chemical composition of a ~50 nm thick POEGA brush was determined using XPS (Figure 4.1). The survey spectrum as shown in Figure 4.1(a) confirms that the polymer is composed only of carbon and oxygen elements. The oxygen:carbon molar ratio was determined to be 0.32:0.67, which agrees very well with the expected value ratio of 0.35:0.65 for POEGA. The high resolution C 1s spectrum was fit with the 3 peaks expected for POEGA. The sp² hybridized carbon atom in the carbonyl group, labeled III in Figure 4.1(b), is
at 287.9 eV. The sp³ hybridized carbon peak at around 285.0 eV was divided into two components: peak I at 284.2 eV corresponding to the -CH₂- in the backbone of POEGA; peak II at 285.7 eV attributable to the -CH- unit in the POEGA backbone and the -CH₂-CH₂- unit in the side chain of POEGA. A molar ratio of 1:7:1 for the three components, I:II:III, yielded that the number of ethylene oxide units is ~ 3, instead of 7 as expected from the grafted POEGA brushes. The possible explanation is that monomers with shorter oligoethylene glycol units might be slightly more reactive if the reaction is diffusion limited.

**Figure 4.1.** XPS spectra of POEGA brushes on an oxidized silicon wafer. (a) survey spectrum, (b) C 1s high resolution spectrum with peak fitting. The solid curve in (b) is the experimental data and dashed curves the curve fits. The peak maximum of the CC/CH component in (b) was referenced to 285.0 eV.

Reflectance-mode FTIR spectrum (not shown) was collected from a 63 nm thick POEGA brush grafted on a silicon wafer. Major peaks in the IR spectrum are as follows: 1112 cm⁻¹ (C-O, ν), 1445 cm⁻¹ (C-H, δ), 1735 cm⁻¹ (C=O, ν), 2858 cm⁻¹ (CH₂, νₛ), and 2935 cm⁻¹ (CH₂, νₐₕ). They confirmed the presence of the chemical functional groups in the POEGA layer.[25]
ToF SIMS characterization of POEGA brush (Figure 4.2) showed characteristic ethylene oxide fragment peaks, including $\text{CH}_3\text{O}^+$, $\text{C}_2\text{H}_5\text{O}^+$ and $\text{C}_3\text{H}_7\text{O}^+$, further confirming the brush chemical composition.

![ToF SIMS spectrum of a 50 nm POEGA brush on silicon wafer.](image)

**Figure 4.2.** ToF SIMS spectrum of a 50 nm POEGA brush on silicon wafer.

### 4.3.2 Water contact angle measurements

At room temperature (~23 °C) in air, the advancing contact angle of all POEGA samples is about 46-47°, and the receding angle is around 30°. The hysteresis between the advancing and receding angle may be the result of swelling of the POEGA brushes upon contact with water during the contact angle measurement.[26, 27]
4.3.3 Thickness measurements

4.3.3.1 POEGA brushes in dry state and water-submerged state

Table 4.1 shows thickness and index of refraction data of both dry and wet POEGA brushes. The dry thickness data of the POEGA brushes from AFM experiments were obtained from the height difference between the POEGA brush and the OTS SAM. The ellipsometry data were collected from the unpatterned region on the same sample, outside of the patterned area, and the data of the wet POEGA brushes were measured under water using the custom-made sample cell with the samples submerged in water.

<table>
<thead>
<tr>
<th>Polymerization Time (hour)</th>
<th>Dry Thickness (nm)</th>
<th>Wet Thickness (nm)</th>
<th>Index of Refraction (from Ellipsometry)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ellipsometry</td>
<td>AFM</td>
<td>Ellipsometry</td>
</tr>
<tr>
<td>2</td>
<td>36 ± 2</td>
<td>32 ± 3</td>
<td>101 ± 4</td>
</tr>
<tr>
<td>11</td>
<td>63 ± 2</td>
<td>56 ± 2</td>
<td>125 ± 3</td>
</tr>
<tr>
<td>20</td>
<td>93 ± 1</td>
<td>91 ± 2</td>
<td>160 ± 2</td>
</tr>
</tbody>
</table>

The thickness of the POEGA brushes increases progressively with the polymerization time, which is expected for a living polymerization. As can be seen, the dry thickness data of POEGA brushes collected from the two different techniques were very close. Since the substrates were completely immersed during polymerization, the patterned and unpatterned regions of the substrate should be exposed to the identical reaction conditions and therefore should give similar thickness results. And as indicated in the increased thicknesses, POEGA brushes adsorb a large amount of water in wet state, and the hydrated polymer chains adopt a fairly extended conformation.

The polymer volume fraction in the swelled polymer brush can be calculated according to effective medium approximation (EMA),[28]
where \( f_p \) and \( f_{H2O} \) are volume fractions of polymer and water, and \( n_p \), \( n_f \), and \( n_{H2O} \) are the indexes of refraction of dry polymer, wet polymer, and water respectively. Assuming the densities of POEGA and water are the same, the polymer volume fraction in the swelled polymer brush can also be calculated directly from the ratio of the dry and wet thicknesses of the polymer layer,

\[
f_p = \frac{d_{dry}}{d_{wet}}
\]

where \( d_{dry} \) and \( d_{wet} \) are the thicknesses of the dry and wet polymer brushes. The calculated polymer volume fractions are summarized in Table 4.2. POEGA takes up about 40-50% of the volume in the swelled state, and this is qualitatively expected since the oligoethylene glycol units in the side chains are able to form hydrogen-bonds with water molecules and therefore retain water inside the polymer layer. Very similar values of polymer volume fraction were obtained from both methods for the two thicker POEGA samples, while there is an 8%-difference between the calculated volume fractions for the thinnest POEGA sample. This rather large difference is attributed the relatively greater surface roughness of the thinnest POEGA film as shown by the thickness data in Table 4.1.

Table 4.2. Volume fractions of dry POEGA in water-swelled POEGA brushes.*

<table>
<thead>
<tr>
<th>Polymerization Time (hour)</th>
<th>POEGA Volume Fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Method 1: EMA Method 2: Thickness Ratio</td>
</tr>
<tr>
<td>2</td>
<td>44 ± 4</td>
</tr>
<tr>
<td>11</td>
<td>54 ± 2</td>
</tr>
<tr>
<td>20</td>
<td>55 ± 1</td>
</tr>
</tbody>
</table>

*: in the EMA calculation, \( n_{H2O} \) is assumed to be 1.330.
4.3.3.2 POEGA brush saturated with water vapor

The response of POEGA brushes to water vapor was tested using environmental ellipsometry. As shown in Figure 4.3, POEGA brush swells when exposed to water vapor. The adsorbed water molecules act as plasticizers in polymers,[29] and the $T_g$ of the water-swelled POEGA film is expected to be decreased.

![Ellipsometry thickness of a POEGA brush as a function of relative humidity. The thickness of the POEGA brush is 35.4 ± 1.1 nm at ambient conditions (24 °C at 35% relative humidity).](image)

The glass transition temperature of the water swelled POEGA can be estimated by a simplified, empirical equation,[30]

$$T_g \approx \frac{T_{gp}}{1 + (X - 1)(1 - \Phi_p)}$$  \hspace{1cm} (4.3)

where $T_g$ is the glass transition temperature of the plasticized polymer, and $T_{gp}$ is the glass transition temperature of the pristine polymer, $X$ is the ratio of polymer glass transition
temperature over solvent glass transition, \( \frac{T_{gP}}{T_{gS}} \), and \( \Phi_p \) is the volume fraction of the polymer. \( \Phi_p \) can be calculated from the thickness data. Assuming the \( T_g \) of POEGA is -50 °C and the \( T_g \) of water is -108 °C,[1, 5] the \( T_g \) values of the plasticized POEGA under variable humidity were calculated according to Equation (4.3) and presented in Table 4.3.

<table>
<thead>
<tr>
<th>Relative Humidity</th>
<th>0%</th>
<th>25%</th>
<th>50%</th>
<th>75%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_g ) of H\textsubscript{2}O Swelled POEGA (°C)</td>
<td>-50</td>
<td>-51</td>
<td>-53</td>
<td>-56</td>
<td>-60</td>
</tr>
</tbody>
</table>

### 4.3.4 Fluorescence studies of unpatterned POEGA brushes

#### 4.3.4.1 Fluorescence spectroscopy of Prodan in POEGA brush

We have used fluorescence spectroscopy to characterize the fluorescent properties of Prodan dissolved in the POEGA brushes. 0.1 mM Prodan solution was spun cast onto/into a 90-nm thick POEGA film at 2000 rpm, and the aerial density of Prodan is ~ 0.2 nm\(^{-2}\). As shown in Figure 4.4, the emission maximum of Prodan is 442 nm in POEGA brush, and as expected, the control POEGA sample does not fluoresce. As a comparison, the emission maximum of Prodan in PMMA film is at 418 nm (unpublished result). This large red shift of Prodan emission in the POEGA matrix is very likely due to the effect of solid state solvation, the solid state analog of liquid state solvation.[31] The electronic transition of Prodan from the ground state to the excited state causes the surrounding solvent molecules, in our case POEGA or PMMA, to experience a new electric field. The solvent responds to this new field either through electron cloud reorganization (i.e., polarizability or electronic relaxation), or through physical translation and rotation. Since the polarizability of POEGA is probably very close to that of PMMA, which
is implied in their relative close refractive index, physical motion inside the polymers, more specifically, the local rotation and translation of segments and/or other subunits, might have more contribution to the solvation of solute molecules. We could qualitatively discuss this solvation effect based on the comparison of glass transition temperatures of POEGA and PMMA. The $T_g$ of POEGA is estimated to be around -50 °C and the $T_g$ of PMMA is about 105 °C.[1] At room temperature, POEGA is in the rubbery state whereas PMMA is in the glassy state, well below its glass transition. We would expect that the energy of the excited state of Prodan is more effectively relaxed or dissipated in the POEGA matrix which has a much lower viscosity. As a result of this lowered excited-state energy, we could observe a red shift in Prodan emission in POEGA.

Figure 4.4. Fluorescent emission spectra of Prodan in a 90 nm-thick POEGA sample and a control sample of POEGA brush (no Prodan). The excitation wavelength is 320 nm.

4.3.4.2 Diffusion of Prodan in POEGA brush

Following the published procedure,[32] fluorescence recovery of Prodan in an unpatterned POEGA brush with a thickness of 45 nm was studied under dry nitrogen (i.e., 0%
relative humidity), 25% relative humidity, 50% relative humidity and 75% relative humidity. The sample was equilibrated for at least 15 minutes prior to the FRAP experiments under each humidity.

Figure 4.5 shows FRAP images at 0% relative humidity, and fluorescence intensity profiles of Prodan at different diffusion times with fitted diffusion curves (according to Fick’s second law). FRAP images and their corresponding diffusion curves under 25%, 50%, and 75% relative humidity are presented in Figure 4.6, Figure 4.7, and Figure 4.8 respectively. The diffusion of Prodan in dry POEGA is very fast, with a diffusion coefficient of 0.6 µm²/s, which could explained by the low $T_g$ of POEGA. As shown in this series of figures, the diffusion coefficient of Prodan in POEGA brushes increases consistently as the relative humidity increases.

**Figure 4.5.** FRAP data of Prodan in a POEGA brush under dry nitrogen. (a) fluorescence recovery images (image size = 119 µm × 119 µm); (b) Experimental (symbols) and simulated (lines) intensity vs radial position as a function of time. The simulated data are for $D = 0.6$ µm²/s.
Figure 4.6. FRAP data of Prodan in a POEGA brush under 25% relative humidity. (a) fluorescence recovery images (image size = 119 µm × 119 µm); (b) Experimental (symbols) and simulated (lines) intensity vs radial position as a function of time. The simulated data are for $D = 0.7 \, \mu\text{m}^2/\text{s}$.

Figure 4.7. FRAP data of Prodan in a POEGA brush under 50% relative humidity. (a) fluorescence recovery images (image size = 119 µm × 119 µm); (b) Experimental (symbols) and simulated (lines) intensity vs radial position as a function of time. The simulated data are for $D = 0.8 \, \mu\text{m}^2/\text{s}$.
Figure 4.8. FRAP data of Prodan in a POEGA brush under 75% relative humidity. (a) fluorescence recovery images (image size = 119 µm × 119 µm); (b) Experimental (symbols) and simulated (lines) intensity vs radial position as a function of time. The simulated data are for $D = 0.9 \, \mu \text{m}^2/\text{s}$.

4.3.4.3 Comparison of diffusion coefficients by FRAP experiments and calculations based on Williams-Landel-Ferry (WLF) equation

The diffusion of a small molecular probe in polymers near $T_g$ can be well described by a modified WLF equation.[33-35]

$$\log D = \frac{C_1(T - T_g)}{C_2 + (T - T_g)} + \log D_e$$  \hspace{1cm} (4.4)

As revealed by the WLF equation, the diffusion coefficient is highly dependent on the difference between $T_g$ of the polymer matrix and the actual temperature.

Figure 4.9 shows the relative diffusivity versus relative humidity from both the WLF calculation and the FRAP data. Assuming that $C_1$ and $C_2$ values are 17 and 50 K respectively,[36, 37] calculations were performed based on Equation 4.4 and the $T_g$ values in Table 4.3. In general, the WLF equation is a relatively good model to describe the diffusion of Prodan in our POEGA brush system. The calculated value and the FRAP data match very well at 25% relative humidity, and they overlap at 50% relative humidity. At 75% relative humidity,
the discrepancy between them becomes obvious. We speculate that as the water content in the POEGA layer becomes higher, association of adsorbed water molecules may occur ("clustering").[29] Instead of plasticizing the whole POEGA layer, water molecules may form small clusters so that the majority of the environment surrounding Prodan molecules is less mobile than what we expected from our $T_g$ calculation (Table 4.3). Therefore, the WLF calculation may overestimate the relative diffusivity under higher relative humidity.

![Figure 4.9](image-url) Relative diffusivity under variable humidity.

### 4.3.5 Patterned POEGA brushes via microcontact printing method

#### 4.3.5.1 AFM of the patterned POEGA brushes

A patterned POEGA brush was prepared following a published procedure.[24] The AFM images of a sample of patterned POEGA brush are presented in Figure 4.10. The darker region in Figure 4.10(a) is the OTS SAM (lower in topography), and the brighter area is the POEGA brush (higher in topography). As can be seen in Figure 4.10(b), the observed height difference between the OTS SAM and the POEGA brush is 88.4 nm. Since the OTS layer has a thickness
of 2.5 nm (as measured by AFM on a microcontact printed OTS SAM), the total thickness of the polymer brush is estimated to be ~ 91 nm. The height contrast in the patterned sample can be clearly shown in Figure 4.10(c). We learned from Figure 4.9 that for the most part, the OTS self-assembled monolayer (SAM) prevents the underlying SiO₂ from reacting with APS so that POEGA brushes primarily grow in the APS modified surface.

Figure 4.10. Tapping mode AFM images of patterned POEGA brushes prepared by microcontact printing of OTS followed by surface initiated ATRP of OEGA. The AFM images were obtained in ambient conditions: (a) topography image; (b) section analysis; (c) surface plot. The PDMS stamp used for creating these patterned POEGA brushes had feature sizes comparable to the resulting POEGA brush.
Figure 4.11 shows a higher resolution image of the patterned POEGA sample. As can be observed in Figure 4.11 (a) & (b), there are small island-like features in the OTS region. If OTS does not completely prevent surface initiator attachment and subsequent polymerization due to defects in the OTS SAM, there may be POEGA growing off of the surface initiator that has inserted into the OTS patterned region. The OTS patterned region has a RMS roughness of ~ 3 nm. The POEGA surface shown in Figure 4.11 (c) & (d) is very smooth, and the RMS roughness is ~ 1.5 nm.

Figure 4.11. AFM images of the OTS patterned area and the POEGA area in the patterned POEGA brush shown in Figure 4.9. (a) & (b) are topography image and 3-D surface plot of the OTS patterned region; (c) & (d) are topography image and 3-D surface plot of the POEGA surface.
4.3.5.2 Diffusion of Prodan in the patterned POEGA brushes

Ideally, since Prodan diffusion on OTS is extremely slow as discussed in the FRAP experiments in Chapter 2, we expect that Prodan diffusion would only occur over our experimental time scale in the POEGA region in an OTS/POEGA patterned sample. Any POEGA region isolated by OTS SAMs would be disconnected from any fresh dye source therefore could not undergo fluorescence recovery after photobleaching.

Figure 4.12. FRAP images of Prodan in a patterned POEGA layer. (a) shows the pattern with a square bleached; (b) shows the fluorescence recovery in this square, and this isolated square recovers fluorescence with repeated bleaching; (c) eventually, the sample is damaged due to repeated bleaching before fluorescence recovery is eliminated.

Figure 4.12 shows FRAP of Prodan in a patterned OTS/POEGA sample. The dark regions correspond to OTS patterned areas, and the brighter regions are POEGA brushes. We observed that fluorescence recovery occurs in isolated squares subsequent to bleaching. As can be seen in Figure 4.12, repeated photobleaching in the same square results in continued recovery, and finally sample damage occurs before fluorescence recovery can be eliminated. We hypothesize that the POEGA islands shown in Figure 4.11 (a), (b) in the OTS region may transport fresh Prodan molecules into the isolated POEGA square therefore fluorescence
recovery can occur in the isolated square. In addition to these POEGA islands that have polymerized in the OTS region, there may exist a thinner layer of POEGA that spans the entire OTS surface allowing for surface diffusion.

4.3.6 Patterned POEGA brushes via photolithography and reactive ion etching

4.3.6.1 AFM of the patterned POEGA brushes

Figure 4.13 shows the AFM images of a typical sample of patterned POEGA brushes using photolithography and RIE. As can be seen in Figure 4.13(a), the brighter region corresponds to POEGA brush and the darker region corresponds to glass substrate. There are both continuous grids and isolated circular islands in the same sample. The height difference between the POEGA brush and the glass substrate is 155 nm, as shown in Figure 4.13(b). The 3-D surface plot in Figure 4.13(c) shows the height contrast among the patterned features. The glass substrate region is scanned in more details at higher resolution, and the 3-D surface plot is shown in Figure 4.13(d). The glass surface is very smooth, with a very small RMS roughness of 0.4 nm. This roughness is expected for a clean glass substrate, and more importantly, the smooth surface topography indicates that there is no apparent polymeric residue on the glass surface. From the AFM characterization, we have confirmed that we have achieved the desired surface patterns, and we would like to test whether Prodan diffusion would only follow the continuous POEGA pathway whereas the isolated POEGA islands will be free of fluorescence recovery due to the diffusion barrier created by the clean glass surface.
Figure 4.13. Tapping mode AFM images of patterned POEGA brushes prepared by surface initiated ATRP of OEGA followed by photolithography and RIE. (a) topography, (b) section analysis and (c) 3-D surface plot of the patterned feature; (d) surface plot of the glass substrate region.
4.3.6.2 FRAP of Prodan in the patterned POEGA brushes

As can be seen in the reflectance and fluorescence images of the patterned POEGA sample, Figure 4.14(a) & (b), the micro-patterning method has generated good surface contrast in the tethered polymer brush. In the fluorescence image, the dark regions should be naked glass, and the brighter regions should be the POEGA brush. Although glass surface was found to have negligible diffusion[32] and was therefore expected to limit diffusion between patterned POEGA regions, we observed fluorescence recovery in the interconnected grids regions as well as in the isolated POEGA islands, as shown in Figure 4.14(c) through Figure 4.14(f). And there is no obvious gradient of fluorescence intensity in the POEGA regions where photobleaching and fluorescence recovery have taken place.

One possible explanation is that the fluorescence recovery may be caused by rotational diffusion of Prodan inside the POEGA brush. Rotational diffusion of Prodan is possible because the experimental temperature is well above the glass transition temperature of POEGA (≈ 70 °C above $T_g$) and thus the mobility of the polymer might be large enough to generate enough free volume to allow Prodan to rotate. Since Prodan molecules are randomly oriented in the polymer layer, and the polarization of the incident laser beam aligns well with a small fraction of them, one set of bleaching exposure may not be sufficient to bleach all of the Prodan molecules in the POEGA layer. Repeated bleaching was carried out in the same area to test this possibility. However, we could still see fluorescence recovery in both continuous and isolated POEGA regions. From this, it appears that rotational diffusion is not likely the cause of the observed fluorescence recovery.
Another possibility is that the naked glass regions are still able to transport dye molecules, and that diffusion from the glass regions to the polymer is significantly slower than within the polymer regions. The naked glass regions still have Prodan molecules or aggregates of Prodan (aggregates have lower fluorescence intensity, and it is more plausible to explain why the glass regions show up as darker regions in the fluorescent images) on the surface, and they carry Prodan to the polymer regions. Once the dye molecules enter the polymer regions, they can diffuse very quickly inside so that there is no experimentally observable fluorescence gradient in the polymer regions.

Fast surface diffusion might as well be the cause of fluorescence recovery in bleached, isolated circles in the patterned samples if there is some residue of polymer left after etching. To confirm that a residue of the polymer layer (in exposed regions) was not responsible for fluorescence recovery in the isolated squares, samples were over-exposed, with the RIE etching time increased to 5 minutes. This etching time should adequately remove all polymers in the exposed areas. However, fluorescence recovery is still simultaneously observed in both the isolated circles and the connected grids subsequent to bleaching. This suggests that the fluorescence recovery in this kind of patterned samples may not be attributed to fast surface diffusion.

Since Prodan diffusion in pristine POEGA brushes shows normal diffusion profiles, in contrast to what we have observed in the patterned samples, we speculate that there might be some unfavorable chemical reactions occurring during the photolithography and RIE process so that the polymer and glass regions have been modified. Although it would be beneficial that we investigate in detail the possible reactions, it is very difficult to do so and it is beyond the scope of our research. We have designed new patterning routes to generate patterned pathways with
potentials to fulfill our goal of guided diffusion of probe molecules in surface-tethered molecular pathways. These routes include: (1) to pattern surface initiators through photolithography and then grow polymer brushes; (2) to create a “buffer” layer between POEGA brushes and photoresists using inert polymers such as polystyrene, poly(methyl methacrylate), or poly(vinyl alcohol), and then pattern the polymers using photolithography and RIE. These approaches will be attempted shortly within our research group.

![Figure 4.14](image)

**Figure 4.14.** FRAP images of Prodan in a patterned POEGA layer under dry nitrogen. (a) and (b) show the reflectance image and fluorescence image of the patterned POEGA brush before FRAP; (c) is the fluorescence image of the sample at 5 seconds after photobleaching; (d), (e) and (f) show fluorescence recovery in the patterned sample at 3 minutes, 6 minutes and 9 minutes after photobleaching, respectively.

### 4.4 Conclusions

Surface initiated ATRP of OEGA is carried out to prepare POEGA brushes on silicate substrates. The chemical structure of the POEGA brushes was confirmed by XPS, FT-IR and
ToF SIMS, and the physical properties were characterized with ellipsometry, and contact angle measurements. The fluorescence emission spectrum of Prodan in POEGA brushes indicates that the local chemical environment is relatively mobile, which is expected from the low $T_g$ of POEGA. FRAP of Prodan in unpatterned POEGA brushes shows that the diffusion of Prodan in dry POEGA is very fast, with a diffusion coefficient around 0.6 μm²/s, which could again be explained by the low $T_g$ of POEGA. The diffusion of Prodan in POEGA under different humidity has been studied using FRAP, and it can be described reasonably well using WLF equation.

Two methods have been applied to pattern POEGA brushes: the first method involves microcontact printing of OTS, backfilling of APS, surface reaction to attach initiator and finally surface-initiated polymerization of OEGA; the second method utilizes photolithography and RIE to pattern POEGA brushes. AFM was used to test patterned POEGA brushes, and showed good topographic contrast between the polymers and the OTS or naked glass substrate. However, so far our patterned polymer brushes are not able to confine Prodan molecules to diffuse exclusively inside the polymer regions. We have designed new experimental routes to overcome possible limitations in the patterning procedure and hopefully to reach the goal of guided molecular diffusion in surface-tethered polymer pathways.

4.5 References


CHAPTER 5

COLLOIDAL INTERACTIONS STUDIED THROUGH THE SELF-ASSEMBLY AND TWO-DIMENSIONAL DIFFUSION OF PNIPAAm BRUSH TETHERED SILICA PARTICLES

5.1 Introduction

Colloids stabilized with polymers have numerous important technological uses, which is evident in their applications in all kinds of everyday products such as cosmetics, pharmaceuticals and paints. Experimental and theoretical effort over the past few decades has resulted in a good understanding of the thermodynamics and kinetics involved in such colloidal systems. This knowledge can not only help in predicting the behavior of colloidal systems, including polymer adsorption mechanism, inter-particle interactions, phase diagrams, kinetics of phase transitions and particle diffusion, but it can also bring insights into other areas of research as well, for example, understanding the transitions between gas, liquid, solid and liquid crystalline phases in colloidal systems would greatly assist in comprehending phase transitions in a broader sense, especially those involved in complex systems such as biomacromolecules.[1-3]

In this chapter, we study a colloid-polymer model system consisted of a hard spherical silica core and a soft PNIPAAm brush shell. Although silica particles and PNIPAAm brushes have been individually extensively studied, there is very little know about silica/PNIPAAm core-shell particles.[4] With the advent of routes for the synthesis of monodisperse silica particles and surface-initiated polymerization,[5-8] we can precisely, independently and systematically control the core and shell sizes in order to do a systematic study on this model system.

The first few questions to ask are: (1) how thick a polymer brush shell or how large the shell/core ratio should be in order to change the phase behavior, (2) how close the particles need to be in order to feel the presence of each other, (3) at what distance does a particle feel the
presence of a flat wall, and (4) most importantly, how do the self-assembly properties and diffusion kinetics of colloids change in response to external stimuli such as temperature gradients, and pH or ionic strength variation.

In an initial effort, in the concentrated regime, we are interested in studying the self-assembly of PNIPAAm-tethered colloids at room temperature and after annealing at elevated temperature. In the dilute regime, we are intrigued to study the two-dimensional diffusion of PNIPAAm-tethered colloids on PNIPAAm brushes under variable temperatures. Due to the well-known LCST transition of PNIPAAm, we expect these systems to exhibit rich and complex phase behaviors. Through these studies, we hope that we can not only obtain phenomenological knowledge about the thermodynamics and kinetics involved in this model system, but also gain some insights into the mechanisms of the observed behaviors on a more microscopic or even molecular level.

5.2 Experimental

5.2.1 Materials

All chemicals were purchased from Acros unless otherwise noted. Aminopropyltriethoxysilane (APS, 99%), 2-bromo-2-methylpropionic acid (BriBuA, 98%), 4-dimethylaminopyridine (DMAP, 99%), \( N, N' \)-dicyclohexylcarbodiimde (DCC, 99%), and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99+%) were used as received. \( N \)-isopropylacrylamide (NIPAAm, 99%) was purified by passing through an inhibitor removal column using a mixture of dichloromethane and n-hexane (v/v \( \sim \) 3:1) as the solvent and then recrystallized. Copper (I) bromide (99.999%) and the inhibitor removal columns were purchased.
from Aldrich and used as received. (Heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane was purchased from Gelest.

5.2.2 Instrumentation

TEM images of the PNIPAAm/SiO₂ particles were acquired using a Philips CM 12 operating at 120 kV. The particle size under variable temperature was characterized by dynamic light scattering (NICOM 380 ZLS) using the 632 nm line of a HeNe laser as the incident light; NICOM software was used to analyze the intensity-averaged particle size. Near-IR spectroscopy was carried out using a microspectrometer consisting of a reflected-light microscope (Zeiss Axiovert 135) with light output coupled into a linear photodiode array spectrometer (Control Development, Inc., South Bend, NJ) via an optical fiber. Video microscopy was carried out using phase contrast microscope (Axiovert 200) equipped with a back illuminated electron multiplying CCD camera (Andor Ixon DV-887 BI) and a programmable heat stage.

5.2.3 Synthesis of PNIPAAm brush tethered silica particles

Monodisperse colloidal silica particles were prepared according to a method developed first by Stöber et al.[5] and modified later by many other research groups. [6, 9]

The preparation of PNIPAAm brush coated silica particles is illustrated in Figure 5.1. The attachment of surface initiator and the subsequent surface-initiated polymerization of NIPAAm on the monodisperse silica particles were carried out using a published procedure with minor changes.[10]

The bare silica colloids (~ 0.5 g) were centrifuged from aqueous suspension, and washed and centrifuged two times with ethanol. The colloids were re-dispersed in 20 mL of ethanol, and then 40 µL of APS was added into the suspension. The reaction proceeded for 30 minutes under
After two centrifuge-and-disperse cycles in ethanol and one cycle in dichloromethane, the colloids were transferred into a glass centrifuge tube with a solution of BriBuA (267 mg) and DMAP (48 mg) dissolved in 40 mL of dichloromethane. The suspension was cooled by an ice bath to 0 °C, and a solution of DCC (413 mg) in 5 mL of cooled dichloromethane was added. The mixture was allowed to warm to room temperature, and the reaction was allowed to continue for 8 hours. Frequent vortexing during the reaction was needed to avoid agglomeration of the colloids. The initiator-tethered colloids were cleaned by 6 cycles of centrifuge-and-disperse in chloroform, and finally dispersed in 10 mL of 1:1 (v:v) mixture of methanol and water.

Figure 5.1. Procedure for tethering of PNIPAAm brushes on silica particles.

NIPAAm (6.3 g, 55 mmol), CuBr (80 mg, 0.55 mmol) and PMDETA (350 µL, 1.65 mmol) were dissolved in 50 mL of 1:1 (v:v) MeOH/H₂O mixture and degassed by two freeze-thaw cycles. The monomer and catalyst solution was then transferred via a canula into the degassed Schlenk tubes containing the surface-initiator tethered colloids. The polymerization
was carried out at room temperature under a nitrogen atmosphere overnight. At the conclusion of the reaction, the Schlenk tubes were disconnected from the nitrogen line. The PNIPAAm tethered colloids were cleaned after multiple centrifuge-and-disperse cycles in ethanol and in water.

5.2.4 Sedimentation of PNIPAAm tethered silica particles

The colloidal assembly of PNIPAAm-tethered particles was carried out in a sedimentation cell. Glass coverslips and glass tubes (5 mm ID, 30 mm length) were cleaned in piranha solution (3:1 v/v mixture of concentrated H\textsubscript{2}SO\textsubscript{4} and 30% aqueous H\textsubscript{2}O\textsubscript{2} solution) (CAUTION: *piranha solutions are strongly oxidizing and should not be allowed to contact organic solvents.*) for 3 hours, then were rinsed completely with copious amount of Millipore\textsuperscript{®} water (18.2 MΩ·cm) and dried under a stream of dry nitrogen. A glass tube is glued to a coverslip using epoxy adhesive to form a sedimentation cell. The assembled cells were treated by the vapor of (heptadecafluoro-1,1,2,2-tetrahydrodecyl)trichlorosilane to render hydrophobic surfaces in a sealed plastic container. 0.5 mL of aqueous suspension of PNIPAAm-tethered particles (~ 0.3% solids) was added into a sedimentation cell, and the cell was capped with a coverslip using high-vacuum grease as the sealant to prevent water evaporation. The sedimentation samples were put onto a leveled stage and allowed to settle under normal gravity. After 10 days, the colloids were completely settled to the bottom of the sedimentation cells, and the samples were removed from the stage for further experiments.

5.2.5 Particle tracking

20 µL of aqueous suspension of PNIPAAm-tethered particles (~ 0.3% solids) was diluted with 1 mL of Millipore water. 200 µL of the diluted colloidal suspension was injected into a
silicone solution holder (GRACE Biolabs, Type PC1-1.0) which has been taped securely onto a glass slide, and a PNIPAAm-tethered coverslip was pressed firmly onto the silicone surface to have a good seal. The sample was then inverted and put onto the programmable heat stage attached to the microscope. Video microscopy of the PNIPAAm/SiO₂ colloids on the planar PNIPAAm-tethered surface was carried out at 22 °C (room temperature) and at 39 °C using phase contrast imaging. Images were collected using a 63× lens (NA = 0.75) with 1.6× magnification at the speed of 10 frames/second, and 400 frames were collected continuously. The trajectories of the colloids were tracked from the video images and analyzed to obtain diffusion coefficients.

5.3 Results and Discussion

5.3.1 TEM Characterization

Figure 5.2 shows TEM images of PNIPAAm/SiO₂ core-shell particles under different magnifications. The dry PNIPAAm shell thickness is 18 ± 4 nm, and the silica core diameter is 467 ± 11 nm. Since the core radius is much larger than the shell thickness, we assume that the properties of the PNIPAAm brush tethered on these spherical particles are the same as those grafted on planar substrates. As shown by the environmental ellipsometry study of PNIPAAm brushes in Chapter 3, we expect that the shell will swell to about 80 nm under room temperature in water. Therefore, the diameter of the hydrated PNIPAAm/SiO₂ core-shell particles would be ~ 630 nm (i.e. its radius is about 315 nm).
Figure 5.2. TEM images of PNIPAAm-tethered silica colloids under different magnifications. The contrast inside the framed area of image (c) is enhanced in order to clearly show the polymer shell.

5.3.2 Dynamic light scattering results

The PNIPAAm-tethered silica colloids were characterized using dynamic light scattering (DLS) to measure the hydrodynamic sizes of the particle under different temperatures. The intensity-averaged particle diameter is 886 nm at room temperature (23 ºC), and it changes to 732 nm and 472 nm at 30 ºC and 40 ºC respectively. While more study is needed to examine the exact values of the hydrodynamic diameter of the PNIPAAm-tethered particles obtained from light scattering, the changing trend of the particle size versus temperature confirmed that PNIPAAm brush on the particles collapses when the temperature is above its LCST transition. Qualitatively, the transition is much sharper after 30 ºC, which is consistent with the ellipsometry observation in Chapter 3. The diameter at 40 ºC appears smaller than the average diameter of the particles at dry state. After LCST transition, the surface of the PNIPAAm brush becomes much more hydrophobic,[11] and we speculate that there is much less drag force experienced by these hydrophobic particles in the aqueous suspension.[12] Since the physics model for the data analysis software of the light scattering instrument may not take into account any change in solvent-particle interactions, the particle size at 40 ºC measured by DLS may be underestimated.
5.3.3 Temperature-response of the colloidal assembly of PNIPAAm/SiO₂ particles

The presence of thermally responsive PNIPAAm on the colloidal surfaces can strongly influence the phase behavior. We expect that PNIPAAm chains undergo coil-to-globule conformational change when heated above LCST, which may induce changes in the assembly of the colloids. By cycling the polymer brush above and below its LCST, and annealing out any kinetically trapped high-energy states, the surface-attached PNIPAAm chains may enable the formation of an equilibrium structure of the lowest possible energy by allowing the colloidal system to explore all available states.

Figure 5.3. Near-IR spectra of a colloidal assembly of PNIPAAm-tethered silica colloids collected at room temperature as formed (labeled as ‘RT’) and after thermal annealing at 55 °C convection oven for 24 hours (labeled as ‘after heating’).

Figure 5.3 shows the near-IR spectra of a sedimented colloidal assembly of PNIPAAm-tethered silica colloids. A spectrum was collected at room temperature after the sedimentation sample was done; the sample was then annealed at 55 °C for 24 hours and then cooled down
completely to room temperature before taking the second spectrum. As can be seen, the colloidal assembly as formed does not show any characteristic peaks over the entire spectrum except a broad hump at around 1200 nm; however, after thermal annealing, there is a distinct peak at 1534 nm for a relatively ordered structure that formed near the center of the sample (the diameter of the area of this ordered structure is ~ 1 mm).

The formation of the relatively more ordered structure after heating indicates that thermal annealing can be a very promising method to anneal the defects formed in a colloidal assembly so as to yield a good crystal. Although classic theories predict that at equilibrium a colloidal system should form a crystal when the volume fraction of the colloids is high enough, such an ideal crystal with the lowest energy is experimentally very difficult to achieve.[1, 2, 13] This is either because the conditions assumed by the theories are not satisfied, or more importantly the dynamics of the system predicts an alternative structure.[1] If the system is trapped in some high-energy intermediate state and there is no sufficient energy for it to overcome the energy barrier, the crystallization process will not occur. For the PNIPAAm coated colloids in the concentrated regime, the hydrated PNIPAAm chains may interdigitate, and the polymer interactions may be strong enough to constrain the particles from any large motion. Therefore the colloidal structure formed at room temperature may have been dictated by the kinetics since the initial two-dimensional assembly near the bottom substrate plays a critical role in determining the final structure. Thermal annealing of the PNIPAAm coated silica particles allows the colloid assembly to detrap from the high-energy state. The PNIPAAm chains will collapse into dense globules above the LCST, and thus the polymer interactions may become smaller so that the “cage” around a colloid is much easier to escape. In the mean time, since the viscosity of water becomes much smaller at higher temperature (55 ºC), a colloid can rattle much
more frequently within its “cage” compared to at room temperature. As a result, the PNIPAAm coated colloids are likely to overcome the energy barrier and reorganize to form a more ordered structure with a lower total energy during the thermal annealing process.

The near-IR diffraction peak due to the colloidal assembly can be described using Bragg’s law:[14]

\[
\lambda = 2d n_{eff} = \left( \frac{8}{3} \right)^{1/2} D \left( \sum_i n_i^2 V_i - \sin^2 \phi \right)^{1/2}
\]

where \(d\) is the characteristic spacing, \(D\) is the center-to-center distance between particles, \(n\) and \(V\) are the refractive index and the volume fraction of each component phase, and \(\phi\) is the angle between the incident beam and the sample normal. In our system, there are three phases: water, silica and water-swelled PNIPAAm. At room temperature, the indexes of refraction of these three phases are 1.33, 1.44, and 1.395 (adapted from chapter 3) respectively, and their volume fractions are 0.30, 0.29, and 0.41 respectively (assuming that the assembly formed by the hydrated particles is almost a close-packed structure). The center-to-center distance of the particles calculated according to Equation 5.1 is 676 nm, which is larger than the estimated diameter of ~630 nm from the above TEM experiments by ~7%. We expect that the center-to-center distance would be slightly larger than the diameter of the hydrated particle since the particles are assumed not to touch each other in the calculation; another cause of this difference comes from the fact that the shell thickness and the core diameter of the PNIPAAm-tethered silica particles are not rigorously monodisperse and have finite distributions.

5.3.4 Two-dimensional Brownian motion of PNIPAAm/SiO\(_2\) colloids on PNIPAAm brush surfaces

The semi two-dimensional diffusion of the PNIPAAm/SiO\(_2\) particles on a PNIPAAm brush surface was studied using video microscopy using phase contrast microscopy. First of all,
qualitatively, we have observed from the video microscopy data some interesting changes in colloidal motion before and after LCST. At 22 °C, the 2-dimensional Brownian motion of the particles on the PNIPAAm surface is stable. Particle-particle collision does not induce aggregation. In contrast, our control experiments showed that PNIPAAm/SiO₂ particles are immobilized on bare silica substrates permanently. At 39 °C, 10-15% of the PNIPAAm/SiO₂ particle population is immobilized. Particle-particle collision is followed by transient deceleration of the 2-D motion, but it does not promote permanent aggregation. Apparently, the presence of hydrated (i.e. water-swelled) PNIPAAm brush has greatly improved the thermodynamic stability of this colloid system, and the stabilization effect is mainly attributed to the high osmotic pressure inside the swelled brush.[15]

Second, from the video microscopy, we could analyze the diffusion kinetics of those mobile particles. Trajectories of a colloid particle at 22 °C and 39 °C are obtained and presented in Figure 5.4.

![Figure 5.4](image-url)  

**Figure 5.4.** Trajectories of PNIPAAm/SiO₂ particles on PNIPAAm brush surfaces at two different temperatures. (a) shows a 39-step trajectory at 22 °C (below LCST), and the time interval between each step is 1 s; (b) shows a 63-step trajectory at 39 °C (above LCST), and the time interval between each step is 0.1 s.
From the trajectories presented in Figure 5.4, we did a time-averaged analysis of the mean-square displacement using Equation 5.2, and then calculated the diffusion coefficient of the 2-D diffusion using Equation 5.3. [16-18]

\[ \left\langle |r(t) - r(0)|^2 \right\rangle = \frac{1}{N_i} \sum_{i=1}^{N_i} |r(t + t_0) - r(t)|^2 \]  

(5.2)

\[ \left\langle |r(t) - r(0)|^2 \right\rangle = 4Dt \]  

(5.3)

Figure 5.5 shows the graphs of mean squared displacement versus time at two different temperatures. At 22 °C, the diffusion coefficient is \( \sim 0.32 \mu m^2/s \), and at 22 °C, the diffusion coefficient is \( \sim 0.94 \mu m^2/s \). The increase in diffusion coefficient is almost 3-fold.

If we assume there is no surface interaction, we could estimate the diffusion coefficient of the colloids using the Stokes-Einstein equation.

\[ D = \frac{k_B T}{6\pi\eta a} \]  

(5.4)

We take into account the changes in the following parameters: (1) viscosity of water decreases from \( 9.54 \times 10^{-4} \) Pa·s (22 °C) to \( 6.66 \times 10^{-4} \) Pa·s (39 °C); (2) particle radius decreases from \( \sim 315 \) nm (22 °C) to \( 285 \) nm (39 °C); (3) temperature increases from 295 K to 312 K. The diffusion coefficient is estimated to be \( 0.7 \mu m^2/s \) at 22 °C and \( 1.2 \mu m^2/s \) at 39 °C (there is about 1.7-fold increase in the calculated diffusion coefficient). As can be seen from the comparison between the experimental data and the calculated values, there is a larger change in the dynamics of the colloids observed in the experiments. We speculate that heating may trigger a transition from “sticky” surfaces to “slippery” surfaces: below the LCST, swelled PNIPAAm chains may interdigitate and slow down particle motion; above the LCST, the PNIPAAm coated particles on the PNIPAAm brush surface have minimal interactions.
Figure 5.5. Mean square displacement versus time. (a) at 22 °C (below the LCST); (b) at 39 °C (above the LCST).

5.4 Future Work

We intend to further our study on colloidal assembly in the concentrated regime by finely tuning the temperature gradient and introducing external triggers such as ionic strength and pH, in order to get a full understanding of the colloidal phase behaviors.

In the preliminary work on the 2-D diffusion of the PNIPAAm/SiO₂ colloids, we have carried out a time-averaged analysis to obtain the diffusion coefficients at two different temperatures. Our future work includes a systematic, variable-temperature experiment. We would observe the colloidal system from room temperature to well above LCST at fine steps of temperature increase, in order to determine the transition point and more details about the change in diffusion kinetics. We would study a large ensemble of particles and analyze the data statistically. For an ideally uniform population of colloids, the ensemble-averaged motion of a large number of particles would yield the identical diffusion coefficient as the time-averaged motion of a single particle.[17] However, in a realistic colloidal system, it is necessary to do a statistical evaluation based upon both the ensemble-averaged and time-averaged analysis as
described by Equation 5.5. And then the diffusion coefficient can be estimated by using Equation 5.3.

\[
\left\langle |r(t) - r(0)|^2 \right\rangle = \frac{1}{N N_t} \sum_{n=1}^{N} \sum_{t=0}^{T} |r_n(t + t_0) - r_n(t_0)|^2
\] (5.5)

Another future effort is to determine the mechanism of the apparent 2-D diffusion on the surface. Instead of a truly 2-dimensional diffusion, what we have observed in our video microscopy is a 2-dimensional projection of the actual diffusion. The particles are able to randomly walk on the brush surface through either a “hopping” mechanism, which involves a single diffusion coefficient, or the particles can move through a multiple “trap-and-release” mechanism, which is best described by two distinct diffusion coefficients.[19] Figure 5.6 schematically represents the two diffusion mechanisms. Through carefully designed experiments (with better time and spatial resolutions), we may be able to distinguish which mechanism is more plausible in our colloidal system.

Figure 5.6. Schematics of two proposed diffusion mechanisms: (a) “hopping” mechanism, in which the particles are constantly engaged at the flat, brush surface and only one diffusion coefficient is needed to describe the particle diffusion; and (b) trap-and-release mechanism, in which the particles can engage with the surface and diffuse at a finite diffusion coefficient for a specific period, and disengage transiently from the surface and diffuse at another speed for another time period.

A longer term goal is to systematically study self-assembly and diffusion kinetics of polymer-tethered particles. Patterned polymer brushes (on a flat surface) will be very interesting for our future experiments since dramatically different polymer structures can be attached in a
single patterned sample, which allows exploring different colloid-surface interactions simultaneously. We can also use polymer brushes with gradient in molecular weight, grafting density and surface energy to systematically investigate the colloid-surface interactions. On the other hand, the chemical compositions of the core and shell, the core diameter, and the shell thickness of core-shell colloids can be independently varied in order to carry out a systematic investigation.

5.5 Conclusions

In summary, we have tethered PNIPAAm brushes onto monodisperse silica particles via surface initiated polymerization, and characterized them using TEM and dynamic light scattering. We have studied the colloidal assembly formed by these colloids by using near-IR spectroscopy, and found that thermal annealing slightly improved the crystallinity of the structure. Preliminary experiments on the semi two- dimensional diffusion of the PNIPAAm/SiO$_2$ particles suggested that PNIPAAm brushes greatly improve the stability of the colloidal system. The diffusion kinetics is very sensitive to the temperature change, and we have observed a three-fold increase in diffusion coefficient, which is greater than the expected ~ 2-fold increase, when temperature is increased from 22 ºC to 39 ºC. The LCST transition of PNIPAAm may have played an important role in determining the diffusion of the colloids, and our speculation is that interdigitation between PNIPAAm chains may slow down the colloidal diffusion at room temperature relative to above the LCST.

5.6 References

CHAPTER 6

CONCLUSIONS

In this thesis, polymer brushes and self-assembled monolayers are utilized to build 2-dimensional transport media on silicate substrates to confine and guide molecular diffusion. Microcontact printing and photolithography combined with surface-initiated atom transfer radical polymerization are the major techniques to construct patterned and unpatterned polymer brushes. Extensive surface characterizations, including AFM, ellipsometry, FTIR, XPS, XRR and etc., are used to confirm chemical identities and physical properties of the polymer brushes; FRAP is used to determine diffusion coefficients of a fluorescent dye, Prodan, in the polymer brushes.

CTS, OTS, PEG SAMs and clean silica surface are tested first for their molecular transport properties. Similar diffusion constants are found for the CTS and PEG layers, and we attributed this result in part to the ability of Prodan to partially intercalate in these layers enabling good dispersion and diffusion. No fluorescence recovery is observed on the OTS SAM or on the clean silica surface. Prodan is thought to aggregate on the OTS SAM, and form hydrogen bonds with the abundant silanol groups on the silica surface. There is no significant change in the rate of diffusion with relative humidity on the PEG layer, but there is a slight increase on the CTS SAM.

Patterned poly(N-isopropylacrylamide) (PNIPAAm) brushes were fabricated on oxidized silicon wafers by surface-initiated atom transfer radical polymerization of N-isopropyl acrylamide from a micropatterned initiator. The patterned surface initiator was prepared by microcontact-printing octadecyltrichlorosilane and backfilling with 3-(aminopropyl)triethoxysilane followed by amidization with 2-bromo-2-methylpropionic acid.
XPS and FTIR confirmed the chemical structure of the surface initiator and the PNIPAAm brushes. Surface analysis techniques, including ellipsometry, contact angle goniometry, and X-ray reflectometry (XRR), were used to characterize the thickness, roughness, hydrophilicity, and density of the polymer brushes. Tapping-mode AFM imaging confirmed the successful patterning of the PNIPAAm brushes on the oxidized silicon substrates. Variable temperature ellipsometry indicated that the lower critical solution temperature of the hydrated PNIPAAm brush was broad, occurring over the range of 20-35 °C. Fluorescence microscopy further proved the successful patterning of the polymer brushes and suggested that the Prodan is localized in the patterned PNIPAAm brushes and excluded from the surrounding octadecyltrichlorosilane regions.

Surface initiated ATRP of OEGA is carried out to prepare POEGA brushes on silicate substrates. The chemical structure of the POEGA brushes was confirmed by XPS, FT-IR and ToF SIMS, and the physical properties were characterized with ellipsometry, and contact angle measurements. The fluorescence emission spectrum of Prodan in POEGA brushes indicates that the local chemical environment is relatively mobile, which is expected from the low $T_g$ of POEGA. FRAP of Prodan in unpatterned POEGA brushes shows that the diffusion of Prodan in dry POEGA is very fast, with a diffusion coefficient of 0.6 μm²/s, which can also be explained by the low $T_g$ of POEGA. The diffusion of Prodan in POEGA under different humidity has been studied using FRAP, and it can be described reasonably well using WLF equation. Two methods have been applied to pattern POEGA brushes: the first method involves microcontact printing of OTS, backfilling of APS, surface reaction to attach initiator and finally surface-initiated polymerization of OEGA; the second method utilizes photolithography and RIE to pattern POEGA brushes. AFM was used to test patterned POEGA brushes, and showed good
topographic contrast between the polymers and the OTS or naked glass substrate. However, so far our patterned polymer brushes are not able to confine Prodan molecules to diffuse exclusively inside the polymer regions. We have designed new experimental routes to overcome possible limitations in the patterning procedure and hopefully to reach the goal of guided molecular diffusion in surface-tethered polymer pathways.

PNIPAAm brushes are tethered onto monodisperse silica particles via surface initiated polymerization, and characterized using TEM and dynamic light scattering. We have studied the colloidal assembly formed by these colloids by using near-IR spectroscopy, and found that thermal annealing slightly improved the crystallinity of the structure. Video microscopy on the semi two-dimensional diffusion of the PNIPAAm/SiO₂ particles suggested that PNIPAAm brushes greatly improve the stability of the colloidal system. The diffusion kinetics is very sensitive to the temperature change, and we have observed a three-fold increase in diffusion coefficient when temperature is increased from 22 °C to 39 °C. The LCST transition of PNIPAAm may have played an important role in determining the diffusion of the colloids, and our speculation is that interdigitation between PNIPAAm chains may have slowed down the colloidal diffusion at room temperature.

From the results of this thesis research, we have learned that the interactions between the probe molecule and the polymer brush, and polymer-polymer interactions between the polymer coated colloids and the polymer tethered planar substrates determine the diffusion rate of small probes in the polymer matrix, and govern phase behavior and diffusion kinetics of the colloids at surfaces. The research may be continued with systematic experiments on constructing transport media for different molecular or ionic species, and studying the interfacial interactions between colloids and surfaces under external stimuli. We expect that the patterned polymer brushes
developed in this thesis have intriguing properties as surface-confined channels for transporting molecules and ions, and surface templates for the formation of ideal colloidal crystals.
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Huilin Tu was born on April 26, 1975 in Jiangxi Province, China. She graduated from Peking University in July 1997 with a bachelor’s degree in chemistry and in July 2000 with a master’s degree in chemistry with a focus on polymer chemistry. Since August 2000, she has pursued a Ph. D. in materials science and engineering at the University of Illinois at Urbana-Champaign under the supervision of Professor Paul Braun. In fall semesters of 2001, 2002, and 2003, she was a teaching assistant for Polymer Chemistry. She has been awarded Mavis Memorial Scholarship in 2003. During her spare time, she enjoyed running and swimming long distances, and cooking. She will stay on campus to do postdoctoral research on surfaces and colloids, working with Professors Paul Braun and Steve Granick.