DEWETTING OF POLYSTYRENE THIN FILMS
ON ORGANOSILANE MODIFIED SURFACES

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DEWETTING OF POLYSTYRENE THIN FILMS
ON ORGANOSILANE MODIFIED SURFACES

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Dissertation

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ABSTRACT

The importance of polymer thin films (< 100 nm) in microelectronics, coatings/paints, adhesives, nanofabrication, or biodevices has promoted extensive studies on the dewetting phenomenon of these thin films. Most of the studies have been focused on the effects of polymer properties on the dewetting and the associated kinetics while the effects of substrates on the dewetting behaviors, which could be crucial in some cases, have rarely been reported. For the few experimental studies that utilized modified substrates, none has systematically varied substrate surface energy (γ_S) to examine its effects on the dewetting. Therefore, in this study, the effects of γ_S on the dewetting process of supported polystyrene (PS, M_n of 63k and 9.3k) thin films were studied. The substrates were modified using various organosilanes under different preparation conditions to systematically vary γ_S, ranging from 13 to 63 mJ/m^2. In particular, the preparation methods included (1) contact printing of octadecyltrichlorosilane on oxidized silicon wafers for different contact times, (2) vapor phase deposition of mixed CF_3- and CH_3-terminated organosilanes with different ratios, and (3) solution deposition of polar organosilanes with functional groups of -COOH, -CH_2Cl, -NH_2, or -SH. On these substrates, the kinetics of dewetting was first investigated as a function of γ_S. Empirical relationships between the rate of hole growth (dewetting velocity, V_R) and γ_S. V_R ≈ 530
exp(-0.13\gamma_S) and 310 \exp(-0.10\gamma_S), were obtained from the dewetting of PS-63k thin films on the -CH_3 and -CF_3/CH_3 covered surfaces, respectively. For PS-9.3k on the OTS surfaces, \(V_R \approx 1.1 \times 10^4 \exp(-0.13\gamma_S)\) was obtained. In analogous to a desorption process, the exponential relationship between \(V_R\) and \(\gamma_S\) was hypothesized to be originated from the energy required to overcome the free energy of adhesion in the dewetting process, which is proportional to \(\gamma_S^{1/2}\).

Second, an origin of the instability of the rim, formed around the dewetting hole, was elucidated in relation to \(\gamma_S\). The rim instability, in terms of undulations of the rim, became more pronounced as \(\gamma_S\) decreased. A narrower and higher rim was also observed as \(\gamma_S\) decreased. A simple material balance of the rim formation verified that \(\gamma_S\) determined the rim profile through the variation of \(\theta_d\). The predicted rim profiles were used in combination with the analysis of the Rayleigh instability of a cylindrical fluid to interpret the rim instability. The model captures the basic trend of the rim instability dependence on \(\gamma_S\).

Third, the possible mechanism of the enhancement of the PS thin film stability on substrates modified using an NH_2-terminated organosilane, aminopropyltriethoxysilane (APTES), was proposed and evaluated. Dewetting suppression was only observed for PS/APTES that was thermally treated at \(\sim 80\) or \(120\) °C prior to annealing the thin film at higher temperatures, and much stronger suppression was observed for PS having a molecular weight higher than \(M_e\) (entanglement molecular weight). For PS thin films
deposited onto non-cured or precured APTES networks, no dewetting suppression was resulted. These results suggested that the penetration of the entangled PS chains into the APTES layer and the thermal crosslinking of the APTES molecules over the penetrated PS chains were responsible for the dewetting suppression.

This study has indicated the importance of $\gamma_S$ in the dewetting kinetics or rim morphology of the dewetting holes and the capability of dewetting suppression by simply modifying the substrate. However, it can be suggested that for the dewetting kinetics, the assumption of the “thermally-activated” dewetting process in our hypothesis could be verified by temperature-dependent studies of $V_R$ with a fixed $\gamma_S$; and for the dewetting suppression of the PS/APTES systems, the interface of PS/APTES could be investigated using X-ray or neutron reflectometry to probe any interdiffusion across the interface. Furthermore, other factors affecting the dewetting behaviors, e.g. film thickness of PS or molecular weights of PS, could also be systematically varied for a fixed $\gamma_S$, providing a possibility of multidimensional combinatorial analysis of the dewetting.
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4.34 Topographical AFM images of APTES surfaces generated by different deposition techniques: solution deposition (a – c), vapor phase deposition (d), and contact printing (e) techniques. For the solution deposition, hexane (a), chloroform (b), and toluene (c) were used. No dramatic topographical differences were observed. Some formation of aggregates on the surfaces generated from the solvents was noticed. The scan size is 2 μm × 2 μm.

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NOTATION

Roman Letters

$A$ Hamaker constant

$d_0$ Minimum cutoff equilibrium distance between surfaces

$\Delta E_{\text{des}}$ Activation energy for desorption

$f_x$ Unknown factors or constants

$G$ Gibbs free energy

$H$ Rim height

$k_B$ Boltzmann constant ($1.3807 \times 10^{-23} \text{ J/K}$)

$k_{\text{des}}$ Desorption rate constant

$L$ Average length of distance between two adsorption/desorption sites

$L$ Correlation (decay) length for polar interactions

$M_n$ Number average molecular weight

$N$ Refractive index

$P$ Ratio of viscosity of liquid and viscosity of medium

$Q$ Growth rate of instability

$R$ Radius of dewetting hole

$R_o$ Radius of curvature of rim

$R_p$ Complex Fresnel reflection coefficient of p-polarized light
$R_s$ Complex Fresnel reflection coefficient of s-polarized light

$S$ Spreading coefficient

$S^d$ Dispersion component of spreading coefficient

$S^p$ Polar component of spreading coefficient

$T$ Time

$T$ Temperature

$T_g$ Glass transition temperature

$V_R$ Velocity of dewetting hole growth ($dR/dt$)

$W$ Rim width

$W_{II}$ Work of adhesion

$W_{III}$ Work of cohesion

$X$ Head group of organosilane

Greek Letters

$\alpha_0$ Original amplitude of thermal fluctuation

$\alpha_b$ Amplitude of instability at breakup

$\beta$ Reduced film thickness

$\Delta$ Relative phase change of incident light

$\delta$ Film thickness

$\Gamma$ Function of $\lambda$ and $R_o$

$\gamma$ Surface energy

$\gamma^d$ Dispersion component of surface energy
\( \gamma^p \)  Polar component of surface energy

\( \gamma_S \)  Substrate surface energy

\( \eta \)  Viscosity

\( \Lambda \)  Area

\( \lambda \)  Instability wavelength

\( \lambda_L \)  Wavelength of light

\( \nu_0 \)  Frequency factor of desorption

\( \Pi \)  Disjoining pressure

\( \pi_e \)  Equilibrium film pressure

\( \theta \)  Contact angle

\( \theta_a \)  Advancing contact angle

\( \theta_d \)  Dynamic contact angle

\( \theta_e \)  Equilibrium contact angle

\( \theta_i \)  Angle of incidence

\( \theta_r \)  Receding contact angle

\( \sigma \)  Desorption sites per unit area

\( \Omega \)  A complex function of \( \lambda \) and \( p \)

\( \Psi \)  Relative amplitude change of incident light
1.1 Importance of Substrate Surface Energy in Polymer Thin Film Dewetting

Ultrathin polymer films (< 100 nm) have extensive technological applications in the areas of paints and coatings, microelectronics, adhesion and lubrication, and nonlinear optics. Scientific interest concerning these films extends to fundamental studies of multilayer adsorption,\(^1,^2\) cell adhesion,\(^3,^4,^5,^6\) and polymer diffusion or adsorption.\(^7,^8\) A key criterion for these applications is the stability of the polymer thin film on a solid substrate. As recent technological applications advance towards smaller scales and more complicated designs, the concomitant applied coating in industrial processing requires thinner and thinner films. However, there are critical limitations in producing very thin polymer films with desirable stability, uniformity, and continuity after aging or thermal processing\(^9\) since the thin films on nonwettable surfaces are generally unstable, i.e. they exhibit dewetting phenomenon.\(^10\) When a polymer thin film is annealed above its glass transition temperature (\(T_g\))\(^11\) and enters its liquid-like state, the film starts to break up, resulting in the exposure of the substrate to the surroundings.\(^12,^13,^14\) Theoretical studies indicate that the dewetting process is initiated and driven by the minimization of system
free energy, which is related to the interaction between the film and the substrate. Most theoretical predictions and experimental studies have focused on properties of the polymer to investigate the kinetics of dewetting and to suppress the dewetting process. Few studies have been performed on the effects of substrate properties, such as substrate surface energy ($\gamma_S$), on the dewetting behavior, even though the substrate surface energy is one critical factor in minimizing the system free energy. Therefore, evaluating the importance of the driving force, more specifically surface and interfacial energies, in the dewetting process and its associated dewetting morphology is essential for both fundamental understanding and technical applications of polymer thin films.

1.2 Scope of Research

The overall objective of this work is to understand the effects of substrate surface energy on the kinetics and morphological pattern formation of PS thin films (< 100 nm) dewetted from substrates modified with organosilanes. The functionality of organosilanes, which could promote a specific interaction with PS and subsequently affect the dewetting process of PS thin films, is also addressed.

Studying dewetting behavior with a wide-ranging variation of substrate surface energy makes it possible to rationalize the effects of substrate surface energy on dewetting kinetics in terms of dewetting hole growth.\textsuperscript{15,16,17} Any turnovers in dewetting phenomena, e.g. the instability of rims formed around dewetting holes, related to the substrate surface energy, can also be identified. A wide ranging variation of the substrate
surface energy ($\gamma_S$) is generated by different coverages of CH$_3$-terminated organosilanes, different mixing ratios of CH$_3$- and CF$_3$-terminated organosilanes, and various polar organosilanes. Dewetting hole growth rates ($V_R$) of PS thin films on various substrates with different surface energies are obtained and compared with theoretical predictions.

Besides the dependence of $V_R$ on $\gamma_S$, during the hole growth, rims formed around the dewetting holes also demonstrated different morphological instability as a function of $\gamma_S$—from a uniform rim with even width and height throughout its circumference to an undulating rim with regularly spaced protrusions. The development of the rim instability was identified as a function of $\gamma_S$. The variation of rim profiles, depending on $\gamma_S$, was examined and compared with a theoretical model, derived from the interaction between PS and the substrates and a simple material balance. A mechanism of the rim instability was suggested based on a Rayleigh instability. Predicting and understanding the rim instability can be important in designing nano/micro-scaled 2-D or 3-D polymeric structures through a controlled manipulation of the dewetting process.

In addition, suppression of the dewetting of PS thin films by modifying substrates with a particular organosilane is accomplished. To suppress or retard the dewetting process is essential in coatings of polymer thin films, where maintaining the continuity and homogeneity of films is the first requirements for their applications. Suppression of the dewetting of PS thin films on NH$_2$-terminated organosilane surfaces was studied and evaluated, and a possible mechanism of the suppression was suggested.
1.3 Overview of the Dissertation

In this chapter, the stability issue of polymer thin films from the perspective of substrate surface energy and the objectives and scopes of this work are briefly presented. Chapter 2 provides literature reviews of surface modification using organosilanes and theoretical aspects of the dewetting of polymer thin films. In Chapter 3, experimental approaches to achieve the objectives are described. Chapter 4 summarizes the main results and discussion of the study, and Chapter 5 concludes this study along with some possible future directions of this research.
CHAPTER II

BACKGROUND

Dewetting of PS thin films on various organosilane modified surfaces is investigated in this work. In this chapter, the molecular structures, self-assembly, and deposition techniques of organosilanes will be provided. Then, a general description of material-substrate interactions, the instability of polymer thin films on surfaces, and the dewetting phenomena of films are presented.

2.1 Organosilane Self-Assembled Monolayers

2.1.1 Organosilanes

Organosilane molecules have attracted much attention for technological applications because of their ability to modify surface characteristics of materials without altering the bulk properties of these materials, as well as for their excellent chemical, mechanical, and thermal stability. Organosilane modified surfaces are widely used as model surfaces for applications in the areas of wettability, chemical resistance, biocompatibility, and lubrication. In addition to the importance of fundamental
Figure 2.1  A structure of an organosilane molecule (a) and its self-assembled monolayer (SAM) (b). Xs indicate head groups that can react with substrates. The functionality in this case is a methyl group, -CH₃. The drawing of the SAM (b) is a part of a cross-linked organosiloxane network.¹⁸
studies, organosilane molecules have been utilized in more practical technological applications such as photolithography, micropatterning, sensors, optoelectronics, and microelectromechanical systems (MEMS).22,23,24,25,26

Organosilane molecules and their derivatives normally have RSiX₃, R₂SiX₂, or R₃SiX structures. The active head group, X, generally chloride or alkoxy, of organosilanes can be chemisorbed on a hydroxylated substrate. The body of the organosilane molecule, R, represents a carbon chain and includes a terminal group that is responsible for the surface functionality (Figure 2.1). Functionality can be -CH₃, -CF₃, -NH₂, -CH₂Cl, -SH, -COOH, etc. When Si/SiOX is used as a substrate, the remarkably strong stability can be achieved by three-dimensional polysiloxane network formation among the silane molecule themselves and between the substrate silanol groups and the organosilane molecules. Therefore, with a proper functional group, i.e. a terminal group with low or high energy, the wettability of organosilane-modified surface can be changed dramatically.

2.1.2 Self-Assembled Monolayers

Self-assembled monolayers (SAMs) are highly ordered molecular assemblies that are formed by a spontaneous adsorption of surfactants on the solid surface of interest via a specific affinity with the substrate.18,27,28,29,30 This results in the formation of thin and uniform molecular monolayers with a strong physical or chemical stability.18,19 Figure 2.2 represents a schematic of SAMs, including the components of a SAM-molecule (head
Figure 2.2 Schematic of SAMs. A molecule that can form SAMs is composed of three major parts: head group (open octagon) that adsorbs on the substrate via physicochemisorption, backbone (rectangular) that supports and maintains the SAM-structure via interchain van der Waals or electrostatic interactions, and an end group (shaded octagon) that endows a specific functionality to the SAMs.\(^\text{18}\)
group, backbone or chain, and end group) in general. The head group participates in exothermic chemisorption on the substrate. Due to the nature of the exothermic process, molecules adsorb until all the possible binding sites are occupied. The backbone or body is normally an alkyl chain. After the adsorption of the head groups on the substrate, the alkyl chains assist in producing an ordered and close-packed self-assembly through inter-chain van der Waals interactions. The end group is the one that determines the functionality of the modified substrate.

There are several types of organic SAMs: n-alkanoic acids on metal oxide surfaces (e.g. Al₂O₃, AgO, or CuO) through acid-base reactions; organosulfur adsorbates on Au, Ag, or Cu from the chemisorption of thiolates; organosilicon on hydroxylated surfaces (silicon oxides, Al₂O₃, glass, etc.) through the physiochemical adsorption of organosilanes; and alkyl monolayers on hydrogen-terminated Si through direct covalent bonds between C and Si.²¹,²⁷ SAMs have been recognized for not only their easy accessibility, design flexibility, and simple self-organizing process, but also their vast applications. SAMs can be used as model systems for fundamental understanding of interfacial phenomena; chemical and biochemical sensors, building blocks or foundations for supra/macromolecular architectures; surface coatings for applications including control of wetting, adhesion, lubrication, and corrosion.²¹,²⁹,²⁷

2.1.3 Mechanism of Organosilane SAM Formation

The growth mechanism of organosilane SAMs can be discussed from two
different perspectives: physicochemical surface reaction of organosilane molecules onto substrates and morphological growth behavior of silane polymerization towards fully-covered monolayers.

2.1.3.1 Reaction Mechanism

A general mechanism of the molecular surface reaction is described as follows (Figure 2.3).\textsuperscript{31,32} First, organosilane molecules are physically adsorbed on a water film present on silicon oxide substrates under ambient conditions (Figure 2.3a).\textsuperscript{33} In a solution deposition technique, it is possible that organosilane molecules are hydrated by water moieties present in the solvent. However, this pre-mature hydration could result in heterogeneous and rough SAMs.\textsuperscript{34} Those adsorbed molecules are then hydrated and bound to surface silanol groups via hydrogen bonding (Figure 2.3b), and then chemically react with the surface silanols to form Si-O-Si, or siloxane bonds, after dehydration (Figure 2.3c). Concomitantly, the hydrolyzed organosilanes can link together to form a polysiloxane network. This 2-dimensional polysiloxane network anchors to the substrate surface by occasional siloxane linkages.\textsuperscript{31,32} The reduced roughness of a substrate surface modified by organosilane SAMs, compared to that of the bare substrate, supports the concept that only occasional bonds of the SAMs attach to the substrate. A polysiloxane network with all of its individual organosilane molecules directly linked to the surface silanols would exhibit the same surface roughness that of the bare substrate.\textsuperscript{31,32}
Figure 2.3 Illustration of physicochemical reaction mechanisms of organosilane SAMs. X: head groups, \(\bigtriangleright\bigtriangleright\bigtriangleright\): alkyl chain, and F: functional group. (a) adsorption of organosilane molecules on a water film adsorbed on the silicon oxide substrates, (b) hydration of adsorbed organosilane molecules and fixation via hydrogen bondings with surface silanol groups, and (c) polymerization between hydrated organosilane molecules and surface silanols or among the molecules after dehydration.\(^{31}\)
2.1.3.2 Growth Mechanism

Two contradictory models have been proposed to explain the growth mechanism of organosilane SAMs: “island” and “uniform” models.\textsuperscript{18,19,29} In the island model (Figure 2.4b), a partially-formed layer is composed of islands with a full layer thickness, and the islands continue to grow until full coverage is achieved. On the contrary, in the uniform model (Figures 2.4a), an organosilane SAM grows homogeneously in film thickness, from a sub-layer thickness for the partial liquid-like state to the full extended layer for the ordered state. Cohen \textit{et al.} first reported that an incomplete SAM was composed of partially ordered islands, observed by FTIR (Fourier transform infrared) spectroscopy.\textsuperscript{35} However, in the work of Wasserman \textit{et al.} and Tidswell \textit{et al.} who employed X-ray reflectivity (XR) and ellipsometry, the uniform growth mechanism was proposed.\textsuperscript{36,37} While those early works were employed “indirect” analytical methods, i.e. FTIR, XR, or ellipsometry, Bierbaum \textit{et al.} was able to directly image the morphological shape of an incomplete organosilane layer using atomic force microscopy (AFM).\textsuperscript{38} They confirmed that partial layers formed in islands, also supported by other AFM studies.\textsuperscript{28}

It is generally accepted that the growth of organosilanes proceeds via the expansion of islands for C\textsubscript{18} trichlorosilane (octadecyltrichlorosilane, OTS) on silicon oxides at room temperature; however, it can be erroneous to assume this mechanism for all cases. It should be noted that when a conclusion of the growth mechanism for a certain organosilane is drawn based on the literature, one must consider only the same organosilane and the same experimental conditions. The final quality of organosilane
Figure 2.4 Illustration of morphological growth mechanisms of organosilane SAMs. (a) uniform model, a uniform growth of SAMs in film thickness; (b) island model, an increased coverage of fully extended islands; (c) combination of uniform and island models, coexistence of thinner (< fully extended) and continuous layer among fully extended islands; and (d) intermediate of uniform and island models, a growth of islands in thickness and lateral dimension.\textsuperscript{18,54}
SAMs is dependent on a proper combination of the degree of polymerization between molecules and the density of surface anchoring, as mentioned in the previous section. The growth mechanism is also sensitive to the type of organosilanes (e.g. chain length, head groups, and functionality), as well as the water content, temperature, and substrate conditions. In addition, it is also critical that a distinction between physically adsorbed and chemically reacted molecules be made in the interpretation of experimental results. Depending on the conditions, the growth mechanism could either follow the uniform model or the island model, or a combination of the two (Figure 2.4c). In some cases, an intermediate (Figure 2.4d) of uniform and island models could also be possible. In general, organosilanes with longer-chains and non-reactive functionality with substrates tend to grow via the island model at higher water contents at reaction temperatures lower than the “critical growth temperatures” of the molecules.

2.1.4 Deposition Techniques

The most common techniques for depositing organosilanes are solution deposition, vapor phase deposition, and contact printing (Figure 2.5). In the solution method (Figure 2.5a), a substrate is immersed in an organosilane solution, normally one to tens of millimolarity, for a certain period of time (normally for hours). The reaction occurs at room temperature or at elevated temperatures. The combination of solvent (e.g. hexane, toluene, alcohol, or mixtures of solvent and surfactant), deposition time, and deposition temperature can be optimally selected to ensure the formation of a
Figure 2.5 Organosilane deposition techniques: (a) solution deposition technique, (b) vapor phase deposition technique, and (c) contact printing
complete homogeneous monolayer. In vapor phase deposition (Figure 2.5b), a substrate is exposed to the vapor of an organosilane, generated from either the neat organosilane or the mixture of heavy mineral oil and the organosilane. Normally, the organosilane or its mixture with mineral oil is placed inside a vacuum chamber, which provides a sufficient low pressure to vaporize the organosilane. Mineral oil, having a very low vapor pressure, serves as a buffer to prevent the organosilane from hydrolysis before it reacts with the substrate, which hinders uniform monolayer formation. However, this technique is limited to organosilanes that have high vapor pressure. Contact printing, recently developed, is the simplest and most convenient method for providing a densely-packed and ordered SAM. In this technique (Figure 2.5c), an elastomeric stamp is inked with an organosilane solution and brought into contact with a substrate. The organosilane molecules on the elastomeric stamp are transferred onto the substrate and react to form SAMs. Generally, contact printing can be done within tens of seconds.
2.2 Polymer Thin Film Dewetting

2.2.1 Wetting and Dewetting

When a liquid (I) spreads over another liquid or a solid (J), the spreading behavior can be predicted by the change of the free energy of the system, $G$ (Figure 2.6). At constant temperature and pressure, the change in $G$ can be expressed as the following:

$$dG = \frac{\partial G}{\partial \Lambda_I} d\Lambda_I + \frac{\partial G}{\partial \Lambda_{IJ}} d\Lambda_{IJ} + \frac{\partial G}{\partial \Lambda_J} d\Lambda_J$$  \hspace{1cm} [2.1]

where $\Lambda$ is the area. Since the free energy per unit area, $\frac{\partial G}{\partial \Lambda}$, is defined as the surface free energy, $\gamma$, and $-d\Lambda_I = d\Lambda_J = d\Lambda_{IJ}$, equation [2.1] becomes

$$-\frac{dG}{d\Lambda_I} = \gamma_J - \gamma_{IJ} - \gamma_I$$  \hspace{1cm} [2.2]

Usually, $-dG/d\Lambda$ is defined as the spreading coefficient, $S_{IJ}$, which indicates the free energy change for the process of spreading I over J. In general, $S_{IJ}$ is simply denoted as $S$. A positive $S_{IJ}$ (i.e. $dG < 0$) means I spreads spontaneously over J (i.e. I wets J).

$S_{IJ}$ can also be written as

$$S_{IJ} = W_{IJ} - W_{II}$$  \hspace{1cm} [2.3]

where $W_{IJ}$ is the work of adhesion ($W_{IJ} = \gamma_I + \gamma_J - \gamma_{IJ}$), and $W_{II}$ is the work of cohesion ($W_{II} = 2\gamma_I$). It suggests that if the interaction between J and I ($W_{IJ}$) is larger than that of I-I ($W_{II}$), I spreads freely over J. Otherwise, additional work is required to cause I to
spread over J, and I will not wet J spontaneously. In the case that I is forced to wet J, I will spontaneously dewet from J when the restraining factors are removed.

2.2.2 Excess Free Energy and Disjoining Pressure

The stability of a polymer thin film (i.e. the possibility of dewetting) is related to its film thickness. Thick films (> 100 nm), due to the gravitational force, can be stable or metastable even if the spreading coefficient, \( S \), is negative.\(^{63,64,65} \) However, for thinner films (< 100 nm), excess intermolecular interaction free energy\(^ {66,67,68,69} \) can be dominant, and spontaneous dewetting can occur when \( S \) is negative.

The non-retarded and additive\(^ {70} \) excess free energy (or the excess Lifshitz-van der Waals energy) per unit area, \( \Delta G \), and the disjoining pressure, \( \Pi \), of a thin film bounded by a substrate and an inviscid fluid (normally air or vacuum) is obtained by pairwise summations of film-film and film-substrate interactions (Figure 2.7). In general, \( \Delta G \) and \( \Pi \) are the sum of antagonistic (attractive/repulsive) long- and short-range interactions,\(^ {71,72,73,74} \)

\[
\Delta G = -\left( \frac{A}{12\pi\delta^2} \right) + S^p \exp\left( \frac{-\delta}{l} \right) \tag{2.4}
\]

\[
\Pi = -\left( \frac{\partial \Delta G}{\partial \delta} \right) = -\left( \frac{A}{6\pi\delta^3} \right) + \frac{S^p}{l} \exp\left( \frac{-\delta}{l} \right) \tag{2.5}
\]

where \( \delta \) is film thickness and \( l \) is a correlation (decay) length for the polar interactions. The terms on the right hand side of equations \([2.4]\) and \([2.5]\) represent, from the left, long-range Lifshitz-van der Waals interactions and short-range polar energies of
Figure 2.6 The spreading of liquid I over solid J (or liquid J). The spreading of liquid I depends on the change of free energy for the system.\textsuperscript{30}
Figure 2.7  Schematic presentation of the film fluid (3) bounded by a substrate (1) and surrounding fluid (2). The evolution of the infinitesimal perturbation of the film fluid leads to the film breakup or deformation, i.e. instability. $\delta_0$ is the initial film thickness.
interactions, respectively.\textsuperscript{71,72,73,74,75,76} The first and last terms are from the 6-12 Lennard-Jones potential.\textsuperscript{75,76} The inclusion of the Born repulsion prevents equations [2.4] and [2.5] from breaking down, mathematically, as the singularity ($\delta \to 0$) is approached.\textsuperscript{75,76}

Since $A > 0$ and $B > 0$, “the nonlinearity stabilizes the solution behavior at small $\delta$”.\textsuperscript{77}

The second term corresponds to either the attractive “hydrophobic force” or the repulsive “hydration force”, which has been found to decay exponentially with film thickness.\textsuperscript{70,72}

This polar intermolecular interaction can be ignored when the polymer film and one of the bounding media (substrate (1) and surrounding fluid (2) in Figure 2.7) are nonpolar.\textsuperscript{72}

$A$ in equations [2.4] and [2.5] is the effective Hamaker constant, which is related to the Hamaker constants for binary interactions of the system components (Figure 2.7):\textsuperscript{18,72}

\[ A = A_{33} + A_{12} - A_{13} - A_{23} \quad [2.6] \]

Since the surrounding fluid is usually vacuum, $A_{12}$ and $A_{23}$ can be omitted. As a result,

\[ A = A_{33} - A_{13} = \sqrt{A_{33}^2} - \sqrt{A_{13}^2} = \sqrt{A_{33}^2} (\sqrt{1} - \sqrt{1}) \quad [2.7] \]

where

\[ A_{ii} = 24\pi d_0^2 \gamma_i^d \quad [2.8] \]

$\gamma_i^d$ is the dispersion component of the surface or interfacial energy, and $d_0$ is the minimum cutoff equilibrium distance between the surfaces (normally, $d_0 \approx 0.158$ nm), which is associated with the extremely short range Born repulsion.\textsuperscript{18,72} From equations [2.7] and [2.8], $A$ can also be related to $S^d$ as:

\[ A = -12\pi d_0^2 \cdot 2\sqrt{\gamma_1^d \gamma_3^d} (\sqrt{\gamma_1^d} - \sqrt{\gamma_3^d}) = -12\pi d_0^2 S^d \quad [2.9] \]
$S^p$, appeared in the second term of equations [2.4] and [2.5], is the polar spreading coefficient, and can be defined as

$$S^p = S - S^d = S + \frac{A}{12\pi d_0^2}$$  \[2.10\]

2.2.3 Thin Film Instability

Polymer thin films become unstable through a spinodal mechanism when the second derivative of $\Delta G$ with respect to $\delta$, $\partial^2 \Delta G / \partial \delta^2$ (spinodal parameter) or $\partial \Pi / \partial \delta$, is negative.\(^7^8\) Since the spinodal parameter is determined by the combination of antagonistic (attractive/repulsive) long- and short-range intermolecular interactions, there should be at least one minimum with $\delta$ or $\delta_{\text{min}}$ (Figure 2.8). In other words, at the range of $\delta_1 < \delta < \delta_2$ (where $\delta_1$ and $\delta_2$ are obtained from $\partial^2 \Delta G / \partial \delta^2 \bigg|_{\delta} = 0$), the film becomes unstable. When a film deforms within the range of $\delta_1 < \delta < \delta_2$, two distinct features across $\delta_{\text{min}}$ can be observed. For $\delta_1 < \delta < \delta_{\text{min}}$, the infinitesimal fluctuation of the film’s free surface directly evolves into bicontinuous ridges, and further breaks up into droplets.\(^7^9^,^8^0\) This is so called the “spinodal dewetting” or the “morphological phase separation”.\(^8^1\) However, for $\delta_{\text{min}} < \delta < \delta_2$, circular holes spontaneously emerge and laterally grow until they coalesce; and then the removed film materials are collected at the borders of coalesced holes and break up into droplets.\(^7^9^,^8^0\) Similarly, metastable thin films, which have a thickness greater than $h_2$ and $\partial^2 \Delta G / \partial \delta^2 > 0$, also dewet through circular hole formation; however, the holes are initiated by defects or heterogeneities on the film or substrate surfaces.\(^8^2\)
Figure 2.8 Qualitative variation of spinodal parameter \( \frac{\partial^2 \Delta G}{\partial \delta^2} \) with respect to the film thickness, \( \delta \). \( \delta_{\text{min}} \): the minimum of \( \frac{\partial^2 \Delta G}{\partial \delta^2} \); \( \delta_1 \) and \( \delta_2 \) where \( \frac{\partial^2 \Delta G}{\partial \delta^2} \bigg|_\delta = 0.78 \).
2.2.4 Morphology of the Dewetting Process

The dewetting process of thin polymer films has various unique features in terms of morphology (Figure 2.9). The infinitesimal evolves, under the condition of \( \frac{\partial^2 \Delta G}{\partial \delta^2} < 0 \), into ruptures or indentations of the film’s free surface. The ruptures grow toward the substrate, and after reaching the substrate, they form holes or dry patches, exposing the substrate to the ambient (Figure 2.9a). These holes grow laterally, resulting from the retraction and transportation of polymer material along rims of the holes (Figure 2.9b). The holes grow further until their circumferences contact those of neighboring holes to form polygonal patterns composed of polymer ridges or ribbons (Figure 2.9c). In the final stages, the polymer ridges disintegrate into spherical droplets due to Rayleigh instability (Figure 2.9d). This is due to an amplification of fluctuations (capillary breakup) of the surface of long cylindrical masses, resulting from the tendency to reduce the surface area.

In this chapter, backgrounds related to surface modification and polymer thin films are reviewed. Especially, how substrate properties, hence their surface energies (\( \gamma_S \)), can be altered by depositing organosilanes molecules is first provided. In brief specifics, the organosilane molecules grafted to a substrate to form a self-assembled monolayer, and the modified substrate adopts the property (e.g. \( \gamma_S \)) of the functional group in the organosilanes. Depending on the physical properties of organosilanes, substrates can be modified through solution deposition, vapor phase deposition, or contact printing techniques.
Figure 2.9  Morphological stages of dewetting of a thin polymer film. A thin film (∼800 Å) of PS ($M_w = 65k$, $PI = 1.03$) on silicon wafer modified with -CF$_3$ terminated organosilane was annealed in air at 160°C. (a) Initial dewetting hole formation. White circular spots are dewetting holes exposing substrate. Gray background is the intact PS thin film. (b) Lateral growth of dewetting holes. (c) Polygon pattern formation with polymer ribbons. (d) Disintegration of polymer ribbons into sessile droplets. The images were taken at 2, 11, 31, and 141 s, respectively, after the sample started to anneal. The sizes of images are 560 μm × 420 μm.
Polymer thin films can be vulnerable to thermal treatments over its glass transition temperature. When a polymer thin film is deposited on nonwettable substrates, it is deprived of its continuity and homogeneity under thermal environments over its glass transition temperature by an irreversible “dewetting” process. Holes are spontaneously emerged throughout the film, exposing bare spots of the substrate. Eventually, the polymer thin film turns into polymer droplets on the substrate. The stability of the film and the kinetics of the hole growth are dependent on the intermolecular interactions within the polymer film and between the polymer film and the substrate.
In this chapter, basic information related to sample preparation and characterization techniques used in this work, including spin-coating, ellipsometry, contact angle measurements, and atomic force microscopy (AFM), is first reviewed, and then the experimental procedures associated with the three major divisions of this work—dewetting kinetics, rim instability, and dewetting suppression—are described. For each of the divisions, sample preparation, processing, and characterization are described in detail in sub-sections.

3.1 Background on Sample Preparation and Characterization Techniques

3.1.1 Spin-coating

Spin-coating is a quick and efficient technique to generate thin films. A coating solution is deposited on a substrate that is either stationary or spinning at a low speed (rpm), and then the solution is spread evenly across the substrate by centrifugal forces by
Figure 3.1 Schematic illustration of spin-coating process (a) and a typical spin-coating profile. After dispensing a coating solution on a substrate that adheres to a rotating plate by the suction from a vacuum pump, the substrate spins, and the solution spreads across the substrate due to the centrifugal forces. The solvent is evaporated, and a uniform and thin film is generated on the substrate. The spin-coating profile starts with dispensing (1), acceleration (2), spin (3), and ends with deacceleration (4).
spinning the substrate at a high speed (Figure 3.1a). During the spinning, the solvent evaporates, and only the coating material is left behind, forming a thin film. The film thickness is normally in the range of 500 ~ 5000 Å.

A typical spin-coating profile is illustrated in Figure 3.1b. After dispensing a coating solution on a substrate (1 in Figure 3.1b), the spin speed of the substrate increases to a preset spin speed with a certain acceleration (2 in Figure 3.1b). Since the acceleration exerts a force on the spreading solution, in addition to the centrifugal force, the acceleration rate is also involved in determining the final coating film thickness and quality. During the spinning step (3 in Figure 3.1b), the substrate spins at a given spin speed (normally 1000 ~ 7000 rpm) and time (10 s ~ 10 min). In general, this step defines the final film thickness. The final film thickness is determined by a balance between the centrifugal force to shear the solution towards the edge of the substrate and the solvent evaporation rate which governs the viscosity of the solution. One can expect that the film thickness would increase as the concentration of the solution increases and the spin speed decreases. In addition, a possibility of shear thinning of the solution may be used to adjust coating parameters. It is also important to ensure that the coating solution wets the substrate by having a proper surface energy (γ): generally γ of the solution > γ of the substrate; otherwise, uniform and full coverage of the final film cannot be guaranteed. The deacceleration rate would have a similar effect on the film properties as the acceleration rate does, but the impact is minimal since the film is already mostly solidified during the spin process (4 in Figure 3.1b). For certain applications, an
additional annealing process for the film may be required to eliminate any residual stress or non-equilibrated features within the film.

3.1.2 Ellipsometry

Ellipsometry is an optical technique that determines thicknesses or refractive indices of thin films by measuring changes in polarization of a visible light after it interacts with (i.e. reflects from) the thin films. The range of film thickness varies up to several thousand angstroms. In principle, when linearly polarized light irradiates a surface at a certain angle of incidence, the light interacts with the film through reflection and transmission, and the light that reflects back from the surface is elliptically polarized. The difference in the polarization state of the reflected light from that of the incident light are measured by its relative phase ($\Delta$) and amplitude ($\Psi$) changes. These changes are related to the ratio of Fresnel reflection coefficients, $R_p$ and $R_s$, which are corresponding to the two components (i.e. p- (in the plane of incidence) and s-(perpendicular to the plane of incidence) components) of the polarized light, respectively (equation [3.1a]).

$$\tan(\Psi)\exp(i\Delta) = \frac{R_p}{R_s} = f(\beta, n_0, n_1, n_2, \theta_0, \theta_1, \theta_2)$$

[3.1a]

where $n$ is refractive index and $\theta_i$ is the angle of incidence. The subscripts, 0, 1, and 2, refer to air, film, and substrate, respectively. $\beta$ (reduced film phase thickness) in the equation [3.1a] can be expressed as

$$\beta = 2\pi \frac{\delta}{\lambda} n_1 \cos \theta_1$$

[3.2b]
Figure 3.2 Optical model used to calculate film thickness \(d\) and the reflective index of the film \(n_1\) in ellipsometry (a) and a schematic description of a nulling ellipsometer where \(L\): light source, \(P\): polarizer, \(C\): compensator, \(\theta_i\): incidence angle, \(A\): analyzer, and \(D\): detector (b). The unpolarized and collimated monochromatic light is linearly polarized through the \(P\), and then circularly polarized through the quarter-wave \(C\). The polarized incident light is elliptically polarized after it travels through the film and reflects from the substrate. The \(A\) measures the changes in the polarization of the light on the reflection. By manipulating the \(P\) and \(A\), the intensity of the reflected light at the \(D\) reaches zero. The arrows, circle, ellipse, and dot represent the electric field vector in the p- and s-planes.89
where $\delta$ is film thickness and $\lambda_L$ is wavelength of the light. Therefore, with the experimentally measured values of $\Psi$ and $\Delta$, one can calculate $\delta$ if $n_1$ is known and vice versa, using equations [3.1a] and [3.2b].

Figure 3.2a represents the optical model used to interpret ellipsometric data. Since $n_1$ (organic films) is only slightly greater than $n_0$ (air), the reflected light ($\Theta$) from the surface of the film is weak. On the other hand, $n_2$ (substrate) is much greater than $n_1$, and the incident light ($\Omega$) that travels through the film and reflects from the interface between the film and the reflective substrate is stronger. The reflected light $\Theta$ is negligible since most of the light would be reflected back to the substrate because $n_2 >> n_1$. As a result, most of the light detected by the detector is from $\Omega$, which can be related to the properties (i.e. thickness and refractive index) of the organic film.

Figure 3.2b represents a schematic diagram of an ellipsometer. An unpolarized monochromatic He-Ne laser is generated from the light source, $L$. This laser is linearly polarized after passing through the polarizer, $P$. When two linearly polarized laser lights propagate in phase with each other, the resulting light will be linearly polarized. After traveling through a quarter-wave plate compensator, $C$, either the p-component or the s-component of the linearly polarized light has a relative phase lag of 90°, resulting in elliptically polarized light. After the two components with the same amplitude and a phase difference of 90° travel through or interact with the film, their amplitudes and phases become arbitrary, and the reflected light from the film becomes elliptically
polarized. The analyzer, $A$, is another polarizer that linearly polarizes the reflected light from the film. The light passing through the analyzer is detected by the detector, $D$. In a null ellipsometer, properties of a sample are determined by adjusting $P$, $C$, and $A$ in order to extinguish or “null” the intensity of the light detected. For simplicity, $C$ is set at $\pm 45^\circ$, and only $P$ and $A$ are adjusted, which vary $\Delta$ and $\psi$, respectively, until $D$ detects a minimum intensity of the light.

3.1.3 Contact Angle Measurement

One of the most common techniques to investigate the quality of SAMs is contact angle measurement. When a drop of a liquid is placed on a perfectly homogeneous and smooth solid surface, at the phase equilibrium with the surrounding vapor phase, the drop normally forms a finite angle of contact with the solid surface.

3.1.3.1 Young’s Equation

The contact angle of a liquid formed on a solid surface depends on the interaction between the liquid and the solid. Such an interaction can be related to the free energy (i.e. surface (free) energy, $\gamma$) of the liquid and that of the solid. Thomas Young was the first to state the relationship between the contact angle and surface energies and interfacial energy in 1855. Based on thermodynamics, when a liquid forms an angle on a solid surface, a slight extension of the drop (angle changes from $\theta$ to $\theta - \Delta \theta$) would result in a series of small change in areas ($\Delta A$s). The solid surface loses $\Delta A$, the solid/liquid
Figure 3.3  Schematics for the derivation of Young’s equation by a change in surface free energy of the system (a) or a force balance of interfacial tensions in the system. The subscripts, SL, SV, and LV, refer to solid-liquid, solid-vapor, and liquid-vapor interfaces, respectively. The $\theta$ is a contact angle, and $\pi_e$ is the equilibrium film pressure.
interface gains $\Delta A$, while the liquid surface gains $\Delta A \cos(\theta - \Delta \theta)$ (Figure 3.3a). Then, the change in surface free energy of the system, ($\Delta G^S$), is

$$
\Delta G^S = \Delta A (\gamma_{SL} - \gamma_{SV}) + \Delta A \gamma_{LV} \cos(\theta - \Delta \theta) \tag{3.3}
$$

where the subscripts, SL, SV, and LV, refer to solid-liquid, solid-vapor, and liquid-vapor interfaces, respectively.\textsuperscript{30} At the three-phase equilibrium

$$
\lim_{\Delta \Lambda \to 0} \frac{\Delta G}{\Delta \Lambda} = 0 \quad \text{or} \quad \frac{dG}{d\Lambda} = 0
$$

and

$$
\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta \tag{3.4}
$$

Equation [3.4] is Young’s equation. Since surface energy (energy/area) is also used interchangeably with surface tension (force/length), Young’s equation can also be interpreted as the x-directional force balance at the three phase contact line (Figure 3.3b).\textsuperscript{62}

It should be noted that $\gamma_{SV}$ and $\gamma_{LV}$ are slightly smaller than the surface energy of the pure solid phase ($\gamma_S$) and liquid phase ($\gamma_L$), respectively.\textsuperscript{90} The adsorption of the molecules of the other phase always occurs at the interfaces, and at equilibrium, the equilibrium pressure, $\pi_{eSV}$ and $\pi_{eLV}$, needs to be included, respectively, in $\gamma_S$ ($\gamma_{SV} = \gamma_S - \pi_{eSV}$) and $\gamma_L$ ($\gamma_{LV} = \gamma_L - \pi_{eLV}$). The $\pi_{eLV}$ is commonly ignored as long as the solubility of the solid in the liquid is very low. The $\pi_{eLV}$ is also neglected for low-energy solid surfaces that form a large $\theta$, and because of a lack of literature values.\textsuperscript{62} In summary, it
would be reasonable to ignore $\pi_c$ for pure liquids on homogeneous and low-energy solid surfaces, in which a finite contact angle is formed.

3.1.3.2 Surface Energy Estimation

By employing contact angle measurements, one can estimate the surface energy of unknown solid surfaces, $\gamma_S$. Surface energy ($\gamma$) can be broken down into components: dispersion ($\gamma_d$) and polar ($\gamma_p$) components, i.e. $\gamma = \gamma_d + \gamma_p$. $\gamma_d$ includes dispersion-force interactions, while $\gamma_p$ includes dipolar, induced polar, hydrogen bonding, and other specific interactions. To estimate $\gamma_S$, it can be convenient if one can first identify the type of surface of interest: purely nonpolar or nonpolar/polar. If the surface is purely nonpolar, then only one nonpolar probe liquid with a known $\gamma_L$ is required for the contact angle measurement. The ambiguous term $\gamma_{SL}$ in Young’s equation [3.4] can be replaced by introducing a “geometric mean” combining rule. The adhesion of the interface S-L (equation [2.3]), $\gamma_S + \gamma_L - \gamma_{SL}$, is equal to the geometric mean of the cohesion of $\gamma_S$ and $\gamma_L$, $2\sqrt{\gamma_S \gamma_L}$. By combining equation [3.4] and the geometric mean, one can derive

$$\gamma_S = \frac{\gamma_L (1 + \cos \theta)^2}{4}$$  \hspace{1cm} [3.5]

where S and L are nonpolar and $\theta$ is the measured contact angle between the probe liquid (L) and the solid surface (S). The measured contact angle ($\theta$) is plugged into equation [3.5] along with the value of $\gamma_L$ to obtain the unknown $\gamma_S$. 

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For a solid surface that is composed of nonpolar and polar characteristics, the surface energy of the surface ($\gamma_S$) may be expressed as the sum of the nonpolar (dispersion, $\gamma_S^d$) and polar ($\gamma_S^p$) components. The $\gamma_{SL}$ term can be eliminated by employing a harmonic or geometric mean combination rule. Similar to the derivation of equation [3.5], the harmonic mean gives

$$\gamma_{SL} = \gamma_S + \gamma_L = \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} - \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}$$

[3.6a]

$$\gamma_L (1 + \cos \theta) = \frac{4\gamma_S^d \gamma_L^d}{\gamma_S^d + \gamma_L^d} + \frac{4\gamma_S^p \gamma_L^p}{\gamma_S^p + \gamma_L^p}$$

[3.6b]

and the geometric mean gives

$$\gamma_{SL} = \gamma_S + \gamma_L = 2\sqrt{\gamma_S^d \gamma_L^d} - 2\sqrt{\gamma_S^p \gamma_L^p}$$

[3.7a]

$$\gamma_L (1 + \cos \theta) = 2\sqrt{\gamma_S^d \gamma_L^d} + 2\sqrt{\gamma_S^p \gamma_L^p}$$

[3.7b]

By utilizing two probe liquids with known $\gamma_L^d$, $\gamma_L^p$, and $\gamma_L$ values and their contact angles ($\theta_1$ and $\theta_2$), the unknown values of $\gamma_S^d$ and $\gamma_S^p$ for a solid surface can be estimated by simultaneously solving the two equations from either [3.6b] or [3.7b] for each probe liquid, giving a value of $\gamma_S = \gamma_S^d + \gamma_S^p$.91

3.1.4 Atomic Force Microscopy

AFM is one type of scanning probe microscopy (SPM), which utilizes a sharp tip to scan a solid surface by the interaction of the tip and the surface. AFM can probe a sample surface with resolution down to sub-angstrom scales, especially in height differences, and generate 3-dimensional topography (or morphology) of the surface. In
virtue of this surface mapping ability, AFM has been applied in areas ranging from semiconductors to cell biology.\textsuperscript{30,92}

Figure 3.4 illustrates the basic principles of AFM operation. Surface topography is probed by the deflection of a cantilever that supports a sharp tip at the end. The scanning can be performed either by moving a tip over the sample (tip scanning) or by moving the sample under the tip (sample scanning). The conical silicon tip is a few microns long with a radius curvature of 5 – 50 nm.\textsuperscript{30} The deflection is determined by the degree of attractive or repulsive interatomic van der Waals forces between the tip and the sample surface during scanning. The “tiny” deflection of the cantilever can be mechanically amplified and probed by a laser beam bouncing off the back of the cantilever onto a position-sensitive photodetector (PSPD). The detector senses the position of the reflected laser beam, and from the difference, the original height change can be calculated. The amplification of the cantilever deflection depends on the length of the cantilever and the distance between the cantilever and the detector.

There are two major modes of AFM operation: contact and non-contact. The terms are defined by the distance between the tip and the sample surface and its corresponding force type. Figure 3.5 represents the interatomic force vs. distance curve.\textsuperscript{92}
3.1.4.1 Contact Mode

In contact mode, the tip approaches the sample surface within a few Angstrom separation. At this distance, electron clouds of the silicon atom at the end of the tip overlap with those from the atoms on the sample surface, resulting in a repulsive force (i.e. positive total van der Waals force) between the tip and the surface (Figure 3.5).\textsuperscript{92,93} Since the tip is repelled and bent away from the surface (Figure 3.5), the cantilever should be long and soft to avoid damaging the surface. The cantilever for the contact mode is typically \( \sim 450 \mu \text{m} \) long with a force constant of \( \sim 0.2 \text{ N/m} \).

Especially in contact mode, there are two additional forces acting on the tip: a capillary force and a cantilever force. It is generally recognized that there is a thin layer of water on surfaces, and the water layer is assumed to be homogeneous. The surface tension of the water layer between the tip and the surface results in an attractive force with a magnitude of \( 10^{-8} \text{ N} \). As long as the contact between the tip and the surface is maintained, the capillary force would be constant. The cantilever force is a force generated to restore the deflection of the cantilever; therefore, it is related to the degree of deflection and the spring constant of the cantilever. Since the cantilever force is also an attractive force in contact mode, the total force exerted on the sample results from a balance between the repulsive van der Waals force and the sum of the capillary force, the deflection force of the cantilever, and the negligible attractive force between the tip and the sample. The total force normally ranges from \( 10^{-8} \) to \( 10^{-6} \text{ N} \).\textsuperscript{92}
Figure 3.4 Schematic of a generalized atomic force microscopy. Surface topography is probed by a cantilever mounted with a tip. The deflection of the cantilever, caused by surface topography, is sensed by a position-sensitive photodetector (PSPD) through the position of the reflected laser beam. The signal from the PSPD is used to construct 3-dimensional surface topography of the sample and to give feedback in order to control the motion of a piezoelectric scanner that is attached either to the sample holder or to the cantilever. The diagram is not to scale.\textsuperscript{92}
Figure 3.5 Illustration of two modes of AFM operation, contact and non-contact, in interatomic force vs. distance curve. The force is repulsive for the contact mode while it is attractive for the non-contact mode. The distance is the separation between an AFM tip and a sample surface.\textsuperscript{92}
The contact mode, depending on the operating conditions, can be further categorized into “constant-height” or “constant-force” mode. In the constant-height mode, the scanner is fixed in its vertical movement, and the topographical data is collected from deflection of the cantilever. Therefore, the mode is applicable only to molecularly smooth samples and advantageous for real-time scanning through the possibility of high scan rates (due to the absence of the response time of feedback signals to control the height of the scanner). In constant-force mode, the deflection of the cantilever is kept constant by controlling the height of the scanner. This mode is commonly used for most applications.92

3.1.4.2 Non-Contact Mode

One feature of non-contact mode distinct from that of contact mode is that the tip vibrates or oscillates at its resonant frequency (typically 250 – 390 kHz) at tens to hundreds of angstroms above the sample surface while scanning. Due to the magnitude of the separation, the force acting between the tip and the surface is an attractive van der Waals force; therefore, the tip is bent towards the sample surface (Figure 3.5). Since the tip is not supposed to be in contact with the surface, the tip is normally shorter and stiffer than that for contact mode. Typical values for the length and the force constant are ~ 125 μm and ~ 42 N/m, respectively. The low total force (~ 10^{-12} N) and little contact between the tip and the surface in the range of the attractive force render the non-contact mode advantageous for soft or elastic materials.
Surface topography is obtained by noting the change in the resonant frequency or vibration amplitude of the tip as the separation changes by the vertical variation of the surface features. The scanner movements designed to maintain a constant resonant frequency and vibration amplitude are transformed into 3-dimensional surface topography images of the sample.
3.2 Dewetting Kinetics as a Function of Substrate Surface Energy

3.2.1 Materials

The organosilanes were all obtained from Gelest, Inc. and used as received. Physical properties and abbreviations of the organosilanes are presented in Table 3.1. The organosilanes were sealed with Parafilm and stored under vacuum in a dry desiccator prior to use to minimize possible irreversible hydrolysis. Organic solvents of toluene, hexane, and acetone were used for sample generation and cleaning. The detailed type of solvents and physical properties are summarized in Table 3.2. Sulfuric acid (Certified ACS Plus) and hydrogen peroxide (30% solution, Reagent, ACS), used for cleaning silicon wafers, were purchased from Fisher and VWR™, respectively. PS ($M_\text{n} = 63k$, PI = 1.03 and $M_\text{n} = 9.3k$, PI = 1.13) was purchased from Polymer Source. Poly(dimethylsiloxane) (PDMS) was used to fabricate elastomeric stamps. For the PDMS, Sylgard® 184, composed of both a vinyl terminated PDMS base elastomer and a Si-H side group PDMS curing agent, was purchased from Dow Corning Corp. The substrates used were 4 in. test Si(100) wafers purchased from Silicon Quest International. Glass slides, used in the polymer thin film generation, were precleaned VWR® micro slides purchased from VWR Scientific Inc. The size was 25 mm × 75 mm, and the thickness was ~ 1 mm. Mineral oil ($\rho$ (density) = 0.862 g/cm$^3$) was purchased from Aldrich Chemical Company, Inc.
Table 3.1  Physical properties of organosilanes used in this study

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>MW(^{a})</th>
<th>D(_{4}^{20\circ})</th>
<th>n(_{D}^{20\circ})</th>
</tr>
</thead>
<tbody>
<tr>
<td>perfluorodecyl-1(H,1(H,2(H,2(H)-trichlorosilane (CF(_3)(CF(_2))(CH(_2))(_2)SiCl(_3))</td>
<td>FTS</td>
<td>581.56</td>
<td>1.703</td>
<td>N/A</td>
</tr>
<tr>
<td>(n)-decyltrichlorosilane (CH(_3)(CH(_2))(_9)SiCl(_3))</td>
<td>DTS</td>
<td>275.72</td>
<td>1.0540</td>
<td>1.4528</td>
</tr>
<tr>
<td>(n)-octadecyltrichlorosilane (CH(_3)(CH(_2))(_9)CH(_2)SiCl(_3))</td>
<td>OTS</td>
<td>387.93</td>
<td>0.950(^{22})</td>
<td>1.4602</td>
</tr>
<tr>
<td>3-aminopropyltriethoxysilane (H(_2)N(CH(_2))(_3)Si(OC(_2)H(_5))(_3))</td>
<td>APTES</td>
<td>221.37</td>
<td>0.951</td>
<td>1.4225</td>
</tr>
<tr>
<td>2-(carboxymethylthio)ethyltrimethylsilane (HOOCCH(_2)S(CH(_2))(_2)Si(CH(_3))(_3))</td>
<td>CTMES</td>
<td>192.35</td>
<td>1.0139</td>
<td>1.4811</td>
</tr>
<tr>
<td>3-chloropropyltrimethoxysilane (ClCH(_2)(CH(_2))(_2)Si(OCH(_3))(_3))</td>
<td>CPTMOS</td>
<td>198.72</td>
<td>1.077(^{25})</td>
<td>1.4183(^{25})</td>
</tr>
<tr>
<td>3-mercaptopropyltrimethoxysilane (HS(CH(_2))(_3)Si(OCH(_3))(_3))</td>
<td>MPTMOS</td>
<td>196.34</td>
<td>1.051(^{25})</td>
<td>1.4502(^{25})</td>
</tr>
</tbody>
</table>

\(^{a}\) Molecular weight (g/mol)

\(^{b}\) Specific gravity measured at 20\(^\circ\)C or otherwise indicated in the table (g/cm\(^3\))

\(^{c}\) Refractive index measured at 20\(^\circ\)C or otherwise indicated in the table
<table>
<thead>
<tr>
<th>Sample generation</th>
<th>Name</th>
<th>MW&lt;sup&gt;a&lt;/sup&gt;</th>
<th>ρ&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Water content</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene-‘BAKER ANALYZED’® HPLC solvent</td>
<td>92.14</td>
<td>0.87</td>
<td>0.0007%</td>
<td>J.T. Baker</td>
</tr>
<tr>
<td></td>
<td>Hexane-‘BAKER ANALYZED’® HPLC solvent</td>
<td>86.18</td>
<td>0.663</td>
<td>0.001%</td>
<td>J.T. Baker</td>
</tr>
<tr>
<td>Sample cleaning</td>
<td>Toluene-Reagent Grade, 99.5% min. by GC</td>
<td>92.14</td>
<td>0.86</td>
<td>N/A</td>
<td>VWR™</td>
</tr>
<tr>
<td></td>
<td>Hexane-Reagent Grade, 98.5% min. by GC</td>
<td>86.18</td>
<td>0.66</td>
<td>N/A</td>
<td>VWR™</td>
</tr>
<tr>
<td></td>
<td>Acetone-Reagent Grade, 99.5% min. by GC</td>
<td>58.08</td>
<td>0.79</td>
<td>N/A</td>
<td>VWR™</td>
</tr>
</tbody>
</table>

<sup>a</sup> Molecular weight (g/mol)

<sup>b</sup> Density (g/cm³)
3.2.2 Sample Preparation

3.2.2.1 Substrate Cleaning

Silicon wafers were cut into 1 cm × 1 cm pieces. The substrates were cleaned by immersing in a freshly prepared piranha solution (70/30 (v/v) of concentrated H₂SO₄ and 30% H₂O₂) for 1 h. The solution was decanted, and the substrates were rinsed thoroughly with deionized water. The cleaned substrates were dried under a stream of N₂ gas and then exposed to UV/ozone (UV/O cleaner model 42, Jelight) oxidization for 6 min immediately prior to the deposition of organosilanes. The entire cleaning process provided silicon wafers with clean and oxidized surfaces containing mainly Si-OH groups.

3.2.2.2 Stamp Fabrication

The stamps were fabricated from silicone elastomers. The elastomer was generated by mixing the Sylgard 184 elastomer base and curing agent according to the prescribed recipe. The mixture was then poured into a plastic weighing dish containing a master template placed on the bottom of the dish. For stamps with a completely flat surface, the master was a piece of silicon wafer treated with FTS (as described below). After the mixture was cured at room temperature for 48 h, the elastomeric stamps were
peeled away from the masters. All the fabricated stamps were extracted with a Soxhlet extractor in toluene for 2 h to remove un-cross-linked PDMS chains.

3.2.2.3 Contact Printing of Octadecyltrichlorosilane

For contact printing of OTS onto a silicon wafer, a cotton swab was dipped into a 2 mM solution of OTS in HPLC-grade hexane. The solution was applied onto the planar silicone stamp by rubbing the cotton swab on the flat surface. The inked stamp was then dried with a stream of N₂ to remove the solvent. After drying, the stamp was brought into contact with the cleaned and oxidized silicon wafer for various lengths of time (1, 10, 20, 30, 60, 90, and 120 s) under finger pressure and removed. Each stamped silicon wafer was stored in a glass Petri dish at room temperature for 1 h to provide sufficient time for OTS molecules to react with the silicon wafer. Then, it was sonicated in toluene inside an ultrasonic cleaner (model 50HT, Aquasonic) for 2 min. The OTS-modified substrates were then dried with N₂ gas and characterized within 4 h. This same procedure was followed for each sample.

3.2.2.4 Vapor Phase Deposition of Mixed Organosilanes

Mixtures of FTS and DTS with various volume ratios were used. For each volume ratio, 200 μL of organosilane mixture in 3 g of mineral oil was thoroughly mixed, poured into a plastic weighing dish, and placed inside an empty glass desiccator. The desiccator was evacuated to a pressure of ca. 10 mTorr and maintained at that pressure for 20 min to
remove trapped air bubbles from the solution. Then, a glass slide, on which the cleaned and oxidized silicon wafers were attached face down using double-sided Scotch tape, was laid across the plastic weighing dish approximately 1 cm above the degassed solution. The assembly was evacuated again to the same pressure and maintained for 1 h. After the organosilane-treated silicon wafers were removed from the desiccator, they were thoroughly rinsed with freshly distilled toluene inside a Soxhlet extractor for 1 h. The samples were then dried with \( \text{N}_2 \) gas and characterized within 4 h.

3.2.2.5 Solution Deposition of Polar Organosilanes

Polar organosilanes, APTES, CTMES, CPTMOS, and MPTMOS, were deposited on cleaned and oxidized silicon wafers using the most common solution deposition method.\(^9\) Clean silicon wafers, as described above, were placed in a 2 mM solution of each polar organosilane in HPLC-grade hexane. The chemisorption of the polar organosilanes was allowed to occur for 1 h at room temperature. The modified substrates were removed from the solution and rinsed in a Soxhlet extractor for 1 h using toluene. The samples were then dried under \( \text{N}_2 \) and stored in plastic Petri dishes prior to characterization, which is normally conducted within 4 h after deposition.

3.2.2.6 Polystyrene Thin Film Generation

The FTS/DTS- and OTS-modified surfaces had low surface energies, so direct spin coating of PS solution onto these surfaces was difficult. Therefore, the "float-off
and pick-up" method\textsuperscript{96} to place a thin film of PS onto each organosilane-modified surface was applied. A 2 wt % PS solution (in HPLC toluene) was passed through a microfilter (Acrodisc 13 mm syringe filter with 0.45 \( \mu \)m nylon membrane, Gelman) to remove any impurities. Then it was spin coated at 3000 rpm for 30 s using a spin coater (P-6000, Specialty Coating Systems) onto a 2.5 cm \( \times \) 2.5 cm microscope glass slide. The glass slides were precleaned by rinsing with toluene, acetone, and deionized water in that order, and then exposed to UV/ozone oxidization for 6 min. The PS thin film placed on the organosilane-treated silicon wafer was dried under ambient conditions inside a glass Petri dish for about 15 h. After drying, the samples were stored in a vacuum oven (~30 in. Hg) at 80 °C for 15 h to eliminate any residual water trapped at the PS film/organosilane-modified silicon wafer interface. PS-9.3k thin films were used only for OTS-modified surfaces

3.2.3 Sample Processing

3.2.3.1 Polystyrene Thin Film Dewetting

The PS thin films on the SAMs of organosilane were annealed at 160 °C using a hot plate under ambient conditions. The annealing temperature and film thickness of 800 Å were chosen by a simple combinatorial method.\textsuperscript{97} At those conditions, the dewetting velocity became measurable over the range of surface energy variation. An optical microscope (Infini Tube, Edmond Scientifics) equipped with a CCD video camera was
used to follow the dewetting process from hole initiation to coalescence. Dewetting behavior was videotaped, and the radius ($R$) of the dewetting holes for selected images at various annealing times ($t$) was measured. The maximum distance of the inside rim (only the dry area) was measured as the diameter, and then it was divided by 2 to obtain the radius. The very early stage (when the hole initiates) and the final stage (when the hole growth starts to level off or holes start to coalesce with each other) of dewetting were not considered in our measurements. The annealing was ceased immediately prior to the coalescence of holes. The dewetting velocity ($V_R$) was obtained from the slope of the linear relationship of $R$ as a function of $t$.

3.2.4 Sample Characterization

3.2.4.1 Atomic Force Microscopy

The surfaces modified with organosilanes were first characterized with AFM (Molecular Imaging Corp., MI 2000) to verify and analyze the formation of organosilane SAMs. Topographic and lateral force images were taken in contact mode using a 450 μm long cantilever having a spring constant of 0.2 nN/nm. Phase images were also taken in non-contact mode to verify the phase separation of FTS/DTS mixed SAMs. A 125 μm long cantilever with a spring constant of 42 nN/nm and a frequency of 320 kHz was used for the non-contact mode scans. Various scan sizes, from 200 nm × 200 nm to 10 μm × 10 μm, were used.
3.2.4.2 Contact Angle

The modified silicon wafer was then examined with contact angle measurements via the sessile drop method. Contact angles were measured using deionized water ($\gamma_{L}^d = 22.0$ mJ/m$^2$, $\gamma_{L}^p = 50.2$ mJ/m$^2$, $\gamma_{L} = 72.2$ mJ/m$^2$) and methylene iodide (MI, $\gamma_{L}^d = 48.5$ mJ/m$^2$, $\gamma_{L}^p = 2.3$ mJ/m$^2$, $\gamma_{L} = 50.8$ mJ/m$^2$) with a Rame-Hart contact angle goniometer, model 100-00. Four images of advancing ($\theta_{A}$) and receding ($\theta_{R}$) angles on two randomly chosen spots from each sample were taken using image-capturing equipment (Dazzle DVC, Dazzle media). The contact angles on both sides of the droplet were measured using the Scion Image package. An average value ($\theta_{avg}$) of all the contact angles was used in calculating surface energy. Owens-Wendt geometric mean with the two-liquid method was applied.$^{90,91}$ The measurements were performed under ambient conditions (1 atm, 24 ± 2°C).

3.2.4.3 Film Thickness Measurement

The thicknesses of the PS thin films were measured using an ellipsometer (model 439, Rudolph Instruments) with a helium-neon laser ($\lambda = 6328$ Å). The angle of incidence was 70° from the normal to the surface. The compensator was set at $± 45^\circ$. A refractive index of 1.592 was used for PS in calculating the film thickness. The accuracy of the film measured with this ellipsometer is ± 2 Å.
3.3 Rim Instability as a Function of Substrate Surface Energy

Since most materials and detailed sample preparation/characterization procedures have already been described in Section 3.2, only brief descriptions of the same procedures are provided in this section. However, unique and relevant procedures for this section are provided in detail.

3.3.1 Sample Preparation

Substrates with different surface energies were generated by contact printing (CP) of $n$-octadecyltrichlorosilane (OTS, from Gelest Inc.) onto cleaned SiO$_X$ surfaces with different contact times to achieve different surface coverages of OTS. Planar silicone stamps used for CP were fabricated using Sylgard® 184 purchased from Dow Corning. The standard procedures can be found in Ref. 10 and references therein. The masters used for fabricating the stamps were pieces (1 cm $\times$ 1 cm) of fluorosilane-modified silicon wafers.$^{98}$ The “ink” for CP was a 2 mM solution of OTS in HPLC-graded hexane (J.T. Baker). The substrates, Si (100) wafers (Silicon Quest International), were cleaned using a freshly prepared piranha solution and then oxidized using a UV/ozone treatment (UV/O cleaner model 42, Jelight) for 6 min. A planar stamp “inked” with OTS solution was brought into contact with each substrate for particular contact times between 1 s and 120 s. PS ($M_n = 9.3k$, PI = 1.13 and $M_n = 63k$, PI = 1.03, purchased from Polymer Source, Inc.) thin films with a film thickness ($\delta$) of $\sim$ 800 Å were placed onto the OTS-modified surfaces using the “float-off and pick-up” method.$^{96}$
3.3.2 Sample Processing

The samples, after drying under ambient conditions for 15 h and then in a vacuum oven at 80°C for 15 h, were annealed at 160°C in air, while the hole growth was monitored using an optical microscope (Infini Tube, Edmond Scientifics). The annealing was terminated when the hole diameter reached certain chosen sizes (e.g. ~ 35 or 55 μm), and then the samples were quenched to room temperature to preserve hole morphology. A separate experiment (by gel permeation chromatography analysis) verified that thermal degradation of those PS thin films after annealing at 160 °C in air was insignificant within the annealing time of interest (< 10 min).

The overall morphology of the dewetting holes was characterized using optical microscopy (IX-70, Olympus) with a differential interference contrast (DIC) prism and an analyzer to enhance color (black and white with a monochrome CCD camera) contrast in the rim height fluctuation. The rim height ($h$), the rim width ($w$), and the dynamic contact angle ($\theta_d$) between the substrates and the PS melts at a dewetting hole diameter ($D$) of ~ 35 μm were obtained by AFM (MI 2000 from Molecular Imaging) in non-contact mode.

The instability wavelength ($\lambda$), or the spacing between the protrusions, was obtained by dividing the angular length of rim (circumference at the middle of rim width) at $D$ of ~ 55 μm by the number of protrusions formed along the rim. Optical microscopic images of at least 50 well-defined dewetting holes ($D$ ~ 55 μm) formed on the substrates
(2 or 3 replicates) with a specific $\gamma_S$ were taken and analyzed to obtain the angular length of the rims and the number of protrusions. The number of discernible protrusions or “nodes”,\textsuperscript{99,100} which were easily noticed along the rim by clear color contrast and/or their multiple color bands, were manually counted from optical microscopic images. $\lambda$ was estimated by dividing the circumference of the rim by the number of protrusions along the rim. In the calculation of the $\lambda/w$ ratio, $w$ was the predicted rim width derived from the material balance with the predicted $\theta_d$ at the size ($D \sim 55 \, \mu m$) of the dewetting holes used to obtain $\lambda$. More detailed experimental descriptions can be found elsewhere.\textsuperscript{10}

3.3.3 Sample Characterization

The surface energies ($\gamma_S$) of OTS-modified surfaces were determined from contact angle measurements (model 100-00, Rame-Hart Inc.) with two probe liquids, deionized water and MI. The values of $\gamma_S$ were estimated using the Owens-Wendt geometric mean equation\textsuperscript{90} with the averaged contact angles (advancing and receding contact angles) of each liquid.

3.4 Dewetting Suppression by Surface Modification Using Amine-Terminated Organosilane

Again, only the detailed sample preparation/characterization procedures that are relevant to this section are provided here.
3.4.1 Sample Preparation

Substrates used were cleaned and oxidized silicon wafers. They were prepared by immersion in a freshly prepared piranha solution for 30 min, then rinsing thoroughly with deionized water, drying under a stream of nitrogen, and finally exposing to UV/ozone for 10 min. 3-aminopropyltriethoxysilane (APTES, NH$_2$(CH$_2$)$_3$Si(OC$_2$H$_5$)$_3$) surfaces were prepared by immersing the substrates into 5 mM of APTES solution in HPLC hexane for 1 h, and then sonicated in HPLC hexane for 1 min to remove loosely attached APTES molecules. $n$-octadecyltrichlorosilane (OTS, CH$_3$(CH$_2$)$_{17}$SiCl$_3$)-modified silicon wafers were generated via the contact printing technique [13] and used as controls. Planar elastomeric stamps used for contact printing were fabricated using Sylgard™ 184, following standard procedures. 1 mM of OTS solution in HPLC hexane was used as the “ink”. The stamp, after being dipped into the OTS solution and dried under a stream of nitrogen, was brought into contact with the cleaned and oxidized silicon wafer for 1 s. The OTS-modified silicon wafers were then sonicated in HPLC hexane for 1 min to remove unreacted OTS molecules.

More APTES surfaces were generated. First, a 50 mM of APTES solution in HPLC hexane was used to generate another type of APTES surfaces (thick-APTES). The cleaned and oxidized Si-wafers were immersed in the solution for 1 h. Second, an additional set of APTES surfaces was generated by employing three different deposition techniques: solution deposition, contact printing, and vapor phase deposition techniques. Three HPLC-graded solvents, hexane, toluene, and chloroform (water %: 0.00006), were
used for the solution deposition technique. The cleaned Si-wafers were immersed into a 5 mM APTES solution in each solvent for 1 h. For the contact printing of APTES, 5 mM APTES solution in HPLC hexane was used, and the contact time was 1 min. For the vapor phase deposition of APTES, 200 μL of APTES in 3 g of mineral oil was used. The desiccator was evacuated to a pressure of ca. 10 mTorr, and maintained for 1 h. After the APTES modification, all samples were sonicated in toluene for 2 min to remove loosely attached APTES molecules.

1.5 wt % of PS ($M_n = 9.3k$, PI = 1.13 and $M_n = 63k$, PI = 1.03) solution in HPLC toluene, filtered through a 0.45 μm Acrodisc® Nylon membrane, was spin-coated at 3000 rpm for 30 s onto the control and APTES substrates. For controls and fresh APTES (without precuring) surfaces, the PS thin films were spin-coated on the substrates within 5 min after the substrates were prepared. For precured APTES surfaces, PS thin films were spin-coated after the APTES layers were cured. PS with a $M_n$ of 9.3k was spin-coated onto the thick-APTES surface. For the APTES surfaces generated by different deposition techniques, 2 wt % of PS with a $M_n$ of 63k was spin-coated. After spin-coating, the samples were dried under ambient conditions for 20 h.

3.4.2 Sample Processing

The curing degree of APTES layers, with or without PS thin films on top of them, was varied by changing the curing temperature, or the curing time at a fixed curing temperature. With a PS thin film deposited, the curing conditions included: (1) inside a
vacuum oven at 80 °C for 20 h, (2) inside a vacuum oven at room temperature for 20 h, (3) inside a vacuum oven at 80 °C for 0.5, 1, 2, 5, 10, and 15 h, and at 120 °C for 0.25, 0.5, 1, 2, 10, and 20 h. Precured APTES layers were cured at 200 °C under vacuum for 20 h prior to the deposition of PS films. After the deposition, the samples were dried under ambient conditions for 20 h and then further cured inside a vacuum oven at 80°C for 20 h. Another set of samples was prepared without the additional curing step inside the vacuum oven. After drying the PS films under ambient conditions for 20 h, the samples were immediately annealed or further cured under ambient conditions for 20 h and then annealed. The treated samples were annealed for 5 h inside a vacuum oven at 135 °C and 170 °C for PS-9.3k and -63k, respectively, to investigate their dewetting behavior. As a separate experiment, freshly prepared APTES samples were also cured inside a vacuum oven at 80 °C and 120 °C for 0.25, 0.5, 1, 2, 3, 5, 10, and 20 h. For the additional thick-APTES surface and the APTES surfaces generated by employing different deposition techniques, the samples were cured inside a vacuum oven at 80 °C for 20 h after drying in the ambient conditions for 20 h. PS-9.3k films deposited on the thick-APTES surface were annealed at 140 °C for 2 h. The samples were then annealed inside a vacuum oven at 170 °C for 1 h or 6 h. One set of the samples was annealed inside a vacuum oven at 170 °C for 50 h with occasional measurements of the hole sizes after taking samples out of the oven. From each APTES surface, the dewetting behavior of one hole, which was randomly chosen, was followed.
3.4.3 Sample Characterization

The APTES and control surfaces were characterized using contact angle measurements (model 100-00, Rame-Hart Inc.) with deionized water and MI. The dispersion ($\gamma^d$) and polar component ($\gamma^p$) of the substrate surface energy ($\gamma_S$) were estimated using Owens-Wendt-geometric mean\textsuperscript{98} with the contact angles of each probe liquid. The contact angle value of each probe liquid was averaged from advancing and receding angles measured at various locations on multiple samples that were generated from different batches (i.e. at least 50 measurements). The values of the surface energy components of water and MI needed for the calculations were obtained from the literature.\textsuperscript{98} In the time- and temperature-dependent curing and precuring studies, contact angles of water and MI were also measured right after each curing of the APTES surface. $\gamma_S$ was estimated using the averaged water and MI contact angles. The modified substrates were also characterized by AFM (Metrology 2000 from Molecular Imaging). The contact angle measurements and the AFM scans were performed within 10 min of sample preparation. The film thickness of APTES was measured by an ellipsometer (L116C, Gaertner Scientific Corporation) using a refractive index of 1.4225. The thickness of PS thin films ($\delta$) was measured to be $\sim$ 550 Å using the ellipsometer. The dewetting characteristics were examined using an optical microscope (IX-70, Olympus) and AFM.
CHAPTER IV

RESULTS AND DISCUSSION

This chapter summarizes all the results of this work. It consists of three main sections. Section 4.2 discusses the dewetting kinetics as a function of substrate surface energy, $\gamma_S$, Section 4.3 describes the instability of rims formed around dewetting holes as a function of $\gamma_S$, and Section 4.4 presents the dewetting suppression of PS thin films on substrates modified with an amine-terminated organosilane.

4.1 Dewetting Kinetics as a Function of Substrate Surface Energy

4.1.1 Introduction

The stability/instability of homogeneous and continuous polymer thin films (< 100 nm) on nonwettable substrates has been extensively investigated due to scientific interest and numerous industrial or technological applications of such films.\textsuperscript{101,102,103,104,105} Especially, the instability of these polymer thin films becomes an issue when they undergo thermal treatments at temperatures over the glass transition temperatures of the polymers.\textsuperscript{106,107} The films enter a liquid-like state and can be
destabilized. The intrinsic thermal fluctuations on the film surfaces spontaneously evolve and are amplified by attractive long-range intermolecular interactions between the films and the surroundings.\textsuperscript{78,73,72,71,79,12,108} This leads to the destabilization of these films and results in their “dewetting” from the substrates.

The amplified surface deformation reaches the substrate, exposing substrates and forming “holes” through the film. The removed material from the hole accumulates around the hole with a ring-shaped “rim”. These holes grow laterally until they coalesce with each other. The removed material forming the rim accumulates as the holes coalesce, forming polygonal networks of liquid ridges. Finally, the ridges break up into droplets (i.e. spherical caps). This dramatic change in structural morphology of polymer thin films is termed “dewetting”.\textsuperscript{12,96,109,110}

Theoretical aspects of dewetting kinetics, i.e. the growth rate of dewetting holes, in the intermediate stage\textsuperscript{109} of lateral hole growth has long been studied.\textsuperscript{111,112,113,114,115,116,117,118} However, experimental studies, performed to study dewetting kinetics, have been mostly limited to the effects of polymer properties.\textsuperscript{111,116,119,120,121,122,123,124} These studies may introduce unknown factor in the polymer properties, and thus the interaction between the substrate and the polymer. From this perspective, it is more desirable to modify substrate properties, e.g. substrate surface energy ($\gamma_S$). $\gamma_S$ is related to the capillary driving force, the spreading coefficient ($S$):\textsuperscript{30}

$$S = \gamma_S - \gamma_L - \gamma_{SL}$$

[4.1]
where $\gamma_S$ and $\gamma_L$ denote the surface energies of the substrate/air and the polymer melt/air interfaces, respectively, and $\gamma_{SL}$ is the polymer/substrate interfacial energy. This indicates that varying $\gamma_S$ by surface modification of the substrate directly and exclusively change the driving force of the dewetting, $S$. Therefore, if other experimental parameters are maintained, the dewetting velocity ($V_R$) can be varied as a function of $\gamma_S$. There have been only a few experimental studies that utilized modified substrates,$^{12,125}$ however, the variation of $\gamma_S$ was limited to a couple of cases.

To systematically study dewetting kinetics over a wide range of $\gamma_S$, PS thin films on surfaces modified with self-assembled monolayers (SAMs) of organosilanes were selected as model systems. Organosilanes having terminal groups of -CF$_3$ or -CH$_3$ were chosen to produce various substrates with different $\gamma_S$. Two sets of surfaces were prepared: one set contained different surface coverage of -CH$_3$ (octadecyltrichlorosilane, OTS) deposited on the surface using contact printing (CP) with different contact times,$^{126}$ while the other contained various ratios of mixed monolayers of -CF$_3$ and -CH$_3$-terminated organosilanes that were grafted to the surface by vapor phase deposition.$^{127}$ Polar surfaces with various $\gamma_S$ values, using organosilanes containing -COOH, -SH, -NH$_2$, or -CH$_2$Cl as the terminal group, were also generated by a solution deposition method.$^{128}$
4.1.2 Generation of a wide range of variation in substrate surface energy

4.1.2.1 Contact Printing of Octadecyltrichlorosilane with Different Contact Times

In the first class of systems studied, Si/SiO$_X$ substrates were modified with different coverages of CH$_3$-terminated OTS molecules. An earlier study$^{129}$ demonstrated that the amount of OTS deposited on SiO$_X$ surfaces increased as the contact time increased. Therefore, the surfaces were generated by contact printing (CP) of OTS to the surface using different contact times from 1 s to 120 s. AFM topographic and lateral force images of the OTS films were examined under ambient conditions to confirm the different OTS coverages (Figure 4.1). At a contact time of 1 s, OTS molecules were sparsely adsorbed throughout the contact area. At a contact time of 10 s, OTS molecules started to assemble and form small circular islands having average heights of 1.89 nm, which were shorter than the fully extended OTS molecules (2.62 nm$^{130}$). This suggested that the molecules were in a less ordered state.$^{131,132,133}$ Because OTS SAMs had much lower friction than that of the Si/SiO$_X$ substrate,$^{134}$ the correspondingly lower friction in the lateral force images verified that these islands consisted of OTS molecules. As the contact time increased (up to 30 s), these islands increased slightly in size. The most important observation was the OTS molecular extension to 2.8 nm indicating the formation of fully extended layers. At the same time, secondary islands with sizes similar to those formed at shorter contact times appeared. It was speculated that the secondary island formation was dominated by the diffusion of OTS molecules from the
Figure 4.1  2 μm × 2 μm SPM topographic and lateral force images of a contact-printed OTS monolayer are presented in the left and right columns, respectively, for each contact time. The higher regions in the topographic images correspond to the lower lateral force regions in the lateral force images, suggesting that these regions were covered with OTS molecules. The OTS domains grew with contact time: (a) with a contact time of 1 s, no visible islands were observed; (b) with a contact time of 10 s, small circular islands (~ 85 nm diameter) were found; (c) with a contact time of 20 s, the number of small islands was remarkably increased, and secondary islands were also observed among the primary islands; (d) with a contact time of 30 s, the islands grew in size and number; (e) with a contact time of 60 s, the density of islands further increased, but the sizes became comparatively uniform; and (f) with a contact time of 120 s, the islands coalesced and started to form a continuous layer.
primary islands as in the case of the solution deposition method.\textsuperscript{130} As the contact time increased further (up to 60 s), the island density increased with an onset of coalescence. With an extended contact time, more islands coalesced to form a continuous monolayer, even though the Si/SiO\textsubscript{X} substrate remained sporadically exposed.

\[ \gamma_S \] of each OTS contact-printed surface was estimated from the contact angles of two probe liquids (liquids 1 and 2), in this study deionized water and MI, using equation [3.7b].\textsuperscript{135} The contact angles values and corresponding surface energy components are summarized in Appendix A. As shown by the surface energies of the OTS contact-printed surfaces in Figure 4.2, \( \gamma_S^p \) decreased as the contact time increased. Since the majority of \( \gamma_S^p \) was from the polar Si/SiO\textsubscript{X} surface, as the contact time increased, more OTS molecules, which consisted of nonpolar -CH\textsubscript{2}- chain units and -CH\textsubscript{3} terminal groups, were transferred to the substrate leading to less exposure of the polar Si/SiO\textsubscript{X} substrate. However, even with a 120 s contact time, sparsely uncovered Si/SiO\textsubscript{X} regions were observed, as the planar stamp (1 cm x 1 cm) was not in intimate contact with the entire substrate. While \( \gamma_S^p \) showed a dramatic change with contact time, \( \gamma_S^d \) remained almost constant (around 24 mJ/m\textsuperscript{2}). In addition, the values of \( \gamma^d \) for -CH\textsubscript{3} groups in OTS molecules (21 mJ/m\textsuperscript{2})\textsuperscript{136} and Si/SiO\textsubscript{X} (24.4 mJ/m\textsuperscript{2})\textsuperscript{75} were similar. Therefore, an increase in OTS coverage might not cause a considerable change in \( \gamma_S^d \). The fact that the values of \( \gamma_S^d \) at 10 and 20 s contact times were slightly higher than those at other times could be the result of exposure of -CH\textsubscript{2}- units (\( \gamma^d = 32 \) mJ/m\textsuperscript{2})\textsuperscript{137} of the OTS chains, as less-ordered OTS SAMs are expected with these contact times.
Figure 4.2  $\gamma_s$ and its dispersion ($\gamma_s^d$) and polar ($\gamma_s^p$) components, represented by ●, ○, and □, respectively, of the contact-printed OTS at different contact times. As the contact time increased, $\gamma_s^p$ decreased dramatically, while $\gamma_s^d$ remained almost constant.
4.1.2.2 Mixed CH₃/CF₃ Monolayers with Different Mixing Ratios

Another set of nonpolar surfaces with different surface energies was generated by vapor phase depositing\textsuperscript{138} mixtures of FTS/DTS with various volume fractions. Since FTS and DTS have matching chain lengths, any topographical effects from chain length differences within the monolayer\textsuperscript{139} that might affect the dewetting process could be minimized. AFM observations for the FTS/DTS monolayer confirmed that there was no noticeable height difference. The scan size was varied from 200 nm × 200 nm to 10 μm × 10 μm. Lateral force and phase images, revealing frictional and mechanical properties of the monolayer, respectively, were also utilized to qualitatively discern possible phase separation of FTS and DTS in each mixed monolayer. Phase-separated FTS and DTS might alter the dewetting of PS thin films as compared to a homogeneous mixed FTS/DTS monolayer. FTS chains likely form helical structures, whereas DTS chains are normally in a planar zigzag structure. C-C bonds would encounter more resistance in rotating with the helical conformation than with the planar zigzag formation. As a result, the frictional force of FTS would be much higher than that of DTS.\textsuperscript{140,141} Also, elongation or compression of CF₂-CF₂ bonds due to the rotational barrier and the helical conformation should produce a layer that is harder than that from CH₂-CH₂ bonds. If phase separation were to occur, it should therefore be observed in AFM images. The frictional force and phase images of the mixed SAMs revealed no clear evidence of prominent phase separation.
\( \gamma_S \) and its components (\( \gamma_S^d \) and \( \gamma_S^p \)) presented in Figure 4.3 were calculated using equation [3.7b]. The contact angle values and corresponding surface energy components are summarized in Appendix A. The \( \gamma_S \) values decreased as the FTS content increased, since the surface consisting of -CF\(_3\) terminal groups (\( \gamma_S = 10.4 \) mJ/m\(^2\)) had a much lower surface energy than that of the -CH\(_3\) terminal groups (\( \gamma_S = 21 \) mJ/m\(^2\)).\(^{138}\) In contrast to Figure 4.2, \( \gamma_S^d \) changed dramatically while \( \gamma_S^p \) remained constant with a value of \( \sim 2.7 \) mJ/m\(^2\). The \( \gamma_S \) of both FTS and DTS was composed mostly of \( \gamma_S^d \). However, the presence of a polar component in the FTS/DTS mixed monolayer was not totally unexpected. One possibility for this occurrence is defects in the mixed monolayer or incomplete coverage of the monolayer, resulting in a slight exposure of the Si/SiO\(_X\) substrate. Another possibility was the strong electronegativity of fluorine present in FTS which might have the ability to form hydrogen bonds with water\(^{142}\) and contribute to \( \gamma_S^p \).

The resulting \( \gamma_S \) (Figure 4.3) did not correlate directly to the composition of the original FTS/DTS mixtures. Provided that the area fractions of FTS and DTS of the modified surfaces are directly proportional to their composition fraction in the mixtures, according to Cassie’s equation,\(^{143}\) a linear correlation between the resulting contact angle and the compositions of the original mixture would be expected if the monolayer had the same composition as the predeposited mixture. As a result, \( \gamma_S \) of the mixed monolayer, estimated from \( \cos \theta \) derived from Cassie’s equation, should be nearly linear over the entire composition of the mixtures. The experimentally measured \( \gamma_S \) of the mixed
Figure 4.3 $\gamma_s$ and its dispersion ($\gamma_{sd}$) and polar ($\gamma_{sp}$) components of the FTS/DTS mixed monolayer generated from vapor phase deposition of FTS and DTS mixtures having different molar ratios are represented by ●, ○, and ■, respectively. To have a more direct comparison to the surface energy estimated using the Cassie equation, the molar ratios instead of the volume ratios were used in this plot. $\gamma_s$ decreased with the increase of FTS content, which had a lower $\gamma_s$ than that of DTS. $\gamma_s$ measured on the mixed monolayer did not vary linearly with the molar ratios of the predeposited FTS/DTS solutions. As DTS content decreased, $\gamma_{sp}$ fluctuated more or less around a certain constant value, while $\gamma_{sd}$ decreased noticeably.
monolayer on a silicon wafer showed FTS domination. It was found that \( \gamma_s \) of the mixed monolayer-modified substrate increased with the logarithmic decrease of the FTS fraction. This suggested that the -CF\(_3\)-terminated organosilane, or FTS, might be preferentially deposited onto the substrate and/or more easily detected.

The possible preferential adsorption of FTS was therefore evaluated. Possible causes from our experimental procedures were eliminated first. On the basis of the higher molecular weight, boiling point, and density of FTS molecules, FTS was less volatile than DTS. As a result, more DTS molecules could be vaporized during the degassing process, leaving insufficient amounts for the deposition process. If this were true, then \( \gamma_s \) of the surface modified with the FTS/DTS 50/50 v/v mixture without degassing should have been higher (due to more DTS molecules) than that of the degassed mixture. We conducted separate experiments of FTS/DTS 50/50 v/v without degassing, and \( \gamma_s \) of the respective modified surface was still similar to the case of the degassed sample (~13.1 mJ/m\(^2\)). Therefore, preferential adsorption was not simply a result of the experimental method. On the basis of the higher values of \( \gamma_s^d \) and \( \gamma_s^p \) of our DTS surface as compared to the closely packed DTS, our DTS formed a disordered, liquidlike structure. The disorder of DTS, probably due to the presence of gauche bonds, could cause a slight shortening of the chain length.\(^{144}\) This shortening then could lead to the preferential adsorption of relatively longer FTS molecules, as in the case of mixed thiols.\(^{145}\) Also, it was reported that the polarity of the component drives its preferential
Figure 4.4 An illustration of the interaction between probe liquid molecules (denoted as the rounded rectangles) and the FTS/DTS mixed monolayer formed on the Si/SiOₓ substrate. The 3-D cross-polymerization among the organosilane molecules and the covalent bonding between the organosilane molecules and the substrate was simplified. (a) With higher contents of FTS, (FTS/DTS 50/50 or 10/90 v/v), the probe liquid molecules mainly interacted with FTS molecules due to the molecular arrangement of FTS (represented by a helical structure and an elliptical terminal group) and DTS (represented by zigzag chains and triangular end groups), the disordered monolayer structure of DTS, and the possible preferential adsorption of FTS molecules. (b) With lower FTS contents (FTS ≤ 1/99), DTS molecules formed a dominant continuous phase and FTS molecules were isolated. As a result, probe liquids sensed both the FTS and DTS molecules.
adsorption.\textsuperscript{146} FTS molecules, containing highly polarizable fluorine, were more polar than DTS molecules.

In addition to preferential adsorption, the arrangement of the FTS and DTS molecules in the mixed monolayer could lead to a preference of FTS over DTS. This could be the combined result of the slightly shorter chain length and smaller terminal group of DTS. The slight shortening of the DTS molecules due to the existence of gauche bonds and the disordered monolayer caused the -CH\textsubscript{3} terminal groups to be positioned underneath the -CF\textsubscript{3} terminal groups (Figure 4.4). The FTS molecules could “stand straight” by virtue of the intramolecular stabilization of the rigid rodlike helical structure of fluorocarbon chains.\textsuperscript{147} The larger -CF\textsubscript{3} terminal groups can act as “an umbrella” in preventing the probe liquids from penetrating and reaching the underlying -CH\textsubscript{3} groups at high FTS content (50 vol % and 10 vol % of the original mixture). We roughly calculated the projected area of a single -CH\textsubscript{3} and -CF\textsubscript{3} group from their van der Waals hemisphere volumes.\textsuperscript{148} The areas occupied by -CF\textsubscript{3} and -CH\textsubscript{3} were \(~23.4\) and \(~12.6\) Å\textsuperscript{2}, respectively. Therefore, more direct contact of the probe liquids with -CF\textsubscript{3} groups contributed to the measured $\gamma_S$. For DTS molecules to be detected, a significant amount of DTS molecules on the substrate was needed. Experimentally, only concentrations of $\geq 99$ vol. % DTS resulted in $\gamma_S$ measurements with a -CH\textsubscript{3} contribution.
4.1.2.3 Polar Organosilane Surfaces

Polar surfaces, whose $\gamma_S$ values are normally high, were generated using -NH$_2$-terminated APTES, -COOH-terminated CTMES, -CH$_2$Cl-terminated CPTMOS, and -SH-terminated MPTMOS with a solution deposition method.$^{130}$ The contact angles values and corresponding surface energy components are summarized in Appendix A.

On the basis of the larger than expected water contact angle hysteresis (\~ 30$^\circ$ for APTES and \~ 20$^\circ$ for the other polar silanes, CTMES, MPTMOS, and CPTMOS), the polar organosilanes might have failed to form close-packed or complete SAMs. The polar organosilanes used in this study only had two or three alkyl units in their backbone. Short alkyl chains (< 4 CH$_2$) form disordered or incomplete monolayers.$^{131,132,133}$ In addition, APTES is known to form multilayers when deposited using the solution deposition method,$^{149}$ resulting in 3-D polysiloxane networks having many possible molecular conformations and orientations.$^{150}$ This incomplete monolayer or random multilayer formation of the polar organosilanes could perturb the sole contribution of $\gamma_S$ to dewetting behavior. To verify the quality of the monolayer, we obtained surface root-mean-square roughness values, \( R_q \), from the topographic SPM images of the organosilane surfaces (Appendix B). The surface roughness provides crude insight into the homogeneity of a surface. All of the organosilane surfaces were scanned. The value of \( R_q \) was estimated by averaging several scans with different scan sizes of the same type of surfaces. We were aware that the values were subject to change for the same sample type depending on the AFM conditions (e.g., scan mode, tip condition, vibration). The scans
were performed under well-controlled conditions and procedures, and the overall trend for different organosilanes was found to be similar within each scan set. The polar surfaces had relatively higher values of $R_q$ than did the nonpolar FTS/DTS surfaces, indicating that the polar surfaces were more likely incomplete and/or multilayers.

4.1.3 Dewetting Velocity versus Substrate Surface Energy

A thin film (~ 800 Å) of PS ($M_n = 63k$ or $9.3k$) was chosen with an annealing temperature of 160 °C. The annealing temperature and the film thickness of 800 Å were chosen by a simple combinatorial method. With these conditions, dewetting velocity (Appendix C) became measurable over a range of surface energies.

After the deposition of organosilanes on silicon wafer, PS thin films were placed on top of those organosilane-modified surfaces mentioned above. The PS thin films on the SAMs of organosilane were annealed under the ambient conditions. Dewetting behaviors were videotaped, and the diameter ($R$) of the dewetting holes for selected images at various annealing times ($t$) was measured (Appendix C). The maximum distance of the inside rim was measured as the diameter. The very early stage (when the hole initiates) and the final stage (when the hole growth starts to level off or holes start to coalesce with each other) of dewetting were not considered in our measurements. The annealing was ceased immediately prior to the coalescence of holes. The $V_R$ was obtained from the slope of the linear relationship of $R$ as a function of $t$. 
4.1.3.1 Dewetting Velocity versus Substrate Surface Energy Using Various Octadecyltrichlorosilane Coverage

The dewetting process varied from a few minutes to 1 h depending on the dewetting behavior of a particular surface. For samples with more than a 20 s contact time, PS thin films dewetted rapidly, leading to the coalescence of dewetting holes within a few minutes. However, for $\gamma_S$ of 63 and 52 mJ/m$^2$, the hole growth slowed and reached a plateau before holes were able to contact each other. Dewetting velocity was extracted from the linear growth period. Hole growth was found to be relatively uniform across the surface for each OTS contact-printed sample. The $V_R$ values reported are the average values of measurements from several locations. At least two OTS surfaces having the same contact times were used. Figure 4.5 summarizes the variation of $V_R$ as a function of $\gamma_S$. For PS-63k, the overall trend is expressed as an exponential relationship with an exponent of -0.13$\gamma_S$ and a coefficient of 530. The large standard deviation of $V_R$ at the 120 s contact time may originate from the dramatic change of $V_R$ on the slight variation of $\gamma_S$ of the three surfaces used. Experiments showed that $V_R$ was very sensitive to $\gamma_S$ in the low $\gamma_S$ region. Furthermore, $\gamma_S$ versus $V_R$ for PS-9.3k was also determined. Except for the molecular weight of the PS, all the other experimental conditions were the same: film thickness (~ 80 nm), substrates (contact-printed OTS surfaces), and annealing temperature (160 °C). Interestingly, the same exponent of -0.13$\gamma_S$ was obtained, and the coefficient was $1.1 \times 10^4$. 

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Figure 4.5 Dewetting velocity, $V_R$, on contact-printed OTS is plotted against $\gamma_S$ for PS-63k and -9.3k. $V_R$ decreased with the increase of $\gamma_S$ with an exponential relationship: $V_R \approx 530 \exp(-0.13 \gamma_S)$. The error bars were generated by measuring $V_R$ at different spots of the same type of samples. Errors in $V_R$ for 1 to 60 s contact times resided within the symbols. The inset represents a plot of $V_R$ as a function of $\gamma_S$ for PS-9.3k. The relationship was $V_R \approx 1.1 \times 10^4 \exp(-0.13 \gamma_S)$. 
4.1.3.2 Dewetting Velocity versus Substrate Surface Energy Using Mixed CH₃/CF₃ Monolayers

The plot of $V_R$ versus $\gamma_S$ in the case of FTS/DTS mixed monolayers is presented in Figure 4.6. As before, the relationship is not linear, but exhibits an exponential trend with an exponent of $-0.10\gamma_S$ and a coefficient of 310. The relatively poor alignment of the data to the fitted line could be the result of difficulties in reproducing the dewetting process, as the data were collected from at least three sets of surfaces over 12 months. The variation was attributed to factors such as ambient conditions, which have been shown to affect the monolayer formation.¹⁵¹

4.1.3.3 Dewetting Velocity versus Substrate Surface Energy Using Polar Organosilane Surfaces

The relationship of $V_R$ and $\gamma_S$ for polar organosilane surfaces was scattered with no discernable trend. The polar terminal groups may have induced interactions (e.g. hydrogen bonding between -COOH or -NH₂ and water molecules) with the molecules of the probe liquids. The polar surface activity could also increase contamination by adsorbing airborne particles, moisture, and organic debris, leading to the alteration of surface properties, and thus $\gamma_S$ of the surface.¹⁵²,¹⁵³ The molecularly disordered and rough surfaces of the polar organosilanes could have higher friction¹⁵⁴ and adhesion forces, which could interfere with the system free energy-driven dewetting process. There could also be additional physical (electrostatic) or chemical interactions between the polar...
Figure 4.6 $V_R$ of a PS thin film on FTS/DTS mixed monolayer was plotted versus $\gamma_S$. The trend line showed a relationship of $V_R \approx 310 \exp(-0.10\gamma_S)$. The error bars were generated from measuring $V_R$ at different spots of the sample.
Figure 4.7  Selected lateral force images of the organosilanes: (a) APTES, (b) SiO$_X$, and (c) 120 s contact-printed OTS. The images from left to right are the organosilane surface (2 μm × 2 μm) before placing a PS thin film, a dewetting hole of the PS thin film (30 μm × 30 μm) from the surface, and the floor of the dewetting hole (5 μm × 5 μm). Residual polymers were detected on the dewetted floor of APTES, and SiO$_X$, but not on the dewetted floor of OTS.
surfaces and the PS thin film; hence, complicating the dewetting behavior. In addition, APTES had been widely used as an adhesion promoter.\textsuperscript{149} The markedly low $V_R$ on the APTES surface implied that the -NH$_2$ terminal group could strongly affect the dewetting behavior.\textsuperscript{155,156} To further investigate the possible interactions, the floor of the dewetting holes was scanned with AFM lateral force imaging (Figure 4.7), since it is believed that lateral force imaging is more sensitive than topographic imaging for detecting the presence of any residuals. The dewetting holes from all polar surfaces had detectable nuclei, which initiated the dewetting, and patches of residual materials. This indirectly indicated an interaction between the PS thin film and the polar surfaces that impeded the dewetting of PS thin films. The scans showed that dewetting holes from the APTES surface had irregular shapes. In addition, the floor of the holes contained a significant amount of PS residuals (Figure 4.7a). The dewetted hole floors from Si/SiO$_X$ also showed a small amount of PS residuals (Figure 4.7b). Conversely, the floor of the dewetted holes from the OTS or FTS/DTS surfaces was very smooth with no noticeable features (Figure 4.7c). This was direct evidence that certain properties of polar surfaces, other than $\gamma_S$, hindered the dewetting process. Detailed investigations on one of the polar organosilanes, APTES, were pursued and reported in Section 4.3.

4.1.3.4 Master Plot of Dewetting Velocity versus Substrate Surface Energy on Organosilane Surfaces

A master correlation of $V_R$ versus $\gamma_S$ for various organosilane surfaces was attempted in order to combine the data obtained from both the nonpolar (various OTS
Figure 4.8 $V_R$ of PS-63k and -9.3k thin films plotted against $\gamma_S$ of all the organosilane surfaces used in this study: (i) PS-63k, vapor phase deposition of different volume ratios of FTS/DTS mixtures (♦), (ii) PS-63k, CP of the OTS monolayer with various contact times (■), (iii) PS-63k, solution deposition of polar organosilanes (-NH$_2$, -COOH, -CH$_2$Cl, and -SH) (△), (iv) PS-9.3k, CP of the OTS monolayer with various contact times (○). For PS-63k, an overall correlation between $V_R$ and $\gamma_S$ could not be obtained due to the dispersity of data for the polar organosiloxane surfaces. When only the surfaces modified with nonpolar organosilanes were chosen, an overall correlation had a relationship of $V_R \approx 620 \exp(-0.13\gamma_S)$. The relationships for PS-9.3k was $V_R \approx 1.1 \times 10^4 \exp(-0.13\gamma_S)$. The error bars were generated by measuring $V_R$ at different spots of the same type of samples.
coverage surfaces and the FTS/DTS mixed surfaces) and the polar surfaces (Figure 4.8). However, the data on the polar surface diverged from the fitted line of data on the nonpolar surfaces. The divergence was not surprising, since other factors could contribute to the dewetting of the PS thin film from the polar surfaces. Therefore, the polar organosilane surfaces might not be suitable for inclusion in the correlation between $V_R$ and $\gamma_S$. For all the nonpolar organosilane-modified surfaces described above, an overall expression of $V_R \approx 620 \exp(-0.13\gamma_S)$ was obtained.

4.1.3.5 Dewetting Kinetics

First, it is hypothesized that the dewetting kinetics of PS thin films can be described by a thermally activated process that follows an Arrhenius-type behavior. According to the work of Wei et al.,157 the isothermal dewetting rates of PS thin films were found to be constant and increased as the annealing temperature increased, suggesting thermally activated dewetting processes. In addition, the data extracted from the study of Karapanagiotis et al.125 also demonstrated the exponential dependence of the dewetting rates of PS films on the inverse of temperature. In the studies158,159,160 of the wetting phenomenon of simple liquids, they also recognized the wetting process as a “shear-modified” activated rate process. A preliminary result of the dewetting rate dependence on the annealing temperature in our case suggested thermally activated dewetting processes. PS-9.3k thin films on the OTS-modified substrates with $\gamma_S$ of $\sim$ 28 mJ/m$^2$ were annealed at 130, 150, and 160 °C, respectively. $V_R$ values were found to
exponentially increase with increasing temperature. From this perspective, $V_R$ would have a form of an isothermal rate constant in it. The rate constant could be analogous to a desorption\textsuperscript{161,162} rate constant if the dewetting process were apprehended as a desorption process of the adhered PS films with an activation energy. Then, the physical reason of the exponential dependence of $V_R$ on $\gamma_S$ could be drawn from the exponential dependence of the rate constant on an activation energy of the process.

Since our purpose in this present study is to elucidate the exponential dependence of $V_R$ on $\gamma_S$, it is supposed that $V_R$ could be simplified as $V_R = f(a$ rate constant, a certain molecular length scale in the movement of the receding PS chains, $...)$. Wei et al.\textsuperscript{157} found that the dewetting velocity is a thermally activated process, but they did not have a length scale in their Arrhenius-type model. On the basis of the concepts of a desorption process and a length component, $V_R$ can be described as

$$V_R = f_s k_{des} L = f_s \nu_0 \exp \left( \frac{-\Delta E_{des}}{k_B T} \right) L$$

[4.2]

where $k_{des}$ is a rate constant for the desorption, $L$ is the average length of distance between two adsorption/desorption sites, $\nu_0$ is a preexponential factor, $\Delta E_{des}$ is an activation energy for the desorption, $k_B$ is Boltzmann’s constant ($1.3807 \times 10^{-23}$ J/K), and $T$ denotes the absolute temperature (K).\textsuperscript{161,162} $f_s$ includes unknown factors or constants except $k_{des}$ and $L$, which would depend on the detailed properties of system components. In this relationship (equation [4.2]), we suppose that the PS chains initially interact with and adhere to the substrates through arbitrary adsorption/desorption sites whose length scales and number density per unit area are to be determined in relation to $V_R$ which is
Figure 4.9 Schematic of PS chain desorption as the dewetting proceeds. The PS film continues to the axis perpendicular to the plane of paper. The PS chains adsorbed at the arbitrary adsorption/desorption sites that are located along the dewetting line are desorbed all at the same time and retracted, resulting in the receding of the dewetting line in the direction perpendicular to it.
resulted from the interaction between the PS films and the substrates. Once the thermal energy renders the PS films a liquid-like state, mobile and thermally activated, the adsorption sites of the PS chains on the substrates along the dewetting line (three-phase contact line), are successively broken at the rate of $k_{\text{des}}$, as the dewetting line moves (Figure 4.9). The separating rate is to be directly reflected in the observed $V_R$, i.e. $k_{\text{des}} \propto V_R$. Since the spreading coefficients of the systems are negative (equation [4.1]), the movement of the dewetting line, perpendicular to the straight dewetting line (at the point under consideration), is in the direction of desorbing PS films. Since the desorption of PS chains from the adsorption sites only happens along the dewetting line all at the same time, there is no coexistence of adsorbed sites by the PS chains and emptied sites along the dewetting line during the receding. If it existed, it might affect $V_R$, as in the desorption kinetics of small molecules, like coverage effects.\textsuperscript{161} In addition, $V_R (dR/dt)$ in our case is kind of a dynamic quantity in terms of length and rate, and $V_R$ is not a function of the coverage variation of desorbing substance, different from a reaction kinetics.

Dewetting phenomenon can be considered as a type of “adhesion failure” between the polymer thin film and the substrate. Since no permanent chemical bond formation is involved between PS and the OTS surfaces or the FTS/DTS mixed surfaces, the activation barrier for PS to dewet from the surfaces would be proportional to the free energy of adhesion between PS and the substrates ($S$), $\Delta G_{\text{PS-S}}$. Considering the direction of the dewetting process, the apparent $\Delta E_{\text{des}}$ is to be proportional to $-\Delta G_{\text{PS-S}}$, which is the energy necessary to separate a unit area of the interface PS-S into the PS and substrate
surfaces.\textsuperscript{90,163} \(-\Delta G_{PS-S}^a\) can be related to the geometric mean of the free energies of PS (\(\gamma_{PS}\)) and \(\gamma_S\) (section 3.1.3.2).\textsuperscript{163}

\[-\Delta G_{PS-S}^a = -(\gamma_{PS} + \gamma_S - \gamma_{PS-S}) \approx 2\sqrt{\gamma_{PS}\gamma_S} \]  \[4.3\]

Assuming \(\Delta E_{des}\) is dominated by -\(\Delta G_{PS-S}^a\) for our system, equation [4.2] can be expressed as

\[V_R = f_x v_0 \exp\left(\frac{-(-\Delta G_{PS-S}^a)}{\sigma k_B T}\right) = f_x v_0 \exp\left[\frac{-(2\sqrt{\gamma_{PS}\gamma_S})}{\sigma k_B T}\right]L [4.4]\]

where \(\sigma\) is adsorption/desorption sites per unit area. The form of this expression demonstrates how \(V_R\) increases as \(\gamma_S\) decreases, in accord with experimental observations. However, in this approach, \(V_R\) is exponentially dependent on \(\gamma_S^{1/2}\), not \(\gamma_S\); therefore, the previous experimental results (Figure 4.8) were replotted in terms of \(V_R\) versus \(\gamma_S^{1/2}\) (Figure 4.9). For a better presentation, Figure 4.9 shows the \(V_R\) versus \(\gamma_S^{1/2}\) relationship on a semilogarithmic scale. From Figure 4.9, exponential relationships between \(V_R\) and \(\gamma_S^{1/2}\) are found, as expected from the model (equation [4.4]). It seems that the simple Arrhenius-type desorption kinetics is able to account for the \(\gamma_S^{1/2}\) dependence of \(V_R\).

The exponents for PS-63k and PS-9.3k on the OTS surfaces are about -1.7\(\gamma_S^{1/2}\), while the exponent for PS-63k on the FTS/DTS surfaces is -0.9\(\gamma_S^{1/2}\). The absolute values of the exponents are altered from the previous values (Section 4.1.3), as a result of plotting \(V_R\) versus \(\gamma_S^{1/2}\). To simply demonstrate the physical validity of equation [4.4], the exponents are compared with the estimated values, \(-(2\gamma_{PS}^{1/2})/(\sigma k_B T)\), from equation
Figure 4.10 $V_R$ of PS-63k and -9.3k thin films plotted against $\gamma_S^{1/2}$: (i) PS-63k on the mixed FTS/DTS surfaces (♦), (ii) PS-63k on the OTS surfaces (■), and (iii) PS-9.3k on the OTS surfaces (○). The $V_R$ versus $\gamma_S^{1/2}$ relationships for each system were also found to be exponential. The corresponding slopes of the curves -0.9, -1.7, and -1.7, respectively.
[4.4] for each system. The $\gamma_{PS}$ values at the annealing temperature of 160 °C for PS-9.3k and PS-63k are estimated to be $\sim 35$ and $37 \text{ mJ/m}^2$, respectively (Appendix D).\textsuperscript{164} Since the exact $\sigma$ values cannot be obtained, they are subject to be assumed as free parameters. The estimated values of $\sigma$ to match the experimentally obtained exponents are $\sim 1.2 \times 10^{18}$ for PS-63k on the OTS surfaces, $\sim 2.3 \times 10^{18}$ for PS-63k on the FTS/DTS surfaces, and $\sim 1.2 \times 10^{18}$ for PS-9.3k on the OTS surfaces. If the distribution of the desorption sites is isotropic, $L \approx \sigma^{-1/2}$.\textsuperscript{160,165,166,167} Hence, with the values of $\sigma$, one can determine the distance between two desorption sites, $L$, for each system, which should be in the order of molecular dimension. The calculated $L$ values are $\sim 0.9$ nm for PS-63k on the OTS surfaces, $\sim 0.7$ nm for PS-63k on the FTS/DTS surfaces, and $\sim 1.0$ nm for PS-9.3k on the OTS surfaces. These values are reasonable in terms of the average length of molecular displacement.\textsuperscript{160,165,166,168} It indicates that the fitted values for $\sigma$ are not physically unrealistic. Therefore, it is possible that the exponential dependence of $V_R$ on $\gamma_S^{1/2}$ originates from the nature of the desorption process. In other words, the dewetting process can be perceived as a type of desorption process that depends on the exponential value of the activation energy, in this case, the negative of the free energy of adhesion, $2(\gamma_{PS}\gamma_S)^{1/2}$. Another approach to confirm the validity of this model is to vary the annealing temperature under a fixed $\gamma_S$, as described in the above. By plotting $V_R$ versus $1/T$ for each $\gamma_S$, the $\Delta E_{des}$ values can be obtained from the exponents.\textsuperscript{157} Finally, the obtained $\Delta E_{des}$ values should be plotted against $\gamma_S^{1/2}$ to verify their dependence on $\gamma_S$. 
It is interesting to find that the slopes, which are \(-2\gamma_{PS}^{1/2}/(\sigma k_B T)\), for PS-9.3k and -63k on the OTS surfaces are similar while different from the exponent for PS-63k on the FTS/DTS surfaces. \(\sigma\) seems to be less sensitive to the molecular weight of PS. Little sensitivity of the activation energy to molecular weight or chemical composition of the polymer was also noticed in the work of Wei et al.\(^{157}\). Thus, the difference in the slopes for PS on the OTS surfaces and that for PS on the FTS/DTS surfaces could be drawn from the difference in morphological structures between the OTS and FTS/DTS modified surfaces. The surfaces modified with OTS molecules, prior to forming the full coverage, consist of OTS islands that can be seen as cylinders oriented perpendicular to the substrate (Figure 4.1) while the FTS/DTS modified surfaces have relatively no physical features (Figure 4.4). This difference results in different magnitudes of surface roughness for each type of surfaces, as indicated in the surface RMS roughness data (Appendix B), and this roughness effect could interfere with the dewetting process. In the case of the OTS surfaces, because of the lack of intermolecular van-der Waals interactions, the molecules at the outer edges of the islands may not be standing straight and packed closely against each other to form an ordered monolayer. Those disordered or dangled OTS molecules from the outer edges could impose different friction into the dewetting interface. Similarly, strong frictional properties of the fluoro components\(^{140,141}\) in the FTS molecules could contribute to smaller \(V_R\) for the FTS-rich surfaces than expected from the \(\gamma_S\) values, resulting in a reduction of \(V_R\) at each \(\gamma_S\). In addition, the existence of polar character for the OTS surfaces (Figure 4.2) might induce sort of “hysteresis-effect” in the \(V_R\) variation relative to the range of \(\gamma_S\), and thus expand the magnitude of \(V_R\)
variation, resulting in the greater exponent compared with that for the nonpolar FTS/DTS surfaces. However, more data of $V_R$ for each set of surfaces need to be collected to confirm the significance of the variation in the slopes and the preexponential parts, and then the actual contribution of PS properties and surface character of each type of surfaces.

Since the equation is developed only to identify the origin of the exponential increase of $V_R$ with $\gamma_S^{1/2}$, it is not our intention at the current moment to predict the absolute values of $V_R$ from the $\gamma_S$ data using equation [4.4]. The desorption kinetics was originally derived based on molecules in the gas phase or solution and primarily applied to small species.$^{161,169}$ Therefore, the unique situation of the desorption of polymer melt itself should be considered for a further development of the model. For instance, viscosity or viscoelasticity of the polymer melt can be included, as a part of $f_x$ components in equation [4.2]. In the studies of wetting process,$^{159,160}$ the viscosity of liquids has been introduced into the wetting model by considering viscous contribution into the activation energy through invoking the Erying theory$^{170}$ of viscosity. Furthermore, when accompanied by more data, the physical rationale behind the difference among $\sigma$’s (thus $L$’s) for each system could be elucidated in relation to the chain length of PS and the substrate surface properties.

For reference, there has been a common model for the growth of dewetting holes$^{171,172,173,174}$ which can be called as the “hydrodynamic model”. It is originated from hydrodynamic studies for wetting behaviors of fluids.$^{160}$ According to the model, the
velocity is derived from a balance between a capillary driving force due to the “uncompensated Young’s force” and a viscous force due to flow in the wedge of the retraction rim, and can be expressed as

\[ V_R = k \frac{\gamma \theta_e^3}{\eta} \]  \[4.5\]

where \( k \) is a numerical coefficient, \( \gamma \) is the surface energy of the liquid, \( \theta_e \) is an equilibrium contact angle between the liquid and the solid surface, and \( \eta \) is the viscosity of the liquid. In addition, especially from the theory of dewetting dynamics, the relationship between \( \theta_e \) and dynamic contact angle \( \theta_d \) can be derived as

\[ \theta_e = \sqrt{2} \theta_d \]  \[4.6\]

\( \theta_e \) values for our case were measured from cross-sectional profiles of the droplets using AFM after further annealing of the samples until the droplets reach a pseudo-equilibrium state (Appendix E). The measured \( V_R \) values were plotted as a function of the measured \( \theta_e \) values with estimated \( \gamma_{PS} \) and \( \eta_{PS} \), as in equation [4.5]. Relatively, linear relationships between \( V_R \) and \( \gamma_{PS} \theta_e^3 / \eta_{PS} \) were found for each system (Appendix F). For equation [4.6], \( \theta_d \) (constant throughout the hole growth) was measured from the cross-sectional profile of the rim when the dewetting hole diameter was \( \sim 35 \mu m \), where a mature rim was formed. For PS-9.3k and -63k on the OTS surfaces, the slope of \( \theta_e \) plotted against \( \theta_d \) was determined to be \( \sim 1.4 \), which was quite close to the theoretical value of \( \sqrt{2} \) (Appendix G). The linear relationships between \( V_R \) and \( \gamma_{PS} \theta_e^3 / \eta_{PS} \) and between \( \theta_e \) and \( \theta_d \) with a coefficient of 1.4 suggested that the hydrodynamic model seems to be valid for our system as well. Macroscopically measured experimental data seem to fit into the model;
however, this model does not have physical relation with the spontaneous dewetting phenomenon and cannot describe the submicroscopic physics behind the phenomenon. Therefore, this model can only explain the relationship between the observed macroscopic quantities.

4.1.4 Summary

Dewetting of PS-63k and -9.3k thin films on substrates having various surface energies was investigated. The surface energy was varied by modifying a silicon wafer through the contact printing of OTS under different contact times or using mixed SAMs with different ratios of -CF₃- and -CH₃-terminated organosilanes. Polar surfaces with -COOH-, -CH₂Cl-, -NH₂-, and -SH-terminated groups were also generated. However, these surfaces introduced complicating factors for the dewetting behavior of polymer thin films. As a result, a simple correlation of dewetting velocity versus surface energy could not be obtained. Therefore, the nonpolar (or minimum polarity) organosilane-modified surfaces were concentrated on in this section. For PS-63k on the -CH₃ and -CF₃/-CH₃ covered surfaces, overall relationships of \( V_R \approx 530 \exp(-0.13\gamma_S) \) and \( 310 \exp(-0.10\gamma_S) \) were obtained, respectively. For PS-9.3k on the OTS surfaces, \( V_R \approx 1.1 \times 10^4 \exp(-0.13\gamma_S) \) was obtained. The exponential dependence of \( V_R \) on \( \gamma_S \) was elucidated by regarding the dewetting kinetics as the rate of desorption process that has an exponential dependence on the activation energy. In this perspective, the activation barrier for the physically adsorbed PS films to dewet from the substrates was the negative of the free energy of adhesion, which was proportional to \( \gamma_S^{1/2} \). The exponential relationship found
in the replotted $V_R$ in terms of $\gamma_S^{1/2}$, with physically reasonable exponents, supported the validity of the proposed rationalization.

The empirical correlation between $V_R$ and $\gamma_S$ can also be utilized to deduce surface energies of previously uncharacterized surfaces. It is difficult to estimate surface energies of miniaturized energy gradient surfaces (micrometer scale) and surfaces containing micron-scaled heterogeneous patterns using contact angle measurements or contact mechanics. By using the dewetting of PS thin films on these surfaces, surface energies of the gradient and heterogeneous surfaces could be roughly deduced from the correlation plots. More detailed studies related to this issue have been published.$^{54,238}$ Those studies involved the generation of energy gradients and heterogeneous surfaces and estimating their surface energies using the correlation plots of $V_R$ versus $\gamma_S$ or dewetting hole size versus $\gamma_S$ obtained by annealing samples for a fixed time.
4.2 Rim Instability as a Function of Substrate Surface Energy

4.2.1 Introduction

Instability of polymer thin films (< ~ 100 nm) has been an issue in applications, such as coatings in micron-scaled devices and nonlinear optics, of these thin films. The failure of thermal stability and continuity, termed “dewetting”, of polymer thin films has led to extensive studies of dewetting phenomena. Recently, construction of 3-dimensional micro/nano-scaled polymer structures utilizing dewetting phenomena has been demonstrated. Dewetting of polymer thin films in a controlled manner with patterned substrates or physical confinements facilitates the production of such structures, which has potential for use in fundamental studies and practical applications. In order to achieve the desired structures using a dewetting process, a comprehensive understanding of the key factors affecting the dewetting process is essential. One such factor is substrate surface properties, such as the surface energy of a substrate ($\gamma_S$). Studies have shown that substrate surface properties affect the early stages of dewetting, such as the nucleation and growth of dewetting holes. In this section, we focus on how the surface conditions, especially substrate surface energy variations, control the early-intermediate stages of dewetting and the formation and development of rims around the dewetting holes during their lateral growth.

Recently, the morphological rim instability of dewetting holes has drawn attention. During the lateral growth of dewetting holes, the removed
polymer materials from the dewetting holes accumulate along the circumference of the exposed substrates, forming ring-like polymer ridges called “rims”. In most dewetting studies, the rims were found to grow evenly in size with the growth of dewetting holes, without altering the overall profile. However, for cases when large equilibrium contact angles occurred or high molecular weight polymers were used, it was observed that this retracting rim became unstable with fluctuations in the rim geometry. In some cases, the fluctuations in the rim profile even caused the formation of “fingers”, which were extended behind the rim growth. This rim instability is believed to be analogous to the Rayleigh instability, which accentuates the destabilization of cylindrical liquids into isolated droplets.

Similar instabilities have been observed in the spreading of thin polymer or liquid films under various driving forces, such as gravitational forces, centrifugal forces, surface tension gradients, or thermal gradients. These instabilities were related to their driving forces, which were easily controlled by varying the inclination of substrate, the speed of rotation, the concentration difference, or the temperature difference. Both theoretical modeling and simulations have attempted to describe the instabilities. However, few experimental studies, regarding the effects of the driving capillary force on the rim instability during the dewetting process, have been systematically performed. To our best knowledge, the only documented substrate effects on polymer thin film dewetting behavior involved the use of a fully nonpolar organosilane-covered substrate and two different types of silicon wafers. For the dewetting process of a liquid, the driving capillary force is the difference between $\gamma_S$ and the sum of the liquid surface tension with the surrounding environment.
tension and the liquid/substrate interfacial tension. Therefore, the rim instability of the dewetting holes is expected to depend on $\gamma_S$.

In this study, the rim instability as a function of $\gamma_S$ will be determined, and an analysis of the rim instability based on the Rayleigh instability will be presented. Rims of dewetting holes of PS ($M_n = 9.3k$) thin films on substrates having surface energies ($\gamma_S$) ranging from 28 to 63 mJ/m$^2$ were studied. The variation of $\gamma_S$ was accomplished by contact printing of octadecyltrichlorosilane (OTS) with different contact times. PS-9.3k, having a molecular weight much less than the entanglement weight of PS ($M_e \sim 19k$), was chosen to minimize the slippage at the PS/substrate interface, which might induce complications in the rim instability. Under the no-slip condition, $\gamma_S$ is the critical factor in determining the development of the rim morphology and rim instability. The morphology and rim profile of the dewetting holes—specifically, the rim height ($h$), the rim width ($w$), and the dynamic contact angle ($\theta_d$) of the rim on the substrate (Figure 4.11)—were evaluated. The spacing (or instability wavelength, $\lambda$) between height fluctuations along the rim was also characterized. All these quantities were compared with an analysis based on the Rayleigh instability, and agreements were found.

4.2.2 Substrate Surface Energy Dependency of Dewetting Hole Morphology

The evolution of the rim instability as a function of $\gamma_S$ is presented in Figures 4.12 and 4.13. To obtain unperturbed rim geometry, holes large enough (inside diameter, $D \sim 35 \mu m$) to have discernible rims but without fully developed rim fluctuations were used
Figure 4.11 Schematic of the cross-sectional profile of a dewetting hole. $\theta_d$ represents the dynamic contact angle formed by the polymer melt on the substrate. $h$, $w$ and $R_o$ are the respective height, width and radius of curvature of the rim, $R$ is the radius of the dewetting hole. The sketch is not scaled, i.e. $h << w$. 
To compare the degree of the rim instability, even larger holes ($D \sim 55 \mu m$) with mature rim instabilities were selected (Figure 4.12). With similar hole size, the amount of PS removed from the holes and accumulated into the rims would be similar, and thus the substrate surface energy effects can be adequately compared. For $\gamma_S$ in a range of 52 mJ/m$^2$ to 63 mJ/m$^2$, relatively circular dewetting holes with some irregularity of the inside edge were observed (Figures 4.12a, 4.12b, 4.13a and 4.13b). The darker colored ring around the outside edge of the rim indicated a slight decrease in height from the original film thickness$^{197}$. Very slight undulation of the rim was also observed in this surface energy range. One might notice that while color bands of the rims, black-white-gray, were similar, $w$ appeared to reduce from Figure 4.12a to Figure 4.12b, suggesting that a reduction in $\gamma_S$ led to a smaller $w$. For a substrate having $\gamma_S$ of $\sim 47$ mJ/m$^2$ (Figure 4.12c), in addition to the slight reduction in $w$ as compared to the case of $\gamma_S \sim 52$ mJ/m$^2$, more color bands (black-white-gray-white) and smaller gaps between the bands were observed, indicating the height of the rim ($h$) also increased. Furthermore, along the rim, occasional protrusions (portions with more color bands) in the height or the $z$-direction and slight circumferential undulations in the $r$-direction occurred, which could be a result of excess protrusion in the $z$-direction.

For a substrate having $\gamma_S$ of $\sim 43$ mJ/m$^2$ (Figure 4.12d), $w$ decreased further while $h$ increased. Protrusions in the $z$-direction further developed and became pronounced enough for the inner part of the rim to bulge slightly in the opposite direction of the rim growth. Similar rim morphological patterns were observed for substrates having $\gamma_S$ down
to \( \sim 30 \text{ mJ/m}^2 \) (Figures 4.12e and 4.12f), while the protuberance in the \( r \)-direction became more conspicuous and well-defined. The rim width continued to decrease while \( h \) continued to increase as \( \gamma_S \) decreased. The transition of the protrusion shape from long mounds along the angular direction (Figure 4.12c) to compact “humps” (Figure 4.12f) was also observed. “Humps” were more developed at lower \( \gamma_S \), and these evolved protrusions could be left behind as the rim developed and could eventually become fingers.

The formation of protrusions, in a sense, was similar to the undulation in the Rayleigh instability.\(^{180,182,186}\) The rim would tend to break and form isolated droplets to minimize its system energy; however, it was constrained by the undewetted film outside the rim. As a result, the protrusions formed due to the instability had to grow only in the \( z \)-direction and the \( r \)-direction. In the case that the inward protrusions or “fingers” grew long enough, they might detach from the rim and form isolated droplets. For a substrate with an even lower \( \gamma_S \) (\( \sim 28 \text{ mJ/m}^2 \)), short fingers emerged from the unstable rim (Figure 4.14c). The rim instability was so pronounced that the circumference of the rim became slightly irregular or “flower-shaped”.\(^{180}\)

Another set of experiments was performed to rule out the dewetting velocity effect on the rim instability. \( V_R \) (\( dR/dt \)) in our study ranged from \( \sim 2 \mu\text{m/min for } \gamma_S \sim 63 \text{ mJ/m}^2 \) to \( \sim 235 \mu\text{m/min for } \gamma_S \sim 28 \text{ mJ/m}^2 \). Since dewetting holes that exhibited a higher degree of rim instability also grew faster, one could argue that \( V_R \) could contribute to the
Figure 4.12  The optical microscope images of dewetting holes of PS-9.3k thin films formed on various substrates; each has a particular substrate surface energy ($\gamma_S$). $\gamma_S$ of each substrate was achieved by modifying the substrate with a certain amount of OTS molecules to form either partial or complete monolayer coverage. The annealing was ceased when the dewetting holes grew to $\sim 55 \, \mu$m in diameter. $\gamma_S$ for the substrates were (a) $\sim 63$ mJ/m$^2$, (b) $\sim 52$ mJ/m$^2$, (c) $\sim 47$ mJ/m$^2$, (d) $\sim 43$ mJ/m$^2$, (e) $\sim 34$ mJ/m$^2$, and (f) $\sim 30$ mJ/m$^2$. As $\gamma_S$ decreased, the instability along the rim became more pronounced. The slight distortion in the bottom left corner of the rim seen in (a) is the result of a dust particle presented in the film. All the images have the same size, and the scale bar is 20 $\mu$m.
Figure 4.13  SPM images of dewetting holes of PS-9.3k thin films on substrates having different $\gamma_S$. $\gamma_S$ are (a) $\sim 63$ mJ/m$^2$; (b) $\sim 52$ mJ/m$^2$; (c) $\sim 47$ mJ/m$^2$; (d) $\sim 43$ mJ/m$^2$; (e) $\sim 34$ mJ/m$^2$; and (f) $\sim 30$ mJ/m$^2$. Dewetting holes with a similar size ($\sim 35.5 \pm 2.3$ μm) were chosen to minimize any size effect, probably insignificant by considering the deviation, on the development of instability. As $\gamma_S$ was decreased, the instability become more distinct. The scanning was performed under contact mode. The scan size for each image was 60 μm x 60 μm, and the z-scale was 1 μm/div.
evolution of the rim instability. Therefore, thin films on the substrate with $\gamma_S$ of $\sim 28$ mJ/m$^2$ were annealed at three different temperatures of 130, 150, and 160 °C to achieve various values of $V_R$. The rim instability of those holes grown under different $V_R$ was similar (Figure 4.14). In all cases, the fluctuation in $h$ was markedly enhanced (indicated by multiple colored bands), resulting in clear “short fingers” in the $r$-direction. $V_R$ for the samples annealed at 130 °C was $\sim 3$ μm/min. If the rim instability were to depend on $V_R$, the rim instability of these samples (Figure 4.14a) should be similar to that of the samples on the substrate with $\gamma_S$ of $\sim 63$ mJ/m$^2$ ($V_R \sim 2$ μm/min, Figure 4.12a) or $\sim 52$ mJ/m$^2$ ($V_R \sim 7$ μm/min, Figure 4.12b) annealed at 160 °C, however, this similarity was not observed. The rim instability was related to neither the hole growth rate nor the viscosity of the PS melts.

On the basis of the experimental observations described above, we propose a qualitative explanation for the evolution of the rim instability with hole growth. Once a dewetting hole forms in the film, under no-slip conditions, the PS melts removed from the hole cannot be immediately merged into the surrounding film, resulting in rim formation around the hole. Driven by the capillary force, more PS is added to the rim as the hole grows, and the unconstrained portion (free from the underneath interface and the undewetted PS film connected to the rim) of the rim increases. The instability of this unconstrained portion becomes similar to the Rayleigh instability and can be easily developed. The protrusions developed from the rim are amplified by thermal fluctuations to minimize total surface free energy of the rim. The flow from the non-
Figure 4.14 The dewetting velocity ($V_R$) having no effect on the rim instability with $\gamma_S \sim 28 \text{ mJ/m}^2$ for PS-9.3k is presented. $V_R$ was varied by annealing the samples at different temperatures: (a) 130°C, (b) 150°C, and (c) 160°C. $V_R$ measured for the samples annealed at (a) 130°C (~ 3 $\mu$m/min) was ~ 80 times slower than that at (c) 160°C (~ 235 $\mu$m/min). If the degree of rim instability were a function of $V_R$, then, the rim instability in (a) should be suppressed far more than that in (c) and similar to that in Figure 4.12a. However, the degree of rim instability observed was similar, and “short finger” formation occurred for all the cases. All three images have the same size with the scale bar of 20 $\mu$m.
protruding portions of the rim to the protrusions are due to the Laplace pressure, which overcomes the stabilizing effect of the surface energy (\(\gamma_{PS}\)) and enhances the instability. Therefore, as the dewetting hole grows, the rim instability starts to evolve and becomes visible in microscopic dimensions. For dewetting holes having the same size, as \(\gamma_S\) decreases, the height of the rim, thus the unconstrained portion, increases. The rim fluctuation emerges and becomes visible at an earlier stage (i.e. smaller hole size) of hole growth.

One thing worth noting is that the OTS islands formed by contact printing have little or no influence on the dewetting process and the rim instability. It was reported that, prior to the formation of droplets, the dewetting process was insensitive to the substrate heterogeneity within a scale less than a micrometer. The spacing between the OTS islands decreased from hundreds of nanometers to probably sub-nanometer with the decrease of \(\gamma_S\), while the observed length scale of the instability (wavelength) was in tens of micrometers (as described below), which was much larger (~ 100 times) than the heterogeneity length scale of the OTS islands. In addition, the development of rim instability was not correlated to the transition of the substrate heterogeneity, (i.e. as \(\gamma_S\) decreased, the degree of the instability continuously increased, while the heterogeneity increased first and then decreased). Only heterogeneities that were able to locally pin the retracting rim were large foreign impurities (in micrometers) occasionally deposited on the surface. Therefore, the OTS surfaces were considered homogeneous with respect to the rim instability and its development.
4.2.3 Predicting Rim Profile Based on Substrate Surface Energy

We have qualitatively discussed the morphological evolution of the rim instability as a function of $\gamma_S$. This section focuses on more quantitative measurements and analysis of the rim instability. As it may be noticed from the optical microscopic and AFM images of the dewetting holes formed on substrates having different $\gamma_S$ (Figures 4.12, 4.13, and 4.14), the sizes of $w$ are different for holes having a similar diameter. This indicates that, to satisfy the material balance, the rim profile should vary with $\gamma_S$ in a predictable manner. The rim profile in the rz-plane likely depends on $\theta_d$, the dynamic contact angle of PS melts formed on a substrate. $\theta_d$ controls the slope of the rim formed on the substrate; thus, it may govern the profile of the rim. $\theta_d$ is related to $\gamma_S$ in the following expression:27

$$\cos(\sqrt{2\theta_d}) = \frac{2\sqrt{\gamma_d^S \gamma_d^p} + 2\sqrt{\gamma_P^S \gamma_P^p}}{\gamma_{PS}} - 1 \quad [4.7]$$

where $\gamma^d$ and $\gamma^p$ are the dispersion and polar components of surface energy, i.e. $\gamma = \gamma_d^S + \gamma_P^p$, and the subscript of $S$ and PS indicate, respectively, the substrate and PS. $\theta_d$ is related to the equilibrium contact angle ($\theta_e$) with a relationship of $\sqrt{2\theta_d} = \theta_e$, which can be derived from the “hydrodynamic theory of dewetting”.211 The anticipated $\theta_d$ values (dashed line in Figure 4.15) were calculated using equation [4.7] with experimentally measured $\gamma_d^S$ and $\gamma_P^p$ and estimated $\gamma_{PS}$ at 160 °C. $\gamma_{PS}$ at 160 °C was estimated to be $\sim$ 30.6 mJ/m$^2$,212 and $\gamma_{PS}^p$ was assumed to be about 1 % of $\gamma_{PS}$,213
Figure 4.15 Dynamic contact angles ($\theta_d$) experimentally measured (indicated as ■) for dewetted PS-9.3k thin films were compared to the values predicted $\theta_d$ (dashed line) using the equation [4.7]. The experimental values of $\theta_d$ (averaged over ~ 50 measurements) were retrieved from cross-sectional profiles of the SPM images as those shown in Figure 4.13. For predicting $\theta_d$, the experimentally measured dispersion and polar components of $\gamma_S$ were used along with the estimated $\gamma$ of PS melt at 160$^\circ$C with the assumption of 1% of polar component in total $\gamma$ of PS melt. As $\gamma_S$ decreased, $\theta_d$ increased with a sharp transition. The error for each measured $\theta_d$ was the standard derivation of ~ 50 measurements. The error bars for $\gamma_S$ were originated from the variation in contact angles of probe liquids used to estimate $\gamma_S$. 

\[
\begin{align*}
\theta_d (^\circ) & \quad \gamma_S (\text{mJ/m}^2) \\
20 & 30 \\
30 & 40 \\
40 & 50 \\
50 & 60 \\
60 & 70 \\
70 &
\end{align*}
\]
The experimental values of $\theta_d$ were obtained from the cross-sectional profiles of the AFM images of the dewetting holes. Only holes with a particular size (~35 μm) on substrates having different $\gamma_S$ were scanned and used. This hole size was chosen to ensure the formation of mature rims while minimizing fluctuations that could alter the intrinsic values of $\theta_d$. Figure 4.15 represents experimentally measured $\theta_d$ values on substrates having different $\gamma_S$ for PS-9.3k. These experimental values agree well with the predicted $\theta_d$ from equation [4.7].

The variation of $\theta_d$ versus $\gamma_S$ symbolizes the rim profile dependency on $\gamma_S$. As $\theta_d$ increases, the cross-sectional contour of the rim becomes higher and narrower. Based on the material balance, the rim volume of each dewetting hole formed on substrates having different $\gamma_S$ should be similar regardless of $\gamma_S$, since $D$ of the dewetting holes was basically same (35.5 ± 2.3 μm). $h$ and $w$, as defined in Figure 4.11, were obtained experimentally from the AFM images which were also used for $\theta_d$. Apparently, as $\gamma_S$ increased, $h$ decreased while $w$ increased (Figure 4.16).

Another quantity worth noting for the instability is the “instability wavelength”, $\lambda$. $\lambda$ of the rim instability was determined using optical microscopic images as those shown in Figure 4.12. The variation of $\lambda$ as a function of $\gamma_S$ for PS-9.3k is shown in Figure 4.17. Overall, $\lambda$ decreased as $\gamma_S$ decreased. It indicated that as $\gamma_S$ decreased, not only the protrusions grew in the $z$-direction, but also the number of them increased. $\lambda$
exhibited a similar trend as that of \( w \) with a transition at a similar \( \gamma_S \) range as those of the other rim parameters, such as \( \theta_d, h, \) and \( w \).

The rim profile (\( w \) and \( h \) at a particular \( \gamma_S \)) can also be predicted using material balance. The volume of PS removed from a dewetting hole should be accumulated into its rim (Figure 4.11), and the volume of the hole and that of the rim are, respectively, presented in equations [4.8] and [4.9]:

\[
\pi \delta (R^2 + \frac{\delta R}{\tan \theta_d} + \frac{1}{3} \frac{\delta^2}{\tan^2 \theta_d}) \tag{4.8}
\]

\[
2\pi \left( R + \frac{1}{2} \left( w + \frac{\delta}{\tan \theta_d} \right) \right) \cdot SA \tag{4.9}
\]

where \( \delta \) (\( \approx 80 \) nm) is the thickness of the initial PS thin film, \( R \) is the radius of the dewetting hole, and \( SA \) is the cross-sectional area of the rim, which has the following form:

\[
\frac{1}{4} \left( w + \frac{\delta}{\tan \theta_d} \right)^2 \left( \frac{1}{\sin^2 \theta_d} - \frac{1}{2} \sin 2 \theta_d \right) - \delta w \tag{4.10}
\]

The material balance equations [4.8] to [4.10] along with the value of experimentally measured \( R \) and the predicted \( \theta_d \) from equation [4.7] were used to estimate the anticipated \( w \) at a particular \( \gamma_S \). For PS-9.3k, the expected \( w \)s for each \( \gamma_S \) (dashed line in Figure 4.16) match well with the measured values. The anticipated \( h \) can also be estimated from the anticipated \( w \) with a relationship (equation [4.11]) derived from the rim geometry, and the values (dotted line in Figure 4.16) also agree reasonably well with the measured values.
Figure 4.16 The experimentally measured rim width \((w,\text{ denoted as } \bigcirc)\) and rim height \((h,\text{ denoted as } \blacklozenge)\) for PS-9.3k as a function of \(\gamma_S\). As \(\gamma_S\) increased, \(w\) increased while \(h\) decreased. The anticipated \(h\) and \(w\) corresponding to each \(\gamma_S\) were estimated using the material balance (equations [4.8] and [4.9]), the rim geometry shown in Figure 4.11 (equation 10), and the predicted \(\theta_d\) in Figure 4.15 (equation [4.7]). The experimentally measured \(w\) and \(h\) agreed reasonably well with the anticipated \(h\) (dotted line) and \(w\) (dashed line) values. The error for each measured value was the standard derivation of at least ~ 50 measurements. The insets (left and right) are schematic drawings of rim geometry (or profile) for low and high \(\gamma_S\) cases, respectively. The drawings are not scaled.
Figure 4.17 The instability wavelength, $\lambda$, of the rim instability as a function of $\gamma_s$ for dewetted thin film of PS-9.3k. As $\gamma_s$ increased, $\lambda$ increased with a transition occurring at $\gamma_s$ between 43 mJ/m$^2$ and 47 mJ/m$^2$. The error for each data point was the standard derivation of at least ~ 50 measurements.
In order to clarify the rim instability dependency on $\gamma_S$, the possibility of slippage of the PS-9.3k film and its effect on the rim instability\textsuperscript{210,211} are evaluated and argued below based on previous related studies, since no direct measurement of the slippage at the interface during dewetting is possible.\textsuperscript{213} The ratio of slip length ($b$)\textsuperscript{192,209} of PS-9.3k ($b \sim 6$ nm) to its film thickness ($\delta \sim 80$ nm) is much smaller than that of a no-slip PS film reported,\textsuperscript{191} suggesting that our systems were likely under the no-slip condition. It is erroneous to apply the theoretical analysis of dewetting dynamics with slippage\textsuperscript{214} to a case of $\delta >> b$, as in our systems. Also, polymer films on high-energy Si/SiO$_x$ and partially silanized Si/SiO$_x$ surfaces are considered not to slip.\textsuperscript{192} In addition, a constant growth rate of the dewetting holes from each of our substrates indicate the no-slip condition\textsuperscript{192,195,209,216,217,218} was valid for our systems. Furthermore, a recent simulation study\textsuperscript{213} suggested that dewetting holes in slipping thin films have less-developed rims.

Slippage likely increases as the substrates become smoother with deposition of more OTS molecules.\textsuperscript{192} If slippage were to affect the rim instability, then the rim instability would have been less pronounced as $\gamma_S$ decreased, which is opposite to what we observed in this study. The suppression of the retracting line instability was also observed experimentally when a viscoelastic adhesive was peeled from a substrate in the presence of strong slippage.\textsuperscript{219} Therefore, the enhanced rim instability at lower $\gamma_S$ cannot
be the result of slippage at the polymer melt/substrate interface, but it is likely the result of rim profiles controlled by $\gamma_S$.

4.2.4 Substrate Surface Energy Dependency of Rim Instability

The rim geometry can be predicted using equations [4.8] – [4.11] for holes with known sizes ($D$), and shows a strong dependence on $\gamma_S$ (Figures 4.12, 4.13, and 4.16). As the dewetting holes grow, different rim profiles result from different $\gamma_S$, and the rim instability emerges at different stages of the hole growth. Rims with higher aspect ratios ($h/w$) on lower $\gamma_S$ substrates seem to be more susceptible to thermal fluctuations and become unstable at an earlier stage of hole growth. This agrees with the quantitative analysis on the growth of the rim instabilities shown in Figure 4.18, which will be discussed below based on the Rayleigh instability.

To simplify our analysis, we made an analogy of the rim instability of dewetting holes to the Rayleigh instability.\textsuperscript{205} In most Rayleigh instability cases, a cylindrical liquid column is surrounded by a medium, and fluctuations are developed along the surface of the liquid, eventually leading the liquid column to break up and form droplets. It can be imagined that the rim around dewetting holes is a liquid thread in the form of a ring. Sekimoto \textit{et al.}\textsuperscript{220} pointed out that this ridge geometry was thermodynamically unstable against surface fluctuations and exhibited behavior like the Rayleigh instability. However, some distinct features in the case of rim instability exist and need to be noted. First, the rim of a dewetting hole is not stationary as in the Rayleigh instability; the rim
continuously expands in both $w$ and $h$ as the dewetting hole grows. Second, one side of the rim is attached to an undewetted film making fluctuations less likely. Third, the rim is not a cylindrical column; instead, it is a flat cylindrical cap with a very small height and a large width. Fourth, the rim is not exposed to only one medium (i.e. air): while its curved surface is exposed to air, its base is in contact with a solid substrate.

For the Rayleigh instability of a cylindrical liquid thread surrounded by another liquid medium, the growth rate ($q$) of the distortion or instability\textsuperscript{199,205,220} is defined as:

$$q = \frac{\gamma_{lm} \Omega(\lambda, p)}{2 R_o \eta_m}$$ \hspace{1cm} [4.10]

where $\gamma_{lm}$ is the interfacial tension between the liquid and the medium, $\Omega(\lambda, p)$ is a complex function of the instability wavelength ($\lambda$) and the ratio ($p$) of the viscosity of the liquid column ($\eta_l$) and the surrounding medium ($\eta_m$), and $2R_o$ is the diameter of the liquid column. In our case, where the rim sits on the substrate with the curved portion exposed to air (Figure 4.11), the growth rate will be quite different for the air-side versus the substrate-side. On the substrate-side, the viscosity of the substrate (silicon wafer) is assumed to be infinite while all other terms in equation [4.12] have finite values. As a result, the growth of the protrusion is almost completely suppressed, and only $q$ of the air-side is important in the development of the instability. In the case of a large $p$ ($p \rightarrow \infty$), $q$ depends primarily on the liquid properties, and according to Tomotika, the expression becomes\textsuperscript{199}

$$q = \frac{\gamma_{lm} \Gamma(\lambda, R_o)}{2 R_o \eta_l}$$ \hspace{1cm} [4.12]
When the surrounding medium is air, the value of \( I(\lambda, R_o) \) is \( \frac{1}{3} \), and equation [4.13] can be simplified to the Rayleigh’s original expression for the instability of a cylindrical column of fluid in air:\(^{200}\)

\[
q = \frac{\gamma_{lm}}{6 R_o \eta} \tag{4.14}
\]

In our case, \( R_o \) is the radius of curvature of the rim as indicated in Figure 4.11. Our rim consists of PS melt at 160 °C, so \( \gamma_{lm} = \gamma_{PS} \cong 30.6 \text{ mJ/m}^2 \),\(^{212}\) and \( \eta = \eta_{PS} \cong 103.8 \text{ Pa-s}. \)

One might expect that the shear thinning behavior of the polymer could affect the viscosity for the cases when the dewetting velocity is large (\( \sim 235 \mu\text{m/min} \)). According to our calculation, the dimensionless strain rate parameter\(^{222}\) is much smaller than 10, indicating the effects of dewetting velocity are unimportant to the viscosity of the polymer melt, and the zero shear viscosity limit can be used for all the calculations.

By using the predicted \( \theta_d, w, \) and \( h \) at each \( \gamma_s \), \( q \) values can be estimated from equation [4.14] and plotted as a function of \( D \) or \( \gamma_s \) in Figure 4.18. In general, for a particular \( D \), the instability grows faster as \( \gamma_s \) decreases; consequently, more pronounced protrusions are expected. As shown in Figure 4.18, for \( \gamma_s \) greater than 49 mJ/m\(^2\), \( q \) is almost independent of \( \gamma_s \) for holes with a specific size, but \( q \) increases sharply as \( \gamma_s \) decreases from 49 mJ/m\(^2\) to 43 mJ/m\(^2\) with a shape transition occurring at \( \sim 46 \text{ mJ/m}^2 \), and then it continues to increase at a slower pace for \( \gamma_s \) less than 43 mJ/m\(^2\). The basic shape of \( q \) as a function of \( \gamma_s \) is similar to that of \( \theta_d \) (Figure 4.15). For a substrate with a lower \( \gamma_s \), \( q \) has a greater value at the moment that the dewetting hole forms and decreases...
quickly as the hole grows. $q$ starts to converge for all the substrates as $D$ approaches $\sim 100 \, \mu m$. For PS thin films used in our study ($\delta \sim 80 \, nm$), the dewetting is likely initiated with fluctuations of the film. The fluctuations grow toward the substrate and finally reach the substrate to form the dewetting holes, and then the holes grow laterally. As soon as the bottom of the fluctuation hits the substrate (still $R = 0$), a rim with a certain width, defined as the initial rim width, is formed. The value of the initial rim width depends on $\gamma_S$ or $\theta_d$. As $\gamma_S$ decreases, i.e. $\theta_d$ increases, the initial rim width decreases. For instance, the initial rim width is $\sim 2.89 \, \mu m$ for $\gamma_S \sim 63 \, mJ/m^2$, while it is $0.67 \, \mu m$ for $\gamma_S \sim 28 \, mJ/m^2$. The relative increases of $w$ and $h$ are smaller for substrates having higher $\gamma_S$, this is why the $q$ value is almost constant for substrates with $\gamma_S$ greater than $49 \, mJ/m^2$, especially when the holes are small ($< 1 \, \mu m$) (Figure 4.18). As the dewetting hole grows from 1 to $10 \, \mu m$, a significant decrease in $q$ occurs for substrates with $\gamma_S$ less than $46 \, mJ/m^2$ (the inset of Figure 4.18), since the relative increases of $w$ and $h$ are larger for these cases. Once the hole grows larger than $10 \, \mu m$ in diameter, the relative increase rates of $w$ and $h$ become comparable for different substrates, and the slopes of $q$ vs. $D$ become similar.

For a substrate having a lower $\gamma_S$, $q$ is always greater as compared to that of a substrate with a higher $\gamma_S$; hence, the rim instability becomes observable earlier or at a smaller dewetting hole, and the rim instability is expected to be more pronounced when similar sized holes are compared. To further verify this statement, one could estimate the time required for a certain amplitude of protrusion (i.e. $\sim 25 \, nm$) to be microscopically
observable by adopting the expression for estimating the breakup time \( t_b \), \( t_b = 1/q \ln(\alpha_b/\alpha_0) \), where \( \alpha_b \) is the amplitude at breakup and \( \alpha_0 \) is the original amplitude) of a stationary liquid cylinder.\(^{205}\) Substituting the \( q \) value predicted using \( R_o \) when the fluctuation hits the substrate, 25 nm for \( \alpha_b \), and 0.3 nm for \( \alpha_0 \),\(^{205}\) the instability should become observable in \( \sim 1.5 \) s for \( \gamma_S \sim 63 \text{ mJ/m}^2 \) and \( \sim 0.1 \) s for \( \gamma_S \sim 28 \text{ mJ/m}^2 \). Experimentally, for \( \gamma_S \) greater than 47 mJ/m\(^2\), the rim instability became microscopically observable\(^{223}\) only after the dewetting hole grew greater than \( \sim 10 \mu\text{m} \), which took tens to hundreds of seconds after the initial hole was formed. Even with the lowest \( \gamma_S \) (28 mJ/m\(^2\)), the emergence of the observable rim instability was still one order of magnitude lower than the analysis predicted. In addition, the ratio of \( \lambda/2R_o \) can be used to evaluate the validity of the theoretical predications. \( \lambda/2R_o \) was found to vary from 0.4 to 2.2 as \( \gamma_S \) decreased from 63 mJ/m\(^2\) to 28 mJ/m\(^2\), which was much smaller than the value (4.51) reported for Rayleigh instability cases.

As mentioned earlier, the analysis was oversimplified; many factors in our polymeric systems could slow down the development of the rim instability, which were not considered in the analysis. The continuous addition of material flow into the rim could dampen out the destabilizing process caused by capillary fluctuations. The rim, which only resembles a very small portion of the cylindrical geometry, is strictly confined by the substrate and connected to the continuous undewetted polymer film, which retards the development of the rim and its instability. Therefore, the rim instability
Figure 4.18  The growth rate ($q$) of instability as a function of $\gamma_S$ and the dewetting hole diameter ($D$) (the inset). Each $q$ vs. $\gamma_S$ plot represents the transition of $q$ as $\gamma_S$ varies at a fixed $D$. The curve from the top to the bottom corresponds to $D$ of 0.1 $\mu$m, 1 $\mu$m, 10 $\mu$m, and 55 $\mu$m, respectively. The inset shows the variation of $q$ as dewetting holes grow (i.e. $D$ increases) on substrates that have a particular $\gamma_S$. The corresponding $\gamma_S$ for $q$ curve from the top to the bottom is 28, 34, 43, 46, 47, 52, and 63 mJ/m$^2$, respectively. $q$ was calculated from equation [4.14].
proceeds much slower than the Rayleigh model predicted. Nevertheless, the basic trend of the substrate surface energy effect on the development of the rim instability was well captured, qualitatively, with the analysis based on Rayleigh instability.

Interestingly, when $\lambda$ was divided by estimated $w$, the ratio was between 3.6 for $\gamma_s \sim 63$ mJ/m$^2$ and 4.6 for $\gamma_s \sim 28$ mJ/m$^2$, which was slightly smaller but comparable to the value of the Rayleigh instability of a cylindrical thread in air. The exact reason behind the agreement is unclear. Nonetheless, it seems that it is not adequate to replace $2R_o$ with $w$ in equation [4.14], otherwise the effect of rim height or dynamic contact angle on the rim instability would be neglected. For all the dewetting holes studied, the maximum aspect ratio ($h/w$) is 0.13 (Figure 4.16), suggesting the height contribution to rim instability could be small but not negligible. For an example, with a similar $w$ ($\sim 4.06 \mu$m), $h$ for $\gamma_s \sim 28$ mJ/m$^2$ ($\sim 0.50 \mu$m) is almost 4 times of that for $\gamma_s \sim 63$ mJ/m$^2$ ($\sim 0.13 \mu$m), and the corresponding values of $D$ were $\sim 58 \mu$m for $\gamma_s \sim 28$ mJ/m$^2$ and $\sim 6 \mu$m for $\gamma_s \sim 63$ mJ/m$^2$. With these dimensions, much greater rim instability was observed for the dewetting holes formed on the lower energy substrates.

4.2.5 Molecular Weight Effect on Rim Instability

It was also investigated that how the entanglement of the PS chains or the molecular weight of PS affected the formation of an irregular rim around the dewetting holes and the development of rim instability. To investigate entanglement effects, thin
films of PS having a molecular weight ($M_n$) of 63k (PS-63k) were subjected to dewetting studies on the same set of substrates.

First, the evolution of the rim instability as a function of $\gamma_s$ was determined for PS-63k and presented in Figures 4.19 and 4.20. Once the holes grew to certain sizes (50 $\sim$ 60 \(\mu\)m in $D$), the instability of the rim formed on each substrate was examined and compared. For $\gamma_s$ in a range 52 mJ/m\(^2\) to 63 mJ/m\(^2\), clean circular dewetting holes were observed (Figures 4.19a, 4.19b, and 4.20a), but the growth of dewetting holes was significantly retarded and almost ceased within our time-scale of annealing (< 1 h), so no detailed instability could be examined at such high $\gamma_s$. $D$ was < 10 \(\mu\)m for the dewetting holes formed on a substrate having $\gamma_s$ of 63 mJ/m\(^2\). The darker colored ring around the hole indicated an underdeveloped rim with a slight increase in height from the original film thickness (Figure 4.19a). For $\gamma_s$ $\sim$ 52 mJ/m\(^2\), the dewetting holes grew up to $\sim$ 30 \(\mu\)m in $D$ and remained almost circular with no visible modulation of the rim (Figures 4.19b and 4.20a).

As observed for a sample with $\gamma_s$ 47 mJ/m\(^2\) (Figures 4.19c and 4.20b), along the rim, occasional protrusions in the $z$-direction and slight circumferential undulations in the $r$-direction occurred, and the undulation in the $r$-direction was the result of the excess protrusion in the $z$-direction. Between 52 mJ/m\(^2\) and 47 mJ/m\(^2\), an interesting characteristic of $w$ was noticed from Figures 4.19b (or 4.20a) and 4.19c (or 4.20b). Intuitively, we can imagine that $w$ increases as the hole grows, since the material
removed from the hole should accumulate in the rim. However, \( w \) in Figure 4.20c was similar to that in Figure 4.20b, while \( D \) was much larger. This again implies that \( \gamma_S \) contributes to the rim profile: as \( \gamma_S \) decreased, \( h \) increased (Figure 4.16).

For a substrate having a \( \gamma_S \) of 43 mJ/m\(^2\), protrusions in the \( z \)-direction developed further and became so pronounced that the inner part of the rim bulged in the opposite direction of the rim growth (Figures 4.19d). Similar rim morphological patterns were observed for substrates having \( \gamma_S \) as low as 34 mJ/m\(^2\) (Figure 4.19e). Note that, for \( \gamma_S \) 34 mJ/m\(^2\), the protrusions were more condensed and broke into individual immature fingers, unlike the wide protrusions in the angular direction seen in Figure 4.20d. The fluctuation in the \( r \)-direction became conspicuous and well-defined. For \( \gamma_S \) 30 mJ/m\(^2\), periodic \( z \)-protrusions and \( r \)-fluctuations overgrew from the rim and turned into short fingers (Figures 4.19f and 4.20d).

In some cases, the fingers extended, and when long enough the finger tip pinched off and formed isolated droplets, similar to the front propagation of Rayleigh instabilities.\(^{224}\) The tip of the finger, while attached to the rim, experienced a minimum stress from the rim, and thus it could easily relax into an individual droplet and left inside the floor of the dewetting hole. For a substrate with an even lower \( \gamma_S \) (\( \sim 28 \) mJ/m\(^2\)), fingers emerged during the early stage of the hole growth, and continue to extend as the dewetting proceeded. In the meantime, more material was lost to the extended fingers.
Figure 4.19 Evolution of the fingering instability along the rim of dewetting hole as a function of substrate surface energy ($\gamma_S$) for PS (63k). The $\gamma_S$ was varied by adsorbing OTS molecules with different coverage. The annealing was ceased when the dewetting holes grew up to a certain comparable size. The $\gamma_S$ for the substrates were (a) $\sim$ 63; (b) $\sim$ 52; (c) $\sim$ 47; (d) $\sim$ 43; (e) $\sim$ 34; and (f) $\sim$ 30 mJ/m$^2$. As the $\gamma_S$ decreased, the fingering instability along the rim became clearly more pronounced. The scale bars are 20 $\mu$m.
Figure 4.20  AFM images of dewetting holes for PS (63k) at different $\gamma_S$. The $\gamma_S$ are (a) 52, (b) 47, (c) 34, and (d) 30 mJ/m$^2$. As the $\gamma_S$ was decreased, the onset and development of fingering instability were pronounced at a similar hole diameter (~ 40 μm). Well-distributed fingers were observed at the $\gamma_S$ of ~ 30 mJ/m$^2$. Contact mode was used for the scanning. The $z$-scale is 1 μm/div for all the images.
and enhanced the outward growth of the portions of the rim in between the fingers. As a result, the circumference of the rim became irregular or “flower-shaped”.

Figure 4.21 represents the difference between the development of the rim instability of PS-9.3k and that of PS-63k with decrease of $\gamma_s$. When $\gamma_s$ was $\sim 49$ mJ/m$^2$, for PS-9.3k (Figure 4.21a), a slight fluctuation of $h$ along the azimuthal direction was observed. These long protrusions along the rim were indirectly visible by darker colored bands. On the other hand, for PS-63k, dewetting holes (Figure 4.21b) showed clearer protrusions indicated by more colored bands for the elliptical parts. As $\gamma_s$ further decreased down to $\sim 28$ mJ/m$^2$, the fluctuation in $h$ was markedly enhanced (indicated by multiple colored bands) for PS-9.3k, resulting in a clear differentiation between the enhanced convex protrusions accompanied by radial undulations and the less undulated rim portions (Figure 4.21c). However, at similar $\gamma_s$, for PS-63k (Figure 4.21d), the protrusions around similar sized dewetting holes were significantly developed over the limit of $w$ and apparently formed “fingers”, which were detached from the rim and formed isolated droplets, and the overall rim contour was distorted from its circular shape.

In comparing the rim instabilities between PS-9.3k and PS-63k, one could argue that the lower $\eta$ (roughly 180 times), and faster $V_R$ (approximately an order of magnitude higher) of PS-9.3k were responsible for suppression of the instability. As indirectly demonstrated in the previous section of 4.2.2, $\eta$ is not a dominant factor in the rim instability, and neither is $V_R$; it simply alters the rate of the dewetting process. To
Figure 4.21 Comparison of $\gamma_S$ effects on the rim profile and instability of dewetted thin films of PS having two different molecular weights. (a) and (c) are resulted from thin films of PS with a $M_n$ of 9.3k, and (b) and (d) are those from PS with a $M_n$ of 63k. They were all annealed at 160$\degree$C. To control possible $\eta$ effect on the rim instability, PS-9.3k was annealed at 160$\degree$C (e), while PS-63k was annealed at 215$\degree$C (f). $\gamma_S$ were selected to be approximately the same for each set to control its effect. For (a) and (b), $\gamma_S$ was $\sim$ 49 mJ/m$^2$, and it was $\sim$ 28 mJ/m$^2$ for (c) – (f). The instability developed with the decrease of $\gamma_S$ for both types of PS thin films; however, the degree of rim fluctuation and finger formation was enhanced for the higher $M_n$ PS (63k). In comparison of the rim instability for PS-9.3k and -63k with the same $\eta$, PS-63k still demonstrated a higher degree of rim instability. The scale bar for (a) – (d) was 20 $\mu$m, and that for (e) and (f) was 100 $\mu$m.
ensure the irrelevance of $\eta$ to the rim instability, PS-63k was annealed at 215 °C (Figure 4.21f) to match $\eta$ with that of PS-9.3k annealed at 160 °C (Figure 4.21e).\(^{221}\) $\gamma_S$ was $\sim 28$ mJ/m\(^2\) for both cases. The diameter of the holes was chosen to be $\sim 60$ μm. The rim instability that emerged in rims for PS-63k was still more developed than that for PS-9.3k. These rims exhibited distinguished and well-distributed short fingers and slight undulation of the outer rim, indicating more evolved rim instability. The effect of viscoelasticity on the destabilization of the rim morphology was also reported by Masson et al.\(^{122}\) According to their study, dewetting holes formed in thin films of PS with higher molecular weights are subjected to the development of fingering instability when the film thickness and the capillary driving force are constant. As in the instability of cylindrical fluid bodies,\(^{225}\) a viscoelastic thread also becomes unstable and easily breaks up into droplets compared with Newtonian threads. However, it is critical to realize that manipulating $\eta$ of polymers by changing the annealing temperature could also alter $\gamma_{PS}$. In order to accurately investigate the molecular weight effect on the rim instability, one should change the annealing temperature to match $\gamma$ of the polymers, since $\eta$ does not appear to affect the rim instability. The estimated $\gamma$ of PS-63k at 215 °C was $\sim 34$ mJ/m\(^2\).\(^{221}\) Because $\gamma$ of PS-63k is a little larger than that of PS-9.3k, the viscoelastic effect due to the entanglement of polymer chains on the rim instability may not be important.
4.2.6 Summary

Rim instability of dewetting holes, developed during the dewetting of PS-9.3k and -63k thin films from substrates having different surface energy ranging from 28 to 63 mJ/m², was investigated. As $\gamma_S$ decreased, more distinct instability was observed with enhanced protrusions in both the vertical and radial directions. The transition from even rims to rims with small circumferential undulations and height fluctuations was observed at $\gamma_S$ of $\sim$ 52 mJ/m². The evolution of protrusions into pronounced features with small “fingers” occurred at $\gamma_S \leq 28$ mJ/m². PS-63k demonstrated more developed rim instability compared with PS-9.3k. It seemed that the entanglement of PS-63k chains promoted the destabilization of rim morphology. However, more controlled experiments are needed to clarify the molecular weight effect on the rim instability by matching $\gamma$ of the two PS systems.

For PS-9.3k thin films dewetted from substrates having different $\gamma_S$, the different degrees of rim instability for the same size holes originated from distinct rim profiles determined by $\gamma_S$. The $\theta_d$ between the PS melts and the substrates was strongly dependent on $\gamma_S$. The larger $\theta_d$ for lower $\gamma_S$ resulted in higher and narrower rims, which were susceptible to destabilization as in the Rayleigh instability, and the instability developed earlier and exhibited more evolved protrusions and fluctuations along the rim. Consequently, the development of the rim instability depended on the rim profile ($h$, $w$, and $\theta_d$) which was determined by $\gamma_S$. The instability was the result of neither slippage at the PS melt/substrate interface nor the dewetting velocity.
A simplified analysis based on the Rayleigh instability of viscous cylindrical fluids was applied to explain the rim instability dependency on $\gamma_S$. The analysis also utilized the rim profile predicted based on $\gamma_S$. This simple model was capable of capturing the basic trend of $\gamma_S$-dependent rim instability, including the sharp shape transition of the instability occurring between 43 mJ/m$^2$ and 49 mJ/m$^2$ observed experimentally. However, the experimentally observed rim instability development was about one order of magnitude slower than the model predicted. The discrepancies between the experimental data and the theoretical prediction likely resulted from some of the detailed geometric and polymeric properties that were not included in the model. A more comprehensive study can be conducted by including some of these details, which may provide a better guide to the understanding of the development of the rim instability occurring during the dewetting of polymer thin films. Nevertheless, this study pointed out that, in addition to the properties of polymer thin films, substrate surface properties, such as surface energy, which have received little attention in the past, should be included in theoretical analyses of polymer thin film behavior.
4.3 Dewetting Suppression by Surface Modification Using Amine-Terminated Organosilane

4.3.1 Introduction

Maintaining the homogeneity and continuity of polymer thin films (< 100 nm) is critical for their applications in the areas of paints and coatings, microelectronics, adhesion and lubrication, and nonlinear optics. However, under normal circumstances, polymer thin films on non-wettable surfaces become unstable and undergo a self-destructive process, termed “dewetting”, once they are annealed at a temperature greater than \( T_g \) of the polymer.\(^{226,227,228,229}\) Holes are formed in the film, and the film eventually disintegrates into polymer droplets. As a result, the properties of the polymer thin film and thus the advantages of using such films vanish. To suppress or inhibit the dewetting process, various modifications of polymer films and/or substrates have been attempted. The retardation of dewetting has mostly been achieved by the addition of foreign materials including nanoparticles, homopolymers, block copolymers, and metal ions into polymer films.\(^{230,231,232,233,234,235,236,237}\)

With nanoparticles or other polymers, they are normally added into the polymer solution and spin-coated with the polymer into the thin films. These foreign materials segregate to the polymer-substrate interface during the spin-coating,\(^{230,231,232,233,234}\) and the preferential segregation is believed to modify polymer-substrate interactions or substrate roughness, leading to inhibition or retardation of dewetting. In the case of metal ions,\(^{237}\)
possible inter- and intramolecular ionomer complexation between sulfonated ionomers and counter metal ions occurs, thus enhancing electrostatic interactions between polymer and substrate. Such modifications made to polymer films clearly alter their characteristics. Further characterization of the altered films is needed to clarify the mechanism of dewetting inhibition. Moreover, the amount of dewetting inhibitors added to fully suppress dewetting causes residual materials to be left in the bulk film, hence, not only are physical, optical, and electrical properties of the film altered, but also the surface chemistry and topology. Those alterations can be critical for the applications of polymer thin films mentioned above; therefore, direct substrate modification is more desirable. Recent studies have shown that surfaces modified by -NH₂-terminated organosilanes could strongly suppress the dewetting of polymer (e.g. PS) thin films.²³⁴,²³⁸

In fact, amine-terminated organosilanes (e.g. 3-aminopropyltriethoxysilane, APTES) have been widely utilized as coupling agents to enhance adhesion between organic materials and inorganic substrates.²³⁹,²⁴⁰,²⁴¹ The structure of an APTES layer is controlled by its molecular nature. The three ethoxy groups in each APTES molecule can be hydrolyzed and react not only with active groups (e.g. -OH) on the inorganic substrate, but also with those of other APTES molecules, resulting in a polymerized network.²⁴⁰,²⁴² In addition, the active –NH₂ terminal group can interact with surface hydroxyl groups as well as the hydrolyzed head groups.²⁴³,²⁴⁴,²⁴⁵ Furthermore, the intermolecular van der Waals forces between the short alkyl chains (three –CH₂) of APTES are insufficient for the molecules to stand straight against each other and form an ordered monolayer.²⁴¹ Therefore, APTES molecules normally form a 3-dimensional multilayer network that
anchors to the substrate with a few chemical bonds.\textsuperscript{246} Under ambient temperature, such a network is relatively loose with a minimum amount of permanent chemical bonds. To tighten the network or increase the crosslinking among APTES molecules, a thermal process is normally required, which provides a window of opportunity for the organic materials, especially those with high glass transition temperatures ($T_g$) or melting points, to interact chemically or physically with the network while it is being irreversibly formed.

In spite of the extensive utilization of APTES as an adhesion promoter, the mechanism of the adhesion enhancement is not well understood. It was suggested that a stronger interaction between the polymer and APTES could exist. The sources of the stronger interaction are possible chemical interaction between $-\text{NH}_2$ and polymers,\textsuperscript{243,247} physical attractions between APTES and polymers,\textsuperscript{242,248,249,250} or simply the network structure of the APTES layers.\textsuperscript{241} As mentioned earlier, the network structure may allow for penetration of polymer chains and anchoring these chains to the network. If the 3-dimensional APTES network allows penetration and/or interlocking of polymer chains while it is being formed, this type of interaction can play a more predominant role in suppressing the dewetting of polymer thin films. Therefore, the main objective of this study is to qualitatively verify this hypothesis, thus providing insight into the process behind the dewetting suppression ability of amino-functional organosilanes.

To elucidate this possible dewetting suppression mechanism of APTES-derivatized surfaces, the dewetting of PS thin films from APTES surfaces and their
corresponding control surfaces was studied. The control surfaces were modified with a methyl-terminated organosilane with a low coverage to achieve a similar surface energy, a primary factor of controlling dewetting, as that of the APTES surfaces. PS with two different molecular weights ($M_n$) of 9.3k and 63k, one below and the other above its entanglement molecular weight (~ 19k),$^{251}$ was used. The degree of APTES curing or the crosslinking density of the APTES network was varied systematically by curing the APTES surfaces at different temperatures and/or for different curing times. The dewetting behavior, in terms of hole size and area density of the holes as well as the polymer residuals left on the hole floors, were carefully examined to verify the above hypothesis.

The dewetting process of a supported polymer thin film is generally initiated and governed by the thermodynamic equilibrium of intermolecular forces within the film and between the film and its underlying substrate.$^{228,252}$ When the intermolecular forces and rheological properties of the film for different polymer film-substrate systems are controlled, the dewetting behavior is expected to be similar for these systems. However, if any additional physical interactions (e.g. interpenetration, interdiffusion, or interlocking) between the polymer chains and the substrate surface exist, the dewetting phenomena can be retarded or inhibited. In the following section, the results of the surface characteristics and surface energy of the substrates will be reported first to show that they are not the contributing factors to the differences in dewetting behavior observed. Then, the thermodynamic considerations of the dewetting process of PS thin film on the substrates will be briefly discussed. After that, the dewetting of PS thin films
from APTES surfaces treated under various conditions will be presented. Finally, based on the dewetting phenomena, possible interfacial structures between the PS thin film and the APTES layer will be proposed.

4.3.2 Characterization of Control and Aminopropyltriethoxysilane-Modified Surfaces

To ensure a monolayer-like, reproducible, and stable APTES layer on Si/SiO$_x$, an anhydrous organic solvent, HPLC hexane, was used. Contact angles of deionized water and MI on the controls and APTES surfaces are summarized in Table 4.1, along with the estimated surface energies. The surfaces were characterized within 10 min after preparation due to the possibility that APTES surfaces could be contaminated by foreign impurities, leading to an alteration of their surface properties. In our case, small silicon debris were occasionally observed on the APTES surfaces after sonication, which could provide nucleation sites for the dewetting of PS thin films.

Both probe liquids showed high contact angle hysteresis (i.e. the difference between the advancing and receding contact angles), $H$, on the control and the APTES surfaces, indicating the surfaces could be molecularly rough and highly polar. The highly polar character of the APTES surface indicated that the APTES network formation was not complete, leaving many uncondensed hydroxyl or ethoxy groups of the molecules. The surface energy of the control was ~ 62 mJ/m$^2$, comparable to that of the APTES surface (~ 61 mJ/m$^2$). If the dewetting process were purely driven by intermolecular interactions within the system, it would be expected that the
Table 4.1  Averaged contact angle values and their hysteresis of deionized water and MI on Control and APTES surfaces and corresponding estimated surface energies.

<table>
<thead>
<tr>
<th>Probe liquid</th>
<th>Control</th>
<th>APTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI</td>
<td>W(^d)</td>
<td>MI</td>
</tr>
<tr>
<td>Contact angle (°) (hysteresis)</td>
<td>45 (13)</td>
<td>33 (20)</td>
</tr>
<tr>
<td>(\gamma) (mJ/m(^2))</td>
<td>(\gamma^d(^a))</td>
<td>(\gamma^p(^b))</td>
</tr>
<tr>
<td></td>
<td>24</td>
<td>38</td>
</tr>
</tbody>
</table>

\(^a\) dispersion component of surface energy  
\(^b\) polar component of surface energy  
\(^c\) total surface energy  
\(^d\) deionized water
dewetting process (or kinetics) for the two types of surfaces is similar, as explained in the following sub-section.

AFM scans showing representative topological features of the two substrates are presented in Figure 4.22. The control surface was relatively smooth with a root-mean-square (RMS) roughness of ~ 0.6 nm, and no visible islands were found (Figure 4.22a). Therefore, the surface energy of the control mainly originates from disordered individual OTS molecules and uncovered SiO\textsubscript{X} surfaces.\textsuperscript{238} For the APTES surface, occasional aggregates with various heights and lateral sizes were observed (Figure 4.22b).\textsuperscript{253,260} The measured film thickness, using ellipsometry, of the APTES layer was ~ 1.5 ± 0.23 nm, indicating more than one monolayer (monolayer thickness: ~ 0.7 nm) was formed.\textsuperscript{256} Figure 4.22c shows a cross-sectional profile (for the white line in Figure 4.22b) of the APTES surface including an aggregate. The aggregate was ~ 6 nm in height and ~ 130 nm laterally. The profile also demonstrated that the APTES surfaces were not molecularly smooth. Roughly, the heights of aggregates ranged from 2 to 9 nm, and their lateral dimensions were in the range of 20 – 300 nm. In spite of the existence of noticeable aggregates, the RMS roughness of the APTES surface was still only ~ 0.6 nm. This small substrate roughness cannot affect the dewetting behavior.\textsuperscript{261} Otherwise, the existence of those aggregates would tend to induce more unstableness to PS thin films on top of the APTES surface by reducing the local film thickness.\textsuperscript{74}
Figure 4.22  Topographical atomic force microscopy (AFM) images of (a) control surface, (b) APTES surface, and (c) a cross-sectional profile of the APTES surface corresponding to the white line in (b). The control surface was relatively smooth and uniform, while sparsely formed aggregates were observed on the APTES surface. The scan sizes were 2 μm × 2 μm, and z-scales were 20 nm.
4.3.3 Polystyrene Thin Film Instability

The instability of PS thin films on the control and APTES surfaces can be anticipated by calculating the disjoining pressure (\( \Pi \)) within the PS films.\textsuperscript{228,252} A negative value of \( \Pi \) indicates that the PS thin film is under attractive interactions, leading to film instability.\textsuperscript{229,262} When only the long-ranged van der Waals interactions are considered,\textsuperscript{228,229,252} the expression for \( \Pi \) is:

\[
\Pi = -\left( \frac{\partial \Delta G}{\partial \delta} \right) = -A_{132} / 6\pi\delta^3
\]  \[4.15\]

where \( \Delta G \) is the total excess free energy per unit area due to the intermolecular interactions, \( \delta \) is the film thickness, and \( A_{132} \) is the effective Hamaker constant (1: substrate, 2: medium, and 3: film), which can be related to dispersive surface energies (\( \gamma^d \)) of each component and simplified as:\textsuperscript{252}

\[
A_{132} \approx -24\pi d_0^2 \sqrt{\gamma_3^d} \left( \sqrt{\gamma_1^d} - \sqrt{\gamma_3^d} \right)
\]  \[4.16\]

where \( d_0 \) is the minimum cut-off equilibrium distance between surfaces (\( \approx 0.158 \) nm), \( \gamma_3^d \) is \( \gamma^d \) PS melt at the annealing temperature, and \( \gamma_1^d \) is the dispersion component of substrate surface energy.\textsuperscript{229,252} The estimated total surface energies of PS melts (\( \gamma_3 \)) are \(~35\) mJ/m\(^2\) and 37 mJ/m\(^2\) for PS-9.3k at 135 °C and PS-63k at 170 °C, respectively.\textsuperscript{251} \( \gamma_3^d \) for both PS melts are assumed to be 99% of the estimated \( \gamma_3 \).\textsuperscript{263} \( \Pi \)s of each system with the estimated \( \gamma_3^d \) and experimentally measured \( \gamma_1^d \) are calculated. The values of \( \Pi \) for the four combinations (two PS and two substrates) are all negative (-3 to -4 N/m\(^2\)), indicating unstable PS films. When considering errors (\( \pm 1\) mJ/m\(^2\)) in the measured \( \gamma_1^d \) and
uncertainty of the predicted $\gamma_3$, the difference between these $\Pi$ values ($\pm 0.5 \text{ N/m}^2$) is likely insignificant.

Once the film is ruptured and dewetting holes are formed, the holes grow laterally driven by the capillary force (i.e. spreading coefficient, $S$), which is originated from a balance between the interfacial energies at the three-phase contact line.\textsuperscript{229} Since only dispersive interactions are predominant, $S$ can be simplified as $S^d$.\textsuperscript{252}

\[ S = S^d = -\frac{A_{32}}{12\pi d_0^2} \]  \hspace{1cm} [4.17]

Averaged $S^d$ values for the four systems studied are -12 mJ/m$^2$. The deviation of $S$ values ($\pm 1.9 \text{ mJ/m}^2$) lies within the uncertainty of the estimated $\gamma_3$. Therefore, instability of the PS films or their dewetting behaviors would not deviate much among the combinations if the dewetting process were solely governed by $\Pi$ or $S$. However, the results, presented in the next four sub-sections, clearly demonstrate that factors other than $\Pi$ and $S$ play important roles in the dewetting behaviors of the PS thin films on the APTES surfaces.

4.3.4 80 °C Curing (Condition 1)

As mentioned earlier, the curing of the APTES layer after the deposition of APTES onto a substrate could provide an opportunity for the APTES network to interlock with PS chains. It could lead to various dewetting suppression of the PS thin films on the APTES surface upon annealing. Figure 4.23 represents optical microscopic images of dewetting holes for PS-9.3k and PS-63k formed on the control and APTES
The samples were cured inside a vacuum oven at 80 °C for 20 h prior to the annealing process. 80 °C was chosen to ensure that no dewetting of PS films occurred during the curing process (i.e. below the T_g of PS). In addition, when treated at 80 °C for 20 h, a certain degree of crosslinking of the APTES layer could be achieved. This was verified by a decrease in the surface energy of cured APTES layer. $\gamma_S$ of APTES decreased to a value of $\sim 41$ mJ/m$^2$ with $\gamma_1^p$ (polar component of surface energy) of $\sim 10$ mJ/m$^2$ and $\gamma_1^d$ of $\sim 31$ mJ/m$^2$. Thermal treatments condensed unreacted ethoxy and/or hydroxyl groups of APTES molecules into siloxane bonds, resulting in the decrease of $\gamma_1^p$. As a result, aminopropyl groups that initially interacted with the unreacted hydroxyl groups or hydroxyl groups from SiO$_X$ substrate via hydrogen bonding were released, exposing them to the surrounding and contributing to the increase in $\gamma_1^d$.

In addition to controlling $\Pi$ and $S$, to possibly eliminate viscosity effects on the dewetting process, the samples with PS-9.3k were annealed at 135 °C ($\eta \approx 3.5 \times 10^3$ Pa-s), while those with PS-63k were annealed at 170 °C ($\eta \approx 3.5 \times 10^3$ Pa-s), inside a vacuum oven. Under these constraints, the degrees or rates of dewetting process of both PS on the control and the APTES surfaces were expected to be similar. For reference, both OTS and APTES molecules, reacted with the substrates, are thermally stable at the annealing temperatures. However, the dewetting holes on the APTES surfaces (Figures 4.23c and 4.23d) were remarkably smaller than those on the controls (Figures 4.23a and 4.23b). The dewetting of PS-63k film on the APTES surface (PS-
Figure 4.23 Optical microscopy images of dewetting holes formed in PS thin films (9.3k and 63k) on control and APTES surfaces. The samples were cured inside a vacuum oven at 80°C for 20 h prior to the annealing process. (a) PS-9.3k and (b) PS-63k film on the control surfaces; (c) PS-9.3k and (d) PS-63k film on the APTES surfaces. The dewetting process of PS thin film on the APTES surfaces was remarkably suppressed, in terms of the dewetting hole size, as compared to that for the control surfaces. PS-63k on APTES surface showed almost no dewetting behaviors. The scale bar was 100 μm.
63k/APTES, Figure 4.23d) was almost unnoticeable—small holes with a diameter \( (D) \) of \(~5 \mu m\) were occasionally observed, and tiny holes \( (D \leq 1 \mu m) \) were also observed throughout the film. For the PS-9.3k film on the APTES surface (PS-9.3k/APTES, Figure 4.23c), a number of dewetting holes with detectable sizes \( (D \text{ varied from } 5 \mu m \text{ to } 30 \mu m) \) were found. However, compared to the PS-9.3k film on the control surface, PS-9.3k/APTES still exhibited a certain degree of suppression with smaller and less numbers of dewetting holes and inhomogeneous hole distribution.\(^{266}\) As pointed out earlier, the silicon debris or impurities on the APTES surfaces could initiate the dewetting at different times, resulting in different sizes and inhomogeneous spatial distribution of the dewetting holes. To clarify, the tiny black dots observed in the undewetted PS films were not the early stage of dewetting holes.\(^{267}\) Topographic AFM scans revealed that those were embossed bumps. Topographic and phase AFM images revealed that those were bumps of foreign impurities with a lateral size < 1 \( \mu m \) (not shown). Likely, the capillary rise of PS melts around the impurities caused them to appear larger than their actual sizes.

Contrary to the dewetting behaviors on the APTES surfaces, on the control surfaces, more progressed dewetting was observed for PS-63k film (PS-63k/control, \( 90 < D < 120 \mu m \) measured from isolated circular holes, Figure 4.23b) as compared to that of PS-9.3k film (PS-9.3k/control, \( D \approx 44 \pm 2 \mu m \), Figure 4.23a). The difference in the hole sizes between PS-63k and PS-9.3k could be mainly due to the slight difference in the estimated \( \gamma_3 \) between them. The higher value of \( \gamma_3 \) for PS-63k resulted in a larger \( S \) value, i.e. increased driving force. Another possibility would be the molecular weight effect on
the dewetting process. Higher dewetting rates were observed for polymers having higher molecular weights.\textsuperscript{268} Interfacial slippage could happen for PS-63k during dewetting,\textsuperscript{269} which enhanced the hole growth, leading to larger holes.

Figure 4.24 represents AFM images of dewetting holes and their cross-sectional profiles through the center of the dewetting holes for PS-63k/control (Figures 4.24a and 4.24b) and PS-63k/APTES (Figures 4.24c and 4.24d). For most dewetting holes on the control surface (Figure 4.24a), no nuclei that initiated the dewetting were found (Figure 4.24b). Some nuclei that were intermittently found were only < 5 nm in height. It indicated that the PS films on the control surface were originally unstable and also very sensitive to any impurities within the system. However, all the dewetting holes (Figure 4.24c) scanned from the PS/APTES cases had large nuclei on the hole floors (Figure 4.24d). Particularly for PS-63k (Figure 4.24d), the heights of all the nuclei were over the initial PS film thickness. This indicated that the PS-63k film on the APTES surface was metastable or nearly stable; therefore, only nuclei, whose sizes were comparable to or greater than the initial PS film thickness, that already disrupted the continuity of the film could barely “initiate” the dewetting.\textsuperscript{267} Opposite to the contribution of molecular weights of PS to the dewetting for the control surfaces, the entangled PS-63k films on the APTES surface demonstrated more dewetting suppression (i.e. smaller holes, Figure 4.24d). The entanglement of PS-63k chains could introduce an additional stabilizing effect for the PS film on the complex APTES network, resulting in more effective dewetting suppression, even against foreign impurities. Due to the absence of chain
Figure 4.24 Topographical AFM images of dewetting holes and their cross-sectional profiles through the center of the dewetting holes for PS-63k on control (a and b) and APTES (c and d) surfaces, respectively. The samples were cured inside a vacuum oven at 80°C for 20 h prior to the annealing process. On the APTES surface, dewetting was nucleated by large impurities (size greater than the initial PS film thickness) that became the nuclei of the hole. On the contrary, dewetting holes on the control surface appeared to be spontaneously initiated, and the hole floors were almost as clean as the initial control surface. The scan sizes were 70 μm × 70 μm for (a) and 30 μm × 30 μm for (c). The z-scales were 500 nm and 200 nm for (a) and (c), respectively.
entanglement, dewetting suppression of the PS-9.3k film would be less effective in response to foreign impurities (Figure 4.24c).

One strong piece of evidence of possible penetration/interlocking between the PS chains and the crosslinked APTES network could be the presence of PS residuals on the hole floors. AFM scans on the hole floors were performed to identify any residuals of PS (Figure 4.25). PS residuals were sparsely detected on the hole floors for the controls (Figures 4.25a – 4.25d), but the value of RMS roughness of the hole floors (~ 0.6 nm) was the same as that of the initial control surfaces. It verified that the amounts of PS residuals left behind were insignificant. To avoid scanning large nuclei on the hole floors for the APTES surfaces, the scanning was performed near the rim of the dewetting holes. For PS-9.3k/APTES, with a z-scale of 20 nm, it was hard to detect any residuals in the topographic image (Figure 4.25e); however, the phase image showed that the hole floor appeared to be covered with irregular ultrathin PS patches (Figure 4.25f). The RMS roughness value obtained from the hole floor slightly increased to ~ 0.7 nm (Figures 4.25e and 4.25f). In addition, it seemed that the PS-9.3k chains left behind were loosely interlocked with the APTES networks. The loosely adsorbed PS chains could contaminate the AFM tips and interfere with the AFM scanning, resulting in AFM artifacts in some of the AFM images, which contained occasional intense and featureless lines, i.e. “streaking”.270 A slight penetration/interlocking between the PS-9.3k film and the APTES network could suppress the dewetting to some extent, but the lack of entanglement between the penetrated PS-9.3k chains and the bulk chains was incapable of preventing the dewetting completely. For PS-63k/APTES, close-packed “bumps” with
Figure 4.25  Topographical AFM (left column) and corresponding phase (right column) images of dewetting hole floors of PS-9.3k/control (a and b), PS-63k/control (c and d), PS-9.3k/APTES (e and f), and PS-63k/APTES (g and h). The samples were cured inside a vacuum oven at 80°C for 20 h prior to the annealing process. Few bumpy PS residuals were sparsely left behind on the control surfaces (a and c). For the APTES surfaces (e and g), PS residuals were irregularly left behind on the floor, easier to be seen from the phase images (f and h). Less PS residuals were left behind on the floor of PS-9.3k/APTES (f) than those for PS-63k/APTES (h). The scan size was 2 μm × 2 μm. The z-scale was 20 nm.
heights of 3 – 4 nm were observed on the hole floors (Figure 4.25g and 4.25h), and
several larger bumps with a height of ~ 10 nm were also found. The RMS roughness
value of the hole floor increased to ~ 0.9 nm. Since no primary chemical bonding
between PS and APTES was possible,\textsuperscript{242} the most likely cause for such a strong adhesion
to retain PS on the substrate was the penetration/interlocking between PS chains and 3-
dimensional APTES network,\textsuperscript{243,244,248,250,271,272} which terminated the growth of dewetting
holes at very early stage of dewetting.

4.3.5 Room Temperature Curing (Condition 2)

A different degree of penetration/interlocking between PS and the APTES layer
was introduced to evaluate its effect on dewetting suppression. To reduce the possible
penetration/interlocking, another set of samples of PS/APTES and PS/control were cured
inside a vacuum oven at room temperature for 20 h, prior to the annealing process.
Generally, the degree of crosslinking of APTES network is increased by curing at a
higher temperature or a longer time.\textsuperscript{244,256,259,264} Curing at an evaluated temperature
increases the siloxane linkage among APTES molecules and between APTES molecules
and surface hydroxyl groups, while treating at room temperature leaves a certain amount
of unreacted ethoxy and/or hydroxyl groups and a loose APTES network.\textsuperscript{259}

Optical microscopic images of dewetting holes formed on the control and the
APTES surfaces are presented in Figure 4.26. The sizes of the holes for the control
surfaces (Figures 4.26a and 4.26b) were comparable to those (Figures 4.23a and 4.23b)
Figure 4.26 Optical microscopy images of dewetting holes formed in PS thin films (9.3k and 63k) on control and APTES surfaces when the samples were cured inside vacuum oven at room temperature for 20 h prior to the annealing process. (a) PS-9.3k and (b) PS-63k film on control surface; (c) PS-9.3k and (d) PS-63k film on APTES surface. The dewetting behaviors of both PS thin films on APTES surfaces were comparable to their corresponding controls. The scale bar was 100 μm.
from condition 1, with \( D \) of 43 ± 3 \( \mu \)m and 100 \( \mu \)m – 130 \( \mu \)m for PS-9.3k and PS-63k films, respectively. This indicated that \( \Pi \) or \( S \) between the PS thin films and the control surfaces and physical or mechanical properties of the PS thin films related to dewetting phenomenon under this curing condition were not altered from those under condition 1.\(^{261,273}\) For PS-9.3k/APTES and PS-63k/APTES (Figure 4.26c and 4.26d), the holes were 46 ± 2 \( \mu \)m and 90 \( \mu \)m – 110 \( \mu \)m in \( D \), respectively, similar to those for the control surfaces. No discernible PS residuals on the hole floor of the PS/APTES systems were observed in the topographic AFM images (not presented). This clearly indicated that, without thermal curing, no dewetting suppression for the PS/APTES systems occurred, and the dewetting behaviors were only dependent on the intermolecular interactions and physical properties of the PS films.

4.3.6 Time- and Temperature-Dependent Curing

Thermal treatment for the PS/APTES systems could result in two major effects on the systems: the degree of curing (i.e. Si-O-Si linkage) of the APTES network and the mobility of the PS chains. In the case of curing APTES at 80 °C, the formation of siloxane bonds among the APTES molecules could be promoted,\(^{244,256,259,264}\) and more covalent bonds between the APTES network and the substrate could form.\(^{256}\) An increased mobility of PS chains at near \( T_g \) (~ 100 °C) could also assist the penetration of the PS chains into the APTES network. Therefore, more effective suppression or inhibition of PS thin film dewetting could result.
To evaluate how the thermal curing process suppressed the dewetting of PS thin films, PS-63k/APTES was cured at 80 °C for different time periods prior to the annealing. Figure 4.27 shows curing time-dependent dewetting suppression, in terms of $D$ (Figure 4.27a) and the number density of the dewetting holes ($N$, Figure 4.27b). With 0.5 h of curing, both $D$ and $N$ of the holes formed after the annealing decreased dramatically from $\sim 90 \mu m$ and $\sim 32 /mm^2$ (no curing) to $\sim 70 \mu m$ and $\sim 17 /mm^2$, respectively. With 1 h of curing, $D$ and $N$ further reduced, respectively, to $\sim 60 \mu m$ and $\sim 7 /mm^2$. With 5 h of curing, dewetting became similar to that of the samples with 20 h of curing, with only small holes ($D \sim 5 \mu m$, $N < 1 \sim 2/mm^2$) sporadically appearing in the film. Considering the fact that $N$ in “spontaneous dewetting” is governed by the thermodynamic equilibrium of the system, our results suggest that thermal curing shifts the equilibrium of the system towards a more stable state.

It was surprising that the penetration/interlocking between the PS chains and the APTES network occurred so rapidly at 80 °C, since the APTES molecules are not fully crosslinked at this temperature and bulk mobility of the PS chains is believed to be still minimal. Therefore, to ensure the sufficient mobility of the PS chains, another set of experiments for PS-63k/APTES was performed by curing at 120 °C for various times. Both $D$ and $N$ decreased more rapidly as compared with those cured at 80 °C. With only 15 min of curing at 120 °C, the holes were already smaller than those for the samples cured at 80 °C for 2 h. Comparing 2 h of curing, $D$ for the curing at 120 °C was only 10% of that for the curing at 80 °C. With 10 h of curing at 120 °C, no holes were found
Figure 4.27  The variation of the dewetting hole diameter ($D$, (a)) and the hole area density ($N$, (b)) as a function of curing times for PS-63k/APTES. The samples were cured inside a vacuum oven at 80°C (□) or 120°C (●) for different amount of times prior to the annealing process. For the curing time of 0 h, the data of $D$ and $N$ were obtained from the samples that were cured inside a vacuum oven at room temperature for 20 h. As the samples were cured for longer times, both $D$ and $N$ were decreased, indicating more effective dewetting suppression or inhibition was achieved. When the samples were cured at 120°C, compared with those cured at 80°C, dewetting was suppressed more rapidly. The error bars represent the standard deviation. The solid and dotted lines are the guide for the eyes.
while small holes were sparsely observed for the curing at 80 °C for 20 h. At 120 °C, the increased mobility of the PS chains and the accelerated crosslinking of APTES network\textsuperscript{244,256,259} seemed to be responsible for the rapid and effective dewetting suppression. Our results indirectly implied that even at 80 °C, the PS chains at and near the interface had enough mobility to achieve the penetrations/interlocking with the APTES network.

To identify the thermal curing effect on the APTES layer itself, $\gamma_S$ of the APTES layers cured under different temperatures for various durations was also estimated using contact angle measurements. Since contact angle measurements are surface-sensitive, any phase change of the APTES surface by the thermal curing can be roughly probed, which is critical in dewetting suppression by the modification of polymer-substrate interface. Figure 4.28a represents advancing ($\theta_a$) and receding ($\theta_r$) contact angles of deionized water and MI measured from the APTES layer cured at 80 °C for various duration. As the curing time ($t$) increased, $\theta_a$ of deionized water markedly increased to a value of $\sim 72^\circ$ from $\sim 47^\circ$ (the freshly prepared APTES) in 0.5 h, and then increased at a slower rate and leveled off in $\sim 3$ h. High $\theta$ of water ($84^\circ \sim 95^\circ$) for thermally cured APTES layers was also reported recently.\textsuperscript{274} Although $\theta_r$ of deionized water increased with the curing duration as well, it only gradually increased to $\sim 50^\circ$ in 5 h of the thermal curing and slowly leveled off at $\sim 59^\circ$ by the end of curing ($\sim 20$ h). It resulted in a large $H$ between 0 h and 5 h with a peak value of $\sim 46^\circ$ at 1 h. The increase of $\theta_a$ and $\theta_r$ of deionized water with the curing duration indirectly verified the further condensation of
unreacted ethoxy and/or hydroxyl groups of APTES molecules into siloxane bonds. \(^{244,256,259,264}\) \(\theta_a\), “hydrophobicity-sensitive”, \([52-56]\) rapidly increased in response to the removal of those hydrophilic groups; whereas, \(\theta_r\), “hydrophilicity-sensitive”, \([52-56]\) only increased slowly likely due to the hydrophilic interaction between water molecules and the uncondensed ethoxy and/or hydroxyl groups. \(^{275,276,277,278,279}\) The trend of \(H\), steeply increasing at first, then decreasing, and finally maintaining at a constant, corresponded to the history of the heterogeneity.

\(\theta_a\) and \(\theta_r\) of MI were not changed significantly with the curing duration, except a slight “dip” between 0 h and 5 h. Since nonpolar MI is insensitive to the variation of the hydrophilic components, it was somewhat expected that \(\theta_a\) and \(\theta_r\) of MI would not vary considerably, and neither did its \(H\). The slight dip of \(\theta_a\) and \(\theta_r\) and the fluctuation in \(H\) between 0 h and 5 h could be simply due to the increase of molecular roughness\(^{280,281}\) by molecular rearrangement during the condensation of unreacted ethoxy and/or hydroxyl groups and the release of aminopropyl chains.\(^{244,256,259}\) During the first hours (< 5 h), the active molecular reorientation of the APTES layer could facilitate molecular penetration/interlocking between the PS chains and the APTES layer, supported by the drop of \(D\) and \(N\) during the hours (Figures 4.27a and 4.27b).

Time-dependent thermal curing of the APTES layer was also performed at 120 °C. \(\theta_a\) of water increased to \(\sim 77^\circ\) within 0.25 h and continued to increase gradually to \(\sim 83^\circ\) in 20 h. Different from the curing at 80 °C, \(\theta_r\) of deionized water quickly increased to ~
Figure 4.28 The variation of advancing ($\theta_a$, diamond symbols) and receding ($\theta_r$, triangle symbols) contact angles for deionized water (filled symbols) and MI (open symbols), (a), and $\gamma$ components ($\gamma^d$: ●, $\gamma^r$: ○, and $\gamma_S$: ■), (b), of APTES layers cured at 80°C for various curing duration ($t$, h). In addition, the transition of $\gamma_S$ of APTES layer cured at 120°C was denoted as □ in (b). The significant increase in $\theta_a$ and $\theta_r$ of water (a) and corresponding decrease in $\gamma^d$ (b) indicated further condensation of unreacted ethoxy and/or hydroxyl groups as the curing continued. Relatively, no variation in $\theta_a$ and $\theta_r$ of MI was observed, and $\gamma^d$ increased slightly, indicating more exposure of the released aminopropyl groups from hydrogen-bondings with those previously unreacted head groups. As a result, $\gamma_S$ also decreased as $t$ increased. At a higher curing temperature of 120°C, $\gamma_S$ decreased more rapidly due to a faster condensation rate. The error bars represent the standard deviation. $\gamma$ components in (b) were estimated by using the averaged values of each probe liquids. The solid and dotted lines are the guide for the eyes.
50° within 1 h and then gradually increased and leveled off at ~ 62° at the end of 20 h of curing. As a result, $H$ increased to a peak value of ~ 46° within 0.25 h, rapidly decreased to the initial value of ~ 25° at 1 h, and then gradually leveled off at ~ 21° until 20 h. $\theta_n$ and $\theta_i$ of MI demonstrated a similar trend as those shown in Figure 4.28a with an overall $2^\circ \sim 3^\circ$ lower in the $H$ values. An earlier stabilization (< 2 h) of the fluctuation in $H$ was noticed, which seemed to indicate a faster molecular rearrangement of aminopropyl groups by faster condensation of unreacted ethoxy and/or hydroxyl groups at the higher curing temperature.

$\gamma_d$ and $\gamma_p$ of the cured APTES layers were estimated based on the contact angles of DI water and MI measured from them (Figure 4.28b). $\gamma_d$ increased from ~ 26 mJ/m$^2$ to ~ 31 mJ/m$^2$ with ~ 1 h of curing and remained at the value until 20 h. $\gamma_p$ noticeably dropped from ~ 35 mJ/m$^2$ to ~ 23 mJ/m$^2$ with 0.5 h of curing, and then slowly reached a value of ~ 10 mJ/m$^2$ in 20 h of curing. The decrease of $\gamma_p$ demonstrated the disappearance of unreacted ethoxy and/or hydroxyl groups, which are highly polar, through the condensation. The slight increase of $\gamma_d$ implied that more released aminopropyl groups (from hydrogen-bonding) were exposed to the surrounding, since aminopropyl groups have relatively higher dispersion component than that of the head groups (i.e. ethoxy and/or hydroxyl) and the siloxane back bone linkage. Due to the slight increase of $\gamma_d$ throughout the curing duration, the variation of $\gamma_S$ was predominated by the marked decrease of $\gamma_p$. $\gamma_S$ decreased and reached a value of ~ 41 mJ/m$^2$ after 20 h of curing. The variation of $\gamma$ components for the APTES layers cured at 120 °C was quite
similar to that for those cured at 80 °C, except that $\gamma_S$ dropped more rapidly (Figure 4.28b) due to a faster reduction of $\gamma^p$ in shorter curing times. The rapid reduction resulted from the faster condensation of unreacted ethoxy and/or hydroxyl groups of the APTES molecules at the higher curing temperature.

The variations of contact angles and $\gamma$ components as a function of curing temperature ($T$) were represented in Figures 4.29a and 4.29b, respectively. The values were obtained from the APTES layers cured at a particular temperature for 20 h. Both $\theta_a$ and $\theta_r$ of water (Figure 4.29a) markedly increased from 47° and 22° to 81° and 59°, respectively, from 25 °C to 80 °C, and then slowly increased with temperature and reached 86° and 62°, respectively, at 200 °C. $H$ of water seemed to remain constant. Higher $\theta_a$ and $\theta_r$ of water at higher curing temperatures indicated more unreacted ethoxy and/or hydroxyl groups were condensed at higher curing temperatures. No significant variation in $\theta_a$ and $\theta_r$ of MI was observed while $H$ of MI seemed to decrease slightly as $T$ increased. More stabilized rearrangement of aminopropyl groups from further condensation of those unreacted groups, i.e. a formation of relatively more uniform and smooth surface structure, could be responsible for the slight decrease in $H$.

The variation of $\gamma$ components with $T$ (Figure 4.29b) exhibited a similar trend as that with $t$ in time-dependent thermal curing (Figure 4.28b)–an increase of $\gamma^d$ and a decrease of $\gamma^p$ with the increase of $T$. Those unreacted head groups condensed more at
Figure 4.29 The transition of advancing ($\theta_a$, diamond symbols) and receding ($\theta_r$, triangle symbols) contact angles for deionized water (filled symbols) and MI (open symbols), (a), and $\gamma$ components ($\gamma^d$: $\bullet$, $\gamma^p$: $\bigcirc$, and $\gamma_S$: $\blacksquare$), (b), of APTES layers cured at various curing temperatures ($T$, °C). The APTES layers were cured at the temperatures for 20 h. With the thermal curing, $\theta_a$ and $\theta_r$ of water increased and leveled off while $\theta_a$ and $\theta_r$ of MI were not altered significantly (a). The slight increase in $\theta_a$ and $\theta_r$ of water and decrease of $\gamma^p$ between 80°C and 200°C indicated a little more removal of unreacted ethoxy and/or hydroxyl groups at higher temperatures. Due to the distinct drop of $\gamma^p$ with the thermal curing, $\gamma_S$ markedly dropped initially between room temperature (25°C) and 80°C and then leveled off for the higher temperatures. The error bars represent the standard deviation. $\gamma$ components in (b) were estimated by using the averaged values of each probe liquids. The solid and dotted lines are the guide for the eyes.
higher temperatures\textsuperscript{244,259} and the aminopropyl groups that were bounded to them via hydrogen-bonding were released and exposed to the surrounding. The slight increase of $\gamma^d$ and the slight decrease of $\gamma^p$ between 80 °C and 200 °C cancelled out each other, thus $\gamma_S$ remained constant.

4.3.7 Precuring of Aminopropyltriethoxysilane Layer prior to Depositing Polystyrene Films

To further clarify that the dewetting suppression for PS/APTES systems was the result of penetration/interlocking between the PS chains and the APTES network formed during the thermal treatment, the APTES layer was precured at 200 °C for 20 h. After the deposition of PS films, the samples were dried and cured as in condition 1. The precuring temperature of 200 °C was chosen to ascertain that there was a maximum crosslinking of the APTES network.\textsuperscript{259} $\gamma_1^d$ and $\gamma_1^p$ of the precured APTES layer at 200 °C were ~ 33 mJ/m\textsuperscript{2} and ~ 7 mJ/m\textsuperscript{2}, respectively. The lower $\gamma_1^p$, as compared with that for the cured APTES layer at 80 °C, indicated more polar hydroxyl and/or ethoxy groups from APTES molecules condensed to form siloxane bonds.

Using $\gamma_1^d = 33$ mJ/m\textsuperscript{2}, $\Pi$ and $S$ values were calculated to be about -1 N/m\textsuperscript{2} and -3 mJ/m\textsuperscript{2} in average, respectively. These smaller values compared with those for the uncured APTES layer (section 4.3.3) indicated that the dewetting of the PS films would be more retarded or suppressed than that observed for condition 1 if such suppression were solely governed by the repulsive intermolecular interactions, i.e. equilibrium
Figure 4.30 Optical microscopy images of dewetting holes formed in (a) PS-9.3k and (c) PS-63k thin films on the precured APTES surfaces with their corresponding topological AFM images obtained from the hole floors, (b) and (d), respectively. The APTES layer was precured inside a vacuum oven at 200°C for 20 h, and then the PS thin films were spin-coated onto the precured APTES surfaces. The samples were dried under ambient conditions for 20 h and then inside a vacuum oven at 80°C for 20 h prior to the annealing process. No dewetting suppression for both PS thin films was noticed with little PS residuals on the hole floors.
In addition, precuring could allow aminopropyl chains to switch from their original “cyclic structure” to “extended open-chain structure”. The extended aminopropyl chains could also penetrate into the PS matrix above (i.e. “compatibility/penetration”), leading to an enhanced suppression. However, our results as shown in Figure 4.30, with both $D$ and $N$ of the dewetting holes, clearly illustrated that there was almost no suppression in dewetting. The results indicated that a fully crosslinked APTES network might not allow a sufficient penetration of PS chains during the later thermal treatment (at 80 °C for 20 h) to suppress dewetting. In other words, the dewetting suppression on the APTES layer is more dominated by conformational penetrations at the interface than by the equilibrium thermodynamics.

Different from $\gamma_3$, chain entanglement, and possible slip effects on the dewetting behaviors for the PS-63k/control system, smaller dewetting holes were observed for PS-63k/procured APTES (Figure 4.30c), compared with those for PS-9.3k (Figure 4.30a). This suggested that a minimum penetration/interlocking between the entangled PS-63k chains and the network could still be possible and slightly retard the dewetting process, which was verified by PS residuals shown as small bumps on the hole floors (Figure 4.30d). However, the hole floor for PS-9.3k was relatively clean (Figure 4.30b), indicating no interlocking between the PS chains and the APTES network.
4.3.8 Overview of Polystyrene/Aminopropyltriethoxysilane Interfacial Structure

Hypothetical structures of the PS/APTES interface depending on different curing or precuring conditions are depicted in Figure 4.31, with an emphasis on the entangled PS-63k chains. When a sample of PS/APTES is cured at room temperature (Figure 4.31a), a low degree of crosslinking between APTES molecules is expected, and those amine groups are bound towards the substrate due to hydrogen bonding with the hydroxyl groups from the SiO$_X$ substrate or unreacted hydroxyl groups of the APTES molecules. Since the PS chains have little mobility at room temperature, they remain flat and oriented parallel, entropically unfavorable, to the interface as the conformation that they are forced to adopt by spin-casting. During annealing, the PS film is dewetted solely driven by the intermolecular interactions within the system, and the dewetting dynamics became similar to that of the PS/control.

When the APTES layer is thermally cured at 80 °C or 120 °C (Figure 4.31b), those unreacted hydroxyl groups of the APTES molecules react with hydroxyl groups of the SiO$_X$ substrate or unreacted hydroxyl groups from neighboring APTES molecules to form siloxane linkages. Amine groups initially hydrogen bonded to these hydroxyl groups are set free, resulting in the extension of aminopropyl chains. A possible affinity between amine and PS could drive those free aminopropyl chains to penetrate into the PS matrix adjacent to them. Concurrently, the confined PS chains at the interface, due to the spin coating process, become mobile during the thermal curing.
near or over $T_g$ of PS. Those mobile PS chains at the interface penetrate into the APTES layer, driven by entropic contributions and enthalpic effects.\textsuperscript{285,286} Likely, the APTES molecules crosslinked each other over the penetrated PS chains. As a result, the interface between the PS thin film and the APTES network becomes a 3-dimensional interdiffused phase. For the PS thin film to dewet from the APTES network, the possibilities are that the penetrated PS chains should be pulled all the way out of the tightly crosslinked APTES network, the PS chains in the upper layers should be disentangled from the penetrated chains, or chain scissions of the penetrated PS chains should occur. Since all three processes are energetically or entropically unfavored, the dewetting is inhibited or at least retarded. This is especially conceivable for PS-63k, whose chains are longer than the entanglement length.\textsuperscript{251} In some cases, both chain ends of PS-63k chains penetrate into the APTES network, leaving the remaining portion to form “loops” that could entangle with bulk PS chains.\textsuperscript{286} Less dewetting suppression with PS-9.3k films (Figure 4.23c) could be explained by the lack of entanglements between the penetrated and bulk PS chains.

When the APTES layer is precured at 200 °C (Figure 4.31c), a maximum crosslinking of the APTES molecules could be achieved.\textsuperscript{259} During the later thermal treatment at 80 °C, the free aminopropyl chains could diffuse or penetrate into the PS matrix; however, the PS chains cannot easily penetrate into the APTES network due to the tight Si-O-Si linkages. Consequently, the PS film is dewetted from the new surface of the siloxane linkages. The interface could be slightly widened by the penetration of the extended aminopropyl chains into the PS film. Therefore, slight dewetting retardation
of the unreacted hydroxyl groups, penetrated into the PS matrix. In (c), during the later precuring step, the APTES molecules diffused into the APTES network while extending aminopropyl precuring step. Dotted lines represent extended siloxane linkage in the 3-dimensional space.

Figure 4.31 Hypothetical interface/interphase structures of PS-63k/APTES under various curing or precuring conditions used in our study: (a) cured at room temperature, (b) cured at 80°C or 120°C, and (c) precured at 200°C, followed by additional thermal treatment at 80°C with PS thin film on top of the cured APTES network. In (a), the APTES layer was minimally crosslinked while amine groups were bound with unreacted hydroxyl groups via hydrogen bonding. PS chains were not able to penetrate into the APTES layer. In (b), PS chains, gaining enough mobility due to the high processing temperature to crosslink the APTES molecules, diffused into the APTES network while extended aminopropyl groups, freed from the hydroxyl groups in virtue of more formation of Si-O-Si linkages of the unreacted hydroxyl groups, penetrated into the PS matrix. In (c), during the later thermal treatment, PS chains were able to diffuse down into the APTES network, however, only down to the top of the highly crosslinked Si-O-Si bonds formed during the precuring step. Dotted lines represent extended siloxane linkage in the 3-dimensional space.
for the entangled PS-63k film (Figure 4.30c), when compared with the PS-63k/APTES cured at room temperature (Figure 4.26d), was achieved.

4.3.9 Effects of Other Factors on Dewetting Suppression of Aminopropyltriethoxysilane-Modified Surfaces

In addition to the effects of thermal curing of the APTES layers on the dewetting behaviors of the PS thin films, other factors that might affect the dewetting behaviors were studied. These factors include water contents in the APTES layer, film thickness of the APTES layer, and qualities of APTES layer.

First, the effect of water contents in the APTES layer on the dewetting suppression was examined with or without vacuum. After the deposition of the PS films on the control and APTES surfaces, the samples were either not cured or cured only at room temperature without vacuum (i.e. ambient conditions) for 20 h, prior to the annealing process. Figure 4.32 presents optical microscopic images taken from the samples after the annealing process. The dewetting behaviors, in terms of $D$, of PS-9.3k and PS-63k on the control surfaces (Figures 4.32a and 4.32b) were similar to the previous results (Figures 4.23a and 4.26a, and Figures 4.23b and 4.26b, respectively). This again indicated that the absence of the curing step or vacuum (after the drying at ambient conditions for 20 h) did not alter the characteristic of the control surface and the physical properties of PS. However, for PS-9.3k and PS-63k/APTES cases (Figures 4.32c – 4.32f), the dewetting behaviors were intermediate between those of the samples cured
inside a vacuum oven at room temperature (Figures 4.26c and 4.26d) and those of the samples cured inside a vacuum oven at 80 °C (Figures 4.23c and 4.23d).

As mentioned above, since no physical alteration happened for the PS films themselves, the absence of vacuum must have affected the properties of the APTES surface or the interface of PS/APTES. Likely, without vacuum, surface water layer would still exist on the APTES surface or be trapped at the interface until the annealing process. It seemed that water contents caused the dewetting to be suppressed during the annealing process, prior to the initiation of the dewetting of the PS films. Otherwise, the dewetting behaviors of the samples not cured should also be the same as those of the samples cured inside a vacuum oven at room temperature (Figures 4.26a and 4.26b), since the residence time of surface water at the PS/APTES interface for the samples was basically the same (i.e. during the drying step at ambient conditions for 20 h). No significant difference in $D$ between the samples that were not cured (Figures 4.32c and 4.32d) and those with the curing at room temperature without vacuum for 20 h (Figures 4.32e and 4.32f) might also support the hypothesis that actual suppression process happened during the annealing. In addition, apparent distinction of dewetting behaviors between the samples cured at room temperature without vacuum (Figures 4.32e and 4.32f) and those cured at room temperature with vacuum (Figures 4.26a and 4.26b) undoubtedly ruled out any possibility of a curing time effect (prior to the annealing) on the dewetting suppression. Since a critical factor that can be related to the vacuuming and the properties of the APTES layer is water, possibly, the presence of water contents at the interface at the moment of the annealing process could promote additional
Figure 4.32  Optical microscopy images of dewetting holes formed in PS thin films with a $M_n$ of 9.3k (left column) and 63k (right column) on the control (a and b) and APTES surfaces (c – d) when the samples were not cured prior to the annealing process. In another set of experiments, samples were cured at room temperature without vacuum (i.e. ambient conditions) for 20 h, prior to the annealing process: (e) PS-9.3k and (f) PS-63k film on APTES surface The dewetting behaviors of both PS thin films on the control surfaces were comparable to those cured inside a vacuum oven at room temperature for 20 h or cured inside a vacuum oven at 80°C for 20 h prior to the annealing process. However, the dewetting behaviors of both PS thin films on the APTES surfaces were intermediate between those cured inside a vacuum oven at room temperature for 20 h and cured inside a vacuum oven at 80°C for 20 h. The presence of surface water at the PS/APTES interface at the annealing process due to the absence of vacuuming seemed to result in the moderate dewetting suppression. The scale bar was 100 μm.
crosslinking of APTES molecules over the PS chains and suppress the dewetting to some extent. A larger variation of the hole size within the samples for PS-9.3k (Figures 4.32c and 4.32e) could be due to the heterogeneity of the distribution of water contents throughout the PS/APTES interface, since the dewetting behavior of shorter and unentangled PS-9.3k chains was likely more sensitive to the details of surface heterogeneity.

Second, the effect of the APTES film thickness on the dewetting behaviors of PS-9.3k films was tested. An APTES film with $\delta$ of $\sim$ 4.6 nm, about three times thicker than that of the APTES film mentioned above, was utilized. The estimated $\gamma_S$ was still $\sim$ 62 mJ/m$^2$ (Table 4.2), similar to the previous value (Table 4.1). Only the hysteresis of contact angles of the probe liquids was decreased (Table 4.2). However, AFM images of the surface revealed remarkable differences in the surface topography. Many tiny aggregates with a height of $\sim$ 5 nm were noticed throughout the surface with a scan size of 2 $\mu$m $\times$ 2 $\mu$m (Figure 4.33a). From a larger scan of 15 $\mu$m $\times$ 15 $\mu$m, a coexistence of two different magnitudes of aggregates was observed (Figure 4.33b). Among larger aggregates with heights of 100 nm $\sim$ 150 nm, those tiny aggregates were filled. $R_q$ values were increased to $\sim$ 0.89 nm and $\sim$ 8.8 nm for scan sizes of 2 $\mu$m $\times$ 2 $\mu$m and 15 $\mu$m $\times$ 15 $\mu$m, respectively.

An optical microscopic image of a dewetted PS-9.3k film on the thick-APTES surface clearly demonstrated effects other than $\gamma_S$ on the dewetting behaviors (Figure
Table 4.2  Contact angle values and their hysteresis of MI and deionized water on the thick-APTES surface and corresponding estimated surface energies.

<table>
<thead>
<tr>
<th>Probe liquid</th>
<th>thick-APTES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle (°) (hysteresis)</td>
<td>MI</td>
</tr>
<tr>
<td>31 (7)</td>
<td>35 (15)</td>
</tr>
<tr>
<td>γ (mJ/m²)</td>
<td>γ&lt;sup&gt;d&lt;/sup&gt;&lt;sub&gt;a&lt;/sub&gt;</td>
</tr>
<tr>
<td>31</td>
<td>32</td>
</tr>
<tr>
<td>δ&lt;sup&gt;d&lt;/sup&gt; ± 2 (Å)</td>
<td>46</td>
</tr>
</tbody>
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<sup>a</sup> dispersion component of surface energy  
<sup>b</sup> polar component of surface energy  
<sup>c</sup> total surface energy  
<sup>d</sup> film thickness  
<sup>e</sup> deionized water
Figure 4.33 AFM images of APTES surface (thick-APTES surface) with different sizes (a and b) and an optical microscopy image of dewetted PS-9.3k film on the thick-APTES surface (c). A 50 mM of APTES in HPLC-graded hexane was used. The film thickness of the surface was ~ 46 Å. Two different dimensions of aggregates with heights of ~ 5 nm or ~ 125 nm were coexisted on the surface (b). PS-9.3k film was annealed inside a vacuum oven at 140°C for 2 h. High number density of dewetting holes was observed, i.e. many nucleation sites. The AFM scan sizes were 2 μm × 2 μm for (a) and 15 μm × 15 μm for (b). The scale bar in (c) is 100 μm.
4.33c). No dewetting suppression was found at all. There were many nucleation sites for the dewetting holes. It seemed that $N$ was even ~ 10 times higher than that of PS-9.3k/APTES cured without heat (Figure 4.26c). Since the heights of the larger aggregates were already beyond the PS film thickness (Section 4.3.4), those aggregates could serve as nucleation sites for the initiation of dewetting holes.

Third, various deposition techniques were used to generate APTES surfaces with different quality, and its effect on the dewetting suppression or behavior was observed. APTES surfaces were generated to observe the effect of deposition techniques on the dewetting suppression or behaviors. The surfaces were generated by solution deposition using hexane, chloroform, or toluene; vapor deposition; and contact printing technique. Figure 4.34 presents AFM images of the APTES surfaces, no dramatic differences were observed. For all the three solution deposition cases, some types of islands or aggregates were formed on the surfaces (Figures 4.34a − 4.34c). With the use of hexane, larger aggregates with a height of ~ 7 nm were presented while those presented for chloroform and toluene were ~ 2 nm in height. Many discernable aggregates were found when chloroform was used while sparsely adsorbed aggregates existed with the use of toluene, confirmed by a slightly higher $R_q$ value for the APTES surface generated from chloroform (Table 4.4). It seemed that the variation in the size and distribution of aggregates could be due to the difference in the polarity of the solvents. It was reported that APTES is relatively more stable in polar organic solvent, for instance, toluene. Since hexane has no polarity (relative polarity of 0.009), relatively unstable APTES molecules in hexane are favored to gather together. It could not only promote physical
Figure 4.34  Topographical AFM images of APTES surfaces generated by different deposition techniques: solution deposition (a – c), vapor phase deposition (d), and contact printing (e) techniques. For the solution deposition, hexane (a), chloroform (b), and toluene (c) were used. No dramatic topographical differences were observed. Some formation of aggregates on the surfaces generated from the solvents was noticed. The scan size is 2 μm × 2 μm.
coherence of the molecules, but also expedite the condensation of them, resulting in larger aggregates. However, in toluene or chloroform (relative polarity of 0.099 and 0.259, respectively),\textsuperscript{288} the APTES molecules are better stabilized and reacted progressively with the substrate to form more uniform layers, resulting in less aggregates (toluene) or smaller and well-distributed aggregates (chloroform). On the APTES surface generated by vapor phase deposition, barely discernible patches of APTES molecules were found (Figure 4.34d). The contact-printed APTES surface seemed to be the smoothest one (Figure 4.34e).

Figure 4.35 represents dewetting behaviors on these APTES surfaces. The samples were annealed inside a vacuum oven at 170 °C for 6 h continuously. Dewetting holes with $D < 10 \, \mu m$ were observed on the APTES surfaces generated from solution deposition (Figures 4.35a – 4.35c). However, the dewetting holes formed on the contact-printed surface grew to 40 μm ~ 50 μm in $D$ (Figure 4.35e), while almost no discernible dewetting holes were observed for the APTES surface generated from a vapor phase, except occasional holes initiated by foreign impurities (Figure 4.35d). The holes on the contact-printed APTES surface were not circular, and their rims even demonstrated some type of instability. Sharply cornered radius of curvature of the inside rim indicated that the rim was locally pinned at the location. Profiles of hole growth on the APTES surfaces, obtained by intermittently measuring $D$ of one hole from each surface, also revealed that more dewetting suppression or retardation was found for the vapor deposited surface, while dewetting holes grew continuously on the contact-printed
surface (Figure 4.36). Hole sizes were not quantitatively comparable to those from the samples annealed at one time (Figure 4.35). It seemed that once annealed samples were quenched, re-annealing the samples might be different from annealing freshly prepared ones continuously for the same amount of total annealing time. Once interdiffused interfaces of PS/APTES network are hardened by quenching, it might not be loosened as the initial state.

We attempted to relate the dewetting behaviors, in terms of $D$, to the magnitude of surface energy components, $R_q$, or $\delta$ of the APTES layers (Table 4.3). However, no quantitative correlations between them were noticed. For instance, higher $\gamma_S$ or higher $R_q$ was not correlated to more enhanced dewetting suppression indicated by smaller $D$. The data were simply all scattered (Appendices H.1 – H.3). The morphology or quantity of PS residuals left on the hole floors (Figure 4.35) provided no further information to differentiate detailed states or structures at the interfaces of PS/APTES.

One plausible hypothesis for the rapid dewetting process on the contact-printed APTES surface could be drawn from $\delta$ of the APTES layer—even it was unable to find a single expression of $D$ as a function of $\delta$. $\delta$ of the APTES layer was $\sim 9$ Å (Table 4.3), which was close to that of APTES monolayer ($\sim 7$ Å). The APTES molecules could form a monolayer through contact printing, exposing aminopropyl groups to the surroundings. Since there would be no interlocking between the monolayer of APTES and the PS chains and no particular chemical interaction between the PS chains and the
Figure 4.35  Optical microscopy images of dewetting holes of PS-63k films formed on the APTES surfaces generated by different deposition techniques (right column) and AFM images of their hole floors (left column). (a) – (c) are the surfaces generated by solution deposition using hexane, chloroform, and toluene, respectively. (d) is vapor phase deposited APTES surface, and (e) is contact-printed APTES surface. Tiny dewetting holes (D < 5 mm) were sparsely observed for (d), while dewetting holes with 40 μm < D < 50 μm were observed for (d). For (a) – (c), dewetting holes with D < 10 μm were observed throughout the surfaces. All the hole floors had PS residuals, and there were no noticeable differences in morphology or quantity of the residuals. The scale bar is 20 μm. The AFM scan size is 2 μm × 2 μm.
Figure 4.36  Profiles of dewetting hole growth of PS-63k formed on the APTES surfaces generated by different deposition techniques.  △: hexane solution; ∗: chloroform solution; ◆: toluene solution; ●: contact printing; and ■: vapor phase deposition techniques.  The samples were annealed inside a vacuum oven at 170°C.  The samples were taken out of the oven intermittently to measure hole diameter (D).  The data were obtained by monitoring one hole from each surface.  The vapor phase deposited APTES surface demonstrated most dewetting retardation or suppression, while no dewetting suppression was observed on the contact-printed surface.
Table 4.3  Contact angle hysteresis values of MI and deionized water; surface energy ($\gamma_S$); root-mean-square roughness; and film thickness of APTES surfaces generated by different deposition techniques: solution deposition, vapor phase deposition, and contact printing techniques.

<table>
<thead>
<tr>
<th>APTES</th>
<th>Hysteresis $^f$ ($^\circ$)</th>
<th>$\gamma_S$ $^c$ (mJ/m$^2$)</th>
<th>$R_q$ $^d$ (nm)</th>
<th>$\delta$ $^e$ ± 2 (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MI$^a$ W$^b$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solution</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hexane</td>
<td>10</td>
<td>34</td>
<td>52</td>
<td>0.625 ± 0.042</td>
</tr>
<tr>
<td>Chloroform</td>
<td>10</td>
<td>26</td>
<td>56</td>
<td>0.454 ± 0.052</td>
</tr>
<tr>
<td>Toluene</td>
<td>4</td>
<td>32</td>
<td>56</td>
<td>0.415 ± 0.010</td>
</tr>
<tr>
<td>Vapor phase</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>deposition</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>11</td>
<td>25</td>
<td>58</td>
<td>0.412 ± 0.021</td>
</tr>
<tr>
<td>Contact printing</td>
<td>6</td>
<td>18</td>
<td>59</td>
<td>0.464 ± 0.082</td>
</tr>
</tbody>
</table>

$^a$ methylene iodide  
$^b$ deionized water  
$^c$ total surface energy  
$^d$ root-mean-square roughness (10 μm × 10 μm)  
$^e$ film thickness  
$^f$ the difference between the average of advancing contact angles and the average of receding contact angles
NH_{2} groups, the PS chains dewetted from the APTES monolayer, similar to the dewetting behaviors on the precured APTES layer (Section 4.3.7). As shown in the optical microscopic images of Figures 4.35a – 4.35d, wider rims, relative to the hole sizes, were observed for the solution deposited or vapor phase deposited APTES surfaces. The wider rims resulted from low \( \theta_{d} \), indicating strong adherence of PS to the surfaces. In addition, the \( H \)s of the probe liquids (both MI and deionized water) on the \textit{thick}-APTES surface (Table 4.2) and the contact-printed APTES surface (Table 4.3), on which no dewetting suppression was observed, were relatively smaller as compared to other APTES surfaces (Tables 4.1 – 4.3). The lower \( H \) of the probe liquids might imply weak adherence of the liquids in receding. Similarly, when the PS melts receded or dewetted from these APTES surfaces, there would be less resistance at the interfaces, resulting in the faster hole growth. At this point, a direct connection between the phenomenon of the low \( H \) of the probe liquids and the interfacial characteristic or structure of the PS/APTES interface may not be drawn, but they could be correlated at least qualitatively.

4.3.10 Summary

In this study, a possible penetration/interlocking between PS chains and 3-aminopropyltriethoxysilane (APTES) network was investigated, and how this penetration or interlocking could retard or inhibit dewetting of PS thin films was discussed. While dewetting occurred spontaneously on the control surfaces where no penetration/interlocking occurred, various degrees of dewetting suppression were observed on the APTES surfaces having similar thermodynamic equilibrium of dewetting.
Complete suppression of dewetting resulted when the APTES network was being crosslinked in the presence of the thin film of PS, having chains longer than the entanglement length, on it. However, only slight retardation in dewetting, as compared to the controls, was obtained when the PS thin film was dewetted from the tightly precured APTES network. In addition, for the thin films of PS having shorter chains, meager suppression resulted when the APTES network was thermally cured with the PS film on it while no dewetting suppression was observed on the precured APTES network. Therefore, two conditions are necessary to achieve dewetting suppression of PS thin films on APTES surfaces: PS chains on top of the APTES surface must be able to penetrate into the APTES network while it is being formed and the PS chains should be sufficiently long and entangled. The formation of the APTES network normally occurred at elevated temperatures; at such temperatures, PS chains could gain enough mobility to rearrange their conformations and penetrate into the APTES network. Realizing such a window of opportunity, a substrate could easily be modified with APTES, with a layer as thin as 1.5 nm, to enhance the stability of polymer thin films without altering the unique characteristics and properties of these thin films.
4.4 Summary of Results and Discussion

In the study of the dewetting kinetics, dewetting hole growth rates \( (V_R) \) of PS thin film with molecular weights \( (M_n) \) of 63k and 9.3k were determined corresponding to various \( \gamma_S \). The various \( \gamma_S \) was achieved by modified the Si/SiO\(_X\) substrates with different coverage of a CH\(_3\)-terminated organosilane, octadecyltrichlorosilane (OTS); with different ratios of CH\(_3\)- and CF\(_3\)-terminated organosilanes; and with various polar group-terminated (-COOH, -SH, -NH\(_2\), or -CH\(_2\)Cl) organosilanes. The \( \gamma_S \) values were varied from 13 to 63 mJ/m\(^2\). Empirical relationships between the rate of hole growth (dewetting velocity, \( V_R \)) and \( \gamma_S \), \( V_R \approx 530 \exp(-0.13\gamma_S) \) and \( 310 \exp(-0.10\gamma_S) \), were obtained from the dewetting of PS-63k thin films on the -CH\(_3\) and -CF\(_3\)/-CH\(_3\) covered surfaces, respectively. For PS-9.3k on the OTS surfaces, \( V_R \approx 1.1 \times 10^4 \exp(-0.13\gamma_S) \) was obtained. The physical rationale of the exponential relationships between \( V_R \) and \( \gamma_S \) was elucidated by regarding \( V_R \) as the rate of desorption process, which was exponentially dependent on the activation energy for desorption. The activation energy for the dewetting process would be the negative of the free energy of adhesion, which is proportional to \( \gamma_S^{1/2} \). The replotted \( V_R \) versus \( \gamma_S^{1/2} \) also demonstrated the exponential dependence of \( V_R \) on \( \gamma_S^{1/2} \) with physically reasonable exponents, indicating the validity of the proposed model.

During the growth of dewetting holes, not only \( V_R \) was varied by \( \gamma_S \), but the morphology of rims formed around the holes also exhibited \( \gamma_S \) dependency. As \( \gamma_S \) decreased, a transition from even ring-shaped rims to undulated wavy rims was observed. This effect of \( \gamma_S \) on the degree or development of rim morphology is investigated in
Sections 4.3. Dewetting holes of PS thin films with a molecular weight ($M_n$) of 9.3k and 63k were studied, which formed on substrates with different coverage of OTS. A possible mechanism of the rim instability was proposed based on different rim geometry or profile depending on the $\gamma_S$. It was found that the variation of $\gamma_S$ affected $\theta_d$ and consequently determined rim profiles. Higher and narrower geometry of rim by lowering $\gamma_S$ seemed to be destabilized easily, as demonstrated in the growth rate ($q$) of the rim undulation as a function of $\gamma_S$, based on Rayleigh instability.

In addition, during the dewetting dynamics study, unusual retardation or suppression of hole growth was noticed on NH$_2$-terminated organosilane, aminopropyltriethoxysilane (ATES). It was unexpected behaviors, judging from its $\gamma_S$. Since the dewetting phenomena is generally better to be avoided, the dewetting suppression was further investigated (Section 4.4). To elucidate the dewetting suppression ability of APTES-modified surfaces, different molecular weights of PS-9.3k and -63k thin films were used, and the curing degree of the APTES network was also varied by changing curing temperature and time (duration). Thermal curing of the APTES-network at 80 °C or 120 °C in the presence of the PS thin film on it was found to be essential to accomplish dewetting suppression. The APTES layers without the thermal curing or precured without the PS thin film on it did not demonstrate any ability of dewetting suppression. On the basis of the experimental results, a possible mechanism of dewetting suppression of the NH$_2$-terminated organosilane surface was proposed in perspective of interfacial diffusion and entanglement between the PS chains and the
APTES networks. Other factors that could influence the dewetting suppression of the APTES surface were studied, including surface water, film thickness, and deposition technique. The existence of surface water at the interface of PS/APTES during the annealing step due to the absence of the vacuum process seemed to enhance dewetting suppression, compared with the case with the vacuuming. To avoid large agglomerates and to suppress dewetting, a proper thickness for the APTES surface was needed. Various deposition techniques for the generation of APTES surfaces produced similar surface properties; however, actual dewetting behaviors on those surfaces were varied. Vapor phase-deposited APTES surface demonstrated the most dewetting suppression, while the contact-printed APTES surface demonstrated no dewetting suppression. An intermediate suppression of dewetting was observed for the APTES surfaces generated by solution deposition. An exact explanation for the behaviors is not definite at this point.
CHAPTER V

CONCLUDING REMARKS AND FUTURE STUDIES

5.1 Concluding Remarks

Dewetting hole growth rates ($V_R$), dewetting kinetics, of PS thin film with molecular weights ($M_n$) of 63k and 9.3k were studied as a function of $\gamma_S$. The variation of $\gamma_S$ was achieved by modified the Si/SiO$_X$ substrates with different coverage of a CH$_3$-terminated organosilane, octadecyltrichlorosilane (OTS); with different ratios of CH$_3$- and CF$_3$-terminated organosilanes. The $\gamma_S$ values were varied from 13 to 63 mJ/m$^2$. Empirical relationships between $V_R$ and $\gamma_S$, $V_R \approx 5.3 \times 10^2 \exp(-0.13\gamma_S)$ and $3.1 \times 10^2 \exp(-0.10\gamma_S)$, were obtained from the dewetting of PS-63k thin films on the -CH$_3$ and -CF$_3$/-CH$_3$ covered surfaces, respectively. For PS-9.3k on the OTS surfaces, $V_R \approx 1.1 \times 10^4 \exp(-0.13\gamma_S)$ was obtained. The physical rationale of the exponential relationships between $V_R$ and $\gamma_S$ was explained by regarding the dewetting process as the rate of desorption process that exponentially depended on the activation energy. Since the negative of the free energy of adhesion, the activation energy for the dewetting process, was proportional to $\gamma_S^{1/2}$, $V_R \propto \exp(-\gamma_S^{1/2})$. The replotted $V_R$ versus $\gamma_S^{1/2}$ also
demonstrated the exponential dependence of $V_R$ on $\gamma_S^{1/2}$ with physically reasonable exponents, demonstrating the physical validity of the proposed model.

In addition, a variation of rim (formed around dewetting hole) morphology was also studied as a function of $\gamma_S$. To isolate $\gamma_S$ effect on the rim instability, dewetting holes with a similar diameter were compared. As $\gamma_S$ decreased, a transition from even ring-shaped rims to undulated wavy rims was observed. As $\gamma_S$ decreased, $\theta_d$ increased and the increased $\theta_d$ altered the rim profile to be higher and narrower. The geometry seemed to be subject to destabilize. The analysis of the growth rate ($q$) of the rim undulation, based on Rayleigh instability, also captured the rim instability dependency on $\gamma_S - q$ was higher for the higher and narrower rims.

Interestingly, dewetting retardation or suppression was noticed on NH$_2$-terminated organosilane, aminopropyltriethoxysilane (ATES). The dewetting suppression was only possible when the APTES layer was thermally (80°C or 120°C) cured in the presence of PS films on top of it. No dewetting suppression was observed from the APTES surfaces cured at room temperature or the precured APTES surfaces. A proposed mechanism of the dewetting suppression of the NH$_2$-terminated organosilane surface indicated that the enhanced adhesion was possible by interfacial diffusion and entanglement between the PS chains and the APTES network. This additional physical interlocking between the APTES surface and the PS chains at the interface enabled the suppression of dewetting. The existence of surface water at the interface was also able to
suppress the dewetting. A thick APTES layer formed with large agglomerates on its surface in fact facilitated the dewetting process. The ability of dewetting suppression of the APTES surfaces was dependent on their deposition techniques. No dewetting suppression was observed for the contact-printed APTES surface, while the solution deposited and vapor phase deposited APTES surfaces demonstrated the dewetting suppression.

5.2 Future Studies

- The strong preferential adsorption of the CF₃-terminated organosilane in the mixed monolayer of CF₃-terminated and CH₃-terminated organosilanes can be verified—whether actually the CF₃-terminated organosilane is more adsorbed on the surface or not. FTIR may be used to detect the ratio of CF₃ to CH₃ groups on the surface.
- In the rim instability, the thickness of PS film can be varied with a fixed \( \gamma_S \) to investigate how the amount of PS materials accumulated in the rim affects the rim instability.
- The molecular weight effect on the rim instability needs to be verified by controlling \( \gamma_{PS} \) with the adjustment of the annealing temperature for PS.
- There was one concern that the developed rim instability for high molecular weight PS-63k (\( > M_c \)) might be due to slippage of entangled polymer at the interface. Comparing the degree of the rim instability of PS-9.3k on low \( \gamma_S \) with that of PS-63k on high \( \gamma_S \) may provide some insights on the issue.
• The interface of PS and APTES can be investigated using X-ray reflectivity. The enhanced adhesion of PS films on the APTES surface might be due to the increased interface width during the thermal curing process.

• The unclear mechanism of different dewetting behaviors on the APTES surfaces generated by different deposition techniques needs to be studied. It may be possible to dye the exposed NH₂ groups in the top portion of the APTES layer with a certain material, and then we can find out whether the mechanism has something to do with the amount of effective NH₂ groups or not.
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223 The minimum height difference to be experimentally observable with the optical microscopy by color contrast was ~ 50 nm. The value was obtained from the height difference between protrusions and non-protruding regions of the rim using the AFM scans.


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APPENDICES
APPENDIX A

CONTACT ANGLES OF MI AND DEIONIZED WATER

Tables A.1 – A.3 provide contact angle values of MI and deionized water measured from the contact-printed OTS surfaces, the FTS/DTS mixed monolayer surfaces, and the polar organosilane-modified surfaces.

Table A.1 Contact angle values of MI and deionized water measured from the contact-printed OTS surfaces.

<table>
<thead>
<tr>
<th>Contact time (s)</th>
<th>MI</th>
<th>Deionized water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_a$</td>
<td>$\theta_r$</td>
</tr>
<tr>
<td>1</td>
<td>49</td>
<td>43</td>
</tr>
<tr>
<td>10</td>
<td>51</td>
<td>43</td>
</tr>
<tr>
<td>20</td>
<td>52</td>
<td>46</td>
</tr>
<tr>
<td>30</td>
<td>54</td>
<td>48</td>
</tr>
<tr>
<td>60</td>
<td>57</td>
<td>51</td>
</tr>
<tr>
<td>90</td>
<td>62</td>
<td>57</td>
</tr>
<tr>
<td>120</td>
<td>59</td>
<td>55</td>
</tr>
</tbody>
</table>

$\theta_a$: advancing contact angle  
$\theta_r$: receding contact angle  
$\theta_{avg}$: averaged contact angle of $\theta_a$ and $\theta_r$
Table A.2 Contact angle values of MI and deionized water measured from the FTS/DTS mixed monolayer surfaces.

<table>
<thead>
<tr>
<th>FTS/DTS mixture ratio</th>
<th>MI</th>
<th>Deionized water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_a$</td>
<td>$\theta_r$</td>
<td>$\theta_{avg}$</td>
</tr>
<tr>
<td>FTS</td>
<td>95</td>
<td>87</td>
<td>91 ± 4</td>
</tr>
<tr>
<td>FTS/DTS 50/50</td>
<td>92</td>
<td>85</td>
<td>89 ± 4</td>
</tr>
<tr>
<td>FTS/DTS 10/90</td>
<td>91</td>
<td>82</td>
<td>86 ± 5</td>
</tr>
<tr>
<td>FTS/DTS 1/99</td>
<td>76</td>
<td>70</td>
<td>73 ± 5</td>
</tr>
<tr>
<td>FTS/DTS 0.1/99.9</td>
<td>65</td>
<td>62</td>
<td>63 ± 5</td>
</tr>
<tr>
<td>FTS/DTS 0.01/99.99</td>
<td>61</td>
<td>60</td>
<td>60 ± 4</td>
</tr>
<tr>
<td>DTS</td>
<td>58</td>
<td>54</td>
<td>56 ± 3</td>
</tr>
</tbody>
</table>

$\theta_a$: advancing contact angle  
$\theta_r$: receding contact angle  
$\theta_{avg}$: averaged contact angle of $\theta_a$ and $\theta_r$

Table A.3 Contact angle values of MI and deionized water measured from the polar organosilane-modified surfaces.

<table>
<thead>
<tr>
<th>Organosilane</th>
<th>MI</th>
<th>Deionized water</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_a$</td>
<td>$\theta_r$</td>
<td>$\theta_{avg}$</td>
</tr>
<tr>
<td>APTES</td>
<td>42</td>
<td>32</td>
<td>37 ± 6</td>
</tr>
<tr>
<td>MPTMOS</td>
<td>39</td>
<td>34</td>
<td>36 ± 6</td>
</tr>
<tr>
<td>CTMOS</td>
<td>50</td>
<td>45</td>
<td>47 ± 7</td>
</tr>
<tr>
<td>CPTMOS</td>
<td>50</td>
<td>41</td>
<td>45 ± 5</td>
</tr>
</tbody>
</table>

$\theta_a$: advancing contact angle  
$\theta_r$: receding contact angle  
$\theta_{avg}$: averaged contact angle of $\theta_a$ and $\theta_r$
APPENDIX B

ROOT MEAN SQUARE ROUGHNESS FOR ORGANOSILANE-MODIFIED SURFACES

Figure B.1 represents surface root mean square (RMS) roughness ($R_q$) values for all the organosilane-modified surfaces: the contact-printed OTS surface, the FTS/DTS mixed monolayer surfaces, and polar organosilane-modified surfaces.
Figure B.1  Surface RMS roughness ($R_q$) for the organosilane-modified surfaces.
APPENDIX C

DEWETTING HOLE GROWTH

Figure C.1 represents a dewetting hole growth (radius, $R$) as a function of time ($t$) and its velocity taken from the slope.

Figure C.1  Dewetting hole growth (radius, $R$) versus time ($t$) and its velocity (the slope).
SURFACE ENERGY ESTIMATION OF POLYSTYRENE MELT

Surface energies ($\gamma$) of the PS-9.3k and -63k thin films at the annealing temperature, 160 °C, were estimated by considering the influences of temperature and molecular weights, according to Ref. [164]. Table D.1 represents the influence of temperature on PS with different molecular weights.

Table D.1 The dependence of surface energy of PS ($\gamma_{PS}$) on temperature ($T$): $\gamma_{PS} = a - bT$.

<table>
<thead>
<tr>
<th>$M_n$ (g/mol)</th>
<th>$a$ (mJ/m$^2$)</th>
<th>$b$ (mJ/m$^2$ °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3400</td>
<td>49.17</td>
<td>0.0956</td>
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<tr>
<td>12,400</td>
<td>45.42</td>
<td>0.0763</td>
</tr>
<tr>
<td>41,200</td>
<td>47.22</td>
<td>0.065</td>
</tr>
<tr>
<td>107,200</td>
<td>52.02</td>
<td>0.0885</td>
</tr>
</tbody>
</table>

The dependence of $\gamma$ of PS ($\gamma_{PS}$) on the molecular weight is given by equation D.1.

$$\gamma_{PS} = \gamma_\infty - C_1 (M_n)^{-1}$$  \hspace{1cm} \text{[D.1]}

where $\gamma_\infty$ and $C_1$ are constants.
APPENDIX E

EQUILIBRIUM CONTACT ANGLE VERSUS SUBSTRATE SURFACE ENERGY

Figure E represents measured equilibrium contact angles ($\theta_e$) as a function of substrate surface energy ($\gamma_s$) for PS-63k on the contact-printed OTS surfaces (○) and on the FTS/DTS mixed monolayer surfaces (■) and for PS-9.3k on the contact printed OTS surfaces (♦). Error bars are standard deviations from the mean.
Figure F represents the verification of a linear relationship between dewetting velocity ($V_R$), equilibrium contact angles ($\theta$), surface energy of PS ($\gamma_{PS}$), and viscosity of PS ($\eta_{PS}$): $V_R \sim k\gamma_{PS}\theta^3/\eta_{PS}$ where $k$ is a numerical constant, as predicted in the theory (equation 4.5). ◆, ○, and ■ indicate the values obtained from PS-9.3k and -63k on the contact-printed OTS surfaces and PS-63k on the FTS/DTS mixed monolayer surfaces, respectively. Relatively linear relationships in $V_R$ versus $\gamma_{PS}\theta^3/\eta_{PS}$ were found with different slopes. The dashed lines were drawn to guide the eye.
$V_R (\mu m/min)$

$\gamma_{PS} \theta_e^3/\eta_{PS} (\mu m/min)$
Figures G represent the verification of the theoretical relationship between equilibrium contact angles ($\theta_e$) and dynamic contact angles ($\theta_d$) in the dewetting dynamics: $\theta_e = \sqrt{2}\theta_d$. The $\theta_e$ and $\theta_d$ values were measured from PS-9.3k (♦) and -63k (○) droplets formed on the contact-printed OTS surfaces, using AFM. It was found that $\theta_e \approx 1.4\theta_d$, agreed well with the theoretical relationship.
APPENDIX H

OTHER FACTORS AFFECTING DEWETTING ON APTES SURFACES

Figures H.1 – H.3 represent diameters of dewetting holes ($D$) of PS-63k formed on the APTES surfaces, generated by different deposition techniques, as a function of substrate surface energy ($\gamma_S$), root-mean-square (RMS) roughness ($R_q$), or APTES film thickness ($\delta$).
Figure H.1  Dewetting hole diameter ($D$) versus substrate surface energy of APTES surfaces ($\gamma_S$). The samples were annealed inside vacuum oven at 170°C for 1 h (□) or 6 h (▲). The dotted and dashed lines are guide to the eye.
Figure H.2  Dewetting hole diameter \((D)\) versus root-mean-square roughness \((R_q)\) of APTES surfaces. The samples were annealed inside vacuum oven at 170°C for 1 h (□) or 6 h (▲). The dotted and dashed lines are guide to the eye.
Figure H.3  Dewetting hole diameter ($D$) versus film thickness of APTES surfaces ($\delta$). The samples were annealed inside vacuum oven at 170°C for 1 h (□) or 6 h (▲). The dotted and dashed lines are guide to the eye.