Unravelling new phenomena in polymer science at both the ensemble and single-molecule levels

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**Unravelling new phenomena in polymer
science at both the ensemble and
single-molecule levels**

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SCHOOL OF PHYSICAL & MATHEMATICA SCIENCES

NANYANG TECHNOLOGICAL UNIVERSITY

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both the ensemble and single-molecule levels**

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LIST OF ABBRECIATIONS

AFM	Atomic force microscopy
SAXS	Small-angle X-ray scattering
WAXD	Wide angle X-ray diffraction
POM	Polarizing optical microscopy
DSC	Differential scanning calorimetry
TEM	Transmission electron microscopy
WFM	Wide field microscopy
FCS	Fluorescence correlation spectroscopy
CCD	Charge-coupled device
SMT/SPT	Single-molecule/particle tracking
MSD	Mean square displacement
DNA	Deoxyribonucleic acid
PEO	Poly (ethylene oxide)
PS	Polystyrene
P2VP	Poly (2-vinyl pyridine)
PEG	Polyethylene glycol

PUBLICATIONS

1. **W. Bi**, J. S. Teguh and E. K. L. Yeow,. Visualizing polymer crystallization in ultrathin layers using a single-macro-molecule tracking method. *Phys. Rev. Lett.* **102**, 048302 (2009).
2. B. Xing, T. Jiang, **W. Bi**, Y. Yang, L. Li, M. Ma, C. K. Chang, B. Xu and E. K. L. Yeow,. Multifunctional divalent vancomycin: the fluorescent imaging and photodynamic antimicrobial properties for drug resistant bacteria. *Chem. Commun.* **47**, 1601-1603 (2011).
3. **W. Bi** and E. K. L. Yeow,. Domain Coalescence-Induced Nucleation and Anomalous Growth of Holes in Thin Polymer Blend Film. *Phys. Rev. Lett.* **106**, 078001 (2011).
4. **W. Bi**, X. Wu and E. K. L. Yeow,. Unconventional Multiple Ring Structure Formation from Evaporation-induced Self-Assembly of Polymers: A Spreading and Receding Mechanism. Submitted (2011).

SUMMARY

Single-(macro) molecule tracking is used for the first time here to study the crystallization process in ultrathin layers of single poly(ethylene oxide) (PEO) chains. Diffusion trajectories of macromolecules diffusing toward the crystal followed by deposition onto the crystal-growth front display different types of motion, such as Brownian and directed motions, prior to crystallization. We show that PEO chains in the amorphous layer and in the less concentrated or depleted zone exhibit Brownian motion of different diffusion rates as a result of heterogeneities in the environment.

The phase evolution of thin polymer blend film of polystyrene (PS) and poly(2-vinyl pyridine) (P2VP) triggered by solvent annealing is examined at both the bulk and single-(macro)molecule levels using wide-field microscopy (WFM). The transitions between different evolutionary stages in the nucleation and growth process are clearly visualized in real-time and without intermittent breaks. The nucleation of PS holes arises from the coalescence and growth of P2VP domains and the holes expand in a complex manner involving the dewetting of PS and the absorption of P2VP domains into the holes.

The formation of multiring deposits of poly(2-vinyl pyridine) P2VP from the evaporation of a P2VP-(2,6-lutidine + water) drop on a glass substrate does not conform to the conventional pinning-depinning mechanism. Instead, ring-like deposits are formed when the droplet undergoes several cycles of spreading and receding where for each spreading event, a P2VP ridge is formed at the contact line when the polymer flows toward the outward advancing edge. A

surface tension gradient created as a result of the solutal-Marangoni effect plays an important role in enhancing the droplet spreading rate.

CHAPTER 1

GENERAL INTRODUCTION

1.1 Crystallization in the ultrathin polymer films

Polymer crystallization is an important process in semi-crystalline polymeric materials and it has a strong effect on their physical properties. To comprehensively understand the nucleation mechanism and kinetics of crystal growth during polymer crystallization, a significant number of studies have been dedicated to understand crystallization in bulk polymeric materials using small-angle X-ray scattering (SAXS) [1,2], wide angle X-ray diffraction (WAXD) [2,3], polarizing optical microscopy (POM) [2,3], differential scanning calorimetry (DSC) [1,4-6], transmission electron microscopy (TEM) [7] and other techniques. On the other hand, crystallization of semi-flexible polymer films on solid substrates is a unique branch of polymer science because the thermophysical properties such as glass transition temperature (T_g), thermal expansion coefficient, molecular mobility, *etc.* [8] of polymers confined in a thin film are considerably different from those of polymers in non-confined environment. The crystallization of polymer films has been investigated in depth using atomic force microscopy (AFM) which allows the morphology of the crystals to be visualized at different times [9-14]. Poly(ethylene oxide) is a common semi-crystalline polymer used to study thin film crystallization due to its simple polymeric chain structure and relatively low melting point (T_m) [9-17]. In the following sections, some special topics will be reviewed involving the crystallization of poly(ethylene oxide) ultrathin films on solid substrates including the nucleation formation, kinetics of crystal growth, thickening process of crystals and conformation of polymer chains in the adsorbed amorphous layer.

The nucleation stage of polymer crystallization, unlike the crystallization of small molecules that occurs when quenched to a temperature below the melting point, is complex because the free motion of the monomers linked together in the polymer chains is limited. Based on the classical nucleation theory, Wunderlich has proposed two nucleation pathways including intermolecular crystal nucleation and intramolecular crystal nucleation [18]. The nucleation process occurring in the initial stages of polymer crystallization of ultrathin films, particularly those with thicknesses less than 10-15 nm, is rarely discussed in the literature because it is difficult to form crystals when

Figure. 1 Schematic picture of the crystallization of polymer chains adsorbed on a substrate.

strong interaction between polymer and substrate is present [19,20]. It is thought that the initial crystal growth begins at the thicker parts of polymer thin film since nucleation is not observed during crystal growth (thickness < 15 nm) (see Figure 1 “thick parts”) (The figures provided in this chapter are adapted

from the literatures where dimensions are not provided. However, in most instance, the thickness of the polymer films falls in the nm to μm range.) [9,10]. Furthermore, the rate of polymer nucleation occurs too rapidly to be observed using conventional experimental techniques such as atomic force microscopy and optical microscopy [9].

Crystallization of poly(ethylene oxide) monolayers adsorbed on the surface of a substrate or confined in the holes of polymer films has been studied extensively by Reiter and Sommer who observed that for polymer films with thickness < 15 nm, quasi-2D polymer crystals with fingerlike or fractal-like patterns are observed utilizing AFM [9]. Monte Carlo simulation has also been carried out to explain the crystallization process of polymer monolayers on the basis of the probabilities of detachment (P_d) and rest (P_r) in the crystallization process similar to that used in the diffusion-limited aggregation model [21]. An expression for polymer monolayer crystal growth has been established [9]:

$$d^2 \sim fD_s \tau_a \sim fD_s \tau_c / (1 - P_d) \sim fD_s \tau_c / (P_r) \sim fD_s \tau_c [1 - \exp(-C_1 \Delta T/T)]$$

where d is the width of the depleted zone, f is an accumulation factor, D_s is a diffusion coefficient, τ_a is an average time for the polymer chain to get attached to the crystal, τ_c is a characteristic time, C_1 is equal to $\Delta h_m / k_B T_m$ where Δh_m and T_m are the heat of fusion per unit volume and the melting temperature, respectively, and T is the crystallization temperature. The molecules move randomly near the crystal with a constant diffusion coefficient D . Based on the above expression for d^2 , the molecules entering the depleted zone can attach themselves to the crystal during τ_a . When a molecule touches the crystal cell,

two possible situations can happen; namely, a molecule desorbs from the crystal with a probability P_d or becomes part of the crystal, which is determined by an accumulation factor (f). In this case, the evolution of crystal growth towards fingerlike morphologies is mapped out by the Monte-Carlo simulation (see Figure 1). Reiter and Sommer, in their subsequent works, further discussed the crystal growth kinetics of poly(ethylene oxide) monolayers in greater details combining both experiment and computational modeling studies [10,22].

The rate of transforming the amorphous poly(ethylene oxide) into the ordered crystalline layer calculated by Reiter *et al.* is relatively lower than the rate of bulk polymer crystallization [10]. In addition, the widths of the fingerlike patterns become broad as the crystallization temperature increases. The width of the fractal patterns of polymers with low molecular weight is significant even at low crystallization temperature whereas that of high molecular weight polymers displays a dramatic change only at high crystallization temperature. The surface smoothness of the fingerlike patterns is affected not only by the crystallization temperature but also by the crystallization time. The adsorbed polymer chains need to further optimize themselves after they have attached and joined the crystal cell. Sommer and Reiter have also proposed a model to explain how polymer chains become upright and arrange themselves in an orderly manner by adjusting several parameters, such as the maximum stretching length of the chains and the interaction energy between crystals [22].

The resulting fingerlike crystals of poly(ethylene oxide) on a surface at low temperature, however, are not in a thermal equilibrium state. When performing thermal annealing at higher temperature below the melting point of

the polymer, the crystal will relax to a new metastable state corresponding to the annealing temperature. The change of morphology of polymer crystal is quite distinct between 51 and 54 °C below the melting temperature [23]. Wang and co-workers have also observed that the transition from nonequilibrium to equilibrium states and the polymer crystal thickens when the temperature increases (see Figure 2) [11].

Figure. 2 The illustration of the thickening of polymer crystal on a substrate with the temperature increasing below the melting temperature.

The effects of the end group of polymer chains on the mechanism of crystallization for polymers adsorbed on substrate have also been studied and the mechanism of nucleation-limited growth is valid for polymers where one end of the chain is terminated with a $-CH_3$ group and the mechanism of “diffusion-limited” growth occurs when both ends of the polymer chains are terminated with a $-OH$ group [14]. Crystallization in the polymer film has also been investigated using video rate atomic force microscopy [24]. Nevertheless, this is inadequate for studying rapid motion of single polymeric chains since

video rate atomic force microscope is equipped with low temporal resolution camera.

While significant attention has been directed towards the study of the kinetics of quasi-2D dimensional crystal growth of polymers adsorbed on a substrate, dynamics of the amorphous polymer chains and chains found in the depletion zone are rarely discussed. In particular, issues such as interaction of the adsorbed amorphous polymer chains with the surface of substrate, interaction between polymers, conformation and motion of the amorphous polymer chains on the substrate have received little attention. Granick and co-workers have made significant effort to understand the properties of adsorbed polymer layers, and have reported several factors influencing the kinetics and mechanical properties of polymer layer adsorbed on the substrate including entanglements, monomeric friction coefficient (ξ_0), near-surface gradients, and time-temperature superposition [25,28-30].

Existence of entanglement of polymer chains in the bulk is well known when the molecular weight exceeds the critical molecular weight (M_c) for entangled macromolecules. On the other hand, the adsorbed polymer chains may interact with the surface of substrate to form loops (see Figure 3) [25]. Some non-adsorbed polymer chains may be trapped in the loop leading to further limitations in the mobility. In this case, entanglement of polymer chains will be enhanced on the surface of the substrate. The monomeric friction coefficient (ξ_0) of polymer chain segments is usually sensitive to temperature and pressure. The T_g of polymers near the surface of a substrate is higher than the bulk value because the thinner thickness of the polymer films, the high interfacial energy between the polymer film and the substrate and the effect of

Figure. 3 Scheme of the conformation of polymer chains adsorbed on the substrate.

the surface of the substrate result in the T_g increase of a polymer film on the substrate [26, 27], and this has an effect on ξ_0 . ξ_0 is also related to the distance of the polymer chain segment from the surface and the distribution of the distance of the polymer from the substrate results in a near-surface gradient in ξ_0 . In addition, the conformation of non-equilibrium polymer chains on the substrate stretch out as much as possible such that the deformation of the adsorbed chains on the surface is impeded.

To comprehend the behavior of the polymer chains adsorbed on the substrate, Granick *et al.* have investigated the diffusion of polymer chains using fluorescence correlation spectroscopy (FCS). For low molecular coverage, the polyethylene glycol (PEG) chains on the substrate adsorb in a pancake conformation to minimize chain-chain interaction (see Figure 4) [28]. The diffusion coefficient (D) of PEG displays a power law relationship with the degree of polymerization (N), namely $D \approx N^{-3/2}$. The reptation model is used to

interpret the strong power law relationship between D and N . The relationship between D and the radius of gyration is $D \approx R_g / \tau_{\text{rept}}$, where R_g ($\approx N^{3/4}$) is the radius of gyration, and τ_{rept} ($\approx N^3$) is the terminal relaxation time scales, and is in good agreement with experiment results. The authors have proposed that a single polymer chain in a very dilute environment on the substrate diffuses by propagation of loops formed by sticking points on the surface. Furthermore, other possible transport mechanisms for a polymer chain adsorbed on the surface include the first-principle model, the reptation model, the amoeba model and the sticky reptation model that follow $D \approx N^{-3/2}$ [29].

Figure. 4 The pancake conformation of a polymer chain adsorbed on the substrate with a low molecular coverage.

Concentration of the polymer chains adsorbed on the surface has a strong effect on the interaction between polymers. Granick and co-worker have found that the diffusion coefficient of polymer chains adsorbed on a substrate is enhanced as the concentration of polymer chains increases, and the diffusion coefficient decreases sharply after approaching a certain polymer concentration [31,32]. This is because of the transition of conformation of the adsorbed polymer chain from a “pancake” morphology in the dilute situation to a “loop-train-tail” conformation in the concentrated situation [33].

Wide field microscopy is here used to study the dynamics of polymer crystal growth on the substrate for the first time, in order to examine the diffusion coefficients of polymer chains in the amorphous layer and depletion zone, and to visualize how single polymer chains attach themselves onto the growing front of a polymer crystal. Details will be discussed in Chapter 2.

1.2 Instabilities of polymer thin films

The stability of polymer thin films on solid surfaces is an important process which finds application in several areas including coatings, adhesives, emulsions and polymer solar cells [34]. In particular, thin films become metastable or unstable when their thicknesses are less than the critical thickness ($e_c = 2\kappa^{-1}\sin(\theta_E/2)$, where $\kappa = (\gamma/\rho g)$, and θ_E , γ , ρ and g are the contact angle under equilibrium, surface tension, density and earth's gravity, respectively) after deposition on the surface due to the existence of the long-range force which yields the energy ($P(e)$) between the thin film and the surface of the solid (see Figure 5) [35-38]. In equation (1),

$$F(e) = \gamma_L + \gamma_{SL} + P(e) + \frac{1}{2} \rho g e^2 \quad (1)$$

where $F(e)$, γ_L , γ_{SL} and $\frac{1}{2} \rho g e^2$ are the free energy, surface tension of liquid film, interfacial tension between liquid and solid and the gravitational energy, respectively. $P(e) = A/12\pi e^2$ where A is the Hamaker constant. If the film thickness $e < 1 \mu\text{m}$, $\frac{1}{2} \rho g e^2$ can be ignored. Under thermal or good solvent treatment, the relatively thick films (more than tens of nm, see Figure 5, $> e_i$)

easily form holes whereas thinner films (e.g., thickness of several nanometers, see Figure 5, $< e_i$) decompose spontaneously (spinodal dewetting) at the early stage followed by rupture of the thin films and subsequent formation of droplets [37,39-43]. To understand the dynamics of the instabilities of thin films, experimental efforts have been focused on three typical thin films including the homogenous films, the bilayers and the multi-component blends. Herein, formation of holes due to heterogeneous nucleation and their growth dynamics in homogeneous and bilayer thin films, and phase domain growth and transformation of phase morphology in blend thin films are briefly reviewed.

Figure. 5 Plot of the free energy $F(e)$ vs. film thickness e . $S = \gamma_{SO} - \gamma_L + \gamma_{SL}$ is the spreading coefficient and e_i is the inflection point (order of 10 nm).

The creation of initial holes in liquid thin films on a non-wettable solid surface plays a crucial role in the subsequent growth of the holes and rupture of

the thin films. Sharma *et al.* have built a model to depict the formation process of the initial holes based on free energy change (ΔF) [44,45]. In equation (2), F , A_s , and S represent the free energy, the initial area of contact between the liquid

$$\begin{aligned}\Delta F &= F_{\text{hole}} - F_{\text{film}} \\ &= (A_s - \pi r_2^2)\gamma_L + (A_s - \pi r_1^2)\gamma_{SL} + S\gamma_L + \pi r_1^2\gamma_S - A_s\gamma_L - A_s\gamma_{SL} \\ &\quad + \pi\rho g \int_0^{h-r_2} (h-x)dx \quad (2)\end{aligned}$$

film and solid surface, and the surface area of the hole bounded between the horizontal planes $x = 0$ and $x = h$ (see Figure 6 for other parameters), respectively. Based on equation (2), the authors have shown that the free energy change ΔF reaches a maximum value as the thickness of the thin film decreases

Figure. 6 Schematic picture of the nucleation of a hole.

and approaches a certain “transitional” thickness which leads to thin film instability. As the thin film continues to thin, a “critical” thickness appears where ΔF is equals to zero. The unstable region existing between the transitional thickness and the critical thickness results in the creation of initial holes. Furthermore, the authors have also discussed the effects of impurities and trapped gaseous bubbles in the thin film on the creation of holes. Tsui and co-workers have also proposed that an energy barrier has to be crossed in order for the nucleation of holes to occur [41].

The growth dynamics of holes in liquid thin films on non-wettable solid surface has been thoroughly investigated by Brochard-Wyart *et al.* and the velocity (V) of the hole expansion is constant and is expressed according to equation (3) [37],

$$V = V^* k \theta_E^3 \quad (3)$$

where $V^* = \gamma/\eta$, (γ and η are the surface tension and viscosity of the fluid, respectively) and k is a constant that depends on the nature and the molecular weight of the liquid. In a separate study, Brochard-Wyart *et al.* have proposed that the hole expansion behavior of liquid A thin film depends on the viscosity and thickness of liquid B thin film below liquid A when liquid A and liquid B are immiscible [38]. The three possible cases are:

Case I: When the viscosity of liquid B (e.g. solid surface) is higher than that of liquid A and liquid B does not move as liquid A dewets, the velocity of the rim obeys equation (3). (See Figure 7a)

Figure. 7 The schematic picture of growing holes. θ_d is the dynamic angle.

Case II: If the viscosity of liquid B on the substrate is low and the thickness is thin (see Figure 7b), the relationship of the radius of the growing hole (R) and time (t) is

$$R^{3/2} \sim V_B^* \theta_E^{1/2} \frac{L}{e^{1/2}} t \quad (4)$$

when the driving force (F_d) and the friction force (F_f) are in equilibrium. In equation (4), $V_B^* = \gamma/\eta_B$ where γ and η_B are the surface tension and viscosity of fluid B, respectively, and e is the thickness of the thin film. The other parameters are shown in Figure 7b. The velocity (V) of the expansion of holes

can be obtained by $V = dR/dt$, where R is the radius of the hole, and (see Figure 7b),

$$V = dR/dt = (V_B^* \theta_E^{1/2} \frac{L}{e^{1/2}})^{2/3} t^{-1/3} \quad (5)$$

Case III: When the thickness of liquid B on the substrate is thick (see Figure 7c), the velocity (V) of the expansion of holes abides

$$V = V_B^* \theta_E^2 \quad (6)$$

where $V_B^* = \gamma/\eta_B$, γ and η_B are the surface tension and viscosity of fluid B, respectively.

Rafailovich's group and Geoghegan's group have further verified the theory proposed by Brochard-Wyart by experimentally studying the growth dynamics of the dewetting hole in bilayer polymer films using optical microscopy, atomic force microscopy and scanning force microscopy. The authors adjusted the viscosity of the upper polymer layer by controlling the polymer molecular weight and found that the growth velocity of holes displays a linear relationship with time when the viscosity of the upper polymer is far less than that of the underlying polymer (**Case I**) whereas $R \sim t^{2/3}$ when the viscosity of the upper polymer is larger than that of the underlying polymer (**Case II**) [46,47]. Composto *et al.* have reported accelerated growth of holes ($D \sim t^\alpha$, $\alpha > 1$, D represents the diameter of hole) for a polycarbonate film dewetting on a poly (styrene-co-arylonitrile) film [48]. The authors have

proposed that the accelerated growth of holes may result from an increase of the dewetting force given by $\gamma_A [\cos \theta_E - \cos \theta_d(t)]$ (θ_E and $\theta_d(t)$ are the equilibrium contact angle and the dynamic contact angle, respectively). If the dewetting force increases, $\theta_d(t)$ decreases. Moreover, An *et al.* have also observed a slight enhancement in the growth of holes when the viscosity of the underlying polymer is low, which is attributed to an increase of θ ($V \approx \theta^3$, θ is the dynamic angle) with time [49]. At present, it is not clear why the upper layer polymer with high viscosity will deform the underlying polymer with low viscosity when the upper layer dewets on the lower layer.

Compared with homogeneous layers and bilayers, the instability of blend films on solid surface is relatively complicated due to the simultaneous existence of dewetting and phase separation of incompatible polymers and the diverse surface morphologies (e.g. bicontinuous, discrete and insular) arising from compositional variation and/or experimental conditions [50-62]. In earlier works, Karim *et al.* have proposed that the instabilities of blend films are ascribed to phase separation/phase roughening leading to changes in surface patterns with annealing time [56]. Composto and co-workers have explained the time evolution of phase morphology using a model involving the interplay of phase roughening and capillary fluctuations caused by a long-range force [59]. Muller-Buschbaum *et al.* have also found that the morphology of blend films develops into droplets with annealing time and have proposed that both phase separation and dewetting play a significant role. In addition, the different initial morphologies of blend films are dependant on the compositions of both polymer components in the blend [57,63]. In blend films, the concentration fluctuations of compositions result in a variation of the local wetting/dewetting

force and lead to a capillary fluctuation. Clarke has developed a thermodynamic model on the basis of the height variation of the polymer film caused by capillary fluctuation [54] and has proposed that both the height fluctuation and the concentration variation may make the blend film more unstable.

At present, the exact reasons behind the instability of multi-component polymer thin films are still not clear due to the coexistence of phase separation and dewetting. In particular, it is difficult to track, without intermittent breaks, the continuous evolution of phase separation, phase growth and dewetting. This problem has been circumvented by employing single molecule tracking technique to understand the dynamics of the instability of multi-component blend films. This will be discussed in Chapter 3.

1.3 The transportation of the solute/suspended particles in the evaporating droplets

A drop of coffee deposited on the surface of a table usually leaves behind a stain after drying. This behavior has several important applications and has received significant experimental attention due to the occurrence of an ordered assembly of solute in the ring stain [64-67] (see Figure 8). Stone and co-workers have found that polystyrene particles in an evaporating drop form an ordered ring-like arrangement when the contact line experiences pinning [68]. When Wong *et al.* evaporated a DNA drop, a lyotropic liquid crystalline DNA ring with a periodic type Z pattern was obtained [69]. Tsukruk *et al.* successfully aligned a ring of guided and arched 1D nanotubes by the evaporation of a drop on the substrate with periodic alternation of hydrophobic and hydrophilic sections [70]. Corwin *et al.* obtained uniformly distributed

cracks of monodisperse silica nanoparticles in a ring when a drop is evaporated [71]. Wang *et al.* have found that noble metal nanoparticles with different shapes and sizes were also able to self-assemble into rings after the drop has dried [72].

Figure. 8 A schematic picture for the formation of ring stains.

To understand the phenomena of coffee ring stain formation, Deegan *et al.* have proposed the model where the formation of coffee ring results from capillary flow [64]. This flow transports the suspended particles into the region of the pinned contact line when the drop evaporates (See Figure 9a) [64]. Based on equation (7), the evaporating flux $J(r)$ can be calculated :

$$J(r) = -D\nabla\phi \quad (7)$$

Figure. 9 Capillary flow in the drop (a), and receding (b) and pinning (c) of the contact line when the drop evaporates.

where D and ϕ are the diffusivity and the concentration of the solvent vapor in air, respectively. The flow velocity $\bar{v}(r)$ can be evaluated according to $\bar{v}(r) \propto J(r)$. In addition, the evaporating flux on the surface of a drop is proportional to $(R-r)^{-\lambda}$, so that $J(r) \propto (R-r)^{-\lambda}$ (where $\lambda = (\pi - 2\theta)/(2\pi - 2\theta)$, and θ is the contact angle). In this case, equation (8) can be deduced :

$$t = \int_{r_t}^R dr / \bar{v} \propto (R - r_t)^{1+\lambda} \quad (8)$$

where t is the time used for transporting the solute through a distance of r (see Figure 9a) to the contact line. To calculate the mass of solute ($M(r, t)$) deposited near the contact line at the early stage, a power law relationship

$$M(R, t) = M(R, 0) \propto t^{2/(1+\lambda)} \quad (9)$$

has been given according to $M(R, 0) \propto (R - r)^2$ ($M(R, 0)$ is the initial mass). In addition, Deegan *et al.* further tested the validity of the model by performing an evaporation experiment using drops containing polystyrene microspheres, and the experimental data agree with the proposed physical model. Deegan *et al.* have also pointed out a couple of effects that influence the model, such as the shape of drops on the substrates, the deposition of some of the solute on the surface of the substrate before arriving at the pinned contact line and Marangoni effect caused by surface tension gradients. The capillary flow proposed by Deegan *et al.* is a great breakthrough for comprehending the driving force behind the formation of a single coffee ring stain.

Besides the formation of a single ring stain after drying of the drop, the multiring stains have also been observed (see Figure 8). In an early work, Adachi *et al.* evaporated a drop of water with polystyrene particles on a glass surface and observed that the contact line undergoes a stick-slip motion. This led to the formation of stripe patterns [73]. On the basis of the experimental data, Adachi *et al.* have proposed that the formation of the stripe patterns and the occurrence of the stick-slip motion result from the competition between a friction force and the surface tension at the contact line. Maeda has also obtained multi-ring collagen deposits when a drop of collagen solution dries up [74]. Deegan has also observed various patterns, such as cellular and lamellar structures, sawtooth patterns *etc.* and proposed the mechanism of self-induced pinning [75]. Subsequently, Deegan performed a series of experiments including varying the concentration and size of polystyrene microspheres in the drop, and drew a conclusion that self-induced pinning is the result of competition between the dewetting of drops and contact line pinning. Deegan

has also emphasized that both the contact line pinning and the evaporation occurring near the contact line play an importance role in the formation of rings. The rings can be formed as long as the contact line is pinned (see Figure 9c), even if the receding of the contact line occurs, such as from A to B and then to C (see Figure 9b). Stone *et al.* have also proposed that multi-ring stains of polystyrene particles arise from the pinning-depinning of the contact line [68]. In the pinning-depinning process, the polystyrene particles were deposited and arranged in an orderly manner near the contact line (see Figure 10a). The steps of the pinning-depinning cycles of the contact lines are random. This observation is different from the strong periodic stick-slip motion reported by

Figure. 10 A schematic picture of different mechanisms of solute deposition.

Adachi *et al* [73]. In addition, the paper published by Chang *et al.* has shown another mechanism different from the one proposed by Stone where capillary dimple near the contact line exists [76]. The formation of the rings is due to the

solute in the contact line region being prevented from flowing towards the drop interior as capillary dimples form (see Figure 10b). This mechanism is also used to explain the formation of DNA ring stains by Chang *et al.* who proposed that the formation of multi-ring DNA stains is the result of the mutual interaction of deposition and stick-receding motion of the contact line [77]. Recently, Thiele *et al.* have modelled the dynamics of a contact line according to the long-wave approximation [78] and have found that both the evaporation-dominated and the convection-dominated mechanisms near the contact line control the pinning and depinning processes of the contact line. The concentration of solute increases substantially when the rate of evaporation is greater than the rate of convection in the contact line region. This results in the stopping (so-called pinning) of the contact line motion. Reversely, the contact line motion displays a slip (so-called depinning) when the convection dominates. In this way, all types of patterns can be explained well by the pinning and depinning of the contact line. However, the exact reason for the pinning is still largely unknown.

Effects of Marangoni flow in the drop has also been explored by Deegan *et al.* [64,75]. Marangoni effect arises from the surface tension gradient created by a non-uniform distribution of temperature, concentration variation of the mixed liquid components or addition of surfactant into the evaporating drop. Hu and Larson [79] have demonstrated by numerical calculations that the recirculation of Marangoni flow will occur when the contact angle is beyond 14° in the evaporating drop. This Marangoni flow results from a temperature gradient (see equation 10). When the drop is contaminated (e.g. with a surfactant),

Marangoni flow will be driven by an extra surfactant concentration gradient (see equation 11).

$$\frac{d\sigma}{Rd\tilde{r}} = \frac{d\sigma}{dT} \frac{dT}{Rd\tilde{r}} \quad (10)$$

$$\frac{d\sigma}{Rd\tilde{r}} = \frac{d\sigma_T}{Rd\tilde{r}} + \frac{d\sigma_S}{Rd\tilde{r}} \quad (11)$$

where σ , R , $\tilde{r}$, $d\sigma_T/Rd\tilde{r}$ and $d\sigma_S/Rd\tilde{r}$ are the surface tension, the contact line radius, $\tilde{r} \equiv r/R$ ($r \leq R$ on the drop surface), the Marangoni stress induced by a temperature gradient and the Marangoni stress induced by a surfactant concentration gradient, respectively. Hu and Larson have proposed that the temperature at the edge of a drop is higher than that at the top of the drop, and the temperature at the top is lower than that of the base of the drop when the contact angle of the drop is more than 14° . In this case, a clockwise recirculation of Marangoni flow occurs radially inwards firstly and then outwards (see Figure 11).

Figure. 11 A schematic picture of Marangoni flow radially directed outwards along the substrate where θ is $>14^\circ$.

In a subsequent work, Hu and Larson have found that the recirculation of the Marangoni flow in an organic solvent drop is stronger than that of water since water is contaminated more easily than an organic solvent [80]. Besides an outward Marangoni flow radially along the substrate, Stone and co-workers have proposed Marangoni flow directed radially inwards along the substrate towards the center of the drop (see Figure 12). Stone *et al.* have derived a relationship between the contact angle and the conductivity between substrate and liquid [81].

$$k_R^{\text{crit}} = \tan(\theta) \cot\left(\frac{\theta}{2} + \frac{\theta^2}{\pi}\right) \quad (12)$$

where $k_R \equiv k_S/k_L$ (k_S and k_L are the substrate conductivity and the liquid conductivity, respectively) and θ is the contact angle. Marangoni flow is directed radially outwards along the substrate when k_R is greater than 2 (see Figure 11), and directed radially inwards along the substrate when k_R is less than 1.45 (see Figure 12).

Figure. 12 A schematic picture of Marangoni flow radially directed inwards along the substrate

Tears of wine are well-known and they result from a concentration variation of water and ethanol at the contact line. Ethanol with a high vapor pressure and low surface tension is evaporated away preferentially. In this case, a surface tension gradient is created between the water-rich contact line with a high surface tension and the bulk solution. This leads to the occurrence of the Marangoni flow from the interior of the solution to the contact line. Conversely, if the phase near the contact line has a low surface tension as compared to the bulk solution, the direction of the Marangoni flow will be reversed.

The dynamics of fluid in an evaporating drop has been investigated using relatively large (*e.g.* micro-scale) particles due to the ease of observing the behavior of the slow moving particles. However, smaller particles (*e.g.* nano-scale particles and polymer chains) are difficult to visualize due to the limited temporal and spatial resolution of conventional techniques. In this case, techniques with high resolution are needed to study the dynamics of fluid in evaporating droplets containing small molecules/particles. In chapter 4 the behaviour of the contact line and the solute close to the contact line of an evaporating binary solvent drop will be examined using WFM in order to elucidate the driving force behind the self-assembled multiring patterns.

1.4 Single-molecule/particle tracking (SMT/SPT) technique

Single-molecule/particle tracking (SMT/SPT) technique is a powerful tool to track the diffusion of single fluorescent molecules/particles and can be achieved by wide field microscopy (WFM) (see Figure 13). The WFM consists of a microscope and a laser source. The excitation light is passed through an excitation filter and reflected into an objective lens before exciting the sample.

The fluorescence from the sample is allowed to pass through the dichroic mirror and an emission filter before being detected by a highly sensitive CCD camera after magnification with a camera lens.

Figure. 13 Scheme of the wide field microscopy set-up. Laser light from the source passes through an excitation filter and is reflected into the objective lens by a dichroic mirror to excite the sample, and then the emission of light from the sample through the dichroic mirror and emission filter is recorded by the CCD camera.

SMT/SPT has been used to explore several biological processes, such as the infection pathways of viruses [82], plasmodium transmission [83], transport of gene carriers [84] and relating phospholipase mobility to activity [85]. In the investigation of the diffusion of single molecules in thin silica sol-gel films by SMT/SPT, Harris *et al.* have demonstrated that the structure of such films is spatially heterogeneous [86]. Hofkens *et al.* and Bräuchle *et al.* have also

applied SMT/SPT to probe the effect of crystal face of the catalyst on the catalysis efficiency and the effect of nano-structures on the diffusion of single molecules [87,88]. In the area of polymer science, Hofkens *et al.* [89] and Tezuka *et al.* [90] have used the SMT/SPT technique to study the diffusion of single polymer chains during polymerization and the diffusion of single ring polymers, respectively.

The diffusion of single molecules/particles is visualized by recording the images of the diffusing molecule/particle using a CCD camera and the fluorescence intensity of the diffraction limited spots in the image frames are fitted using a two-dimensional Gaussian function [91,92,93,94]

$$I(x,y) = A_n \exp(-((x - x_n)^2 + (y - y_n)^2)/w_n) \quad (13)$$

in order to determine the position of each single molecule/particle accurately. In equation (13), A_n , w_n , and (x_n, y_n) represent the peak height of the Gaussian distribution, width at position (x_n, y_n) and the co-ordinate of the center position of the diffraction limited spot, respectively. The error of the resulting position (x_n, y_n) for each diffraction limited spot depends on instrument resolution, the density of sample points, and the signal-to-noise ratio of the data [95]. After obtaining the position of a single molecule/particle in each frame with time, the mean square displacement $\langle r(t_n)^2 \rangle$ can be calculated by [91]

$$\langle r(t_n)^2 \rangle = \frac{1}{j-n} \sum_{i=1}^{j-n} r_{i,i+n}^2 \quad (14)$$

where $r_{i,i+n}$ is the distance moved between frames i and $i+n$, and j is the total number of frames. Based on the functional relationship of the mean square displacement $\langle r(t)^2 \rangle$ with time interval t , the motion of single molecules/particles are divided into random motion, directed motion and confined motion (see Figure 14) in two dimension.

Figure. 14 Three plots of $\langle r^2(t) \rangle$ vs. time t for different motions are shown.

Case I : The expression for random motion is described by [91,93,94]

$$\langle r(t)^2 \rangle = 4Dt \quad (15)$$

where D is the diffusion coefficient.

Case II : The expression of directed motion is [96]

$$\langle r(t)^2 \rangle = 4Dt + (Vt)^2 \quad (16)$$

where D and V are the diffusion coefficient and drift velocity, respectively.

Case III : The expression for confined motion is [91]

$$\langle r(t)^2 \rangle = r_{\max}^2 [1 - \exp(-4Dt/r_{\max}^2)] \quad (17)$$

where $r_{\max}^2$ represents a maximum mean square displacement for longer times.

For the case of random motion, to test the distribution of each step when a single molecule/particle diffuses, an equation is extracted from the classic diffusion theory [97], namely, [91,93,94]

$$q(r, t) = (r/2Dt) \exp(-r^2/4Dt) \quad (18)$$

where $q(r, t)$ is the distribution of displacement in time t . According to equation (15), equation (18) can be transformed into

$$q(r, t) = (2r/\langle r(t)^2 \rangle) \exp(-r^2/\langle r(t)^2 \rangle) \quad (19)$$

When r^2 (the squared step length) is equal to u ,

$$p(u, t) = (1/\langle r(t)^2 \rangle) \exp(-u/\langle r(t)^2 \rangle) \quad (20)$$

where $p(u, t)$ is the distribution of the squared step length in time t . In this case, the cumulative probability is obtained by

$$P(U, t) = \int_0^U p(u, t) du = 1 - \exp(-U/\langle r(t)^2 \rangle) \quad (21)$$

where $P(U, t)$ is the cumulative probability distribution. When the value of u is not larger than U , an exponential decay function is established

$$C(U, t) = 1 - P(U, t) = \exp(-U/\langle r(t)^2 \rangle). \quad (22)$$

1.5 Outline of the Thesis

The outline of the thesis is as follows:

Chapter 1. General introduction and a general review of the literature on crystallization of ultrathin polymer films, instabilities of polymer thin films, transportation of solute/suspended particles to the contact line of evaporating droplets to form ringlike deposits and single-molecule/particle tracking technique are given.

Chapter 2. Wide-field microscopy is used for the first time to study the crystallization process of single poly(ethylene oxide) chains in ultrathin layers deposited on a substrate. Various types of motion, such as Brownian and directed motions, are observed just before crystallization.

Chapter 3. Both wide-field microscopy and atomic force microscopy are utilized to investigate the evolution of morphology change of binary blend film with annealing time. A new mode of nucleation mechanism involving

domain coalescence is proposed. In addition, the inclusion of poly(2-vinyl pyridine) domains during hole expansion results in irregular shaped holes and accelerated hole growth.

Chapter 4. Multiple ring deposits of poly(2-vinyl pyridine) from the evaporation of a P2VP-binary solvent drop on a glass substrate were formed by a spreading and receding mechanism which is different from the conventional pinning and depinning mechanism. We have demonstrated that a surface tension gradient created as a result of a solutal-Marangoni effect plays an important role in enhancing the droplet spreading rate.

1.6 Bibliography

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CHAPTER 2

Visualizing polymer crystallization in ultrathin layers using a single-macro-molecule tracking method

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2.1 Introduction

Polymer crystallization is a fundamental process in polymer physics and is known to occur in thermoplastic materials commonly used in the aerospace, automobile and microelectronics industries. An extensive number of studies have been dedicated to understand the transition processes of (semi)flexible polymers in their random amorphous states to ordered crystalline states [1,2]. In particular, the kinetics of crystal growth in bulk samples have been examined using small-angle X-ray scattering (SAXS), polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). Recently, atomic force microscopy (AFM) was utilized to probe the crystallization behavior of thin films of poly(ethylene oxide), PEO, on the surfaces of solid substrates [3-7]. Fractal-like crystals were observed and their growth dynamics was described using a model that considers the diffusion-limited transport of polymeric chains and the probability of their attachment to the crystal front [8]. However, these techniques yield only ensemble-averaged information on the thickening dynamics of lamellar crystals and do not provide information on the kinetics of mobile polymers in the vicinity of the crystals just before crystallization. Understanding the dynamics of the transportation pathways of single macromolecules prior to crystallization yields a better insight into the driving force behind crystal growth.

Single-(macro)molecule tracking (SMT) *via* wide-field microscopy (WFM) has been used to track, in real-time, important processes occurring in biological systems and inorganic materials [9-13]. In this study, WFM is used to probe the behavior of diffusing polymers at different regions from the crystal

(*i.e.*, amorphous layer and less concentrated/depleted zone), and the motions of polymeric chains prior to crystallization.

2.2 Experimental

2.2.1 Materials

α -Methoxy ω -amino terminated poly(ethylene oxide) ($M_n = 5000 \text{ g mol}^{-1}$, $M_w/M_n = 1.06$, PEO) with a radius of gyration $R_g = 2.6 \text{ nm}$ was obtained from Polymer Source Inc., and the photostable dye, Atto647N NHS-ester, was purchased from Atto Tec GmbH. Anhydrous dimethylsulfoxide (99.9%, Aldrich, DMSO), and tetrahydrofuran (spectrophotometric grade, Sigma Aldrich, THF) were used as received.

2.2.2 Labeling of PEO with Atto647N

The PEO was labeled by the reaction of its terminal amino group, NH_2 , with the NHS-ester moiety of Atto647N. 2.5 mg of PEO was dissolved in 1 mL of DMSO at 40°C , followed by the addition of 1 mg of Atto647N NHS-ester into the solution. The solution was then allowed to react under stirring for 4 h. Subsequently, 1 mL of the resulting solution was dispersed into 10 mL of ultrapure DI water. Free dye was removed from the solution by using a high performance dye removal column (Thermo Scientific). The eluate was further treated with a new dye removal column, and this step was repeated at least three times. Labeled PEO was stored at -20°C and protected from light when not in use.

2.2.3 Preparation of PEO sample for wide-field microscopy study

Monolayer of PEO on glass surfaces was prepared following the procedure by Zhai and co-workers [3,4,5]. Glass coverslips (Menzel-Gläser) were placed in a water-saturated UV-ozone atmosphere for more than 10 h to achieve a high density of OH groups on the surfaces. The treated coverslips were then cleaned using the method described in reference [14]. The THF solution containing 0.02 wt % of unlabeled PEO was prepared by sonicating an appropriate amount of unlabeled PEO in THF at 30°C for 5 min. 2 μ L of the labeled PEO solution was diluted in 0.5 mL of THF, and 1 to 2.5 μ L of the resulting solution was added into 1 mL of the unlabeled PEO solution. The final concentration of labeled PEO is $\sim 10^{-10}$ M which is suitable for single-molecule spectroscopy. An ultrathin PEO film is prepared by dropping the polymer solution, containing both labeled and unlabeled PEO, onto a clean coverslip at room temperature. The sample was dried at ambient condition for at least 8 h before further drying in an evacuated desiccator for more than 24 h. The dried sample was heated to 75°C for 5 min to allow the crystals to melt completely, and then allowed to cool to 45°C. The sample was then maintained at 45°C using the warm microscope stage (Linkam Scientific Instrument (DC60)) for subsequent wide-field microscopy experiments.

2.2.4 Wide-field microscopy

The wide-field fluorescence microscopy setup consists of a microscope (IX 71, Olympus) and a 633 nm HeNe laser source (35 mW, Melles Griot). The excitation light was tuned to be circularly polarized using $\lambda/4$ and $\lambda/2$ waveplates and expanded *via* a beam expander (ThorLabs) before being focused onto the back-focal plane of an oil immersion objective lens (100 $\times$,

N.A. 1.3, Olympus). An excitation filter (Z633/10, Chroma) was used to filter the excitation light. The fluorescence was passed through a dichroic mirror (Z633rdc, Chroma) and an emission filter (HQ645lp, Chroma) and subsequently detected by a highly sensitive CCD camera (CascadeII 512B, Photometrics) after magnification with a $3.3\times$ camera lens. The dimension of a wide-field fluorescence frame was measured to be $24.7 \times 24.7 \mu\text{m}^2$ using a stage micrometer, and the power density was adjusted to be about 0.165 kW cm^{-2} . The integration time of the CCD camera is 34.6 ms per frame.

2.2.5 Single-macromolecule tracking

The fluorescent images of single molecules appear as diffraction-limited spots of radius $\sim 297 \text{ nm}$. Fluorescent spots in each image were located using the Image-Pro Plus software (AMS version 5.5.1, MediaCybernetics). Only clear and discernible diffraction spots are tracked in all our analysis. In order to obtain the position of the molecule, (x_n, y_n) , the intensity distribution of each spot was fitted to a two-dimensional Gaussian function with peak intensity A_n and width w_n [15,16]:

$$I(x,y) = A_n \exp(-((x - x_n)^2 + (y - y_n)^2)/w_n) \quad (1)$$

A macromolecule positioning accuracy of $\pm 22 \text{ nm}$ was obtained from the variance of position measurements of an immobile particle. 100 frames were captured for this immobile particle. The intensity distribution of the particle in each frame was fitted to equation (1). In this case, an average value of x_n and y_n with $\pm 22 \text{ nm}$ was obtained from 100 frames. Pixel size of our camera is $512 \text{ pixel} \times 512 \text{ pixel}$. Number of pixels for the particle is about $15\sim 20 \text{ pixel} \times$

15~20. Each pixel $\times$ pixel represents about $48.2 \times 48.2 \text{ nm}^2$. In addition, the error of accuracy of position depends on the signal-to-noise ratio of the data. Therefore, the positioning accuracies of the different particles are different.

The mean square displacement (MSD) analysis is performed by determining the mean square displacement of a molecule $\langle r(t_n)^2 \rangle$ as a function of different delay time, $t_n = n\delta t$, where n is the number of frames and δt is the time interval between frames. The value of $\langle r(t_n)^2 \rangle$ is obtained using the following expression [15]:

$$\langle r(t_n)^2 \rangle = \frac{1}{j-n} \sum_{i=1}^{j-n} r_{i,i+n}^2 \quad (2)$$

where $r_{i,i+n}$ is the distance moved between frames i and $i+n$, and j is the total number of frames.

2.3 Results and discussion

2.3.1 Mean square displacement (MSD) analysis

Figure 1(a) shows a wide-field fluorescence image of a PEO sample maintained at 45°C for 35 h and trajectories of the diffusion of several PEO chains are shown in Figure 1 (b). At this time, no crystals are formed and the polymeric chains undergo random motion in the amorphous layer (see Movie 1). Mean square displacement (MSD) analysis is performed by calculating the mean square displacement ($\langle r^2(t) \rangle$) for different delay times (t), and the diffusion coefficient (D) for Brownian motion in two dimension is obtained

Figure. 1 (a) Wide-field fluorescence image of a PEO sample maintained at 45°C for 35 h. (b) Trajectories of the diffusion of several PEO chains.

Figure. 2 Trajectory of the diffusion of a PEO chain obtained by SMT at 35 h (inset). The $\langle r^2(t) \rangle$ against t plot obtained by MSD analysis (●) is in good agreement with the $\langle r^2(t) \rangle$ against t plot obtained using $\langle r^2(t) \rangle$ from equation (1) (◆). The straight line is the linear fit for the first 6 s of the MSD plot using the equation $\langle r^2(t) \rangle = 4Dt$ where $D = 2.9 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$.

Figure. 3 The $\langle r^2(t) \rangle$ vs. t plot for the next 86 steps of the trajectory shown in Figure 2 (M1 in Figure. 1 (b)).

from the relationship $\langle r^2(t) \rangle = 4Dt$. Figure 2 shows the single- macromolecule trajectory of a representative polymeric chain corresponding to 260 steps (9 s) (see M1 in Figure 1 (b)). The plot of $\langle r^2(t) \rangle$ against t (Figure 2) reveals a straight line ($D = 2.9 \times 10^{-14} \text{ m}^2\text{s}^{-1}$) for the first $t = 6$ s followed by a faster motion for the next 3 s with $D = 4.4 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ (see Figure 3), possibly arising from a less constrained environment. This may arise from a reduced polymer-surface interaction, less entanglement and different loop tightness. It is still not clear which factor dominates, however, the trajectory clearly shows the motion changing as it moves into different regions. The latter is not unexpected for long trajectories since the molecule has a probability of returning to a location close to its initial position at long times [17]. An alternative method of obtaining MSDs is to determine the probability that the squared displacement (r^2) exceeds a value U for a given t , $C(U, t)$:

$$C(U, t) = \exp[(-U)/\langle r^2(t) \rangle] \quad (3)$$

Mono-exponential decays of $C(U, t)$ at different delay times (see Figure 4) and a good agreement between the plots of $\langle r^2(t) \rangle$ against t based on equation 3 and the MSD analysis (Figure 4) suggest that only one type of motion is present in the trajectory.

MSD analysis corresponding to the first 30 steps (1 s) of the trajectory was performed on 60 polymeric chains and the linear plots of $\langle r^2(t) \rangle$ against t are given in Figure 5. Each PEO chain has a characteristic D value that ranges from 1×10^{-15} to $3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$. At the single-molecule level, the nano-environment of the crowded amorphous layer may contain 1-2 layers of PEO such that the

Figure. 4 Plot of cumulative probability of r^2 for three delay times (0.2, 2.0 and 4.5 s) for molecule M1 in Figure 1 (b). The decay curves are fitted using a mono-exponential decay function (see equation 3).

Figure. 5 $\langle r^2(t) \rangle$ against t plot for 60 PEO polymeric chains obtained at 35 h.

adsorbed chains adopt a train-loop-tail conformation (such as chains “a and b” in Figure 6) with the loops forming barriers [18,19]. The chains diffuse by a hopping process where segments are desorbed and adsorbed at a new random position. In their immediate environment, individual polymeric chains experience different fractions of potential adsorption sites with the surface and different polymer-surface interactions due to heterogeneities in surface topography and surface chemistry [18,19]. Furthermore, non-adsorbed chains can thread through surface-attached loops such that these polymers undergo reptation diffusion of varying rates as a result of different loop tightness and the presence of a near-surface gradient of monomeric friction coefficient [18,19]. These will lead to the non-homogeneous behavior observed in Figure 5.

Figure. 6 Depiction of the conformation of the adsorbed PEO chains on glass surface [Ref. 18 and 19].

A typical wide-field fluorescence image of a PEO sample maintained at 45°C for 47 h shows fractal-like crystal patterns (see Figure 7(a)) similar in shape to the ones measured previously by AFM [3,4,5]. This suggests that a diffusion-limited aggregation mechanism for crystal growth is in operation

Figure. 7 (a) Wide-field image of a PEO sample maintained at 45 °C for 47 h.
(b) Trajectories of the diffusion of several PEO chains.

[20,21]. After 47 h, crystallization is incomplete since mobile chains are visible outside the perimeter of the crystal (see Movie 2 and Figure 7 (a)). Polymers far removed from the crystal edge, such as those found in region A of Figure 7 (a) (*i.e.*, type A polymers), display Brownian motion kinetics similar to those observed after a waiting time of 35 h. On the other hand, a significantly larger proportion of polymers close to the crystal (*i.e.*, type B polymers), where the separation between the polymer and the crystal edge is within 1 to 2 diffraction limited spots ($< 1 \mu\text{m}$ where the radius of a diffraction spot is $\sim 297 \text{ nm}$), undergo slower random motion. Examples of type B polymers are found in region B of Figure 7 (a). From the linear plots of $\langle r^2(t) \rangle$ against t , we note that 97% of 100 type B polymeric chains analyzed (see Figure 8) showed D values smaller than $1 \times 10^{-13} \text{ m}^2\text{s}^{-1}$, whereas 68% of the same number of type A polymers studied exhibited $D < 1 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ (see Figure 9).

Figure. 8 $\langle r^2(t) \rangle$ against t plot for 100 type B polymeric chains obtained after 47 h. The straight line D corresponds to the linear function $\langle r^2(t) \rangle = 4Dt$ where $D = 1 \times 10^{-13} \text{ m}^2\text{s}^{-1}$.

Figure. 9 $\langle r^2(t) \rangle$ against t plot for 100 type A polymeric chains obtained after 47 h. The straight line D corresponds to the linear function $\langle r^2(t) \rangle = 4Dt$ where $D = 1 \times 10^{-13} \text{ m}^2\text{s}^{-1}$.

The diffusion coefficient (D_{2D}) obtained using a 2D diffusion model ranges from 1×10^{-15} to $3 \times 10^{-13} \text{ m}^2\text{s}^{-1}$ as reported. In the case of random 3D motion, the mean-square displacement $\langle r^2(t) \rangle = 6D_{3D}t$, where D_{3D} is the corresponding 3D diffusion coefficient [13,22,23]. For similar mean-square displacements, $D_{3D} = 2D_{2D}/3$ which clearly shows that 3D motion does not explain the large D dispersion in our experiments. Furthermore, diffusion of molecules in 3D biological membranes and mesoporous silica systems of similar volumes has been well characterized using a 2D diffusion analysis [13,22,23].

2.3.3 AFM results

The discrepancy in diffusion rate behavior observed between type *A* and type *B* polymers is ascribed to the presence of a less concentrated/depleted zone between the crystal and the amorphous layer [3-7]. The thickness of the amorphous layer and the less concentrated/depleted zone was measured using a scanning probe microscope (D3100V, Veeco Digital Instruments) using a Si tip in the tapping mode. The average thickness of the amorphous layer is *ca.* 3 nm (**A** in Figure. 10) while the thickness of the less concentrated/depleted zone (**B** in Figure. 10) is < 3 nm. The thickness of the amorphous layer is in agreement with the film thickness of the PEO films reported in references [3-8] (*i.e.*, 3 to 5 nm). The less concentrated/depleted zone results from the extraction of the chains adsorbed on the glass surface towards the growing crystal front. Therefore, a concentration gradient is created on the surface of the substrate close to the crystal such that the surface has a low surface coverage of polymers and may not be molecularly covered [6]. In this case, the polymers adopt a more pancake like conformation such that the proportion of monomeric contacts for each chain increases [24,25]. In addition, the relatively more mobile non-adsorbed chains are significantly reduced. Therefore, it is not unexpected to observe the absence of fast moving polymers in the less concentrated/depleted zone (see Figure 10).

Figure 10. a) AFM image of the crystal formed in our ultrathin PEO film. b) Cross-section plot of the amorphous layer (A) and less concentrated/depleted zone (B), and the crystal (C). (D) represents the bare glass surface.

2.3.4 Investigation of the dynamics of attachment and detachment of PEO chains at crystal front

We next examine the motion of PEO chains prior to crystallization. In this case, single PEO chains displaying diffusion toward the crystal followed by deposition onto the crystal edge are investigated. In general, polymers either diffuse randomly or display a directed motion toward the crystal. The most common motion is shown in Figure 11 where a polymeric chain undergoes Brownian motion toward a crystal before attaching itself onto the crystal-growth front. For this particular polymer, it subsequently undergoes desorption from the crystal surface and diffuses away from it (see Movie 3).

Figure. 11 Trajectories of the diffusion of a PEO chain before attachment onto the crystal (Begin 1 $\rightarrow$ End 1) and after detachment (Begin 2 $\rightarrow$ End 2) (inset). Linear $\langle r^2(t) \rangle$ against t plots are obtained for both trajectories based on the MSD analysis.

From the linear plots of $\langle r^2(t) \rangle$ against t (see Figure 11), the diffusion coefficients before attachment and after detachment are $8.6 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ and $7.3 \times 10^{-14} \text{ m}^2\text{s}^{-1}$, respectively, suggesting that the two random motions are not significantly different. The polymer thus moves with a single type of motion.

Figure 12(a) shows the trajectory of another polymeric chain just before it crystallizes. The diffusion behavior is analysed by plotting the cumulative probability of the squared displacements for different time delays (*i.e.*, equation 3). The plots for three delays, 34.6 ms, 138.4 ms and 276.8 ms are given in Figure 12(a). The decay profiles are best described using a double-exponential decay function indicating that the macromolecule is diffusing randomly in two diffusion regimes. This is clearly depicted in the trajectory (see Figure 12(a) and Movie 4) that shows the polymeric chain initially diffusing towards the crystal followed by a significantly slower random motion when the macromolecule is next to the crystal surface. The polymer then moves away from the crystal before diffusing back to the surface and attaching itself onto the crystal-growth front. The diffusion coefficients are obtained by fitting the mean square displacement $\langle r^2(t) \rangle$, derived from equation 3, against t . The linear plots in Figure 12(b) yield $D = 6.2 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ and $0.6 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ for the fast and slow diffusion motions, respectively. A plausible reason for the occurrence of dual diffusion motion for the PEO chain is the different environment experienced by the polymer.

Figure. 12 (a) Trajectory of the diffusion of a PEO chain displaying two types of motion before attachment onto the crystal edge (inset). The plots of $C(U, t)$ against r^2 for three delay times (34.6, 138.4 and 276.8 ms) are best described using a double-exponential decay function. (b) Plots of $\langle r^2(t) \rangle$ against t for the polymer shown in b) for the fast (■) and slow (●) diffusion motions.

Directed motion of macromolecules towards the crystal surface before attachment is observed and is illustrated by the trajectory of the PEO chain in Figure 13 (see Movie 5). The $\langle r^2(t) \rangle$ against t plot deviates from linearity and curves upward with increasing t . By fitting the curve using the equation $\langle r^2(t) \rangle = 4Dt + (Vt)^2$ [22], a drift velocity of $V = 1.7 \times 10^{-7} \text{ ms}^{-1}$ and a diffusion coefficient of $D = 0.6 \times 10^{-14} \text{ m}^2\text{s}^{-1}$ are obtained. This behavior suggests the interplay between the polymer-surface and polymer-crystal interaction, however, the exact nature of the motion remains unclear and more work is needed to fully understand its properties. Finally, crystallization is completed after $> 65 \text{ h}$, and a typical crystal pattern is given in Figure 14 (see Movie 6).

Figure. 13 Trajectory of a PEO polymeric chain exhibiting directed motion towards the crystal edge (inset). The plot of $\langle r^2(t) \rangle$ against t is fitted using the equation $\langle r^2(t) \rangle = 4Dt + (Vt)^2$.

Figure. 14 Wide-field microscopy images of a PEO sample maintained at 45°C for > 65 h.

2.3.5 Effect of the labeled dye on the motion of PEO chains

The aromatic Atto647N dye may affect both the transportation of the polymer on the substrate and its probability of attachment to the crystal. The interaction between the moderately hydrophilic dye and the glass substrate is weak compared to the interaction between the hydrophilic PEO and substrate. A possible outcome is that the dye can create a tail and reduce the attachment of the PEO segments located near it. Due to surface heterogeneity, the extent of this effect is not homogeneous for all the chains, and becomes one of several plausible factors affecting the diffusion dynamics of individual chains moving toward the crystal. The presence of the bulky dye may also alter the probability

of chain attachment to the crystal front and the time taken for the chain to undergo folding and orientation inside the lamellae. This will likely affect the degree of perfection of the crystal. It is, however, not clear from the wide-field microscopy experiment how the attached dye perturbs these factors.

2.4 Conclusion

Wide-field microscopy is used for the first time here to study the crystallization process of single PEO chains in ultrathin layers deposited on a substrate. Various types of motion, such as Brownian and directed motions, are observed just before crystallization. PEO chains in the amorphous layer and in the less concentrated/depleted zone exhibit Brownian motion of different rates as a result of heterogeneities in the environment. It would be interesting to see how the entropic differences in the non-crystalline regions can influence the chain diffusion for ultrathin films as reported recently for a solution-crystallized sample of polyethylene [26].

2.5 Movie captions

Movie 1. At 35 h

Movie 2. At 47 h

Movie 3. Macromolecule (circled) diffusing towards the crystal and undergoing attachment onto the crystal. Subsequently, it detaches from the crystal and moves away from it. Movie recorded at 47 h.

Movie 4. Macromolecule (circled) undergoing diffusion before attaching itself onto the crystal growth-front. Movie recorded at 47 h.

Movie 5. Macromolecule (circled) undergoing directed motion towards the crystal before attaching itself onto the crystal growth-front. Movie recorded at 47 h.

Movie 6. At > 65 h.

2.6 Bibliography

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CHAPTER 3

Domain Coalescence-Induced Nucleation and Anomalous Growth of Holes in Thin Polymer Blend Films

This chapter is adapted from: “Domain Coalescence-Induced Nucleation and Anomalous Growth of Holes in Thin Polymer Blend Film, Wuguo Bi and Edwin K. L. Yeow, *Phys. Rev. Lett.* **106**, 078001 (2011).”

3.1 Introduction

The judicious control of the morphology of thin polymer blend films has led to several important applications including microelectronics fabrication and optical lithography in the semiconductor industry [1,2]. A significant amount of attention has been directed toward understanding phase behavior changes in polymer blends induced by thermal annealing [3,4,5]. Due to the slow morphology change associated with thermal annealing, it is difficult to track, without intermittent breaks, the continuous evolution of phase separation, phase growth and dewetting using traditional techniques such as atomic force microscopy (AFM) and optical microscopy. Therefore, important information such as the transition mechanism between different evolutionary stages is either ambiguous or unavailable.

One of the aims of this work is to visualize, in real-time and without in-between breaks, the phase growth and dewetting processes occurring in polymer blend films at both the ensemble and single-macromolecule levels using wide-field fluorescence microscopy (WFM). Single-macromolecule tracking *via* WFM has recently been utilized by us [6] and Hofkens *et al.* [7] to study important polymer behavior such as crystallization and polymerization. In previous investigations of polymer dewetting by the nucleation and growth mechanism, the origin of nucleation is often unclear [8]. In this chapter, we show that domain coalescence triggered by solvent annealing is responsible for the nucleation of holes in our polymer blend systems. Dewetting occurs when the polymers are mobilized by vapor treatment as discussed by Müller-Buschbaum and co-workers [9].

3.2 Experimental

3.2.1 Materials

Polystyrene PS of various molecular weights ($M_w = 290K$ ($M_w/M_n = 2.23$), $M_w = 135.5K$ ($M_w/M_n = 1.13$), $221K$ ($M_w/M_n = 1.08$)) were purchased from either Sigma Aldrich or Polymer Source Inc. while α -Amino, ω -carboxy terminated poly(2-vinyl pyridine) P2VP ($M_w = 13K$ ($M_w/M_n = 1.3$) and $M_w = 140.6K$ ($M_w/M_n = 1.04$)) and amino terminated polystyrene ($M_w = 355K$, $M_w/M_n = 1.18$) were obtained from Polymer Source Inc. The photostable dye, Atto647N NHS-ester, was purchased from Atto-Tec GmbH. Anhydrous dimethylsulfoxide (DMSO, 99.9%, Aldrich), anhydrous ethylbenzene (99.8%, Sigma Aldrich), chloroform ($CHCl_3$, spectrophotometric grade, Sigma Aldrich), methanol (MeOH, HPLC/spectro grade, Tedia) and cyclohexane (99.9%, Fisher Scientific) were used as received.

3.2.2 Labeling of P2VP and PS with Atto647N

The α -Amino, ω -carboxy terminated poly(2-vinyl pyridine) was labeled by the reaction of its terminal amino group, NH_2 , with the NHS-ester moiety of Atto647N. 10 mg of α -amino, ω -carboxy terminated poly(2-vinyl pyridine) was dissolved in 1 mL of anhydrous DMSO at 40 °C, followed by the addition of 1 mg of Atto647N NHS-ester into the solution. The mixture was then allowed to react under stirring for 4 h. The labeled P2VP was precipitated out by adding the DMSO P2VP solution into triply distilled DI water and recovered by centrifugation. The procedure for removing free dyes is as follows: the recovered P2VP was first dissolved in MeOH and then precipitated out by adding the MeOH P2VP solution into DI water before extraction by

centrifugation. The free dye removal procedure was repeated at least three times.

The amino terminated polystyrene was labeled by the reaction of its terminal amino group, NH_2 , with the NHS-ester moiety of Atto647N. 31 mg of PS was dissolved in 1 mL of mixture solution consisting of 0.5 mL of anhydrous DMSO and 0.5 mL of anhydrous ethylbenzene at 40 °C, followed by the addition of 1 mg of Atto647N NHS-ester into the solution. The mixture was then allowed to react under stirring for 4 h. The labeled PS was subsequently precipitated out by adding the DMSO PS solution into MeOH and recovered by centrifugation. The procedure for removing free dyes is as follows: the recovered PS was first dissolved in CHCl_3 and then precipitated out by adding the CHCl_3 P2VP solution into MeOH before extraction by centrifugation. The free dye removal procedure was repeated at least three times.

3.2.3 Preparation of thin PS:P2VP blend films

A polymer blend mixture was prepared by dissolving 65% (wt) of non-labeled PS ($M_w = 290\text{K}$) and 35% (wt) of non-labeled P2VP in CHCl_3 . The mixture was further diluted to a concentration of 0.01 g/mL in CHCl_3 and filtered using a syringe drive filter unit (PVDF Durapore, Millipore). Labeled P2VP (ca. 10^{-7} M) and labeled PS ($M_w = 355\text{K}$, ca. 10^{-9} M) were added into the polymer blend mixture for ensemble and single-macromolecule experiments, respectively. Thin polymer blend films were prepared by spin-coating the resulting solution onto cleaned glass coverslips (Menzel-Glaser). The glass coverslips were pre-cleaned by sonication in acetone (HPLC, Tedia) for 10 min followed by sonication in aqueous sodium hydroxide (Scharlau) for 30 min and then sonication in DI water for 10 min. The last step was repeated three times.

The thickness of the film, measured using an ellipsometer (autoSE, Horiba Jobin Yvon), was ca. 72 nm. Similar procedure is used for the preparation of the blend with composition PS:P2VP = 50%:50% and 30%:70% and molecular weight ratio PS:P2VP = 135.5K:13K, 221K:13K and 355K:13K. The initial thickness of each film is measured to be < 80 nm using an ellipsometer.

In the WFM solvent annealing experiment, the samples were placed inside a sealed chamber saturated with CHCl_3 vapor produced by warming a bottle of CHCl_3 solvent (see Figure 1 for a scheme of the experimental set-up). To image the PS/P2VP interface using AFM, the PS layer was removed by immersing the samples in cyclohexane for > 3 h and then dried by blowing Ar gas.

Figure. 1 Schematic of the solvent annealing experiment.

3.2.4 Atomic force microscopy (AFM) and wide-field microscopy (WFM)

The morphologies of the surface of the blend film and the PS/P2VP interface were measured using an atomic force microscope, AFM, (D3100V, Veeco Digital Instruments) with a Si tip operating in the tapping mode.

The wide-field fluorescence microscopy is discussed in Chapter 2. The power density for this project was adjusted to about 0.413 kW cm^{-2} . The integration time of the CCD camera is 34.6 ms per frame.

3.2.5 Data treatment (center-center distance between colliding domains)

The perimeter of a P2VP domain is extracted from its binary image created using the thresholding method in the Photoshop software (Version 7.02, Adobe, threshold value = 148). A domain is thus considered to be confined within the perimeter. The reliability of the perimeter is tested by calculating the diameter of 100 domains recorded at 130 s after the start of solvent annealing using WFM. An average value of $403 \pm 27 \text{ nm}$ is obtained which is in agreement with the value ($390 \pm 11 \text{ nm}$) measured using AFM. The center-center distance between two domains is obtained using the ImageJ software (National Institute of Health).

3.2.6 Single-macromolecule tracking

Analysis method of the fluorescent images of single molecules has been discussed in Chapter 2. The trajectory of motion of a single PS chain moving in a straight track is fitted to a linear function using the Origin 8.0 software. The coordinate of the chain after each time step is calculated based on its perpendicular (*i.e.*, shortest) projection onto the straight line.

3.3 Results and Discussion

3.3.1 Analysis of AFM and WFM images

Phase separation between the strongly incompatible PS and P2VP occurs during spin-coating which results in a distribution of cylindrical-like P2VP domains surrounded by an inter-connected PS layer as observed by AFM (data for PS:P2VP = 65%:35% is shown in Figure 2). Thick and thin regions in the surface morphology of PS indicate an uneven solidification of PS during spin-coating [1,10]. The selective removal of PS reveals a wetting layer of P2VP covering the glass surface due to the strong enthalpic affinity between P2VP and glass [11]. For the PS:P2VP = 65%:35% blend film, the thicknesses of the P2VP wetting layer, P2VP domain and PS layer are approximately 20 nm, 55 nm and 50 nm, respectively (see Figure 2). The polymer blend film remains stable in air and dewetting is induced only after the film is placed inside a sealed chamber saturated with chloroform (a common solvent for PS and P2VP) vapor. AFM images of the blend film show progressively larger size P2VP domains followed by film rupture at increasing solvent annealing times (see Figure 3).

In order to understand the rapid phase growth and dewetting dynamics and the relationship between them, WFM is utilized to track the evolution of the processes in real-time starting from 130 s after the start of annealing when the P2VP domains are discernible and clearly imaged in Figure 4. Figure 4a shows the wide-field fluorescence image (bulk experiment with only P2VP chains labeled with dye) of a PS:P2VP = 65%:35% blend film recorded at 130 s after the start of solvent annealing (see Movie 1). The P2VP domains, comprising of a relatively large number of labeled P2VP chains, appear as bright near-circular

spots. Upon further solvent annealing, neighboring P2VP domains within close proximity (separation $<$ domain size) undergo coalescence to form larger domains (Figures 4b and 4c). The coalescence dynamics is studied by plotting l versus Δt , where l is the separation between the domain centers and the coalescence time $\Delta t = t_c - t$, where t is the time and t_c is the time when they

Figure. 2 AFM images of the PS:P2VP = 65%:35% blend films recorded (a) after spin-coating, and (b) after removal of PS phase by dissolution in cyclohexane. A scratch by a sharp blade removes the polymer and exposes the surface of the glass substrate to the AFM tip. The schematic picture of the blend film is shown in (c).

Figure. 3 AFM images of PS:P2VP = 65%:35% blend films recorded (a) after spin-coating, and (b)-(f) at various times after the start of solvent annealing. The AFM image for each time is recorded using a different polymer blend sample.

Figure. 4 WFM images of a PS:P2VP = 65%:35% blend film recorded at different times after solvent annealing. The near-circular white dots in (a) are P2VP domains whereas the dark background represents the inter-connected PS layer. Domain coalescence between two P2VP domains is highlighted in (b) and (c).

Figure. 5 The linear plot of l vs. Δt (a) for a pair of P2VP domains given in (b). The domains (domains P and Q in Movie 1) approach each other (i and ii) before colliding (iii) and undergoing shape relaxation (iv).

collide. A linear relationship exists between l and Δt as illustrated for a typical pair of P2VP domains in Figure 5. From the AFM image in Figure 6, it is observed that the PS layer sandwiched between two closely spaced P2VP domains is vertically thinner than the outer PS layer. This results in a higher capillary pressure in the trapped PS layer (thickness = a_1) as compared to the thicker outer layer (thickness = $a_2 > a_1$), and a pressure gradient of $\Delta P = \gamma (a_1^{-1} - a_2^{-1})$, where γ is the surface tension, gives rise to a hydrodynamic flow of PS from the thin region (trapped PS) toward both sides of the thick regions (outer

PS). Siggia [12] and McMaster [13] have shown that the thinning of the trapped PS progresses linearly with time. By treating the coalescence time to be the time taken to remove the trapped PS [14], the P2VP domains approach each other with $l \sim \Delta t^1$ as experimentally observed. We note that early stage domains

Figure. 6 AFM image of the PS:P2VP = 65%:35% blend film recorded at 130 s after solvent treatment. The inset shows the enlarged image of the area enclosed within the white box. (b) shows the sectional view along line b in the AFM image. (c) shows the sectional view along line c in the AFM image. The trapped PS is higher than the P2VP domains but lower in thickness (ca. 15 nm) when compared with the outer PS.

(*i.e.*, formed during spin coating) are too small to be tracked accurately using the current WFM set-up. The trapped PS is still lower in thickness than the outer PS (see Figure 7) and the collision dynamics of early stage domains arising from the pressure gradient should be similar to that of later stage domains (*i.e.*, domains at ~ 130 s after solvent treatment).

Figure. 7 (a) AFM image of the PS:P2VP = 65%:35% blend film recorded after spin-coating. The inset shows the enlarged image of the area enclosed within the white box. (b) shows the sectional view along line b in the AFM image. (c) shows the sectional view along line c in the AFM image.

After collision, the deformed P2VP domain (Figure 5b(iii)) reduces its surface area by undergoing interface-tension-driven shape relaxation to an equilibrium cylindrical-like domain (Figure 5b(iv)), and the latter can further coalesce with a neighboring domain. A dewetting PS hole is formed when the enclosed P2VP domain becomes sufficiently large (ca. 500 nm radius), causing the PS-rich layer to dewet from the underlying P2VP layer *via* rapid hole growth (Figures 4d - 4f and Movie 1). In the nucleation and growth process of liquid films on non-wetting surfaces, the change in the free energy from hole creation (ΔG) leads to a potential barrier ΔG_t that corresponds to the maximum ΔG when a hole of transition radius r_t is created [15,16]. An initial hole, of radius $r > r_t$, capable of undergoing expansion is formed when ΔG_t is crossed [15]. The formation of PS holes smaller than r_t is thermodynamically not feasible [15] and these holes are prevented from collapsing by the enclosed P2VP domains. On the other hand, dewetting PS holes with sufficiently large radii (*e.g.*, ca. 500 nm) are created from domain coalescence which is the passage taken to overcome ΔG_t .

As the PS hole widens, the surrounding PS layer pushes smaller P2VP domains into neighboring holes (see domain X in Movie 1) causing the latter to grow irregularly. It is also observed that a separate group of P2VP domains are initially pushed away from an expanding hole before slowing down and absorbed into the hole (see domain Y in Movie 1). A simple model illustrated in Figure 8, is proposed to rationalize this behavior. We begin by noting that the width of the PS rim surrounding a hole is, on average, ca. 2 μm (from Figure 9) and the driving force for dewetting is given by $F_d = \gamma_1 + \gamma - \gamma_2$, where γ_1 , γ and γ_2 are the PS/P2VP interfacial tension, PS surface tension and P2VP surface

Figure. 8 A schematic illustration of the entry of a P2VP domain into a hole at various time stages ($t_4 > t_3 > t_2 > t_1$). The P2VP domain (a) is outside the rim of the hole, (b) enters the rim, (c) is ca. 1 μm away from the hole and (d) enters the hole.

tension, respectively. Upon dewetting, the rim pushes the P2VP domain away from the hole while collecting the PS layer between the two entities (Figure 8a). When the PS layer has been removed, the rim advances ahead of the P2VP domain causing the rim to tear and the domain to move into the rim (Figure 8b). The velocity of the affected portion of the rim decreases when the resistance force from the non-wetting P2VP domain is greater than F_d and the domain comes to a near complete halt at ca. 1 μm away from the hole (Figure 8c and Movie 1). The PS separating the hole and domain is subsequently pulled aside by the moving rim found at both sides of the disrupted rim, allowing the P2VP domain to flow into the hole (Figure 8d).

Figure. 9 AFM image of a PS:P2VP = 65%:35% blend film recorded at 147.6 s after the start of solvent annealing. The rim width of the hole measured is ca. 2 μm.

The break-up of the rim is visualized by tracking single labeled PS ($M_w = 355K$) chains using WFM. An advantage of single-molecule spectroscopy over ensemble-level studies is the ability to observe the effects of the surrounding environment (*e.g.*, incoming domains) on the motion of individual PS chains

located throughout the rim. In this case, each macromolecule appears as a diffraction-limited spot and its position is determined by fitting the intensity distribution to a 2D Gaussian function (see Chapter 2). The reptation motion of PS is inhibited by entanglement (entanglement molecular weight for PS $M_e = 10$ kg/mol) and the effect of random motion is neglected in further analysis. In Figure 10a, the trajectories of motion for a pair of PS chains (chains *A* and *B*) located in the rim (*i.e.*, perimeter of the hole) diverge rapidly away from each other (see Movie 2). This is due to the separation of the two polymeric chains by the entry of a domain.

In order to investigate the intrinsic dewetting dynamics of PS holes, we examine the trajectories of individual PS chains that move in straight tracks and are located in undisrupted portions of the rim. In this case, the motion of the PS chain is due to hole expansion. The trajectories of motion for two typical PS chains in the same rim are shown in Figure 10b (chains *C* and *D*, Movie 2) along with the corresponding linear fits. Given that the bin time for each step in the trajectory is $T = 0.346$ s, the distance moved by a polymeric chain within a period of T increases as the dewetting progresses. This is also evident in the plot of the displacement of the chain with respect to its initial position (d) (calculated from the linear fit of the trajectory) versus time (t) as shown for chains *C* and *D* in the inset of Figure 10c. In general, the hole growth is best described by the relationship $d \sim t^\alpha$, where $\alpha = 2$ and 1.4 for chain *C* and chain *D*, respectively. The distribution of $\alpha > 1$ for 60 single PS chains located in different rims is displayed in Figure 10c which clearly indicates the presence of accelerated hole growth.

Figure. 10 The trajectories of motion of (a) two PS chains (*A* and *B*) located in the rim and affected by the entry of a P2VP domain and (b) two PS chains (*C* and *D*) located in the rim and moving in linear tracks. *S* and *E* are the start and end of a trajectory, respectively. The plots of d vs. t for chains *C* and *D* are given in the inset of (c) and fitted to $d = At^\alpha$, where $\alpha = 2$ and 1.4 for chains *C* and *D*, respectively. The distribution of α for 60 PS chains is given in (c).

Brochard-Wyart *et al.* have theoretically classified the dewetting dynamics at a polymer-polymer interface into two classes depending on the viscosities of

the polymers [17]. In the case when the lower layer is more viscous than the dewetting layer, hole radius r increases linearly with t (*i.e.*, $r \sim t$) whereas $r \sim t^{2/3}$ when a highly viscous polymer dewets from a low-viscosity liquid [17]. The unusual acceleration in hole growth for a polycarbonate/poly(styrene-*co*-acrylonitrile) stratified system has been reported by Composto *et al.* [18] who have proposed several plausible mechanisms to explain the behavior including a time-dependent variation in the dynamic contact angle θ_d . In this case, the uncompensated Young's force $F_d = \gamma (\cos \theta_e - \cos \theta_d)$, where θ_e is the equilibrium contact angle, increases as θ_d decreases with time due to the deformation of the polymer-polymer interface by the vertical component of the surface tension of the dewetting layer.

In order to assess the role of θ_d in our system, the contact angle of PS on P2VP is determined by examining the AFM images at the start of hole growth and just before hole collision/film rupture. We note, by selective removal of PS, that the triple line is lifted up and no visible trench is present (see Figure 11). Furthermore, as the dewetting progresses with time, the volume of P2VP under the triple line increases, hence enhancing the separation between the triple line and the glass substrate (see Figure 11). This is supported by the WFM images of holes which reveal a relatively bright perimeter as compared to hole interior (Movie 1). A probable explanation is the continuous accumulation of P2VP chains at the three phase contact line after the domains are absorbed into the hole. A change in the contact angle occurs with θ_d decreasing from an average value of $29 \pm 1^\circ$ at the start of hole growth to $22 \pm 1^\circ$ before hole collision/film rupture. The driving force F_d , therefore, increases during hole expansion when the equilibrium contact angle $\theta_e = 51 \pm 1^\circ$. In addition, the frictional force, F_v ,

on the rim is dependent on the viscous dissipation within the lower P2VP layer and is reduced upon increasing the thickness (h) of P2VP (*i.e.*, $F_v \sim h^{-1}$) [17]. F_v may decrease as more P2VP accumulates at the three phase contact line leading to further hole acceleration. The presence of a distribution of α suggests that the

Figure. 11 AFM image of the PS/P2VP interface of a PS:P2VP = 65%:35% blend film after selective removal of PS recorded at 147.6 s after the start of solvent annealing. θ_d is the dynamic contact angle.

acceleration dynamics and hence environment of individual chains are heterogeneous in nature. This behavior can be ascribed to i) non-uniform changes in θ_d and F_d , especially for chains close to disrupted portions of the rim, and ii) influences of neighboring dewetting holes that provide opposing forces. It is necessary to note that many questions remain, among them the clarification of the exact nature of the driving force behind hole acceleration. Several issues such as the quantitative correlation between θ_d and F_d require further experimental attention (*e.g.*, using non-trivial time-resolved experiments) [18,19].

Finally, the film undergoes rupture (Figure 4g) when PS holes collide into each other, and droplets of PS are formed (Figure 4h). The influence of blend compositions on phase separation and dewetting of thin blend films has been discussed in the past [20,21]. Polymer blend film of composition PS:P2VP = 50%:50% displays similar domain coalescence-induced nucleation and anomalous growth of holes (see Movies 3). Due to the high density of larger domains, shape relaxation process after P2VP domain collision induces hydrodynamic flow that can lead to further coalescence (*i.e.*, direct hydrodynamic interaction) [22].

3.3.2 Molecular weight ratio and fluid composition of polymers

Domain coalescence-induced nucleation is also observed for thin blend films of various molecular weight ratios of PS:P2VP = x :13K (where x is ~ 130 K to ~ 350 K). We have investigated a series of molecular weights where the molecular weight of PS ranges from ~ 130 K to ~ 350 K while maintaining the molecular weight of P2VP at 13K (*i.e.*, samples with ratio PS:P2VP = 135.5K:13K (Movie 4), 221K:13K (Movie 5), 290K:13K, 355K:13K (Movie 6)

were studied). It is observed that for all the samples investigated, the domain coalescence-induced hole formation mechanism takes place and the center-center distance between colliding domains varies linearly with time. However, the time taken for the initiation of dewetting *via* hole growth increases with an increase in the PS molecular weight (see Figure 12) due to an increase in viscosity. PS of molecular weight < 135K was not studied since the phase growth and dewetting processes occur too rapidly to be tracked accurately using the current wide-field microscopy set-up.

Figure. 12 Relationship between molecular weight of PS (M_w) and initiation time of dewetting by hole growth (t) after solvent treatment.

When a P2VP of molecular weight 140.6K is used, large continuous islands of P2VP are observed after spin-coating (see Figure 13). Slow diffusion and convective rearrangement processes during spin-coating may lead to the coalescence of P2VP domains (see Figure 13). We have, therefore, chosen P2VP of molecular weight 13K in order to study well-defined and

near-cylindrical P2VP domains. Our choice of PS:P2VP molecular weight ratios are in line with those used by Han *et al.* to study pattern formation in PS:P2VP blend films upon solvent-induced phase separation [23,24].

Figure. 13 AFM image of PS:P2VP = 135.5K:140.6K (left panel) and 221K:140.6K (right panel).

Off-critical compositions (*e.g.*, PS:P2VP = 65%:35% and 50%:50%) were chosen so that only discrete domain growth was studied. Preferential wetting of the P2VP layer on the glass substrate may be the cause for the off-critical composition behavior seen in the PS:P2VP = 50%:50% system [3]. When the composition of the blend is PS:P2VP = 30%:70%, a near-critical composition is reached and a bicontinuous growth is observed (see Movie 7).

3.3.3 Effect of chloroform

Chloroform (solubility parameter $\delta = 19.0 \text{ MPa}^{1/2}$ [25]) is chosen to be the (good) solvent that solubilizes both PS ($\delta = 17.8 \text{ MPa}^{1/2}$ [25]) and P2VP ($\delta = 20.4 \text{ MPa}^{1/2}$ [26]). Since PS and P2VP are incompatible (Flory-Huggins polymer-polymer interaction $\chi = 0.1$ [27,10]), phase separation occurs during

spin-coating to reduce the effective interfacial energy as observed experimentally [10,27]. In the presence of the chloroform vapor, the homogeneous layers are replaced by layers of PS/chloroform and P2VP/chloroform hence decreasing the glass transition temperature, viscosity, surface and interfacial tensions of the polymers [9]. The effect of lubrication in our system is unclear at the present moment. Previous studies involving solvent-driven dewetting of PS on various substrates [9,28,29] did not observe significant surface lubrication effects and mechanisms such as entropy driven autophobic dewetting and instability caused by polar interaction were proposed.

3.4 Conclusion

In summary, we have demonstrated, using a combination of WFM and AFM, a new mode of nucleation mechanism involving domain coalescence. In addition, the inclusion of P2VP domains during hole expansion results in irregular shaped holes and accelerated hole growth.

3.5 Movie captions

Movie 1. Bulk experiment with P2VP polymers labeled with dye and recorded at 130 s after the start of solvent annealing. P2VP domains *P*, *Q*, *X* and *Y* are highlighted. Composition of blend is PS:P2VP = 65%:35% and molecular weight ratio PS:P2VP = 290K:13K.

Movie 2. Single-(macro)molecule experiment with a low concentration of labeled PS chains. Chains *A*, *B*, *C* and *D* are highlighted. Composition of blend is PS:P2VP = 65%:35%.

Movie 3. Bulk experiment with P2VP polymers labeled with dye and recorded at 130 s after the start of solvent annealing. Composition of blend is PS:P2VP = 50%:50% and molecular weight ratio PS:P2VP = 290K:13K.

Movie 4. Bulk experiment with P2VP polymers labeled with dye and recorded at 130 s after the start of solvent annealing. Composition of blend is PS:P2VP = 65%:35% and molecular weight ratio PS:P2VP = 135.5K:13K.

Movie 5. Bulk experiment with P2VP polymers labeled with dye and recorded at 130 s after the start of solvent annealing. Composition of blend is PS:P2VP = 65%:35% and molecular weight ratio PS:P2VP = 221K:13K.

Movie 6. Bulk experiment with P2VP polymers labeled with dye and recorded at 130 s after the start of solvent annealing. Composition of blend is PS:P2VP = 65%:35% and molecular weight ratio PS:P2VP = 355K:13K.

Movie 7. Bulk experiment with P2VP polymers labeled with dye and recorded at 130 s after the start of solvent annealing. Composition of blend is PS:P2VP = 30%:70% and molecular weight ratio PS:P2VP = 290K:13K.

3.6 Bibliography

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CHAPTER 4

Unconventional Multiple Ring Structure Formation from Evaporation-induced Self-Assembly of Polymers: A Spreading and Receding Mechanism

This chapter is adapted from: “Unconventional Multiple Ring Structure Formation from Evaporation-induced Self-Assembly of Polymers: A Spreading and Receding Mechanism, Wuguo Bi, Xiangyang Wu and Edwin K. L. Yeow, *Phys. Rev. Lett.* submitted.”

4.1 Introduction

The evaporation of a sessile drop is a simple, convenient and cost effective method of creating self-assembled patterns of functional materials (*e.g.*, polymers, semiconductor particles and biological systems such as DNA) on solid substrates. The self-organization of the solute, upon drying of the sessile drop, has been demonstrated to give rise to different pattern morphologies including the well-known single coffee ring stain [1-3], multiring structures [4-7] and uniform film deposits [1-3]. Deegan *et al.* have proposed a physical model to explain the single ring deposit observed in a coffee ring stain [1]. In this case, a non-volatile solute is transported to and trapped at the pinned contact line (CL) of a stationary drying droplet by an outward capillary flow arising from both CL pinning and enhanced solvent evaporation at the edge of the sessile drop. On the other hand, multiple rings are observed when the CL undergoes a series of pinning-depinning events with the solute flowing towards the edge and accumulating at the CL when it is pinned (*i.e.*, “stick”) [4-7]. Depinning occurs when either a dominating inward capillary force or an evaporation-induced rupture of the solvent at the edge (or close to it) causes the CL to “slip” to a new position such that a new solute ring is subsequently formed.

The evaporation of polymer-mono solvent drops has previously been characterized using experimental techniques such as optical microscopy [8] and particle image velocimetry [9]. These techniques, however, suffer from limited temporal and spatial resolution and do not provide detailed information on the dynamics of the motion of both the CL and the polymer moving in close vicinity to the leading edge. Such information is important as it provides a more complete picture of the overall surface patterning mechanism. In this study, we will utilize

wide-field microscopy (WFM) to visualize, in real-time and with minimal intermittent breaks [10,11], the behaviour of the CL and the solute, poly(2-vinyl pyridine) P2VP, close to the CL in order to elucidate the driving force behind the self-assembled multiring pattern of an evaporating binary solvent drop.

4.2 Experimental

4.2.1 Materials

Amino terminated poly(2-vinyl pyridine) P2VP ($M_w = 140,600$ and $M_w/M_n = 1.04$) and Atto647N NHS-ester dye were obtained from Polymer Source Inc and Atto-Tec GmbH, respectively. Anhydrous dimethylsulfoxide (DMSO, 99.9%, Aldrich), 2,6-lutidine (98+%, Alfa Aesar), n-decyltriethoxysilane (98%, Alfa Aesar), sulfuric acid (H_2SO_4 , 96.7%, Schedelco), hydrogen peroxide (H_2O_2 , 30%, Scharlau), toluene ($\geq 99.5\%$, HPLC/spectroscopy grade, Sigma Aldrich) and methanol (MeOH, HPLC/spectroscopy grade, Tedia) were used as received.

4.2.2 Labeling of P2VP with Atto647N

The amino terminated poly(2-vinyl pyridine) was labeled by the reaction of its terminal amino group, NH_2 , with the NHS-ester moiety of Atto647N. 100 mg of amino terminated poly(2-vinyl pyridine) was dissolved in 1 mL of anhydrous DMSO at 40 °C, followed by the addition of 1 mg of Atto647N NHS-ester into the solution. The mixture was then allowed to react under stirring for 4 h. The labeled P2VP was precipitated out by adding the DMSO P2VP solution into DI water and recovered by centrifugation. The procedure for removing free dyes is as follows: the recovered P2VP was first dissolved in

MeOH and then precipitated out by adding the MeOH P2VP solution into DI water before extraction by centrifugation. The free dye removal procedure was repeated at least three times.

4.2.3 Sample preparation

All experiments were conducted in ambient conditions. Since the lower critical solution temperature of the binary solvent is $\sim 34\text{ }^{\circ}\text{C}$ [12], water (*W*) and 2,6-lutidine (*L*) are completely miscible in the mixture compositions used here at room temperature ($24\text{ }^{\circ}\text{C}$).

Binary mixtures of DI water and 2,6-lutidine in various compositions (*i.e.*, wt% of 2,6-lutidine:wt% of water = 60%:40%, 70%:30% and 90%:10%) were used in the wide-field microscopy experiments. Different concentrations of P2VP solutions (*i.e.*, 0.0002, 0.001, 0.002, 0.005 and 0.008 g of P2VP dissolved in 1 g of solvent) were prepared by dissolving the labeled and unlabeled P2VP in the binary solvent such that the final concentration of the labeled P2VP is *ca.* 10^{-8} - 10^{-9} M and *ca.* 10^{-6} M for the wide field microscopy and confocal fluorescence microscopy experiments, respectively.

The glass coverslips (Menzel-Glaser, thickness #1) were pre-cleaned by sonication in acetone for 10 min followed by sonication in aqueous sodium hydroxide for 30 min and then sonication in DI water for 10 min. The last step was repeated three times. The coverslips were further heated in a “piranha” solution (70% H_2SO_4 and 30% H_2O_2 v/v) for 1 h and then sonicated in DI water for at least three times. The cleaned coverslips were subsequently rinsed with DI water and dried by blowing argon over the coverslips before being exposed to ozone in an UV-ozone reactor (PSD Series, NovaScan) for 30 min. The coverslips were used immediately after cleaning.

The procedure to prepare silanized surface is as follows. The cleaned coverslips were first dried in a vacuum oven (Thermo Scientific) at 50 °C for 1 h. The coverslips were then introduced into a flask containing 50 μ L of n-decyltriethoxysilane dissolved in 5 mL of toluene and allowed to react for 1 h. Subsequently, the silanized coverslips were washed with toluene followed by MeOH and then dried by argon flow. The modified coverslips were further dried under vacuum for 5 h.

4.2.4 Contact angle, surface tension and confocal fluorescent imaging measurements

An optical contact angle and surface tension meter (KSV CAM 101) is used to measure the contact angles of the sessile drops (0.5 ± 0.1 μ L) and the surface tensions of the binary mixtures. Each measurement was repeated at least 3 times and an average value taken.

A confocal fluorescence microscope (Nikon, Eclipse TE2000-E) equipped with a 633 nm HeNe laser and a 2 $\times$, N.A. 0.06 (Nikon) objective lens is used to record the confocal fluorescent images.

4.2.5 Wide-field microscopy (WFM)

The setup of the wide-field fluorescence microscopy has been discussed in Chapter 2. In this chapter, a water immersion objective lens (60 $\times$, N.A. 1.2, Olympus) or an air objective lens (20 $\times$, N.A. 0.4, Olympus) was used. The dimension of a wide-field fluorescence frame was measured to be 41 $\times$ 41 μ m² for the 60 $\times$, N.A. 1.2, water objective lens, and 123 $\times$ 123 μ m² for the 20 $\times$, N.A. 0.4, air objective lens, using a stage micrometer, and the power density

was adjusted to be about 0.512 kW cm^{-2} . The integration time of the CCD camera is 34.6 ms per frame.

4.2.6 Fluorescence correlation spectroscopy (FCS)

The FCS measurements were performed using a time-resolved confocal microscope (MicroTime 200, PicoQuant). The excitation source used is a 635 nm pulsed diode laser (LDH-P-C-635B, PicoQuant) with a repetition rate of 20 MHz. The excitation light passed through an excitation filter (Z636/10, Chroma) and directed *via* a dichroic mirror (Z638rpc, Chroma) into an inverted microscope (IX71, Olympus) before being focused onto the sample through a water objective lens (60 $\times$, N.A. 1.2, Olympus). The correction collar of the water immersion objective was optimized in order to obtain the highest signal-to-noise ratio and the fluorescence was subsequently collected by the same objective lens. The fluorescence was then passed through the dichroic mirror, an emission filter (HQ685/70, Chroma) and refocused through a pinhole (50 μm in diameter) before being detected by an avalanche photodiode (SPCM-AQR-15, Perkin-Elmer). The excitation intensity of the laser beam used was 8.7 kW cm^{-2} .

The lateral radius (ω_0) and axial $1/e^2$ -radius (z_0) of the confocal volume were determined by measuring the autocorrelation function of Atto655-COOH in water. The triplet state formation quantum yield of Atto655-COOH is negligible and the fluorescence intensity fluctuations arise from the translational diffusion of the dye [13]. Assuming that the confocal volume can be approximated by a 3-dimensional Gaussian function, ω_0 and z_0 were obtained by fitting the autocorrelation function ($G(t)$) of Atto655-COOH in water using the following equation:

$$G(t)=G_0\left(1+\frac{t}{\tau}\right)^{-1}\left(1+\frac{t}{\kappa^2\tau}\right)^{-\frac{1}{2}} \quad (1)$$

The eccentricity of the confocal volume is defined by $\kappa = z_0/\omega_0$, and the diffusion time (τ) is related to ω_0 and the diffusion coefficient D via

$$\tau = \frac{\omega_0^2}{4D} \quad (2)$$

The diffusion coefficient of Atto655-COOH in water at 23 °C is previously reported to be $D = 404 \mu\text{m}^2 \text{s}^{-1}$ [13].

4.3 Results and Discussion

4.3.1 WFM and the confocal fluorescence microscopy study

Figure 1(a) shows the confocal microscope image of a typical multiring deposit left by a 0.5 μL P2VP-($L + W$) drop on the surface of a glass coverslip. The concentration of P2VP is 0.002 and the solvent composition is wt% of L :wt% of $W = 60\%:40\%$. The multiring structure of P2VP shows similar physical features as the self-assembled multiring patterns of other functional materials (*e.g.*, polystyrene particles and DNA) where pinning of the triple line is a necessary condition for the formation of ring deposits (*i.e.*, by the advection and accumulation of solute at the pinned edge before depinning occurs) [4-6]. Two distinct pattern morphologies are observed in this study depending on the stage of

Figure. 1 Confocal fluorescent image of a typical multiring deposit left by a 0.5 μL P2VP-(L(60%) + W(40%)) drop on a glass substrate at (a) high contrast and (b) low contrast (Movie 1).

evaporation. Fine ring-like solute deposits (Figure 1(a)) are initially formed during evaporation followed by significantly thicker CL deposits (Figure 1(b)) found towards the end of the evaporation and prior to complete dry up of the solvent. We will first focus on the fine multiple rings. For the P2VP system studied here, the evolution of the steps leading to the formation of a ring-like solute deposit is visualized using WFM and the time-lapsed WFM fluorescent images of a typical CL in motion during droplet evaporation are presented in Figures 2(a)-(c) (see also Movie 2). Movie 2 initially shows P2VP flowing outwards to the edge of the drop (not captured by the camera) before the CL retracts rapidly to an equilibrium position (Figure 2(a)). From there, the CL again spreads outwards (Figure 2(b)) to a new position (Figure 2(c)) with P2VP continuously flowing towards the advancing CL (*i.e.*, CL is not pinned) and forming a polymer ridge at the edge. When the drop stops spreading and begins to recede, the P2VP ridge is left behind as a ring-like deposit on the substrate.

Multiple ring stains are formed by the repeated cycles of spreading and receding (Movie 3).

Figure. 2 WFM images of a CL at (a) the beginning of a spreading process (1.9 s after the start of measurement), (b) 6.1 s after the start of measurement and (c) the end of the spreading process (14.0 s). A P2VP deposit is observed.

4.3.2 Contact angle measurement

For a 0.5 μL sessile drop with a solvent composition of wt% of L :wt% of $W = 60\%:40\%$, the radius of the drop (1.5 mm) is shorter than the capillary length ($\kappa^{-1} = (\gamma/\rho g)^{1/2} \approx 2$ mm, where γ is the surface tension of the liquid (39.0 mN m^{-1} , $\rho = 987.5$ kg m^{-3} [12] is the liquid density and g is earth's gravity) of the binary mixture, and flattening of the drop by gravity can therefore be neglected [14].

Figure 3 shows the evolution of the contact angle (θ) with evaporation time for a 0.5 μL binary solvent drop (wt% of L :wt% of $W = 60\%:40\%$) with a P2VP concentration of 0.002. The time variation of θ occurs in two different time scales, where for the short time scale, a periodic rise and fall in θ is observed (see

inset of Figure 3). In this case, the decrease in θ for each cycle corresponds to the continuous reduction in the contact angle when the CL undergoes a spreading event to form a solute ring. The histogram of the time taken for a series of CL (95) to complete a spreading event (from WFM) and the histogram of the time taken for θ to decrease to a minimum value in 65 independent oscillation cycles are in good agreement with each other (Figure 4). In particular, the histograms were

Figure. 3 Plots of the contact angle θ vs. evaporation time t for sessile drops with compositions of wt% of L: wt% of W = 60%:40% (“curve a”) (amplification of the first 50 s is given in the inset) and 90%:10% (“curve b”) on a glass surface. The concentration of P2VP is 0.002.

fitted to a Gaussian distribution that yielded a mean CL spreading time of 8.0 s and a mean θ decay time of 6.9 s. When the wetting angle becomes equal to the receding angle, the CL retracts to a new position and a rapid rise in θ towards an equilibrium value (θ_e) is observed for each cycle. In the long time scale, θ varies

Figure. 4 The histogram of the time taken for a series of CL (95) to complete a spreading event (i) and the histogram of the time taken for θ to decrease to a minimum value in 65 independent oscillation cycles (ii). The histograms were fitted to a Gaussian distribution that yielded a mean time of 8.0 s and 6.9 s for (i) and (ii), respectively.

according to the relatively slow evaporation rate and composition of the binary solvent. Figure 5 shows that the initial contact angle θ_i of a binary mixture with a P2VP concentration of 0.002 dips slightly from $13.5^\circ (\pm 0.3^\circ)$ to $12.2^\circ (\pm 0.4^\circ)$ when the wt% of L :wt% of W changes from 60%:40% to 65%:35% and then remains relatively unchanged for solvent compositions from 65%:35% to 75%:25%. However, for binary mixtures with a wt% of $L > 75\%$, an increase in the concentration of 2,6-lutidine leads to a drastic drop in θ_i . From Figure 3, θ_e does not vary significantly ($13.2^\circ (\pm 0.3^\circ)$) within the first 75 s of the measurement indicating that during evaporation the composition of the binary

Figure. 5 The plots of the initial contact angle (θ_i , $\square$) and surface tension (γ , Δ) vs. wt.% of L for a binary solvent with a P2VP concentration of 0.002.

mixture most likely remains in the range of wt% of L :wt% of $W = 60\%:40\%$ and $75\%:25\%$. After 75 s, the relatively fast decline in the contact angle is attributed to a smaller drop volume and a higher fraction of 2,6-lutidine (wt% $> 75\%$) remaining in the solvent during evaporation. This is possible since water (vapour pressure, $P = 23.8$ mmHg at 25°C) is known to evaporate faster than 2,6-lutidine ($P = 5.65$ mmHg at 25°C).

4.3.3 Rate of spreading

We next investigate the speed of an advancing CL when it spreads to form a ring deposit. In this case, a plot of the change in drop radius $\Delta R(t) (= R(t) - R(0))$ as a function of time t for a spreading event is obtained from the WFM experiment and a typical example is given in Figure 6 (corresponding to the CL in Figure 2 (a) and Movie 2). We consider the initial time (*i.e.*, $t = 0$ s) to be the time when the drop begins to spread and $R(0)$ is assumed to be 0 for convenience.

The $\Delta R(t)$ vs. t plot in Figure 6 is best described using a power-law expression $\Delta R(t) \sim t^\alpha$, where the power-law exponent $\alpha = 0.9$. The histogram for the distribution of α for a collection of 30 independent spreading events (see inset of Figure 6) indicates that α lies between 0.4 and 1.

Figure. 6 A typical plot of $\Delta R(t)$ vs. t for a CL undergoing spreading is fitted to a power-law expression, $\Delta R(t) \sim t^\alpha$ with $\alpha = 0.9$. The inset shows the histogram of α for 30 independent spreading CLs.

We propose a model based on the pre-existence of an ultrathin (a few nm) precursor film ahead of the droplet edge (see Figure 7) to explain the spreading effect [15]. The binary solvent mixture consisting of water and 2,6-lutidine is utilized because the pure solvent components display different (i) extent of wetting on glass surface and (ii) ability to solubilise P2VP. According to our contact angle measurements, 2,6-lutidine completely wets the glass surface used in this study (contact angle = 0°), whereas water forms a thin sessile drop on the

glass substrate with an equilibrium contact angle of $\theta_e = 3.3 \pm 0.3^\circ$ (see Figure 8).

Therefore, 2,6-lutidine has a greater affinity to spread on a glass surface. The

Figure.7 Schematic drawing of (half) a sessile drop.

Figure. 8 Representative images of a drop of (a) 2,6-lutidine on a glass surface showing complete wetting , and (b) water on a glass surface that forms a thin sessile drop with an equilibrium contact angle of $3.3 \pm 0.3^\circ$.

greater dewetting of a drop of the binary (2,6-lutidine + water) mixture has been proposed to arise from both local composition fluctuation and surface tension fluctuation [16]. Since 2,6-lutidine, as compared to water, has a greater propensity to spread on glass, the precursor film and the transition region between the precursor film and the edge of the drop are likely to be

2,6-lutidine-rich (Figure 7). According to the Tanner's law, if the spread of the drop is due to the capillary force F_c acting on the CL, then $\Delta R(t)$ varies with t according to a power-law relationship with $\alpha = 0.1$ [17]. Clearly, F_c does not completely describe the enhanced spreading of the triple line during the formation of ring-like deposits. Given that the solubility parameters of P2VP, 2,6-lutidine and water are $20.4 \text{ (J cm}^{-3})^{1/2}$ [18], $19.3 \text{ (J cm}^{-3})^{1/2}$ [19] and $47.9 \text{ (J cm}^{-3})^{1/2}$ [20], respectively, P2VP prefers to be solubilized in an environment rich in 2,6-lutidine and the polymer will therefore aggregate at the transition region of the advancing edge. This leads to a sharp increase in the P2VP concentration at the transition region as compared to the adjacent solvent. Figure 9 shows that the surface tension of binary solvent increases as the concentration of P2VP in the

Figure. 9 Plot of the surface tension (γ) of the binary solvent (wt% of 2,6-lutidine:wt% of water = 60%:40%) against different concentrations of P2VP (*i.e.*, 0.002, 0.09, 0.18).

binary solvent increases. The aggregation of P2VP, therefore, may result in an increase in the surface tension at the transition region as compared to the bulk droplet. In this case, a surface tension gradient ($\Delta\gamma$) created drives an outward solutal-Marangoni flow that aids in the CL spreading [21,22]. Furthermore, the elevated spreading rate can also be attributed to the relaxation of the no-slip boundary condition due to the presence of the precursor film and the reduction of the advancing angle by the accumulation of P2VP at the CL. As the binary solvent drop undergoes spreading and the contact angle decreases (inset of Figure 3), P2VP molecules are rapidly transported to the advancing CL, *via* the solutal-Marangoni effect and a curvature-induced Laplace pressure, to form a P2VP ridge at the leading edge. However, the outward flow of P2VP occurs too fast for the velocity to be determined accurately using WFM.

Another factor to consider is the Marangoni flow, arising from the different volatilities and surface tensions of the pure solvent components, that opposes spreading. Since water has a lower boiling point than 2,6-lutidine and the evaporation rate is enhanced at the edge, the major component of the remaining solvent in the vicinity of the edge during evaporation is 2,6-lutidine which has a lower surface tension (31 mN m^{-1}) than the bulk binary solvent (39.0 mN m^{-1}) (Figure 5). Therefore, when the effect of P2VP on the surface tension is neglected, a solvent-Marangoni flow along the solvent/vapour interface from the edge to the interior of the drop is induced. From the WFM experiment, it is observed that while most of the P2VP chains close to the edge flow toward and accumulate at the CL, P2VP chains located away (*e.g.*, 10 - 20 μm) from the CL and near the free surface are carried back from the outer to the inner regions of the drop *via* the solvent-Marangoni flow (Movie 4). This suggests that the

solvent-Marangoni flow is effective over a short distance d_l spanning from the P2VP-rich end of the edge (*i.e.*, transition region) to the adjacent solvent region A with a lower P2VP concentration (see Figure 7). On the other hand, the solvent-Marangoni force operates between region A, which is relatively richer in 2,6-lutidine due to preferential evaporation, and the bulk binary mixture over a distance d_2 . The overall driving force acting on a polymer chain by the two opposing Marangoni forces is $F \sim \Delta\gamma_{solute} + \Delta\gamma_{solvent}$, where $\Delta\gamma_{solute} = (\gamma_T - \gamma_A)/d_l$ and $\Delta\gamma_{solvent} = (\gamma_A - \gamma_B)/d_2$. γ_T , γ_A and γ_B are the surface tension of the transition region (assumed to be that of pure P2VP, 46.7 mN m⁻¹ [23]), surface tension of the solvent in region A (assumed to be that of 2,6-lutidine) and surface tension of the bulk binary solvent, respectively. In this case, the majority of P2VP close to the edge are transported to the CL by the solutal-Marangoni flow ($F > 0$ when $\Delta\gamma_{solute} > \Delta\gamma_{solvent}$) whereas a portion of chains further away from the CL experience $\Delta\gamma_{solvent} > \Delta\gamma_{solute}$ ($F < 0$) and are eventually brought back to the drop interior by the solvent-Marangoni flow. It is worth noting that the exact length of d_l is not known [24], however, an estimate value of $d_l = 10 \mu\text{m}$ is assumed based on the WFM experiment and the fact that for a water droplet of a similar dimension, the radial distance from the CL where evaporation is most effective ranges between 10 – 20 μm [25]. The magnitude of the solutal-Marangoni flow is determined by the Marangoni number, $Ma = \Delta\gamma d_l / \eta D$, where η is the viscosity of 2,6-lutidine (0.93 mPa s) [12] and the diffusion coefficient of P2VP in 2,6-lutidine is determined by fluorescence correlation spectroscopy (FCS).

The diffusion coefficient of dye-labeled P2VP ($\sim 10^{-9}$ M) in a 2,6-lutidine solution contained within a well was measured using FCS. Given that the quantum yield of the triplet state formation of Atto647N is negligible [26], the

autocorrelation function of the labeled P2VP in 2,6-lutidine (Figure 10) is fitted using equation (1) which yields a diffusion coefficient of $D_L = 38.4 \pm 1.5 \mu\text{m}^2 \text{s}^{-1}$. Clearly, $M_a > 10^6$ indicates that the solutal-Marangoni flow is important.

Figure. 10 The autocorrelation function of the dye labeled P2VP in 2,6-lutidine.

The distribution of α values observed in Figure 6 indicates that the rate of spreading is not constant throughout the CL may vary with different spreading cycles. Figure 1a clearly shows that the top left edge of the drop is stationary during evaporation because the CL is strongly pinned to the substrate whereas the mobile parts of the CL are not dominated by efficient pinning and can therefore undergo repeated spreading and retraction to form the overall skewed multiring structure. For instance, inhomogeneous distributions in surface roughness, chemical heterogeneities, amount of solute trapped at the edge and solute- (or solvent-) substrate interaction are capable of reducing the speed of the CL to different extents depending on the location of the CL on the substrate.

An interesting feature, observed from the WFM experiment, is the instability of the polymer ridge to small perturbation which leads to the formation and growth of P2VP fingers. From Movies 2 and 3, we note that the P2VP fingers grow by constantly moving along the CL in either direction and coalescing with neighbouring fingers to form larger ones. In addition, a portion of the newly arrived P2VP chains at the thin regions (*i.e.*, valleys with relatively low P2VP concentrations) are attracted to thicker regions (*i.e.*, fingers with relatively high P2VP concentrations) possibly by the solutal-Marangoni effect and osmotic pressure imbalance that push the chains to move from low to high concentrations [8]. Gonuguntla and Sharma have also ascribed the periodic polymer patterns observed along an evaporating droplet edge to thermocapillary effect arising from a temperature difference between the valleys and fingers and the presence of Benard convection cells along the CL [8].

4.3.4 Effects of solvent composition

We examine the effects of solvent composition, while maintaining the P2VP concentration fixed at 0.002, on the morphology of the self-assembled surface pattern. When the fraction of 2,6-lutidine is increased such that wt% of *L*:wt% of *W* = 70%:30%, the number of fine solute rings significantly decreases and the time taken to reach the stage where thick P2VP rings are deposited is shortened (Figure 11 (a), also see Movie 5). Upon increasing the wt% of *L* to 90%, the sessile drop undergoes an initial fast spreading to an equilibrium state and only thick ring deposits are visible under the confocal fluorescence microscope (*i.e.*, fine multiple ring structures are absent) (Figure 11 (b), also see Movie 6). Furthermore, the plot of θ vs. evaporating time does not display

Figure. 11 A typical confocal fluorescent image of a stain deposited on a glass substrate by a drop of binary solvent (wt% of 2,6-lutidine:wt% of water = 70%:30% (a), 90%:10% (b)) with a P2VP concentration of 0.002.

any periodic oscillation in θ (Figure 3, “curve b”). This suggests that for solvent compositions with a high 2,6-lutidine fraction, the sessile drop does not undergo repeated spreading and receding and the CL is efficiently pinned to the substrate after achieving equilibrium such that the solute is transported to the edge by advection (WFM Movie 7). A possible explanation is the greater affinity of the 2,6-lutidine component in the binary mixture at the leading edge to wet the glass surface (Figure 8). The transition region is therefore richer in 2,6-lutidine and P2VP as the relative concentration of 2,6-lutidine in the binary mixture increases which will cause the CL to effectively pin to the glass surface either by a strong solvent-substrate or solute-substrate interaction. For the binary mixture with wt% of L :wt% of $W = 60\%:40\%$, the droplet needs to evaporate for a longer period of time before reaching the right solvent composition to effect complete pinning of the CL and formation of thick solute deposits. Therefore, the mechanism for the formation of thick solute rings found at the later stage of evaporation (*i.e.*, pinning and depinning of the CL) is

different from the case for fine solute rings which involves repeated spreading and receding of the CL.

4.3.5 Effects of solute concentration

To examine the effects of solute concentration, the amount of P2VP is varied while maintaining the same solvent composition (wt% of *L*:wt% of *W* = 60%:40%). We observed that when the concentration of P2VP is reduced from 0.002 to 0.001 and 0.0002, the droplet moves randomly on the glass substrate with fine ring-like deposits trailing behind the tracks as evaporation progresses

Figure. 12 Typical confocal fluorescent images of a stain deposited on a glass substrate by a binary mixture drop (wt% of 2,6-lutidine:wt% of water = 60%:40%) with a P2VP concentration of (a) 0.0002 (also see Movie 8) and (b) 0.001. The drops move randomly on the glass surface.

(*i.e.*, the drop is displaced from its initial position) (Figure 12). The reason behind the lateral movement of the drop is unclear at the present moment. A plausible explanation may be due to an imbalance of Marangoni force arising from a heterogeneous vapour pressure distribution of the solvent components

[27]. On the other hand, when the P2VP concentration is high (*e.g.*, 0.005 and 0.008), multiple ring structures are formed by the spreading and receding mechanism (Figure 13). However, the number of fine ring-like solute deposits decreases as the concentration of P2VP increases. Clearly, at an initial high polymer concentration (*e.g.*, 0.008), sufficient amounts of P2VP can aggregate at the 2,6-lutidine-rich transition region at the leading edge to induce complete pinning of the CL at short times whereas at an initial intermediate polymer concentration (*e.g.*, 0.002), the amount of P2VP is insufficient to drive an efficient pinning process and the solutal Marangoni-induced spreading of the CL becomes important. At an initial low P2VP concentration (*e.g.*, 0.0002), too few P2VP chains are available for trapping at the transition region to immobilize even a small portion of the CL.

Figure. 13 Typical confocal fluorescent images of a stain deposited on a glass substrate by a binary mixture drop (composition wt% of 2,6-lutidine:wt% of water = 60%:40%) with a P2VP concentration of (a) 0.005 and (b) 0.008 (also see Movie 9).

4.3.6 Effects of a confined environment and a silanized surface on the multirings of P2VP

The effect of evaporation in a confined environment is also studied by trapping the binary mixture (wt% of 2,6-lutidine:wt% of water = 60%:40% with P2VP concentration of 0.002) between a glass surface and a piece of cylindrical glass rod with radius of 3 mm (Figure 14). As evaporation progresses, the CL of the trapped drop gradually recedes toward the glass rod (see Movie 10). The important point to note is that for the concave liquid/vapour interface, the outside pressure is now larger than the pressure inside the liquid, and an inward acting Laplace pressure dominates and inhibits any solutal-Marangoni induced spreading.

Figure. 14 Schematic drawing liquid confined between a solid substrate and a cylindrical rod.

In addition, the effects of a silanized glass cover slip was also examined by allowing a sessile drop (wt% of 2,6-lutidine:wt% of water = 60%:40% with P2VP concentration of 0.002) to dry on a glass surface pre-treated with n-decyltriethoxysilane. According to the WFM experiment, the CL of the drop is

strongly pinned to the substrate, possibly from surface roughness and/or solvent-*n*-decyltriethoxysilane interaction, and a single solute ring is deposited on the substrate when the drop dries up (inset in Figure 15). The contact angle θ did not exhibit any periodic oscillation with time (Figure 15), hence concurring with the WFM observation that the CL does not undergo repeated spreading and receding events.

Figure. 15 Plots of the contact angle *vs.* evaporation time t for sessile drops with compositions wt% of *L*:wt% of *W* = 60%:40% (a typical confocal fluorescent image of a single solute ring is given in the inset) on a silanized surface. The concentration of P2VP is 0.002.

4.4 Conclusion

In conclusion, we have shown that multiple ring deposits of P2VP from the evaporation of a P2VP-binary solvent drop on a glass substrate are not formed *via* the conventional pinning-depinning mechanism [4-7]. Instead, ring-like solute deposits are formed when the droplet undergoes several cycles of spreading and retraction where during each spreading event, the P2VP flows towards the outward advancing edge forming a polymer ridge that is deposited when the CL recedes. A surface tension gradient created as a result of the solutal-Marangoni effect aids in enhancing the droplet spreading rate.

4.5 Movie captions

Movie 1. Formation of multiring P2VP deposits, recorded using a confocal fluorescence microscope, for a 0.5 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.002 evaporating on a glass substrate. The movie has been adjusted to play at a rate $10\times$ faster than the real time.

Movie 2. Formation process of a typical ring recorded by WFM using a $60\times$, N.A. 1.2 objective lens for a 0.5 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.002 on a glass substrate.

Movie 3. Formation process of a typical ring recorded by WFM using a $20\times$, N.A. 0.4 objective lens for a 0.5 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.002 on a glass substrate.

Movie 4. WFM movie of P2VP molecules carried back from the outer to the inner regions of a 0.5 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.002 by the solvent-Marangoni flow. The movie was recorded by lifting the objective to focus on a layer of the liquid away from the CL and close to the free surface of the drop.

Movie 5. Formation of multiring P2VP deposits, recorded using a confocal fluorescence microscope, for a 0.5 μL P2VP-(L(70%) + W(30%)) drop with a P2VP concentration of 0.002 evaporating on a glass substrate. The movie has been adjusted to play at a rate $10\times$ faster than the real time.

Movie 6. Formation of P2VP deposits, recorded using a confocal fluorescence microscope, for a 0.5 μL P2VP-(L(90%) + W(10%)) drop with a P2VP concentration of 0.002 evaporating on a glass substrate. The solute deposits are formed by a pinning-depinning mechanism. The movie has been adjusted to play at a rate $10\times$ faster than the real time.

Movie 7. Formation of a thick solute deposit for a 0.5 μL P2VP-(L(90%) + W(10%)) drop with a P2VP concentration of 0.002 on a glass substrate. The CL is pinned. The WFM movie was recorded using a 60 $\times$, N.A. 1.2 objective lens.

Movie 8. Formation of multiring P2VP deposits, recorded using a confocal fluorescence microscope, for a 0.5 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.0002 evaporating on a glass substrate. The movie has been adjusted to play at a rate 10 $\times$ faster than the real time.

Movie 9. Formation of multiring P2VP deposits, recorded using a confocal fluorescence microscope, for a 0.5 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.008 evaporating on a glass substrate. The movie has been adjusted to play at a rate 10 $\times$ faster than the real time.

Movie 10. WFM movie of the gradually receding CL of a trapped 1 μL P2VP-(L(60%) + W(40%)) drop with a P2VP concentration of 0.002 toward the glass rod.

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4.7 Perspective

In this thesis, wide-field microscopy is effectively used to study the dynamics of polymer crystallization, phase growth and dewetting dynamics of thin polymer films and the transportation kinetics of polymer chains in an evaporating droplet. This powerful and convenient technique provides a new window to elucidate several unanswered questions in polymer science. For polymer crystallization, WFM will be expanded to uncover the crystallization dynamics of other semi-crystalline polymers. The information on phase separation and dewetting of polymer can be applied to the paint industry where knowledge regarding the stability of thin coats of paint is essential. Further work can be extended to look to multi-binary systems consisting of more than two types of polymers. The new mechanism that drives multi-ring pattern formation will be extended to confined configuration where control judicious environmental conditions such as evaporation rate will lead to better control of the spreading/receding dynamic and hence thickness of the deposits. This has important implication in inkjet-printing and surface patterning industries. Finally, super resolution single molecule techniques such as STORM and PALM will be used in the future to map the evolution of morphology change in polymer bulk heterojunction. Understanding the shape of the conducting domain is important for the design of better molecular device.