LIQUID CRYSTAL ALIGNMENT AND RELAXATION DYNAMICS
AT SURFACE MODIFIED THIN POLYMER FILMS

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CHAPTER 1

INTRODUCTION

1.1 Soft Matter

Soft-condensed matter physics or soft physics has emerged as an important sub-field of the broader field of condensed matter physics [1]. It includes materials such as complex fluids, liquid crystals, surfactant solutions, polymers, colloids, emulsions, microemulsions, membranes, and biomaterials. Among these, liquid crystals are one of the most extensively studied owing to their technological importance in display and photonic applications in addition to the physical realizations of theoretical concepts in which to test those ideas.

1.1.1 Liquid Crystals

Liquid crystals (LC) [2] are mesomorphic phases intermediate between the crystalline solid and isotropic liquid. These phases can be obtained by varying the temperature (thermotropic) of pure organic molecular system or concentration of a surfactant in a solvent (lyotropic\(^1\)) [3]. The molecules comprising thermotropic LC are generally rod-like with strong dipoles and/or large dielectric anisotropy owing to the presence of easily and preferentially polarizable substituents. In the least ordered nematic phase, the long axes of the molecules align, on average, along a common direction specified by a unit vector \(\mathbf{n}\) called the director (\(\mathbf{n}\), and \(-\mathbf{n}\) are indistinguishable). At high temperature or low density, these molecules diffuse and rotate freely about

\(^1\)This system is beyond the scope of this work and therefore shall not be discussed in detail.
all axes and form a homogeneous isotropic fluid (Fig. 1.1a). In this phase, the system is invariant under arbitrary translational and rotational symmetry operations. As the temperature is reduced, one obtains the nematic (N) phase, in which the molecules align along the director, \( \mathbf{n} \), which is invariant under arbitrary translation but only under rotations about the axis parallel to \( \mathbf{n} \) (Fig. 1.1b). This is known as the nematic phase, which has a lower symmetry than the isotropic phase. The order parameter \( S \) describes the extent of ordering of the molecular long axes with respect to the director \( \mathbf{n} \). If \( \theta \) is the angle between the direction of local molecular axis and \( \mathbf{n} \), then in terms of a distribution function \( f(\theta) \),

\[
\langle S \rangle = 2\pi \int_0^\pi f(\theta)S(\theta)\sin \theta d\theta.
\]

with \( S(\theta) = \left( \frac{3}{2}\cos^2 \theta - \frac{1}{2} \right) \). The value of \( \langle S \rangle \) is non-zero in the nematic and zero in the isotropic phase [2]. The function \( f(\theta) \) is maximum around \( \theta = 0 \) or \( \pi \) and minimum for \( \theta \approx \frac{\pi}{2} \).

As the temperature is further reduced below the N phase, the smectic A (SmA) phase is often obtained in which the molecular centers of gravity segregate into a one-dimensional stack of two-dimensional fluid layers. Molecular long axes align on average along the layer normal (Fig. 1.1c). In some systems, a layered structure known as the smectic-C (SmC) phase, forms with liquid-like in-plane order but with the molecular long-axis tilted away from the layer normal (Fig. 1.1d). Different molecular arrangements within each layer are possible resulting in several different more ordered smectic type phases. The cholesteric state exhibited by pure compounds of chiral molecules is sometimes referred to as the twisted or chiral nematic (N*). It can also be obtained upon addition of chiral molecules to the nematic phase. In this state, the direction of average molecular alignment rotates in a helical pattern as
Figure 1.1: Schematic representation of the position and orientation of anisotropic molecules in the (a) isotropic, (b) nematic, (c) SmA, (d) SmC, and (e) crystalline solid. The direction of the average molecular alignment is specified by a unit vector \( \mathbf{n} \). The layer normal in the smectic phases is indicated by the unit vector \( \mathbf{m} \).
Figure 1.2: Schematic representation of the cholesteric phase. The director rotates in a helical pattern. The distance between equivalent molecular orientations correspond to one pitch, \( p \).

shown in Fig. 1.2. The pitch (distance between equivalent molecular orientations) depends on the concentration (or, degree of chirality) of chiral molecules [4, 5].

As a result of the orientational order, LCs exhibit dielectric (magnetic) anisotropy upon the application of an electric (magnetic) field, as well as optical birefringence \((\Delta n = n_\parallel - n_\perp)\), where \(n_\parallel\) and \(n_\perp\) are refractive indices for light having polarization parallel or perpendicular to \(n\) respectively [6]. Upon distortion/perturbation of the uniform \(n\) state, the elastic constants \(K_1, K_2\) and \(K_3\) corresponding to splay, twist, and bend, respectively, restore the system to its equilibrium configuration. The elastic free-energy density in the perturbed state is described by the Oseen-Frank theory [2]

\[
F = \frac{1}{2} \left[ K_1 (\nabla \cdot n)^2 + K_2 (n \cdot \nabla \times n)^2 + K_3 (n \times \nabla \times n)^2 \right]
\]  

(1.2)

These distortions have been studied extensively, specifically in constrained or confined systems where the ordering of molecules is profoundly affected. That is, the anisotropic surface potential offered by the bounding substrate enhances the orientational order in the nematic phase within a finite distance (penetration depth) of
the substrate. This phenomenon is of great interest because of their application in electrooptical devices (Fig. 1.3a).

Bounded by two parallel but especially treated surfaces, the director \( \mathbf{n} \) can adopt one of two orientations, either nearly parallel (homogeneous alignment) or perpendicular (homeotropic alignment) to the surfaces. In the homogeneous alignment, the director is usually tilted slightly with respect to the substrate surface (illustrated in Fig. 1.3b) depending on the physical and chemical interaction with the substrate. In general, the direction of \( \mathbf{n} \) on a substrate is referred to as the easy axis. It is characterized by the polar angle \( \theta_o \) and azimuthal angle \( \phi_o \) (Fig. 1.4). The polar and azimuthal anchoring energies \( F_p(\theta) \) and \( F_a(\phi_o) \) specify the energy required to deviate the LC director from \( \theta_o \) and \( \phi_o \), respectively. The LC ordering at the substrate interface is phenomenologically described by the ratios of the surface tensions of the surface \( (\gamma_s) \) and the liquid crystal \( (\gamma_{LC}) \). If \( \gamma_s < \gamma_{LC} \), the intermolecular forces exceed the LC-surface forces resulting in a homeotropic alignment. Homogenous alignment is achieved when the surface anchoring forces are dominant [7].

The ordering is usually imposed by the surfaces limiting the LC or by an external field. Various surface treatments are being developed to achieve tailored alignment patterns. Surfaces such as rubbed polymer films, LB films, vacuum deposited dielectric layers, thin polymer films exposed to linearly polarized UV are known to contain grooved surfaces and induce alignment in LCs. From the substantial amount of work done to verify what really aligns LC, a coherent picture emerges. That is, LC ordering is attributed to the anisotropy in the surface morphology [8, 9, 10, 11] and the LC anchoring strength is due to the intermolecular interactions [12, 13, 14] between the LC and the surface.
Figure 1.3: Schematic representation of (a) a basic LCD which consists of a liquid crystalline material sandwiched between two substrates with conductive but optically transparent films. Upon application of an electric field across the substrate, the LC molecules undergo Fredericks transition resulting in a reorientation of the director parallel to the field for LC materials with positive dielectric anisotropy and (b) the different molecular ordering at the surface.
Figure 1.4: Liquid crystalline director orientation at the substrate. $\phi_o$ corresponds to the preferred azimuthal angle and $\theta_o$ to the preferred polar angle.
Figure 1.5: Structural representation of monomeric unit ethylene (a) and of polymer polyethylene (b). The number of monomer units determines the degree of polymerization.

1.1.2 Polymers

Besides liquid crystalline materials, polymers are another class of important soft-matter, specifically in the preparation of thin films. Polymers or macromolecules consist of a large number of molecular units linked together by covalent bonds and typically are represented by organic compounds containing carbon atoms together with hydrogen, oxygen, nitrogen, halogens, etc. [18], an example of which is shown in Fig. 1.5. These covalent bonds are regarded as vectors $\vec{b}_i$ of identical magnitude $b$ (Fig. 1.6), but different directions as a consequence of the unrestricted possible conformations of the adjacent bonds, in the absence of external influences. The vector sum of all the $\vec{b}_s$ along the polymer chain defines end-to-end distance, $R_{EE} = \sum_{i=1}^{n} \vec{b}_i$. That is, $R_{EE}$ is the distance between two terminal atoms of the polymer chain. In the event of the chain being pulled straight, the total length is known as the contour length, $L$ and is equal $nb$, where $n$ is the number of links/chains. The mean square
Figure 1.6: The end-to-end distance, $R_{EE}$ describes the distance between two terminal atoms of a polymer ball such that $\bar{R}_{EE} = \sum_{i=1}^{n} \bar{b}_{i}$.

of the end-to-end distance $<R_{EE}^2>$ is given by

$$\langle R_{EE}^2 \rangle = nb^2$$

$R_{EE}$ however is difficult to measure. Instead, radius of gyration, $R_g$ is often used since this quantity can be measured by light scattering. $R_g$ is the average distance from the center of the gravity to the chain segment and is related to $R_{EE}$, and $\langle R_{g}^2 \rangle = \frac{1}{6} \langle R_{EE}^2 \rangle$ in the limit of very high molecular weight ($M_w$).

In the bulk, polymers combine elastic and viscous properties of both, the fluid and solids and they are generally addressed as viscoelastic materials. They are soft materials because of the relative ease with which they respond to elastic forces. They distort in response to modest shears, and thermal fluctuations play an important, if not dominant, role in determining their properties. As a consequence of strong
temperature dependence of their physical properties, the range of applications for polymers is limited. One such limit is the glass transition temperature, below which the system turns into an amorphous solid.

The Glass Transition

Upon cooling any liquid (except liquid helium), a solid phase forms. For materials whose constituents are highly symmetric (such as single atoms, hard spheres or even long rods), this solid phase is invariably a crystalline phase. In the crystalline phase, the material is characterized by a unit cell which is repeated over macroscopic distances resulting in a phase with long-range positional order. This transition from the liquid to crystalline phase at the melting temperature, $T_m$, is a first-order transition characterized by discontinuities in the first derivative of Gibbs free energy with respect to temperature. At this transition, quantities such as the heat capacity and specific volume change discontinuously. The former manifests in the latent heat of transition.

There are materials however in which another kind of transition takes place. A transition from the liquid phase to a state that can support static shear and no long-range order is present - a glass. This occurs in place of crystallization because the constituent molecules possess some intrinsic order which frustrates crystallization. For example, atactic polymers (polymers with random stereochemistry) and random copolymers are usually unable to crystallize and thus form a glass on cooling. In other systems, for a sufficiently high cooling rate, there is insufficient time for the molecules to make the rearrangements necessary to develop long-range order to form the crystalline state, and despite the fact that the crystalline state has the lower free energy, a kinetically stable glass is formed. This is the case for a wide variety of
metals, inorganic salts, small organic molecules and polymers [15].

The ability of so many substances to form glasses on cooling lies in the empirical fact that the viscosity of glass-forming liquids dramatically increases upon cooling, so that the molecular rearrangements needed for crystallization do not take place on experimental time-scales. Generally, the viscosity of glass forming liquids is well described by the Vogel-Fulcher-Tammann (VFT) relation [16],

$$\eta = \eta_0 e^{B(T - T_o)}$$  \hspace{1cm} (1.3)

This equation describes a viscosity which appears to diverge at a temperature $T_o$. Experimentally, however, the material will undergo a transition to the glass state at a higher temperature, $T_g$. This transition is marked by apparent discontinuities in quantities that are second derivatives of Gibb’s free energy of the system and properties such as the expansivity and the heat capacity [17]. However, the experimental glass transition, despite its superficial similarity to a second order phase transition, is not a true phase transition. The glass transition cannot be assigned a unique transition temperature. The apparent transition temperature depends on the time scale over which the measurement is made as well as the thermal history of the sample. Hence, it is generally more accurate to refer to it as a glass transition region rather than a single glass transition temperature.

The $T_g$ is intrinsically related to the structural relaxation and to the segmental mobility of the polymers. The main relaxation process which takes place in the liquid-glass transition region is the so called $\alpha$-relaxation. The structural relaxation dynamics of glass forming materials are generally well described and characterized by
the Kohlrausch-Williams-Watts (KWW) [19] stretched exponential function

\[ \phi(t) = \phi_0 e^{-\left(\frac{t}{\tau}\right)^\beta} \]  

(1.4)

For short relaxation times (\( \sim \) min) the stretch parameter \( \beta \) describes the shape of
the relaxation time distribution: \( \beta = 1 \) for a distribution with a single relaxation

time; \( \beta < 1 \) for a distribution with a long tail of short relaxation times and \( \tau \) is the
average relaxation time constant. Ideally, a single relaxation time constant (\( \tau = 1 \))
is assumed to characterize the relaxation behavior. However, this is not true for real
polymers, since polymer molecules can exhibit many different modes of relaxation
processes, ergo the time constant \( \tau \) varies with temperature \( T \) and the variation of
the average relaxation time \( \langle \tau \rangle = \tau_o \int f(t)dt \) generally obeys the empirical VFT [16]
temperature dependent equation

\[ \langle \tau \rangle = \tau_o e^{\frac{B}{T - T_o}} \]  

(1.5)

where, the parameter \( \tau_o \) is a microscopic relaxation time. Here, \( B \) describes the
fragility of the glass former, and \( T_o \) for polymers is generally \( T_o \sim T_g - 50K \). The
dynamical behavior of bulk polymers is well-described by Eqns. 1.4 and 1.5.

While the dynamics of bulk polymers is well established, the interest in the dyna-
mical behavior of the polymer surfaces is fairly recent and originated mainly as
a consequence of the increasing number of applications which ranges from coatings,
and dielectric layers, to lubricant surfaces in addition to the observation that some
polymeric systems have surface properties dependent on its environment.

Polymers restructure in conformity to the surface properties of the interfacial
Figure 1.7: Motions in a randomly coiled polymeric chain: (a) rotation about the side-group bond, (b) segmental and (c) macromolecular scale.

medium [20]. Intuitively, polymers on free surfaces are more mobile than the underlying (buried) polymer layers. On the other hand, if the interfacial phase is thermodynamically hostile (e.g., the polymer segments are strongly bound to a substrate), it can work as a hard wall and limit the mobility of surface chains.

In thin films of polymeric materials, several hierarchies of motion co-exist as illustrated in Fig. 1.7. A first kind of motion is the rotation around the backbone and side-group bonds (Fig. 1.7a). On a larger spatial scales, the typical polymeric movements involve either a large segmental (Fig. 1.7b) or macromolecular mobility (Fig. 1.7c). The latter mechanism controls many properties of interest in the bulk, melt and solution of polymers. As for thin films, outdiffusion of chains from the bulk towards the surface or reorganization of segments in the domain-like surface structure profoundly affects the polymer surface properties. Also, the short range reorientation of side-groups can have a dominant effect on the surface properties [21].

Because of these constraints, the dynamics of polymer films becomes different
from that of the bulk and the surfaces, and interfaces affect properties of the materials within a finite distance from the interface.

1.2 Literature Review

In light of increasing evidence that the interfacial morphology plays a dominant role in LC alignment, it is essential to understand not only the interfacial structure and morphology but also the polymer chain dynamics at the interfaces. In this dissertation we investigate both the dynamics and the morphology of thin polymer surfaces. The following sections provide comprehensive reviews of the past studies of the alignment mechanism of LCs and the relaxation dynamics of thin polymer films. This should make it evident why the work described in this dissertation is important.

1.2.1 Alignment of Liquid Crystals

A variety of techniques for controlling the LC alignment near a surface have been empirically developed using surface modifications by methods such as vacuum deposition of metals oxides [22], physical or chemical adsorption of surface active agents [23], deposition of polymer films [24] followed by rubbing or mechanical scribing. Adsorption of amphiphilic compounds [25] induces homeotropic alignment whereas Langmuir-Blodgett films [26] and rubbed polymer thin films, especially of polyimide, cause homogeneous alignment. A director pretilt of $\sim 23^\circ$ is obtained on obliquely-evaporated SiO films [27] and of approximately $5^\circ$ on rubbed polyimide films [28]. These effects suggest that the LC alignment is a result of primarily the mechanical interactions relating to the surface morphology and anisotropic elasticity of LC molecules [29]. Physicochemical interactions such as hydrogen bonding, van der
Waal’s interactions, dipole-dipole interactions between LC molecules and the substrate also play an important role and determine the surface anchoring energy.

There has been great interest in understanding the alignment effects specifically on rubbed polyimide films which possess a grooved morphology [30] and oriented polymer chains [31, 32] where the director *n* lies nearly parallel to the rubbing direction. From the technological viewpoint, rubbing generates undesirable electrostatic charges, mechanical charge and dust particles. It also reduces the yield of thin film transistor based (active matrix addressed) devices. The use of photoalignment on UV sensitive polymer films [33], such as cinnamoyl or photochromic molecule containing polymers eliminates these problems. Morphological anisotropy on these films is induced via linear photopolymerization of polymers with cinnamoyl such as poly(vinyl)4-methoxycinnamate (PVMC) [34] or of similar groups capable of undergoing a photochemical dimerization. Photochromic molecules such as azobenzene containing two isomeric configurations, the *cis* (Z-isomer) and the *trans* (E-isomer) have also been shown [35] to yield photoalignment. Polarization photochromism, affected by the absorption of light induces isomerization from *cis* to *trans* or vice-versa. This fixes a greater proportion of the *trans* configuration in the photostationary state inducing optical and morphological anisotropy. Photoalignment is also induced via photodegradation of UV sensitive polyimide materials [38, 39, 4]. The photoalignment on different photosensitive polymers is caused by different chemical changes in the film and results in a homogeneous alignment with preferred azimuthal orientation either parallel or orthogonal to the direction of the polarization of light. Schadt, et.al. [34] attributes this anisotropy to the depletion of the cinnamate side-chains as a consequence of the (2+2) cycloaddition reaction along the axis of polarization resulting
in the formation of cyclodimers. The orientation of the unreacted side chains and the principal photoproducts is perpendicular to the incident UV field believed to align (or interact) the LC molecule in this direction. However, x-ray reflectivity work on these films as well as on Langmuir-Blodgett films of 12-8(poly)diacetylene (PDA) [36, 37] attributes the alignment to surface roughness anisotropy caused by UV irradiation.

In azo-containing polymers, the alignment stems from photoinduced molecular orientation of photochromic units that also eventually leads to surface roughness anisotropy. The absorption probability of incident polarized light is maximum for molecules with transition moment parallel to $\mathbf{E}$. The excited molecules reorient to a state that is independent of their original orientation. This reorientation is enhanced by configurational changes, since isomerization from $\text{trans}$ to $\text{cis}$ reduces the bulk volume [41]. Hence, the alignment layer develops an anisotropy with the maximum number density of the azo units, and hence the easy axis located perpendicular to the direction of UV’s polarization. The easy axis of photoexposed polyimide is perpendicular to the polarization of the incident UV. This is attributed to the anisotropic dissociation of photosensitive bonds as revealed in spectroscopic studies [42]. Further studies have confirmed this [43] and the alignment direction was shown to change when the polarization direction of the UV field was changed.

Furthermore, a comprehensive XRR study on polyvinyl alcohol (PVA), polyimide (PI) and polystyrene (PS) films [10] also showed that the anisotropy in the surface roughness of the substrate determines the direction of LC alignment.

Studies of the anchoring transition (homeotropic to homogeneous alignment) of LC in chemically derivatized PVA\textsuperscript{2} systems [44] and fluropolyvinyl cinnamate [45]

\textsuperscript{2}PVA alignment layer reacted with trifluoroacetic anhydride (TFAA) in the gas phase to substitute -OH groups to -OCOF\textsubscript{3} groups
have shown that the LC director reorientation with temperature is due to the reorientation of the flexible polymer fragments and of the main polymer chain. Modeling of the "surface viscosity" for gliding of LC [46] also showed that the director reorientation on polymer surface is determined by the rate of rearrangement of the polymer chains rather than by the surface friction of the LC.

Evidently, the study of the relaxation dynamics of polymer surfaces is important and should reveal important details about the alignment mechanism and provide useful information about chain mobility.

1.2.2 Relaxation Dynamics of Thin Polymer Films

The large surface-to-volume ratio of thin films allows one to explore molecular confinement effects and interfacial interactions. The film thickness becomes an important parameter, as this can be reduced down to a scale comparable to the polymers' radius of gyration, $R_g$. By appropriately reducing the thickness of the film, one can perturb the conformation of the polymer molecules and eventually affect the polymers' mechanical properties such as diffusivity, viscosity, and glass transition temperature. Among these properties, the dependence of the glass transition temperature $T_g$ on the confining dimension is least understood.

Measurements of $T_g$ in Thin Polymer Films

The classical methods for measuring $T_g$ in bulk polymers are differential scanning calorimetry (DSC) and dilatometry. These methods measure the heat capacity and/or expansivity which are related to the glass transition. These techniques however require 10-50 mg of material (polymer) and as such are not suitable for measurements in thin films where the amount of material is less than 1 mg. However, it is relatively
straight forward to measure directly or indirectly the expansivity of very thin films and to determine the value of $T_g$.

Currently, there are four techniques which have been effective in determining the value of $T_g$ in thin polymer films. These techniques are ellipsometry, x-ray reflectivity (XRR), Brillouin light scattering (BLS) and positron annihilation light spectroscopy (PAS). In ellipsometry and XRR, the film thickness or a quantity related to the thickness of the film is measured and a discontinuity in the slope of this value versus temperature yields the $T_g$ value. In BLS, the measured frequency shifts are strong functions of the material density and a kink in the frequency shift versus temperature appears at the $T_g$. In PAS, the measured quantity is related to the lifetime of the positrons trapped in nanometer sized voids in the sample. Their lifetime gives the average free volume size in the samples, which is related to density and thus, the value of $T_g$ can be inferred.

The first ellipsometry measurement [47] of the $T_g$’s dependence on film thickness $h$ was performed on a large number of polystyrene films with three different molecular weights $M_w$ ($M_w = 120 \times 10^3, 501 \times 10^3$ and $2900 \times 10^3$; $R_{EE} = 225, 460$ and $1110$ Å) on hydrogen-passivated silicon (Si-H) substrates. Results showed a reduction in $T_g$ from its bulk value for $h < 400$ Å, described by the empirical relation

$$T_g(h) = T_g^{bulk} \left[ 1 - \left( \frac{\alpha}{h} \right)^\delta \right]$$  \hspace{1cm} (1.6)

The best fit of the data to Eq.(1.6) was obtained for $\alpha = 32$ Å and $\delta = 1.8$. This quantitative agreement between the measured $T_g$ values of polymers, with molecular weight $M_w$ values differing by a factor of 25, provided a strong evidence that the confinement of polymer was not responsible for the reduction in the $T_g$ values. Instead, it was suggested that the reduction was caused by the presence of
a liquid-like layer at the polymer-air interface, with the substrate having only a little effect. Similar results were obtained from x-ray reflectivity measurements [48] of PS ($M_w = 233 \times 10^3; R_{EE} = 310$ Å) on Si-H substrates in film thicknesses between 91 Å and 1988 Å, and from positron annihilation lifetime spectroscopy (PAS) [49] measurements for PS ($M_w = 260 \times 10^3, R_{EE} = 330$ Å) on similar substrates.

Subsequent ellipsometry measurements [50] for poly(methyl)methacrylate (PMMA) films ($M_w = 100 \times 10^3; R_{EE} = 220$ Å) on two different substrates revealed the dominant effect of polymer-substrate interaction on $T_g$ values measured for uncapped supported films (air-polymer-substrate). For PMMA deposited onto the native oxide coating of Si wafers ($150$ Å < h < 1200 Å), the measured $T_g$ values increased with decreasing film thickness, h, whereas for PMMA films deposited onto Au-coated Si wafers ($300$ Å < h < 1300 Å), the $T_g$ decreased as h was reduced. It was proposed that a strongly attractive interaction between PMMA and the Si native oxide due to hydrogen bonding was responsible for the increase in $T_g$ with decreasing h. The PMMA-Au interaction is much weaker leading to a decrease in $T_g$ with decreasing h. This qualitative difference in the thickness dependence of $T_g$ for the two substrates revealed the strong influence of the polymer substrate interaction on $T_g$. Similar results were reported for poly 2-vinyl pyridine [P(2)VP] films on SiO$_x$[51].

A reduction in $T_g$ below the bulk value was also observed in polystyrene films, both, supported and free standing with BLS, photon correlation spectroscopy and quartz crystal microbalance techniques [52]. The first measurement of $T_g$ for thin freely-standing polymer films was done using BLS studies. These studies on single ($M_w = 767$ K) polymer revealed very large reductions (~70 K) in the value of $T_g$ compared to supported films with decreasing film thickness [53]. The behavior of $T_g$
for supported films is well described by Eqn. 1.6 whereas, for freely-standing films, it is a linear function of film thickness (also $M_w$ dependent). In contrast, the values of $T_g$ measured with XRR showed an increase from 20-50 K above the bulk $T_g$ with decreasing film thickness [54].

It is clear from the above discussion that the $T_g$ of thin polymer films has a substantial dependence on the film thickness, nature of the substrate, and molecular weight. Because $T_g$ is related to segmental mobility of polymer chains, a number of studies on chain mobility/structural relaxation were performed to understand it in confined geometry.

Measurements of Chain Mobility and Structural Relaxation

A polymer chain has a large number of relaxation modes, ranging from very small segmental motions to center of mass diffusion. The $T_g$ is usually thought of as being associated with relatively small-scale segmental motions. Hence, in thin films, any thermal anomalies in the segmental mobility are reflected in the value of glass transition temperature.

Chain mobility measurements of PS films using the fluorescence recovery method after patterned photobleaching [55] showed that the lateral diffusion coefficient of the polymer chains ($M_w = 30 \times 10^3; R_{EE} = 120 \text{ Å}$) was substantially lower than its bulk value for films with thicknesses much larger than $R_{EE}$. The results of these experiments, which are in agreement with Zheng et al. [56], demonstrate that the chain mobility is strongly influenced by substrate effects. Higher (than bulk) mobility at the free surface is expected, but has yet to be observed directly. Atomic force microscopy of 2000 Å thick PS films ($1.7 \times 10^3 < M_w < 1800 \times 10^3; 30 < R_{EE} < 900 \text{ Å}$), for which $h$ was much larger than $R_g$, revealed enhanced mobility of the polymer chains
at the free surface for small molecular weights \(M_w < 27 \times 10^3\) [57]. These results show that the surface region of low \(M_w\) PS films is "rubberlike" at a temperature 70 K below the bulk \(T_g\), whereas the surface region of PS films with larger \(M_w\) is glassy at room temperature.

Recently, it was shown that room temperature buffing of thin polymer films orients the polymer side groups along the buffing direction, even for high-\(T_g\) polymers such as polyimide \((T_g > 400^\circ\mathrm{C})\) [13, 58]. The ability to rearrange the chains at free polymer surface is an evidence for the existence of a surface region of enhanced mobility. Near-edge x-ray-absorption fine structure (NEXAFS) has been used to study the relaxation of the buffed state of PS films on Si wafers with native oxide layer [59]. Results showed that a full relaxation of the buffed and oriented state did not occur for temperatures less that the bulk \(T_g\).

In simulations [60, 61, 62, 63, 64, 65] of polymers at temperatures near \(T_g\), confined by both free surfaces and hard neutral walls, it is found that the chain mobility in the surface layer is highly anisotropic with a mobility enhancement (reduction) parallel (perpendicular) to the walls. The effect of these anisotropic changes on the chain mobility near a free (or neutral) solid surface on the value of \(T_g\) is not clear, and the situation is further complicated by the possibility of interactions between the polymer and the solid substrate. Experimentally, the measured \(T_g\) for a given uncapped supported film seems to depend strongly on the details of the polymer substrate interaction, as indicated by the behavior of polymer films on different substrates in Ref. [59]. In addition, the reduction in \(T_g\) observed in Ref. [59] reveals the importance of the free surface.
In summary, several studies [47, 48, 49, 50, 51, 52, 53, 54] indicate that thin polymer films have glass transition behaviors substantially different from bulk polymer. However, we are far from understanding the causes of these effects. It must also be recognized that while shifts of the $T_g$ in thin films clearly indicate that there are differences between the segmental mobility properties of polymers in the bulk and in thin films, glass transition temperatures by themselves are only an indirect probe of the mobility. Also, many techniques for probing relaxations of polymer surfaces involve physical contact between a probe and the surface of a polymer. Hence, it would clearly be highly desirable to measure the mobility of polymer segments near surfaces, interfaces, and in thin films more directly without the physical contact between probe and polymer surface.

In this dissertation, we describe a simple technique to directly probe the polymer chain dynamics and measure the glass transition temperature simultaneously. Additionally, we investigate the surface morphology of thin polymer films mostly used for LC alignment using a surface-sensitive XRR technique. The XRR was chosen because it probes not only composition/structure of surfaces but also of buried interfaces. The results of both experiments should give us a more coherent picture of what really aligns LC in confined systems in the absence of fields.

In the following chapter, the sample preparation and theoretical and experimental details of the techniques are discussed. The dynamical study on the relaxation of polymer chains on rubbed films, probed by measurements of optical retardation, is presented in Chapter 3. Chapter 4 describes the results of the study of the morphological features of polymer films using x-ray reflectivity. Results on the alignment stability with temperature in UV exposed films are described in Chapter 5. Finally,
Chapter 6 provides a summary and main conclusions derived from this work.
REFERENCES


CHAPTER 2

EXPERIMENTAL TECHNIQUES

The general description of the materials used, the sample preparation, and the experimental techniques are discussed in this chapter. Optical retardation measurements were carried out to determine the relaxation dynamics of rubbed film as well as the optical anisotropy of surface treated films. X-ray reflectivity was performed to investigate the morphological features of the films.

2.1 Materials and Preparation

All polymer films used in this work were prepared on glass substrates, cleaned in an ultrasonic bath filled with detergent water at 60°C for 15 minutes then rinsed with deionized water, methanol and isopropanol (IPA). Complete wetting by IPA was used to determine the cleanliness of the substrate (i.e. when IPA did not form droplets at the substrate). Drying and IPA evaporation were carried out inside an oven set at 100°C for 15 minutes to eliminate residual solvent.

To create homogenous uniform film of polymer, polymer solution (polymer dissolved in appropriate solvent) was spin coated on the glass substrate. Film thickness was controlled by adjusting the spin coating speed, spin time, and the concentration of polymer in the solution. Solvent evaporation was done either by using a hot plate or by placing the substrate inside a vacuum oven (Napco, Model 5851) at an elevated temperature. Depending on the type of polymer, the glass substrate was hard baked at appropriate temperatures in a homemade oven.
Anisotropy in the film was induced either by rubbing or by exposing to linearly polarized ultraviolet (UV) light. Surface modification of the polymer film by rubbing was carried out with the use of a velvet cloth and the extent of rubbing was controlled by varying the number of rubs on the film. A sheet polarizer (Oriel, Model 27320) or Glan-Taylor polarizer was used to linearly polarize the UV light from a Xenon lamp (Oriel, Model 66021) of wavelength range 320-400 nm. The dosage of UV irradiation was controlled by changing the exposure time, source intensity, and the distance of the sample from the UV source.

2.1.1 Polystyrene

Thin films of polystyrene with $M_w = 48.5 \times 10^3$ were prepared by spin coating a PS solution in toluene (Aldrich-HPLC grade) on a glass substrate at 3000 rpms for 30 sec. This was followed by solvent evaporation inside an oven at 100$^\circ$C for one hour. Cast films were prepared using an effective zero spin speed, dried under vacuum conditions for 24 hrs to completely remove the solvent, and then annealed for 5 minutes at 105$^\circ$C (378 K) to erase thermal history and residual birefringence created by spin coating.

2.1.2 Polyimide

A polyimide (PI) is typically prepared by curing a polyamic acid (PAA) film, a polymeric precursor solution of dianhydrides and diamines in polar solvents such as $N$-methylpyrrolidone (NMP), $N,N$-dimethylformamide (DMF), $N,N$-dimethylacetamide (DMAC) and tetramethyleurea (TMU) [1]. A thin film is formed by spin coating the PAA on the substrate followed by thermal curing cycle (soft-baking to evaporate the solvent and hard-baking to carry out imidization). The film thickness uniformity and
morphology are controlled by the solvent composition, polymer composition, molecular weight, viscosity, spin speed and spin time. During the curing cycle, the precursor converts from a flexible, soluble polymer to a rigid mesomorphic polyimide (Fig. 2.1). The curing process involves an (intra-chain) cyclization reaction to form imide linkage [2].

Commercially available polyimide films (Nissan, Chemicals SE610 and SE 7311) were prepared by coating the polyimide precursors, PAA, on the substrate at 3000 rpm for 30 sec., which effectively yielded ~250 Å films. Evaporation of the solvent (soft-baking) was carried out in an oven set at 100°C for 10 minutes, followed by imidization (hard-baking) in a homemade oven with a quartz window to facilitate UV exposure whenever appropriate. Hard baking temperature was 220°C and 200°C for SE610 and SE7311, respectively.

2.1.3 Azopolymers

Thin films of azopolymers were also prepared by spin coating a 10% solution of azopolymer in dichloroethane onto glass substrates. The materials PA and PB were laboratory synthesized comb-like polymers with azobenzene side chains (see Fig. 2.2). The side-chains of PA contain hydrophobic alkyl tail -C₄H₉ attached to the azobenzene moiety (Fig. 2.2a) whereas PB contain NO₂ end groups (Fig. 2.2b). Both azopolymers have liquid crystalline properties: nematic 112-140°C and 44°C - SmA - 52°C - N - 55°C for PA and PB, respectively. At room temperature, both azopolymers are crystalline solid.

To determine the effectiveness and stability of the film as an alignment layer for liquid crystals, the substrates were assembled to form cells with a gap of 5μm. Nematic liquid crystal ZLI 4975 with the nematic-to-isotropic transition temperature, $T_{N→I} =$
Figure 2.1: Formation of poly(amic acid) from the reaction of pyromellitic dianhydride (PMDA) and diaminodiphenyl amine (ODA) solution in DMAc solvent. The poly(amic acid) is converted to polyimide by thermal imidization.
Figure 2.2: Molecular structure of azopolymers, (a) PA, containing alkyl tail -C₄H₉ attached to the azobenzene moiety, and (b) PB containing NO₂ end groups.
85°C was filled into the cell in the isotropic phase via capillary action. Controlled cooling at 1 K/min was done before edges of the cells were sealed using 5-minute epoxy.

LC alignment and textures were determined using a polarizing microscope. Uniform appearance under the microscope which alternates between bright and dark as the sample is rotated indicated homogeneous alignment. The appearance of \textit{schlieren} nematic textures or domains indicated planar aligned or misaligned sample.

2.2 Experimental Details

All polymer films were characterized using optical retardation which provides a measure of induced anisotropy and x-ray reflectivity for thickness and roughness anisotropy measurements. Experimental details are described below.

2.2.1 Optical Retardation

In an optically birefringent material, the light propagates with two distinct speeds depending on the orientation of the electric field vector relative to the optical axis of the material. Two refractive indices $n_o$ and $n_e$ correspond to the ordinary and extraordinary waves in optically uniaxial materials. When the two waves with different polarizations propagate and emerge from a birefringent material, the relative phase is different from their initial value and the phase difference is called the phase retardation, $\delta$ given by [3]

$$\delta = \frac{2\pi}{\lambda} d \Delta n$$

where $\lambda$ is the wavelength of light, $d$, the thickness of the medium and $\Delta n = n_e - n_o$ is defined as the optical birefringence. When an isotropic material is mechanically compressed or stretched, the material becomes optically anisotropic or birefringent
[3], a phenomenon called photoelasticity. In the case of polymer films, anisotropy can be induced by mechanical rubbing [4, 5] or exposure to linearly polarized UV light [6]. The small phase retardation of these modified films can be measured with high sensitivity using a photo-elastic modulator as discussed below.

Photo-elastic modulators (PEM) are resonant devices, producing oscillating birefringence at a fixed frequency which operate on the basis of photoelasticity of a material (piezoelectric effect). A photoelastic rectangular head (ex. fused Silica) is made to vibrate with a natural resonant frequency of about 50 Hz sustained by a piezoelectric transducer attached to the end of the bar. The transducer is driven by an electronic circuit (PEM controller) which controls the amplitude of vibration. An oscillating birefringence appears at the center of the head making a linearly polarized light acquire a sinusoidal phase retardation. Optical retardation of the films, in this study, was measured using an optical set-up consisting of a PEM (PEM90, Hinds Instruments) and two crossed polarizers shown in Fig. 2.3. The polarizers are oriented at 45° relative to the optical axis of the PEM and the sample is mounted on a heating stage (Mettler) placed between the PEM and the analyzer.

A plane polarized light of amplitude $E_0$ coming out of the first polarizer can be represented as [7]

$$\vec{E} = \frac{E_0}{\sqrt{2}} \left( i + j \right) e^{-iwt} \tag{2.1}$$

and the field $\vec{E}'$ after the PEM is

$$\vec{E}' = \frac{E_0}{\sqrt{2}} \left[ i e^{i\Delta(\delta + \alpha)} + j e^{i\Delta(\delta + \alpha)} \right] e^{-iwt} \tag{2.2}$$

where $\delta$ and $\alpha$ are the optical phase retardation of the sample and PEM respectively, $\alpha = \alpha_0 \cos(\Omega t)$, in which $\alpha_0$ is the amplitude of the sinusoidal retardation function
Figure 2.3: Experimental set-up for the optical retardation measurement.
of PEM and $\Omega$ is the angular frequency of the modulator. The electric field coming through the analyzer (second polarizer) is

$$E'' = \frac{1}{\sqrt{2}} (\hat{i} - \hat{j}) \cdot \hat{E}$$

$$= \frac{E_o}{2} \left[ e^{\frac{i}{2}(\delta + \alpha)} - e^{\frac{i}{2}(\delta + \alpha)} \right] e^{-iwt}$$

$$= E_o \sin \left( \frac{\delta + \alpha}{2} \right) e^{-iwt}$$  (2.3)

The intensity seen at the detector (photodiode) is then

$$I_d = |E''|^2 = \frac{I_o}{2} \left[ 1 - \cos \delta \cos \alpha + \sin \delta \sin \alpha \right]$$  (2.4)

where $I_o = |E_o|^2$. Fourier series expansion of this equation yields

$$I_d = \frac{I_o}{2} \left[ 1 - \cos \delta J_0(\alpha_o) + 2 \sin \delta J_1(\alpha_o) \cos(\Omega t) + 2 \cos \delta J_2(\alpha_o) \cos(2\Omega t) \right] + HOHT^1$$  (2.5)

where $J_i$s are the Bessel functions of the $i$th order. The first three terms are the DC component, and the first (1f) and second (2f) harmonics of the optical signals. Introducing a proportionality constant $K$, we get

$$V_0 = K \left[ 1 - \cos \delta J_0(\alpha_o) \right]$$

$$V_1 = 2K \sin \delta J_1(\alpha_o) \cos(\Omega t)$$

$$V_2 = 2K \cos \delta J_2(\alpha_o) \cos(2\Omega t)$$  (2.6)

where $V_1$ and $V_2$ are peak voltages representing the amplitudes of the signal waveform.

By adjusting the amplitude $\alpha_o$ so that the DC signal ($V_0 = V_{dc}$) becomes a constant and independent of the samples retardation $\delta$, the DC signal can be used to normalize the AC signals ($V_1$ and $V_2$). This happens when $J_0(\alpha_o) = 0$ or $\alpha_o = 2.405$ radians

\footnote{higher-order harmonic terms}
and using this as the reference signal from the modulator controller, $V_1$ and $V_2$ can be easily detected with a lock-in amplifier (LIA). The LIA presents $rms$ voltages related by $V_{rms} = \frac{V_{peak}}{\sqrt{2}}$, therefore the ratios between the AC signals to the DC signal become

$$R_1 = \frac{V_{1(rms)}}{V_{dc}} = \sqrt{2} \sin \delta J_1(2.405)$$

$$R_2 = \frac{V_{2(rms)}}{V_{dc}} = \sqrt{2} \cos \delta J_2(2.405)$$

(2.7)

By tuning the PEM at $\alpha_0 = 2.405$ and monitoring the signal on the LIA (EG&G Princeton Applied Research, Model 5210), the optical retardation $\delta$ of the sample expressed as

$$\delta = \tan^{-1} \frac{V_{1(rms)}J_2(2.405)}{V_{2(rms)}J_1(2.405)}$$

can be determined while rotating the sample with respect to the surface normal. The LIA, PEM and the motor-controlled rotation stage were interfaced to a PC via a GPIB board. The sensitivity of this method enabled us to measure the phase retardation with a precision of $\pm0.01{}^\circ$

A commercially available heating stage from Mettler-Toledo model FP82HT (temperature range: room temperature to 375 °C) was used for precise thermal measurements ($\pm0.4{}^\circ$C for $20{}^\circ$C $\leq T \leq 100{}^\circ$C and $\pm0.6{}^\circ$C for $100{}^\circ$C $\leq T \leq 200{}^\circ$C). Attached to the heating stage was a temperature controller (Mettler FP90) for controlled heating of 1 to 20 °/min. The FP82HT allowed simultaneous optical measurements and heating/cooling of the polymer films.

2.2.2 X-ray reflectivity

Over the last few decades, the investigation of surfaces and interfaces with x-ray scattering methods has grown enormously and x-ray reflectivity has emerged as a powerful technique for the investigation of the morphology of polymer surfaces and
interfaces [8], as well as the various structures of biological membranes [9], Langmuir-Blodgett films [10], micro-emulsion [11] and liquid crystal phases [12]. The high spatial resolution $\sim 5 \text{Å}$ provides a means of probing density gradients across the surface as well as the rms surface roughness of the material on a submolecular level. X-ray reflectivity was used in this work to probe the morphology of polymer films typically used for LC alignment and prepared with different surface modification methods such as rubbing and exposing to linearly polarized UV light. The basic principles of x-ray reflectivity emphasizing on the specular as well as the diffuse scattering in polymer thin films is discussed including the experimental details.

Basic Principles of X-ray Reflectivity

The scattered x-rays are characterized by an output wave vector $k_{out}$, an angle $\beta$ to the surface and an angle $\phi$ with respect to the plane of incidence as illustrated in Fig. 2.4. The difference between the incident and output wavevectors defines the wave transfer $\mathbf{q} = k_{out} - k_{in}$ whose Cartesian components under the notation shown in Fig. 2.4 are [13]

\begin{align*}
q_x &= k [\cos(\beta) \cos(\phi) - \cos(\alpha)] \\
q_y &= k \cos(\beta) \sin(\phi) \\
q_z &= k [\sin(\alpha) + \sin(\beta)]
\end{align*}

where $k = 2\pi/\lambda$.

To extract a quantitative information on the surface structure of the material in the direction of layer formation ($z$-axis), specular reflectivity is measured. This is carried out by measuring the reflected intensity as a function of the incidence angle $\alpha$, or wavevector transfer $q_z$ along the surface normal while maintaining the *specular*
Figure 2.4: General x-ray scattering geometry. The surface lies in the xy-plane.

conditions, i.e. $\alpha = \beta$ and $\phi = 0$ (or equivalently $q_{xy} = 0$).

Reflectivity arises from the contrast of the gradient of the refractive index along the surface normal of the media. The refractive index of a material is

$$n = 1 - \delta + i\beta \quad (2.11)$$

to within a good approximation. The $\delta$ is directly related to the electron density $\rho(\hat{z})$ written as

$$\delta = \frac{\rho(\hat{z})\lambda^2 e}{2\pi} \sim 10^{-6} \quad (2.12)$$

That is, the real part of the refractive index is slightly smaller than unity. The imaginary component $\beta$ which accounts for the absorption is expressed as

$$\beta = \frac{\mu\lambda}{4\pi} \quad (2.13)$$
and is usually one or two orders of magnitude smaller than $\delta$. $\lambda$ is the x-ray wavelength, $\rho(z)$ the electron density function along the surface normal $z$, $r_e$ the classical electron radius ($2.82 \times 10^{-13}$ cm), and $\mu$ the linear mass absorption coefficient. Because $q$ contains no component parallel to the surface in the specular condition, no information about the in-plane structure/correlations can be obtained. Such information can be obtained from the off-specular diffuse scattering, i.e., when $\alpha \neq \beta$, which shall be discussed later in this chapter. At the interface separating the two media of refractive indices $n_1$ and $n_2$, Snell’s law [13] of refraction yields

$$n_1 \cos \alpha = n_2 \cos \beta_r$$

(2.14)

If the interface is between air or vacuum to a solid or liquid, $n_1=1$ and Eqn. 2.14 becomes

$$\cos \beta_r = \frac{1}{n_2} \cos \alpha$$

(2.15)

For most materials, the real part of the index of refraction for x-rays is slightly smaller than unity ($n_2 < 1$). A critical angle $\alpha_c$ exists, below which total external reflection of x-rays occurs. That is, x-rays do not penetrate far into the medium. Instead, all incoming radiation is reflected with a small loss due to absorption. The angle of refraction $\beta_r = 0$ when

$$\cos \alpha = \cos \alpha_c = n_2$$

(2.16)

To a very good approximation, $\alpha_c \approx (2\delta)^{\frac{1}{2}}$. The change in the refractive index from one medium to another give rise to reflectivity. The reflectivity $R$, at an ideal interface as a function of the glancing incidence angle $\alpha$, or x-ray momentum transfer $q_z = (4\pi/\lambda) \sin \alpha$ along the surface normal, is given by the well-know Fresnel formula
[3] and is written as

\[
R(q_z) = |r|^2 = \frac{q_z - \sqrt{q_z^2 - q_c^2}}{q_z + \sqrt{q_z^2 - q_c^2}}
\]

where \( r \) is the reflection coefficient, and \( q_z \) and \( q_c \) are as described above.

Figure 2.5 shows examples of reflectivity profiles (Eqn. 2.17) as a function of the \( q_z \) for a fixed value of electron density \( \rho = 0.75 \text{ Å}^{-3} \) and different ratios of electron density to absorption coefficient \( (\rho/\mu) \). The absorption only plays a role in the vicinity of the critical angle, leading to the ”rounding” in this region and is essentially negligible for large \( q_z \).

Reflectivity of Thin Films

A stratified media is much more complex than the single interface. In almost all cases, layer systems are present where the scattering from all interfaces is to be taken into account. Consider the scattering of x-rays from two sharp interfaces or film of thickness \( d \) and uniform electron density \( \rho(z) = \rho_o \) on a substrate. Here, there are two step changes in the reflection coefficients; at the air-film and film-substrate interfaces shown in Fig. 2.6. The reflectance of the sample in terms of the reflectances of the film-substrate, \( r_{fs} \) and at the air-film interface \( r_{af} \), is written as [3]

\[
r = \frac{r_{af} + r_{fs} \exp(\text{in}q_zd)}{1 + r_{af}r_{fs} \exp(\text{in}q_zd)}
\]

for which the reflectivity \( R \) is given by \( R = r^*r \) or

\[
R(q_z) = \left| \frac{r_{af} + r_{fs} \exp(\text{in}q_zd)}{1 + r_{af}r_{fs} \exp(\text{in}q_zd)} \right|^2
\]

where \( r^* \) is the complex conjugate of \( r \). The indices \( a, f \) and \( s \) correspond to air, film and substrate respectively. This equation yields oscillations well-known as the Kiessig fringes [14] characteristic of a uniform film thickness which stem from interfaces of the
Figure 2.5: Normalized Fresnel reflectivity $R_F$ with the wavevector $q_z = (4\pi/\lambda)\sin2\theta$ of an air/glass interface. $\rho_{\text{glass}} = 0.75$ Å$^{-3}$ for $\lambda = 1.54$ Å at different $\rho/\mu$ ratios: solid line (1), long-dashed line (1/50) and dashed-dot line (1/100).
Figure 2.6: Schematic diagram of the beam path in a uniform film of thickness \( d \) on a substrate.

Reflected waves at the air-film and film-substrate interfaces. The period of the these fringes provides an accurate measure of the film thickness \( d \) for which \( q = 2\pi n/d \). As an example, Fig. 2.7 shows a calculated reflectivity for a film with thickness \( d = 250 \) Å on glass substrate of \( \rho_{\text{glass}} = 0.75 \) Å\(^{-3}\) and \( \rho_{\text{film}} = 0.35 \) Å\(^{-3}\) with \( \lambda = 1.54 \) Å. The amplitude of these fringes depends on the electron density contrast between the top and the bottom film interface as well as uniformity (or, roughness) and morphology of the film. The top (air/film) interface usually displays the strongest scattering due to the relatively large electron density change across it.

Reflectivity of Non-ideal Surfaces: Roughness

The specular reflectivity from a macroscopically homogenous surface is alternatively well-described by the Born approximation [15]

\[
R(q_z) \simeq R_F(q_z) \left| \int_{-\infty}^{+\infty} dz \frac{d}{dz} \left[ \frac{\langle \rho(z) \rangle}{\rho_\infty} \right] e^{-s^2q_z^2} \right|^2
\]

(2.20)

where, \( R_F(q_z) \) is the Fresnel reflectivity from an ideally flat and sharp interface in Eqn. 2.17, \( \rho_\infty \) is the electron density in the bulk subphase and \( \langle \rho(z) \rangle \) is the average
Figure 2.7: Calculated x-ray reflectivity of a film with thickness $d = 250$ Å (solid line) and Fresnel reflectivity $R_F$ of the substrate (dashed line).
density profile ("average" over area defined by the x-ray coherence lengths in the x-y plane) across the interface at height $z$ along the surface normal. That is, the interface between a film and a substrate is not infinitely sharp and a surface roughness is associated with it over an appropriate coherence length ($l_c$) in the x-y plane. Shown in Fig. 2.8 are flat and rough surfaces over the coherence length $l_c$. The influence of roughness on the specularly reflected intensity is estimated by Beckmann and Spizzichino [16], simplifying Eqn. 2.20 to

$$R(q_z) = R_F \exp(-4q_z^2\sigma^2)$$  \hspace{1cm} (2.21)

The exponential part is a Debye-Waller-like factor which accounts for the scattering from a rough surface described by a Gaussian surface roughness $\sigma$. The reflectivity is sensitive to the surface roughness and is damped at higher $q_z$ values by this factor. Reflectivity profiles of a smooth and a rough interface are shown in Fig. 2.9.

In the layer system, interface roughness has to be included in the calculation of the specular reflectivity. This can be done easily for $rms$ roughness which are
Figure 2.9: Schematic diagram of a smooth/flat surface (solid line) and rough surface (dash-line) with $\sigma = 10$ Å.
much smaller than the respective layer thickness by replacing the Fresnel reflectivity (Eqn. 2.17) by the modified reflectivity (Eqn. 2.21). Reflectivity profiles with the same parameters used for the calculation of the curve in Fig. 2.10 is considered for the three cases: \( \sigma_{af} = 0, \sigma_{fs} = 10 \ \text{Å}, \sigma_{af} = 10 \ \text{Å}, \sigma_{fs} = 0 \) and \( \sigma_{af} = 10 \ \text{Å}, \sigma_{fs} = 10 \ \text{Å} \). It can be seen that roughness essentially damps or washes away the modulations stemming from the interference of the x-rays reflected from the film and substrate surfaces. The amplitude of modulation remains unaffected only if the roughnesses are identical, but the intensity drops more quickly than in the case of sharp interfaces. If at least one interface is sharp, i.e. \( \sigma = 0 \), the general decrease is equal to the Fresnel reflectivity, with superimposed damped oscillations. This result can be generalized: for large wavevectors \( q_z \), the interface with the smallest roughness in the multilayer stack determines the reflectivity. All other contributions with larger roughnesses "die" more quickly.

2.2.3 X-ray Diffuse Scattering

Rough interfaces dampen the specularly reflected intensity considerably. This missing intensity is diffusely scattered at exit angles \( \alpha \neq \beta \), i.e., in off-specular conditions. Corrections of the specular scattering is taken into account as a continuous profile rather than a sharp interface. However, the specular reflectivity is sensitive only to the vertical density profile \( \rho(z) \) of the sample. Lateral surface correlations/features give rise to diffuse scattering which provides information about lateral inhomogeneities of interfaces. Off-specular diffuse scattering is typically monitored by measuring the scattered intensity from a given surface within the plane of incidence \( (\phi = 0 \text{ or } q_y = 0) \) at non-specular conditions, i.e. \( \alpha \neq \beta \) (typically \( \alpha - \beta \approx 0.05^\circ \)) or \( q_z \neq 0 \).
Figure 2.10: Calculated reflectivity profiles of a film with thickness, \( d = 250 \text{ Å} \) for various rms roughness \( \sigma_{\text{rms}} \): (a) \( \sigma_{af} = 0, \sigma_{fs} = 0 \), (b) \( \sigma_{af} = 10 \text{ Å}, \sigma_{fs} = 0 \), (c) \( \sigma_{af} = 0, \sigma_{fs} = 10 \text{ Å} \) and (d) \( \sigma_{af} = 10 \text{ Å}, \sigma_{fs} = 10 \text{ Å} \). The curves are shifted vertically by two decades for clarity.
The electron density of a sample is described in three dimensions by \( \rho(\mathbf{x},y,z) \). It is convenient to separate the vertical profile \( \rho(z) = \langle \rho(x, y, z) \rangle \) from the lateral correlations \( \delta \rho(x,y,z) \) in the following manner: \( \rho(x,y,z) = \rho(z) + \delta \rho(x,y) \). The vertical profile \( \rho(z) \) is sampled by the specular reflectivity and \( \delta \rho(x,y) \) accounts for the diffuse scattering [17]. Although the vertical profiles of \( \rho(z) \) can be solved analytically, the full scattering problem including the diffuse scattering from the fluctuations \( \delta \rho(x,y,z) \) can only be solved by applying certain approximations. Using the kinematical approximation [18], the scattering function \( S(\mathbf{q}) \) is written as

\[
S(\mathbf{q}) = \frac{(\Delta \rho)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \int \exp\{q_z^2 \mathbf{C}(\mathbf{R})\} \times \exp\{-i(\mathbf{q}_{xy} \cdot \mathbf{R})\} d\mathbf{R} \quad (2.22)
\]

where, \( \mathbf{q}_{xy} \) is the in-plane scattering vector and \( \Delta \rho \) is the density contrast between the two materials next to the interface. The integration of Eq. (2.22) has a delta function behavior since \( \mathbf{C}(\mathbf{R}) \to 0 \) for \( |\mathbf{R}| \to 0 \), thus, \( S(\mathbf{q}) \) can be separated and written as,

\[
S(\mathbf{q}) = S_{\text{spec}}(\mathbf{q}) + S_{\text{diff}}(\mathbf{q})
\]

where

\[
S_{\text{spec}}(\mathbf{q}) = \frac{(\Delta \rho)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \delta(q_{xy}) \quad (2.23)
\]

and

\[
S_{\text{diff}}(\mathbf{q}) = \frac{(\Delta \rho)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \times \int [\exp\{q_z^2 \mathbf{C}(\mathbf{R})\} - 1] \exp(-i q_{xy} \cdot \mathbf{R}) d\mathbf{R} \quad (2.24)
\]

Here, \( \sigma \) is the rms roughness of the interface and \( \mathbf{C}(\mathbf{R}) \) is the height-to-height in-plane correlation function which provides a complete statistical description of the surface and is related to the probability of finding a point \( \mathbf{P} \) at position \( \mathbf{R}(X,Y) \) with the same height \( z(\mathbf{P}) \) above the mean interface as at the origin \( \mathbf{O} \) (Fig. 2.11).
2.2.4 Description of the Experimental Set-up

A Rigaku 12 kW rotating anode x-ray generator with CuKα radiation with a pair of Si(111) single crystal as monochromator and analyzer arranged in a non-dispersive geometry and a series of tantalum slits (S1, S2 and S3) to collimate and define beam size, were used to carry out the x-ray reflectivity measurements, illustrated in Fig. 2.12. The x-rays were generated as a result of the emission of electrons from a tungsten filament running a ~ 1.0 amps current. Circulating chilled water kept the rotating anode from overheating due to the incident heat flux. The electrons were accelerated toward a rotating (6,000 rpms) copper target by a potential difference of ~ 60 kV. These electrons knock-out electrons from an inner valence shell of the target atoms creating a vacancy. X-ray photons were emitted when electrons from an outer shell filled this vacancy by dropping to lower energy levels and giving up energy difference between the shells. The transitions between shells (K,L,M, etc.) have associated characteristic energies (and wavelengths) and appear as emission lines in the x-ray spectrum. The uncollimated and "white" (i.e., of many different wavelengths) x-ray
Figure 2.12: Experimental setup for high resolution x-ray reflectivity measurement. $S_1$, $S_2$ and $S_3$ are the slits for collimation. The monochromator and analyzer are Si(1 1 1) crystals. Samples are mounted on a Huber four-circle goniometer.

radiation passed through a beryllium window at a take-off angle of $\sim 6^\circ$, with an effective spot size of 0.5 mm $\times$ 1.0 mm.

The beam was then collimated by the tantalum slit S1 before impinging on the monochromator Si(1 1 1), fine tuned to select the $K_\alpha$ doublet. For copper, the $K_\alpha$ doublet has wavelengths $\lambda_{K_{\alpha_1}}=1.54056$ Å and $\lambda_{K_{\alpha_2}}=1.54439$ Å with an intensity ratio of 2:1. The presence of the doublet can smear finer features in the x-ray reflectivity scans, specifically in the specular scans, increasing the complexity of data analysis. To avoid this complexity, $K_{\alpha_2}$ was cut off by means of slit S3. The slit S2, as well as slit S3 further collimated and defined the beam cross-section (horizontal and vertical directions) before it hit the sample mounted on the goniometer. The Huber four-circle diffractometer allowed sample orientation in any desired configuration defined
by Euler’s angles $\theta$, $2\theta$, $\chi$, and $\phi$. Four stepping motors, driven by Advanced Control System’s MCU-2, on the diffractometer control the step-sizes with a precision of 0.00025° in $\theta$ and 2$\theta$ arcs, 0.0025° for $\chi$ arc, and 0.005° for $\phi$ arc.

Over a long time interval, deposition of Tungsten (from the cathode filament) on the anode surface can result in a decrease in the amount of photons emitted by the target. In addition, power fluctuations also cause fluctuations in the incident flux of the x-ray beam impinging on the sample. To avoid the effect of these fluctuations, a small percentage of the incident beam was scattered by a mylar sheet into a second Na(Tl)I detector mounted perpendicular to the beam, after the monochromator. This was used to monitor the beam intensity so as to average over power fluctuations of the source. Air absorption and background scattering of x-ray beam were minimized by means of vacuum beam path from the anode to the sample.

The scattered beam was eventually Bragg scattered by the analyzer, Si(111) into a second Na(Tl)I scintillation detector to measure the scattered beam intensity. The scattered x-ray hit the Na(Tl)I scintillation detector which generated a signal through excitation of NaI atoms. Emission of photon followed as a result of the de-excitation of the atoms. This caused ejection of electrons from a photocathode which were accelerated and multiplied between plates of successively higher potential. This signal was passed through a preamplifier (see Fig. 2.13), the output of which is proportional to the incident x-ray. This signal was then fed to a linear amplifier where proportionality of pulse amplitude to incident energy was also maintained. A single channel analyzer (SCA) was used to reject with pulses amplitude less than $V_1$ volts or greater than $V_2$ volts (the latter discrimination was accomplished using an anti-coincidence circuit in which a pulse greater than $V_2$ triggered both levels $V_1$ and $V_2$). The two
Figure 2.13: Control electronics schematic of the goniometer motor controllers, and signal amplification for monitor and detector.
levels defined a window with level \( V_1 \) serving as the baseline. In this way, the Cu\( K_\alpha \)
distribution was determined and the window centered on it and widened so as to accept \( \sim 90\% \) of the signal.

A personal computer with Linux operating system running SPEC was used to control angular positions, counting and timing via GPIB and Scientific Solution Labmaster boards.

2.2.5 Resolution Function

The instrumental resolution is determined by the geometry and components used in the experiment, such as, slits, monochromator, analyzer, etc. In the case of in-plane scattering \( (q_y = 0) \), the total differentials of Eqns. 2.8 and 2.10 assuming grazing angles are

\[
\delta q_x = \frac{\Delta \lambda}{\lambda} q_x + k (\sin \alpha \Delta \alpha + \sin \beta \Delta \beta) \quad (2.25)
\]
\[
\delta q_z = \frac{\Delta \lambda}{\lambda} q_z + k (\cos \alpha \Delta \alpha + \cos \beta \Delta \beta) \quad (2.26)
\]

where \( \delta q_x \) and \( \delta q_z \) are the resolutions parallel and perpendicular to the surface, \( \frac{\Delta \lambda}{\lambda} \) is the wavelength spread, \( \Delta \alpha \) and \( \Delta \beta \) are the angular divergence and acceptance of the incoming and outgoing radiation, respectively. In the case when \( \alpha \approx \beta \approx \theta \) and \( \Delta \alpha \approx \Delta \beta \), Eqns. 2.25 and 2.26 simplify to \( \delta q_x \approx 2k \sin \theta \Delta \alpha \) and \( \delta q_z \approx 2k \cos \theta \Delta \alpha \). The angular divergence \( \Delta \alpha \) of the beam is mainly determined by the distances, slit sizes and optical elements (mirrors, monochromator and analyzer crystals) of the experimental set-up. However, in the small angle regime, \( \Delta \lambda \) can be measured by determining the width of the primary beam at arm-zero\(^2\) where the full-width-at-half-maximum (FWHM) = 2\( \Delta \alpha \). This yields good approximations for \( \delta q_x \) and \( \delta q_z \).

\(^2\)The arm-zero scan was performed by rotating the analyzer and the detector on the \( 2\theta \) arm through the direct beam.
The $\delta q_y$ can be determined by placing the crystal in the sample position and rocking the sample.

For our x-ray experiments with Si(111) crystals as monochromator and analyzer, $\frac{\Delta \lambda}{\lambda} \approx 10^{-4}$ and the FWHM = 0.00318° ($\Delta \alpha = 0.00159^\circ$). Hence, the resolutions $\delta q_x \approx 1 \times 10^{-5}$ and $\delta q_z \approx 2.2\times10^{-4}$ Å$^{-1}$ were obtained, for the transverse in-plane diffuse and specular scans, respectively. This allowed a probe of lateral and vertical length scales up to $x_{\text{max}} = 2\pi/\delta q_x \sim 10^5$ Å and $z_{\text{max}} = 2\pi/\delta q_z \sim 10^4$ Å, respectively. The out-of-plane resolution $\delta q_y \approx 1.7 \times 10^{-2}$ Å$^{-1}$.

2.2.6 Specular and Diffuse Scans

Specular ($q_\perp = 0$) or longitudinal scans (Fig. 2.14) were performed to gain information about the electron density profile in the direction perpendicular to the substrate as well as the vertical roughness. These scans were carried out by varying the magnitude of $\mathbf{q}$ while keeping its direction perpendicular to the substrate. This was done by maintaining a 2:1 ratio in the angle for the detector (2$\theta$) position and sample ($\theta$) orientation. In this way, the incident ($\alpha$) and scattered ($\beta$) [refer to Fig. 2.4] wavevectors make the same angle with the surface ($\alpha = \beta$), so that the momentum transfer vector is always perpendicular to the surface $\mathbf{q} = (0, 0, q_z)$. This probes the periodicities and structural features along the surface normal.

The coherent beam of the x-ray acquires some angular divergence when reflected from rough surfaces which increases with an increase in the rms roughness. This causes an additional contribution to the specular scattering. To obtain this additional contribution from the lateral roughness, off-specular scans were performed. The off-specular scans were carried out with a constant offset of the scattering vector from the specular condition, ($\beta = \alpha + \delta$, where $\delta = 0.05^\circ$) introducing an in-plane
Figure 2.14: Scattering geometry illustrating the specular, off-specular and rocking scans. Double arrow lines represent the specular and off-specular scans.
component to the q-vector, \( q = (q_x, 0, q_z) \). The true specular scattering was obtained after the off-specular contribution was subtracted from the specular scan data.

Rocking (\( \omega \)) scans were performed by fixing the detector position (\( 2\theta \)) at the specular angle and rocking the sample about the specular position (\( \theta \)). Such scans are done at a small but constant in-plane component of the momentum transfer vector. Hence, the \( \omega \)-scan probes the distribution of the in-plane domains: the rougher the surface, the wider the rocking scan.

2.2.7 Goniometer Alignment and Data Correction

Prior to specular scans, the sample and the goniometer were aligned in the following manner. The detector was brought to zero-arm (\( 2\theta = 0 \)) position and the sample was placed vertically in the sample holder whose center of rotation is the center of the diffractometer. Then the sample was moved laterally into the direct beam until the intensity at the detector was cut by one-half the initial intensity. The sample was rotated about the \( \theta \) and \( \chi \) axes so as to maximize the intensity (i.e. to ensure that the samples' face is parallel to and in the exact center of the incident beam). This process was repeated until the maximum zero-arm intensity is halved. To find the specular condition, the detector position was fixed at some value of \( q \) and a \( \theta \)-scan carried out to find the maximum reflected intensity.

Due to finite sample size, specular scans performed at very low angles (\( \leq 0.6^\circ \)) have to be applied the "footprint correction". This arises from the projection of the incident beam (or footprint) on the sample being larger than the sample size in the scattering plane. And so, only a fraction of the incident intensity is intercepted by the sample. By considering the geometry of the experimental set-up, this effect can be corrected and the data then analyzed. Assuming the incident beam intensity is
uniformly distributed over the horizontal width of the slit $S_3$ (Fig. 2.12), the intensity must be divided by a factor of

$$\left[ \frac{L}{w_{slit} \sin \theta} \right] \text{ for } \theta < \arcsin \frac{w_{slit}}{L}$$

(2.27) to apply the footprint correction. Here, $L$ is sample length, $w_{slit}$ is the horizontal slit width and $\theta$ is the angle of incidence.

2.2.8 X-ray Coherence Length

Coherence length is the distance on the sample over which a photon in the scattered beam will interfere coherently at the detector. In the case of x-ray reflectivity (See Fig. 2.15), this beam coherence is considered, both in the beam direction (longitudinal coherence length, $l_\parallel$) and in the direction orthogonal to the incident beam (transverse coherence length, $l_\perp$). The $l_\parallel$ is related $[19]$ to the natural linewidth of the radiation, $\Delta \lambda$ by

$$l_\parallel = \frac{\lambda^2}{\Delta \lambda}$$

(2.28) When performing the x-ray reflectivity measurements, the beam direction is actually at a slight angle to the sample surface. Hence, a factor of $\cos \theta$ is necessary to account for the geometry. For our experimental set-up, the $l_\parallel$ is $\sim 4000$ Å based on Eqn. 2.28 and the natural linewidth of the $\text{CuK}_{\alpha1}$ line of $6.12 \times 10^{-4}$ Å $[20]$. For the thin films considered in this study, $h < 1000$ Å, the longitudinal coherence length exceeds the film thickness where, the beam scatters coherently over the entire thickness of the film. The presence of Kiessig fringes in the specular scans is its evidence. The transverse coherence length ($l_\perp$) is related $[19]$ to the distance from the final slit, $S_3$ in Fig. 2.12 to the sample, $R$ and to the horizontal width, $d_{slit}$ of $S_3$ by

$$l_\perp = \frac{R \lambda}{2d_{slit}}$$
Figure 2.15: Representation of the elongated coherence area of the x-ray beam.
Substitution of the parameters specific to our experimental setup yields $l_\perp \sim 300 \text{ Å}$. The morphological contributions from the two directions are separable to the degree of elongation of the beam coherence. The longitudinal/transverse ratio ($l_\parallel/l_\perp$) of coherence lengths was calculated to be $\approx 13:1$ for our experimental conditions. Hence, the scattering arising from contributions from the film morphology has about 13 times the coherence length in the longitudinal direction, sampling more heavily roughness correlations in that dimension. The roughness of the film as "seen" by the beam will therefore differ for samples possessing anisotropic morphology. That difference is detectable upon rotation of the film about the substrate normal. Thus, the elongated coherence area can be used to gather information about anisotropic roughness in films with in-plane anisotropy such as rubbed thin polymer films, LPUV exposed PI films including in-situ [21] UV exposed PI films.
REFERENCES


CHAPTER 3

RELAXATION OF CHAIN ORIENTATION IN POLYMER THIN FILMS

An investigation of the dependence of $T_g$ on the film thickness of polyimide, polystyrene and azo-polymers films on glass substrates as well as the mobility at the surface was carried out using a simple optical method. The method employed to probe the polymer-air surfaces was based on earlier NEXAFS work on rubbed polymer surfaces [1]. The orientational order in polymer chains created with surface treatments, such as rubbing, induces optical anisotropy in the film. This anisotropy is a direct measure of the orientational order and serves as a sensitive probe of the relaxation process at the surface when its temperature is raised to near the bulk $T_g$ values. This type of measurement has not been carried out in the past as judged from the literature surveyed and is the core of the work presented here. The dynamical relaxation of the rubbed films are modelled using the typical dynamical Kohlrausch-Williams-Watts (KWW) relaxation equation (Eqn. 1.4) to determine the $T_g$’s of such films.

There is no marked change in the optical birefringence with temperature up to 375 °C (maximum temperature limit of the heating stage) for both polyimide (rubbed and LPUV exposed) and the LPUV exposed azopolymers. This is not surprising for the case of polyimides owing to its thermal, mechanical and chemical stability even beyond its bulk $T_g$. The absence of the relaxation in the azopolymer alignment films could possibly be due to the strong substrate-polymer interaction. In this chapter, the dependence of $T_g$ on film thickness of polystyrene as well as the chain dynamics
is discussed.

3.1 The Relaxation Model

The relaxation dynamics of glass forming materials is described by KWW *stretched exponential* function [2, 3]. Based on this model, the time dependence of birefringence \( \Delta n \) at temperature \( T \) of oriented polymer film can be written as

\[
\Delta n(t) = \Delta n_o \exp \left[ - \left( \frac{t}{\tau} \right)^\beta \right]
\]  

(3.1)

where, \( \tau \) is the average relaxation time, and \( \beta \), is the relaxation exponent which is related to the distribution of relaxation times in the polymer: \( \beta = 1 \) for a distribution with a single relaxation time and \( \beta < 1 \) for a distribution with a long tail of short relaxation times.

In a more general form, Eq. 3.1 can be expressed in the form of an integral

\[
\Delta n(t) = \Delta n_o \exp \left[ - \int_0^t \frac{\beta \tau^{\beta-1}}{\tau^\beta} dt \right]
\]  

(3.2)

where, \( \beta \) is constant for an isothermal process. When \( \Delta n \) relaxation changes with temperature, which is the case in our study, \( \beta \) becomes temperature dependent. Assuming that the temperature is linearly related to time by \( T' = T_o + \alpha t' \), where \( T_o \) is the initial temperature and \( \alpha \) is the heating rate. The temperature dependent \( \Delta n \) can then be written as

\[
\Delta n(T) = \Delta n_o \exp \left[ - \int_{T_o}^T \frac{\beta (T' - T_o)^{\beta-1}}{(\tau (T')^\beta)} dT' \right]
\]  

(3.3)
Assuming a simple Arrhenius type temperature dependence below \( T_g \), and a Williams-Landel-Ferry (WLF) [4] temperature above \( T_g \), the relaxation time is written as

\[
\tau(T) = \tau_{T_g} \exp \left[ -\frac{\Delta E}{R} \left( \frac{1}{T} - \frac{1}{T_g} \right) \right] \quad T < T_g
\]

\[
= \tau_{T_g} \times 10^{\frac{c_1(T-T_g)}{c_2(T_g-T)}} \quad T \geq T_g
\]

(3.4)

where, \( \Delta E \) is the activation energy, \( R \) is the Rydberg gas constant, \( c_1 = 13.7 \) and \( c_2 = 50.0 \) K are WLF parameters [5] and \( \tau_{T_g} \) represents the relaxation time at \( T_g \). Based on previous works, [6, 7, 8, 9]

\[
\tau(T) = \tau_{T_g} \exp \left[ \frac{\langle \tau \rangle_{T_g} \beta}{\Gamma \left( \frac{1}{\beta} \right)} \right]
\]

(3.5)

where \( \langle \tau \rangle_{T_g} \) is the average relaxation time at \( T_g \) and \( \beta \) is the KWW relaxation exponent, whereas \( \tau_{T_g} \) at the \( \alpha \)-relaxation ranges between 0.5 to 20 sec. [6]. In this study, \( \tau_{T_g} = 5 \) sec is chosen for which the \( T_g \) obtained (\( \sim 370K \)) for the cast film is similar to the bulk \( T_g (\sim 378K) \) determined by DSC. This choice of \( \tau_{T_g} \) is valid because cast films are considered to have bulk-like behavior. Also, the choice of \( \tau_{T_g} \) is arbitrary and the same arbitrariness is also present in choosing the onset and endset points for \( T_g \) in the DSC measurements.

3.2 Data Analysis

The \( T_g \)s of the films are determined from the fits of Eqn. 3.3 to the relaxation data. To test the integrity of the model, three fitting procedures were carried out: (i) both \( \Delta E \) and \( \beta \) were parameterized, (ii) \( \beta \) was fixed while \( \Delta E \) was parameterized, and (iii) both \( \Delta E \) and \( \beta \) were fixed. Any dependence of relaxation time or relaxation exponent on penetration depth is considered negligible. Hence, the values of \( T_g, \Delta E \)
and $\beta$ determined from the fits are averages over the film depth perturbed by rubbing. The first fitting procedure yielded $\Delta E = -202 \pm 34$ kJ/mol and $\beta = 0.38 \pm 0.05$ where the error is the standard deviation of all the fits. In the second fitting procedure, $\beta = 0.36$ was fixed, and $\Delta E$ was parameterized which yielded $\Delta E = -207 \pm 28$ kJ/mol. In the third case, $\Delta E$ and $\beta$ were fixed at $-205$ kJ/mol and 0.36, respectively. All fitting procedures resulted in the same trend of $T_g$ as a function of film thickness although, in the third case, the errors from the fits were not as good as the first two cases. For relaxations of PS below $T_g$, $\Delta E$ and $\beta$ are typically in the range $-188$ to $-209$ kJ/mol [6] and 0.24 to 0.4 [4, 7], respectively. This study yielded $\Delta E$ and $\beta$ values which lie within the range affirming the validity of this model.

3.2.1 Sample Preparation

Solutions of polystyrene with $M_w = 48,500$ g/mol ($R_g = 56$ Å), polydispersity index = 1.03 in toluene (Aldrich, HPLC grade) were prepared in various concentrations. Twenty-four hours were allowed for complete dissolution of the polymer before filtering the solutions twice using 0.45 µm PTFE filters. Filtering was done to remove the dusts from the solution. After which, films were prepared by spin coating on glass substrates which were previously soaked in sulfuric acid and Nochromix solution for 24 hours, rinsed with deionized water from a Millipore MilliQ water purifying system, and dried with nitrogen gas. The film thicknesses were controlled by varying the spin coating speed as well as the polymer solution concentration. Cast films were prepared using an effective zero spin speed. The samples were allowed to dry under vacuum for 24 hrs to permit complete removal of the solvent. They were then annealed for 5 minutes at $105^\circ$C to remove residual birefringence created by spin coating and thermal history. The thin films were rubbed using a velvet cloth to saturation so that
further rubbing did not change the initial retardation, and the cast films were rubbed with varying rubbing strengths.

To ensure that the annealing process did not cause the films to dewet and that the rubbing did not significantly alter the film thickness, x-ray reflectivity measurements described in Chapter 2 were performed on a select film (125 Å) before and after annealing/rubbing. The relative invariance of the reflectivity profiles of the film before annealing (before birefringence measurements) up to the completion of the experiment (Figs. 3.1a-d) indicates that the film thickness did not significantly change to within an experimental error of 5 Angstrom and that dewetting did not occur. An XRR profile characteristic of a dewetted film is shown in Fig. 3.1e for the film annealed for over an hour at 105°C.

3.2.2 Retardation Measurements

Optical retardation measurements were carried out using the set-up described earlier except that the film/sample was mounted inside a heating stage for controlled heating. The rubbed samples stage were oriented such that the rubbing direction was along the vertical (perpendicular to the optic axes of the PEM). Films of thickness 58, 125, 150, 280, 480, 540, 1150 Å and 10 μm were studied.

For thin polymer films heated above \( T_g \), a relaxation process leading to thermodynamical equilibrium ensued [10]. As a consequence, spontaneous dewetting resulted where a homogeneous film tore up and holes in the polymer film were created. These holes grew in lateral size building a cellular pattern which dewetted further until a stable droplet formation was reached [11].

The rubbing process is known to cause alignment of polymer chains and has been shown to create a grooved surface. This birefringence is dominated by the “form
Figure 3.1: Reflectivity profiles of a 125 Å PS film on glass substrate at room temperature (a) before annealing, (b) after annealing for 5 minutes at 105°C, (c) after rubbing, (d) after the birefringence measurement and (e) after several hours of heating at 105°C which indicates a dewetted film. The curves are shifted vertically for clarity.
birefringence” associated with the roughness of the surface [12]. A theoretical formulation based on uniform grooves predicts a positive birefringence for rubbed films [13]. The birefringence of the PS films in this study was found to be negative, indicating that form birefringence was negligible and that the reorientation dynamics probed in this work are associated with the changes in the orientation of PS chains. This is demonstrated by the cooling curve for the 480 Å film shown in Fig. (3.2) along with its Δn relaxation curve (heating) where the retardation remains unchanged (zero) indicating a permanent randomization of the PS chains after complete relaxation.

3.3 Results

3.3.1 Relaxation as a Function of Film Thickness

The Δn relaxation curves as well as the theoretical fits of the rubbed cast PS film (10 μm) and the thin films with thicknesses h = 58, 281 and 480 Å upon heating are shown in Fig. 3.3. For the sake of clarity, other films studied are not shown. The initial retardation becomes progressively higher for thicker films because more and more chains align upon rubbing. On heating, the retardation of the film decreases monotonically and becomes zero at temperatures above \( T_g \). This decrease in the retardation is associated with the (random) reorientation of the PS chains. The difference in the relaxation dynamics of different films is manifested in the temperature at which the films are completely relaxed, \( T = 360K \) and \( T = 385K \) for the 58 Å and the cast film respectively. This relaxation behavior is indicative of enhanced chain mobility in thinner films which results in a reduction of \( T_g \). The maximum film thickness up to which the optical retardation technique is valid is \( h < 58 \) Å which is about the size of the radius of gyration, \( R_g \) of the polymer used in this study (\( R_g = 56 \) Å). For
Figure 3.2: Relaxation curve of the 480 Å film (○) and its cooling curve (∗). Heating was controlled at 1 K/min whereas cooling was uncontrolled.
Figure 3.3: Optical retardation curves upon heating to bulk $T_g$ for (○) 10 $\mu$m, (▼) 480 Å, (△) 280 Å and (◊) 58 Å PS films. Experimental data of other films used in the analysis are not shown for clarity.
$h < 58$ Å, dewetting occurred during the heating cycle. Since the rate of relaxation is
a strong function of the heating rate and the physical properties of the polymer layer,
quantitative analysis of the relaxation dynamics requires a physical model. From the
fits to the model discussed above (Eqn. 3.1), $T_g$'s of the thin films are determined
and are shown in Fig. 3.4 as a function of thickness. The $T_g$ of the cast and the 300
Å films are close to the $T_g^{bulk}$ as measured by DSC and other dynamics techniques
and it drops by 15-20 K as the film thickness approaches 58 Å.

Furthermore, enhanced mobility with decreasing film thickness is illustrated in
Fig. 3.5 which shows a plot of the area under the normalized relaxation curves with
film thickness. The area decreases with film thickness indicating fast relaxation dy-
namics.

3.3.2 Relaxation as a Function of Rubbing Strength

A series of experiments performed by van Aerle[1] on rubbed polyimide films have
shown that the depth of penetration of rubbing increases with rubbing pressure or
rubbing density and that the total retardation of the film is expressed as follows:

$$|\delta| = \int_0^h \frac{2\pi \Delta n(z)dz}{\lambda}$$

(3.6)

where, $\Delta n(z)$ is the birefringence at a distance $z$ from the surface, $h$ is the overall
film thickness and $\lambda$ ( = 632.8 nm) is the wavelength of light used. On the basis of
these results, the influence of the penetration depth on the relaxation dynamics of the
rubbed films can be determined. The cast film ( 10 μm) was rubbed with different
rubbing strengths and the relaxation curves as well as the fits to the curves are shown
in Fig. 3.6. After each run (cycle), annealing was done for 30 minutes at 110°C
to erase any residual retardation. It is evident that the initial retardation becomes
Figure 3.4: The $T_g$'s determined from fits to the KWW model of the films with different thicknesses.
Figure 3.5: Area under the normalized relaxation curves for all the films studied.
Figure 3.6: Relaxation curves as a function of temperature of the cast film rubbed to different extent: ○ 3×, △ 6×, ○ 9 × and ○ 12×. Solid lines represent fits to equation 3.1.
progressively higher with rubbing strength, as expected since stronger rubbing causes more PS chains to align. Also, as illustrated in Fig. 3.6, the rate of relaxation is faster for the lightly rubbed films. This is an indication that the molecules at the polymer-air interface are more mobile than the interior molecules. Although it can be argued that by increasing the rubbing strength, the molecules become highly extended with nonlinear relaxation times resulting in a faster relaxation, quantitative analysis of the relaxation curves in our study proves otherwise. $T_g$'s of the cast film rubbed to different degrees were determined from the fits to the relaxation curves and shown in Fig. 3.7. On the horizontal axis is the initial retardation related to the effective rubbing depth ($d_{eff}$) which is proportional to the rubbing strength. Results show that $T_g$ increases with rubbing depth. This essentially means that molecules closer to the film-air interface relax faster than the molecules farther from the film-air interface. The similarity of the $T_g$ drop between the effects of film thickness and effects of $d_{eff}$ suggests that the mobility at the polymer-air interface influences the dynamics more than the PS-substrate interface.

3.3.3 Comparison with Previous Results

A comparison of the results with previous studies [14, 15, 16] is illustrated in Fig. 3.8. The PS films studied were spin-coated on etched silicon, aluminum coated glass substrates, and plain glass substrates. The solid line in the Fig. 3.8 (Ref.[14]) becomes an extrapolation for thicknesses below 130 Å, where significant deviations between it and the supporting data begin to occur. For film thicknesses greater than 130 Å, the results of the three studies agree well. These investigations suggest that the $T_g$ of the polymer film is not significantly affected until the film thickness falls below 200-300 Å. In contrast, Wu and coworkers have reported an increase in $T_g$ for
Figure 3.7: $T_g$ as a function of rubbing depth, $\Delta n_{eff}$ determined from the fits of the relaxation curves to the KWW model.
Figure 3.8: Comparison of $T_g/T_{gbulk}$ as a function of film thickness, $h$ with previous studies on similar systems: ○ this study, ◊ Forrest et.al. [15], - Keddie et.al. [14] and -- Fukao et.al. [16]
PS on silicon substrates by 60 K for films as thick as 400 Å [17].

The reduction in $T_g$ of 20 K for a lightly rubbed surface of a thick cast film indicates that the polymer chains at the surface is more mobile than in the bulk. In comparison, results from a study on free-standing PS ($M_w = 767 \times 10^{-3} \text{ g/mol}$) films [18, 19] show a large reduction in $T_g$ ($\sim 70 K$) for film thickness, $h < 700$ Å and the film thickness limit, $h_{\text{limit}}$ at which the $T_g$ drops is directly proportional to the molecular weight. This suggests that the effect of the free surface extends roughly 350 Å into the film.

In this study, the rubbing strength dependence of the $T_g$ suggests that the free surface effect penetrates to a depth of greater than 150 Å into the PS film. This agrees with the free-standing film studies to within an order of magnitude. However, the magnitude of the change observed in the birefringence of supported films are far lower than in free-standing films. The results of this study indicate that a polymer’s mobility increases in films of decreasing thickness. This does not agree qualitatively with many diffusion measurements in the literature. For example, the diffusion of fluorescent probes at 376 K in PS films deposited on quartz\(^1\) substrates decreases roughly by an order of magnitude as the film thickness decreases from 5600 Å to 800 Å [20]. PS diffusion at 426 K is slowed roughly by 2 orders of magnitude near a Si surface relative to the diffusion far from the surface [21] and lateral diffusion at 413 K of fluorescent labeled polymer chains decreases by a factor of 2 as the film thickness decreases from 2000 Å to 600 Å [22]. Based on these diffusion measurements it can be concluded that a polymer’s mobility should decrease as the film thickness decreases. However, the reasons for such long-range effects on diffusion constants are not clear.

\(^1\)Quartz has similar surface properties to that of glass
and require further investigation.

Previous ellipsometry measurements [23] for poly(methy)methacrylate (PMMA) films on two different substrates ($SiO_2$ and Au-coated Si) revealed the dominant effect of polymer-substrate interaction. For PMMA deposited unto the native oxide coating of Si wafers (150 Å < $h$ < 1200 Å), the measured $T_g$ values increased with decreasing film thickness, $h$, whereas for PMMA films deposited on to Au-coated Si wafers (300 Å < $h$ < 1300 Å), the $T_g$ decreased as $h$ was reduced. The strong attractive interaction between PMMA and the Si native oxide is due to hydrogen bonding believed to be responsible for the increase in $T_g$ with decreasing $h$. The PMMA-Au interaction is much weaker leading to a decrease in $T_g$ with decreasing $h$. Similar results were obtained for poly 2-vinyl pyridine [P(2)VP] films on $SiO_x$ [24]. The decrease in $T_g$ observed in this work and the studies of Keddie et.al, Forrest et.al. on supported films and Fukao. et.al. is attributed to the absence of the polar interaction in the PS - $SiO_2$ and PS-glass system.

3.4 Conclusion and Recommendations

The use of a simple technique to probe polymer relaxation in ultra-thin films has been demonstrated. The relaxation of the rubbed PS films in different thickness films supported on glass substrates has provided significant evidence for faster relaxations in thinner films. Also, using the relaxation model based on KWW, the glass transition temperature $T_g$ of PS films as a function of thickness as well as of the rubbing (strengths) depths have been determined. Reductions of 15 – 20$K$ in $T_g$ for films of thickness less than 250 Å correlates very well with previous results on similar systems [3, 4, 6]. The dependence of $T_g$ on rubbing depth provides the evidence that chain mobility is enhanced at the polymer-air interface relative to the polymer-substrate
interface and is undoubtedly responsible for the reductions in $T_g$ of thin films. To confirm that polymer-substrate interaction is playing a role in the dynamics of polymer in confined dimensions, similar measurements on attractive polymer-surface systems should be carried out. Measurements on thin polymers with $T_g$ different than that of PS should also be carried out.
REFERENCES


CHAPTER 4

MORPHOLOGICAL ANISOTROPY OF SURFACE MODIFIED THIN POLYMER FILMS

Although it has been established that alignment effects are controlled via anisotropic alignment layers, the predominant factor controlling the alignment remains a controversy. Previous studies have shown that rubbing of polyimide film gives rise to a grooved morphology [1] and oriented polymer chains [2, 3]. The long molecular axis of LC lies parallel to the rubbing direction indicating that the surface morphology predominantly influences the alignment. Rubbing of PS films however results in a LC homogenous alignment perpendicular to the rubbing direction in the azimuthal direction [5] although a grooved morphology is expected to have been generated along the rubbing direction [6]. In addition, a number of studies of the photoalignment method claim to have shown that the LC orientation can be changed without altering the surface morphology [7] implying that surface morphology plays a minor role. Previous work on the photoalignment method has also shown that the interaction of LC with anisotropic layers clearly determines the azimuthal preferred orientation. To understand these contradicting observations, the effects of rubbing and photoalignment on the surface morphology of several polymer films typically used for LC alignment requires further investigations at a submolecular level. X-ray reflectivity is an excellent technique for this purpose.

The morphological features of rubbed polystyrene and polyimide films as well as the photoaligned PI and azopolymers are discussed in this chapter.
4.1 Data Analysis: A General Description

Prior to spin coating of polymer films, surface roughness, $\sigma_{rms}$, average electron density, $\rho_{ave}$ and absorption coefficient, $\beta$ of the glass substrate were determined using the x-ray reflectivity. Figure 4.1 shows the specular scan of the glass substrate used. Fit to the theoretical curve, represented by solid line gives $\sigma_{rms} = 4.45 \ (\pm 0.16)$ Å and $\rho_{ave} = 0.741 \ (\pm 0.00039) \text{ Å}^{-3}$ and $\beta = 82.6 \ (\pm 2.5)$. The value of $\rho_{ave}$ is in close agreement with $\rho = 0.72 \text{ Å}^{-3}$ [8] for a similar glass. All polymer films were coated on glass substrate taken from the same batch or big piece of glass on which the x-ray reflectivity was carried out to avoid repeated scanning for each film preparation.

Surface treatments such as rubbing and exposure to UV light were carried out without removing the substrate from the sample stage of the XRR set-up so that the same area was scanned after repeated surface treatments.

The x-ray reflectivity measurements (specular, off-specular and $\omega$-scans) were performed before and after surface treatments in the two in-plane orientations (x and y). The x-orientation is arbitrarily defined as the rubbing or UV polarization direction illustrated in Fig. 4.2. All specular reflectivity data, shown in this work, unless otherwise specified was corrected for the beam footprint and off-specular diffuse scattering, so that the total reflected intensity is the true specular scattering then normalized with respect to the incident beam intensity.

CPlot, a Linux and C-based plotting software, was used to model the reflectivity curves (Eqns. 2.21 and 2.19) and to determine the parameters for the substrate, as prepared and surface modified films. Nonlinear least square fitting based on Marquardt algorithm built in the CPlot software was used to fit the experimental data.
Figure 4.1: Specular reflectivity of the glass substrate used in the experiment. The line is the theoretical curve of Eqn. 2.18 with the corresponding parameters: $\sigma_{rms} = 4.45 \text{ Å}, \rho_{ave} = 0.74100 \text{ Å}^{-3}$ and $\beta = 82.6$
Figure 4.2: Orientation of the sample with respect to the direction of modification. The y-orientation is a result of a $90^\circ$ rotation of the sample about the substrate normal so that x-ray scattering plane is perpendicular to the direction of uniaxial surface treatment.
The quality of the fits were determined from $\chi^2$ defined as

$$\chi^2 = \frac{1}{N-n} \sum_i \left( R_i^{exp} - R_i^{fit} \right)^2$$

(4.1)

where $R^{exp}$ is the experimental data and $R^{fit}$ is the fit data calculated using the fit parameters. $N$ is the total number of data points and $n$ is the number of parameters to be fitted. The convergence of the fit procedure was determined by the epsilon test [9].

4.2 Polystyrene

The spin coating of polystyrene solution results in a nearly isotropic distribution of the phenyl rings. This isotropic distribution assumes no periodic layering thereby modeling of the reflectivity curves of the system does not require any electron density modulation of the film in the perpendicular direction. Fitting addresses a case of thin polystyrene film with rough air-film and film-substrate interfaces. The roughness and density associated with the substrate independently determined a priori are kept constant.

The specular scans as well as the $\omega$-scans for the as prepared PS film in the $x$- and $y$-orientations shown in Fig. 4.3 reveal similar reflectivity profiles indicating an isotropic film in the two in-plane directions. The well-defined Kiessig fringes indicate a uniform film thickness of $d = 342.67 \pm 0.5$ Å. The films average bulk electron density ($\rho_{film}$) and surface roughness ($\sigma_{film}$) were parameterized to model the measured reflectivity yielding the fit to Eqn. 2.18 shown as solid lines in the figure. Fit to the data yields $\rho_{film} = 0.347 (\pm 0.005) \text{ Å}^{-3}$ and $\sigma_{film} = 6.9 (\pm 0.2) \text{ Å}$; $6.0 (\pm 0.04) \text{ Å}$ for $x$- and $y$-orientations, respectively. The data shown represents the measured specular scattering. The $y$-orientation scan has been shifted vertically two orders of magnitude
Figure 4.3: X-ray reflectivity curves of PS film in the (o) x-orientation and (Δ) y-orientation of a film of thickness d = 342.67 Å (a) prior to rubbing and (b) after rubbing 6 times. The well-defined fringes before rubbing characterize a uniform film. The fringes are nearly washed out in both directions but are more pronounced in the y-orientation. The inset shows the ω-scans of the film.
for clarity.

The effect of rubbing on the specular scans is illustrated in Figs. 4.4 and 4.5 in the two in-plane orientations of the film. There is an observable change in the surface morphology of the film in both orientations. The amplitude of the Kiessig fringes in both orientations is gradually washed out upon rubbing which attributed an enhancement of the surface roughness. The fringes, however, remained better-defined in the $y$-orientation (see in Fig.4.3) while they were almost washed-out in the $x$-orientation.

Fits to the rubbed PS film data using Eqn. 2.18 in both orientations revealed increasing surface roughness. The values of the fit parameter, $\sigma$, are summarized in Table 4.1 along with the corresponding extent of rubbing and the measure of the goodness of the fit $\chi^2$ for the two orientations.

<table>
<thead>
<tr>
<th>Number of Rubs</th>
<th>$\sigma_{rms}^y$</th>
<th>$\chi^2(10^{-5})$</th>
<th>$\sigma_{rms}^x$</th>
<th>$\chi^2(10^{-5})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.93</td>
<td>4.480</td>
<td>11.31</td>
<td>20.15</td>
</tr>
<tr>
<td>2</td>
<td>11.20</td>
<td>2.959</td>
<td>12.10</td>
<td>1.806</td>
</tr>
<tr>
<td>3</td>
<td>12.33</td>
<td>1.856</td>
<td>16.70</td>
<td>2.014</td>
</tr>
<tr>
<td>4</td>
<td>14.50</td>
<td>2.201</td>
<td>16.84</td>
<td>9.041</td>
</tr>
<tr>
<td>5</td>
<td>16.20</td>
<td>3.145</td>
<td>18.10</td>
<td>10.87</td>
</tr>
<tr>
<td>6</td>
<td>17.73</td>
<td>4.630</td>
<td>20.15</td>
<td>16.26</td>
</tr>
</tbody>
</table>

Theoretical fits to the data after 6 rubs yield $\sigma_{rms}^x = 20.15 \pm 0.05 \text{ Å}$ which is higher than $\sigma_{rms}^y = 17.73 \pm 0.05 \text{ Å}$ giving a surface roughness anisotropy, $\Delta \sigma =$
Figure 4.4: Polystyrene film reflectivity profiles after repeated rubbing in the x-orientation. The film was scanned after each rubbing until fringes were nearly washed out. The lines are the theoretical fits to the experimental data. The inset shows the orientation of the sample for these scans.
Figure 4.5: Specular reflectivity of the polystyrene film in the y-orientation after each rub. Scans are shifted vertically by one decade for clarity. Rubbing direction is orthogonal to the scattering plane.
\( \sigma_{\text{rms}} - \sigma_{\text{rms}}^y = 3.52 \, \text{Å} \). The diffuse-scans which provide lateral inhomogeneities shown at the inset of Fig. 4.3 clearly shows an increase in diffuse scattering indicating a roughness increase. The PS main chain (backbone) aligns along the rubbing direction orienting the phenyl rings (side-groups) perpendicular to the rubbing direction. The phenyl groups being strongly interacting appear to form linear structures in the y-direction [4]. This accounts for the more pronounced surface roughness in the x-orientation. It has been shown that LC alignment on rubbed PS is along the direction perpendicular to rubbing [5]. This means that the preferential direction of LC alignment is along the smoother of the two directions.

Typically, fitting is done by fixing parameters such as the absorption coefficient, \( \beta \) which is an intrinsic property of the material and average electron density, \( \rho \), at the values determined from the scans taken before the surface treatment (in this case rubbing). Better quality fits, however, were obtained (shown in Figs. 4.4 and 4.5) only when other parameters were also varied. Since the \( \beta \) only plays a role in the vicinity of the critical angle leading to the rounding, the \( \rho \) was treated as an adjustable parameter. Results yielded a change in the electron density shown in Fig. 4.6. The decrease is more pronounced in the y-orientation. This change in the electron density in the film is typically seen as a kink (and corresponds to films critical angle) below the glass critical angle, and it moves to the left as the electron density decreases. However, the scans performed did not include scattering much below the critical angle. To confirm this point, a qualitative check was done on another PS film. Similar scans covering \( q_z \ll q_{\text{crit}} \) on a PS film prepared under similar conditions were performed. Figure 4.7 illustrates this aspect. A shift of the kink to the left indicates a decrease in the average electron density.
Figure 4.6: Electron density change in a rubbed PS film.
Figure 4.7: Reflectivity scans near the critical angle. The dashed-line makes the initial position of the kink and is drawn as a guide to eye. Shift of the kink to the left indicates that average electron density of the rubbed film is decreasing.
4.3 Polyimide

Morphology of rubbed and photoaligned PI film of SE 7311 was studied. The film was obtained by spinning the solution of polyamic acid on the substrate. Soft baking followed at 100°C for 10 minutes. The film studied for rubbing was hard baked inside an oven set at 200°C whereas the photoaligned PI film was hard-baked and exposed to UV simultaneously. Hard-baking was for one hour and UV exposures was done 30 minutes. Reflectivity measurements were also carried out in two orientations. The direction of rubbing and polarization of UV was chosen as the x-orientation. A collimated beam from Xe lamp (Oriel, Model No. 6295) was linearly polarized using an Oriel UV sheet polarizer and the intensity at the films surface was maintained at approximately 6 mW/cm².

4.3.1 Rubbed Polyimide

Unlike polystyrene, where spin coating results in uniform homogenous films isotropic distribution of the phenyl rings, PI film assumes a periodic layering of the chains as a result of its tendency for the imide chains to orient parallel to the plane of the film up to a thickness of 100 μm [10]. In modeling the reflectivity curves, the PI film was assumed as a stack of 2-layers having constant but different electron density in each layer. This assumption stems from the fact that the degree of in-plane orientation of the imide chains is higher at the air-film interface than at the film-substrate interface [11]. Although an electron density profile (EDP) can be defined a priori to model the reflectivity curves, no previous EDP is known for PI films. The quality of the fits obtained from the 2-layer model yield good fits to the experimental data. The fitting parameters of the underlying film as well as of the substrate are kept constant. Figure
Figure 4.8: Specular reflectivity scans of polyimide film (a) before and (b) after rubbing in the (o) x- and (△) y-orientations. Data shown is corrected for the off-specular and diffuse scattering. The inset contains ω scans for corresponding orientations at \( q_z = 0.065 \).
4.8a shows the specular reflectivity scans of the nearly isotropic PI film of uniform thickness \( d = 218.5 \, \text{Å} \) with their corresponding theoretical fits. A small anisotropy arises from the flow during the spinning of the polyamic acid.

The curves yield a surface roughness of the top film \( \sigma = 13.4 \pm 1.0 \, \text{Å} \) \( (\chi^2 = 7.68 \times 10^{-4}) \) and the ratio of the electron density of the top layer (\( \rho_t \)) to the underlying layer (\( \rho_b \)), \( \rho_t/\rho_b \) is 0.77 \( (\pm 0.001) \).

Upon rubbing, the well-defined fringes are smeared out in both directions as a result of increased surface roughness. Although the anisotropy in the roughness of the rubbed PI is not obvious from the experimental reflectivity curves, the theoretical fits yield parameters \( \sigma^x_{\text{rms}} = 19.4 \pm 1.0 \, \text{Å} \) \( (\chi^2 = 6.23 \times 10^{-4}) \) and \( \sigma^y_{\text{rms}} = 26.5 \pm 1.0 \, \text{Å} \) \( (\chi^2 = 5.28 \times 10^{-4}) \) evident of a roughness anisotropy \( (\Delta \sigma = 5.1 \, \text{Å}) \). The reorientation of the molecular chain axis along the rubbing direction and/or out-of-plane orientation of the imide chains in the top layer accounts for the increased surface roughness of the rubbed film which is clearly seen in the increase of the diffuse scans.

The thickness of the film in the rubbing direction increased slightly by about 2 Å and decreased by about 4 Å in the orthogonal direction whereas the ratios of the electron densities, \( \rho_t/\rho_b \) are 0.815 \( (\pm 0.005) \) and 0.728 \( (\pm 0.005) \) in the x- and y-orientation, respectively.

4.3.2 \textit{In situ} UV Exposed Films

Among the different schemes for inducing LC alignment, rubbing dominates because of the strong surface anchoring and good chemical and thermal stability. However, as a consequence of rubbing, electrostatic charges and dust particles are generated which could have adverse effects to the desired performance of LCDs. Polarized UV-exposure of photosensitive polymer films eliminates these problems as discussed
in Chapter 1. This technique induces anisotropy on the surface of the exposed film: linear photopolymerization (LPP) for poly(vinyl)4-methoxycinnamate (PVMC) and poly(vinyl cinnamate (PVCi) films [14, 15], while anisotropic dissociation of photosensitive bonds for polyimides[16]. However, linearly photopolymerized PVMC and PVCi as alignment layers deteriorate with time whereas linear photodissociation in polyimides creates photoproducts which result to poor thermal and chemical stability compared with the rubbing method. A non-contact method using in situ linearly polarized ultraviolet (LPUV) light exposure of polyimide was reported [13] to have improved the thermal stability. The alignment PI film is prepared by simultaneous exposure to LPUV during imidization. This has the advantage over the conventional method \(^1\) such that the processing time is reduced and the surface anchoring is enhanced ergo, the thermal stability as well.

While the morphological anisotropy of PVMC and PVCi has been studied using high resolution x-ray reflectivity [18, 19], the in situ LPUV alignment film is fairly recent and has not been explored. The polyimide SE 7311 anisotropic film prepared by the in situ method induced LC alignment perpendicular to the UV polarization direction (x-direction). That is, LC alignment was in the y-direction.

The anisotropic surface roughness of the in situ films provided by the specular reflectivity scans and the \(\omega\)-scans are shown in Fig. 4.9. This is confirmed from the theoretical fits of a 2-layer model described above with \(\sigma_{rms}^{x} = 19.4 \pm 1.0 \text{ Å} \ (\chi^2 = 1.31 \times 10^{-3})\) and \(\sigma_{rms}^{y} = 15.5 \pm 2.0 \text{ Å} \ (\chi^2 = 1.64 \times 10^{-3})\). Again, the smoother direction is the easy axis of LC alignment. Ratios of the electron densities, \(\rho_e/\rho_b = 0.967 \text{ and } 0.913 \) in x- and y-orientations also indicate an anisotropic film. Diffuse

\(^1\)LPUV exposure is done after the imidization
Figure 4.9: Specular Reflectivity profiles of \textit{in situ} exposed polyimide thin films. The inset shows the $\omega$ scans in the two different orientations.
scans show a different profiles in the two orientation. These might arise from the contribution of photo products or unimidized components film near the surface in the direction perpendicular to the substrate [16].

4.4 Azopolymer

To complete this study, we looked at the morphological anisotropy of azopolymers as alignment layers. Initial interest on these materials stems from its excellence as optical data storage. Later, it is found that thin polymer films with azo moiety can be used for (re)alignment of LCs [17]. Such LC (re)alignment is possible via the trans-cis isomerization accompanied by the reorientation of the azobenzene pendant groups perpendicular to the direction of the UV polarized light [20]. Azopolymer film PA was prepared by spin coating 10% solutions of azopolymer and dichloroethane on a pre-cleaned glass at 2500 rpm. Drying was carried out at room temperature for two days to ensure that solvent is completely removed.

Scans of the as-prepared PA film of thickness ~1800 Å determined from the Kies-sig fringes, in both orientations are slightly different as shown in Fig. 4.10 indicating a film that is anisotropic. This anisotropy arises due to the flow during the spin-coating process which may not always be avoided. A theoretical fit yields rms surface roughness, \( \sigma_{rms}^x = 33.0 \pm 2.0 \, \text{Å} \) \( (\chi^2 = 2.56 \times 10^{-5}) \) and \( \sigma_{rms}^y = 28.5 \pm 2.0 \, \text{Å} \) \( (\chi^2 = 2.42 \times 10^{-5}) \) in the two orthogonal orientations giving a roughness anisotropy \( \Delta \sigma = 4.5 \pm 2.0 \, \text{Å} \).

Upon UV irradiation, roughnesses significantly increased as revealed by the theoretical fits to the reflectivity curves shown also in Fig 4.10 with fit parameters, \( \sigma_{rms}^x = 42.7 \pm 2.0 \, \text{Å} \) \( (\chi^2 = 2.38 \times 10^{-4}) \) and \( \sigma_{rms}^y = 30.5 \pm 2.0 \, \text{Å} \) \( (\chi^2 = 2.32 \times 10^{-4}) \) in both orientations giving a roughness anisotropy \( \Delta \sigma = 12.2 \pm 2.0 \, \text{Å} \). This is evident from the change in amplitude of the Kiessig fringes in the reflectivity scans.
Figure 4.10: Specular Reflectivity profiles of azopolymer PA: (a) without UV exposure, and (b) after 30-minute UV exposure. The insets are the \( \omega \) - scans in the two different orientations.
Although washing out of the Kiessig fringes is not obvious from the reflectivity data, quantitative analysis by theoretical fits clearly reveals the increased roughness. The enhancement of the surface roughness in the x-orientation for PA is 5× than that of the y-orientation indicating that y- is relatively smoother than x. The electron densities in both directions did not significantly change before and after LPUV.

Although the as prepared film of azo polymer showed roughness anisotropy greater than the anisotropy of the rubbed PI, it cannot be ruled out that even the as prepared films can partially align LC cells. The bigger picture is that LC aligned in the smoother direction.

4.5 Conclusion

Using a highly sensitive x-ray reflectivity technique which is a quantitative structural and morphological probe of a surface and buried interfaces in the submicron level, we have studied the morphology of thin polymer films of polystyrene, polyimide and azopolymers. These polymer films are typically used to induce liquid crystal molecular ordering on surfaces upon modifying the surface by rubbing or exposing to linearly polarized UV light. Liquid crystal molecules align, on average, in the azimuthal direction orthogonal to rubbing in the case of thin polystyrene film, but parallel to rubbing direction in the case of the polyimide film. Both polyimide and azopolymer exposed to linearly polarized UV induce liquid crystal molecular ordering perpendicular to the polarizer axis in the azimuthal direction.

The anisotropy of the coherence area of the x-ray beam makes it possible to study the morphological anisotropy of these films. Reflectivity scans of initially (relatively) isotropic films of polystyrene film show an enhanced roughness upon rubbing in the direction parallel to the rubbing axis. In contrast, the polyimide show an enhanced
roughness in the direction perpendicular to the rubbing axis. This is qualitatively indicated by the washing out of the Kiessig fringes and quantitatively confirmed by the roughness values from theoretical fits to the data. Reflectivity scans of the polyimide and azopolymer exposed to linearly polarized UV (in-situ method for polyimide) reveal more rough films in the direction parallel to the UV polarizer axis. This direction of increased roughness or more rough direction is perpendicular to the azimuthal direction of the liquid crystal alignment. In other words, liquid crystal molecular ordering is in the smoother direction.

Although this is not the first time the x-ray reflectivity technique is used to study morphological anisotropy of LC alignment layers,² our results in this study unambiguously seals or establishes the fact that liquid crystal molecular ordering imposed by alignment films is not chemical in nature but depends profoundly on physical effect (anisotropic morphology).

For complete characterization of the films in this study, quantitative analysis has to be carried out by fitting the ω-scans data.

²Previous x-ray reflectivity works include alignment layers such as Langmuir Blodgett films, SiO, PVMC, PDA, etc.
REFERENCES


CHAPTER 5

THERMAL STABILITY OF ALIGNMENT LAYERS

5.1 Introduction

While both chemical and thermal stability are important for the performance of the display device, thermal stability (surface anchoring) is necessary in the design process of the devices. The thermal process can damage the anisotropic orientation of the polymer units induced by LPUV resulting in a deterioration of the alignment properties. In the earlier discussion (previous chapter), the non-contact method \textit{in situ} LPUV exposure during imidization of UV sensitive polyimide is reported to be more thermally stable over the conventional method [1].

This chapter delineates the work and results involved in the preparation of polyimide alignment layers using \textit{in situ} method by varying the processing parameters such as soft- and hard-bake temperatures and duration, UV intensity and exposure time. The goal was to determine/develop a pattern for best alignment with a specific PI, and then deduce a general pattern applicable to other types of PI or UV-sensitive films. Also, we will determine the thermal stability of the different thin polymer films as alignment layers for liquid crystals.

5.2 Results and Discussion

5.2.1 Optical Retardation

It has been shown in a number of studies that anisotropic films induce alignment/ordering of LC molecules at the LC-substrate interface. To check the anisotropy
of the films prior to assembly, optical phase retardation, $\delta$ was measured using the method described in Chapter 2 (Fig. 2.3) except that the film/sample was mounted on a rotation stage. The signal was monitored while rotating the sample with respect to the surface normal. Figure 5.1 shows a representative retardation curve of an anisotropic PI film. From the corresponding curve of the film, the magnitude of $\delta$ was determined. The following are the results for the different processing parameters (soft\(^1\)- and hard-bake temperature and duration, UV intensity and time\(^2\)):

**UV-Exposure Time**

Figure 5.2 shows that $\delta$ increases with UV exposure time for both for SE7311 and SE7511 yielding a maximum upon completion of hard-bake time. The photoexposure during hard-baking facilitates immediate photodissociation of the polymer chains or inhibits imidization along the direction of the polarization of light resulting in anisotropic imidization in the direction perpendicular to the UV polarization. This is confirmed by probing the $\delta$ with time during the *in situ* process (Fig. 5.3) using the same experimental set-up in Fig. 2.3. The sample however was mounted on a hot stage (Mettler) to allow simultaneous exposure to LP UV in which the polarization was horizontally oriented. The line is a fit to a typical kinetics equation [2]

$$\delta(t) = C \left[ 1 - \exp^{-\alpha t} \right]$$

(5.1)

where $C$ is a constant related to the retardation saturation for a given temperature and UV intensity, and $\alpha$ is the reaction rate associated with the UV sensitivity of the polymer.

\(^1\)Variation of soft-bake temperature is inconsequential as it is associated only with the solvent evaporation. Bake temperature in the remainder of the text refers to the the hard-bake temperature

\(^2\)Time reference is the onset of hard-baking unless specified
Figure 5.1: Representative retardation curve obtained while rotating the sample about the its surface normal.
Figure 5.2: Dependence of optical retardation with time for • SE7311 and △ SE7511. The points are determined from their corresponding δ curves after the alignment layer preparation and before cell assembly. The line is drawn as a guide to the eye.
Figure 5.3: Dependence of optical retardation for SE7311 with time probed during the *in situ* process. The line is a fit of the data to Eqn. 5.1.
Hard-bake Temperature

The reaction mechanism during hard-baking involves a rapid imidization at an initial stage then a tapering off at a plateau [3]. Imidization rate slows down at the plateau region. The reaction rate is determined by the bake temperature, $T_b$, i.e. increasing the temperature favors a faster reaction (imidization) therefore baking time to complete imidization is shortened. In contrast, decreasing $T_b$ favors a slower reaction increasing the bake time for complete imidization. Photoexposure simultaneous with hard-baking can alter the reaction path. Two reactions, imidization and immediate photodegradation of the imide chains, can occur. The rate determining step (faster reaction) is dependent on the amount of photoexposure and bake temperature [4].

To determine the optimum and effect of temperature on $\delta$ upon varying the bake temperature, UV exposure time was fixed at $t = 1$ hour and the UV lamp power was set at 500W in the bake temperature range of $180^\circ C \leq T \leq 220^\circ C$. The limits of the temperature were constrained within the commercially suggested bake temperature without UV, $T = 200^\circ C$, beyond which, the polyimide film becomes brittle and below which, imidization isn’t complete within the duration of suggested bake time (1 hour). The results shown in Fig.5.4 demonstrate an increase of $\delta$ for $180 \leq T \leq 200^\circ C$ and a decrease for $T \geq 200^\circ C$ indicating that imidization is the faster reaction perpendicular to the polarization of UV light at $T = 200^\circ C$. Otherwise, photodissociation is the rate determining step.

The $\delta$ was probed during the in situ process at different temperatures and shown in Fig. 5.5 confirming that anisotropic imidization is optimum at $T = 200^\circ C$ with $\alpha = 0.0059$ min$^{-1}$. The fits to Eqn. 5.1 yield $\alpha = 0.0043 \pm 1.0 \times 10^{-4}$, 0.0059
Figure 5.4: Dependence of optical retardation for SE7511 with bake temperature. The points were determined from the δ curve after the preparation.
(±7.9×10⁻⁵) and 0.0032(±2.0×10⁻⁴) for 180, 200 and 220 bake temperatures, respectively.

UV-Intensity

Varying the UV intensity affects the anisotropic imidization and/or photodissociation rate. This is illustrated in the δ curves at various UV intensity in Fig. 5.6 for SE7311. From fits to Eqn. 9, α = 0.003 (±1.1×10⁻⁴), 0.0059 (±7.9×10⁻⁵) and 0.0044 (±7×10⁻⁵) for UV = 400, 500 and 600 Watts, respectively, indicating that anisotropic imidization rate is faster for the processing parameter combination of T = 200°C and UV lamp power = 500 W. At appropriate UV intensity and temperature, optimum retardation can be achieved. To illustrate that UV sensitivity is dependent on the material, the δ of PI alignment layers prepared by the normal method (i.e., no UV during hard-baking) was measured while exposing to same amount of LPUV (conventional). Figure 5.7 clearly shows that SE7511 is more sensitive to UV than SE7311 where α = 0.0092 (±1.4×10⁻⁵) and 0.0064 (±2.0×10⁻⁵) for SE 7511 and SE7311 respectively.

5.2.2 Nematic LC Alignment and Thermal Stability

LC alignment was examined from direct observation of the textures of LC cells assembled from the in situ prepared films. Films with δ ≤ 1.0 × 10⁻³ (i.e. PI alignment layers baked below and above 200°C and UV exposed below 30 minutes) did not give good alignment or no LC alignment at all characterized by the appearance of a nematic schlieren texture shown in Fig. 5.8a. Figure 5.8b is a representative photomicrograph of a cell with good alignment obtained from in situ prepared PI layers showing a dark appearance when UV polarization direction coincides with the
Figure 5.5: Dependence of optical retardation for SE7311 with time probed during the \textit{in situ} process for $\circlearrowleft$ - 180$^\circ$C, $\Diamond$ - 200$^\circ$C and $\triangle$ - 220$^\circ$C. The UV lamp power was set at 500 W and the line shown are fits to a kinetics equation Eqn. 5.1.
Figure 5.6: Dependence of optical retardation for SE7311 with time probed during the *in situ* process for $\circ$ - 400 W, $\diamond$ - 500 W and $\triangle$ - 600 W. The bake temperature was set at 200°C and the lines shown are fits to a kinetics equation Eqn. 5.1.
Figure 5.7: Optical retardation of ○ - SE7511 and △ - SE7311 probed during the in situ process and their corresponding fit lines.
Figure 5.8: Photomicrograph of (a) Schlieren texture, and (b) dark texture.

axis of one of the cross polarizers. Otherwise, the appearance becomes bright and is maximum when polarization direction is rotated through 45°.

The sample cells were then subjected to thermal annealing near the $T_{N-I}$ of the liquid crystal used (100°C) at different durations. The results are tabulated in Table I along with that of the cells with PI alignment layers prepared by the rubbing and the conventional methods where o indicates aligned cells and × indicate appearance of nematic schlieren texture or LC domains (Fig. 5.9) depending on the processing conditions and PI used. Rubbing produces the most stable alignment layer. However, between the two UV methods of inducing anisotropy on the film, the in situ method yields alignment layers of higher thermal stability over the conventional one. Several factors account for the enhancement of thermal stability. In the conventional method, photodissociation of imide bonds occurs after the imidization is completed leaving shorter segments of imide chains and other photoproducts in the direction of LPUV,
Figure 5.9: Representative photomicrographs of the annealed cells after LC alignment is lost. Depending on the PI, processing conditions of the alignment layers, either a (a) disclination lines, or (b) micro-domains of LC are observed.
and longer chains in the azimuthal orthogonal direction[5]. The mobility or relaxation of these shorter segments is limited since the UV exposure is carried out below the PIs glass transition temperature. As a consequence, there is a significant strain energy stored in these films which is released at higher temperatures during thermal annealing causing the polymer chains to relax randomly. Consequently, alignment of LC molecules is lost.

Table 5.1: Thermal stability for the two PI alignment layers. The cells were annealed at 100°C. The symbol ◯ indicates a uniform alignment texture and ×, an appearance of disclination lines or micro-domains.

<table>
<thead>
<tr>
<th>PI</th>
<th>Method</th>
<th>Annealing Time(Hrs)</th>
<th>at 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>7311</td>
<td>Rubbing</td>
<td>◯</td>
<td>◯</td>
</tr>
<tr>
<td></td>
<td>Conventional</td>
<td>◯</td>
<td>◯</td>
</tr>
<tr>
<td></td>
<td>In situ</td>
<td>◯</td>
<td>◯</td>
</tr>
<tr>
<td>7511</td>
<td>Rubbing</td>
<td>◯</td>
<td>◯</td>
</tr>
<tr>
<td></td>
<td>Conventional</td>
<td>◯</td>
<td>◯</td>
</tr>
</tbody>
</table>

On the other hand, in the in-situ method, thermal imidization and photodissociation occur simultaneously causing anisotropic imidization. Moreover, since LPUV exposure is carried out at high temperature, the mobility of polymer chains is higher. The shorter imide segments and/or photoproducts that reorient and become perpendicular to the direction of polarization are likely to undergo imidization and thus increase the number and length of the chains in that direction. Thus, the resulting
alignment films are free of strain energy, hence more stable, and more effective as LC alignment layer than the conventionally prepared films. Also, depending on the amount of UV during the in-situ process, imidization in the direction of LPUV can be inhibited favoring faster imidization in the perpendicular direction.

To determine the most stable alignment layer, the effect of LPUV exposure time for SE 7311 was studied. UV exposure was fixed at 400W of lamp power and the samples were annealed at 100°C, slightly above the $T_{N-I}$ of the liquid crystal. The results are summarized in Table II. Alignment layers exposed to UV less than the bake duration yield a more stable alignment upon annealing. Upon removal of UV during the in-situ process, photodissociation ceases. This allows more time for the photoproducts/smaller segments to imidize or relax in the remaining baking time. Hence, the alignment layers are more stable.

Table 5.2: Thermal stability of alignment layer SE7311 at different exposure times. The cells were annealed at 100°C.

<table>
<thead>
<tr>
<th>UV Exposure Time(min)</th>
<th>Annealing Time (Hrs)</th>
<th>0</th>
<th>24</th>
<th>48</th>
<th>72</th>
<th>96</th>
<th>108</th>
<th>132</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>50</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>o</td>
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<td>o</td>
<td>o</td>
<td>x</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>x</td>
</tr>
</tbody>
</table>

Thermal stability of rubbed polystyrene film as alignment layer for liquid crystal was also tested. This was done on an assembled cell with rubbed PS as alignment
layer. Liquid crystal E7 was injected near the $T_{NI}$ via capillary method then sealed with epoxy. The assembled cell with homogeneously aligned liquid crystal was then subjected to thermal annealing at 100°C. Less than an hour of annealing was enough to obtain the Schlieren texture similar to Fig. 5.8a indicating a loss of alignment.

5.3 Conclusion

It has been demonstrated that the in-situ method has far better thermal stability and require less processing time over that of the conventional method. The results have shown that optimum processing parameters of the in-situ method both in anisotropy and thermal stability is material dependent. That is, UV sensitivity and baking temperatures of the polymer are important factors. Optimum bake temperature is about similar with the commercially suggested temperature and the exposure time for optimum thermal stability is at least 20 minutes short of the baking time. The morphological anisotropy of the films prepared using this method showed that LC aligns in the direction with less roughness.

The loss of alignment upon prolonged annealing of the LC cells indicates that either LC has degraded or that the alignment layer lost the surface morphology necessary to align the LC. The earlier can be ruled out owing to the stability of the LC used within the annealing temperature range. Hence, one can deduce that the latter case is more likely the reason for the loss of LC alignment.
REFERENCES


CHAPTER 6

SUMMARY

From the outcome of this study, it is apparent that the dynamical behavior of a polymer specifically polystyrene in thin film geometry shows substantial differences from the bulk. This is most strongly indicated by the measurements of thickness dependent values of the glass transition temperature. Reductions of 15-20 K in the glass transition temperature for thin films of thickness less than 250 Å correlates very well with previous results on similar systems. In addition, we have shown that the chain mobility is enhanced at the polymer-air interface relative to the polymer-substrate interface as deduced from the results of the dependence of \( T_g \) on rubbing strength. This is a very important result because, unlike the behavior of \( T_g \) which is quite well characterized, the ideas such as mobile layers at the free surface and reduced density values in thin films systems from experiments are as yet inconclusive. Many techniques for probing relaxation of polymer surfaces involve physical contact between a probe and the surface of a polymer which could lead to misinterpretations of the results. Clearly, the optical method in this study involved only a direct measure of the chain mobility without the physical contact between probe and polymer surface. Hence, our results establish the mobility of chains at the free surface. The role of polymer-substrate interaction however, in the dynamics of thin polymer, needs to be further explored using similar method on attractive polymer-surface systems.

For more than two decades now, surface morphology and LC-substrate interaction have been subjects of interest due to the profound effect surfaces have on the ordering
of molecules. This subject is sufficiently mature, and we have seen from this study that the behavior of liquid crystal molecules is dependent on surface morphology. Knowledge of \( r_m \) roughness (perpendicular and parallel to the surface) is of great importance in understanding the exact nature of the surface. This can be obtained from the x-ray reflectivity technique which is a highly sensitive quantitative structural and morphological probe of a surface in the submicron level. It also probes buried interfaces as well. We exploited the anisotropy of the coherence area of the x-ray beam to study the morphological anisotropy of thin polymer films of polystyrene and polyimide and azopolymer. All films exhibit an anisotropic morphology upon rubbing or exposing to linearly polarized ultraviolet light.

Reflectivity of the initially nearly isotropic polystyrene (polyimide) films shows that the film became rougher in the direction parallel (perpendicular) to rubbing indicated qualitatively by the \textit{washing out} of Kössig fringes and quantitatively by the theoretical fits to the data, as opposed to the direction of rubbing. In the case of LPUV exposed polyimide (\textit{in-situ}) and azopolymer, reflectivity shows that films are more rough in the direction parallel to the UV polarizer axis. This direction of increased roughness or more rough direction is orthogonal to the azimuthal direction of the alignment of the long molecular axis of liquid crystals as expected from well-known Berreman’s calculation. Here, we have determined that liquid crystal molecular ordering on thin films is dictated by the physical effect (anisotropic morphology) rather than chemical in nature. This is further implicated by the results of the instability of LC alignment on the studied thin films upon thermal annealing and by the increased mobility of polymer chains at the surface with temperature.
Clearly, chain relaxations and surface properties and/or morphologies have important implications for the technological systems where very thin films are employed such as the liquid crystal display industry.