Anisotropic surface morphology of poly(vinyl 4-methoxy-cinnamate) and 12-8(poly)diacetylene thin films induced by linear photopolymerization

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Drastically different morphological anisotropy was induced by linear photopolymerization in thin amorphous films of poly(vinyl 4-methoxy-cinnamate) (PVMC) and Langmuir-Blodgett films of 12-8(poly)diacetylene (PDA) deposited on glass substrates. Examination of these films by x-ray reflectivity reveals that the PVMC films became rough while PDA thin films became smooth along the direction of polarization of uv light. The elongated x-ray coherence area inherent to the reflectivity technique allowed quantitative determination of changes in the film morphology and structure.

Although photopolymerization has played an important role in modern material science and technology for decades, the use of polarized uv light in obtaining polymer thin films with the desired anisotropic surface properties, particularly for liquid crystal alignment, has only been recognized recently [1]. Homogeneous alignment (planar and uniaxial), currently used in virtually all liquid crystal devices, requires an easy axis on the substrate surface which has traditionally been obtained by buffing. It has been generally believed that buffing creates a microgrooved morphology and stretched hydrocarbon chains in polymer thin films to align liquid crystal molecules [2]. The disadvantages of this technique are static charge buildup and nonuniformities. The technique of fabricating anisotropic alignment layers using linear photopolymerization (LPP) eliminates these problems. The success of LPP technique naturally raises two fundamental questions: what is the microscopic origin of liquid crystal alignment and how does LPP change the surface anchoring to achieve the desired alignment.

In this paper, we demonstrate that surface topology contributes to the alignment. We report the results of our x-ray reflectivity studies of two systems: a thin (112 Å) poly(vinyl 4-methoxy-cinnamate) (PVMC) film and a nine-molecule-thick Langmuir-Blodgett (LB) film of 12-8(poly)diacetylene (PDA) on flat glass substrates. These films were polymerized with linearly polarized uv light. It was found that the surface of PVMC thin films became rougher, while that of PDA thin films became smoother along the polarization direction. An elongated x-ray coherence area allowed the probing of the anisotropic roughness in orthogonal in-plane directions. Possible mechanisms responsible for the morphological changes in these thin films are discussed.

The specular reflectivity $R(q)$ of x rays from a single (air-substrate) interface can be described by the Fresnel formula multiplied by a Debye-Waller-like factor [3,4] as

$$R_1(q) = \left| \frac{q - q_s}{q + q_s} e^{(-qq_s\sigma^2/2)} \right|^2 = |r_{as}|^2, \qquad (1)$$

where q and q_s are the magnitude of the x-ray momentum transfer vectors in air and the glass substrate, respectively, and σ is the rms value of interfacial roughness treated as a random distribution of atoms or molecules with respect to an average plane. For a film of thickness t and x-ray refractive index n deposited on the substrate, the reflectivity of x rays can be written [5] as

$$R_2(q) = \left| \frac{r_{af} + r_{fs} \exp(inqt)}{1 + r_{af}r_{fs} \exp(inqt)} \right|^2, \qquad (2)$$

where r_{af} and r_{fs} are the x-ray reflectances at the air-film and film-substrate interfaces, respectively. The interference between the waves reflected from these two interfaces generates Kiessig fringes, which provide accurate measurements of the film thickness, electron density gradients, and the rms roughnesses at the two interfaces. For a Langmuir-Blodgett film consisting of periodic internal structure, one needs to take into account the Bragg scattering and interference between the reflected and Bragg scattered waves [6].

The determination of the anisotropy in film's morphology is made possible by unequal coherence lengths of the x-ray beam in different directions. The incident x-ray beam has the longest coherence length in the direction of the incident wave vector, which depends primarily on the source and the monochromator. The coherence length in the two transverse directions is determined by the experimental geometry. Consequently, the incident x-ray beam has an elongated coherence length volume, which is several thousand angstroms in one direction and a few hundred angstroms in the transverse out-of-plane directions. Evidently, scattering experiments coherently probe sample volumes that are elongated. The orientation of the long coherence length direction on the substrate surface can be changed by rotating the film about the momentum transfer vector. For isotropic surfaces this should not change the measured reflectivity. However, if the surface is anisotropic, the reflectivities obtained in the two orientations will be different. This allows one to probe the anisotropy in surface morphology.

The PVMC thin films were prepared by spin coating from an anisole solution onto 52×52 mm soda-lime glass plates, purchased from Donnally Applied Films, in a Class 100 clean room. The film was then dried for 1 h at 100 °C. Nine-layer PDA films were prepared according to the standard Y-type Langmuir-Blodgett deposition technique [7] on clean glass in a chamber with controlled humidity (30%) and temperature (25 °C). The PDA material was dissolved in chloroform, spread on a distilled water subphase in a Lauda trough, and given sufficient time for the solvent to evaporate. A constant surface pressure of 30 mN/m was maintained to ensure dense packing within each monomolecular sublayer. The deposition ratio for the PDA films was between 0.95 and 1.05 [7]. Both PVMC and the Langmuir-Blodgett films were then polymerized using isotropically and linearly polarized 14 mW/cm^2 of uv light ($\lambda < 330$ nm) at 24 °C and 40% humidity for 40 min. The layer structure and polymer backbone formation upon polymerization of these films are shown in Fig. 1.

X-ray reflectivity measurements were carried out using a four-circle x-ray diffractometer with a 18-kW Rigaku rotating anode source and Si(1 1 1) resolution described in Ref. [8].

Scans were conducted before and after rotating the sample by 90° about the scattering vector, i.e., surface normal, thus bringing the two in-plane directions (x and y, with x parallel to the polarization direction) into the scattering plane. The glass substrate was studied using x-ray reflectivity before the films were deposited. From the fits of the reflectivity to Eq. (1), the electron density and the surface roughness of bare substrate were found to be 0.78 ± 0.06 Å^3 and 3.5 ± 0.5 Å, respectively.

The "monomer" PVMC films were examined by x-ray reflectivity in a darkened environment. The polymerizing effect of the x-ray beam on the monomer film during the measurement can be ruled out as physically the same film exhibited profound changes in reflectivity upon linear polymerization with uv light at a later time.

The reflectivity scans in the x and y orientations were identical, showing that the film was isotropic prior to photopolymerization. The rms roughnesses of monomer film were found to be 2.2 ± 0.5 Å and 1.6 ± 0.5 Å in the x and y directions, respectively.

Isotropic polymerization [Fig. 2(a)] produced equally more pronounced fringes in both the x and y orientations with slightly higher rms roughnesses of 2.9 ± 0.5 Å and
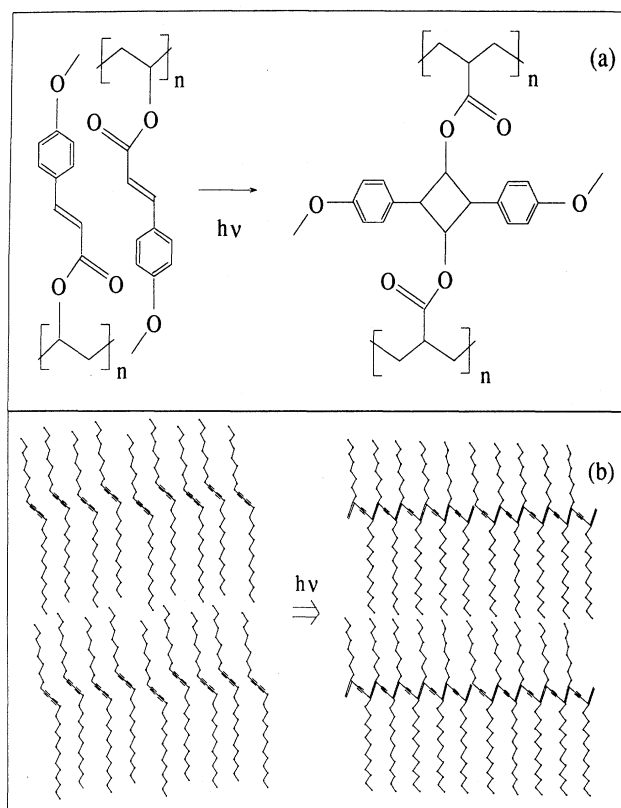

FIG. 1. (a) 2 + 2 cycloaddition mechanism of PVMC induced by LPP, with polymer main chains shown in square brackets. (b) Molecular positions in a PDA bilayer become better defined upon formation of π bonds within the plane of the layers during polymerization along the direction of the electric field of uv light. The zigzag lines represent alkyl chains and triple lines, carbon-carbon triple bonds.
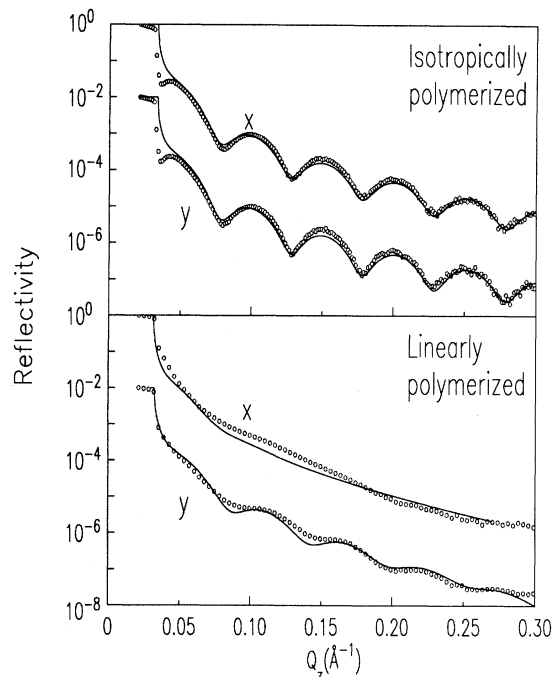

FIG. 2. (a) Specular reflectivity scans on isotropically polymerized PVMC in the x and y directions, showing equally pronounced Kiessig fringes, which indicate a uniform film in both directions. (b) Specular reflectivity scans of linearly photopolymerized PVMC with sample in the x and y orientations. Kiessig fringes in the y direction indicate film uniformity, while fringes have been "washed out" in scans in the x orientation due to film roughening. Solid lines are theoretical fits to Eq. (1).

2.2±0.5 Å, respectively. However, upon polymerization with linearly polarized uv light, the fringes remained well defined in the y direction, but were washed out in the x direction [Fig. 2(b)]. Fits to the linearly polymerized film data in the y direction using Eq. 2 yielded a film thickness of 111.6±2.0 Å and ratio of average electron density of the homogeneous film to the underlying substrate of 0.31±0.06 Å^3 (in agreement with the value for isotropically polymerized films 0.37±0.06 Å^3). The values of film thickness and electron density were then fixed at these values to fit the data obtained for the x direction, as the well-defined fringes in the y direction unambiguously determined these quantities. Roughness at the air-film interface was found to be much higher, 7.7±0.5 Å and 25.7±0.5 Å in the y and x directions, respectively. The quality of the fit was apparently poor due to complex surface morphology which may not be completely accounted for by the Debye-Waller-type factor. Translation of the sample perpendicular to q_z, so as to illuminate different regions on the surface, yielded identical results, indicating that the morphological anisotropy was global in nature.

The results can be explained by the model proposed by Schadt [1], which involves the $(2+2)$ photoinduced cycloaddition leading to preferential depletion of cinnamic acid side chain molecules along the axis of polarization,

forming cyclodimers with their long axes aligned perpendicular to the axis of polarization [Fig. 3(a)]. Uniaxial alignment of liquid crystal molecules deposited on top of this LPP film was previously attributed to dispersion (van der Waals) forces. We believe that this alignment arises primarily due to fissures and molecular mismatch introduced during bond formation after LPP. The observed directional roughening of the film strongly suggests that it plays an important role, as it does in buffed surfaces.

The measured x-ray reflectivity of nine-layer monomer 12-8 diacetylene LB films was analyzed using coherent superposition of the Bragg scattered and specularly reflected x rays. Longitudinal scans of the monomer film in the two orthogonal directions in the plane of the substrate exhibited the similar features—poorly defined Kiessig fringes due to variations in the overall film uniformity. Isotropic polymerization yielded pronounced Kiessig fringes in both directions [Fig. 4(a)] suggesting uniform, isotropic surface morphology. However, upon linear polymerization [Fig. 4(b)] the Kiessig fringes became well pronounced when the sample was oriented in the x direction, but remained poorly defined for the y direction. In the case of an odd number of layers in the LB film, a monolayer was considered in addition to an integer number of bilayers, which formed the "unit cell" of this film.

The structure factor determines the relative intensities of higher-order Bragg peaks, which is directly related to the distribution of electron density within the unit cell.
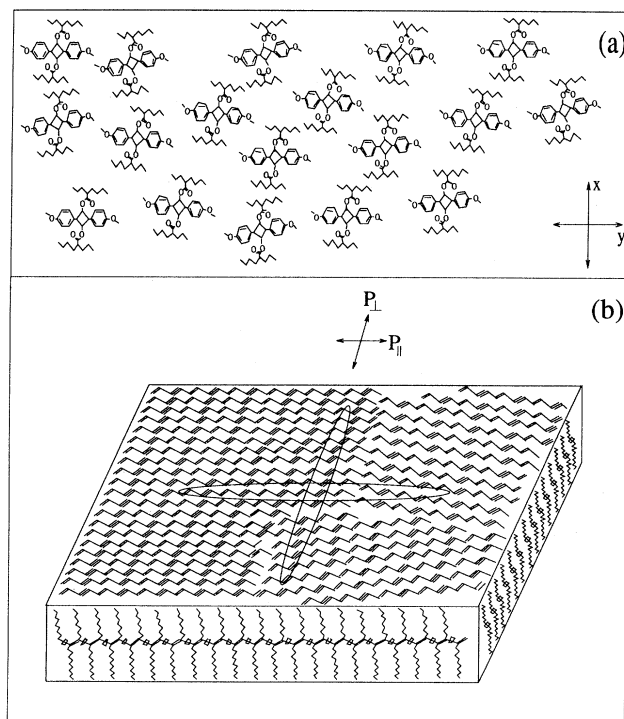

FIG. 3. (a) Uniaxial in-plane ordering of linearly polymerized PVMC films. LPP gave rise to a more uniform film due to cyclodimer and main-chain alignment in the y direction, while reducing uniformity in the x direction. (b) Orientation of π bonds formed upon LPP in PDA films with respect to the elongated beam coherence area. $P_{\parallel}$ and $P_{\perp}$ indicate directions parallel and perpendicular to the initial polarizer directions.
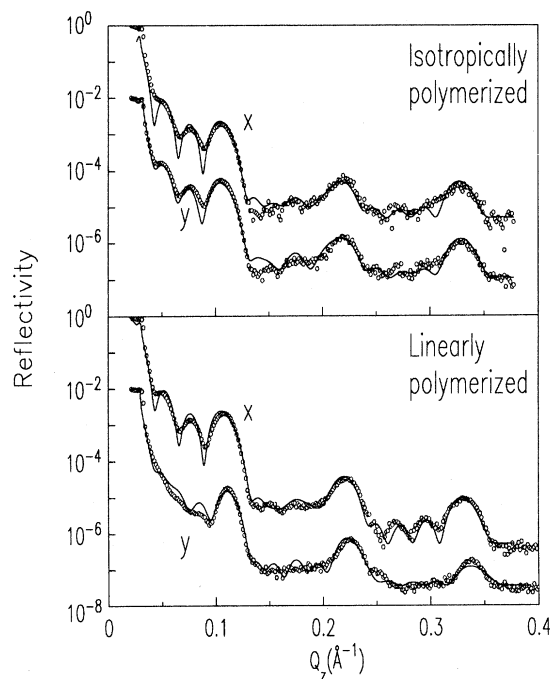

FIG. 4. Reflectivity curves of nine-layer PDA film for (a) isotropically polymerized and (b) LPP samples. Kiessig fringes are equally well defined in the isotropically polymerized sample. They become pronounced in the x direction in the LPP sample while remaining monomerlike in the y direction.

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A histogram representation of electron density modulation of the film was drawn, with the head groups and double-bond regions represented as crests with higher effective electron densities than the alkyl chains and methyl end-groups having a higher preponderance of hydrogens and greater intermolecular carbon-carbon spacing represented as troughs.

Roughness at the air-film interface decreased significantly in the x and y directions of the isotropically polymerized PDA film and in the x direction of the linearly polymerized film. Representative monomer films exhibited essentially the same roughness in the two orthogonal directions at the air-film interface, 25.2 ± 0.5 Å and 26.5 ± 0.5 Å. Upon polymerization by unpolarized uv light, the roughness decreased to 3.4 ± 0.5 Å and 4.2 ± 0.5 Å for the two orientations. However, for the linearly polymerized film, the results were quite different. Fits gave the roughness for the linearly polymerized film to be 5.1 ± 0.5 Å in the x direction, and 19.6 ± 0.5 Å in the y direction. Although both of these values were lower than that found in the monomer film, the decrease was much less for the y direction. The electron density function was modified by linear polymerization and the fits show that the full base width of the crests at the sites of head groups narrowed upon polymerization, changing from 4.4 ± 0.1 Å to 2.3 ± 0.1 Å, suggesting that they are better confined in the z direction and are in better registry with each other than in monomer films. Bilayer thickness of the monomer was 55.7 ± 0.4 Å in both the x and y directions. It increased by 1.5 Å upon isotropic polymerization, which is in agreement with previous results [9].

The fact that 12-8 diacetylene is known to undergo polymerization during which intermolecular linkages form within the plane of a layer [9] suggests that "ribbons" of π bonds formed along the direction of polymerization [Fig. 3(b)]. Previous work utilizing isotropically polarized light has established that rearrangement of the alkane pendant groups leads to fibrillization parallel to the polymer backbones and submicrometer-size crystallites [10,11]. We find that the formation of polymer bonds in effect "straightened" the layers so as to improve the overall film quality [Fig. 1(c)]. No such linkages formed in the perpendicular direction and the film essentially retained its apparent monomer form and roughness. It should be noted that the possibility of preferential π-bond formation due to molecular orientation arising from the "dip direction" inherent to the Langmuir-Blodgett deposition method could not be the cause of the observed anisotropic roughness because exposure to isotropically polarized light would then have produced the same effect.

LPP technique induces spatially preferential polymerization due to a well-defined orientation of the electric field of polarized light. There is a high probability of exciting a molecule that has its transition moment (i.e., initially unsaturated bond) oriented along that direction. Two studies [11] have reported observation of domains in multilayer PDA films in which polymer backbones form in a specific direction within a single domain and a different, independent direction in neighboring domains. The direction of bonding in highly ordered submicrometer sized domains depends on the packing and preferred tilt direction of diacetylene molecular segments [12]. This segment makes an angle of $\sim 120°$ with respect to the alkyl pendant groups and allows uniaxial topochemical polymerization to occur [13]. All the bonds in a particular domain therefore have a high probability of excitation due to a particular orientation of the incident electric vector with respect to the bond, so that in PDA films the smallest "reactive site" is the domain, while in PVMC films it is a pair of molecules as the structure is amorphous. However, in both films, bond formation in the direction of the axis of polarization gives rise to a uniaxial rough surface, which exhibited a "rougher" film direction in the direction parallel to the polarization axis in PVMC films and parallel to that axis in PDA films due to specific geometrical arrangements of reactive sites in the two physical systems examined.

To summarize, anisotropy in the morphology of spin-coated PVMC films and Langmuir-Blodgett deposited PDA films resulting from linear photopolymerization has been determined. Taking advantage of the elongated beam coherence area inherent to the reflectivity technique, we find that PDA LB films became more uniform in the direction of the polarization while remaining "monomerlike" in the perpendicular direction. The preferential bond formation in PVMC films induced roughness in the direction parallel to the polarization of light but left the perpendicular direction unchanged.

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