X-ray investigations of Langmuir-Blodgett multilayer films of side-chain liquid crystal copolymers

R. Geer[a]; S. Qadri[b]; R. Shashidhar[a]; A. F. Thibodeaux[c]; R. S. Duran[c]

[a] Code 6900, Naval Research Laboratory, Washington, D.C., U.S.A. [b] Code 6600, Naval Research Laboratory, Washington, D.C., U.S.A. [c] Department of Chemistry, University of Florida, Gainesville, Florida, U.S.A.

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X-ray investigations of Langmuir–Blodgett multilayer films of side-chain liquid crystal copolymers

by R. GEER†, S. QADRI‡ and R. SHASHIDHAR*†

† Code 6900 and ‡ Code 6600, Naval Research Laboratory,
Washington, D.C. 20375-5000, U.S.A.

A. F. THIBODEAUX and R. S. DURAN

Department of Chemistry, University of Florida,
Gainesville, Florida 32611-2046, U.S.A.

X-ray reflectivity studies on Langmuir–Blodgett multilayer films of side-chain liquid crystal polymers are reported. The films have a high degree of lamellar order. The layer periodicity is independent of the type of monolayer deposition, implying a reorientation of the side group mesogens following the deposition process. X-ray reflectivity from thin films displays subsidiary maxima permitting a quantitative measure of the change in side-chain density between multilayer and monolayer. A unit cell density profile is calculated for thick films assuming a symmetric unit cell.

1. Introduction

The discovery of ferroelectric behaviour in certain smectic liquid crystal meso-phases has prompted intense research aimed towards controlling macroscopic properties for the purposes of application. Recently, ferroelectric side-chain polymers have been synthesized to combine the ferroelectric properties of the monomeric side-chain mesogen with the structural features of the polymer [1–16]. It has been found that some of these polymers, namely, copolymers wherein the side groups are attached to only a fraction of the available positions in the backbone [9, 15, 16], form stable monolayers at an air–water interface. These monolayers have been transferred to suitably prepared substrates to form Langmuir–Blodgett (LB) multilayers [17–20]. Such multilayers have been shown to exhibit ferroelectric polarization similar to that of the bulk [21]. In this paper we report X-ray investigations of ferroelectric side-chain copolymer multilayer films. These results show that the multilayers have a high degree of lamellar order, the layer structure being independent of the type of deposition of the LB layer. We also show that the density profile of the multilayer along the layer normal is essentially the same as that of the bulk. The quantitative differences in the side group density between the multilayers and the bulk are discussed.

2. Experimental

The copolymer (10PPB-CO) is derived from a chiral liquid crystalline mesogen, (R)-4-(1-ethoxycarbonylethoxy)phenyl 4-[4-dec-9-enyloxyphenyl]benzoate (10PPB2),

* Author for correspondence.
Professor R. Shashidhar, Center for Bio/Molecular Science & Engineering, Code 6900, Naval Research Laboratory, Washington D.C. 20375-5348, U.S.A. Ph: (202)404-8424, Fax: (202)767-1295.

which by hydrosilylation is used to substitute approximately 30 per cent of the siloxane backbone units. The remaining silicons carry only methyl groups. This imparts a certain 'freedom' for the packing of side-group units within the layer plane. The synthesis is described elsewhere [15]. The phase sequence for bulk samples of the copolymer is

$$T_g-15^{\circ}\text{C}\text{—smectic C*}\text{—}136^{\circ}\text{C}\text{—smectic A}\text{—}156^{\circ}\text{C}\text{—isotropic.}$$

T_g is the glass transition temperature. Monolayers were formed at the air–water interface. A computer controlled film balance (KSV LB5000 with alternate dipping capability) was used to prepare LB films on a hydrophobisized silicon wafer. The details of monolayer and multilayer formation are given in [19]. The mean molecular area of the copolymer repeat unit is approximately 40 Å at a surface pressure of $0.025 \, \text{N m}^{-1}$. Brewster angle microscopy and isotherm hysteresis measurements [22] have established that the side chains are expelled from the subphase during compression. Polished silicon (100) substrates were used for deposition. Flatness of the wafers ranged from 3–10 Å with a miscut of <0.1 mrad. The substrates possess a native oxide film approximately 20 Å in thickness. Hydrophobization of the silicon wafers was achieved with a 2–5 per cent by volume solution of octadecyltrichlorosilane in 99 per cent anhydrous hexadecane.

Multilayers were deposited at surface pressures between $0.010 \, \text{N m}^{-1}$ and $0.027 \, \text{N m}^{-1}$ at a temperature of 25°C. For X-type deposition the monolayers were transferred during downstroke only. Monolayers were deposited during both up- and down-stroke for Y-type films. X-ray reflectivities for the films were measured on a two-circle goniometer using CuK_α radiation from a rotating anode X-ray generator (Rigaku RU-400). The X-ray beam was collimated by 0.12° entrance and exit slits along with a Soller slit placed in front of the analyser (graphite). The in-plane resolutions were $\Delta_{qx} = 5 \times 10^{-4} \, \text{Å}^{-1}$ and $\Delta_{qz} = 8 \times 10^{-4} \, \text{Å}^{-1}$. The out of plane resolution, $\Delta_{qy} \approx 0.2 \, \text{Å}^{-1}$, was determined by the slit height. The diffracted intensity was measured using a scintillation detector.

3. Results and discussion

Figure 1 shows specular scans for X- and Y-type films, both consisting of 50 deposition strokes. The mosaic of the layer normals is 0.11°, as measured from scans in which the ω axis is varied while the 2θ axis is fixed (rocking curves). Well-formed layers are evident from the four sharp reflections seen for both films. The layer spacing $d = 46.4$ Å is also the same, and is slightly larger than the bulk value of 42 Å. The similarity of the data in figure 1 indicates that the *interlayer structure is independent of deposition*. This implies that upon transfer, the mesogenic side chains reorient from the monolayer configuration to produce interdigitated layers similar to bulk samples. This reorientation is distinct from interlayer diffusion common in LB films of conventional amphiphilic molecules. Such diffusion for our materials is suppressed due to the large radii of gyration of the polymer backbone.

On decreasing the film thickness, subsidiary maxima can be resolved in the X-ray reflectivity, analogous to N-slit optical diffraction. This is shown in figures 2 and 3 for Y- and X-deposited films, respectively. Insets contain the corresponding transfer ratios for each deposition stroke. The average transfer for figure 2 was 0.90 (normalized to 1.0 for complete transfer). The upstroke deposition is clearly poorer, with an average transfer of 0.82 compared to 0.97 for the downstroke. For the X-type deposited film (see figure 3), the average transfer was 0.95. The number of smectic layers, N_L, in
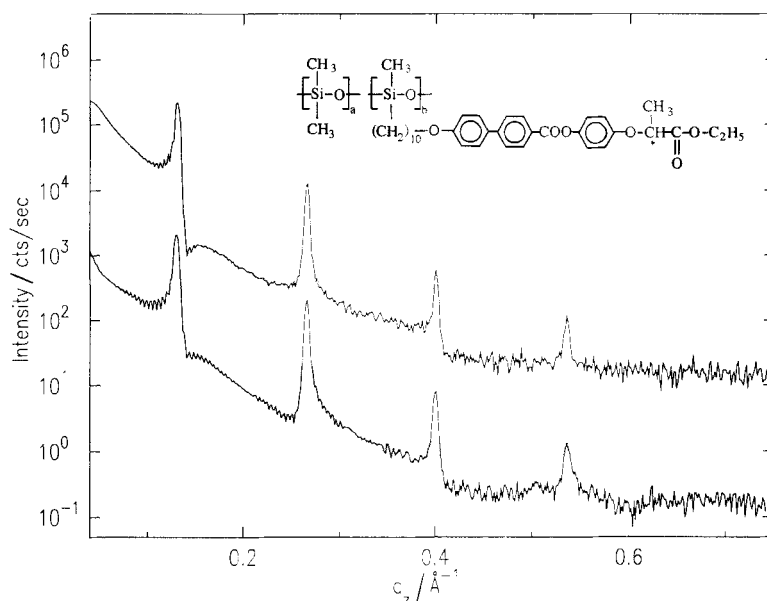
Figure 1. X-ray reflectivity for Y- (upper curve) and X- (lower curve deposited multilayer films (50 deposition strokes each) of the copolymer 10PPB2-CO. The layer spacing $d = 46.4$ Å for both films. The inset shows the chemical structure of the copolymer. $b = 1 > a = 0.3$ is the relative concentration of mesogenic groups occupying the siloxane sites.
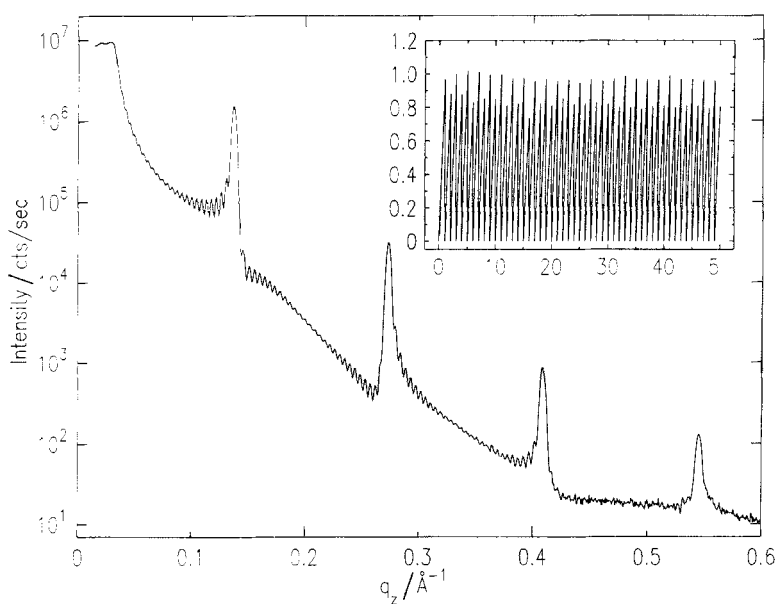
Figure 2. X-ray reflectivity and transfer data (inset) for a 30-layer film. Film thickness is determined from the number of subsidiary maxima.
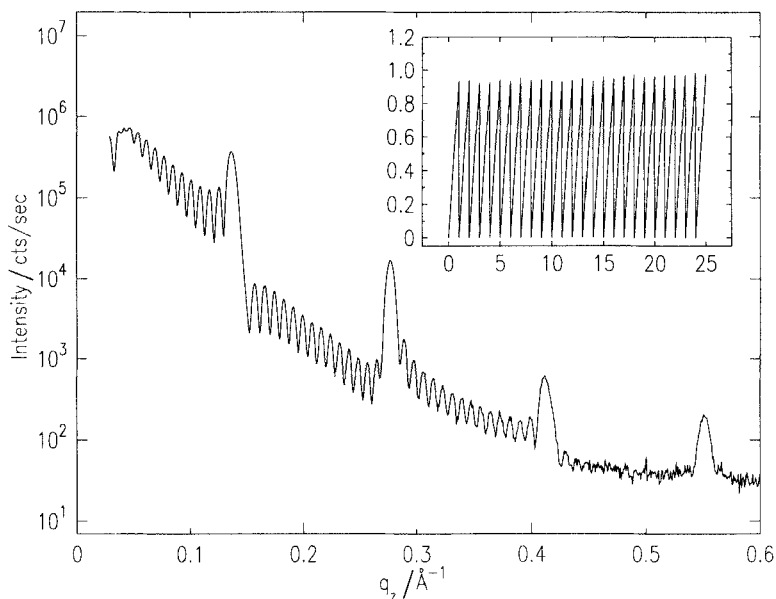
Figure 3. X-ray reflectivity and transfer data (inset) for a 16-layer film.

each film is determined from the $N_L - 2$ subsidiary maxima; $N_L = 30$ for figure 2 and $N_L = 16$ for figure 3. This information provides a quantitative measure of side-chain reorientation. Let ρ and ε denote average mass density and layer spacing, respectively. The subscripts Mo, Mu, and B refer to the monolayer, multilayer or bulk, respectively. Normalizing for the area of the film,

$$N_{dep}\rho_{Mo}\varepsilon_{Mo} = N_L\rho_{Mu}\varepsilon_{Mu}$$

where N_{dep} is the area under the transfer plots and N_L is the number of layers as determined from the reflectivity. For the data in figures 2 and 3, $N_{dep}/N_L = 1\cdot49$. For a series of seven films studied, ranging from 13 to 30 layers in thickness, $N_{dep}/N_L = 1\cdot49$ $\pm 0\cdot12$. N_L was independent of the type of deposition and monolayer surface pressure at transfer, and is determined solely by the amount of material transferred. From this ratio, $\rho_{Mu}\varepsilon_{Mu} = 1\cdot49\rho_{Mo}\varepsilon_{Mo}$ which reflects the increase in mesogen density due to side-chain interdigitation. A rough comparison can be made with bulk values, noting that the area/(polymer repeat unit) of the monolayer at deposition is approximately 40 Å², as compared to the bulk value of 23 Å² (calculated using the side chain nearest neighbour spacing from bulk X-ray measurements). This yields $\rho_B\varepsilon_B = 1\cdot74\rho_{Mo}\varepsilon_{Mo}$, which implies $\rho_B/\rho_{Mu} = 1\cdot29$. Hence, although larger than that of the monolayer, *the average multilayer density, ρ_{Mu} is only 78 per cent of the bulk value.* This results, in part, from the layer thickness of the multilayer film (46·4 Å) which is slightly larger than that of the bulk (42 Å), although a possible difference in the tilt angles could also be playing a role. The scaling of the observed multilayer film thickness with the mass of transferred copolymer implies side-chain reorientation even for the first monolayers transferred. This is further supported by the consistency of the film layer spacing d (plotted against N_L in figure 4). No systematic dependence on the layer number, the monolayer surface pressure at transfer, or the deposition type is observed.
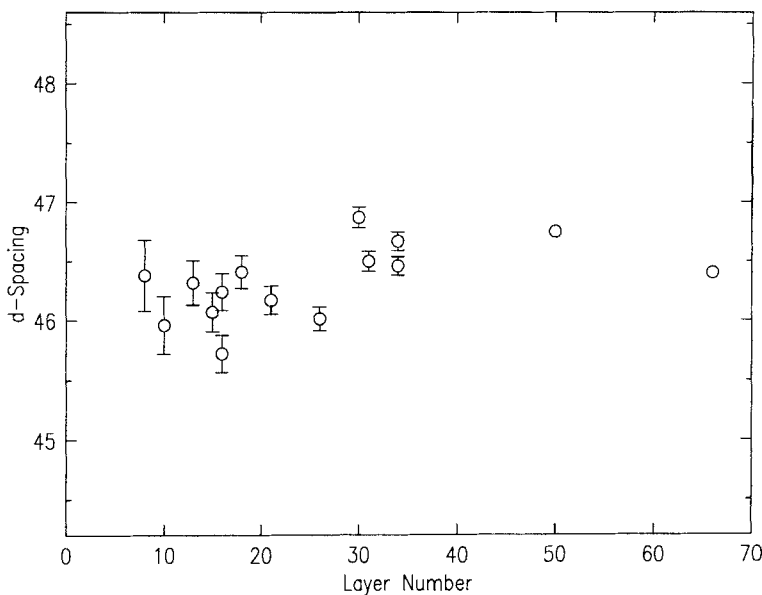
Figure 4. d-spacing as a function of N_L. The larger errors for smaller N_L are primarily due to finite-size broadening of the primary maxima.

These results show that the deposition of each layer is a dynamic process. The side groups have the freedom to interdigitate and pack with respect to the lower layer. We shall now calculated the relative density profile of the unit cell of the LB multiplayer film. For this purpose we assume a symmetric unit cell. The density profile can then be expressed in terms a Fourier cosine series,

$$\rho(z) = \rho_0 + \sum_n a_n \cos \frac{n^2 \pi z}{d},$$

where d is the smectic layer spacing and ρ_0 is the average electron density along the layer normal. The electron density variation, $\Delta \rho = \rho(z) - \rho_0$, can be determined from our experimental data with the proper choice of sign for the a_n. Figure 5 shows the unit cell density profile for a 67-layer (100 deposition strokes) film. The Fourier amplitudes, a_n, were determined by normalizing the data for the Fresnel reflectance and subtracting the specular diffuse scattering as determined from rocking scans. The resultant integrated intensities, proportional to $|a_n|^2$, were normalized to the first Bragg peak. Of the 16 possible sign combinations of the fourier amplitudes, half result in a phase shift of the unit cell by π. Assuming acceptable values for the relative electron densities of mesogen and backbone regions of the unit cells [22], we are left with only one reasonable combination. These coefficients are $a_1 = 1$, $a_2 = 0.53$, $a_3 = -0.14$, $a_4 = -0.10$. Distinct mesogen and backbone regions can be seen. The troughs are due to the alkyl regions of the mesogen groups. The profile of figure 5 closely resembles that of similar polysiloxane side-chain polymers studied by Davidson and Levelut [23]. Our samples, however, show much less backbone confinement due, in part, to the low grafting rate of the side chains which decreases the effective smectic field seen by the backbones. Also, the deposition of the films occurs close to the glass transition temperature of the copolymer which may inhibit complete interdigitation of the side
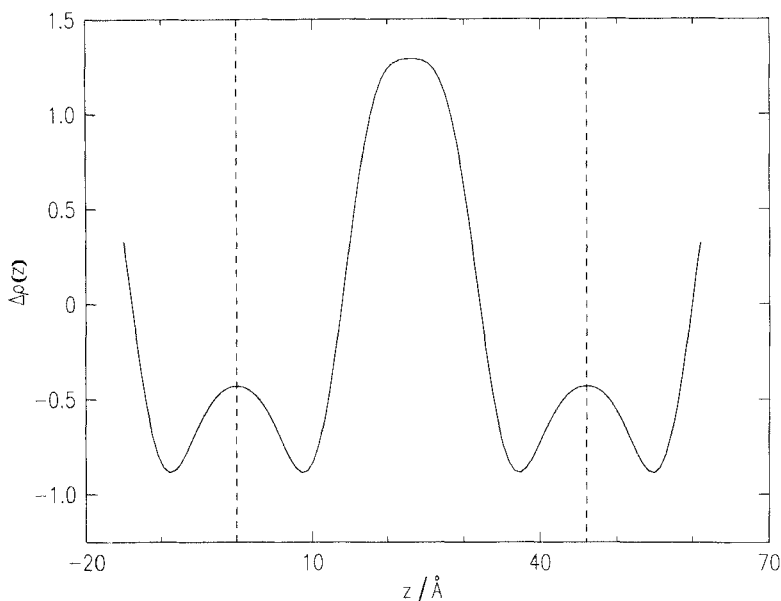
Figure 5.   Relative density profile of the unit cell of an approximately 67-layer thick multilayer.
Dashed lines indicate boundaries of the unit cell. The smaller peaks result from
localization of the backbone.

chains. This is a possible cause for the 10 per cent increase in the multilayer layer
spacing compared to the bulk.

In summary, we have performed X-ray reflectivity measurements for several
Langmuir–Blodgett multilayer films of a side-chain liquid crystal copolymer. Upon
deposition, the side chains reorient and interdigitate to form smectic layers very similar
to bulk samples. The average density of the multilayers is roughly 78 per cent of bulk.
Calculated density profiles are in qualitative agreement with those calculated earlier for
similar polymeric systems, but show a smaller degree of backbone confinement.

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