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Oligo(vinylidene fluoride) Langmuir-Blodgett films studied by spectroscopic ellipsometry and the density functional theory

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Thin films of amphiphilic vinylidene fluoride oligomers prepared by Langmuir–Blodgett deposition on silicone substrates were investigated by comparing experimental and theoretical mid-infrared (IR) spectra. The experimental spectra were obtained using infrared spectroscopic ellipsometry. Theoretical spectra were calculated using density functional theory. Excellent correspondence of major IR bands in both data sets shows that the molecular backbone is oriented with the long axis normal to the substrate plane. This is in contrast to poly(vinylidene fluoride) LB films, in which the polymer chains are parallel to the substrate. © *2008 American Institute of Physics*.
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I. INTRODUCTION

The study of poly(vinylidene fluoride) (PVDF) and its copolymers has spanned more than four decades, with particular attention to ferroelectricity and related physical properties, such as the piezoelectric and pyroelectric responses. The discovery of piezoelectricity in PVDF in 1969 (Ref. 1) generated much interest in transducer applications. The second major milestone was the discovery a decade later of the reversible ferroelectric-paraelectric phase transition[2] in copolymers of PVDF with, e.g., trifluoroethylene (TrFE), dramatically increasing interest in this system by enabling more fundamental studies of ferroelectricity and by providing a means for studying and optimizing the properties within the binary phase diagram poly(vinylidene fluoride—trifluoroethylene) [P(VDF-TrFE)].[3] In the 1980s, there was much progress in the fundamental understanding of ferroelectric copolymer structure, phases, and thermodynamics[4] as well as the development of practical electromechanical devices used for, e.g., pressure sensors, ultrasound transducers, and sonar transducers.[5] PVDF and its copolymers are also excellent insulators used in high-voltage power transmission lines, high-energy density capacitors, and ion-exchange membranes for fuel cells and batteries, and potentially for nonvolatile memories.[6] Materials based on PVDF are also promising due to its low cost, ease of processing, low toxicity, and high chemical stability. In parallel with the laboratory work, there were similar advances in analytical and computational modeling, the latter advancing steadily with improvements in computing power and improved techniques for quantum computational solid state physics.[7] Even with all these advances, the study of ferroelectric polymers was hampered by the fact that the method of crystallization from solution generally produces polymorphous samples with incomplete macroscopic alignment. (One notable exception is the "extended-chain" crystals developed by Ohigashi *et al.*[8])

Several important innovations in the 1990s further advanced the field of ferroelectric polymers. One was the application of Langmuir–Blodgett (LB) deposition to the VDF copolymers,[9] enabling the first studies of ultrathin ferroelectric polymer films. The LB films are much more suitable for fundamental research than are solvent-formed films because the LB films are highly crystalline, uniformly oriented, and range in thickness from one to hundreds of nanometers. These films exhibit two-dimensional ferroelectricity, in which the ferroelectric state is insensitive to film thickness down to nanometer thickness.[10] Another significant innovation in molecular ferroelectrics was the recent demonstration of ferroelectricity in VDF oligomer crystals.[11–13] The VDF oligomers, which consist of finite-length linear VDF chains terminated by, e.g., CF_3 and iodine, appear to be functionally equivalent to PVDF but are easier to handle and to crystallize. The fixed length of the oligomers lends itself to nanoscale structuring that is difficult to impose on random polymers. Encouraged by this work, we have synthesized a series of VDF oligomers (described in detail below) suitable for the production of self-assembled nanoscale structures.

In this paper we demonstrate through detailed analysis of the infrared spectroscopic ellipsometry data that the VDF chains in the VDF oligomer LB films, unlike the case of PVDF and its copolymers, tend to be oriented normal to the

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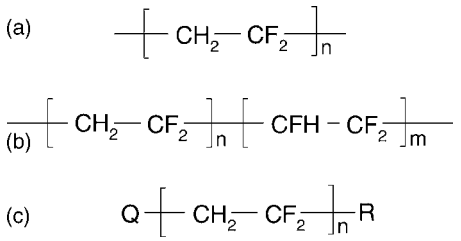

FIG. 1. Molecular structures of (a) PVDF, (b) P(VDF-TrFE) copolymer, and (c) VDF oligomers; n and m denote numbers of VDF (CH_2-CF_2) and TrFE ($CFH-CF_2$) units, respectively, and Q and R are terminal groups.

substrates, and consequently the in-plane component of their polarization dominates. This feature opens new avenues of possible application of molecular ferroelectrics.

II. EXPERIMENTAL

Figure 1 shows the general formula of the VDF oligomers. Their synthesis and detailed characterization will be reported separately. For the purpose of this paper, two different oligomers have been selected: (i) $Q=CF_3$, $R=$iodine, and $n=15$, and (ii) $Q=CH_3$, $R=OH$, and $n=14$. Both samples were prepared on electronic grade silicon (100) wafers as substrates. Films of 20 monolayers (ML) were made by the horizontal (Schaefer) LB deposition using an automated LB trough (NIMA 622C) filled with purified water (>18 MΩ cm). A few milliliters of a solution of the oligomer (0.05%) in dimethyl sulfoxide (DMSO) were dispersed on the surface of the water (stabilized at 25 °C) and slowly compressed to the target pressure of 5 mN/m, which was kept constant during the film transfer. Following the deposition both samples were annealed at 125 °C for 1 h. Additionally we prepared a comparable sample of 25 ML of P(VDF-TrFE) 65-35 copolymer as a reference. Infrared (IR) ellipsometric spectra $\Psi(\theta,\bar{\nu})$ (anisotropy of reflectance) and $\Delta(\theta,\bar{\nu})$ (retardance), where θ is the angle of incidence and $\bar{\nu}$ is the wavenumber, were recorded using a variable angle spectroscopic ellipsometry system (IR-VASE, J.A. Woollam Co., Inc.), comprising a Fourier-transform IR spectrometer and a rotating-compensator variable-angle ellipsometer, with spectral resolution of 4 cm^{-1} and the incidence angle $\theta=65°$. The WVASE32 software package was used for controlling the ellipsometry system and as well for further data analysis. The ellipsometry spectra Ψ and Δ are related to the complex ratio of reflection coefficients for light polarized parallel (r_p) and perpendicular (r_s) to the plane of incidence: $\rho(\theta,\bar{\nu})=r_p/r_s=\tan(\Psi(\theta,\bar{\nu}))\exp(i\Delta(\theta,\bar{\nu}))$.

Theoretical IR spectra of isolated oligomers were computed using a commercial package PQS,[14] which implements density functional theory (DFT).[15] We used the popular hybrid potential B3LYP (Refs. 16 and 17) in combination with the split-valence basis set 6-31+G* with polarization and diffuse functions on heavy atoms.[18,19] The atom of iodine, which is beyond the 6-31 G basis set was handled with the Los Alamos effective core potential (LANLDZ) double-zeta valence basis set.[20] The calculations were performed on shorter molecules consisting of nine VDF units in order to reduce the time of the calculations. We expect that eventual differences between vibrational spectra of VDF oligomers of different lengths are insignificant comparing with differences between calculated and experimental spectra. The structures were fully optimized, and the vibrational frequencies were computed for the optimized geometry. The obtained force fields were then processed with the scaled quantum mechanical (SQM) procedure[21–23] using the standard (transferable) set of scaling factors as in Ref. 22. The polarized IR spectrum was obtained by splitting each calculated vector of IR transition dipole moment (TDM) into two components: one parallel to the long molecular axis (defined as the axis of the lowest moment of inertia of the molecule) and one perpendicular to the long molecular axis. The IR intensities were then calculated as squares of the corresponding TDMs.

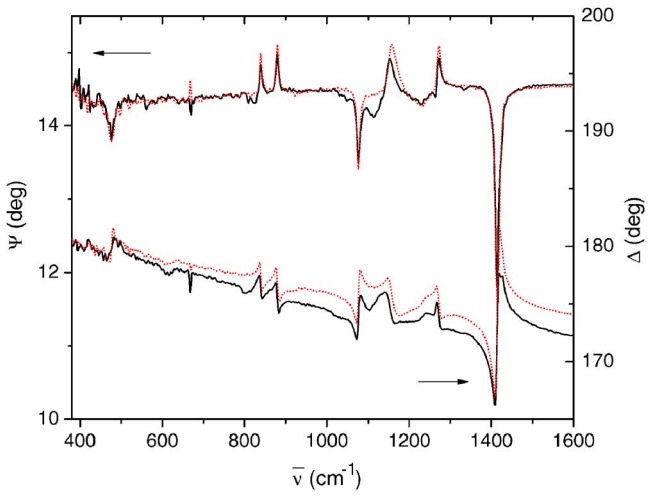

FIG. 2. (Color online) Ellipsometric spectra Ψ and Δ for both VDF oligomer LB samples. Solid black lines—iodine-terminated oligomer; dotted red lines—OH terminated one.

III. RESULTS

Figure 2 shows the ellipsometric spectra Ψ and Δ for both oligomer samples. As there are no fundamental differences between the spectra of both materials, further discussion will be focused on the iodine-terminated oligomer, but the conclusions will apply to both.

The intrinsic optical properties of the film were obtained from the extrinsic ellipsometry spectra Ψ and Δ by applying the following procedure.[24–26] We created a uniaxial model for the polymer layer with distinct in-plane and out-of-plane complex dielectric constants, each with a number of Lorentz oscillators of the form[26] $\varepsilon(\bar{\nu})=\varepsilon_1(\bar{\nu})+i\varepsilon_2(\bar{\nu})=\Sigma A_k/(\bar{\nu}_k^2-\bar{\nu}^2-iB_k\bar{\nu})=\{n(\bar{\nu})+ik(\bar{\nu})\}^2$, where $\varepsilon_1(\bar{\nu})$ and $\varepsilon_2(\bar{\nu})$ are the real part and imaginary part of the dielectric constant tensors, $n(\bar{\nu})$ and $k(\bar{\nu})$ are the refractive index and attenuation constant tensors, A_k is the amplitude of the absorption oscillator, $\bar{\nu}_k$ is the absorption oscillator central frequency, B_k is the absorption oscillator bandwidth, and $\bar{\nu}$ is the frequency (wavenumber). Thus the oscillators correspond to the absorption bands in the infrared spectrum. By fitting the model to the experimental data using the least-squares method (see Fig. 3), we extracted the major infrared bands along with the information on their polarization (in plane or out of plane, see Table I).

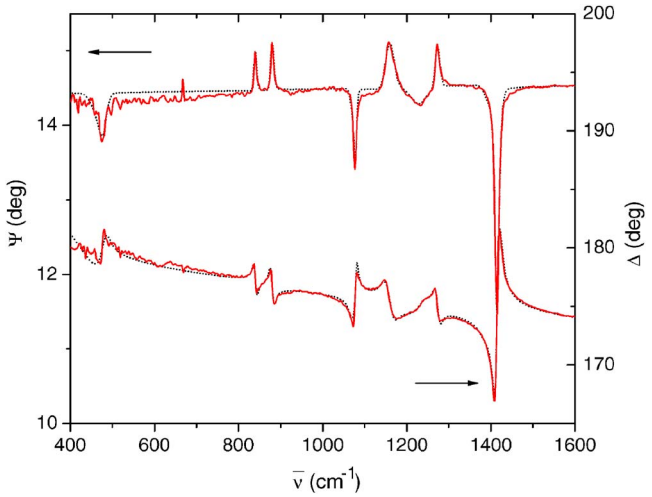

FIG. 3. (Color online) Model fit to the experimental Ψ and Δ data for iodine-terminated VDF oligomer. Solid red line—experimental data; dotted black line—fit.

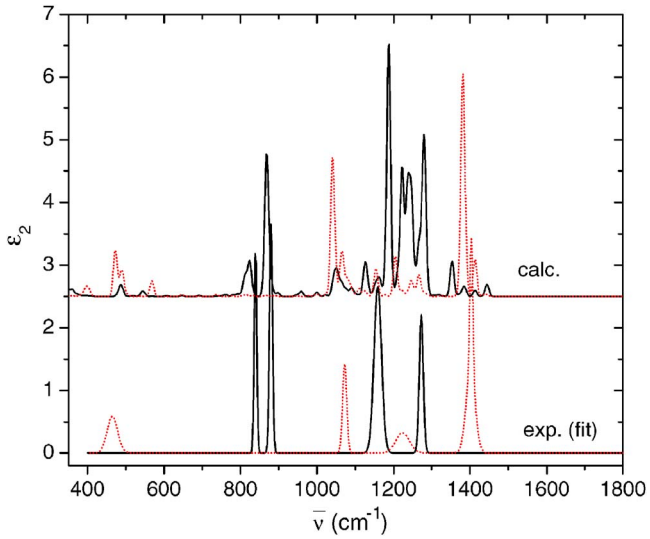

FIG. 4. (Color online) Comparison of experimental and DFT oscillators. Upper panel (shifted for clarity)—DFT oscillators; lower panel—oscillators extracted from the ellipsometry data; solid black lines—perpendicular (DFT) and in-plane (ellipsometry) modes; dotted red lines—parallel (DFT) and out-of-plane (ellipsometry) modes.

Comparing the infrared spectrum extracted from the ellipsometry experiment with the model spectrum calculated from DFT (see Fig. 4) shows an excellent correspondence between the two data sets within the limits of the applied model. The average difference of frequencies between the two data sets is $\approx 18\ \mathrm{cm}^{-1}$, which is reasonable considering the approximations inherent in the DFT calculations and from neglecting the influence of intermolecular interactions in the real sample when calculating a spectrum of a single isolated molecule. Surprisingly, the resulting deviations between the observed and calculated frequencies are much lower in our case than those obtained by Ramer *et al.*[27] for PVDF (on average 44 cm^{-1} for the same set of bands). They performed DFT calculations of PVDF in a unit cell, using plane wave pseudopotentials, which seem much more appropriate for the modeling of highly crystalline systems. In general, DFT calculations do not provide as accurate a prediction of frequencies as the empirical force fields,[28–30] but on the other hand the *ab initio* methods do not use empirical parameters of any kind, and therefore should be more reliable in the modeling of much broader range of material properties. It is worth noting here that the potential energy distribution (PED) analysis of our data reveals substantial differences as compared to the empirical spectra presented in Refs. 28–30, but a more detailed discussion of this issue is beyond the scope of the present paper and will be published separately. Here, we would like to point out two observations.

(i) The experimental IR spectrum of the VDF oligomer (see Fig. 4) closely resembles the spectrum of β-PVDF with *all-trans* conformation of the polymer chain, where the frequencies of most of the major bands are the same to within 2 cm^{-1} (see Table I and Refs. 28–30). This makes the VDF oligomers convenient model systems for studies on PVDF.

(ii) The absorption bands visible as out of plane by the ellipsometry correspond to parallel as determined by the DFT, and those seen as in plane by the ellipsometry correspond to the calculated perpendicular ones (Fig. 4).

TABLE I. Major infrared absorption bands extracted from the ellipsometry spectra. Key: ν—stretching; δ—bending. Values in brackets are relative contributions in %.

Freq. (cm^{-1}) Obs.	Calc.	Assignment (PED)	Polarization
466	474	νCC(55)+δCCF(23)+δCFF(8)+νCF(8)	∥
840	822	νCF(76)+νCC(17)	⊥
880	872	νCF(89)	⊥
1072	1040	νCC(64)+νCF(31)	∥
1159	1190	νCF(86)+νCC(10)	⊥
1273	1280	νCF(77)+νCC(14)	⊥
1404	1380	νCC(81)+δCCH(9)	∥

The latter observation means that the molecular long axes of VDF oligomers are on average oriented out of plane, in contrast to PVDF LB films, in which the polymer chains are oriented in plane. The difference in molecular orientation is illustrated by the ellipsometry spectra of LB films of VDF oligomer and P(VDF-TrFE) copolymer shown together in Fig. 5. Some bands that have TDMs in plane in the case of the oligomer have these moments out of plane in the case of the copolymer, and vice versa. It is especially clear for bands in the range of 800–900 cm^{-1}, which are essentially CF stretching bands.

The average direction of the C-F bonds is a good approximation of the direction of the spontaneous polarization. LB films of PVDF and its copolymers possess an out-of-plane polarization that may be exploited by embedding the polymer films into a capacitor with electrodes parallel to the film plane. The polarization of the oligomer LB film is predominantly in plane and cannot be easily addressed in the same geometry. On the other hand the oligomer LB films seem suitable for all applications where the in-plane polarization is necessary.

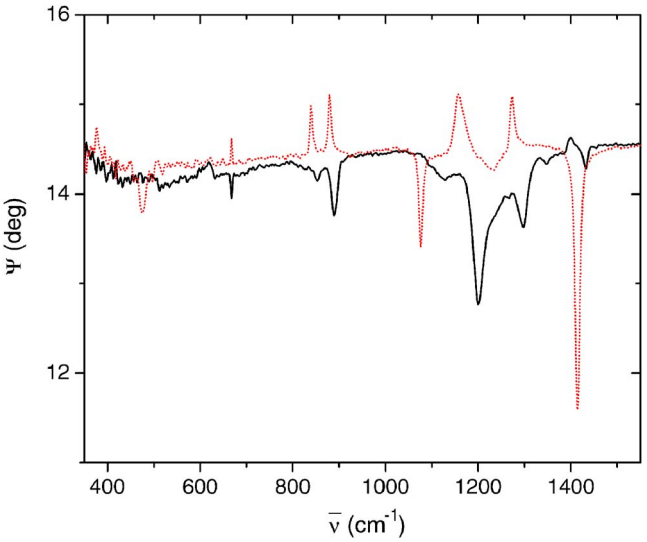

FIG. 5. (Color online) Comparison of Ψ spectra of iodine-terminated oligomer (dotted red line) and P(VDF-TrFE) 65-35 copolymer (solid black line). Please note that ellipsometry is a phase sensitive technique, and a change of the sample thickness affects the way how the IR bands are seen. For example, the strong band at ≈1400 cm^{-1}, which is an absorptive band in the case of the oligomer sample, looks like a dispersive one in the copolymer spectrum. The rather large difference in sample thickness is caused by the molecular arrangement: molecules of the oligomer stand up on the substrate, which results in ≈4 nm/ML, and long chains of the copolymer lie on the substrate, which gives 1.6 nm/ML.

IV. CONCLUSIONS

We have shown experimental evidence that VDF oligomer LB films exhibit molecular arrangement with the molecular backbone normal to the sample substrate, whereas the chains of LB films of PVDF and its copolymers LB films are predominantly parallel to the substrate. This is a fundamental difference that needs to be taken into account when considering the use of VDF oligomers in practical applications.

The techniques employed in the present work, spectroscopic ellipsometry along with the DFT calculations, complement each other in a way that is very useful when detailed information on the orientation of organic molecules in thin films or nanostructures is desired.

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