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Communications to the Editor

Monolayers and Langmuir–Blodgett Films of a Ferroelectric Side-Chain Polymer and Its Constituent Mesogen

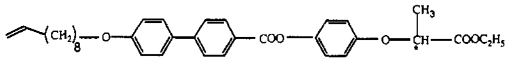
Introduction. Compounds exhibiting the chiral smectic C, or smectic C* (S_{C^*}), phase show ferroelectric properties.[1] It is known that the S_{C^*} phase is highly influenced by an interface with a dissimilar material.[2] In fact, the molecular ordering in the vicinity of the interface may differ significantly from the bulk where ordering is established due to self-organization. This concept was used by Clark and Lagerwall in developing fast electrooptic effects using ferroelectric liquid crystals.[2] The resulting surface-stabilized ferroelectric liquid crystal devices depend on these surface interactions. The molecules of the S_{C^*}-forming material in direct contact with a surface-treated conducting glass substrate are anchored in the plane of the substrate. This results in an untwisting in the macroscopic helix of the structure, which in turn leads to a bistability and bulk ferroelectric properties. Therefore, a more detailed knowledge of ordering in S_{C^*} materials, both low molecular weight and polymeric, near interfaces is of fundamental interest and practical importance.

In these experiments, the Langmuir trough is used to probe lateral interactions of monolayers of S_{C^*}-forming materials at a planar air/liquid interface. The preparation of Langmuir–Blodgett (LB) multilayer films is also described. LB layers formed of S_{C^*}-forming materials in carefully designed experiments may allow model interfaces to be studied using the stepwise development from a two-dimensional monolayer deposited at a solid substrate surface to a three-dimensional bulk-layered system of the liquid crystal. The LB multilayers may also be useful as model thin films to understand the dynamics of the molecular reorientations in switching.

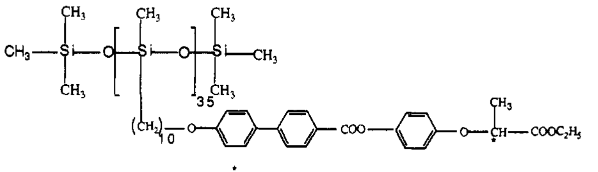
In this paper we report the first investigations of the monolayer properties of a side-chain polymer with a siloxane backbone and its low molecular weight side-chain mesogen and the successful LB multilayer preparation. The chemical structures of the substances and their approximate bulk transition temperatures are shown in Figure 1. For simplicity the side-chain compound will be called the "monomer" in the following text; its structure is slightly different than a monomer repeat unit of the polymer shown which is formed by grafting the monomer to a siloxane prepolymer. In the bulk both compounds exhibit similar liquid crystalline polymorphism.

Experimental Part. The synthesis and characterization of the above compounds are described in more detail elsewhere.[3] Monomer purity was checked by GC, TLC, elemental analysis, and ^{1}H solution NMR, and there were no indications of trace impurities. The polymer was purified by several reprecipitations from tetrahydrofuran solution into methanol.

For monolayer studies and the formation of LB multilayers, a commercially available computer-controlled film balance (KSV 5000) equipped with both Wilhelmy plate and floating barrier surface pressure measurement systems, dipping attachment, and temperature control was used. Monolayers were obtained by spreading chloroform solutions of the compounds (spectroscopic grade, Eastman Kodak, Rochester, NY) at concentrations of about 0.5 mg/mL and at starting areas of about 120 Å^2 or larger per molecule, which is of special relevance for the polymer.[4] A stock solution was prepared and immediately used. The water used for the subphase was prepared by a Millipore apparatus (>18 MΩ cm specific resistance).



10PPB2 $S_{I}^{*}{}_{/F}^{*}$ 55.5) cr 67.0 S_C^* 95.4 S_A 125.4 i



10PPB2P T_g 25 cr 58 S_C^* 178 S_A 215-222 i

Figure 1. Chemical structures of compounds used in this study. The asterisk designates the chiral atom, and bulk transition temperatures are listed below each compound.

During isotherm and dipping measurements, the compression rate of the monolayers was not higher than 10 cm^2/min. LB films were built up on hydrophilic glass substrates, PTFE sheets, and glass or quartz plates hydrophobized with trichlorooctadecylsilane (Aldrich) and immediately used for the transfer. All substrates were rigorously cleaned with alkaline H_2O_2 solution before use. The depositions were carried out at a constant film pressure of 50 mN/m with the exception of one dipping run, which was done at 35 mN/m. The temperature, *T*, was 27 °C. Typical dipping rates were 1 mm/min. Optical absorption spectra were monitored from LB films deposited onto quartz substrates using a Perkin-Elmer Lambda-9 spectrophotometer.

Results and Discussion. Both the monomer and polymer spread to form stable monomolecular films. Isotherms were found to be repeatable and showed little hysteresis upon decomposition below the collapse point. Figure 2 shows typical isotherms for the solvent-induced spreading of the polymer and monomer. The compression curve indicates that the monomer is able to form condensed monolayers only in the region above about 20 mN/m. However, the polymer organizes in the whole range as a condensed film, being highly incompressible above about 25 mN/m up to a pressure of 69 mN/m. In the high-pressure region the polymer film was observed to be very viscous. Therefore, the floating barrier was preferred to the Wilhelmy plate for measuring the applied surface pressure.[4] All the measurements discussed below are from the floating barrier pressure sensor.

The collapse of the polymeric monolayer starts at an area of 24.3 Å^2. This area, in which the side chains are assumed to be densely packed, approximately corresponds to the cross-sectional area of a benzene ring oriented perpendicular to the air/water interface. From this, one might also assume that the side chain is extended perpendicular to the air/water interface.

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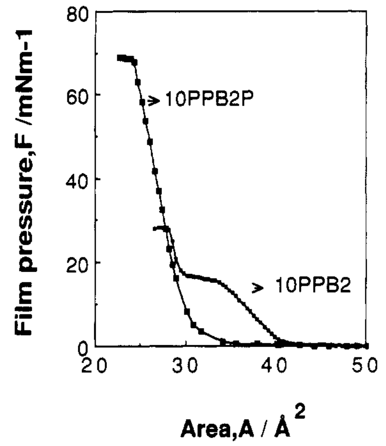

Figure 2. Compression curves of the polymer and monomer on water at T = 27 °C.

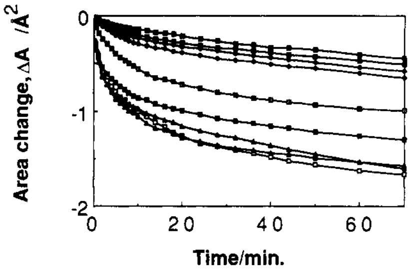

Figure 3. Surface area change vs time for the polymer at constant applied surface pressures. The constant pressures from the upper to lower curve are 50, 40, 30, 20, and 10 mN/m at a compression rate of 2 cm^2/min and 50, 30, 20, and 10 mN/m at a compression rate of 50 cm^2/min.

Extrapolation of the linear high-pressure regions of both isotherms to zero pressure results in approximately the same area of 30 Å^2, indicating the same mesogenic unit orientation for both the monomer and polymer in comparable pressure regions. This implies that, at intermediate applied surface pressures, the molecular areas are dominated by the packing of the mesogens rather than the polymer backbone. The question also arises if the ester group attached to the chiral carbon atom forms part of the hydrophilic headgroup for the polymer and mesogen. Miscibility investigations and surface potential measurements in progress may give answers to this question.

In spite of the same mesogenic orientation, there is a remarkable difference in film stability between the two compounds. Compared to the mesogen, the polymer passes directly to a condensed phase without an apparent liquid-like phase or biphasic region. The collapse pressure of the polymer is also substantially higher than that of the mesogen. The presence of the siloxane backbone thus enhances the film stability of the polymer with respect to its collapse pressure.

The polymer film stability may be seen clearly from the small change in the molecular areas in isobaric creep measurements as represented in Figure 3. The films were compressed to the different surface pressures indicated in the figure at 2 or 50 cm^2/min, respectively. The molecular area change was then measured as a function of time. A comparison of the curves shows that they all have the same features: after a sharp drop in the first 25 min, the area changed nearly linearly with time, depending only on the initial compression speed and not significantly on the applied surface pressure. The initial time dependence may reflect molecular packing rearrangements immediately after the compression was completed. The area change is seen to be smaller as the film is compressed more slowly. Furthermore, the stability was also influenced by the pressure to which the polymer film was compressed. The molecular area decrease at the lower pressures is greater. Similar experiments on the monomer showed the initial area decrease to be significantly faster.

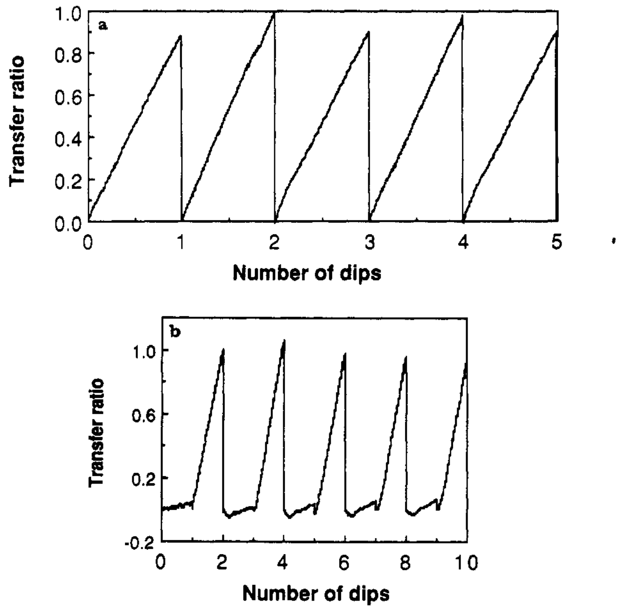

Figure 4. Transfer data vs number of dippings for the polymer: (a) at 50 mN/m, (b) at 35 mN/m. The odd dip numbers correspond to the upstroke.

Summarizing, the most stable films are formed if they are slowly compressed and kept at very high pressures. Thus, the short-term temporal stability of the polymeric monolayers appears to be dominated by relaxations brought about by the backbone conformation.

LB film deposition experiments were performed on a variety of different substrates under various conditions. In this section, results from the polymer are discussed. In spite of the high viscosity of the polymer, which has often been observed to be unsuitable for dipping,[5] LB films could be transferred. At a pressure of 50 mN/m films were transferred onto hydrophobic substrates by drawing downward and upward through the air/water interface at a rate of 1 mm/min. When hydrophilic substrates were used at the same pressure, one layer deposited on the first upstroke with a transfer ratio of 1. During subsequent dips, a layer would deposit on the upstroke and quantitatively "peel off" the substrate on the next downstroke. It should be noted that these first investigations were undertaken without drying the film after upward dipping and without any delay time, which is often described[6] as necessary for a successful transfer of a large number of layers.

As mentioned above, layers were deposited onto hydrophobic substrates at pressures of 50 mN/m. Figure 4a shows that under these conditions layers could be deposited on both the upstroke and downstroke (Y-type deposition) with a transfer ratio of about 1. However, at 35 mN/m (Figure 4b) there was only transfer during the upstroke, and Z-type deposition was observed.[7] Subsequent X-ray diffraction studies showed two orders of reflections in the small-angle region for the Y-type layers corresponding to spacings of 63 and 31.5 Å^2. The Z-type layers showed similar reflections with the intensity of the second-order peak reinforced. The observed layer spacing is less than the approximately 40 Å expected for a double layer of fully extended side chains; thus, the side chains are likely

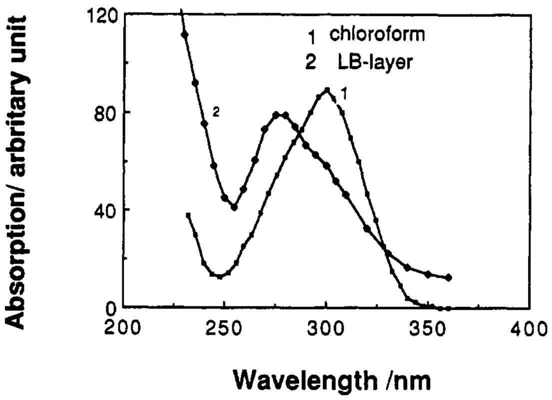

Figure 5. UV–vis spectra of the polymer taken from LB multilayers and a chloroform solution.

to be tilted on average with respect to the layer plane.[4] The above effects manifest the large differences in the polymer/substrate interactions and how these depend upon the conformation of the liquid crystalline molecules.

Transferred LB layers were also studied by UV spectroscopy. For transferred LB layers, a linear relationship of peak intensities to layer number was observed up to more than 100 layers. This, with the X-ray data, indicates homogeneous transfer. Figure 5 shows the nonpolarized spectra obtained from a chloroform solution of the polymer and the LB layers. A distinct hypsochromic shift is observed for the LB multilayers compared with the solution. The bands are shifted from 300 nm (aromatic π–π^* transition) in the solution spectrum to 280 nm for the LB multilayers. A similar shift can be observed if the bands of the LB layers and of a cast film are compared.[4] The shift is indicative of a linear aggregation of mesogenic units with their transition moments parallel to each other, arranged perpendicular or slightly tilted to the stacking direction (H-aggregation).[8] Spectroscopic investigations by IR and UV–vis with polarized light are in progress. They may give more insight into the properties of the ferroelectric polymer at the interface.

In summary, monolayer film formation has been observed for a ferroelectric liquid crystalline side-chain polymer and its corresponding monomer. The polymer formed much more stable films than the monomer. The polymer films could be transferred onto hydrophobic substrates, where, depending on the applied surface pressure, Y- and Z-type deposition was observed. The LB technique is thus an efficient method of systematically manipulating the layer-to-layer stacking order of this polymer in manners that are impossible by bulk techniques. For instance, diffraction studies indicate the LB layers have a tilted layered structure similar to that usually observed in C* phases. At room temperature the lateral positional ordering of the side chains should be similar to that of the higher order smectic phase seen in the bulk. Investigations are in progress to determine at what temperature the S_{C^*} phase develops in these LB films. It should also be noted that Y-type ordering cannot be induced in bulk smectic layers of the polymer by other techniques. Thus model polymeric conformations can be observed and investigated. Further studies on these effects with an alternate layer LB trough are in progress.

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