Bilayer-structure Langmuir films without an inversion center

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Polar multilayer Langmuir films of bilayer structure have been observed for the first time. An irreversible phase transition has been observed. At this transition the structural period of the films changes, the pyroelectric coefficient decreases by a factor of 40, and the dielectric constant goes through a maximum as a function of the temperature.

The ability to synthesize structurally polar multilayer Langmuir films from monomolecular Langmuir layers on the surface of water, which was first demonstrated by Blinov *et al.*,[1] has stimulated research on the synthesis and properties of noncentrally symmetric multilayer Langmuir films without an inversion center but with pyroelectric and piezoelectric properties[2–6] as well as quadratic nonlinear-optics properties.[7–9] Such films are of interest for use in uncooled pyroelectric heat-radiation detectors, thermometers, pressure gauges, optical-waveguide modulators, and frequency converters. According to the present understanding,[1–9] bilayer-structure multilayer Langmuir films synthesized from monolayers of a single chemical compound are assumed to have an inversion center. Researchers have accordingly concentrated their efforts either on synthesizing structures with a monolayer period[1,2,5–8] or on synthesizing superlattices with a bilayer period from two different, alternating monolayers.[3,4,9]

In this letter we report the observation of bilayer-structure polar multilayer Langmuir films consisting of molecules of a single chemical compound. We also report the first study of the temperature dependence of the pyroelectric and dielectric properties of polar multilayer Langmuir films.

The films are synthesized from monomolecular layers of *p*-octadecyl aminoazobenzene-*p*′-sulfamide (AS) layers, with the chemical formula $H_{37}C_{18}$-NH- -N═N- -SO_2NH_2, by the Langmuir-Schaefer method.[10] For experiments we fabricated some samples in the form of thin-film capacitors in which the dielectric layer was the multilayer Langmuir film of AS. The thicknesses of these multilayer films ranged from 30 to 70 monolayers (700–1600 Å).

The fact that these films exhibit a pyroelectric effect confirms that the structure of the multilayer Langmuir films of AS is polar. The pyroelectric coefficient $\gamma_n = dP_n/dT$, where P_n is the normal component of the spontaneous polarization, and T is the temperature, is determined by the well-known dynamic method.[2] The value of γ_n of these AS films is $\sim 1.6\times 10^{-10}$ C/(cm^2·K) (at $T = 20\,^\circ$C). This figure is comparable to values published previously for multilayer Langmuir films of similar molecules [$\sim 3\times 10^{-10}$ C/(cm^2·K); Refs. 1 and 2]. The measurements of the temperature dependence (curves a in Fig. 1) of the pyroelectric coefficient, the real part of the

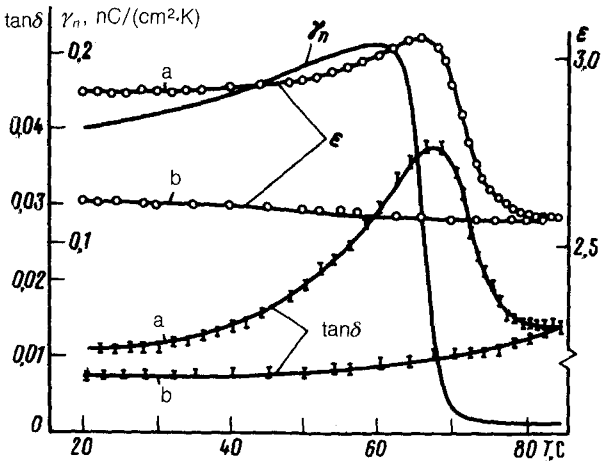

FIG. 1. Temperature dependence of the pyroelectric coefficient γ_n, the real part of the dielectric constant (ϵ), and the dielectric loss tangent $\tan\delta$ (at 1 kHz).

dielectric constant (ϵ), and the dielectric loss tangent ($\tan\delta$) in these films reveal that an irreversible phase transition, unrelated to a melting of the film (its melting point is $\sim 115\ ^\circ$C), occurs at ~ 63–$66\ ^\circ$C. At this transition, the value of γ_n decreases irreversibly by a factor of 40; ϵ and $\tan\delta$ go through maxima at $T = 66\ ^\circ$C. When the measurements are repeated, the curves of $\epsilon(T)$ and $\tan\delta(T)$ (curves b in Fig. 1) reveal no structural features and are reversible.

The periodicity of the structure of the AS films along their thickness is measured on an AMUR-K small-angle x-ray diffractometer[11] with a position-sensitive detector having an angular resolution of 0.02°. In these measurements we use CuKα radiation, at the wavelength 1.54 Å. Figure 2 shows x-ray diffraction patterns of a film 70 monolayers thick, according to measurements (a) before and (b) after the film was heated to 85 °C. The structural period along the thickness of the film found from the Bragg condition is $d_p = 45.5 \pm 0.5$ Å in a film which has not been heated and $d_p = 20.6 \pm 0.4$ Å in one which has been heated. Corresponding results were found for several other samples. The value found for the period, $d_p = 45.5$ Å, corresponds to a bilayer packing of molecules since the length of the AS molecule is about 39 Å. This

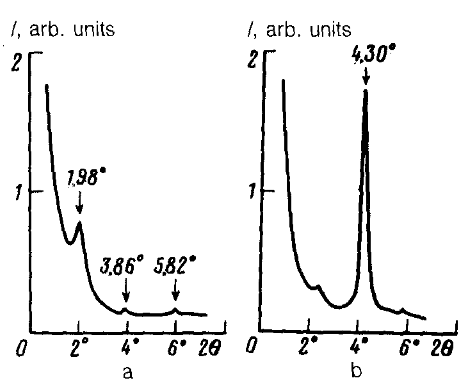

FIG. 2. X-ray diffraction patterns of multilayer Langmuir films of AS. a: Before heating. b: After heating. I—Intensity of the diffracted radiation; 2θ—angle between the incident and diffracted beams.

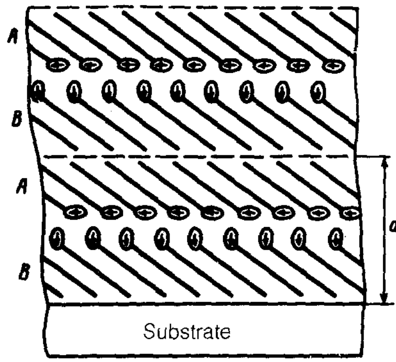

FIG. 3. Schematic diagram of a possible packing of molecules with dipole moments in different orientations in the even (A) and odd (B) layers of a bilayer structure. The arrows represent the dipole moments of the molecules.

was an unexpected result. It contradicts the general belief that a pyroelectric effect is exhibited by films with a multilayer structural period, and it disappears when we go to a structure with a bilayer period. Let us examine some other experimental facts in an effort to suggest a model to explain this result. The films were synthesized as a result of the transfer of an AS monolayer from the surface of water to a substrate by immersing the substrate through the water-monolayer interface and then extracting it from the water through a clean surface, without a monolayer. In this manner, one monolayer is transferred in a single immersion-extraction cycle. The thickness of such a monolayer in a multilayer Langmuir film is $d_e = 23 \pm 2$ Å, according to a measurement of the thickness of the multilayer film with an interference microscope. This thickness is roughly half the observed structural period, $d_p = 45.5$ Å. It may be that half of the molecules undergo an orientation reversal in each transferred monolayer, with the result that a bilayer structure forms, as occurs in multilayer Langmuir films of salts of carbonic acids during X-type deposition.[12] In the bilayer structure that forms with a period of 45.5 Å, molecules 39 Å long should have 2 canted orientation (Fig. 3). The particular molecules that were used have the shape of a slightly bent rod, at one end of which there is a comparatively small group ($-SO_2NH_2$, with a volume amounting to ~ 0.1 of the volume of the molecule). This small group is basically responsible for the dipole moment of the molecule. A particular feature of this molecule is that the dipole moment makes an angle with the axis of the molecule. To explain the polar properties of multilayer Langmuir films of AS, we might suggest that the dipole molecules in the even and odd layers of the bilayer structure have different orientations, as shown schematically in Fig. 3. The molecules might have approximately the same orientation with respect to the normal.

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