

Pyroelectric activity in polar hemicyanine Langmuir-Blodgett multilayer films

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The Langmuir-Blodgett (LB) films of hemicyanine dyes were prepared by LB technique. The films showed pyroelectric effect. The pyroelectric coefficient measured by the method of integrated charges was $12 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ at room temperature, and the relationship between the orientation of DAEP dye in the films and temperature was studied by polarized Fourier transform infrared spectroscopy (FTIR) spectroscopy and Second harmonic generation (SHG). It was indicated that the observed pyroelectricity can be ascribed preliminarily to the structure modification of the polar head groups and the deterioration of the film framework (the first-order phase transition) resulted in the change of spontaneous polarization with temperature.

OCIS codes: 190.4710, 300.6340, 190.2620, 040.3060, 160.1890.

It has been known that Langmuir-Blodgett (LB) films are well-organized thin organic assemblies capable of various functions if molecular compositions are suitably designed. For example: X- and Z-type LB films and alternate LB films consisting of two different amphiphiles have noncentrosymmetric structure and are expected to show piezoelectric, pyroelectric, and various nonlinear optical properties^[1]. Since the beginning of the 1980s, more and more researchers focused on the pyroelectric effect of noncentrosymmetric LB films, for the reason that if the molecule is well-polarized, we need not apply an external electric field to remain the pyroelectricity of the conventional materials such as ferroelectric ceramic^[2-7]. And LB films offers real advantages over polyvinylidene fluoride (PVDF) and ceramic materials in terms of their lower dielectric constants and dielectric loss values which are typically ~ 2.5 and 0.01 . On the other hand, one of the impressive properties of LB films is an opportunity to vary the multilayer structure of the films with an accuracy of one monolayer. The optimum thickness of a pyroelectric film is of the order 30 nm , and the LB film technique is particularly well suited to providing well-ordered films of this thickness.

In the present paper, the relationship between pyroelectricity and temperature in Z-type LB films consisting of hemicyanines was investigated. The pyroelectricity of the multilayer films was measured by a static method in

the temperature range from 20 to 65°C . It was found that the pyroelectric coefficient increased with the raise of temperature and the value was obtained to be $12 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ at room temperature.

The active material hemicyanine dye E-N-docosyl-4-[2-(4-diethylaminophenyl)ethenyl] pyridinium bromide (DAEP) used in this work was synthesized following Girling *et al.*^[8] and purified by our laboratory. The Z-type DAEP LB multilayer samples were fabricated using an automated KSV 5000 two-compartment Langmuir trough. The deposition method has been described in earlier publication^[9,10] and will not be repeated here. We have prepared the films consisted of 25, 53 and 66 monolayers, respectively.

We used glass plates coated with indium tin oxide (ITO) as a substrate. After depositing monolayers, top aluminum electrodes with dimensions of 1.8 cm^2 were evaporated on the top of the films to form a sandwich structure (capacitors) ready for the measurements of pyroelectric coefficient. The charge integration measurement^[11,12] was performed at various temperatures to characterize the pyroelectric coefficient in the samples, the experimental setup was shown in Fig. 1. The curves of pyroelectric coefficient p with temperature T can be gotten using the equation $p = \Delta Q / (\Delta T) = C(\Delta U / \Delta T) / S$.

Polarized infrared spectra were recorded on a Bio-Rad FTS-185 Fourier transform infrared spectroscopy (FTIR) spectrophotometer equipped an DTGS detector. The s- and p-polarized radiation from a Perkin-Elmer wire grid polarizer was incident on the sample plane at 0° or 45° off the surface normal. The substrates for the infrared transmission measurements were ZnSe plates.

The experimental setup used for transmitted second harmonic generation (SHG) measurements was shown in Fig. 2. The incident fundamental beam ($1.064 \mu\text{m}$, 30 ps pulsewidth, 10-Hz repetition rate, 2 mJ per pulse) was produced by a mode-locked Quantel Nd:YAG laser. The transmitted SHG signals from the samples were detected by a photomultiplier tube (PMT) and a boxcar

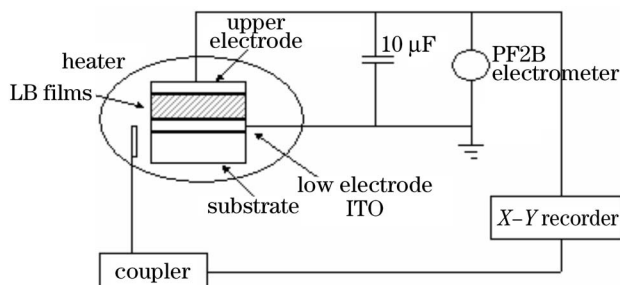


Fig. 1. Experimental setup for pyroelectric coefficients measurement.

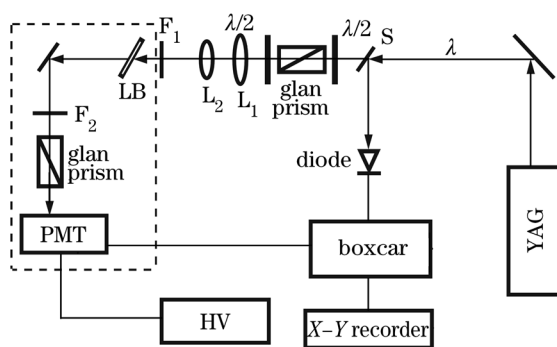


Fig. 2. The experimental setup for transmitted SHG measurements. F₁: filter; S: beam splitter; L₁ and L₂, condensing lenses; LB: samples; F₂: 532-nm interference filter; PMT: photomultiplier.

integrator. The SHG intensities I_{sp} (s-in, p-out) and I_{pp} (p-in, p-out) from samples were measured and normalized to that of a reference (Z-cut quartz plate). The substrates used for LB multilayer deposition were K₉ or quartz glass plates of size 30×18×2 (mm) for the SHG measurements.

The pyroelectric behaviors of these Z-type LB films were investigated using a static technique. Since the pyroelectric coefficient is $p = dP/dT$, where P is the total (spontaneous and field-induced) polarization, the temperature dependence of polarization (on an arbitrary scale) was calculated by integrating pyroelectric voltage, which is proportional to the pyroelectric coefficient. The pyroelectric coefficients of the Z-type hemicyanine LB films are shown as functions of temperature in Fig. 3. It was found that the value of p is obtained to be $12 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ at room temperature. The coefficients raise gradually with increasing temperature. The values measured here are very similar to those obtained for polysiloxane/monolayer icosylamine LB films^[13]. While the temperature raised, the heating movement of molecules was advantageous to disordering the orientation of molecular dipole moments. Thus, the enhancement of temperature was more easy of the modification of polarization and resulted in the enlargement of pyroelectric coefficient.

Previous investigators have attributed the origin of the pyroelectric effect in LB films to the changes in molecular volume, molecular orientation and the degree of

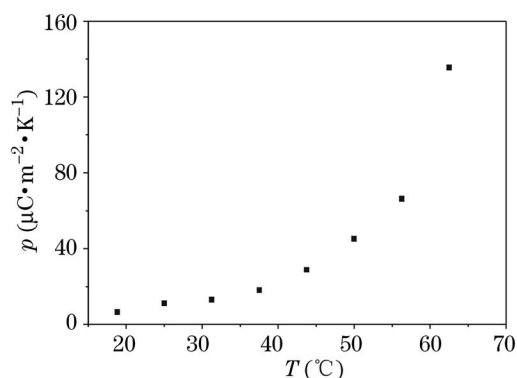


Fig. 3. Pyroelectric coefficient p versus temperature for Z-type LB films of hemicyanine dye (66 monolayers, 165 nm).

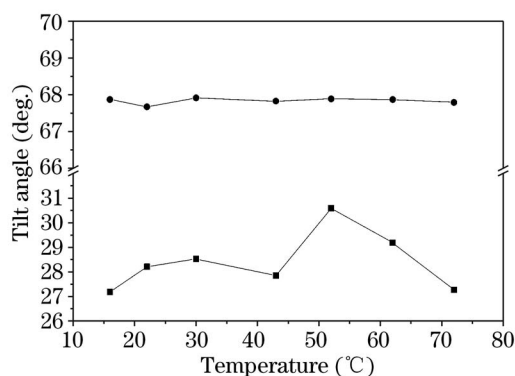


Fig. 4. Temperature dependence of the orientation angle of the hydrocarbon chain and chromophore of hemicyanine molecules in the LB films.

proton transfer upon heating/cooling^[4-6,14]. In order to elucidate the mechanism responsible for the pyroelectric behaviour of hemicyanine LB films, a series of FTIR absorption and SHG experiments were performed.

The orientation angle of the transition moments of the major bands were calculated by infrared linear and UV-visible absorption dichroism^[15-17]. The temperature dependence of the orientation angle of the hydrocarbon chain and chromophore for hemicyanine molecules in the LB films are shown in Fig. 4. For the chromophore of hemicyanine, the orientation angle is almost constant in the temperature range from 16 to 72 °C. While that for the hydrocarbon chain axes are almost constant up to about 45 °C and begins to change upon further heating. This is just a characterization of the first-order phase transition. It should be noticed that this temperature (45 °C) at which the orientation angle starts to change for the hydrocarbon chain axes is in good agreement with the above-mentioned temperature at which the pyroelectric coefficient starts to increase for the same films (Fig. 3). Thus, the pyroelectricity in this film can be ascribed preliminary to the structure modification of the polar head groups (molecular volume due to thermal expansion) and/or to the change in the molecular orientation^[12,17,18]. The other evidence for a phase transition is obtained from the peak position shift (from 2917 to 2926 cm^{-1} , from 2850 to 2855 cm^{-1}) of infrared transmission spectra in the same sample.

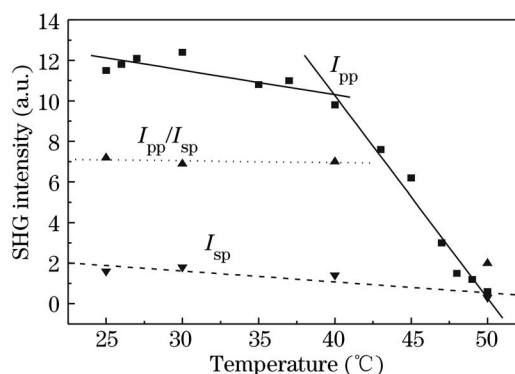


Fig. 5. Temperature dependence of SHG signs for DAEP in the LB multilayers.

On the other hand, our measured SHG intensities I_{pp} and I_{sp} from DAEP in the LB multilayers versus temperature are shown in Fig. 5. We found that the ratio I_{pp}/I_{sp} kept almost constant up to about 40 °C and reduced rapidly with further increasing temperature. It was again suggested that the SHG intensity reduction of I_{pp}/I_{sp} could originate from the deterioration of the film framework (the first-order phase transition) and the phenomenon resulted in the change of spontaneous polarization P with temperature.

In summary, the Z-type LB films of hemicyanine dye possessed the required noncentrosymmetry for the observation of the pyroelectric effect. The pyroelectric coefficient obtained for a 66-monolayer sample is $12 \mu\text{C}\cdot\text{m}^{-2}\cdot\text{K}^{-1}$ at room temperature. The pyroelectricity observed can be ascribed to the structure modification of the polar head groups and the deterioration of the film framework (the first-order phase transition) resulted in the change of spontaneous polarization P with temperature. The organic LB film materials have potential application to infrared pyroelectric heat detector.

This work was supported by the National Natural Science Foundation of China (No. 19704004, 10274014, 60378035), the Oversea Student Foundation of the Ministry of Education of China, "Shu Guang" Project of Shanghai Municipal Education Commission and Shanghai Education Development Foundation, and the Opening Topic supported by the National Laboratory for Infrared Physics of Chinese Academy of Science. S. Ma's email address is shma@fudan.edu.cn.

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