

A study of pyroelectric and dielectric properties of alternate layer fluorodeconoylmonoitaconate Langmuir–Blodgett films

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Abstract

The pyroelectric effect of ¹H, 1H₁, 2H₁, 2H- per fluorodeconoylmonoitaconate monomer/eicosylamine and ¹H, 1H₁, 2H₁, 2H- per fluorodeconoylmonoitaconate polymer/eicosylamine alternate layer LB films has been studied in this work. The quasi-static method has been employed to measure the pyroelectric coefficients, dielectric constant and dielectric loss of these assemblies. Relatively high (for LB films) pyroelectric coefficients of 4.9 μC m⁻² K⁻¹ for the monomer/amine and 3.9 μC m⁻² K⁻¹ for the polymer/amine have been obtained. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The pyroelectric effect [1] is the temperature-dependent spontaneous electric polarization within a material possessing non-centrosymmetric structure. It is well known that pyroelectric Langmuir–Blodgett (LB) films generate an electrical current whenever their ambient temperature changes [2]. In this work, we will discuss the origin of pyroelectricity for ¹H, 1H₁, 2H₁, 2H- per fluorodeconoylmonoitaconate monomer/eicosylamine and ¹H, 1H₁, 2H₁, 2H- per fluorodeconoyl-

monoitaconate polymer/eicosylamine alternate layer LB films. Fig. 1 shows the structures of the three materials used to fabricate alternate layer acid/amine LB films.

Previous work has shown that a tilting mechanism [3] and proton transfer [4] between carboxylic acid and amine head groups play an important role in the pyroelectric effect. These materials are very interesting because (i) the Van der Waals forces between adjacent chains are much weaker in fluorocarbons compared to hydrocarbons and the corresponding freedom of motion may contribute to the pyroelectric effect, (ii) the carbon–fluorine bond is very polar and could contribute to the spontaneous polarisation, and (iii) acid/amine interactions between head

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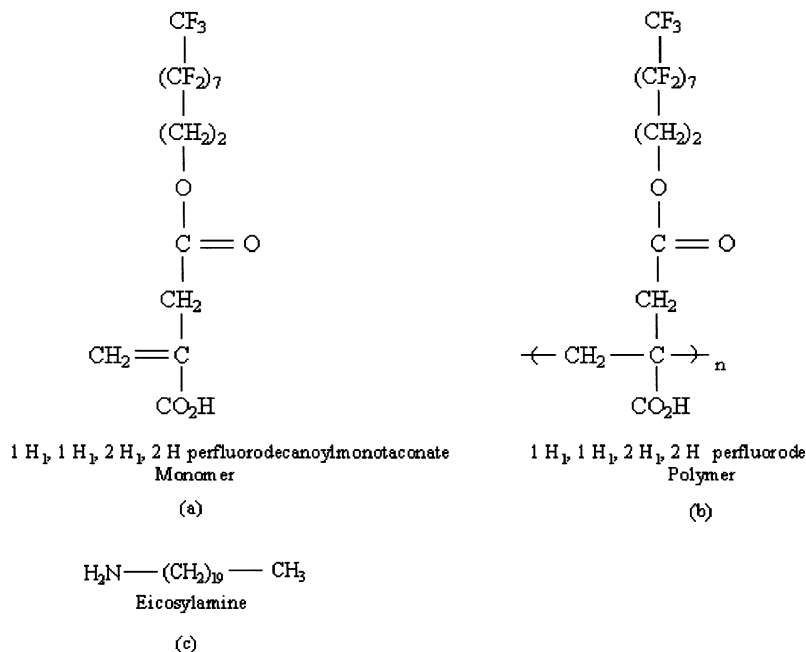


Fig. 1. The structure of the materials (a) monomer (b) polymer and (c) amine.

groups may increase the pyroelectric activity of these films.

2. Experimental

Monomer, polymer and amine were each dissolved in chloroform using approximately 0.7, 0.4, 0.5 mg ml⁻¹ concentrations, respectively. These solutions were spread onto an ultra-pure water (Elga UHP system) subphase contained within a constant perimeter, single compartment Langmuir trough. The water subphase has pH 5.9 and solutions are spread at room temperature. After evaporation of the solvent, each monolayer was compressed at a rate of approximately 0.7% s⁻¹ and the surface pressure was monitored using the well-known Wilhelmy plate method. The surface pressure against surface area was plotted as a function of the area enclosed using an *x-y* chart recorder. This procedure was repeated for each material to yield their surface pressure–area (*Π-A*) isotherm graphs.

Monomer, polymer and amine monolayers at

the water surface were transferred onto aluminised glass substrates using an alternate layer Langmuir–Blodgett trough at a pressure 22.5 mN m⁻¹ for each material. Monomer or polymer was deposited as the first layer when the substrate was withdrawn from the first compartment before depositing amine as the second layer when the substrate was inserted into the second compartment. The upstroke deposition rate for monomer and

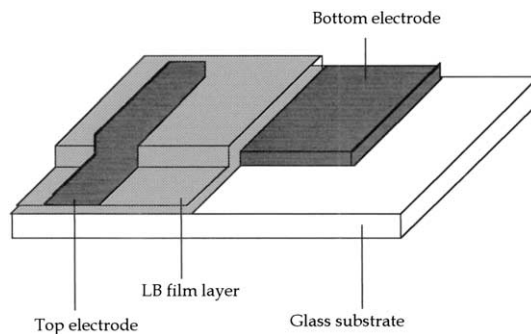


Fig. 2. A schematic diagram of the pyroelectric device structure.

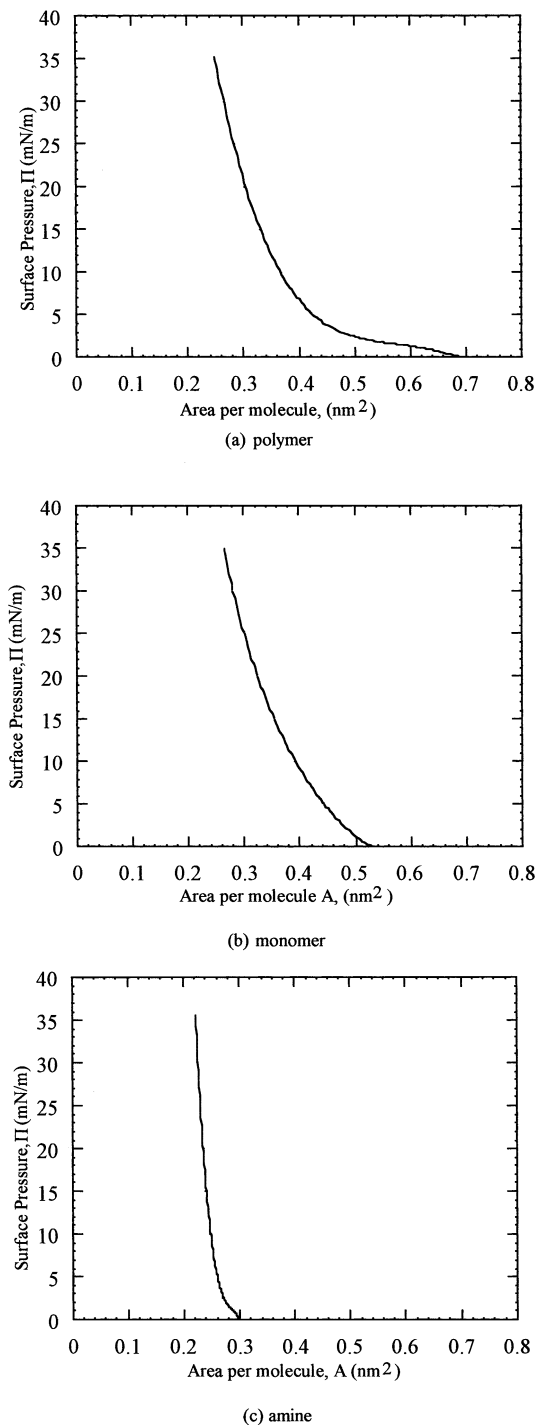


Fig. 3. Isotherm graphs of (a) polymer, (b) monomer and (c) amine.

polymer was 25 mm min^{-1} and the downstroke deposition speed for amine was 100 mm min^{-1} . The resulting monomer/amine and polymer/amine alternate layer LB films were assessed using the quasi-static pyroelectric technique and a dielectric bridge.

A schematic diagram of the pyroelectric device structure with the top and bottom electrodes (50 nm thick) is shown in Fig. 2. The pyroelectric activity was measured using a quasi-static technique described in the literature [5]. In this technique, the pyroelectric sample was heated and cooled by a non-radiative source in a controlled manner facilitating a small temperature change ($\pm 1 \text{ K}$) using a Peltier heating device. A Keithley 614 electrometer was used to measure the resulting current that is generated by the pyroelectric sample between two electrodes. The peak-to-peak pyroelectric, I_{pp} , current produced is related to the change in temperature by the relation:

$$I_{pp} = \Gamma A \frac{dT}{dt} \quad (1)$$

where Γ is the pyroelectric coefficient, A is the area of overlap of the upper and lower electrodes and dT/dt is the temporal rate of change of temperature. Therefore, with knowledge of the values of A and dT/dt , a measurement of the pyroelectric current allows the pyroelectric coefficient to be attained. In practice a triangular temperature profile (produced by sequentially heating and cooling the sample in a linear ramp fashion) imposed upon the sample produces a square wave current output whose peak-to-peak value can easily be obtained.

In this experiment, pyroelectric coefficients of monomer/amine and polymer/amine alternate layer LB films were obtained over the temperature range $18\text{--}38 \text{ }^\circ\text{C}$.

The dielectric properties of monomer/amine and polymer/amine alternate layer LB films were investigated by measuring the capacitance and loss tangent of such films using a Philips Model PM 6304 RCL meter. The dielectric constant (relative permittivity) and dielectric loss were obtained at room temperature. The values of the capacitance for polymer/amine LB film over the thickness range from 9 to 31 monolayers was measured at the operation frequency 600 Hz.

3. Results and discussion

Fig. 3 shows the isotherm graphs of (a) polymer, (b) monomer and (c) amine, respectively. An area per monomer unit for the polymer (a) is found to be $\sim 0.37 \text{ nm}^2$. This value is significantly larger than the 0.21 nm^2 exhibited by similar monomer materials such as fatty acids. The larger value is attributed to the bulky coupling side-group between monomer units and the tendency for fluorinated chains to repel. A very similar area per repeat unit is found for the monomer analogue as expected. It can be seen that the onset of surface pressure occurs at higher area per monomer unit in the case of the polymer compared to that of the monomer. This is interpreted as the gradual alignment of polymer chains compared to the more sudden transition from liquid to quasi-solid phases in the case of the monomer. The area per molecule for the fatty amine is $\sim 0.25 \text{ nm}^2$; this isotherm shows a very abrupt liquid–solid transition indicative of a rigid material on the water subphase.

The pyroelectric coefficient of 19 monolayer monomer/amine and polymer/amine LB films as a function of temperature is given in Fig. 4. Unfortunately, it is not possible to measure the pyroelectric coefficient of monomer/amine LB film

after 28°C because thermal current dominates our pyroelectric signals. In the polymer/amine LB films, the pyroelectric coefficient is measured between 18 and 38°C . It can be seen that the monomer/amine LB film has a larger pyroelectric response than the polymer/amine LB films. This is attributed to the fact that monomer molecules are not tethered together and are therefore more free to reorientate than the polymer molecules. This polymer tethering at the carboxylic end of the molecule restricts motion of the headgroup.

Fig. 5 shows a plot of capacitance and dielectric loss of the LB film device at room temperature. It is clear that the dielectric loss of monomer/amine and polymer/amine LB films is very low. The dielectric loss is an important parameter to obtain the figure of merit of the pyroelectric materials. A plot of reciprocal capacitance ($A\epsilon'\epsilon_0/C$) versus the number of transferred monolayers (N) is given in Fig. 6. An estimation of dielectric constants are made using the gradient of the plot in Fig. 6. The dielectric constants are obtained $\epsilon' = 2.8$ for such LB films (based estimated on a bilayer thickness estimate of 4.0 nm).

Table 1 shows the figure of merit, F , for each LB film assembly. F is a commonly used figure of merit defined as:

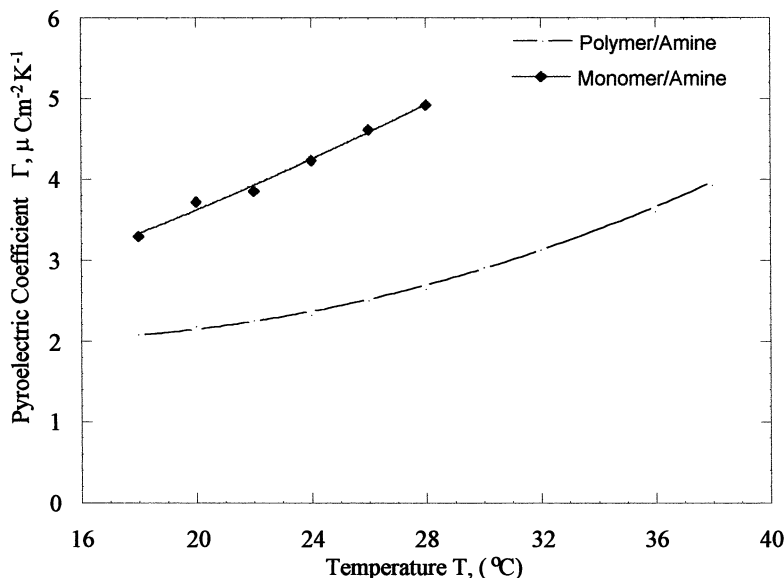


Fig. 4. The temperature dependent pyroelectric coefficients of monomer/amine and polymer/amine LB films.

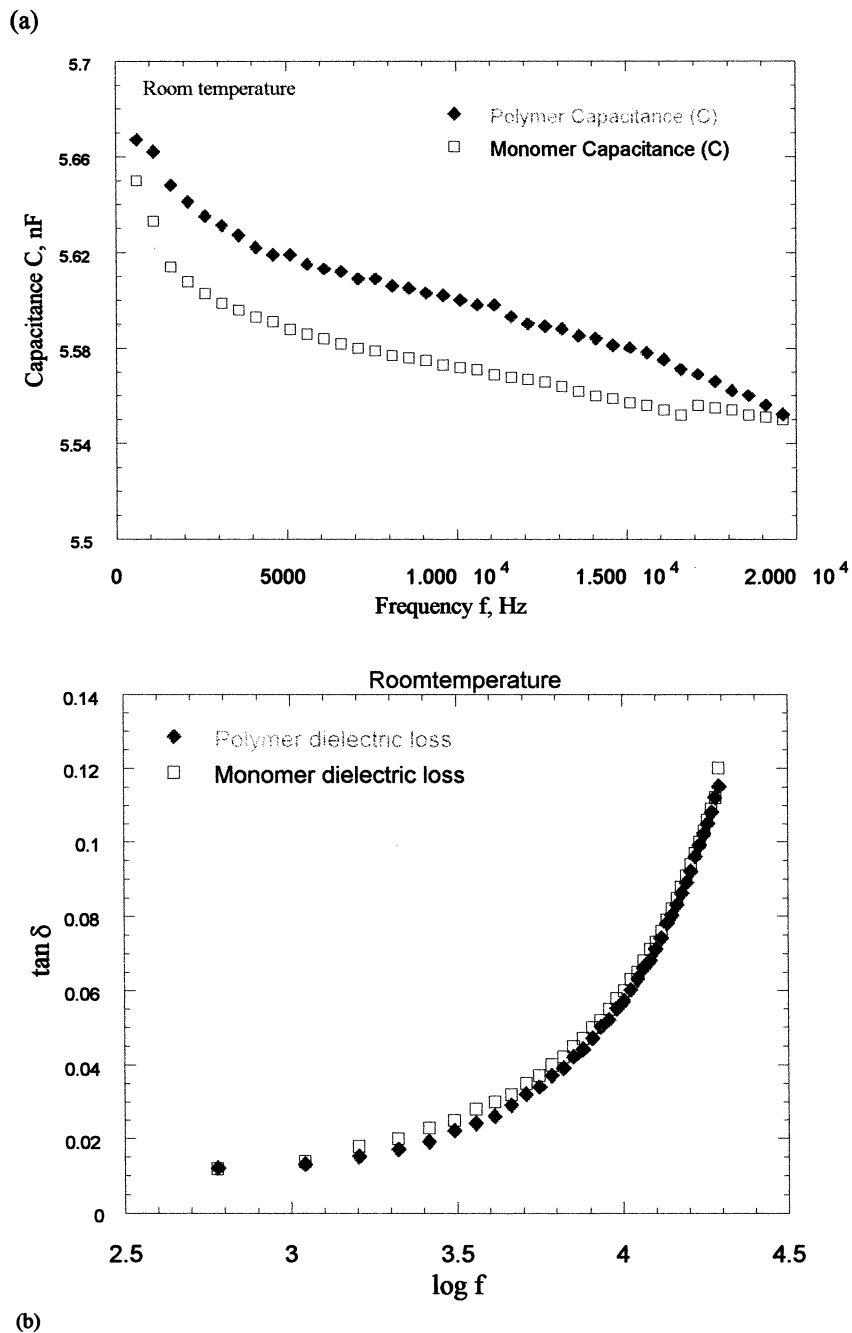


Fig. 5. A plot of (a) capacitance and (b) dielectric loss of monomer/amine and polymer/amine LB films.

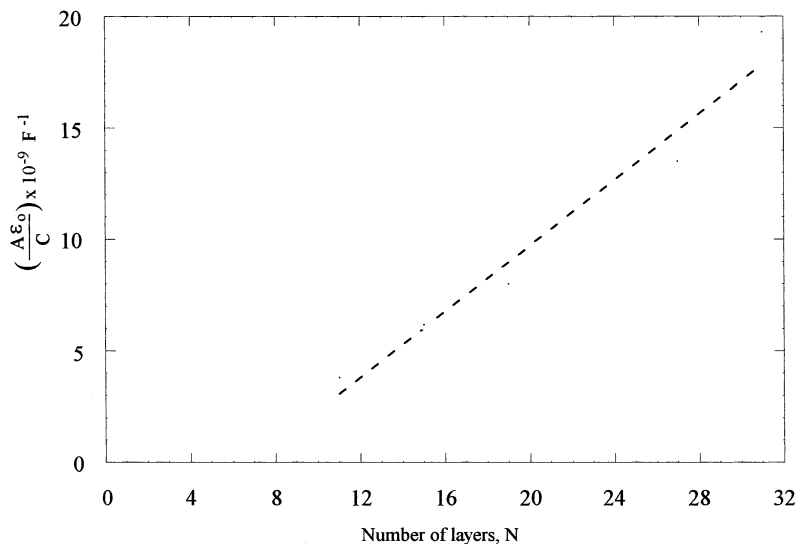


Fig. 6. A plot of reciprocal capacitance versus the number of transferred monolayers.

Table 1

The figure of merit for these LB films

Alternate layer LB films	Γ ($\mu\text{C m}^{-2} \text{K}^{-1}$)	ϵ'	$\tan \delta$	F ($\mu\text{C m}^{-2} \text{K}^{-1}$)
PS50/eicosylamine	9.6	2.6	0.011	56.7 (30 °C)
Monomer/eicosylamine	4.9	2.8	0.011	27.9 (28 °C)
Polymer/eicosylamine	3.9	2.8	0.012	21.3 (38 °C)

$$F = \Gamma / (\epsilon' \tan \delta)^{1/2} \quad (2)$$

The value for the monomer/amine LB film $F = 27.9 \mu\text{C m}^{-2} \text{K}^{-1}$ and polymer/amine LB film $F = 21.3 \mu\text{C m}^{-2} \text{K}^{-1}$ have been calculated using estimated dielectric constants and dielectric loss values. These values are compared to the F value for a polysiloxane (PS50) [6]/amine LB film reported in the literature which is the largest figure of merit for acid/amine LB films yet reported. The lower values obtained in this work suggest that tethering at the carboxylic acid headgroup end of the molecule actually hinders the pyroelectric process.

4. Summary

^1H , 1H_1 , 2H_1 , 2H - per fluorodeconoylmonoitaconate monomer/eicosylamine and ^1H , 1H_1 , 2H_1 , 2H - per fluorodeconoylmonoitaconate polymer/eicosylamine alternate layer LB assemblies have been

prepared using the alternate layer LB deposition technique. The pyroelectric activity has been investigated for these LB films. The alternate layer monomer/amine LB films give higher pyroelectric activity ($4.9 \mu\text{C m}^{-2} \text{K}^{-1}$) than the alternate layer polymer/amine LB film ($3.9 \mu\text{C m}^{-2} \text{K}^{-1}$). These coefficients are much higher than most of the other LB materials. In our future work, we will try to synthesize and study new materials which have different side groups in order to increase the pyroelectric detector performance. We will study the thin film structure using techniques such as infra-red spectroscopy, Raman spectroscopy and X-ray/neutron reflectometry.

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