

# A theoretical model for the pyroelectric response in Langmuir–Blodgett films

R. Çapan<sup>a,\*</sup>, İ. Başaran<sup>a</sup>, T.H. Richardson<sup>b</sup>, D. Lacey<sup>c</sup>

<sup>a</sup>Balikesir Üniversitesi Fen-Edebiyat Fakültesi Fizik Bölümü, Balikesir 10100, Turkey

<sup>b</sup>Department of Physics and Centre for Molecular Materials, University of Sheffield, Hounsfield Road, Sheffield S3 7HR UK

<sup>c</sup>School of Chemistry, University of Hull, Hull HU6 7RX, UK

## Abstract

Understanding the structure of pyroelectric materials is important to elucidate the nature of the temperature-dependent microscopic and macroscopic electric polarisation. Pyroelectric materials must have a non-centrosymmetric structure. Previously, researchers [C.A. Jones, PhD thesis, University of Durham, (1987); *J. Mater. Chem.* 1 (1991) 819; *Langmuir* 11 (1995) 4623] have reported the pyroelectric effect of non-centrosymmetric ultrathin LB films prepared using the alternate layer Langmuir–Blodgett (LB) deposition technique. They have proposed three main mechanisms to explain the origin of the pyroelectric activity, namely, tilting, proton transfer, and ionic processes.

Linear and cyclic polysiloxane materials with aliphatic and aromatic side groups have been studied in this work. These materials have been alternately deposited with eicosylamine to form the active pyroelectric material in metal–LB film–metal (MIM) devices, whose pyroelectric coefficients have been measured using a quasi-static measurement technique [W.H. Majid, Abd., PhD thesis, Univ. of Sheffield (1994); *Mater. Sci. Eng., C, Biomim. Mater., Sens. Syst.* 3 (1995) 197; *Thin Solid Films* 327–329 (1998) 369]. The relation between pyroelectric mechanism(s) and microscopic and macroscopic pyroelectric response for polysiloxane/eicosylamine alternate layer LB films will be explained in this work. Results indicate that the physical mechanism by which the pyroelectric activity arises in the LB films is critically dependent upon their structural quality, the ions within the multilayer arrangement and the molecular dipole moments of the molecules.

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## 1. Introduction

In recent years, organic materials [1–9] have been extensively studied as a pyroelectric material because of their easy synthesis, high quality, and low cost compared with other pyroelectric materials such as ceramics and single crystals. Pyroelectric materials that exhibit a temperature-dependent pyroelectric current must have a non-centrosymmetric structure. Langmuir–Blodgett (LB) film deposition technique is a suitable method to produce a pyroelectric device. In this technique, highly ordered monomolecular film at the air–water interface is transferred onto a solid substrate to build non-centrosymmetric multilayer assemblies. Three different types of LB film such as X-type, Z-

type and alternate layer (AL)-type LB films exhibit a temperature-dependent spontaneous electric polarisation. However X- and Z-type films suffer from poor structure and stability compared with AL-type LB films [10].

It has been well known that LB films are well-organised thin organic assemblies for pyroelectric applications. There have been several reports dealing with the pyroelectric effect of non-centrosymmetric LB films since the beginning of 1980s. The pyroelectric effect of X- and Z-type LB films of azobenzene-containing amphiphiles has been studied by Blinov [11,12]. Smith et al. [13–15] reported the detection of pyroelectric activity in non-centrosymmetric Langmuir–Blodgett multilayer films of structure ABABA... where A and B are monolayers of different materials. These works indicated that the pyroelectric effect in the alternate layer LB films involved a thermal expansion of the film and temperature-dependent tilting of molecules. AL-type LB films have been extensively investigated by Colbrook using 22-tricosenoic acid, 1-docosylamine, 4-octadecylbenzoic acid, 4-tetradecyloniline [10,16], and organo-ruthenium com-

\* Corresponding author. Tel.: +90-266-249-33-58; fax: +90-266-249-33-60.

E-mail addresses: rcapan@balikesir.edu.tr (R. Çapan), ibasaran@balikesir.edu.tr (İ. Başaran).

plexes [17,18]. Poulter et al. [19] observed the pyroelectric coefficient  $1.1 \mu\text{C m}^{-2} \text{K}^{-1}$  in the AL-type LB films consisting of the ruthenium complexes and behenic acid derivatives. Kamata studied the relationship between pyroelectricity and molecular orientation of 5-(*p*-dodecyloxyphenyl) pyraxine-2-carboxylic acid and deuterated stearic acid alternate layer LB films [7], pyraxine derivatives and stearic acid alternate layer LB films [20]. He measured the pyroelectric coefficient  $1.8 \mu\text{C m}^{-2} \text{K}^{-1}$  at  $43^\circ\text{C}$ .

The pyroelectric effect in polysiloxane/eicosylamine AL-type LB films is firstly reported in 1992 [21,22]. The pyroelectric coefficient of these films is measured to be approximately  $2 \mu\text{C m}^{-2} \text{K}^{-1}$ . The pyroelectric activity of polysiloxane/eicosylamine AL-type LB films is improved from 2 to  $15 \mu\text{C m}^{-2} \text{K}^{-1}$  using different polysiloxane backbone and side groups [23,24]. This is one of the largest static pyroelectric coefficients ever reported for an AL-type LB film assembly.

## 2. Experimental

### 2.1. Materials

Aliphatic and aromatic pendant side chains containing carboxylic acid head groups is chosen for substitution onto several different polymer backbones in order to study the pyroelectric mechanism(s) between acid and amine interactions when they are codeposited with eicosylamine. It is well known that the acid–amine interaction between head groups leads to pyroelectric effect. Fig. 1 shows a schematic diagram of materials used in this work. The number of side chains on each polysiloxane depends on the fraction of silicon–hydrogen bonds along the performed polymer backbone. More details of these materials are given in literature [25].

### 2.2. LB film preparation and pyroelectric measured system

The solvents used for preparing all polysiloxane solutions were a mixture of chloroform and 2-ethoxyl ethyl-

acetate (1:1 volume ratio). The typical concentration of the polysiloxane solutions were 0.2–0.3 mg/ml. Eicosylamine was dissolved in chloroform using approximately 0.5 mg/ml. Each polysiloxane investigated in this was codeposited with eicosylamine to form ABABA... AL-type LB film multilayers by using a two-compartment Langmuir trough. The deposition pressure for each polysiloxane and eicosylamine were used 22.5 mN/m. Transfer ratios for polysiloxane and eicosylamine monolayers were close to unity ( $>0.9$ ) in all cases. All monolayers of polysiloxane and eicosylamine were deposited aluminised glass substrate to fabricate Metal–LB film–Metal (MIM) device. Aluminium was used as bottom and top electrodes of the device. In this work, these electrodes were thermally evaporated and the thickness of bottom and top electrodes was 50 nm. This device was placed in an evacuated pyroelectric test chamber and the pyroelectric activity of such LB films was measured using the quasi-static measurement technique. The device was heated by a nonradiative source in a controlled manner so that the temperature will vary about a constant ambient by a very small amount, typically about 1 K. The temperature gradients were 0.01 K/s. The pyroelectric coefficients were calculated using Eq. (1) after measuring the square wave pyroelectric current profile and the triangular wave profiles taken from quasi-static measurement system. Eq. (1) is given by:

$$I = \Gamma A \left[ \frac{dT}{dt} \right] \quad (1)$$

where  $I$  is the pyroelectric current,  $A$  is the electrode area,  $(dT/dt)$  is the rate of change of temperature, and  $\Gamma$  is the pyroelectric coefficient. All pyroelectric coefficients of polysiloxane/eicosylamine alternate layer LB films will be detailed in the Result and Discussion section.

### 2.3. Result and discussion

A group of cyclic and linear polysiloxanes substituted with either aliphatic and aromatic acid side chain has been

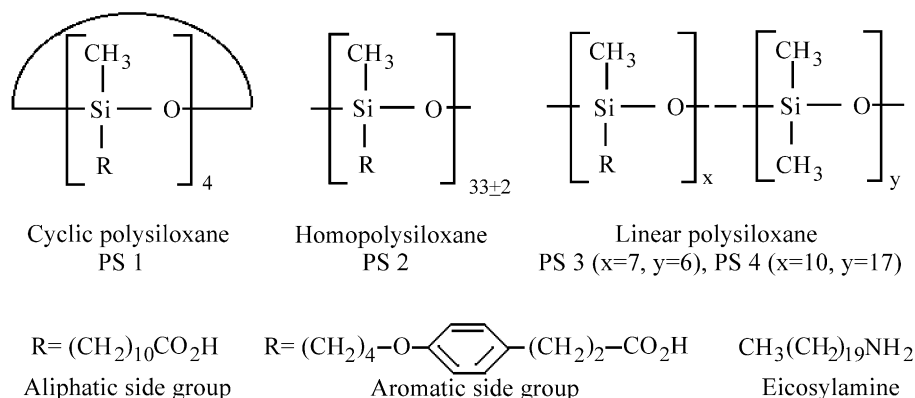


Fig. 1. The chemical structure of materials.

used to fabricate polysiloxane/eicosylamine AL-type LB films. The pyroelectric coefficients of such LB films using aliphatic and aromatic side groups is given in Fig. 2. The temperature range is chosen between 15 and 30 °C. It is very clear that the highest pyroelectric coefficients are exhibited by aromatic substituted side group. The pyroelectric coefficients for all polysiloxanes substituted with aromatic side group are nearly four times higher than the polysiloxanes substituted with aliphatic side chains. The lengths of side chain between aliphatic and aromatic groups are similar although their dipole moment is clearly different. The incorporation of a phenoxy ring into the pendant side group has increased the pyroelectric activity in polysiloxane/eicosylamine AL-type LB films, and the magnitude of

dipole moment in the side groups is increased because of the inclusion of phenoxy ring. These results show that the original objective of improving the pyroelectric activity by the inclusion of the additional molecular dipole within the side chain groups has been achieved.

Many researchers in this field have suggested that a dipole tilting and a proton transfer mechanisms exhibit a temperature-dependent pyroelectric activity. These two mechanisms depend on the free volume and the density of acid–amine pairs. In this work, these two main mechanisms have been studied to create the free volume due to the unsubstituted silicon and to create the density of acid–amine pair using polysiloxane and eicosylamine head groups. The density of acid/amine pairs are calculated using

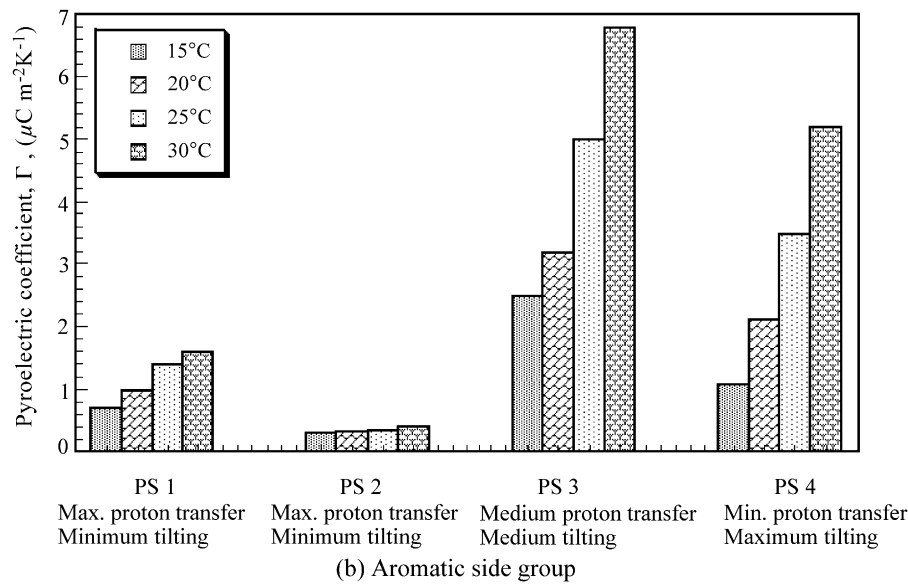
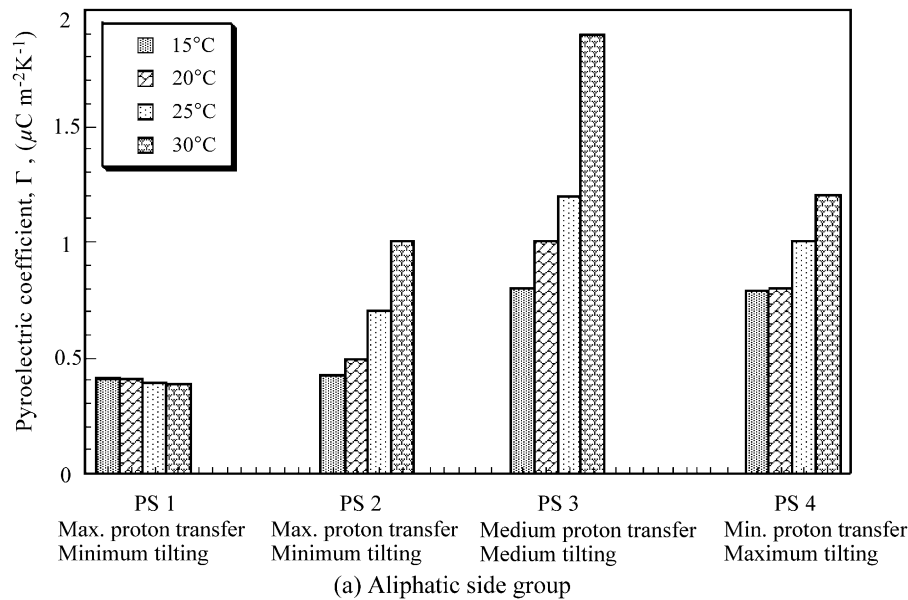


Fig. 2. The pyroelectric coefficients of PS 2, PS 3 and PS 4/eicosylamine LB films.

Table 1  
The density of acid/amine pairs with aliphatic and aromatic side groups

Materials	Acid/amine density ( $\text{nm}^{-2}$ )	
	Aliphatic	Aromatic
PS 1	$4.35 \pm 0.01$	$3.33 \pm 0.01$
PS 2	$4.54 \pm 0.01$	$7.14 \pm 0.01$
PS 3	$2.34 \pm 0.01$	$3.85 \pm 0.01$
PS 4	$1.68 \pm 0.01$	$2.65 \pm 0.01$

the number of acid groups per molecule and area per molecule; they are summarised in Table 1. PS 1 and PS 2 have the highest degree of the side chain substitution. However, the experimental result for PS 1 with aromatic acid side chain exhibited a low acid/amine density. They have the largest density of acid–amine pairs and the smallest free volume created from unsubstituted silicons. PS 3 has the intermediate degree of the side-chain group. This means that it has the intermediate free volume and the intermediate density of acid–amine pairs. PS 4 has the largest free volume and the lowest density of acid–amine pairs.

It can be seen from Fig. 2 that material PS 3 with both side groups has larger pyroelectric coefficients than the other materials. These results indicate that dipole tilting and proton transfer mechanisms lead a temperature-dependent pyroelectric activity, and there is a trade-off between the two mechanisms. Also, the pyroelectric effect strongly depended on the chemical structure of the materials.

In order to study the incorporation of ions within alternate layer LB films, PS 3 is selected to produce 21

monolayers of PS 3/eicosylamine AL-type LB films using a cadmium chloride subphase on a 50-nm-thick aluminised glass substrate. X-ray photoelectron spectroscopy (XPS) results [24] confirm that cadmium ion is bound between carboxylic head groups, and chloride ion interacts with the protonated amine head groups. The pyroelectric coefficient of 21 monolayers of PS 3/eicosylamine AL-type LB films is given in Fig. 3. It is very clear that the incorporation of ions within AL-type PS 3/eicosylamine LB film assemblies leads to a significant improvement of pyroelectric effect. These results suggested that a temperature-dependent ionic mechanism plays an important role in the pyroelectricity.

The total macroscopic pyroelectric effect of PS 3/eicosylamine AL-type LB films may be created from sum of primary and secondary pyroelectric effects. The total macroscopic pyroelectric effect can be defined as:

$$\Gamma_{\text{total}} = \Gamma_{\text{primary}} + \Gamma_{\text{secondary}} \quad (2)$$

where  $\Gamma_{\text{primary}}$  is the primary pyroelectric effect, and  $\Gamma_{\text{secondary}}$  is the secondary pyroelectric effect.

It is well known that the primary pyroelectric effect is a temperature-dependent spontaneous polarisation. The secondary pyroelectric effect arises from any mechanical stress which is the result of thermal expansion. Majid [4] has studied the secondary pyroelectric effect using PS 3/eicosylamine AL-type LB films. The results showed that the pyroelectric effect of this LB film does not depend largely on the secondary pyroelectric effect. The pyroelectric effect of the PS 3/eicosylamine AL-type LB films arises mainly

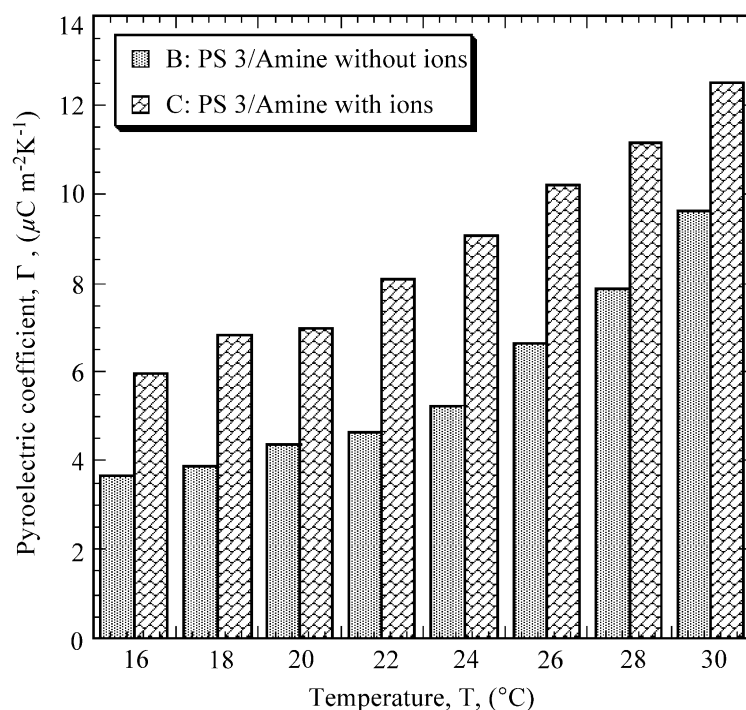


Fig. 3. The pyroelectric coefficient of PS 3/eicosylamine LB films with and without ions.

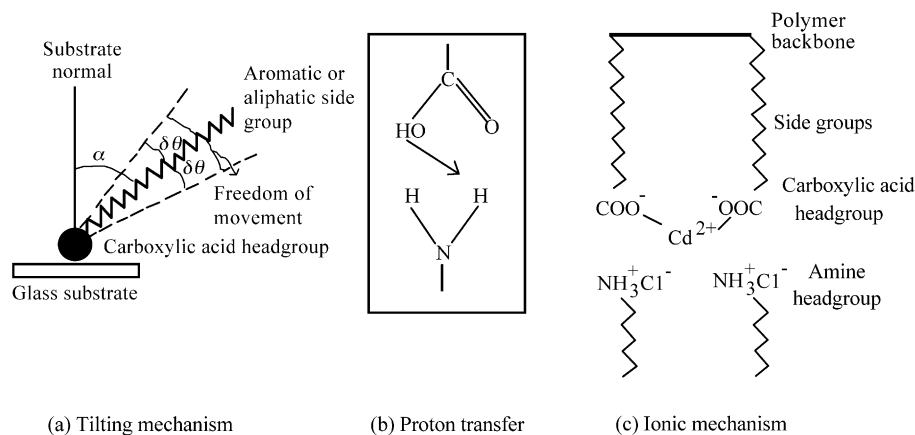


Fig. 4. A schematic diagram of three main mechanisms for the pyroelectric activity.

from the primary pyroelectric effect which can be defined as:

$$\Gamma_{\text{primary}} = \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 \quad (3)$$

$\Gamma_1$  depends on the dipole moment of the nature of the materials.  $\Gamma_2$  is created from the free volume in the film structure which is known as tilting mechanism.  $\Gamma_3$  comes from proton transfer between acid and amine head groups.  $\Gamma_4$  is exhibited from ionic mechanism which depends on the ions within the LB films. These four terms exhibit a temperature-dependent pyroelectric activity in the polysiloxane/eicosylamine AL-type LB films. The pyroelectric activity in our LB films is critically dependent upon their structural quality of the total molecular dipole moment, the degree of acid/amine pairs and the ions inside the LB film structure. Fig. 4 shows a schematic diagram of three main mechanisms. They lead the pyroelectric activity.

### 3. Summary

Pyroelectric effect in the AL-type LB films using polysiloxane and eicosylamine materials has been studied and the relationship between pyroelectricity and molecular structure for these LB films is discussed in this work. This work showed that the pyroelectric effect in AL-type polysiloxane/eicosylamine LB films can be improved due to a structural modification of the materials; for example, the addition of phenoxy ring into the side chain increases the pyroelectric activity due to an increase in dipole moment. Polysiloxane/eicosylamine AL-type LB film with aromatic acid chain always gives a larger activity than the LB film with aliphatic acid chain. The primary pyroelectric effect in the polysiloxane/eicosylamine AL-type LB films is dominant, and four main terms are involved in the pyroelectric process. Pyroelectric effect in AL-type LB films is strongly dependent on the free movement of molecules, degree of acid/amine pairs and ions within the film structure.

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