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Pyroelectric superlattices based on copolysiloxane/calix[8]arene alternate layer LB films

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Abstract

The pyroelectric effect in alternate layer LB superlattices incorporating interacting lamellae of carboxyl and amino moieties has been investigated. Three distinct systems have been studied, namely (a) a copolysiloxane carboxylic acid/aliphatic amine alternate multilayer, (b) a calix[8]arene carboxylic acid/calix[8]arene amine alternate multilayer, and (c) a hybrid system consisting of a copolysiloxane carboxylic acid/calix[8]arene amine multilayer. In all superlattices there occurs proton transfer between acid and amine moieties leading to a temperature-dependent electric polarisation which is reinforced by added contributions from dipolar reorientation effects. This paper describes how the pyroelectric coefficient can be enhanced by utilising a hybrid alternate layer LB film superlattice containing a 50:50 copolysiloxane substituted with polar aromatic side-chains terminated with carboxyl groups, which is co-deposited with a calix[8]arene molecular basket substituted with primary amine groups. The pyroelectric activity of the copolysiloxane acid/calix[8]arene amine system is substantially higher and stable over a wider temperature range than either of the other two superlattices, giving a pyroelectric coefficient of 10.2 μC m^{-2} K^{-1} at 25°C. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pyroelectric effect; Amino moieties; LB film

1. Introduction

Pyroelectric materials exhibit a temperature-dependent spontaneous polarisation and include the well-known perovskites [1] (e.g., barium titanate) and certain organic materials including poly(vinylidenedifluoride) (PVDF) [2]. Electroded pyroelectric thin films generate an electrical current when their electrodes are connected via a suitable ammeter or electrometer, provided their temperature is in the process of changing. Thus, an active material acts as a current source when it is heated or cooled but cannot supply current if held at constant temperature. Although the most sensitive pyroelectric materials are inorganic ceramics, much interest has been directed towards organic competitors such as PVDF. In both cases, electrical poling is usually necessary after preparing thin films of these materials in order to induce pyroelectric activity. Conse-

quently, considerable effort has recently been devoted to the study of alternate layer Langmuir–Blodgett assemblies which are inherently polarised and require no post-deposition poling treatments.

Our previous research effort towards the optimisation of pyroelectric LB films has focused on two distinct molecular architectures, namely (i) a copolysiloxane acid/aliphatic amine alternate layer LB film assembly [3] and (ii) a calix[8]arene acid/calix[8]arene amine alternate layer system [4]. In both these systems, there exists interacting lamellae of acid and amine moieties. Proton transfer between the acid and amine groups leads to a modification of the electric polarisation within the superlattice and subsequently to pyroelectric behaviour, since the relative population of protonated acid/amine pairs is temperature-dependent. This process is schematically shown in Fig. 1. Additionally, there are further contributions to the macroscopic polarisation which arise due to the dipolar nature of the substituted phenyl rings in the copolysiloxane and calixarene molecules. Orientational changes in the average alignment of these dipoles also lead to a contribution to the overall pyroelectric activity. By optimising both the condi-
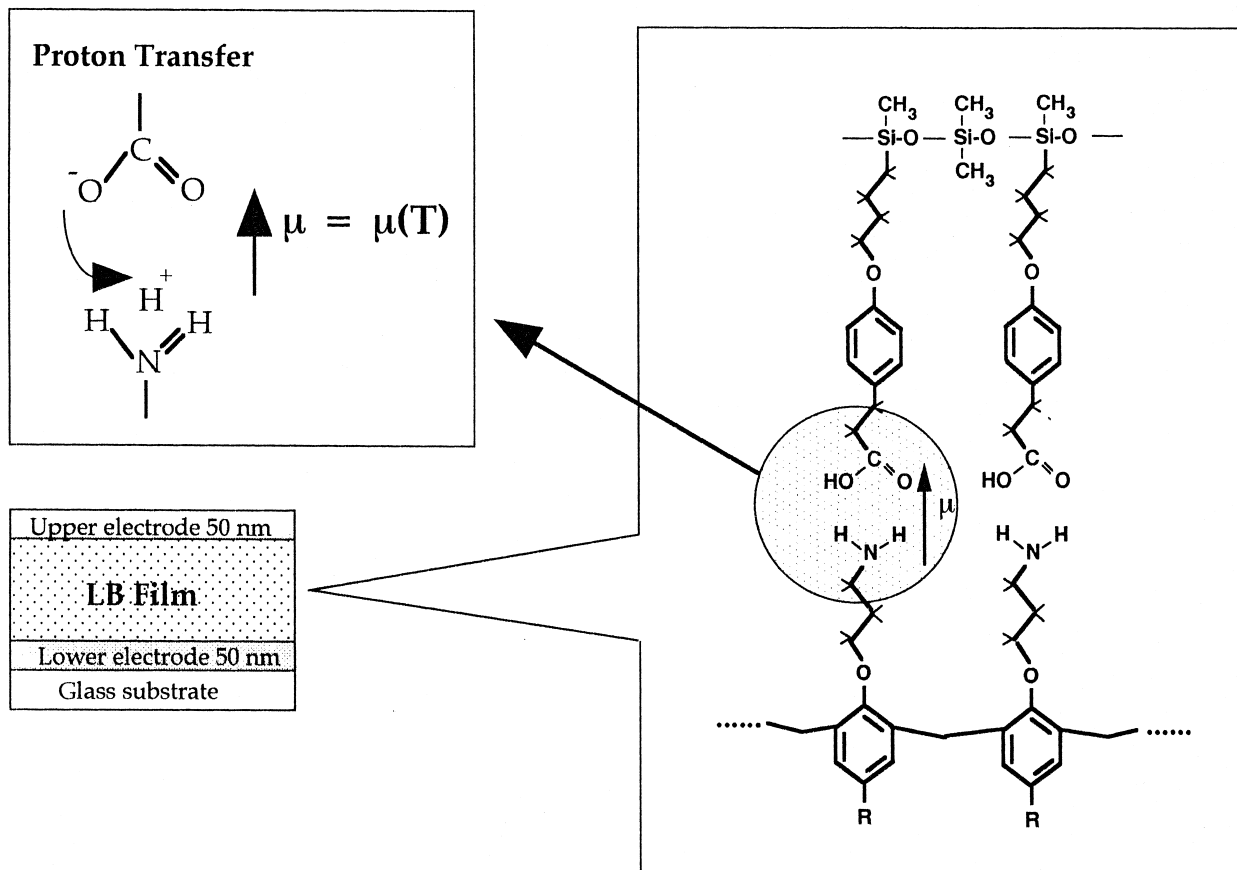
Fig. 1. The pyroelectric effect in an alternating acid/amine LB superlattice.

tions for LB assembly and the device geometry, we have been able to produce, from both copolysiloxane and cal-

ixarene systems, pyroelectric coefficients up to 15 μC m^{-2} K^{-1} at 25°C which is currently the highest value reported
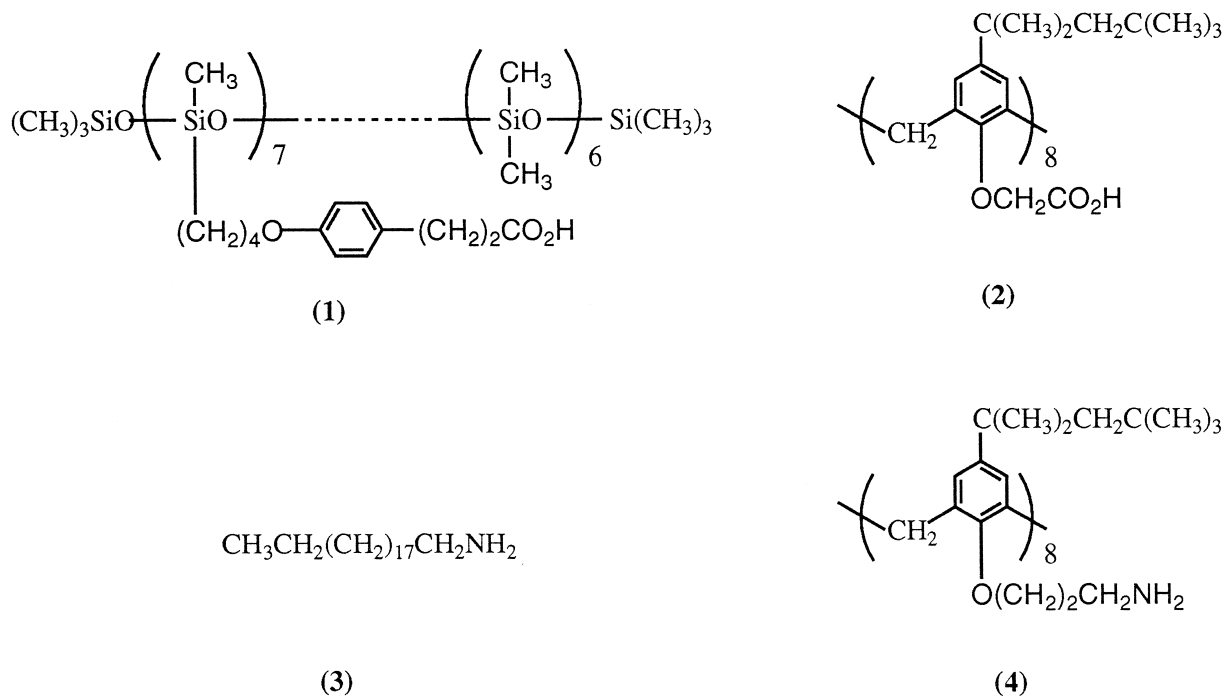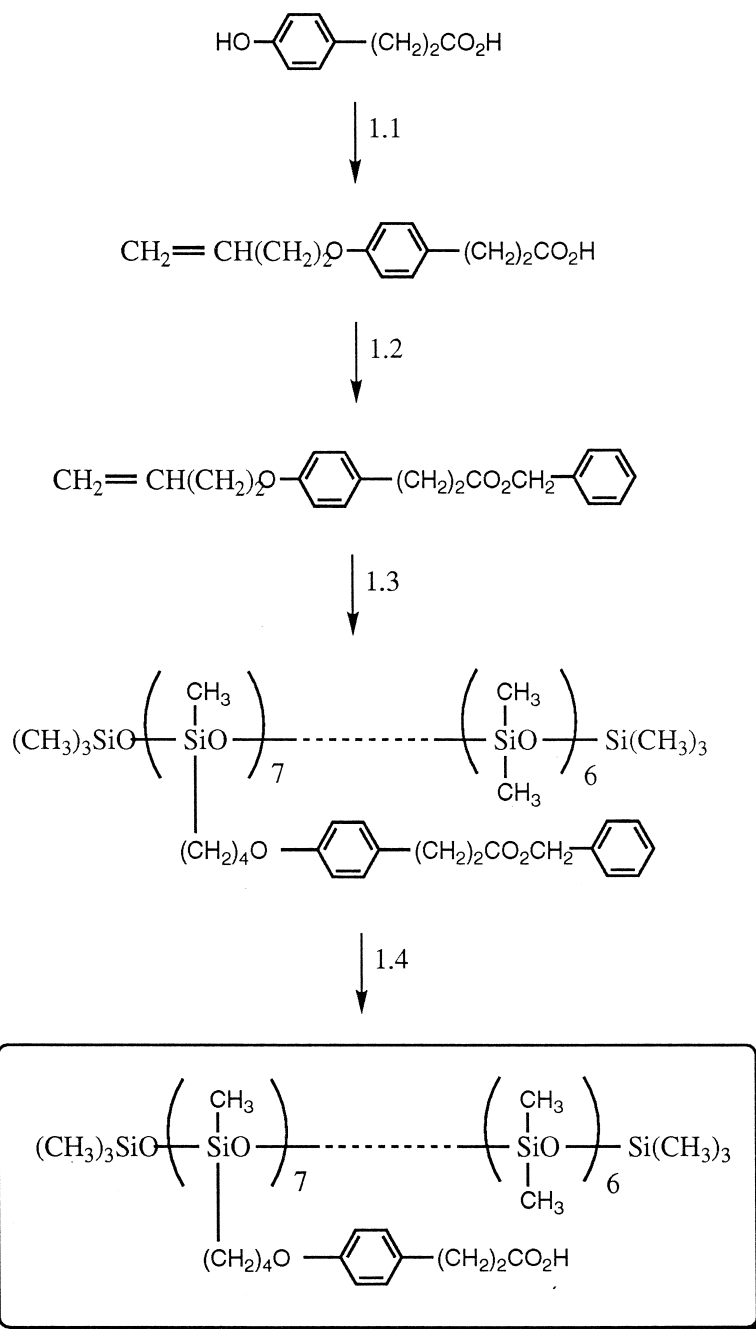

CH$_3$CH$_2$(CH$_2$)$_{17}$CH$_2$NH$_2$

(3)

Fig. 2. Structure of carboxylic acids and amines used to prepare alternating acid/amine LB superlattices.

$$HO-\langle\bigcirc\rangle-(CH_2)_2CO_2H$$

↓ 1.1

$$CH_2\!=\!CH(CH_2)_2O-\langle\bigcirc\rangle-(CH_2)_2CO_2H$$

↓ 1.2

$$CH_2\!=\!CH(CH_2)_2O-\langle\bigcirc\rangle-(CH_2)_2CO_2CH_2-\langle\bigcirc\rangle$$

↓ 1.3

$$(CH_3)_3SiO\left(\begin{array}{c}CH_3\\|\\SiO\\|\end{array}\right)_7 - - - - - -\left(\begin{array}{c}CH_3\\|\\SiO\\|\\CH_3\end{array}\right)_6 Si(CH_3)_3$$

$$(CH_2)_4O-\langle\bigcirc\rangle-(CH_2)_2CO_2CH_2-\langle\bigcirc\rangle$$

↓ 1.4

$$(CH_3)_3SiO\left(\begin{array}{c}CH_3\\|\\SiO\\|\end{array}\right)_7 - - - - - -\left(\begin{array}{c}CH_3\\|\\SiO\\|\\CH_3\end{array}\right)_6 Si(CH_3)_3$$

$$(CH_2)_4O-\langle\bigcirc\rangle-(CH_2)_2CO_2H$$

1.1 (i) $CH_2\!=\!CH(CH_2)_2Br$, NaOH, CH_3OH, H_2O; (ii) HCl (aq)

1.2 $C_6H_5CH_2OH$, *N,N*-dicyclohexylcarbodiimide, 4-pyrrolinopyridine, CH_2Cl_2

1.3 PS 50, H_2PtCl_6, toluene

1.4 5% Pd / C, C_2H_5OH / $CH_3CO_2C_2H_5$, H_2

Scheme 1.

C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$

OH

↓ 2.1

C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$

(CH$_2$ ... OH)$_8$

2.2   2.4

C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$ C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$

(CH$_2$ ...)$_8$ (CH$_2$ ...)$_8$

O(CH$_2$)$_2$CH$_2$N (phthalimide)   OCH$_2$CO$_2$CH$_2$CH$_3$

↓ 2.3   ↓ 2.5

C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$ C(CH$_3$)$_2$CH$_2$C(CH$_3$)$_3$

(CH$_2$ ...)$_8$ (CH$_2$ ...)$_8$

O(CH$_2$)$_2$CH$_2$NH$_2$ OCH$_2$CO$_2$H

2.1 NaOH, CH$_2$O, p-xylene

2.2 3-bromopropyl phthalimide, K$_2$CO$_3$, KI, acetone

2.3 33% CH$_3$NH$_2$ / C$_2$H$_5$OH

2.4 ethyl bromoacetate, K$_2$CO$_3$, KI, acetone

2.5 NaOH, C$_2$H$_5$OH
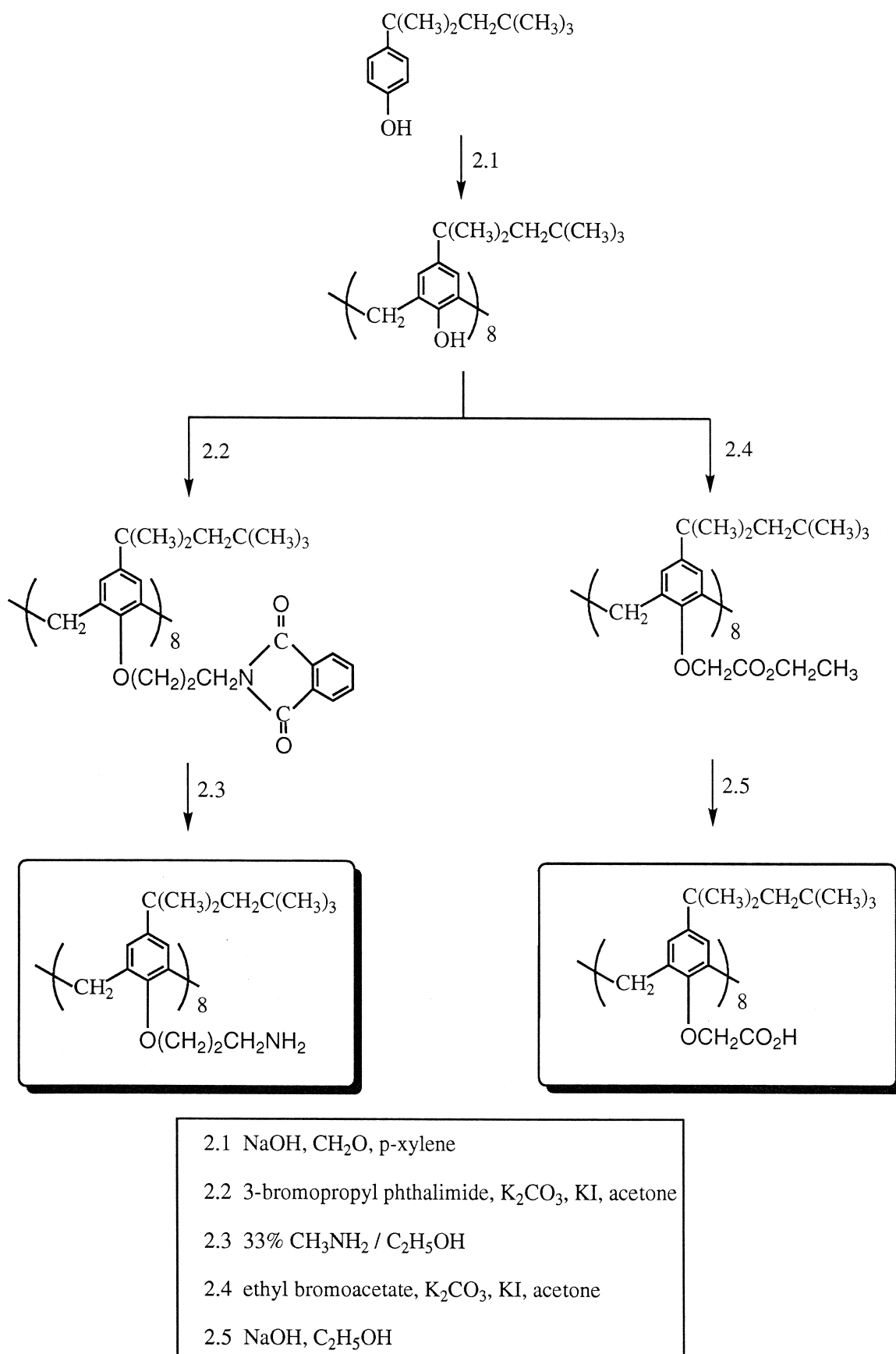
Scheme 2.

for an LB assembly measured by the reliable quasi-static technique.

2. Experimental

The structures of materials used in this investigation are shown in Fig. 2. The synthetic route to the copolysiloxane acid **1** is shown in Scheme 1, for the calix[8]arene acid **2** and amine **4** in Scheme 2 and for eicosylamine **3** in Scheme 3. All the compounds were prepared using known chemistry and the structure of the materials was confirmed by a combination of ^1H NMR, infra-red spectroscopy and mass spectrometry. The purity of the materials was checked by HPLC. For details of their preparation and purification, the reader is directed towards Refs. [3–7]. The Petrarch polysiloxane backbone was purchased from Fluorochem.

A single compartment Langmuir trough was used to measure surface pressure — area isotherms for the materials in Fig. 2. The isotherms (presented in our previous publications [3–7]) enabled cross-sectional areas per molecule (repeat unit) to be derived.

Alternate layer LB films of various combinations of the materials shown in Fig. 2 were prepared using an alternate layer Langmuir trough possessing a central fixed barrier accommodating a rotating drum to which was attached the substrate. The substrates used were glass plates coated with 50 nm of thermally evaporated aluminium. In all cases, the subphase was ultra-pure water (Elga System UHP), pH ~ 6.0 after stabilisation and the temperature was $\sim 20°C$. Upper aluminium electrodes (50 nm) were thermally evaporated on top of the deposited LB films at a very low rate ~ 0.1 nm s^{-1}. The pyroelectric test device configuration is shown in Fig. 1. In all cases, 13 layer superlattices were prepared (seven layers acid/six layers amine).

The pyroelectric coefficient ($\Gamma = dP/dT$; the rate of change of electric polarisation with respect to temperature) was measured using a quasi-static technique described in

detail elsewhere [7]. Briefly, however, the electroded sample was heated and cooled in a triangular wave fashion (amplitude $< 1°C$, frequency < 0.02 Hz) about a mean temperature which could be varied from 15 to 60°C. The electrodes were connected together via a sensitive electrometer (Keithley 614), the analogue output of which was fed into a computer (via an A–D converter) or a chart-recorder. The pyroelectric effect results in the generation of a current flow when the temperature changes and follows the relation:

$$i_{pp} = \Gamma A (dT/dt)_{tot} \qquad (1)$$

where i_{pp} is the peak-to-peak pyroelectric current variation, A is the overlap area of the metal electrodes and $(dT/dt)_{tot}$ is the total rate of change of temperature with respect to time.

The use of a triangular wave temperature profile facilitates the straight-forward determination of the pyroelectric coefficient, Γ, since the current response generated is a square-wave whose amplitude is proportional to Γ.

In this paper, we detail results from our preliminary investigation into a new acid/amine system based on a copolysiloxane incorporating a carboxylic acid moiety (structure **1** in Fig. 2) and a calix[8]arene amine (structure **4** in Fig. 2). These results are then compared to those found for our original two acid/amine systems, i.e., copolysiloxane acid/aliphatic amine LB assembly (structures **1** and **3** in Fig. 2 respectively) and calix[8]arene acid/calix[8]arene amine assembly (structures **2** and **4** in Fig. 2, respectively).

3. Results and discussion

Table 1 details the deposition conditions for each material investigated. Fig. 3 shows a plot of the peak-to-peak current vs. the total rate of change of temperature (heating rate plus cooling rate). The linear relationship confirms that the current produced is indeed pyroelectric in origin. The gradient of this graph can be used to estimate the pyroelectric coefficient, Γ. The inset to Fig. 3 depicts a typical current profile in response to the triangular wave temperature cycle stimulus.

Fig. 4 shows the temperature-dependence of the pyroelectric coefficient for the three superlattice architectures I, II and III. Superlattice I shows the strongest temperature dependence with nearly a three-fold increase in pyroelectric activity between 16 and 30°C. However, the temperature dependence of the pyroelectric activity profile has two distinct regions. Below 25°C, the temperature dependence of the pyroelectric activity is small and is very similar to that found for superlattices I and II. However, above 25°C, the pyroelectric coefficient for superlattice I increases dramatically with increase in temperature and at 30°C, the temperature beyond which the superlattice becomes unsta-

$$CH_3CH_2(CH_2)_{17}CH_2OH$$

$$\downarrow \text{3.1}$$

$$\boxed{CH_3CH_2(CH_2)_{17}CH_2NH_2}$$
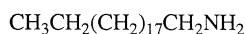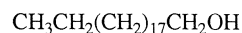
3.1 (i) triphenylphosphine, bromotrichloromethane, benzene; (ii) sodium azide, tetrabutylammonium bromide, DMF; (iii) triethylphosphite, benzene; (iv) HCl (aq); (v) NaOH

Scheme 3.

Table 1
Deposition conditions for superlattice architectures I, II and III

Alternate layer superlattice		Solvent	Deposition surface pressure, Π (mN/m)	Deposition rate, R (mm/min)
I	Copolysiloxane acid (**1**)	Ethyl acetate/chloroform 1:4	22.5	25
	Aliphatic amine (**3**)	Chloroform	22.5	100
II	Calix[8]arene acid (**2**)	Chloroform	25	25
	Calix[8]arene amine (**3**)	Chloroform	25	100
III	Copolysiloxane acid (**1**)	Ethyl acetate/chloroform 1:4	22.5	25
	Calix[8]arene amine (**3**)	Chloroform	25	100

ble, where superlattice I exhibits a pyroelectric coefficient of 9.2 μC m^{-2} K^{-1}. Conversely, the pyroelectric coefficient of the all-calixarene superlattice II exhibits little temperature dependence and is stable up to a temperature of around 45°C, where the superlattice exhibits a pyroelectric coefficient of 8.0 μC m^{-2} K^{-1}. Due to the temperature dependency profile found for superlattice I, below 25°C superlattice II has the higher pyroelectric activity but above 25°C their positions are reversed, up to a temperature of 30°C where superlattice I becomes unstable.

The most interesting feature of Fig. 4 is the fact that the pyroelectric coefficient for superlattice III is higher than that found for superlattices I and II over the whole temperature range investigated, 16–60°C. Below 25°C, the pyroelectric coefficient for superlattice III is larger by a factor of ~ 2 than either superlattice I or II and is stable up to a temperature of 60°C, where it exhibits a pyroelectric coef-

ficient 13.8 μC m^{-2} K^{-1}. The combination of the polymeric acid and the calixarene has produced a superior pyroelectric LB superlattice, both in terms of pyroelectric activity and stability.

An analysis of the area per molecule (or per repeat unit in the case of the copolysiloxane) measured from the Langmuir isotherms enables the surface (areal) density of acid/amine pairs to be estimated. Table 2 shows these values with the pyroelectric coefficients at 20°C. There is a correlation between Γ and the proximity to unity of the ratio of the surface densities of carboxyl and amino groups. The maximum contribution of the proton transfer mechanism to the measured pyroelectric activity is expected to occur when equal numbers of carboxyl and amino groups interact at the interfaces between adjacent acid and amine monolayers within the superlattice. However, as we have shown in previous work on copolysiloxanes [7], an addi-
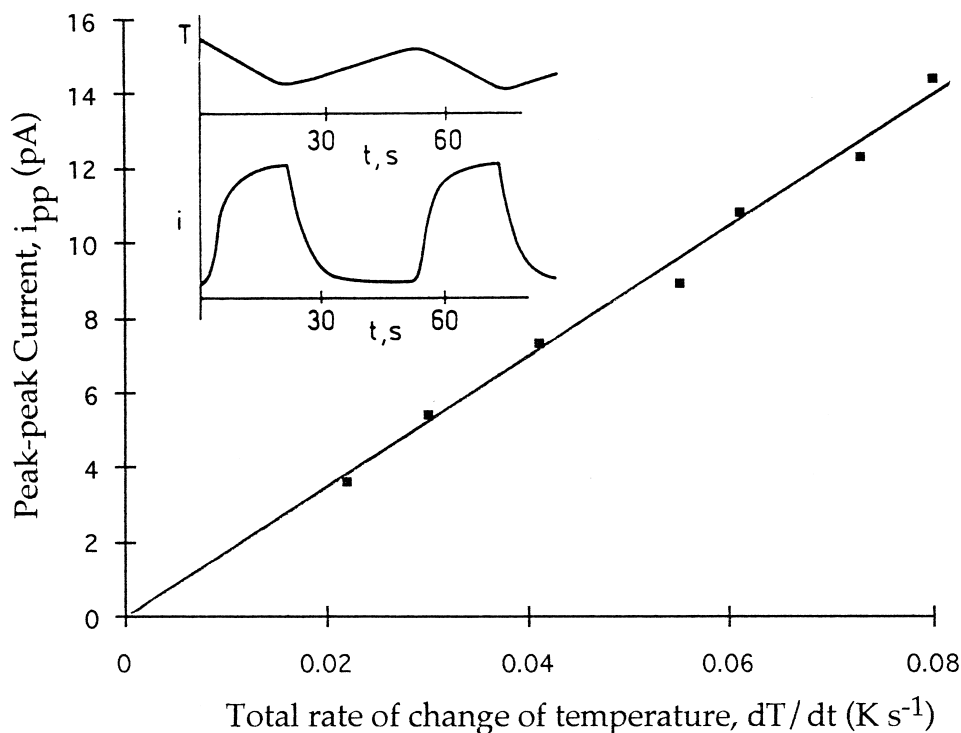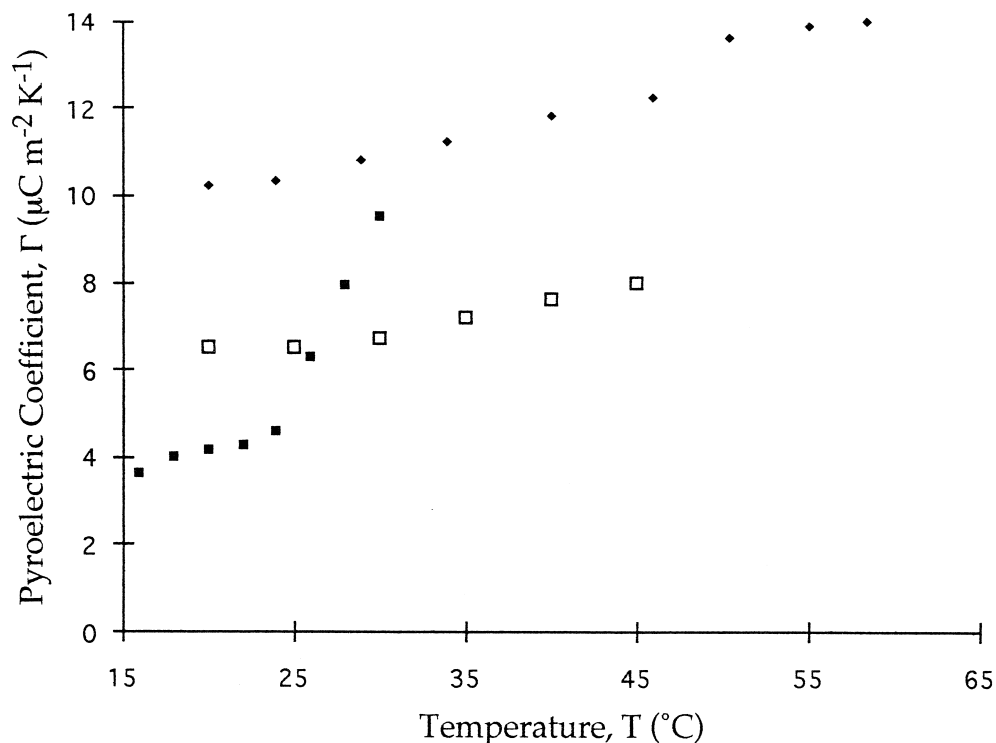

Fig. 3. Plot of peak-to-peak current against the total rate of change of temperature for an acid/amine LB superlattice.

- ■ Superlattice I: copolysiloxane acid (**1**) / aliphatic amine (**3**)

- □ Superlattice II: calix[8]arene acid (**2**) / calix[8]arene (**4**)

- ◆ Superlattice III: copolysiloxane acid (**1**) / calix[8]arene amine (**4**)

Fig. 4. Plot of pyroelectric coefficient against temperature for the three superlattice architectures I, II and III.

tional dipolar tilting mechanism contributes to the pyroelectric activity. In order for this mechanism to become significant, molecular dipoles (such as the substituted phenyl rings in the polysiloxane and calixarene molecules) must experience some free volume in which they can reorientate to minimise their energy. The selection of the copolysiloxane acid alternated with the calix[8]arene amine produces a superlattice in which there is a near 1:1 stoichiometry of the carboxyl: amino population combined with relatively loose packing of molecular dipoles. The highly closed packed structures of benzoic acid/phenylamine superlattices investigated by Colbrook and Roberts

Table 2
Analytical data for superlattice architectures I, II and III

Alternate layer superlattice		Area per molecule[+] a_m (nm^2)	Surface density of acid groups, ρ_{CO_2H} (nm^{-2})	Surface density of amine groups, ρ_{NH_2} (nm^{-2})	Ratio of ρ_{CO_2H}/ρ_{NH_2}	Γ at 20°C (μC m^{-2} K^{-1})
I	Copolysiloxane acid (**1**)	0.26	1.92*			
	Aliphatic amine (**3**)	0.21		4.76	0.40	4.15
II	Calix[8]arene acid (**2**)	3.13	2.56			
	Calix[8]arene amine (**3**)	3.85		2.08	0.48	6.50
III	Copolysiloxane acid (**1**)	0.26	1.92*			
	Calix[8]arene amine (**3**)	3.85		2.08	0.92	10.2

[+] see Refs. [3–7].

[8] did not facilitate significant dipolar reorientation and, as a result, the pyroelectric coefficients were relatively low $(1.0–1.5 \ \mu C \ m^{-2} \ K^{-1})$.

4. Conclusion

The pyroelectric activity of acid/amine alternate layer LB films can be enhanced by tuning the stoichiometry of the carboxyl and amino group populations at the interfaces between adjacent monolayers. By choosing an aromatic substituted linear copolysiloxane acid 1 and a calix[8]arene amine **4**, the surface densities of carboxyl and amino groups can be closely matched. This condition corresponds to the optimisation of the contribution of the proton transfer mechanism to the measured pyroelectric activity. Furthermore, the copolysiloxane backbone and the calixarene ring both accommodate reorientation of the electric dipoles associated with either the molecular moments (e.g., the aromatic side groups attached to the polysiloxane backbone), or the acid or amine headgroups themselves.

In the present system, the ratio of acid:amine surface densities is ~ 0.9. Thus, there is further scope for improvement in the pyroelectric activity of our new system both in terms of optimising the conditions for LB formation, (e.g., the use of divalent metal ions in the subphase, layer thickness) and in device geometry. In later studies, new superlattices will be studied in the hope that even better matching can be achieved and that this leads to further enhancements in the measured pyroelectric coefficients.

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