Langmuir–Blodgett Films of Side-chain Polysiloxanes: Synthesis, Characterisation and Pyroelectric Behaviour

Tim Richardson,[a] **Simon Holder**[b] **and David Lacey**[b]
[a]*Department of Physics, University of Sheffield, Hounsfield Road, Sheffield S3 7RH, UK*
[b]*School of Chemistry, The University of Hull, Hull HU6 7RX, UK*

Four aliphatic acid side-chain polymers have been synthesized and evaluated, based upon two different polysiloxane backbones, namely poly(methylsiloxane) and poly(methylsiloxane–dimethylsiloxane). A study of their behaviour at the water/air interface has shown that stable, fluid molecular films are formed that can be transferred as monolayers onto hydrophilic substrates. Their surface pressure–area isotherms indicate that bunching of the polysiloxane backbones may occur at relatively high surface pressures. The alternate layer deposition process has been used, in which the polysiloxane is co-deposited with a monomeric aliphatic amine (icosylamine). This ABABA··· sequential transfer has been monitored using the piezoelectric quartz crystal microgravimetric technique in which the alternate layer is assembled on top of a bulk quartz crystal, the oscillation frequency of which is measured precisely. The relationship between the frequency change and the number of transferred polysiloxane/monomer icosylamine bilayers is linear for the three materials that could be deposited, indicating that the deposition process is highly reproducible. The pyroelectric effect in these films has been studied. These data indicate that the level of activity is not simply related to the fraction of the silicon units along the backbones which are substituted with aliphatic acid chains. There is likely to be a trade-off between the density of acid/amine interactions and the free volume in which molecular tilting can occur.

Keywords: *Langmuir–Blodgett film*; *Polysiloxane*; *Pyroelectricity*

1. Introduction

Many researchers have studied the Langmuir and Langmuir–Blodgett (LB) film properties of a wide variety of preformed polymers,[1] but relatively little attention has been devoted to such characterisation of polymers synthesized using polysiloxane backbones.[2] This paper describes four aliphatic acid substituted polysiloxane LB materials[3] that form stable Langmuir films which can be subsequently deposited onto solid substrates such as glass and aluminium/aluminium oxide. The molecules, shown in Fig. 1, are synthesized from two polysiloxane backbones, namely poly(hydrogenmethylsiloxane) and poly(hydrogenmethyldimethylsiloxane). Their chemical syntheses and the preparation and characterisation of Langmuir layers will be discussed in sections 2 and 3. Alternate layer polysiloxane/monomer icosylamine (see Fig. 1) LB films have been assembled in an attempt to obtain aliphatic acid/amine interactions, which each produce a strong dipole moment.[4] Within monomer fatty acid/fatty amine alternate layer films, these dipole moments have been found to be aligned in a direction approximately normal to the plane of the substrate. Because of the alternating ABABA··· structure, the planes of ordered dipoles which exist between these acid and amine monolayers are repeated throughout the assembly, giving rise to a large macroscopic polarisation. Such polar structures are of considerable interest when seeking materials which exhibit the pyroelectric effect.[5] However, a constant polarisation is insufficient for this phenomenon to occur; the polarisation must be temperature dependent. The pyroelectric properties of these polysiloxanes, substituted to varying degrees with aliphatic acid side-groups, have been studied and are discussed in section 6.

2. Experimental

2.1 Preparation of Polysiloxanes (Fig. 2)

Materials

Undecen-10-oic acid was purchased from Aldrich and used as received. Hexachloroplatinic acid was purchased from
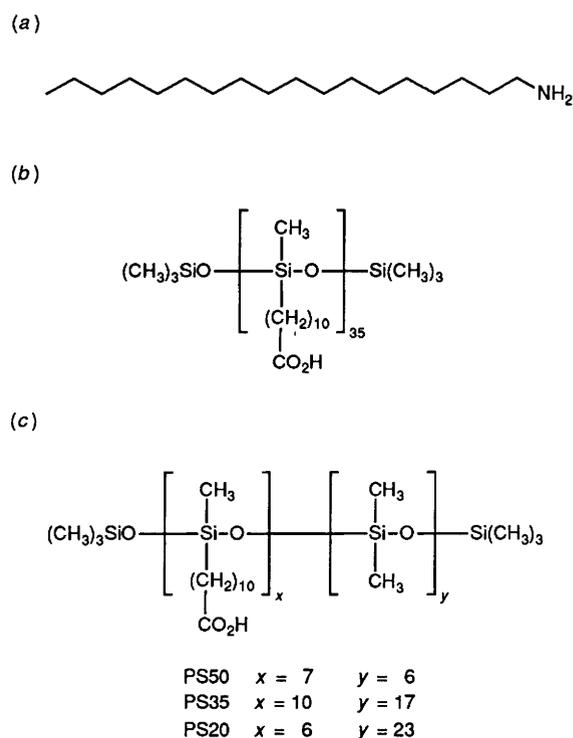
(*a*)

(*b*)

(*c*)

PS50	x = 7	y = 6
PS35	x = 10	y = 17
PS20	x = 6	y = 23

Fig. 1 The compounds studied in this research, (*a*) icosylamine, (*b*) polysiloxane homopolymer (PS100), (*c*) the three polysiloxane copolymers (PS50, PS35 and PS20)

Aldrich and made into solution by dissolving the acid (0.1 g) in isopropyl alcohol (1 cm³) which was then added to toluene (10 cm³). Poly(methylsiloxane) and the poly(methylsiloxane-*co*-dimethylsiloxane) were purchased from Petrarch Systems. Toluene was refluxed over calcium hydride and distilled under nitrogen. Dichloromethane and chloroform were refluxed over phosphorous pentoxide and distilled.

$CH_2{=}CH(CH_2)_8CO_2H$

$CH_2{=}CH(CH_2)_8CO_2R$

1a, b

Homopolymer 1

Copolymers 3a, b, c

Homopolymer 2

Copolymers 4a, b, c

Fig. 2 Synthesis scheme of the homopolysiloxanes and copolysiloxanes

Techniques

The structures of the mesogens, polymers and copolymers were confirmed by ^{1}H NMR (CDCl$_3$ solvent, TMS reference, 270 MHz multinuclear) and infrared spectroscopy (thin film, KBr disc). Samples of spectroscopic data are detailed with the relevant compound syntheses described below. Purities and polydispersities of the polymers and copolymers were determined by gel-permeation chromatography. However the system used was calibrated against polystyrene standards and therefore the molecular weights recorded were outside the systems calibration range.

Discussion

The hydrosilylation process initially proved extremely difficult owing to extensive crosslinking between the siloxane chains, which occurred owing to the presence of the acid precursors of the esters (**1a** and **1b**) in the reaction mixtures. Once free of the acids, the reactions proceeded without problems. Yields were low owing to the resultant substituted polysiloxanes exhibiting a large degree of miscibility in the methanol used during the purification procedure. The lower molecular weight polymers tended to remain in the methanol/dichloromethane mixture. Thus extreme care had to be taken to ensure complete removal of the monomer whilst minimising the amount of polymeric product lost. This problem is currently circumvented by the application of chromatographic size-exclusion techniques.

There is some doubt as to the stability of the acid-substituted homo- and co-polysiloxanes. After periods of usually 1–3 months, gel formation in the bulk liquid is sometimes observed. The gel is often insoluble but after filtration the remainder of the compound proves to be unaffected original product. The cause of this gel formation is as yet unknown but is currently under investigation.

Synthesis

Preparation of tert-*Butyldimethylsilyl Undec-*10-*enoate* (**1**). Imidazole (0.11 mol) was added to a stirred solution of undec-10-enoic acid (0.0543 mol) and *tert*-butylchlorodimethylsilane (0.056 mol) in dry dimethylformamide (CaH$_2$, 15 cm^3) and then left for 16 h at room temperature. The reaction mixture was poured into an excess of water and extracted with petroleum fraction (b.p. 40–60 °C) (3 × 50 cm^3). The combined petroleum fractions were then washed with a saturated aqueous solution of sodium hydrogen carbonate and dried (MgSO$_4$). The crude ester was purified by distillation under reduced pressure to give the *tert*-butyldimethylsilyl undec-10-enoate as a colourless liquid: yield, 12.1 g (74.7%); b.p. 108–110 °C, 0.1 mmHg. The purity of the compound was checked by HPLC (single peak). IR (thin film) v_{max}/cm^{-1} 3095 (C—H str), 1745 (C=O str), 1650 (C=C str). δ_H, 0.25 (s, 6 H, CH$_3$—Si), 0.9 (m, 9 H, CH$_3$—C), 1.3(m, 10 H, CH$_2$), 1.6 (m, 2 H CH$_2$—CH$_2$—CO$_2$), 2.1 (m, 2 H, CH$_2$—C=C), 2.3 (m, 2 H, CH$_2$—CO$_2$), 4.9 (t, 2 H, CH$_2$=CH), 5.8 (m, 1 H, CH=CH$_2$). $m/z = 390$ (M^+).

*Preparation of Benzyl Undec-*10-*enoate* (**2**). Undec-10-enoic acid (0.1 mol) was dissolved in a stirred mixture of methanol (360 cm^3) and water (40 cm^3). The solution was titrated to pH 7.0 with an aqueous solution of potassium carbonate (20%). The solvent was removed under reduced pressure and the resultant white solid was stirred with benzyl bromide (0.21 mol) in dimethylformamide (300 cm^3) for 16 h at room temperature.

The potassium bromide precipitate was filtered off, the solvent was removed under reduced pressure and the residue was dissolved in ether (150 cm^3). The ether solution was washed successively with water (3 × 100 cm^3), a saturated

aqueous solution of sodium hydrogen bicarbonate (3 ×100 cm^3) and water (3 ×100 cm^3) and then dried (MgSO$_4$). The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (C60 silica gel, dichloromethane), giving the product as a slightly yellow liquid. The purity of the compound was checked by thin-layer chromatography (CHCl$_3$). IR (thin film) v_{max}/cm^{-1} 2920, 2840 (C—H str), 1745 (C=O str), 1640 (C=C str). δ_H, 1.25 (m, 10 H, CH$_2$), 1.6 (m, 2 H, CH$_2$—CH$_2$—CO$_2$), 2.1 (m, 2 H, CH$_2$—C=C), 2.3 (m, 2 H, CH$_2$—CO$_2$), 4.95 (t, 2 H, CH$_2$=C), 5.1 (s, 2 H, CO$_2$—CH$_2$), 5.8 (m, 1 H, CH$_2$=CH—), 7.35 (m, 6 H,—C$_6$H$_5$).

Preparation of Homopolymer 1. A mixture of poly(methylsiloxane) (5.7 mmol/Si—H) and *tert*-butyldimethylsilyl undec-10-enoate (1) (6.7 mmol) was dissolved in dry toluene. The chloroplatinic acid solution (1 drop) was then added and the reaction mixture was then gently heated under reflux conditions.

Infrared spectroscopic analysis for the Si—H absorption band (2160 cm^{-1}) was carried out on a small sample of the mixture every 24 h. If the Si—H absorption band was then detected and showed no obvious decrease in intensity (in relation to the carbonyl absorption band at 1745 cm^{-1}), a further aliquot of the catalyst (1 drop) was added to the reaction mixture and the reaction allowed to continue for a further 24 h. This procedure was repeated until no, or very few, unreacted Si—H sites were detectable by infrared spectroscopic analysis of reaction mixture samples. Normally the reaction was complete or near completion within 72 h. A small amount of oct-1-ene was added to the reaction mixture to eliminate any unreacted sites.

The toluene was removed from the reaction mixture by distillation under reduced pressure and the residual yellow-brown viscous liquid was dissolved in the minimum volume of dichloromethane. Methanol was then added (*ca.* four times the volume of the dichloromethane added) and a viscous liquid–gel composite settled to the bottom of the tube. The mixture was then centrifuged for 30 min and the supernatant liquid removed. The dichloromethane–methanol and centrifugation procedure was performed four or five times. After the final addition of dichloromethane the resulting solution was filtered, to remove solid residuals, using a PTFE membrane filter (0.5 mm pore size), and the solvent then removed from the filtrate. The final product was a yellow–brown viscous liquid, yield 0.87 g (42%). IR (thin film) v_{max}/cm^{-1} 2960, 2920, 2850 (C—H str, CH$_3$ and CH$_2$), 1745 (C=O str), 1255 (Si—C str), 1150–1000 (Si—O str). δ_H, 0.1 (m, 9 H, CH$_3$—Si), 0.5 (t, 2 H, Si-CH$_2$—CH$_2$), 1.3 (m, 12 H, CH$_2$), 1.6 (m, 2 H, CH$_2$—CH$_2$—CO$_2$), 2.3 (m, 2 H, CH$_2$—CO$_2$).

Table 1 shows the molecular weights/polydispersities for this compound and all the copolymers synthesized in this work.

Preparation of Copolymer 3a. Copolymer 3a was prepared in a similar way to homopolymer 1 but using a mixture of (50–55%) methylsiloxane (45–50%) dimethylsiloxane copolymer (2.94 mmol/Si—H) and *tert*-butyldimethylsilyl undec-10-enoate (1) (3.5 mmol) dissolved in dry toluene. Purification was carried out in the same manner as described for homopolymer 1. The final product was obtained as a brown viscous liquid, yield 0.72 g (55%).

Preparation of Copolymer 3b. Copolymer 3b was prepared in a similar manner to homopolymer 1 but using a mixture of (30–35%) methylsiloxane (65–70%) dimethylsiloxane copolymer (5.4 mmol/Si—H) and benzyl undec-10-enoate (2) (5.5 mmol) dissolved in dry toluene. Purification was carried out in the same manner described for the preparation of polymer 3. The final product was obtained as a light-yellow highly viscous liquid, yield 1.17 g (47%).

Preparation of Copolymer 3c. Copolymer 3c was prepared in a similar manner to homopolymer 1 but using a mixture of (15–18%) methylsiloxane (82–85%) dimethylsiloxane copolymer (5.4 mmol/Si—H) and benzyl undec-10-enoate (2) (5.5 mmol) dissolved in dry toluene. The final product was obtained as a light-yellow highly viscous liquid, yield 1.35 g (40%).

Preparation of Homopolymer 2. Homopolymer 2 (3 mmol/—CO$_2$Si—) was dissolved in chloroform (10 cm^3) and stirred under a dry nitrogen atmosphere. To the stirred solution was added boron trifluoride in diethyl ether [10 mmol of BF$_3$ (48%) in Et$_2$O]. The reaction mixture was stirred for 6 h at room temperature and then the solution was neutralised by the addition of aqueous sodium hydroxide (1–2% m/v). The product was extracted into chloroform (3 × 30 cm^3) and the combined chloroform extracts were washed with water and dried (MgSO$_4$). The chloroform was removed by distillation under reduced pressure giving a viscous brown liquid (100% yield). The structure of homopolymer 2 was confirmed by infrared spectroscopy and ^{1}H NMR and the purity checked by GPC. IR (thin film) v_{max}/cm^{-1} 3000–2500 (broad band; O—H str of dimer), 1705 (C=O str).

Preparation of Copolymer 4a. The procedure followed for the preparation of copolymer 4a was similar to that outlined for the preparation of polysiloxane 4 but using *co*-polysiloxane 3 (0.41 mmol/—CO$_2$Si—) and boron trifluoride in diethyl ether [2 mmol of BF$_3$ (48%) in Et$_2$O]. The final product was a brown viscous liquid, 100% yield.

Preparation of Copolymers 4b *and* 4c. The relevant copolymer (3b or 3c) was dissolved in ethyl ethanoate (50 cm^3), 5% Pd (0.2 g) on charcoal was added and the mixture was stirred under an atmosphere of hydrogen for 48 h. Subsequently, the

Table 1 Characterisation of the homopolysiloxanes and copolysiloxanes

compound	code	R	x	y	M_w^*	M_w	D
1a		Si(CH$_3$)$_2$C(CH$_3$)$_3$	—	—	—	—	—
1b		CH$_2$C$_6$H$_5$	—	—	—	—	—
homopolymer **1**		Si(CH$_3$)$_2$C(CH$_3$)$_3$	46±2	—	16 146	12 100	1.38
homopolymer **2**	PS100	H	46±2	—	11 344	8 900	1.40
copolymer **3a**		Si(CH$_3$)$_2$C(CH$_3$)$_3$	7±1	6±1	3 110	4 450	1.23
copolymer **3b**		CH$_2$C$_6$H$_5$	10±1	17±1	4 760	7 320	1.72
copolymer **3c**		CH$_2$C$_6$H$_5$	6±1	23±3	3 870	3 300	1.37
copolymer **4a**	PS50	H	7±1	6±1	2 310	2 550	1.35
copolymer **4b**	PS35	H	10±1	17±1	3 860	5 650	1.89
copolymer **4c**	PS20	H	6±1	23±3	3 330	2 770	2.17

M_w^*=molecular weight average, calculated; M_w=molecular weight average, recorded (GPC); D=polydispersity (GPC).

catalyst was filtered off and the solvent removed under reduced pressure. The products were obtained as light-yellow viscous liquids in 100% yield.

3. Langmuir Film Preparation and Characterisation

Langmuir films of all four polysiloxanes were prepared using solutions of concentration 1.0×10^{-4}–2.5×10^{-4} mol dm^{-3} in Aristar grade chloroform (BDH). The solutions were spread dropwise onto the cleaned water surface (18 MΩ, Milli-Q water system) of a constant-perimeter, single-compartment trough, allowing several minutes after spreading for the solvent to evaporate. The surface pressure–area (π–A) isotherms are shown for PS100, PS50, PS35 and PS20 in Fig. 3 and, for reference purposes, are compared with the isotherm of the unsubstituted homopolymer backbone.

The unsubstituted backbone of the homopolymer shows an expanded isotherm [Fig. 3(a)]. The already high compressibility of the monolayer, $-1/A(\mathrm{d}A/\mathrm{d}\pi)$, increases further within a 'plateau' region in which the polymer chains begin to pile up and form an unstable, multilayered film. It is astonishing, however, that the backbone alone can withstand even the low surface pressures (<10 mN m^{-1}) observed here; other researchers have seen this behaviour previously. Fig. 3(b)–(e) show the π–A isotherms of the substituted polysiloxanes. Overall, the monolayer becomes more expanded as the degree of substitution decreases. However, the exception to this trend is PS50, which exhibits the most condensed isotherm. From

these isotherms and the knowledge of the number of polymer molecules on the water surface, the area per polymer molecule at a given surface pressure and, furthermore, the area per siloxane unit, can be calculated. Table 2 shows these areas for the four substituted molecules studied. Also shown are the area values obtained by extrapolation of the high-pressure region of each isotherm. Whilst in the case of these materials, the former values are more meaningful, the extrapolated values are included for completeness and to give an indication of the compressibility of the Langmuir layers. The area per siloxane subunit at a surface pressure of 26 mN m^{-1} for PS50 is 0.22 nm^2. This values agrees well with the area normally measured for monomeric fatty-acid molecules and suggests that this Langmuir film is indeed monomolecular. The area per residue for PS100 is 0.15 nm^2, which is lower than expected and suggests that not all of the PS100 molecules reside within a monolayer. Furthermore, the values of the area per siloxane subunit measured from the isotherms of molecules PS35 and PS20 are considerably lower than the expected cross-sectional area of an aliphatic acid chain. If the polysiloxane backbones are as elongated as possible, the area occupied by each molecule should be directly proportional to the number of siloxane units even when the backbone is only partially substituted. However, the lower values obtained for PS35 and PS20 suggest that either (i) the Langmuir films of these materials are now imperfect and contain regions in which each film is several molecules thick or (ii) the polysiloxane backbone has somehow bunched or coiled such that the side-
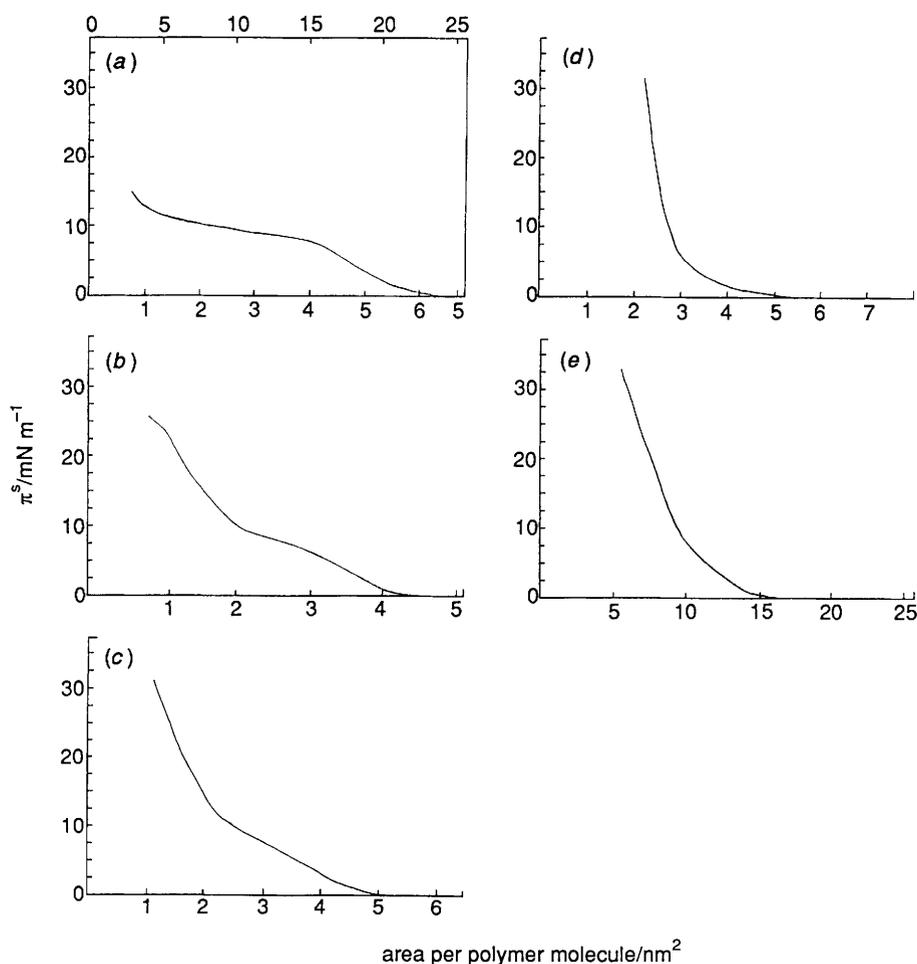

Fig. 3 Surface pressure–area isotherms of (a) the homopolysiloxane backbone, (b) PS20, (c) PS35, (d) PS50 and (e) PS100, at pH 5.9 spread from chloroform

Table 2 Langmuir film areas for the polysiloxane oligomers studied in this work and their associated areas per siloxane unit

oligomer	area per oligomer at 26 mN m^{-1}/nm^2	area per siloxane unit at 26 mN m^{-1}/nm^2	area per siloxane unit extrapolated at 26 mN m^{-1}/nm^2
PS100	6.80	0.15	0.23
PS50	2.35	0.18	0.23
PS35	1.40	0.05	0.09
PS20	1.10	0.04[a]	0.07[a]

[a] At 20 mN m^{-1}.

groups become more closely packed. To a first approximation, the flexibility of the polysiloxane backbones would be expected to increase as the degree of substitution decreased; bunching or coiling may therefore be observed where the backbones are only lightly substituted. Work is in progress to clarify the origin of these low residue areas.

The Langmuir layers of these materials, although relatively compressible, are all extremely stable (the area loss $<0.5\%$ h^{-1}) and single layers can be transferred onto hydrophilic substrates with very high transfer ratios (>0.95). In addition to being very stable on the water surface, these substituted polysiloxanes are extremely fluid. A qualitative test of the degree of rigidity of a Langmuir film is to apply a suction device (normally used for cleaning the water surface) to the layer at a point several centimetres from the surface pressure transducer (in this case, a Wilhelmy plate) and to observe the response of the trough barrier which controls the area available to the film. The trough is set up in the deposition mode so that ideally the barrier would move smoothly inwards (decreasing area) immediately after material has been removed or transferred onto a substrate. In the case of all four substituted polysiloxanes, the barrier response was indeed smooth and immediate even though suction was applied at a distance of 20 cm from the Wilhelmy plate.

4. LB Film Deposition

Monolayers of all four substituted polysiloxanes were transferred onto Al/Al$_2$O$_3$ substrates. In this paper, our results of alternate-layer deposition are described in which each polysiloxane is co-deposited with monomeric icosylamine. The surface pressures used were 26 mN m^{-1} for PS100, PS50 and PS35 and 20 mN m^{-1} for PS20. The icosylamine was deposited at 27.5 mN m^{-1}. For all molecules except PS20, high transfer ratios (>0.9) were obtained for both the polysiloxane and the icosylamine layers. Typically, multilayer films containing 13 layers of the polysiloxane alternated with 12 layers of icosylamine were assembled on an aluminium-coated glass substrate. Upper electrodes were deposited by thermal evaporation of aluminium (40.0 nm, area $=2.5 \times 10^{-5}$ m^2) to form a capacitor structure in which the LB film is the insulating material. The pyroelectric behaviour of these alternate-layer superlattices is discussed in section 5. Interestingly, in the case of PS20, the first monolayer of both the polysiloxane and icosylamine could be transferred effectively, but no deposition at all was observed for the subsequent PS20 layer.

A convenient method of assessing the reproducibility of the deposition technique during the assembly of an alternate layer film is the piezoelectric quartz crystal microgravimetric technique (commonly used in metal coating systems). This involves the measurement of the resonant frequency of a quartz crystal oscillator (in this case 6 MHz crystals are used) using a frequency counter as a function of the number of layers that have been transferred onto the surface of the electroded crystal. The change in resonant frequency, Δf, has been shown

to be directly proportional to the mass of material deposited onto the crystal[6]:

$$\Delta f = \frac{2f_0^2 \Delta m}{A\phi} \qquad (1)$$

where f_0 is the resonant frequency at the beginning of the experiment, Δm is the mass change and ϕ is a term involving material constants for quartz. For alternate-layer LB films, the frequency change per bilayer (one polysiloxane monolayer plus one icosylamine layer) should be related directly to the mass of the bilayer. Thus,

$$\Delta f = \frac{2f_0^2 N \delta_B}{A\phi} \qquad (2)$$

where N is the number of polysiloxane/icosylamine bilayers and δ_B is the mass per bilayer. The plots of Δf versus N are shown for PS100, PS50 and PS35 in Fig. 4. Clearly, the linear relationships confirm that the transfer process is highly reproducible. It is also interesting to note that the gradients of the graphs indicate that the mass per unit area of the bilayers, m_x (where x is 100, 50 or 35 referring to bilayers containing PS100, PS50 and PS35, respectively), does not follow the originally anticipated direct proportionality with the degree of side-group substitution along the polysiloxane backbone. The plots suggest that $m_{100} > m_{35} > m_{50}$; further research is currently being directed at investigating the relationship between the magnitude of the pyroelectric coefficient and the density using the quartz crystal technique.
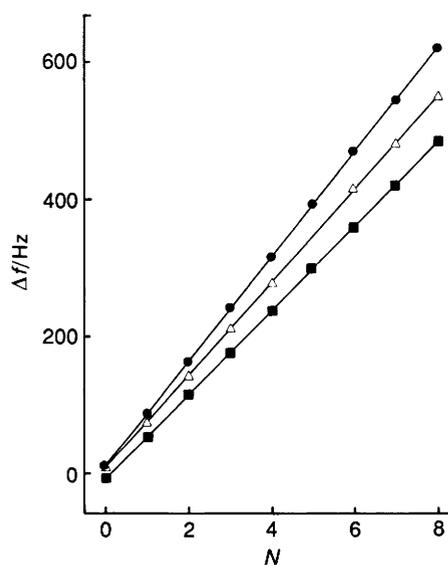

Fig. 4 Quartz microbalance plots for polysiloxane LB films. ●, PS100; △, PS35; ■, PS50.

5. Pyroelectric Activity in Polysiloxane/Monomer Icosylamine LB Films

The pyroelectric behaviour of these alternate-layer LB films was investigated using a static technique which has been described elsewhere.[7] All measurements were made under vacuum ($<10^{-2}$ Torr) in order to remove water incorporated into the films during deposition. Pyroelectricity is the phenomenon in which a charge is generated at the surface of a material in response to a rate of change of temperature and can be expressed as:

$$i = pA\frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

where i is the current that flows when the electroded material is short-circuited, A is the electrode area and $(\mathrm{d}T/\mathrm{d}t)$ is the rate of change of temperature. The pyroelectric coefficient, p, is therefore the current density measured per unit rate of change of temperature. The pyroelectric coefficients of the polysiloxane/icosylamine LB films are shown as functions of temperature in Fig. 5. The coefficients can be seen to rise gradually with increasing temperature. The values measured here are very similar to those obtained for monomeric tricosen-22-oic acid/1-docosylamine alternate-layer LB films.[8] The effect is reversible in the temperature range shown. The
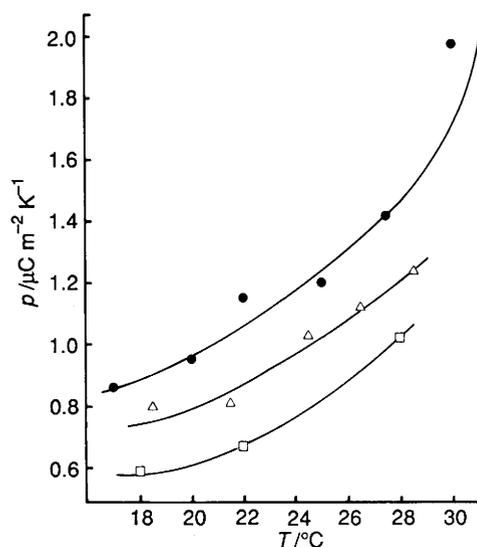
largest response is observed for the film containing PS50 and not that containing the fully substituted molecule, PS100. At first inspection, this may appear somewhat surprising since the density of acid/amine interactions, which are thought to give rise to the pyroelectric effect, is expected to be at its maximum in the alternate layer incorporating the homopolymer, PS100. However, recent studies by Petty et al.[9] have shown that a significant contribution to the activity in some monomer acid/monomer docosylamine alternate layer films may arise through a dipolar tilting mechanism. The PS35/icosylamine film, however, gives an intermediate pyroelectric response suggesting that there may be a trade-off between contributions arising from both proton transfer between the acid and amine headgroups and reorientation of the dipoles through a tilting process.

6. Summary

The syntheses and Langmuir film behaviour of four aliphatic acid substituted polysiloxanes have been reported. Three of these materials can be alternated with monomeric icosylamine to form multilayer LB film assemblies. Their pyroelectric characteristics have been studied and show that the properties of these materials are not simply related to the degree of substitution of the side-groups. Our future work is aimed at investigating the relative permittivities of these LB films and their layer structure.

Fig. 5 Pyroelectric effect in polysiloxane LB films (the pyroelectric coefficients are determined to an accuracy of $\pm 3\%$)

References

1. R. H. Tredgold and C. S. Winter, *J. Phys. D*, 1982, **15**, L55.
2. W. Retlig, J. Naciri, R. Shashidar and R. S. Duran, *Thin Solid Films*, 1992, **210/211**, 114.
3. T. Richardson, G. G. Roberts, S. Holder and D. Lacey, *Thin Solid Films*, 1991, **210/211**, 299.
4. P. Christie, G. G. Roberts and M. C. Petty, *Appl. Phys. Lett.*, 1986, **48** 1101.
5. R. W. Whatmore, *Rev. Prog. Phys.*, 1986, **49**, 1335.
6. G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206.
7. M. Poulter, *D. Phil. Thesis*, Oxford University, 1992.
8. P. Christie, C. A. Jones, M. C. Petty and G. G. Roberts, *J. Phys. D*, 1986, **19**, L167.
9. J. Tsibouklis, M. Petty, Y. Song, R. Richardson, J. Yarwood, M. C. Petty and W. J. Feast, *J. Mater. Chem.*, 1991, **1**, 819.