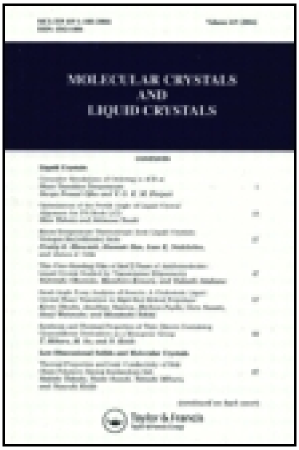

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Copolysiloxanes as Pyroelectric Langmuir-Blodgett Films

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COPOLYSILOXANES AS PYROELECTRIC LANGMUIR-BLODGETT FILMS.

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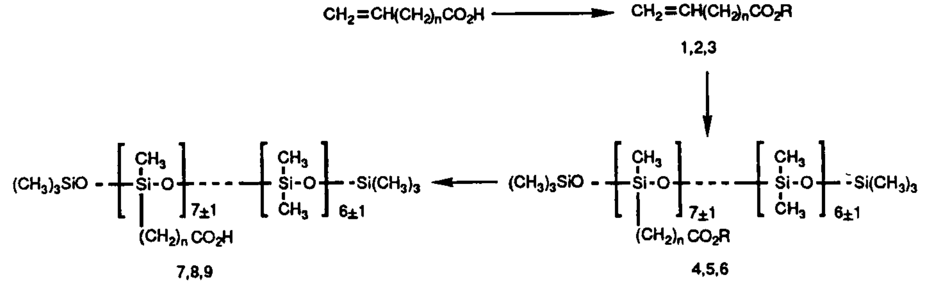
Abstract A series of aliphatic acid side-chain copolysiloxanes based on a poly(hydrogenmethyldimethylsiloxane) backbone have been synthesised and evaluated. The length of the aliphatic acid side-chain of each compound has been varied in order to examine the effect on the Langmuir film properties. The surface pressure - area isotherms have indicated that each copolysiloxane forms a stable monomolecular layer on a pure water subphase. Alternate layer structures, in which each siloxane copolymer is co-deposited with a monomeric eicosylamine, have been prepared in order to measure their static pyroelectric coefficients. The magnitude of the coefficient increases as the length of the aliphatic acid side-chain is reduced. The thickness dependence of the coefficient has also been characterised for one of the copolysiloxane derivatives and shows that the pyroelectric effect is greatest for a 25 layer sample (13 layers of copolysiloxane 8 / 12 layers of eicosylamine).

INTRODUCTION.

Alternate layer LB films containing aliphatic acid and amine functional groups are of interest to researchers studying the pyroelectric effect, in which the spontaneous polarisation is temperature-dependent[1]. The interaction of such groups aligned in adjacent monolayers gives rise to a strong polarisation[2] whose magnitude has been found to change with temperature. It is therefore useful to study different systems in which carboxylic acid and amine groups interact in order to understand the physical and chemical factors which enhance or reduce the pyroelectric effect. The low dielectric constant and dielectric loss displayed by most polar LB films (relative to inorganic ferroelectric crystals or polyvinylidene difluoride and its copolymers) makes them attractive materials for exploitation in pyroelectric heat-sensing applications. However, at present, their pyroelectric coefficients are insufficiently high to enable the necessary sensitivity to non-linear temperature change to be achieved; values in excess of $20\mu Cm^{-2}K^{-1}$ are ideally required. It is important that research aimed at optimising the pyroelectric performance of LB film systems is directed towards determining the future role of such molecular layers in pyroelectric sensors. The principle objective of the work described in this paper is to examine the relationships between the pyroelectric coefficient of copolysiloxane / monomer eicosylamine alternate layer LB films and the length of the aliphatic acid side-chains substituted onto the siloxane backbone.

PREPARATION OF COPOLYSILOXANES.

The copolysiloxanes were synthesised using the synthesis procedure outlined below:

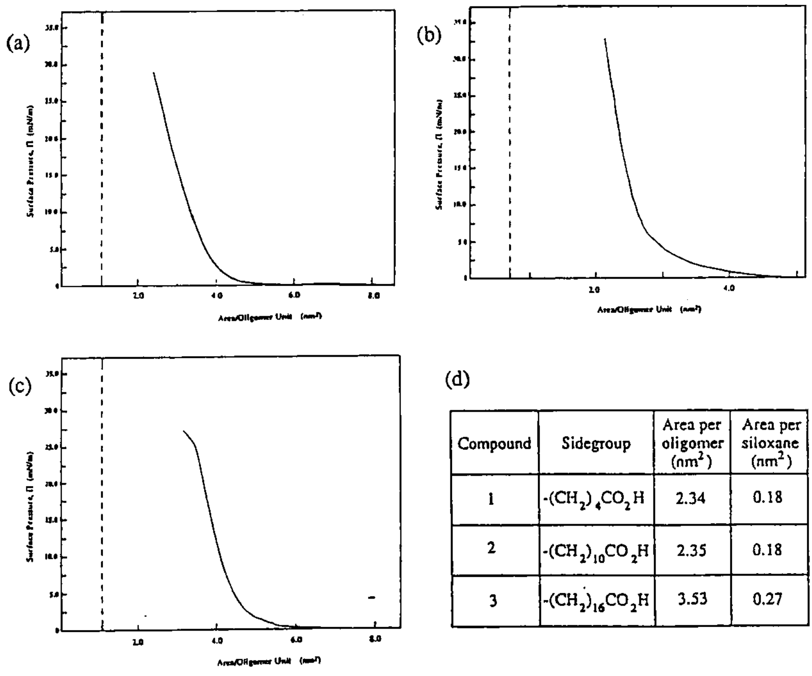


Compound	n	R
1,4	4	$-CH_2C_6H_5$
2,5	10	$-SiC(CH_3)_2C(CH_3)_3$
3,6	16	$-CH_2C_6H_5$

Copolysiloxane	n
7	4
8	10
9	16

LANGMUIR FILM PREPARATION AND CHARACTERISATION.

Stable Langmuir films of copolysiloxanes **7**, **8** and **9** were prepared using solutions of concentration (1.5 - 2.5) x 10^{-4} mol l^{-1} in chloroform. In the case of **9** a small amount (5% by volume) of 2-ethoxyethylacetate was used in conjunction with the chloroform (95% by volume) to improve the solubility. After spreading onto a water suphase at pH 5.9, the surface pressure - area isotherms of each compound were recorded and are shown in Figure 2(a) - (c). It can be seen that the areas per molecule in the high pressure region (20 - 30mNm^{-1}) are approximately 2.0 - 3.0nm^2. These areas are so large because they correspond to the oligomeric units each of which contains several siloxane residues. The areas per siloxane unit are shown in Figure 2(d) and are very close to the expected cross-sectional area of aliphatic acid chains. Therefore, since the polar carboxylic acid groups are strongly bound to the water surface, these data suggest that the oligomeric molecules form a monolayer and are orientated such that the aliphatic acid side-chains protrude approximately orthogonally from the water surface and the siloxane backbone lies parallel to it.



(d)

Compound	Sidegroup	Area per oligomer (nm^2)	Area per siloxane (nm^2)
1	$-(CH_2)_4CO_2H$	2.34	0.18
2	$-(CH_2)_{10}CO_2H$	2.35	0.18
3	$-(CH_2)_{16}CO_2H$	3.53	0.27

FIGURE 2 Π - A isotherms and area data for copolysiloxanes 7, 8 and 9.

LB DEVICE PREPARATION.

LB multilayer films of the copolysiloxanes 7, 8 and 9 each deposited alternately with monomeric eicosylamine have been prepared using Al/Al_2O_3 coated glass substrates. The deposition surface pressures were 26mNm^{-1} for the copolysiloxanes and 27.5mNm^{-1} for the eicosylamine. The transfer ratios were similar in all cases and were close to unity. In order to assess the pyroelectric effect, it is necessary to fabricate a metal-insulator-metal (MIM) device in which the LB film forms the insulating dielectric layer. The aluminium film on glass formed the lower electrode of the MIM device and the upper electrode was formed by thermal evaporation of a 50nm aluminium layer at a rate of 0.1 - 1.0nms^{-1}.

PYROELECTRIC BEHAVIOUR.

The pyroelectric response of these alternate layer LB assemblies has been measured using a static technique which has been described in detail in the literature[3]. In this method, the MIM structure is heated and cooled in a controlled manner and the resulting pyroelectric current which is generated by the LB film is measured using a sensitive electrometer or picoammeter. The current,

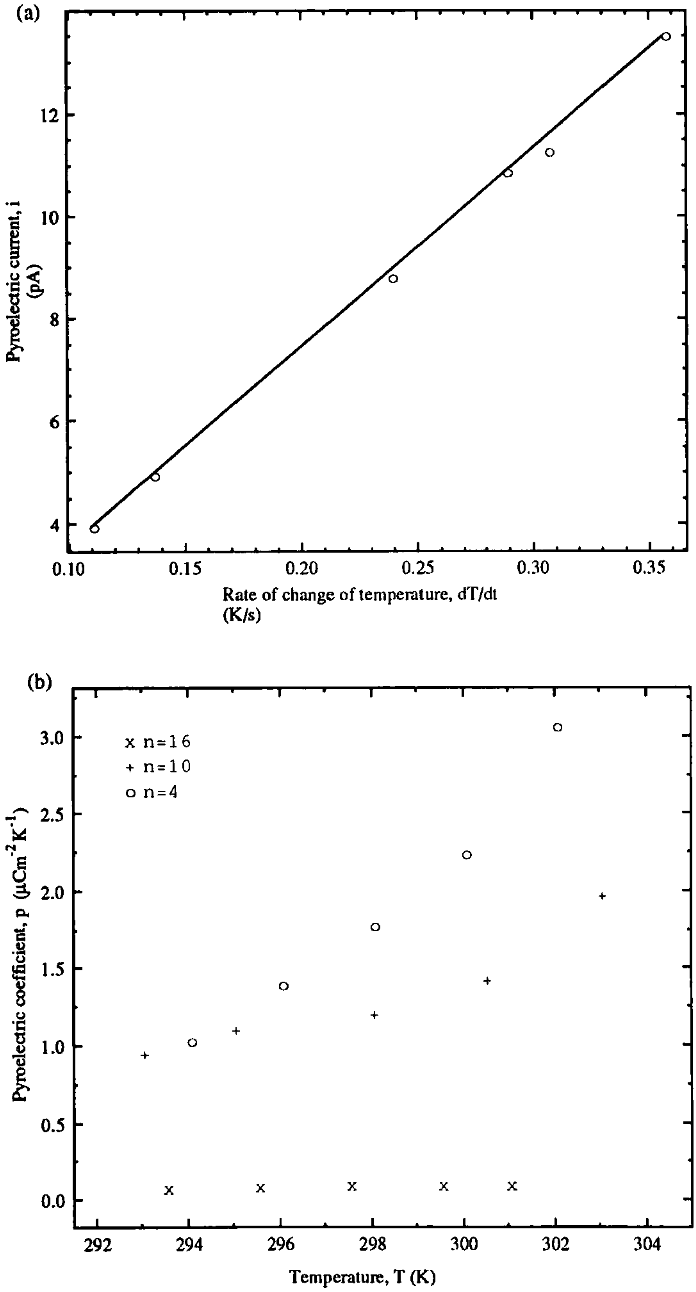


FIGURE 3 (a) Pyroelectric current versus rate of change of temperature and (b) the variation of the pyroelectric coefficient with temperature for the three different side-group chain lengths substituted onto the siloxane backbone.

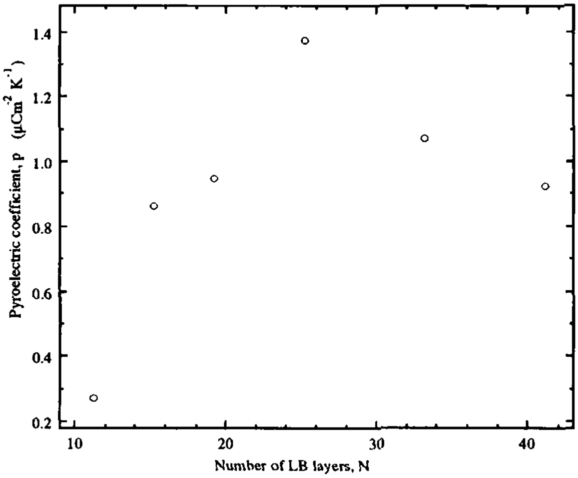


FIGURE 4 Variation in the static pyroelectric coefficient as a function of the number of transferred LB layers.

i_p, is related to the temperature of the LB film[4] by:

$$i_p = p\ A\ (dT/dt) \qquad (1)$$

where p is the pyroelectric coefficient (the rate of change of polarisation P with respect to temperature, dP/dT), A is the electrode area and dT/dt is the rate of change of temperature. Normally, the heating and cooling is performed in such a way that the temperature varies in a triangular waveform; in this case, the pyroelectric current profile is a square waveform whose amplitude is used to determine the pyroelectric coefficient.

Figure 3(a) shows the linear variation of the pyroelectric current as a function of the rate of change of temperature for the copolysiloxane **8** / eicosylamine LB film. This confirms that the relation described in equation (1) is obeyed and that the current arises due to the pyroelectric effect. This linearity is also observed in the other copolysiloxane films. The pyroelectric coefficients of the LB films were measured over the temperature range 293 - 303K. Figure 3(b) shows the temperature dependence of p for the LB films containing compounds **7**, **8** and **9**. The coefficients for all three alternate layers rise gradually with increasing temperature.This is perhaps due to the increasing mobility of observed dipoles in this temperature region although this has not yet been confirmed. However, it is striking that the magnitude of the coefficient increases as the chain length of the aliphatic acid side-groups substituted onto the siloxane backbone is shortened. The value of p obtained for the -$(CH_2)_4CO_2H$ derivative/eicosylamine LB film at 300K (3.1μCm^{-2}K^{-1}) is one of the largest reported coefficients for an LB structure.

Figure 4 shows the variation in the pyroelectric coefficient as a function of the number of transferred layers for the copolysiloxane 8 / eicosylamine LB sample. An optimum value is observed for the structure containing 25 laternating layers, i.e. 13 copolysiloxane monolayers interspaced with 12 eicosylamine monolayers. The origin of this thickness dependence is currently being investigated.

SUMMARY.

Three side-chain copolysiloxanes have been synthesised which form highly stable, condensed monolayers on a water subphase. The alternate layer LB deposition technique has been successfully employed to produce copolysiloxane acid / eicosylamine pyroelectric devices. The pyroelectric coefficients of such LB multilayers increases as the length of the copolysiloxane aliphatic acid side-chain decreases and depends also on the number of monolayers which are built up within the LB stack. Our future work is aimed at studying the pyroelectric behaviour of copolysiloxanes containing aliphatic acid side-chains of other lengths and observing the effect of introducing aromatic side-groups into the aliphatic side-chain.

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