Eur. Phys. J. B **45**, 33–37 (2005)
DOI: 10.1140/epjb/e2005-00161-0

The European Physical Journal B

Pyroelectric behavior and dielectric properties of linear copolysiloxane/eicosylamine superlattice

A.R.M. Yusoff[a] and W.H. Abd. Majid

Material Science Laboratory, Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

Received 25 October 2004 / Received in final form 30 December 2004

Abstract. The pyroelectric behavior and dielectric properties of a superlattice containing a Langmuir-Blodgett (LB) film of alternately monomeric eicosylamine and linear copolysiloxane substituted with aromatic acid side chains have been investigated in the temperature range of 13 – 29 °C. The pyroelectric coefficient of the superlattice increases with temperature, exhibiting the highest coefficient of $6.2 \pm 0.2\ \mu\text{cm}^{-2}\ \text{K}^{-1}$ at 29 °C. The dielectric behavior of the superlattice is investigated by examining the dielectric loss and capacitance in the frequency range of 10^2 to 10^5 Hz. The maximum loss values for all temperatures in the range occur at a frequency ∼5000 Hz which correspond to a relaxation time of 3.18×10^{-5} s. The Cole-Cole plots obtained experimentally are found to be broad and fall inside the semicircle derived from the Debye relaxation theory. However, they agree fit with the semi-empirical Cole-Cole relaxation model. The parameter α obtained from the Cole-Cole relaxation model decreases with temperature indicating the rise in the internal degrees of freedom of the dipole in the superlattice.

PACS. 77.22.-d Dielectric properties of solids and liquids – 77.70.+a Pyroelectric and electrocaloric effects

1 Introduction

Pyroelectricity arises due to a change in spontaneous polarization as a result of a change of temperature. Spontaneous polarization is the dipole moment per unit volume in the absence of an external field. In order to exhibit pyroelectric activity, the dipole moment per unit volume of a device has to be non-zero and the polarization related to the dipole moment is temperature-dependent. The pyroelectric effect [1] has been observed in a wide range of materials such as barium titanate, triglycyne sulfate, polyvinylidene difluoride and various Langmuir-Blodgett (LB) materials.

This paper discusses the dependence of pyroelectricity on temperature of a superlattice containing an alternate layer Langmuir-Blodgett (LB) film of linear copolysiloxane (A) substituted with aromatic acid side chains with monomeric eicosylamine (B). The molecular structure of the linear copolysiloxane is shown in Figure 1. The two organic materials forming the superlattice are deposited alternately such that an ABABA... molecular arrangement is achieved. Such a molecular arrangement produces a non-centrosymmetric structure with a non-zero total polarization. Thus, the superlattice is expected to manifest pyroelectric properties. Other examples of alternate structures which show the pyroelectric effect have been investigated by Coolbrook et al. [2], Smith et al. [3], Jones et al. [4], and Kamata et al. [5].

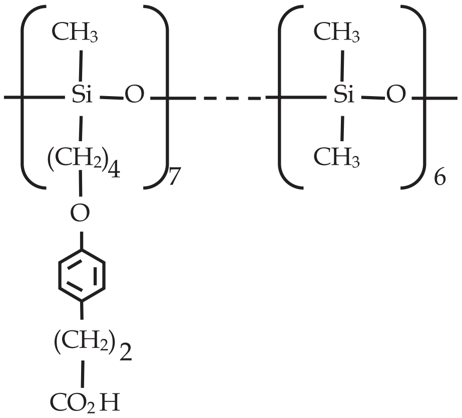

Fig. 1. Molecular structure of linear copolysiloxane.

A study of the dielectric behavior of the superlattice has also been performed in order to determine the dielectric loss and its temperature dependence. The dielectric response of a polymer such as linear copolysiloxane occurs due to several factors including the interaction between polymer chains, the presence of specific molecular groupings and effects related to interactions within specific molecules themselves. In this research, no attempt has been made to identify the detailed source of the dielectric relaxation. However, the most likely source of the

---

[a] e-mail: `abdrashid_4@hotmail.com`

dipole moment in the superlattice comes from the side chain of the linear copolysiloxane and the molecular dipole of eicosylamine.

2 Theory

Pyroelectric effect

The pyroelectric activity of a device is normally represented by the pyroelectric coefficient, which is related to the change in polarization as a result of a small change in the temperature of the device. The relation can be represented by

$$\Delta P = \Gamma \Delta T \tag{1}$$

where ΔP is the change in polarization, Γ is the pyroelectric coefficient and ΔT is the change in temperature. The change in polarization is equivalent to the change in the surface charge density on a device, which can be detected by charge integration or by measuring the short circuit current. Thus, the rate of change of polarization can be represented by a current I_p known as the pyroelectric current where $I_p = \Gamma A \frac{dT}{dt}$. Parameter A and $\frac{dT}{dt}$ is the electrode area of the device and the rate of temperature change, respectively. If a triangular temperature profile is applied to the device, then a square wave pyroelectric current is obtained. The rate of temperature change can be calculated from the gradient of the triangular wave, while the pyroelectric current can be obtained from the amplitude of the square wave. Thus Γ can be evaluated as I_p, A and $\frac{dT}{dt}$ are measurable parameters.

Dielectric properties

The Debye relaxation model has been widely used in describing the way the molecules respond to the applied field [6]. It is based on two assumptions: that the polarization reaches an equilibrium state exponentially and that the superposition principle is applicable in the relaxation phenomena. The Debye dispersion equation is given by

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau}. \tag{2}$$

It can be separated into real and imaginary components. Plotting its real and imaginary components against the frequency of the applied field will give a dispersion curve. The maximum loss is located at frequency, $\omega_{\max}$ whereby $\omega_{\max}\,\tau = 1$. Hence, the relaxation time τ can be obtained experimentally by locating this position.

The Debye model was originally used with dipoles (molecules) that can be rotated in viscous liquid solutions [7]. Thus this simple theory cannot be used to explain other viscous relaxation processes. Modifications to the model have to be made to fit the experimental data to the theory. One of the suggestions proposed is the Cole-Cole dielectric relaxation model, which can be represented by

$$\varepsilon(\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + (j\omega\tau)^\alpha}, \tag{3}$$

where $0 < \alpha \le 1$. α is a parameter added to specify the breadth of the experimental relaxation peaks.

In order to determine which dielectric relaxation model is best for a particular experimental result, a Cole-Cole diagram is plotted. A Cole-Cole diagram is a plot of the imaginary permittivity ε'' against the real permittivity ε'. According to Debye theory, the Cole-Cole plot is a semicircle and according to Cole-Cole theory the plot is a skewed arc.

3 Experimental details

Sample preparation

A polar alternate layer Langmuir-Blodgett (LB) film has been built from a linear copolysiloxane substituted with aromatic side chains (A) and a monomeric eicosylamine (B). The two polar organic materials are deposited alternately by using a two-compartment Langmuir trough to form an ABABA... molecular arrangement of 31 monolayers (16 linear copolysiloxane monolayers alternating with 15 eicosylamine monolayers) on a glass substrate coated with 500 Å of aluminium. An ultra-pure water (18 MΩ) subphase at pH 5.9 at a temperature of 20 °C was used. The deposition pressure for the linear copolysiloxane and monomeric eicosylamine was 22.5 mN m^{-1} and in the range of 20–25 mN m^{-1}, respectively.

Pyroelectric effect and dielectric characterization

The pyroelectric and dielectric activity of the superlattice was measured from a capacitor-type device in which the superlattice formed the dielectric material. The upper electrodes, which consist of 500 Å thick aluminium strips, were evaporated initially at a rate of 1 Å s^{-1} for the first 50 Å, followed by a gradual increase in the rate to <5 Å s^{-1} to prevent damage to the superlattice. The bottom electrodes of the device also have a thickness of 500 Å and the overlapping electrode area is 17.9×10^{-6} m^2. The thickness of the sample as measured by the Plasmos SD 2300 ellipsometer is 65 ± 4 nm.

All pyroelectric measurements are performed in an evacuated earthed chamber (at least 1.33 Pa), as described in detail in reference [8]. A Keithley 617 electrometer is used to measure current from the pyroelectric cell. The pyroelectric current profiles are recorded using the analogue output of the electrometer and a suitable chart recorder. Each pyroelectric measurement consists of ~10 full cycles of heating and cooling about a mean temperature which can be adjusted by a peltier heater such that the temperature dependence of the pyroelectric coefficient can be evaluated over a desired temperature. In this experiment a range of 13 to 29 °C was suitable.

For dielectric measurements, the BNC connection from the sample chamber to a PM6304 programmable automatic RCL meter was connected via a 1 m wire lead. The parallel equivalent circuit was chosen throughout the frequency range from 100 Hz to 100 kHz and the measurement was carried out over the temperature range of 13 to 29 °C.

NO measurements were carried out at higher temperatures to avoid damaging the sample.

4 Pyroelectric behavior

Figure 2 shows the pyroelectric activity of the superlattice containing the linear copolysiloxane substituted with aromatic acid side chains over the temperature range of 13 to 29 °C. The pyroelectric activity of the superlattice increases as the temperature of the device increases from 13 to 29 °C. The highest pyroelectric activity is measured at 29 °C where the coefficient of the activity is $6.2 \pm 0.2\ \mu\,\mathrm{cm}^{-2}\ \mathrm{K}^{-1}$ which is a relatively high value for a superlattice containing LB films. The majority of LB pyroelectric devices made from other types of organic compounds have yielded coefficients in the range of $0 - 2\ \mu\,\mathrm{cm}^{-2}\ \mathrm{K}^{-1}$.

5 Dielectric dispersion curves

The dielectric behavior of the superlattice was investigated by examining the dielectric loss and capacitance of the superlattice. The plot of dielectric loss (tan δ) and capacitance (C) of the device is reported in reference [9]. The dielectric loss (tan δ) is low, about 0.01, in the frequency range of 0–1000 Hz. This is very encouraging as a low value of the dielectric loss for pyroelectric sensors is necessary in the frequency range at which they are used in an applied environment, which is about 50–300 Hz.

If the sheet resistance of the electrodes can be assumed to be small and negligible, then the capacitance, C, of the device at each frequency is equal to the measured value and can be related to the real permittivity, ε', as given by

$$C = \frac{\varepsilon_o \varepsilon' A}{t}. \tag{4}$$

Parameters ε_o, A and t are the absolute permittivity of free space (8.85×10^{-12} Fm^{-1}), the electrode area of the device and the thickness of the superlattice, respectively. From the equation, the real permittivity, ε' of the device can be calculated at each frequency. The equation $\varepsilon'' = \varepsilon'$ tan δ relates the real permittivity, ε' with the dielectric loss, tan δ, of the device. The parameter ε'', which corresponds to the imaginary permittivity, can therefore be calculated for each frequency investigated.

The maximum loss values are obtained by plotting the real permittivity, ε' and the imaginary permittivity, ε'' against frequency. The values are reported to occur at a frequency of ~5000 Hz [9]. This frequency corresponds to the critical frequency at which $\omega_{\max} = 1/\tau$, where τ is the relaxation time. The calculated value of τ for the device is 3.18×10^{-5} s. This analysis also assumes that the interfacial polarization, that arises due to charges that are not locally bound in atoms, molecules or the structures of solids of the device can be neglected.

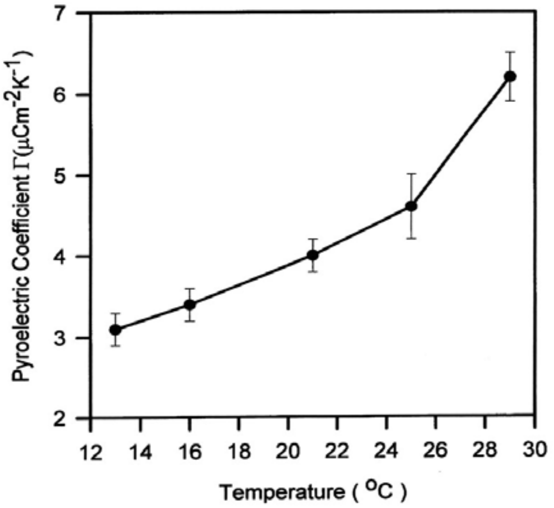

Fig. 2. The temperature dependence of pyroelectric coefficient, Γ of a 31 layer superlattice containing linear copolysiloxane alternating with eicosylamine.

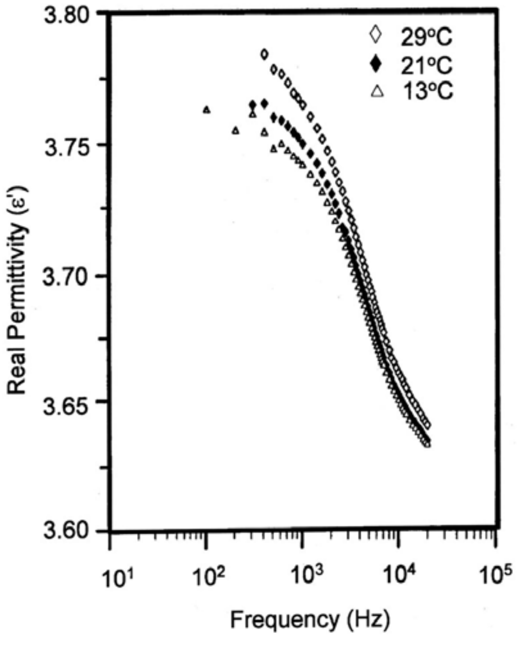

Fig. 3. The frequency dependence of real permittivity (ε') of the 31 layer superlattice containing linear copolysiloxane alternating with eicosylamine.

Figures 3 and 4 show the frequency dependence of the real relative permittivity ε' and the imaginary relative permittivity ε'' of the device measured at 13, 21 and 29 °C, respectively. It appears that the difference in the real permittivity ε' measured at low and high frequencies, which is also called the "strength of the relaxation", is smaller at low temperature (13 °C). As the temperature increases from 13 to 29 °C, the strength of the relaxation increases. The frequency at which the maximum loss value occurs

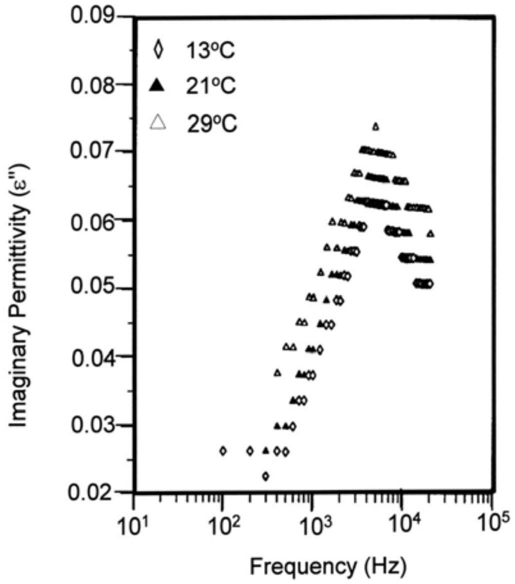

Fig. 4. The frequency dependence of imaginary permittivity (ε') of the 31 layer superlattice containing linear copolysiloxane alternating with eicosylamine.

is unaffected by the increase in the temperature over this range. However, the magnitude of the maximum loss increases with measurement temperature. The ε'' dispersion curves measured at low temperatures also appear broader than those measured at high temperatures.

6 Debye and cole-cole relaxations

Figure 5 shows the curve-fitted Cole-Cole plots of the dispersion curves of the superlattice obtained at various temperatures. From the figure it can be seen that the induced permittivity, ε_∞ (which is obtained by extrapolating the value to the frequency $\omega = \infty$) of the relaxation varies with temperature around 3.57 ± 0.02. Static permittivity of the relaxation, ε_s (which is obtained by extrapolating the value to the frequency $\omega = 0$) increases as the temperature increases. The difference between ε_s and ε_∞ is reflected by the diameter of the Cole-Cole plot semi circle. The difference $\varepsilon_s - \varepsilon_\infty$ corresponds to the orientation polarization that is related to the rotation molecules in the ac field. It appears that $\varepsilon_s - \varepsilon_\infty$ increases with temperature.

The estimated values of ε_s and ε_∞ obtained from the Cole-Cole plot which are derived experimentally are then used to extract ε according to both the Debye and Cole-Cole relaxation theory. It has been found that the Cole-Cole plot obtained experimentally is broad and falls inside the semicircle of the Cole-Cole plot derived from the Debye relaxation theory. The phenomenon is illustrated in Figure 6.

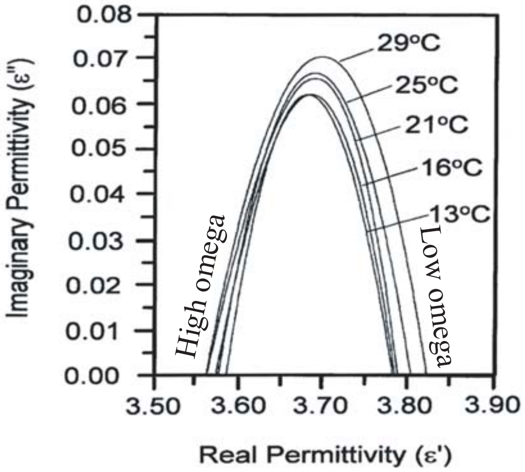

Fig. 5. Cole-Cole plots of the dispersion curves obtained at several temperatures.

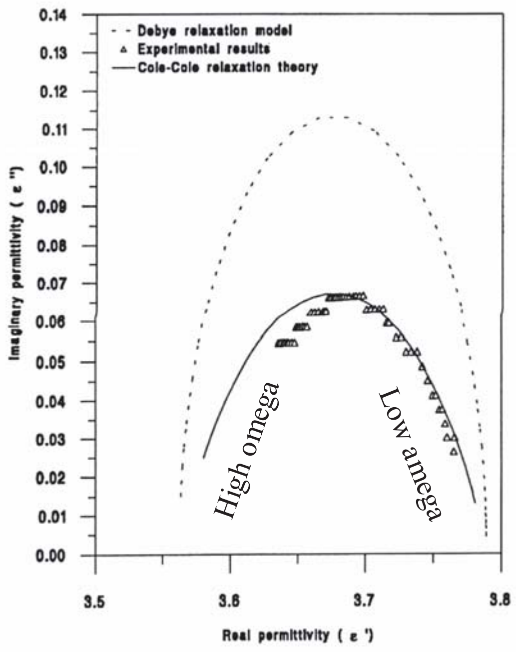

Fig. 6. Cole-Cole plots of the dispersion curves at 21 °C obtained from experiment, Debye relaxation theory and Cole-Cole relaxation theory.

7 Discussion

The Cole-Cole relaxation theory is expressed in equation (3). When $\alpha = 1$, this model should behave like the Debye relaxation model. The ε_s, ε_∞, $\varepsilon_s - \varepsilon_\infty$ which are obtained from the experimental Cole-Cole plots and the α value which is derived from the Cole-Cole relaxation model for the relaxations measured at several temperatures are tabulated in Table 1.

The Debye relaxation model assumes that the interactions between the molecules in the dielectric are negligible. Therefore, there exists only one relaxation time τ.

Table 1. The static permittivity ε_s, induced permittivity ε_∞, $\varepsilon_s - \varepsilon_\infty$ and α parameters obtained from Cole-Cole plots of various temperatures.

Temperature (°C)	ε_s	ε_∞	$\varepsilon_s - \varepsilon_\infty$	α
13	3.78	3.59	0.19	0.71
16	3.79	3.57	0.22	0.69
21	3.79	3.56	0.23	0.68
25	3.81	3.57	0.24	0.64
29	3.82	3.56	0.26	0.63

However, in reality the inter-molecular interactions in dipolar dielectrics are not negligible [7]. The intermolecular interactions in an LB film are expected to be large and certainly not negligible. Consequently, the relaxation process may not be described in terms of the simple Debye equation as demonstrated by our experimental results, where α is found to be less than 1. In this case, the experimental results are better described by the Cole-Cole relaxation theory. The Cole-Cole relaxation theory corresponds to a superposition of a group of Debye processes with a range of dynamically distributed relaxation times about τ. Molecules of long chain polymers such as linear copolysiloxanes are expected to have a much broader relaxation due to the wide range of forces that are required to restrain the orientation of the segmental dipoles. Consequently, the relaxations of such polymers are very broad which results in a large spread of relaxation times.

The parameter α can be used to specify the breadth of the experimental relaxation peaks even though the exact form of the distribution of relaxation times in the Cole-Cole equation is not based on any specific model. The value of α increases with decreasing internal degrees of freedom of the molecules, which leads to weaker intermolecular interactions. As the temperature increases, the molecules obtain more energy to vibrate and therefore the internal degree of freedom of the molecules increases. As a result there are more inter-molecular interactions in the dielectric and hence α is expected to decrease. In our case, the value of α follows this trend. It decreases as the temperature increases. Therefore it shows that the internal degree of freedom of segmental dipoles in the superlattice increases with temperature.

8 Conclusions

The dielectric properties of a superlattice composed of alternating layers of linear copolysiloxane/eicosylamine molecules have been shown to follow the Cole-Cole dielectric relaxation model. This indicates that the inter-molecular interactions in the superlattice are not negligible. The parameter α, which is used to specify the breadth of the experimental relaxation peaks of the superlattice in the Cole-Cole relaxation theory, decreases with temperature suggesting that the internal degree of freedom of the molecules increases. One way of achieving this is by tilting the molecular axes of the superlattice closer to the substrate normal. The pyroelectric coefficient exhibited by the superlattice also increases with temperature. Therefore it can be suggested that the pyroelectric activity of the superlattice depends on the dipolar tilting mechanism. When the temperature increases, the molecular axes of the superlattice tilt closer to the substrate normal. As a result, the change in spontaneous polarization, which is temperature dependent, increases causing a significant increase in the pyroelectric activity of the superlattice.

References

1. R.W. Whatmore, Ferroelectrics **118**, 189 (1991)
2. R. Colbrook, T. Richardson, G.G. Roberts, A. Smallridge, S.G. Davies, Ferroelectrics **118**, 209 (1991)
3. G.W. Smith, M.F. Daniel, J.W. Barton, N. Ratcliffe, Thin Solid Films **132**, 125 (1985)
4. C.A. Jones, M.C. Petty, G.G. Roberts, G. Davies, J. Yarwood, N.M. Ratcliffe, J.W. Barton **155**, 187 (1987)
5. T. Kamata, J. Umemura, T. Takenaka, N. Koizumi, J. Phys. Chem. **95**, 4092 (1991)
6. A.R. Blyth, *Electrical properties of polymer* (Cambridge University Press, New York, 1977)
7. A. Chelkowski, *Dielectric Physics* (Elsevier Scientific Publisher Company, Amsterdam, 1980)
8. T. Richarson, W.H. Abd. Majid, R. Capan, D. Lacey, S. Holder, Supramolecular Science **1**, 39 (1994)
9. W.H. Abd. Majid, T.H. Richardson, *Proceeding of IEEE Conference, Port Dickson, Negeri Sembilan, Malaysia (2001)*
10. C.C. Ku, R. Leipins, *Electrical properties of polymers: chemical principle* (Carl Hansen Verlag, 1987)