

Ferroelectric Langmuir-Blodgett multilayers incorporating metallic cations

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Ferroelectricities in Langmuir-Blodgett (LB) films (Z-type) of arachidic acid (AA) and the effect of incorporating metallic cations on ferroelectricity were investigated by the electric polarization measurements and surface pressure/area isotherms. For Z-type AA LB multilayer and the AA LB films incorporating metallic ions (Ba^{2+} , Mn^{2+} and Mg^{2+}), typical hysteresis loops of the samples were observed and confirmed existence of the remnant polarizations in the LB films. Their corresponding remnant polarizations were found to be 15, 180, 650 and 780 μCm^{-2} , respectively. Therefore, the three maximum ratios of remnant polarizations up to 12 (180/15), 43 (650/15) and 52 (780/15) folds were obtained. The enhancement of ferroelectricity in AA LB films was observed for the first time. It was demonstrated that the enhancement of ferroelectricity in the LB films could be created by incorporation of metallic ions (*ionic transfer mechanism*) into the LB film structures of the samples. These novel approaches can be employed to create strong ferroelectric LB films to make ferroelectric thin-film device for practical applications.

Key words: ferroelectricity, alternate LB films, hysteresis loop, metallic cation

1. INTRODUCTION

Pyroelectric materials are a polar solid and has been taken interested since 1960's. Today it is one of important materials used in infrared detectors.¹ With the development of the devices, the focus point on the materials applied has been transferred from bulk materials to film ones. Ferroelectric material is a kind of pyroelectric materials in which spontaneous polarization can be reversed with the direction change of external electric field. Observation of ferroelectric hysteresis loop could be considered as a criterion for a ferroelectric material.² If we can get ferroelectric hysteresis loop in the material, it suggests that the materials have ferroelectricity and therefore pyroelectricity too.

The Langmuir-Blodgett (LB) film is a well-organized ultrathin molecular film³. Moreover, LB deposition technique can be used to fabricate artificially ordered ultrathin organic molecular films at molecular level (nanometer scale) and the thickness can be controlled precisely. Especially, weak-polar molecules may be organized into well-ordered LB films. Thus, noncentrosymmetric LB films can be fabricated by choosing organic molecules with high performance and

suitable deposition modes, for example, X-, Z-type LB films and the alternate Y-type LB multilayer films. The noncentrosymmetric LB films often show piezoelectric, pyroelectric, ferroelectric, nonlinear optical properties, and so on⁴⁻⁶. A.V. Bune et al. and S. Ducharme et al. investigated the ferroelectric properties of PVDF polymer in LB films^{7, 8}. The hemicyanine dyes (DAEP, polar molecules) and nitrogencrown (NC, weak-polar ones) used by our group were fabricated to Z-type LB films and their ferroelectric hysteresis loops were monitored in the LB films^{9, 10}. It was shown that ferroelectricity might exist in LB films of organic small molecules. However, most of LB films, e.g. PVDF and DAEP molecules, were made of organic molecules with stronger polarity, of which intrinsic dipole moment is found to be ~ 8 D (D is the dipole moment unit—Debye, $1\text{D} = 3.336 \times 10^{-30}\text{Cm}$). To our knowledge, there are few papers available which investigate ferroelectricities in LB films of weak-polar organic molecules incorporating metallic cations and their physical mechanisms. In this paper, weak-polar arachidic acid (AA, the magnitude of its intrinsic dipole

moment is estimated to be 2.0D) molecule was used to fabricate noncentrosymmetric LB films and ones incorporating metallic cations. The ferroelectric properties in these LB films were measured, and the mechanisms associated with the enhancement of the ferroelectricity due to incorporated metal cations (e.g. barium, manganese and magnesium ion) were also discussed.

2. EXPERIMENT

AA ($\text{CH}_3(\text{CH}_2)_{18}\text{COOH}$) was used in this work and it is spectral reagent grade obtained from The First Reagent Plant of Shanghai.

Four LB multilayer samples A, B, C and D were fabricated respectively by a computer-controlled KSV 5000 two-compartment Langmuir troughs (KSV Instrument Ltd, Finland). The AA was spread from chloroform solutions onto the aqueous subphase in two separate compartments of the Langmuir trough. The subphase was doubly distilled, de-ionized water at 20°C with pH value 5.5-6.0. The substrates were glass plates coated with a hydrophilic indium-tin-oxide (ITO) layer as the grounded lower electrode. Samples A, B, C and D used in this work are: AA Z-type LB multilayer films as well as AA Z-type LB multilayer films incorporating barium, manganese and magnesium ions (barium chloride, manganese chloride and magnesium chloride was added in the subphase at the concentration of 10^{-4} mole $^{-1}$), respectively. The multilayers were deposited during upstrokes and/or downstrokes at a constant pressure of 28mNm $^{-1}$. In the experiments, the upstroke speed was 5mm/min and downstroke speed was 3 mm/min. The transfer ratio ($\text{TR} = 1 \pm 0.05$) could be displayed and recorded automatically by a computer during deposition. After deposition of the LB films, an aluminum layer of 50 nm thickness and 3.14 mm 2 area were then coated on top of the films as the upper electrode to form sandwich structures (capacitors) in order to measure the ferroelectric properties in all of the samples.

The ferroelectric hysteresis loops of the samples were recorded on a RT66A standard ferroelectric instrument (Radiant Technologies, Inc., United States). The current generated in the sample was recorded by applying voltages of reversal directions and different magnitudes between the upper and lower electrode of the sample, which eliminates the effect of standard capacitance used in Sawyer-Tower measurement circuits on the sample capacitance. Thus, "the false ferroelectric hysteresis loop" arising from thermal effect and/or lower resistivity could be removed to ensure the accuracy of the measurements.

3. RESULTS AND DISCUSSION

Ferroelectrics is observed in a pyroelectric material, whose spontaneous polarization reverses direction with

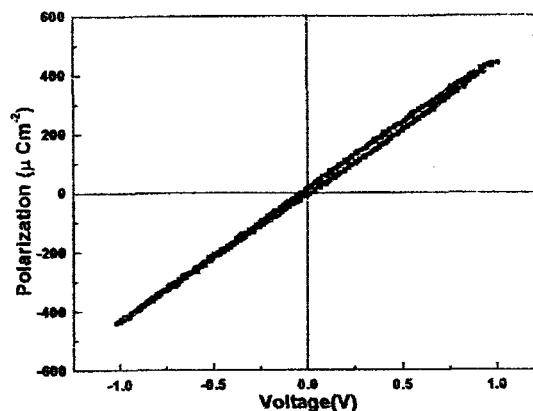


Figure 1. Hysteresis loop of polarization in a Z-type AA LB film (14 layers).

the reversal of external electric field. The measured electric polarization P versus the applied external electric field E shows a typical ferroelectric hysteresis feature. The typical hysteresis loops of the samples observed confirmed that the ferroelectric properties exist in the

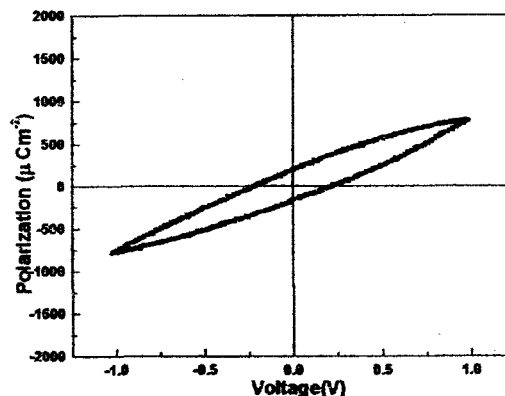


Figure 2. Hysteresis loop of polarization in a Z-type AA LB film (14 layers) incorporating Ba $^{2+}$ ions.

samples. LB films are a well-organized organic ultrathin molecular film. The spontaneous polarization of an organic LB film is firmly built into the organized molecular monolayers and/or multilayers structure without requirement of poling, if organic polar materials are used in LB films 9 . Spontaneous polarization of the LB film mainly depends on the reorientation of molecular dipole moment and charge transfer due to electron or ion displacement 11 . The macroscopic electric polarizations of the ferroelectric materials will vary with changes in ambient surroundings (e.g. temperature, external electric field, etc.) so that the materials exhibit pyroelectric and ferroelectric properties. The ferroelectric hysteresis loops of samples A, B, C and D were measured. The results indicated that the ferroelectric hysteresis effects exist in samples A, B, C and D, as shown in Figure 1, Figure 2,

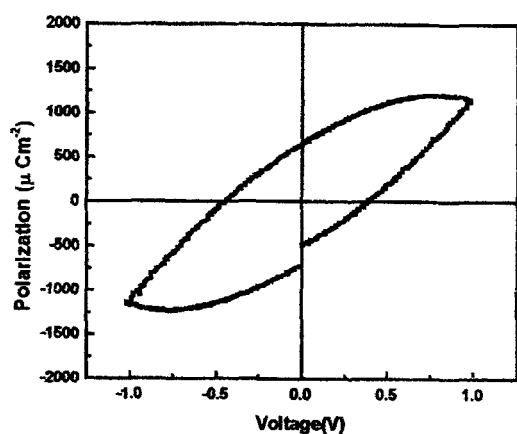


Figure 3. Hysteresis loop of polarization in a Z-type AA LB film (14 layers) incorporating Mn^{2+} ions.

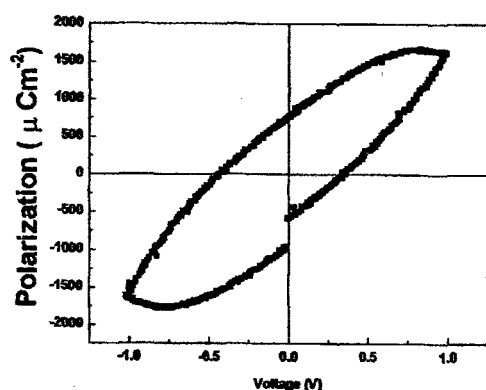


Figure 4. Hysteresis loop of polarization in a Z-type AA LB film (14 layers) incorporating Mg^{2+} ions.

Figure 3 and Figure 4, respectively. We found that ferroelectric hysteresis effect was barely observed in sample A (Figure 1) because the value of remnant polarization is too small (only $15 \mu\text{C m}^{-2}$).

Sample B, C and D, consist of the same molecule AA and fourteen monolayers, similar to sample A, the only difference is that Ba^{2+} , Mn^{2+} and Mg^{2+} ions are incorporated into sample B, C and D, respectively. Their remnant polarizations were found to be 15, 180, 650 and $780 \mu\text{C m}^{-2}$, (Figure 1, 2, 3 and 4). The results indicated that the ferroelectric property is too weak in sample A and strong in sample B, C and D. Since AA molecule is weak-polar organic molecule leading to weaker spontaneous polarization in AA Z-type films, the typical ferroelectric hysteresis loop could be barely observed in sample A (Figure 1). However, after Ba^{2+} , Mn^{2+} and Mg^{2+} ions were incorporated into AA Z-type films, protons transfer occurs between arachidic acid molecules and Ba^{2+} , Mn^{2+} or Mg^{2+} ions. Namely, two protons in AA molecule were substituted by one Ba^{2+} , Mn^{2+} and Mg^{2+} ion, so that arachidic salts were formed in LB films¹². Therefore, the dipole moments of arachidic salt

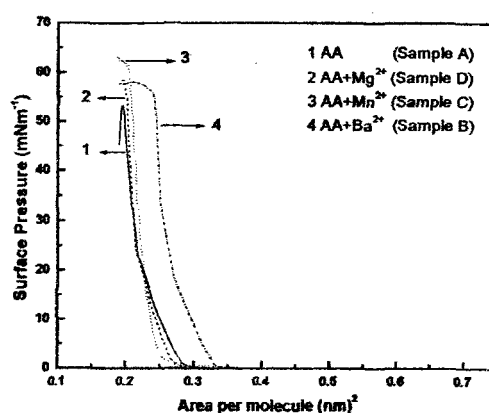


Figure 5. Surface pressure-molecular area isotherms.

molecules in the LB film could be significantly changed due to the difference of ionic transfer (charges transfer) between the metallic cations originated from the size of ion-radius ($\text{Mg}^{2+} < \text{Mn}^{2+} < \text{Ba}^{2+}$) or the different ionization energy ($\text{Mg}^{2+} > \text{Mn}^{2+} > \text{Ba}^{2+}$) and the molecular spontaneous polarization of sample B, C and D were enhanced subsequently. Thus, the remnant polarization could be enhanced by up to 12 (180/15), 43 (650/15) and 52 (780/15) folds after Ba^{2+} , Mn^{2+} and Mg^{2+} ions were incorporated into the LB film with changing an external electric field (as shown in Fig 2, 3 and 4). It was shown that the enhancement of ferroelectric properties actually exists in sample B, C and D due to metallic (barium, manganese and magnesium) ions incorporated into the LB films.

On the other hand, the occupied molecular area was also changed when Ba^{2+} , Mn^{2+} and Mg^{2+} ions were incorporated into AA Z-type films (given in Figure 5). The result showed that the molecular area occupied by sample B, C and D increased, as compared to that of sample A. The decrease of occupied molecular area stem from the increase of molecular dipole moment per unit volume, which consequently enhance molecular spontaneous polarization of sample and in turn reduce the polarization. For the sample incorporating metallic ions, the molecular spontaneous polarization relies on a trade-off between the protons transfer and change of occupied molecular area. It is suggested that, for sample B, C and D, only the former (protons transfer) dominated and then resulted in enhancement of remnant polarization. However, as shown in surface pressure-molecular area isotherms (Figure 5), for sample D, the enhancement of occupied molecular area was the smallest; for sample C middle and for sample B the largest. Thus the decrease of molecular dipole moment per unit volume of sample D was the smallest so that its remnant polarization was the largest, as mentioned above. Based on the same reason, one could understand that the remnant polarization of sample C was larger and that of sample B the smallest.

Table I summarizes the observed ferroelectric experimental results of sample A, B, C, D and their respective remnant polarization. By comparing sample A, B, C and D, we found that their corresponding remnant polarizations were enhanced by up to 12, 43 and 52 folds correspondingly, while incorporating barium, manganese and magnesium ions into AA LB multilayer films. This observation suggested that charge transfer (proton transfer) effect of metallic ions incorporated in the LB films plays an important role in enhancing the spontaneous polarization of LB films.

Table I. The observed ferroelectric results and value of remnant polarization

Sample	Materials	LB film type	Ferroelectric hysteresis loop	Remnant polarization P_r ($\mu\text{C m}^{-2}$)
A	AA	Z	✓	15 ± 2
B	AA Ba ²⁺	Z	✓	180 ± 10
C	AA Mn ²⁺	Z	✓	650 ± 20
D	AA Mg ²⁺	Z	✓	780 ± 20

4. CONCLUSIONS

In summary, we have for the first time measured the enhancement of ferroelectricity, found in AA LB multilayer films incorporating metallic cations. The analyses mentioned above demonstrate that there are several approaches to obtain stronger ferroelectric LB films: (i) to choose organic molecules with strong polarity⁹, (ii) to incorporate metallic ions (such as Ba²⁺, Mn²⁺ and Mg²⁺ ions, etc.) into the LB films using ions transfer (charges transfer) to enhance the polarity of material molecules and to increase the spontaneous polarization. The ferroelectric LB films with enhanced performance can be fabricated by means of LB deposition techniques to satisfy the requirement for manufacturing practical ferroelectric thin film devices.

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