Measurement of flexoelectric coefficient in the relaxor ferroelectric terpolymer Poly(vinylidene-trifluoroethylene-chlorofluoroethylene)

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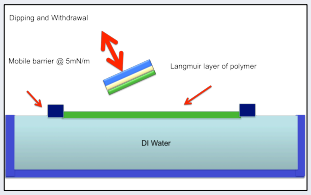
INTRODUCTION

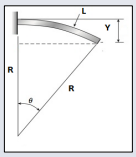
- The conventional electromechanical phenomenon, piezoelectricity has been widely studied in ferroelectrics.
- There is also an unconventional electromechanical phenomenon known as flexoelectricity where the strain gradient effects the polarization in a way similar to an applied electric field. [1,2]
- The flexoelectric coupling between strain gradient and electrical polarization is present in all materials. In piezoelectric materials, however, separation of piezoelectric and flexoelectric signal is a major challenge, because the piezoelectric signal dominates the measurements.
- The goal of this work is to develop an approach to measuring the **flexoelectric coefficient μ**, which is a measure of the polarization induced for a given strain gradient in piezoelectric materials. A phenomenological estimate [3] of the flexoelectric coefficient for crystalline dielectrics is given as the ratio of the electric charge to the lattice constant (e/a), which is of the order of 10^{-10} C/m. [3]
- We report a study of the flexoelectric effect in ferroelectric copolymer of vinylidene fluoride and trifluoroethylene, P(VDF-TrFE) and a relaxor terpolymer variant containing chlorotrifluoroethylene, P(VDF-TrFE-CFE). [4]

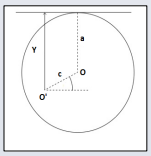
EXPERIMENTAL APPROACH

- Langmuir–Blodgett films of the ferroelectric co-polymer PVDF-TrFE (70:30) [5] and terpolymer P(VDF-TrFE-CFE) (55.8:35:9.2) were fabricated using the horizontal Schaeffer technique.
- The Langmuir layer was dispersed on a sub phase of ultra pure water using di-methyl sulfoxide as solvent for the copolymer and dimethylformamide for the terpolymer.

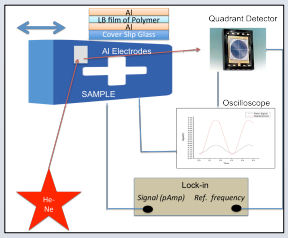


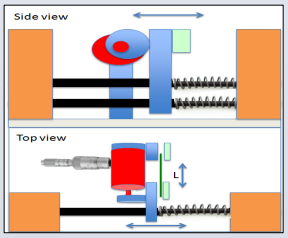
- Films were then deposited at the constant surface pressure of 5 mN/m by touching the cover slip substrate having evaporated Al electrodes to the surface of ultrapure water.
- Film thickness was controlled by number of deposition steps. After that the copolymer sample was annealed at 135°C and the terpolymer sample sample at 135 °C for 90 minutes and allowed to cool at 0.5 °C/minute.





- In order to generate strain, the sample was treated as a cantilever under a load.
- The sample was clamped at both ends one held rigidly and the other allowed to vibrate periodically by a dc motor and camshaft arrangement producing sinusoidal oscillations of one cantilever end.



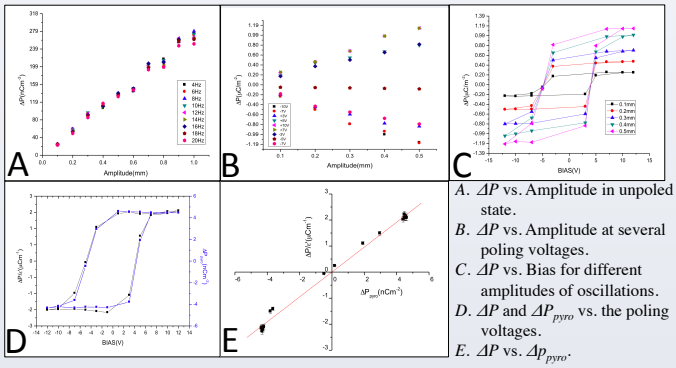


- The amplitude was varied by changing the off-center distance c of the cam head. The displacement was monitored by reflecting a He-Ne laser from the sample onto a quadrant photodetector.
- A lock-in amplifier locked was used to measure the current as a function of amplitude and frequency.

RESULTS AND DISCUSSIONS

- The change in film polarization due to the piezoelectric and flexoelectric effect is: $\Delta P_p = d\gamma\varepsilon$ and $\Delta P_f = \mu\varepsilon'$ where P is polarization, d is the piezoelectric coefficient, γ is the Young's modulus of the polymer, μ is the flexoelectric coefficient, ε is the strain and ε' is the strain gradient.
- In case of the ferroelectric copolymer the polarization state was measured by a pyroelectric method in the as grown unpoled state as well as after poling at different voltages (D, E). (The pyroelectric response is proportional to polarization.) The net polarization change in the sample is: $\Delta P = (\varkappa P_r + \mu)\varepsilon'$ where $\varkappa$ is a constant and P_r is the remnant polarization. The intercept of the ΔP vs. ΔP_{pyro} graph (E) gives an upper limit for μ.

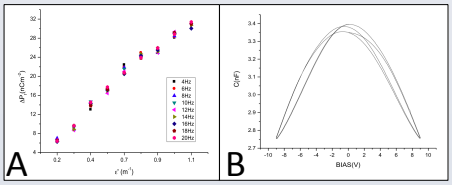
RESULTS FOR THE FERROELECTRIC COPOLYMER P(VDF-TrFE)



A. ΔP vs. Amplitude in unpoled state.
B. ΔP vs. Amplitude at several poling voltages.
C. ΔP vs. Bias for different amplitudes of oscillations.
D. ΔP and ΔP_{pyro} vs. the poling voltages.
E. ΔP vs. Δp_{pyro}.

RESULTS FOR RELAXOR FERROELECTRIC TERPOLYMER P(VDF-TrFE-CFE)

- The terpolymer has negligible piezoelectric contribution. The slope of the graph of ΔP_f vs ε' (A) gives the flexoelectric coefficient μ.



A. ΔP_f vs. ε'
B. Capacitance vs. Voltage

CONCLUSIONS

- Due to the large contribution of the piezoelectric effect we could only put an upper limit on the flexoelectric coefficient $\mu < 4.7 \pm 0.2$ nC/m for the ferroelectric copolymer.
- In addition, we have measured the flexoelectric coefficient μ of relaxor terpolymer as 30 ± 1.5 nC/m.
- We plan to investigate the temperature dependence of flexoelectric effect in a future work.

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