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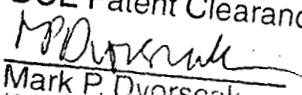
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FINAL REPORT FOR JULY 2001-JUNE 2005
TITLE: NANOSCALE STRUCTURAL ENGINEERING OF FERROELECTRIC POLYMERS

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This proposal is based on unique two-dimensional films of PVDF and its copolymers with trifluoroethylene, P (VDF-TrFE). which have been made here at the University of Nebraska-Lincoln. The films are made by Langmuir-Blodgett (LB) deposition, which affords precise control of thickness from 0.5 nm (one monolayer) to hundreds of nm. The monolayers form excellent crystals. The stated goals of this proposal were to elucidate the correlation between the electrical and structural characteristics of these thin films as well as to make and characterize multilayers and composites.

[A]We have successfully made and characterized the interactions in the following set of multilayers and composites

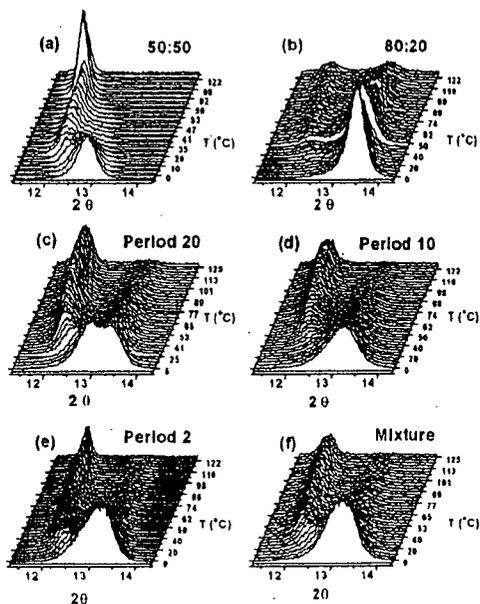| Ferroelectric (A)	Ferroelectric (B)	STRUCTURE OF MULTILAYER	NAME OF SAMPLE
PVDF(80%) -TrFe (20%)	PVDF(50%)- TrFe (50%)	$A_{10}B_{10}$-Sample1 $[A_5B_5]_2$ Sample2 $[A_1B_1]_{10}$ Sample3	Period 20 Period 10 Period 2
50% mixture of A and B spread on LB trough		$[A(50\%)B(50\%]_{20}$	Mixture

Figure 1. X-ray diffraction data at a variety of temperatures on heating and cooling. The coexistence of the ferroelectric and paraelectric phases is clearly visible.

Our goal in fabricating the set of samples is to look for the interaction between multilayered samples . Interaction effects will be manifested by a change in the transition temperatures of the multilayer samples, where the transition temperature will now occur at a temperature in between those of the individual constituents of the layers. The copolymer ratios were chosen so as to have the largest disparity in transition temperatures while still retaining good crystallinity. The 80/20 copolymer has a transition temperature above 130°C, whereas the 50/50 transition temperature is close to 60°C.

We have made a careful series of runs with the set of samples as well as comparison samples of pure 80/20 and pure 50/50. We investigate the transition temperature using x-ray diffraction at the Advanced Photon Source using closely spaced temperature steps over the range –5 °C to 125 °C, at temperature intervals of 5 °C far from the phase transition temperature, and 3 °C near it. The paraelectric phase and the ferroelectric phase of the copolymers have different lattice spacings, and we track the transition temperature by

watching the evolution of the two diffraction peaks with temperature. This is clearly shown in Fig. 1, which shows the evolution of the two peaks in all samples on heating. At low temperatures, only the higher angle ferroelectric peak is present, whereas at high temperatures, one sees only the paraelectric peak in most samples. At temperatures between these two extremes, there is a coexistence of the phases. The transition width of these samples is large and x-ray diffraction provides valuable insight into the amount of material undergoing a phase transition. In order to study the nature of the interaction in more detail, we use the following procedure. The integrated intensity of the x-ray diffraction peaks is proportional to the amount of material in that particular phase. We fit the peaks to a Lorentzian with a background subtraction, taking particular care in the coexistence region to fit to overlapping peaks. We plot the integrated normalized intensity of the higher angle ferroelectric peak and the lower angle paraelectric peak as a function of temperature(fig. 2). Clearly, the 80/20 sample never converts fully into the paraelectric phase. The thermodynamic critical temperatures of all samples are tabulated in Table 1. We define the thermodynamic critical temperatures as follows: the temperature T_0 is the temperature at which the paraelectric phase first appears as the sample is heated, the upper critical temperature T_1 is the final appearance of the ferroelectric phase. Thus, the critical temperatures were determined by extrapolating the XRD peak intensity data in Fig. 6; T_0 by extrapolating the paraelectric peak intensity to zero, and T_1 by extrapolating the ferroelectric peak intensity to zero.

Figure 2. The integrated area under the ferroelectric and paraelectric x-ray peaks for the 50/50, the 80/20 and the $[A_5B_5]_2$ samples on heating. The crossover point at which the integrated intensities are equal is chosen as the transition temperature. Clearly the 80/20 sample has a transition temperature above 135°C

The critical temperatures of the 50:50 sample, extrapolated by this method are very clearly defined and give values of T_0 and T_1 of 9 ± 1 °C and 85 ± 8 °C. This is because the transition region is fairly narrow and the critical temperature is low. However, the gradual transition of the 80:20 sample together with the high value of Tc, lead to great uncertainty in the values of T_0 and T_1. At the highest temperature of 120°C, a mere 50% of the material has undergone the transition, whereas at the lowest temperature of –27C, the paraelectric peak is already present. Over the temperature range we have, we are not able to even define a T_1 for the 80:20 sample.

The period 20 sample has two resolvable ferroelectric peaks as expected due to its sample structure. We fit the data to two ferroelectric peaks as well as a single paraelectric peak to obtain the date shown in figure 6. If we model it as two separate non interacting films of 80:20 and 50:50 and take the arithmetic mean of the two pure copolymer samples' peak intensities, we obtain $T_0 = 2.5\pm3$°C, $T_1 = 265\pm35$°C, and $T_{1/2} = 63\pm3$°C. The measured values from the Period 20 sample are $T_0 = 30\pm5$°C, $T_1 = 170\pm8$°C, and $T_{1/2} = 57\pm6$°C. At first glance this discrepancy may lead us to the conclusion that in fact this period 20 sample does show evidence of interaction,
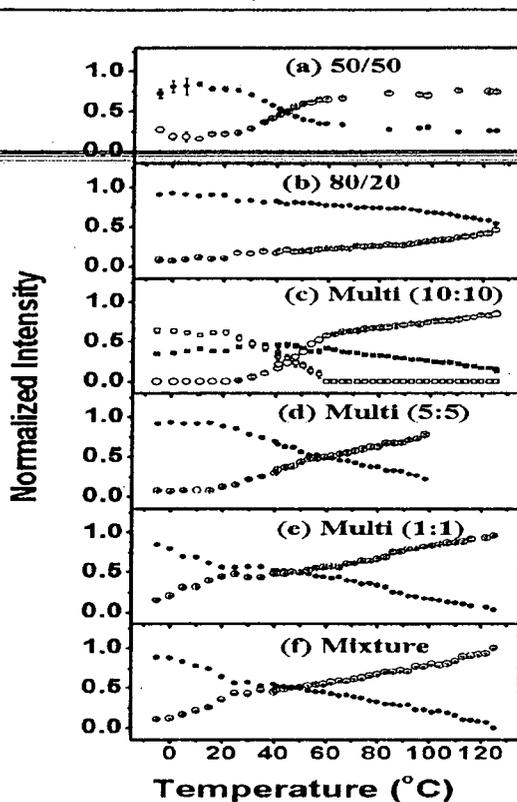
leading to a higher T_0 and a much lower T_1. However, the peak intensities of the Period-20 sample are heavily weighted by the contribution of the higher crystallinity 50:50 material(evident in figure 3). This weighting is likely to result in a lower T_1 and higher T_0, closer to the values of the 50:50 sample, compared to the model in which we assumed equal weighting of the peaks from each material. Under these circumstances, we have no unambiguous evidence of interactions in the period 20 sample.

The transition temperatures shown in table 1 indicate that for the period10 sample, T_0 is close to that of the all 50:50 sample, whereas for the Period 2 and mixture sample, To is lower, and in-between that of the 50:50 and 80:20 copolymers. T_1 for all three samples is approximately the same, and well above that for 50:50. The phase transition region is much wider than for the 50:50 sample, but clearly lower than that of the 80:20 sample. The behavior of the transition temperature is strong evidence for interlayer coupling; the ferroelectric-to-paraelectric phase transition in these films is strongly influenced by the proximity of the 80;20 and 50:50 copolymers, leading to a behavior intermediate to that of the pure samples. Although we do not have enough quantitative information to extract an exact interaction length, we see that as the number of interfaces increase in going from the period 10 to period 2 sample, T_0 drops quite dramatically. Another clue to the interaction comes from looking at the rate of passage through the transition as a function of temperature. In the pure copolymer samples [see Fig 6 (a, b)], we see that at lower temperatures (below 80C) the transition rate of 50:50 is faster than 80:20, whereas the situation is reversed at higher temperatures (above 60C) . The period-20 sample in Fig. 6(c), clearly shows evidence of this behavior-the two independent ferroelectric peaks track the transition rates of the all 50:50 and all 80:20 samples respectively. The Period-10, Period-2, and the Mixture samples in Fig. (d,e,c) however, do not show evidence of this reversal—in all three samples the transition rates are almost constant over the whole temperature range, yet more evidence of interactive behavior.

	Transition Temperature			
	Synchrotron XRD			Capacitance
	$T_0(°C)$	$T_1(°C)$	$T_{1/2}(°C)$	$T_{c+}(°C)$
50:50	9±1	85±8	43±2	70±4
80:20	-40 ↓	-	138±12	133±4
Period20	30±5	170±8	57±6	97±20
Period10	9±4	134±8	60±6	101±11
Period2	-18±1	128±10	35±15	114±5
Mixture	-14±1	131±1	49±3	105±6

The observations made on the Period-10, the Period-2, and the Mixture sample above give us insight into the interaction between the two ferroelectric copolymers over a wide temperature range. We note that the lower transition temperature, T_0, and the higher transition temperature T_1 occur in two different regimes. At and below T_0 the samples are all fully ferroelectric. Hence all the interactions occur between ferroelectric phases of the 50:50 and 80:20 material.
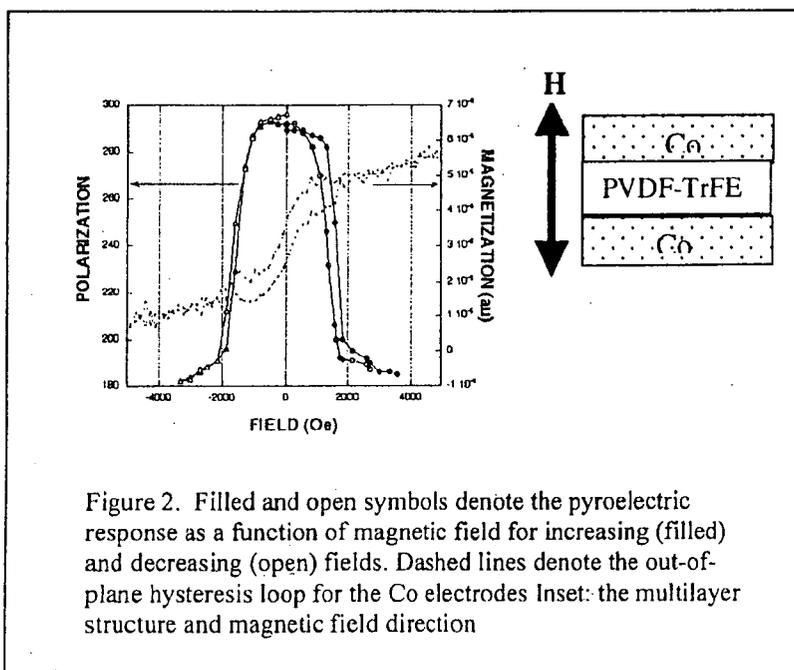
Between T_0 and T_1, there exists a heterogeneous mixture of ferroelectric and paraelectric phases. In this regime, one can envisage an interaction driven by the polarization of the ferroelectric phase on the paraelectric phase, thereby increasing T_1 and/or changing the transition rate as compared to the pure samples.

In this scenario, the values of T_0 and T_1 for the period-10, period-2 and mixture samples can be described as follows. For the period-10 sample, the value of $T_0 = 9±4°C$ is close to that

of the model describing the arithmetic mean of the intensities of the 80:20 and 50:50 sample ($T_0 = 2.5\pm3^\circ$C). This indicates that in the all ferroelectric phase, there is little or no interaction in the period-10 sample. The much lower T_0s of the Period-2 and the Mixture samples is a strong indication of the existence of interaction in these samples in the ferroelectric phase. The Period-10, the Period-2, and the Mixture have similar transition rates over the entire transition region with the peak intensities changing at approximately $0.008\pm0.002(^\circ C)^{-1}$. This could be interpreted as evidence that in this mixed paraelectric-ferroelectric phase region, the interaction has a fairly long length scale and is insensitive to the shorter period. However, the fact that the structural information of the samples when they are heterogeneous is not confirmed should not be overlooked. In order to be conclusive, further structural studies of these multilayer samples is necessary.

[B] Interactions between ferroelectric and ferromagnetic films

Our most recent experiments measure the magneto electric coupling of a thin multi-layer film sandwich of ferromagnetic Cobalt (300 Å)/ferroelectric PVDF/TrFE (75 nm)/ ferromagnetic Cobalt (130 Å), revealing an unexpectedly large effect. The sputtered magnetic and LB deposited ferroelectric layers of the samples have been carefully characterized using the Magneto- Optical Kerr Effect (MOKE) and the pyroelectric response, respectively. In order to avoid inclusion of Co in the PVDF, thin films of Al (2 nm thick) were deposited directly above the ferroelectric, forming a barrier between the PVDF-TrFE and the Co. The out-of-plane magnetic hysteresis loops of the cobalt are typical magnetic hard-axis loops. After electrical saturation, the pyroelectric response is measured as a function of perpendicular magnetic field shown in figure 1. Large magneto-electric coupling is observed, with the pyroelectric response decreasing by ~30% on application of a 2 kG field, an unexpectedly large effect. All measurements were made at room temperature.

Figure 2. Filled and open symbols denote the pyroelectric response as a function of magnetic field for increasing (filled) and decreasing (open) fields. Dashed lines denote the out-of-plane hysteresis loop for the Co electrodes Inset: the multilayer structure and magnetic field direction

We emphasize that this is not a magnetic poling effect in which the structure of the film is irreversibly changed by the application of a magnetic field; rather it is a fully *reversible* change of the polarization as can be seen in the increasing and decreasing field sweeps (aside from a small hysteresis). The effect is symmetrical with respect to positive and negative field. The polarization changes most rapidly in the region where the hysteresis loop is open, compatible with what one would expect from magnetostrictive effects. In the configuration shown, the ferroelectric is essentially unclamped, (i.e. in constant stress) in the out-of-plane direction; hence out-of-plane magnetostriction should have essentially no effect on the electrical properties via the piezoelectric coefficient. Careful calculations indicate that effect of in-plane magnetostriction is many orders of magnitude too small to account for ~ 30% change in the polarization.

<u>Future Experiments</u>: The ability to *substantially* change the electrical polarization with a magnetic field opens a wide arena of possibilities, but a number of questions need to be answered. How is the effect related to the magnetization, magnetostriction coefficients, and magnetic orientation of the electrodes? Is the reduction in polarization solely due to a rotation of the ~~polarization into the plane of the sample or are up and down ferroelectric domains formed? If so,~~ what happens to the structure of the ferroelectric? In order to investigate the underlying mechanism, we plan to explore this phenomenon using different FM materials (hard and soft), with differing easy axes (in-plane and out of plane), differing magnetostrictions (Co vs. Permalloy), with different combinations of top and bottom electrodes and study the effect of magnetic fields using the pyroelectric effect as well as x-rays to look at the structural changes. The structure of these long chain highly anisotropic molecules dictate that a rotation in the polarization be accompanied by a change in the lattice parameter , which should be easily visible in x-ray diffraction experiments.

CONFERENCE PRESENTATIONS

1. Phase Transition of Multi-layered Ferroelectric Copolymer Thin Films
2003 APS March at Austin

2. EMF 2003 (The 10th European Meeting on Ferroelectricity) at Cambridge, England" Study of Interactions between Poly(vinylidene fluoride-trifluoroethylene) copolymers in Multilayered Copolymer LB Thin" Films

3. Magneto-electric coupling in ferromagnetic Cobalt/ferroelectric P(VDF-TRFE) multilayer thin films, Poster presentation at the MRS Fall meeting Nov 2005 Boston.

PAPERS

1. The Effect of Interlayer Interactions on the Ferroelectric-Paraelectric Phase Transition in Multilayered Thin Films of Vinylidene Fluoride-Trifluoroethylene Copolymers, JK Kim[1], Hoydoo You[2], Stephen Ducharme[1], S. Adenwalla[1] to be submitted to Phys. Rev B.

2. Magnetoelectric coupling in ferromagnetic cobalt /ferroelectric copolymer ultra-thin multilayer films, Mengjun Bai, Marucs Natta, Andrew Baruth, Krintin Kraemer, Stephen Ducharme, S. Adenwalla· in preparation.