1. Project Progress

In the second year, we have focused on electrostriction in poly(ether-b-amide) (PEBAX) multiblock copolymers to understand the fundamental physics of electrostriction in ferroelectric polymers. From the constitutive equation for electrostriction, we get:

\[ S_3 = s_3T_{33} + Q_{31}E_3^2 \]  \hspace{1cm} (1)

where \( S_3 \) is the electric field-induced strain along 3 (i.e., stretching) direction, \( s_3 \) is the compliance along the 1 direction, \( T_{33} \) is the stress along the 1 direction, \( Q_{31} \) is the electrostriction coefficient, and \( E_3 \) is the polarization along the 3 direction. Here, piezoelectric effect from spontaneous polarization is ignored, because our uniaxially stretched PEBAX film does not have any remanent polarization. From this equation, the first term is the contribution from Maxwell pressure and the second term is the contribution from electrostriction. \( T_{33} \) is induced by the Maxwell pressure \( T_{33} = D_3^2/\varepsilon_0 \varepsilon_r \), where \( D_3 \) is electric displacement along the 3 direction. Note, \( D_3 = P_3 + \varepsilon_0 E_3 \), where \( \varepsilon_0 \) is the vacuum permittivity and \( E_3 \) is the electric field along the 3 direction. The Maxwell contribution should mostly originate from the actuation of soft amorphous phase in PEBAX, whereas the electrostriction should originate from the actuation of the crystalline nylon-12 phase.

![Stress-strain curve](image1.png)

**Fig. 1.** (A) Stress-strain curve for quenched (Q) P7033 sample. (B) Corresponding 2D WAXD patterns during in-situ uniaxial stretching of Q P7033 at room temperature. The stretching direction is vertical.

**Fig. 1A** shows the stress-strain curve for the P7033 PEBAX sample with 25 mol.% poly(tetramethylene oxide) (PTMO) at room temperature. The in-situ two-dimensional (2D) wide-angle X-ray diffraction (WAXD) patterns at different stretching ratios are shown in **Fig. 1B**. Beyond 300% stretching ratio, obvious crystal orientation from nylon-12 blocks is observed. At 600% stretching ratio, crystals are highly oriented with the chains along the stretching direction.

The electrostriction study is carried out by simultaneous measurements of electric displacement-electric field (D-E) and \( S_1-E \) loops, as shown in **Fig. 2.** At room temperature, D-E loop shows certain ferroelectric hysteresis (**Fig. 2A**). As a result, the \( S_1-E \) loops also show broad loops (**Fig. 2B**). Different from poly(vinylidene fluoride) (PVDF)-based terpolymers, this PEBAX sample exhibits negative electrostriction. Namely, upon apply electric film to the film normal direction, the quench and stretched (QS) P7033 film shrinks, rather than expands. When the temperature increases to 75 °C, which is above the glass transition temperature \( T_g \sim 45 \) °C of the nylon-12 blocks, broad D-E loops are seen in **Fig. 2C**. After subtraction of the AC electronic conduction (the blue horizontal loop), relatively narrow double hysteresis loops are seen with an apparent dielectric constant of 38. The corresponding \( S_1-E \) loops become much narrower (**Fig. 2D**). Again, negative \( S_1 \) is observed, indicating shrinking of the QS P7033 film, and a 0.4% strain is achieved. It is interesting to see that when the electric field is >160 MV/m, certain saturation in \( S_1 \) is reached.
Simultaneous measurements of (A,C) two continuous bipolar D-E and (B,D) longitudinal strain (S$_1$) loops for the QS700% P7033 sample at 200 MV/m at (A,B) room temperature and (C,D) 75 °C, respectively. For D-E loops, subtraction of AC electronic conduction (shown as the blue horizontal loops) from the experimental data (black loops) results in neat ferroelectric loops (red loops).

Fig. 2. Schematic models of (A) crystalline phase and (B) amorphous phase in uniaxially stretched PEBAX films upon the application of a high electric field. The stretching direction is vertical and the electric field is along the normal direction (the blue arrow) of the stretched film. Small red arrows represent the amide groups.

The negative S$_1$ electrostriction in QS P7033 can be understood using the proposed mechanism in Fig. 3. First, nylon-12 crystals contain antiferroelectric arrangement of amide dipoles. Upon electric poling, every other dipoles are twisted to orient in a parallel mode. As a result of twisted chain conformation, the crystal will shrink in the chain direction (Fig. 3A). Meanwhile, there is also Maxwell pressure, primarily squeezing the random amorphous phase, which include both amorphous nylon-12 and PTMO to elongate the sample (Fig. 3B). Under high enough poling electric field, the Maxwell elongation overwhelms the nylon-12 crystal shrinking, a saturation of shrinking S$_1$ is obtained.

2. Program Impact
This project has initiated a new direction of the PI’s research in the fields of electromechanical actuation, which results in a grant application to NSF. A visiting PhD student has been working on the project and trained for scientific research.

3. Publications