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Investigation of Ferroelectricity in Poly(methyl vinylidene cyanide)

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The ferroelectric and piezoelectric properties of newly synthesized polymer systems have been studied. To date PVDF and its copolymers P(VDF-TrFE) have provided the bulk of the knowledge pertaining to ferroelectricity in polymers. Recently, ultrathin ferroelectric films of P(VDF-TrFE) 70:30 have been fabricated using the Langmuir-Blodgett technique [4]. In this study, various new polymers have been synthesized by chemically altering the PVDF structure. This alteration was performed in order to enhance the amphiphilic nature of the polymer and thus improve the LB film quality and control. Various chemical groups have been used to replace the electropositive hydrogen and electronegative fluorine found in the traditional PVDF chemical structure, including Nitrile, Ester, and Methyl groups. In all cases the resulting chemical structure provides for a net dipole moment directed from the electronegative side of the monomer to the electropositive side. However, to obtain ferroelectricity these microscopic dipoles must first pack in a manner such that a reversible macroscopic dipole is obtained. Both structural and dielectric studies have been performed on a number of newly synthesized systems. The structural properties of these new materials were probed using both temperature-dependent x-ray diffraction and differential scanning calorimetry, while dielectric properties were investigated using electric field and temperature-dependent capacitance and polarization measurements.

Keywords: ferroelectricity; polymer; Langmuir-Blodgett

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1. INTRODUCTION

Ferroelectricity has been observed in a relatively small number of crystalline polymers [1]. By far the most widely studied is polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (TrFE), tetrafluoroethylene (TeFE), and other units [2]. Ferroelectricity has long been studied in both solvent-cast and spin-coated films of PVDF and P(VDF-TrFE) [1, 2]. The application of the Langmuir-Blodgett (LB) method to the fabrication of films of P(VDF-TrFE) [3] has produced highly crystalline, oriented ferroelectric films as thin as a nanometer [4]. Encouraged by the relative simplicity of making ferroelectric polymer films by LB deposition, we have begun work on a series of similar potentially ferroelectric polymers. For the present study several new polymer systems have been synthesized by replacing the electropositive hydrogen and the electronegative fluorine with various chemical groups such as nitrile, ester, and methyl groups, thus maintaining the key feature leading to ferroelectricity, a net dipole moment perpendicular to the polymer backbone. While these groups do somewhat change the structure of the polymer the nonconjugated C-C backbone and the long cylindrical shape of the molecules is maintained. However, for ferroelectricity to exist in these newly synthesized materials the packing of chains must result in a polar crystal structure that possesses a reversible polarization. Here we report the initial results from a study of the structural, dielectric, and possibly ferroelectric properties of one of these new polymers. The most promising candidate to date is poly(methyl vinylidene cyanide) or PMVC, which exhibits excellent crystallinity in powder and cast film form, makes excellent LB films, and exhibits dielectric hysteresis.

2. EXPERIMENTAL METHODS

The chemical structure of PMVC is such that each fluorine atom found in PVDF has been replaced by an electron-accepting cyano group (CN), while one of the hydrogen atoms has been replaced by an electron-donating methyl group (CH₃). The chemical structure of PMVC can be viewed in the inset of Fig. 1.

Studies of PMVC have required several sample fabrication methods. Powder, cast, and Langmuir-Blodgett samples have all been used throughout this study. Cast films were created by dissolving PMVC into dimethyl sulfoxide or CHCl₃ and casting the solution onto an appropriate substrate such as Si(100) or aluminum-coated glass. LB films used in capacitance measurements were fabricated using the horizontal Schaefer variation in which

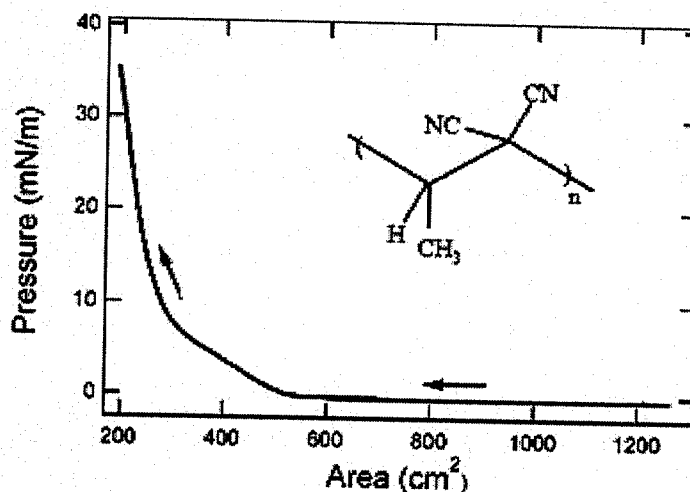


Figure 1. Langmuir isotherm recorded at 25°C from a PMVC/DMSO solution and inset chemical structure of PMVC.

17 monolayers were successively transferred from the water subphase to an aluminum-coated (50 nm) glass substrate [3, 4]. The pressure versus area isotherm for PMVC is displayed in Fig. 1. PMVC displays classic Langmuir film behavior, where the transition between the two-dimensional gas to liquid phase and the liquid to solid phase are indicated by the abrupt changes in slope at approximately 550 cm² and 300 cm² respectively. After deposition an additional 50 nm of aluminum was evaporated onto the surface of the film, creating a simple capacitor. The Langmuir-Blodgett sample fabrication procedure has been described in greater detail elsewhere [4].

Capacitance measurements were employed to study the dependence of the dielectric constant on electric field and temperature. A ferroelectric-paraelectric phase transition is accompanied by a large change in the spontaneous polarization and a peak in the dielectric response. Thus, observation of a peak in the capacitance versus temperature data could be an indication of a ferroelectric phase transition. Polarization switching should also be accompanied by a dielectric peak, resulting in so called "butterfly" curves. The capacitance was measured with a Hewlett-Packard 4192A impedance analyzer operating at 1 kHz with an amplitude of 0.1 V. In the temperature-dependent capacitance studies a ramp rate of 1 K per minute was used.

Differential scanning calorimetry (DSC) of the powder form of PMVC was used to identify a possible phase transition. A first-order ferroelectric-paraelectric phase transition will manifest itself as a peak in the heat flow. The area of this peak is equal to the latent heat of the observed transition. In conjunction with capacitance measurements, DSC provides an excellent

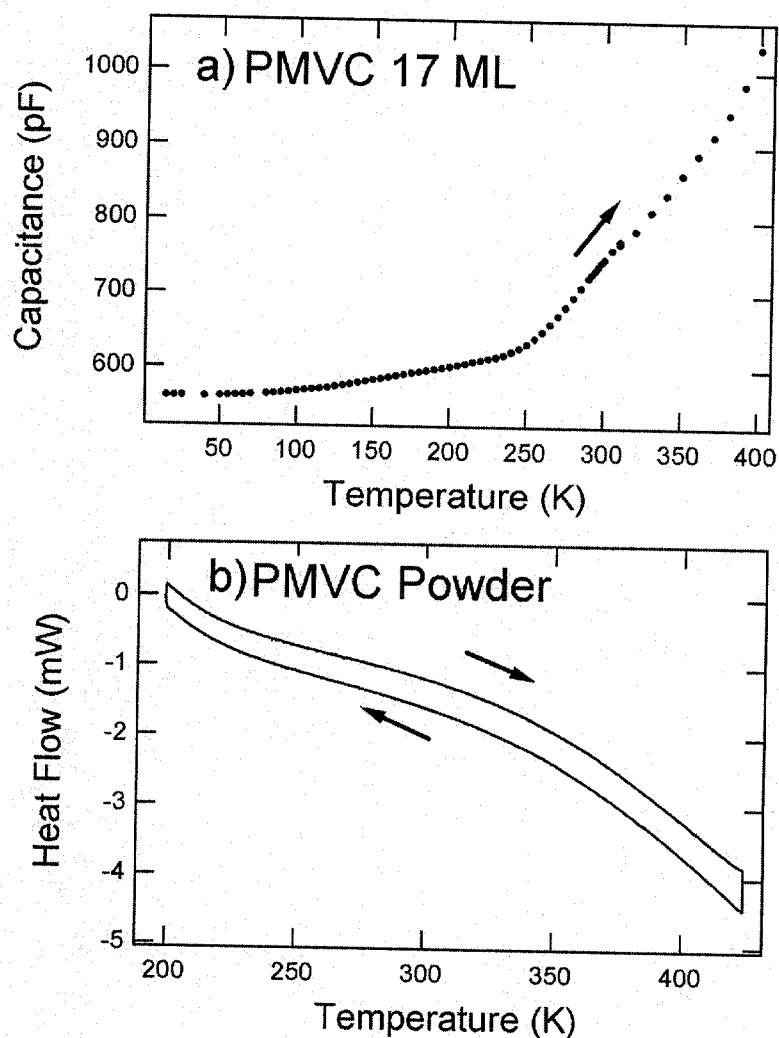


Figure 2. a) Capacitance as a function of temperature upon heating taken from a 17 ML Langmuir-Blodgett PMVC sample. b) Sample heat flow versus increasing and decreasing temperature taken using DSC from a powder sample of PMVC.

probe in establishing the existence and order of a ferroelectric transition. All calorimetry studies were performed on a Perkin Elmer PYRIS 1 differential scanning calorimeter using $0.011 \pm .001$ g of PMVC powder, and a rate of 1 K per minute.

Crystal structure was determined using theta-2theta X-ray diffraction of powder samples. The X-ray diffraction measurements were carried out on a theta-2theta Rigaku diffractometer, using $\text{CuK}\alpha$ radiation (wavelength = 1.54 \AA).

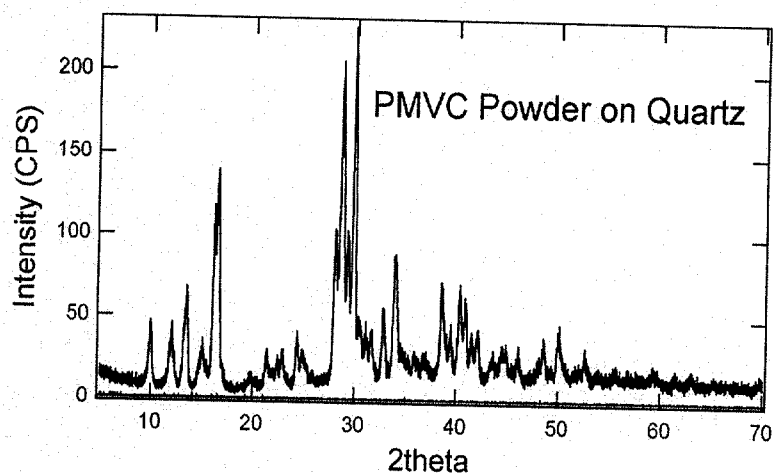


Figure 3. Theta-2theta X-ray diffraction scan taken from a powder sample of PMVC on a zero-background quartz substrate (represented by the bottom flat line) at 25°C.

3. RESULTS

Temperature-dependent capacitance and DSC measurements are shown in Figs. 2a and 2b respectively. Neither measurement shows a peak that might be due to a ferroelectric transition in the temperature range of 15 K to 400 K, though the change in slope at 250 K may indicate a more subtle transition. In addition, both DSC and dielectric measurements indicate the melting temperature is greater than 400 K.

The XRD data taken from a powder PMVC sample is shown in Fig. 3. The uppermost data set was taken from a PMVC sample on an amorphous quartz substrate. The background signal from the quartz substrate is negligible, as shown in Fig. 3. It is clear that PMVC possesses a relatively large degree of crystallinity when compared to other ferroelectric polymers [2, 4]. It is possible that the XRD data corresponds to several crystalline phases as is the case in similarly cast PVDF films [2]. It should also be noted that the sample was heated to approximately 150°C with no indication of a structural phase change observed using XRD, again consistent with DSC and capacitance versus temperature studies.

Figure 4 shows a clear “butterfly” pattern in the dielectric constant of the LB film consistent with polarization hysteresis. The two clear peaks at +4.5 V upon increasing voltage and -6.0 upon decreasing would then correspond to the coercive voltage. This is not, however, enough to prove that there is a switchable spontaneous polarization, the fundamental requirement for ferroelectricity. More direct evidence in the form of pyroelectric

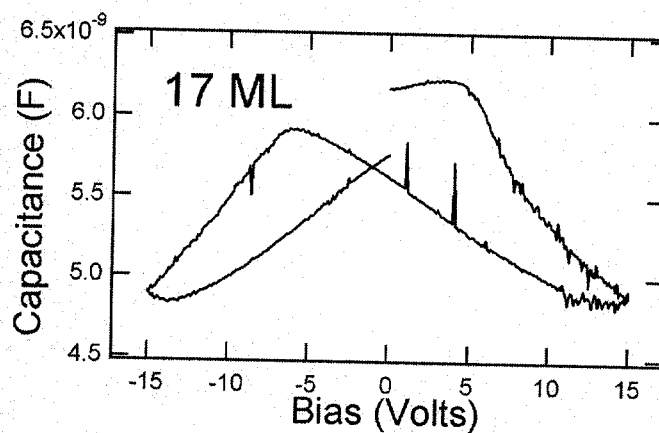


Figure 4. Capacitance versus voltage curve taken from a 17 ML Langmuir-Blodgett film of PMVC at 20°C.

and switched charge measurements is necessary for a more conclusive determination.

4. FUTURE MEASUREMENTS

The preliminary studies of PMVC show that it is highly crystalline, can be made into excellent quality LB films, and exhibits “butterfly” dielectric hysteresis consistent with polarization reversal. Further study of the structure and direct measurements of the polarization and switching properties is required. Also, studies performed on varying molecular weights as well as additional synthesized chemical variants of PMVC are currently underway.

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