Preparation and characterization of new ferroelectric polymers

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Abstract. The odd polyamide series is shown to be a new class of ferroelectric polymeric materials based on the demonstration of the J–E and D–E hysteresis loops of the oriented and unoriented odd polyamide films. Both the remanent polarization (P_r) and coercive field (E_c) of the odd polyamides linearly increase with increasing amide content of the molecules. The ferroelectric response of the samples can be greatly enhanced by uniaxial drawing at room temperature.

1. Introduction

A ferroelectric material is defined as one which possesses a spontaneous polarization whose direction can be reversed by the application of an external electric field. In order to determine whether a material is a ferroelectric, it is essential that the material be shown to exhibit a dielectric hysteresis loop. Investigations of piezoelectricity in polymers have been carried out since 1924 [1], but no significant results had been observed until 1969 when Kawai [2] discovered that a large piezoelectric response could be induced in uniaxially drawn poly(vinylidene fluoride) (PVF_2 or PVDF) by application of an electric field. Since then, piezoelectricity, pyroelectricity and ferroelectricity in PVF_2 and its copolymers have been extensively studied [3–6]. It was indeed an achievement that it was finally recognized that the true origins of ferroelectricity in PVF_2 films originated from dipole orientation in the crystalline regions. Meanwhile, extensive research efforts have been devoted to searching for new ferroelectric polymers.

In 1977, Litt *et al* [7] pointed out that the structures of odd polyamides are also polar and the dipole direction can be switched; these polyamides would meet the requirement to be ferroelectric. Polyamide 11 (or PA-11) is a representative choice for this new series since the unit cell can be prepared in a polar form, and uniaxial orientation followed by bulk electric field treatments align the unit cells in the field direction. Reorientation of the units cells in PA-11 in response to electric fields has been proven by x-ray diffraction [8] with *ex situ* studies while dipole reorientation has been shown by infrared techniques [9, 10].

As described by Mitsui *et al* [11], the usual procedure to examine whether a certain kind of material is ferroelectric or not is as follows. First, a thin film of the given material is fabricated and electrodes are applied to the opposing sides of the film by coating metals such as gold or aluminium. Then this thin film capacitor is inserted in a hysteresis bridge [12]. Further, in a dielectric, the charge Q is proportional to the magnitude of the electric displacement D that generally is defined as:

$$D = \varepsilon_0 E + P \tag{1}$$

where ε_0 is the vacuum permittivity, E is the electric field, which is proportional to V in magnitude, and P is the polarization which corresponds to the magnitude of the surface charge bound at the electrodes by the polarized dielectric. Therefore, the D–E hysteresis behaviour under the application of an alternating electric field can be considered as a characteristic of ferroelectric materials.

In the present study, an applied electric field generated by a high voltage power supply was employed in the D–E measurements. An autoranging picoammeter was connected in series to the specimen for the measurement of the current flow, I, during poling. Since I is defined as:

$$I = \int_a J \, da = \int_a \frac{dq}{dt} \, da = \frac{dQ}{dt} \tag{2}$$

where dt is an element of time, da is an element of area and J is the current density which is equal in magnitude to the charge dq that in a unit time crosses unit area of the surface of the electrodes. As articulated in the forgoing discussion, the surface charge dq is related in magnitude to the electric displacement dD, thus

$$J = \frac{d(\varepsilon_0 E + P)}{dt} = \frac{dD}{dt}. \tag{3}$$

Therefore, we have

$$D = \int_t J \, dt. \tag{4}$$

Normally, dc conduction also contributes to the measured value of J, but it can be subtracted by using the following empirical equation [13]:

$$J_{dc} = aE + b\exp(cE) \tag{5}$$

where a, b, c are constants. Then the electric displacement is obtained by integrating the corrected current density with respect to time.

Usually the sample was pretreated before poling by applying a static electric field for the purpose of field-sweeping out most of the mobile ionic species, so that the ionic conduction is reduced dramatically during the following poling procedure. In addition, since it has been found that, during the poling procedure, both the ionic conduction and the coercive field measured for the odd-numbered polyamides are greatly affected by moisture absorption, especially for the lower-order odd polyamides, during poling, samples were placed in a silicone oil bath with a desiccant and with a dry air purge at room temperature. A triangular shaped electric field pulse with maximum amplitude of 150–250 MV m^{-1} was used and the period of the triangular voltage waveform was 640 seconds.

The objective of this study is to prove that both PA-5 and PA-7 are also ferroelectric polymeric materials. In addition, we want to know whether the P_r and E_c values are influenced by the amide content of the remanent polarization observed in ferroelectric PVDF [8]; unoriented films were examined in this study.

2. Experiment

PA-5 ($[-(CH_2)_4-CO-NH-]_n$, poly(5-aminopentanoic acid), or poly-5-aminopentanoamide, or polyamide 5) and PA-7 ($[-(CH_2)_6-CO-NH-]_n$, poly(7-aminoheptanoic acid), or poly-7-aminoheptanoamide, or polyamide 7) powders were melted between aluminium foil at 270 and 240 °C, respectively, and pressed into thin films in a hot press. Then, the molten films were rapidly quenched in an ice bath. In the case of PA-5, in order to minimize the depolymerization,

PA-5 powders were heated at 100 °C for 12 hours under vacuum. Then, the quenched samples were uniaxially stretched to a draw ratio of 3:1 at room temperature.

The uniaxially drawn films were evaporation coated with gold electrodes on opposing sides of the film and then poled using a triangular voltage waveform with a period of 640 seconds and field pulse with maximum amplitude of 150–250 MV m^{-1}. Because the polyamide samples, especially PA-5, are very sensitive to moisture, which, when present, produces very high ionic conductivity, it is extremely important to apply a static electric field for some time before poling, for the purpose of field-sweeping out the mobile ionic species. During poling, the specimen was usually placed in a silicone oil bath containing a desiccant while a dry air purge was bubbled through at the same time. In this way, the ionic conduction was significantly reduced.

Unoriented samples, i.e. melt quenched but without drawing films, were also poled in this way for the purposes of comparison.

3. Results

In order to ensure that samples were well poled films, the poling procedure was only considered complete when the measured current density J exhibited no further increases for additional cycles. Six to eight cycles were usually required to obtain a well poled sample. The measured current density contained a certain amount of dc conduction and this was subtracted to yield the corrected current densities, J, versus the applied electric field, E; curves are shown in figures 1(a) and (b) for the melt-quenched and cold-drawn PA-5 films. By integrating the corrected current density with respect to time, the typical $D–E$ hysteresis behaviour for these polyamide films, shown in figure 1(c), is obtained. PA-5 exhibited a sharp current peak, which usually indicates a polarization reversal phenomenon. Similar measurements were carried out for other odd polyamide samples in this study. The apparent coercive fields, which were determined by the value of the field where the polarization passes zero in the $D–E$ plots (the intercept on the electric field axis of figure 1(c)), are usually found to be 90–95 MV m^{-1}. The value of the remanent polarization, P_r, for PA-5, determined by the intercept of the hysteresis loops with the D-axis, is observed to be $\sim$140 mC m^{-2}. Figures 2(a) and 2(b) show the $J–E$ and $D–E$ plots determined from PA-7 films. The coercive field and the remanent polarization have been found to be 92–96 MV m^{-1} and 98–110 mC m^{-2}, respectively. Figures 1 and 2 strongly indicate that both melt-quenched and cold-drawn PA-5 and PA-7 exhibit $D–E$ hysteresis behaviour under the application of an alternating electric field, which is typical of ferroelectric materials.

It was found that during the poling procedure, both the ionic conduction and apparent coercive fields measured for the lower-order odd polyamides are strongly affected by moisture absorption. Compared to the higher-order odd polyamides, PA-5 is much more sensitive to moisture, because of the higher density of hydrogen bonding amide groups in its molecular chains. The absorbed moisture results in extremely high ionic conduction so that break-down often occurs during poling. Usually, a dry-air purge can effectively reduce the ionic conduction during the poling process, but is found to increase the apparent coercive field by $\sim$20%. This requires the application of much higher electric fields ($E_{max} = 250$ MV m^{-1}) to switch the dipoles.

Since uniaxial stretching can significantly enhance the remanent polarization in PVF$_2$ [8], both drawn and undrawn PA-5 films were examined in this study. The results are shown in figures 3(a) and 3(b). It has been noticed that compared to that observed from drawn PA-5, the switching curve of the undrawn PA-5 sample is contracted, and the value of P_r obtained, which is found to be about 86 mC m^{-2}, is lower than that obtained in oriented PA-5. However, the
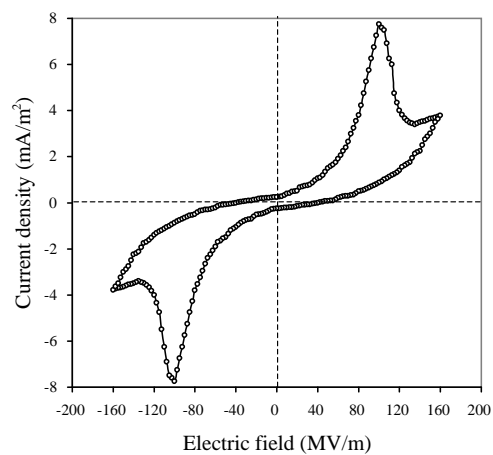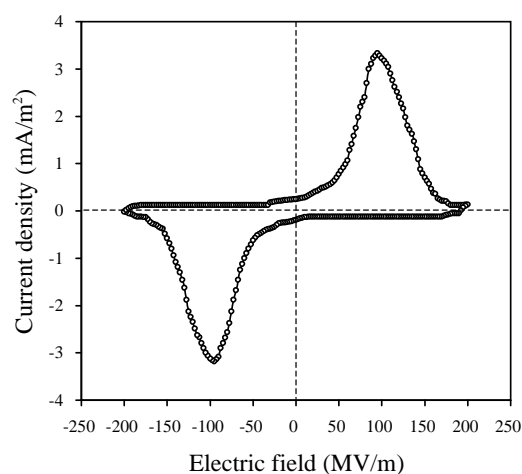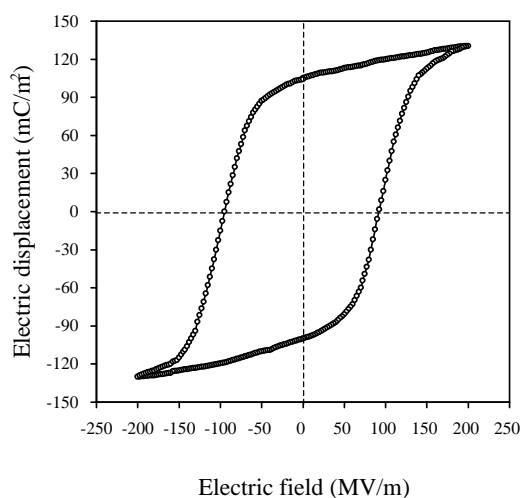
(a)
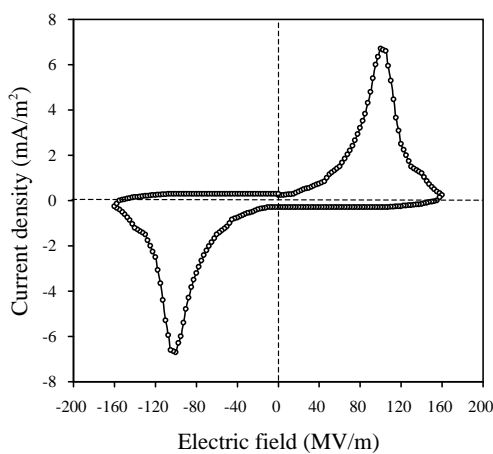
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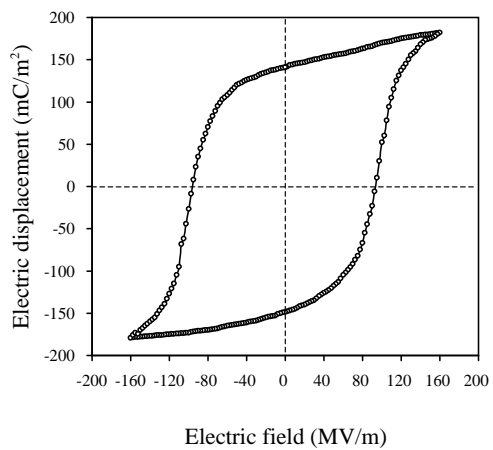
(c)

Figure 1. (a) Current density J against electric field E for oriented PA-5. (b) Current density J, ionic conduction subtracted, against electric field E for oriented PA-5. (c) Electric displacement D against electric field E for oriented PA-5.

(a)

(b)

Figure 2. (a) Current density J, ionic conduction subtracted, against electric field E for oriented PA-7. (b) Electric displacement D against electric field E for oriented PA-7.

coercive field, which is $\sim$110 MV m^{-1}, is smaller than that observed in the oriented sample under the same experimental conditions.

4. Discussion

Figures 1(c) and 2(b) strongly indicate that both melt-quenched and cold-drawn PA-5 and PA-7 exhibit D–E hysteresis behaviour under the application of an alternating electric field, which is typical of ferroelectric materials.

With hydrophilic materials like the odd-numbered polyamides, the water content is an additional complementary variable. The coercive field was observed to be $\sim$100 MV m^{-1} for undried and oriented PA-5 samples (not shown in this paper), but increased to $\sim$120 MV m^{-1}
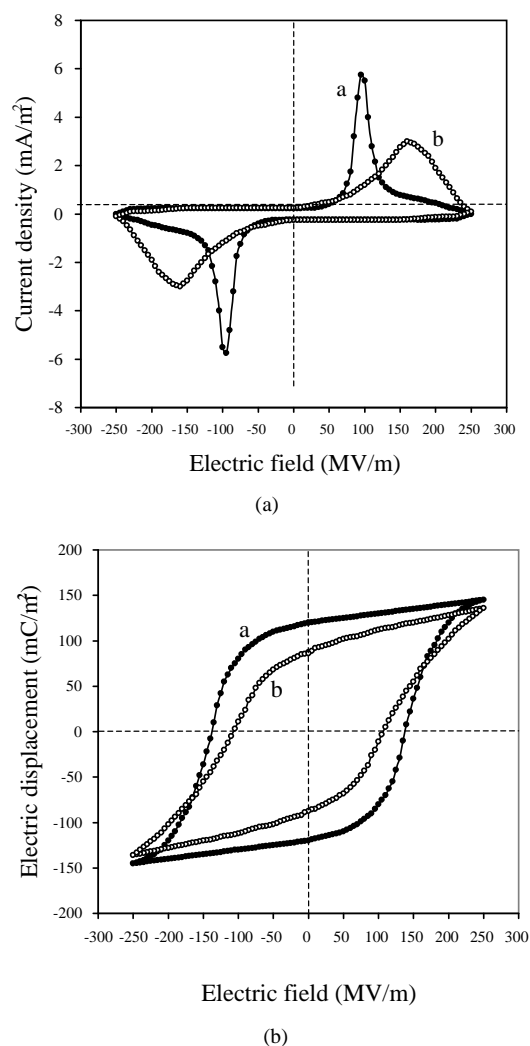
(a)

(b)

Figure 3. (a) Corrected current density J against electric field E for a, oriented, and b, unoriented, PA-5. (b) Electric displacement D against electric field E for a, oriented, and b, unoriented, PA-5.

when a dry-air purge was used (see curve a in figure 3(b)). It is generally believed [14] that the absorbed water exists in the amorphous regions of the polymers. This may be due to strained metahydrogen bonds present in the chain folds and other noncrystalline regions, which are disturbed and reformed with water molecules. An early review of the sorption of water by polymers, written by McLaren *et al* [15], pointed out that the water molecules might just be filling in the intermolecular spaces in the amorphous regions. Therefore, the increase in the apparent coercive field may be explained on the basis of a two-phase model, i.e. amorphous–crystal series structure, consisting of amorphous regions with dielectric constant ε_a and crystalline regions with dielectric constant ε_c. Then, the relationship between the dielectric constant and voltage drops across each phase can be described by the equation $V_a / V_c = \varepsilon_c / \varepsilon_a$ where V_a represents the voltage across the amorphous phase and V_c is the voltage across the crystalline phase. During the poling process, the dry-air purge can effectively reduce the

moisture content of the amorphous regions. As a result, this decreases ε_a, which in turn leads to a higher voltage drop across the amorphous regions. With the total voltage applied to the sample unchanged, the voltage drop across the crystalline regions will be decreased. In order to acquire the energy needed to obtain dipole switching in the crystalline regions, a higher external electric field is required and an increase in the apparent coercive field is observed. Actually, this is an oversimplified model used to interpret the observed phenomenon.

As reported previously [8], melt-quenched and cold-drawn PA-11 films exhibit much larger remanent polarization than those of melt-quenched but unoriented samples do. The remanent polarization increases by almost 50% for the oriented films. A similar phenomenon has also been observed during the poling of melt-quenched and unoriented PA-5. The value of P_r was enhanced by 40% for PA-5 after uniaxial stretching. Since the ferroelectric response originates from the crystalline regions, the result may be attributed to the large increase in the orientation of the molecular chains resulting from the deformation. The higher the orientation, the more the dipoles in the crystalline regions, which can be rotated about their chain axis by the external field, can contribute to the observed ferroelectric response. Furthermore, the melt-quenched and unoriented PA-5 films contain much less crystalline material because the molecular chains are not oriented. This may cause the material to be more sensitive to moisture. According to the foregoing discussion, when the dry-air purge and the desiccant were used during poling, the water content in the amorphous region was largely reduced. Therefore, a much higher apparent coercive field is needed to overcome the energy barrier to switching the dipoles. In an unoriented PA-5 film, the initial dipole orientation is random, so the distribution of energies required to switch the dipoles is broader, which results in a broader switching peak during poling as observed in the J–E plot of unoriented PA-5 shown in figure 3.

In addition, we can predict that there is no trace of ferroelectric behaviour in any of the even numbered polyamides which were prepared and poled under the same conditions as the odd numbered polyamides. The major reason is that the all-*trans* arrangement of the molecular chain results in a net dipole moment in the odd numbered polyamide molecules but zero dipole moment in the even polyamide molecules. According to Slichter's model [16] of the α-form odd numbered polyamides have a large dipole moment in the crystalline regions; however, the dipole moment directions are reversed on successive amide groups in the case of the even polyamide molecules which results in a zero dipole moment for the chain. Therefore, one should expect to be able to detect significant ferroelectric activity in these odd numbered polyamides if proper sample history and poling procedures can be found.

5. Conclusions

In conclusions, the odd polyamide series constitute a new class of ferroelectric polymers. The remanent polarization of the odd polyamide series was observed to increase linearly with increasing amide content of the molecules and the coercive field also showed a linear increase with amide group density of the molecules. In addition, it was found that both uniaxially drawn and undrawn odd-numbered polyamide films exhibited ferroelectric hysteresis behaviour, and that the ferroelectric response could be significantly enhanced by uniaxial orientation as is the case for PVF_2.

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