

Infrared spectroscopic study on electric-field-induced dynamics of polymer chains in a ferroelectric melt-quenched cold-drawn film of nylon-12



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ABSTRACT

We studied the intensity changes of the infrared bands of a ferroelectric melt-quenched, cold-drawn film of nylon-12 as a function of an external cyclic stepwise electric field with the polarization perpendicular to the draw direction. The infrared bands assigned to the NH stretching and amide I modes exhibited butterfly-shaped hysteresis loops characteristic of ferroelectric materials, whereas the intensity changes of the infrared bands assigned to the CH₂ antisymmetric and symmetric stretching modes were small and showed no butterfly-shaped hysteresis loops. These results indicate that only the amide groups were inverted under the external electric field. We proposed a molecular mechanism explaining the ferroelectric properties of nylon-12: the amide groups in the antiparallel β -sheet structure are inverted by the external electric field to form new hydrogen bonds, generating two stable states in a nearly double-minimum potential.

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1. Introduction

Ferroelectric polymers have attracted considerable interest because of their potential applications in flexible piezoelectric sensors, pyroelectric actuators, and ferroelectric memory devices. Poly(vinylidene fluoride) (PVDF) and its copolymers have been widely investigated as ferroelectric polymers [1]. Their ferroelectricity originates from the inversion of their polymer chains containing polar $-\text{CH}_2\text{CF}_2-$ groups. Nylons are also known to exhibit ferroelectric polymer behavior.

A nylon polymer chain has an alternating structure of a polar amide group ($-\text{NHCO}-$) and a methylene chain [2–6]. Nylon with an odd number of carbon atoms in the unit of its polymer chain is called odd-numbered nylon, and that with an even number of carbon atoms is called even-numbered nylon. They form “parallel” or “antiparallel” β -sheet structures [7]. The extended linear polymer chains of nylon-11 and nylon-12 are shown in Fig. 1. The repeating unit of the nylon-11 chain is $-(\text{CH}_2)_{10}\text{CONH}-$, and it has a permanent electric dipole moment originating from the amide group. Thus, nylon-11 is expected to exhibit ferroelectric properties, depending on its crystal form. The repeating unit of the nylon-12 chain is $-(\text{CH}_2)_{11}\text{CONH}-(\text{CH}_2)_{11}\text{CONH}-$. The chain has two

alternating amide groups. As the permanent electric dipole moment of each amide group has the opposite direction, the repeating unit of the polymer chain has no permanent electric dipole moment. Thus, no ferroelectric properties are expected for any crystals of nylon-12. No ferroelectric properties are also expected for any crystals of other even-numbered nylons.

A melt-quenched, cold-drawn film of nylon-11 (δ' form [8]), which assumes a “smectic”-type structure [9], has been experimentally demonstrated to exhibit ferroelectric properties. Curiously, however, nylon-6 exhibits ferroelectricity [10–12]. Nylon-6 has crystalline structures such as its α - and γ -forms [13,14] that do not exhibit ferroelectricity. A melt-quenched film of nylon-6 exhibited a broad X-ray diffraction peak similar to that of the smectic δ' form of nylon-11 [11]; moreover, the film exhibited ferroelectricity [10,12]. Nylon-12 has solid structures such as its α -, γ -, and γ' -forms [15–17]. The thermally stable crystalline γ -form has a monoclinic lattice with the following structural parameters: $a = 0.958 \text{ nm}$, $b = 3.19 \text{ nm}$, $c = 0.479 \text{ nm}$, $\beta = 120^\circ$ ($Z = 2$); the space group is $P2_1/a$ (C_{2h}^5) [15]. The polymer chains form a parallel β -sheet structure. The crystalline α -form has a monoclinic lattice with $a = 0.98 \text{ nm}$, $b = 0.32 \text{ nm}$, $c = 0.85 \text{ nm}$, and $\beta = 65^\circ$ ($Z = 4$) [16]. The α - and γ -forms showed no ferroelectric properties. A melt-quenched film of nylon-12, which is designated as the γ' -form, showed a broad X-ray diffraction peak [17]. The γ' -form likely assumes a smectic structure. The ferroelectric properties of nylon-12 were not reported. In this study, we report a $D-E$

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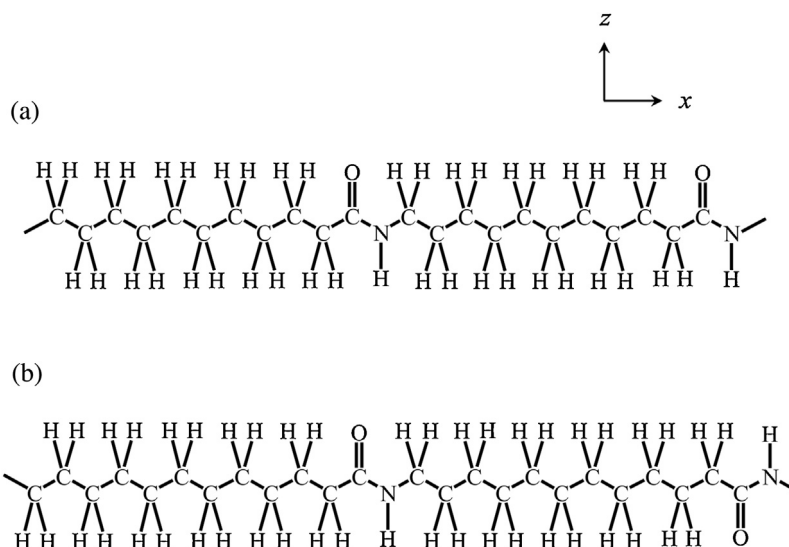


Fig. 1. Polymer structures of (a) nylon-11 and (b) nylon-12.

hysteresis loop characteristic of ferroelectricity for a melt-quenched, cold-drawn film of nylon-12. The observations of the ferroelectric properties for even-numbered nylons seem to be inconsistent with the above consideration of no permanent electric dipole moments in the repeating unit of the extended polymer chain. It is important to clarify the mechanism of the observed ferroelectric properties of even-numbered nylons.

The infrared spectra of various forms of polyamides have already been reported [9,18,19], as have the spectra of the α - and γ -forms of nylon-12 [20,21]. The infrared bands assigned to the amide I (CO stretching) and amide II (mixture of NH in-plane bending and CN stretching) modes are sensitive to hydrogen bonding and to the materials' secondary structures, such as the α -helices and β -sheets of proteins, polypeptides, and polyamides [22].

Infrared spectroscopy is a powerful tool for studying the dynamics of polymer chains induced by an external electric field. Naegele and Yoon [23] observed that the intensity of an infrared band of ferroelectric PVDF exhibits a butterfly-shaped hysteresis loop when an external electric field is cycled positively and negatively. These butterfly-shaped hysteresis loops were reported not only for PVDF homopolymer but also for its copolymers [24–26]. Recently, we investigated the electric-field-induced

effects on the infrared spectra of a melt-quenched, cold-drawn film of nylon-11 [27]. We proposed a new molecular mechanism that explains the ferroelectric properties of nylon-11. In this mechanism, the amide groups in the antiparallel β -sheet structure are inverted by the external electric field to form new hydrogen bonds, whereas the methylene groups were not inverted under the applied external electric field.

In the present study, we report the electric-field-induced effects on the infrared spectra of a ferroelectric melt-quenched, cold-drawn film of nylon-12, and propose a molecular mechanism of ferroelectric properties of nylon-12.

2. Experimental

A melt-quenched, cold-drawn film of nylon-12 (Sigma–Aldrich) was prepared by melt-pressing a pellet between aluminum foil sheets at 230 °C and under a pressure of 10 tons using a universal film maker (S. T. Japan), followed by quenching in ice water. After removal of the aluminum foil sheets, the film was uniaxially drawn to a ratio of 3:1 at room temperature.

Au was evaporated onto both surfaces of a 15 μm thick, melt-quenched, cold-drawn film as electrodes; the thicknesses of the Au layers was 15 nm. The area of each deposited electrode was

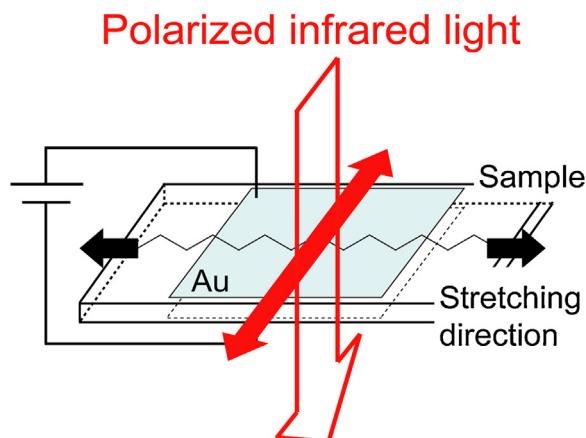


Fig. 2. Schematic structure of a measurement cell.

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