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A giant pyroelectric effect of a rigid rod-like polymer, poly[(s)-(-)-2-propionic acid methyl isocyanate]

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Electric activity of a rigid rod-like polymer, poly[(s)-(-)-2-propionic acid methyl isocyanate] (Pc*IC), in a solid state is reported. A measurement of a displacement-field hysteresis loop reveals that Pc*IC chain systems possessed polarization for which the direction can be inversed by an external field. Remanent polarization and a coercive field were determined to be 16.4 mC/m^2 and 15.7 MV/m, respectively, at 20 °C. The polymer also exhibited the excellent pyroelectricity. A pyroelectric coefficient of about 300 μmC/m^2 K at 95 °C was one magnitude larger than those of other pyroelectric polymers and was almost comparable with those of some inorganic pyroelectric materials. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1978981]

Intermolecular bonding, ranging from weak van der Waals forces through stronger hydrogen bonds, often determines several properties of polymers.[1] Some intermolecular-hydrogen-bond forming polymers have attracted great interest in their electroactivities, such as piezoelectricity, pyroelectricity, and ferroelectricity.[2–9] Intermolecular hydrogen bonds in these polymers are responsible for the long-range ordering of dipoles in a chain system.[4,5] Some naturally occurring polymers, like polypeptides, also exhibit similar electric functionalities due to intermolecular hydrogen bonds. In previous work, ferroelectric ordering of the dipoles was seen in some of the polypeptides during the lyotropic phase.[10] The intermolecular-hydrogen-bond stimulating electroactivities are not specific to the macromolecular materials. Our previous report demonstrated the dipole ordering formed in the self-assembled disk-like molecules with three amide groups.[11] These materials should be applied for the thin-film electro-optic devices and infrared sensors by utilizing their flexible structural features.

We addressed the electroactivities of polyisocyanate (PIC) derivatives, one kind of nylons or polyamides.[12] A group of polyisocyanates is called 1-nylon, and their main chains consist of the repetition of the -CO-NR-monomer units.[13–15] Here, *R* denotes some hydrocarbon side chains. The main chains of the PICs formed rigid helical structures, because of the repulsive interactions between neighboring side chains. Nitrogen atoms differ from other nylons in that the main chains are capped by the side chains, and the intermolecular hydrogen bonds are repulsed. In spite of this, the PIC chain system possesses a macroscopic polarization for which the polarity is inversed in response to an external field.[12] The macroscopic polarization in the PICs is likely caused by C=O dipole ordering along a helical axis.[16] The polarization inversion is associated with the glass transition behaviors: the polarization is probably attributed to a short-range dipole cluster in the amorphous region, namely, the dipole glass state.[17]

In the present letter, we report the electrical functionalities of one of the PIC derivatives: poly[(s)-(-)-2-propionic acid methyl isocyanate] (Pc*IC) (Fig. 1). The side chain of

the Pc*IC contains chiral carbon atoms. In general, the PIC chain takes either of a right- or left-handed helical structure, because these two conformations have the same potential energy with each other.[18,19] The single chains formed the racemic conformation, that is, the right- and left-handed helixes are equally mixed. When the side chains with the chiral carbon atoms are introduced, the helicities of the monomer units are uniquely determined and the single chain takes one-handed helical conformations.[20,21] The features are explained by the so-called "chiral majority rule." When all the chains take one-handed helical conformations, the dipoles should be oriented in the same direction along the helical axis and the single chain potentially possesses giant polarization. Our present study demonstrated that a Pc*IC chain system has an extremely large pyroelectric coefficient, as well as the macroscopic polarization, the direction of which is inversed. The pyroelectric coefficient is the one magnitude larger than those of other pyroelectric polymers and is comparable with those of inorganic pyroelectric materials.

We synthesized Pc*IC with the anionic polymerization method. The details were reported in a previous study.[22] The starting material was CH$_3$-CO-C*H(CH$_3$)-N=C=O. The catalyst was NaCN. The monomer and catalyst were dissolved into *N*, *N*-dimethyl formamide. The polymerization reaction was conducted at −58 °C under a dried nitrogen atmosphere. The synthesized polymers were purified in water and methanol several times. The Pc*IC formed a lyotropic
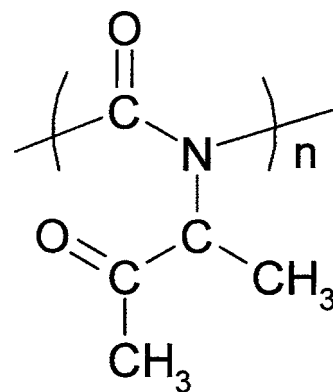

FIG. 1. Chemical formulas of Pc*IC.
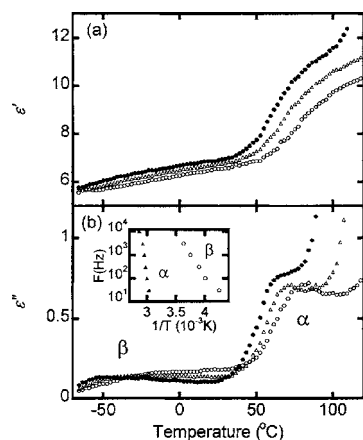
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FIG. 2. Temperature dependence of the real and imaginary parts of the dielectric constant ε' (a) and ε'' (b).

FIG. 3. Displacement (D)-field (E) hysteresis loop of Pc*IC at 20 °C.

liquid crystalline phase when it was dissolved into chloroform, hexafluoro-2-propanol, and toluene. The electric properties of the Pc*IC are characterized by a temperature dependence of the dielectric and pyroelectric coefficients and a displacement (D)-field (E) hysteresis loop. The details were reported in elsewhere.[9,23] The sample was polymer thin films that were sandwiched with aluminum thin layers for these measurements. An aluminum layer was deposited on a glass substrate with a vacuum deposition method. The Pc*IC was then dissolved into chloroform and it was cast and dried on the substrate. Finally, another aluminum layer was deposited again with the same method. The typical thickness of the polymer layer was 10–50 μm.

Figure 2 shows the temperature (T) dependence of the real (ε') and imaginary (ε'') parts of the dielectric coefficient of Pc*IC. The three curves shown in the figure are the data measured at 100 Hz, 1 kHz, and 10 kHz in frequency of the applied ac field. The T-ε'' curves exhibited frequency dispersion in the regions of 30–80 °C (region I) and −60–30 °C (region II). In each region, the curves have peak α in region I and peak β in region II. Both of the peak temperatures T_α and T_β increased, as the frequency of the applied field increased. A thermal analysis with a differential scanning calorimeter (DSC-3100, MAC Science) allows us to observe an endothermic change due to a glass transition was observed at 35 °C. The dispersion in region I is likely to be related to the glass transition phenomenon.[24,25] The monomer units of the Pc*IC have carbonyl (C=O) dipoles in their main chains and carbonyl ester (C=O-O) dipoles in their side chains. When the glass transition happened, the long-range segmental motion of the main chains was allowed and cooperative motions of the C=O and C=O-O dipoles occurred. However, peak β in region II should be due to β relaxation of the side chain. The cooperative motions of the C=O-O dipoles in the side chains began after the side chain started to rotate at the temperatures higher than T_β.

The frequency dependences of T_α and T_β is shown in the inset of Fig. 2(b). The plots are drawn in the Arrhenius scale. Both of the relationships are reproduced with linear functions in the scale. The slopes of the graphs give the activation energies that are required for segmental motions.[24] With the least square fitting, the activation energies were determined to be ΔE_α=31 kcal/mol for peak α and ΔE_β=9.6 kcal/mol for peak β. Both of the T-ε' and T-ε'' traces give sharp increases at the temperatures increase above 80 °C. The
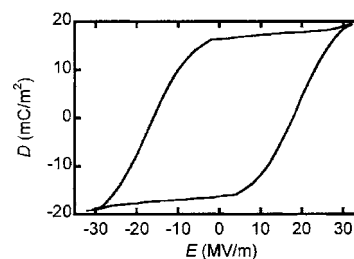
changes may be caused by ionic conduction due to the polar end groups of the polymers. Otherwise, NaCN, which was used as the catalyst, might remain among the chains, even though the synthesized polymers were purified in ethanol and water several times. The impurities that were contaminated in the chains were responsible for the ionic conduction at higher temperatures.

Figure 3 shows the D-E hysteresis loop that was measured at 20 °C. The experimental results indicate the macroscopic polarization formed spontaneously. The direction of the polarization can be inversed in accordance with the polarity of the external field. The features of the D-E hysteresis loop are characterized by two physical quantities: coercive field and remanent polarization.[26] The coercive field E_c is the quantity of the field at D=0, while the remanent polarization D_r is the quantity of the displacement at E=0. From the present hysteresis loop, these two parameters were determined to be E_c=15.8 MV/m and D_r=16.4 mC/m^2, respectively. Some of the intermolecular-hydrogen-bond-forming polymers also revealed hysteresis phenomena. The remanent polarization was 80–100 mC/m^2 for 7-nylon,[2] 60–120 mC/m^2 for 11-nylon,[2] 30–80 mC/m^2 for polyurea,[8] and 50 mC/m^2 for polyurethane.[9] The remanent polarization of the Pc*IC was a bit smaller than those of these polymers. As mentioned earlier the nitrogen atoms of the Pc*IC were capped with the side chain, and the intermolecular hydrogen bonding interaction was repulsed. The Pc*IC chains were clearly packed less tightly in the solid phase. Thus, the ordering parameters of the dipoles were smaller and the material exhibited smaller remanent polarization than the other polymers did. The measurement was also conducted at temperatures lower than T_β. The hysteresis was not recorded at these temperatures.

In our previous study, the hysteresis property was observed in another polyisocyanate derivative: the poly (n-hexyl isocyanate) (PHIC).[12] The side chains of the PHIC lacked the chiral carbon atoms and polar groups. The hysteresis was observed only at temperatures higher than the glass transition temperature T_g or α relaxation temperature T_α. The macroscopic polarization occurred along the helical axis, and it was responsible for the polarization inversion. The motions of the dipoles were frozen at temperatures below T_g, while the long-range dipole motions were likely to occur at temperatures higher than T_g. On the contrary, the present Pc*IC chain system exhibited the hysteresis property even at temperatures lower than T_g, although it was not found at temperatures lower than T_β. The monomer units of the Pc*IC have CO-O dipoles as well as CO dipoles. Among them, the ordering of the CO-O dipoles in the side chains were likely responsible for the polarization inversion. At temperatures higher than T_β, the side chains were likely to rotate and the
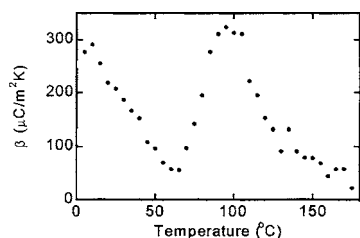
FIG. 4. Temperature dependence of Pc*IC pyroelectric coefficient.

CO-O dipoles changed their direction according to the polarity of the external field.

The quantity of the CO-O dipoles is estimated to be $\langle\mu\rangle=1.7$ Debye. When all the dipole moments in the chain systems are oriented in the same direction, the remanent polarization should be $D_r=\rho\langle\mu\rangle N_A/M=26$ mC/m^2. Here, $\rho=0.96$ g/cm^3 is the weight density of Pc*IC, $M=113$ is the molecular weight of the monomer unit, and N_A is Avogadro's number. The experimentally determined remanent polarization of 16.4 mC/m^2 corresponded to 63% of the ideal quantity. We concluded that the CO-O dipoles were highly oriented in the chain system.

The present experimental results alone could not sufficiently determine if the Pc*IC chain systems formed a ferroelectric dipole ordering state. A dielectric anomaly was not seen at all in the T-ε' and T-ε'' curves. The coordinate motions of the dipoles were closely related to the β transition process; the polarization inversion occurred only at temperatures higher than T_β. Rather, the dipole ordering may occur in the noncrystalline region of the crystal, namely, the dipole-glassy state.

The temperature-dependent pyroelectric coefficient is shown in Fig. 4. The poling treatment was conducted in the atmosphere before the signal measurement. The temperature was 90 °C and the applied dc field was 15 MV/m. After the poling treatment, the sample was cooled down to room temperature at a rate of 3 °C/min. The poling procedure was conducted under a dc electric field of 15 MV/m at 90 °C. The pyroelectric signal decreases monotonously in temperature region II. In temperature region I, the signal has a peak at 95 °C. The dispersion of the pyroelectric signals in the regions I and II is likely associated with the surface changes modulating after the α and β relaxes, respectively.

Notice that the pyroelectric coefficient at 95 °C was as large as 310 μC/m^2 K. The quantity was by one magnitude larger than that of the poly(vinlyidene fluoride), the most prominent pyroelectric polymer that has ever been known.[26] This quantity is also comparable with those of inorganic pyroelectric materials, such as lead zirconate titanate and BaTiO$_3$.[27] Although the remanent polarization from D-E hysteresis was much smaller than those of the other electrically functional polymers, the pyroelectric coefficient was by one or two magnitudes larger than theirs. The pyroelectric signal may occur from a mechanism that differs from other pyroelectric polymers.

In general, the pyroelectric signal is caused by temperature change in macroscopic polarization.[26] The polarization change predominantly occurs due to either of the following two mechanisms. The primary pyroelectricity is known as the true pyroelectricity, and it is purely proportional to the polarization change against the temperature change at a con-

stant strain.[28,29] The secondary pyroelectricity is referred to as the false pyroelectricity and it is attributed to piezoelectricity stimulated by volume expansion. In most cases, the pyroelectric signals of the inorganic materials are predominantly determined by the primary effect, while those of the polymers are determined by the second effect.

Upon expanding the volume of the Pc*IC chains, the stretching motions with the coordinate along the helical axis likely becomes active. The vibrational mode should probably be related to the longitudinal acoustic mode (LAM) or accordion mode for which a vibrational coordinate extends the entire chain.[30,31] When the thermal energy is applied to the chain system and the LAM mode becomes active, the modulations of the CO-O and C=O dipoles are synchronized to the LAM stretching motion. The large polarization change is followed by synchronized oscillation of the entire dipoles that are attached to the main chains. The extremely large pyroelectric signal can be attributed to the polarization change that is accompanied by the LAM mode.

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