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Polymer 47 (2006) 5141–5144
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Electric activity in rigid rod-like polymer, poly(β-hydroxybutyrate)

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Received 21 January 2006; received in revised form 22 April 2006; accepted 6 May 2006
Available online 26 May 2006

Abstract

Poly(β-hydroxybutrate) (PHB), one of the most promising environmental friendly polymers, was found to be rich in electric activities. Our experimental results demonstrated that the PHB exhibited ferroelectric behavior, as well as pyroelectric behavior. A remanent polarization of the PHB system was as large as 67 mC/m^2 at 100 °C from a displacement–field hysteresis loop, while it possessed pyroelectric coefficient as large as 20 μC/m^2 K after a poling procedure. The remanent polarization exhibited unique temperature dependence and it increased rapidly at the temperatures higher than 80 °C. The polarization due to the ester dipole ordering is likely formed in the direction perpendicular to the helical axis.

Keywords: Dielectric; Pyroelectric; Ferroelectric

1. Introduction

Poly(β-hydroxybutyrate) (PHB) (Fig. 1) is known as environmental friendly thermoplastic materials, since the PHB is synthesized biologically in a number of microorganisms and it is degradable by bacteria in soil [1]. The PHB has attracted a great of interests in that its thermoplastic properties are similar to those of polypropylene [2]. From these reasons, great amounts of experimental and theoretical studies have been performed so as to investigate the structural and thermal behaviors of PHB as well as its plastic and biomedical applications.

The PHB has also attracted as one of the greats of electrically active polymers. The mechanically stretched PHB chains are rich in shear piezoelectricity [3]. The promising electrical activity is closely associated with their asymmetric structures due to formation of helical chain conformations. The similar shear piezoelectricity was found in the other helical polymers, such as poly(Γ-methyl D-glutamate) [4] and poly(L-lactic acid) [5]. The mechanism of shear piezoelectricity in helical polymers was explained in pretty generalized forms [6]; the rigid rod-like helical chains have the polarization in the direction parallel to the helical axis. When the chains experience the external stress, rotational motions are stimulated around the helical axis and the polarizations change their magnitudes. Consequently, the shear piezoelectricity comes about in helical chain systems. The polarization along the helical axis direction may potentially bring about the occurrence of the elongation piezoelectricity or pyroelectricity.

In the present letter, we report the dipole ordering behaviors of PHB in the solid state. The PHB's exhibited a displacement–field hysteresis behaviors as well as a pyroelectricity. These experimental results shed light on new potentials of the helical polymers. The ferroelectric dipole ordering behavior was found in the other helical polymer, poly(Γ-methyl D-glutamate), in their lyotropic liquid crystalline phase in the previous work [7]. On the contrary, the ferroelectric properties of the helical polymers in the solid phase have not yet been reported, except for our previous preliminary study about poly(L-lactic acid) [8].

2. Experimental

PHB was prepared by Monsanto Japan Limited. The displacement (D)–field (E) hysteresis loop and pyroelectric signal were investigated so as to characterize the electric properties of PHB. The details of the experimental apparatuses were reported in our previous work [9]. The D–E hysteresis loop was recorded with the following method. A triangular electric field (E) of 0.03 Hz in frequency was applied between the electrodes, and a current (I) was recorded with a multimeter (TR8652, ADVANTEST). An unnecessary ionic conduction component was superposed on the experimentally-determined I–E curve. The magnitude of the ionic conduction component was determined by measuring the I–E

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doi:10.1016/j.polymer.2006.05.010

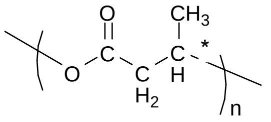

Fig. 1. Chemical formula of PHB.

trace in a range $E>0$ and $E<0$. Before the conversion from the *I–E* hysteresis loop to *D–E* hysteresis loop, the ionic conduction component was extracted from the *I–E* curve. The *D–E* curve was derived by integrating *I* as a function of *E*. Pyroelectricity refers to a thermal energy–electric energy conversion process.

The pyroelectric coefficient β is defined as a temperature (T) derivative of polarization (dP/dT). So, the observation of the pyroelectric signal indicates the existence of polarization (P) in the chain systems. The thin film sample painted with blackbody (bismuth black) was exposed to light emitted from a pulsed semiconductor laser (630 nm, 10 mW, a repetition rate of 10 Hz). The light energy from the semiconductor laser was converted into the thermal energy on the blackbody. The beam radius on the blackbody was about 500 μm. The thermally induced current, which is proportional to β, was detected with a lock-in amplifier (5610A, NF Corp.). In this method, the temperature increasing and decreasing rates were determined only quantitatively, and thus the absolute value of β cannot be determined. A temperature-dependent thermally stimulated current (TSC) was measured simultaneously. The derivative of the TSC signal against the temperatures also gave the pyroelectric coefficient. The absolute value of β was calibrated using the TSC data. The measurement was conducted with the heating rate of 3 °C/min.

The sample was thin polymer layers that were sandwiched with the aluminum thin layers and it was fabricated with a following method. First, the aluminum layer was deposited on the SiO_2 substrates with a vacuum evaporation method. Second, chloroform solution of PHB was cast and dried on the aluminum layers. After drying for 24 h, the thin film with homogeneous thickness remained on the aluminum layers. The typical thickness of the polymer layer was 50 μm. Finally, the aluminum layer was again deposited on the polymer layers with the vacuum evaporation method. The thermal properties of PHB were characterized with differential scanning calorimeter (DSC-3100, MAC Science).

3. Results

Fig. 2 exhibits the DSC traces of PHB. The samples were prepared with two different methods. The measurement was performed in the heating process. The heating rate was 3 °C/min. Fig. 2(a) and (b) are the traces of the sample without any thermal processing and the one annealed at 200 °C. An endothermic peak is observed in both curves at around 150 °C. It is attributed to the melting of the chains. In the curve (a), the endothermic change due to glass transition is seen at $T_g \sim 0$ °C. The transition is related to long-range segment motions. The dielectric spectrum was also measured with LCR meter (HP4284A, Hewlett–Packard). The corresponding dielectric relaxation behavior was observed at $T_g \sim 0$ °C. The dielectric relaxation strength was determined to be as small as $\Delta\varepsilon = 1.5$ in 100 Hz. The monomer units of the PHB chains contain polar ester C=O–O– bonds. The glass transition is associated with the rotational motion of the C=O–O– dipoles around the main chains. The exothermic peak due to the crystallization is found at around $T_c \sim 30$ °C in the cast and dried sample (Fig. 2(a)); some portions of the chain segments were frozen in the noncrystalline state. These segments reoriented so as to form the crystalline phases during the heating process.

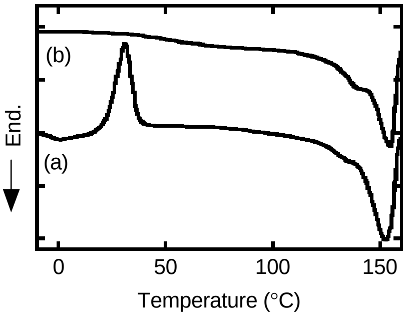

Fig. 2. DSC trace of (a) cast and dried PHB film and (b) film annealed at 200 °C.

Fig. 3 is the *D–E* hysteresis trace of the cast and dried sample. The frequency of the external field was 0.03 Hz. The hysteresis behavior was found at the temperatures higher than 80 °C, but not at the temperatures lower than 70 °C. The hysteresis behavior was not recorded correctly at the temperatures higher than 110 °C, because a component due to unnecessary ionic conduction was contaminated in the trace and hence it was impossible to extract the component due to the polarization inversion. The experiments were also performed for the annealed samples, but the hysteresis behavior was not observed.

The *D–E* hysteresis loop is characterized with two physical quantities, remanent polarization and coercive field. The remanent polarization D_r is defined as the quantity of the displacement at $E=0$ MV/m, while the coercive field E_c is defined as the quantity of the field at $D=0$ mC/m^2. From the hysteresis curves, the remanent polarization and the coercive field are determined to be $E_c=30$ MV/m and $D_r=5.3$ mC/m^2 at 80 °C, $E_c=27$ MV/m and $D_r=23$ mC/m^2 at 90 °C, and $E_c=29$ MV/m and $D_r=67$ mC/m^2 at 100 °C. The coercive field is almost independent of the temperatures, while the remanent polarization rapidly increases as the temperature increases.

The hysteresis behaviors were observed in several ferroelectric polymers, such as poly vinylidene fluoride [10], poly(vinylidene fluoride-*co*-trifluoroethylene) (p(VDF-*co*-TrFE)) [11], odd-numbered nylon [12], poly urethane [13] and poly urea [14]. The remanent polarizations of these ferroelectric polymers were ~100 mC/m^2 for PVDF [10], ~100 mC/m^2 for p(VDF-*co*-TrFE) [11], 60–100 mC/m^2 for 11-nylon [12], ~50 mC/m^2 for poly urethane [13], 30–80 mC/m^2 for poly

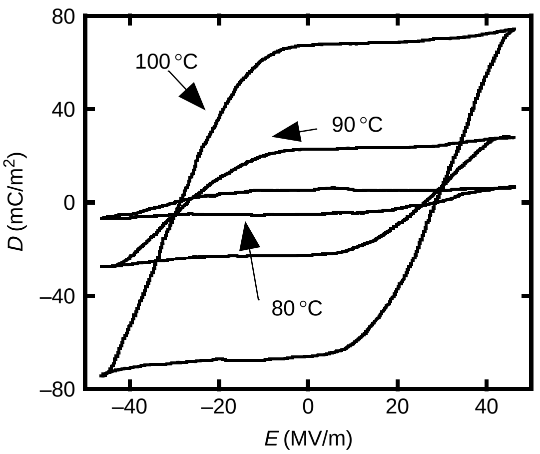

Fig. 3. Displacement–field hysteresis loop of PHB at 80, 90, and 100 °C.

urea [14]. The remanent polarization of the present PHB was as large as $D_r = 67$ mC/m^2 at 100 °C, and it was almost comparable with those of the other ferroelectric polymers.

Fig. 4 is the temperature dependence of the pyroelectric signal of the PHB. Before the measurement, the poling procedure was conducted for the samples; the field intensity was 30 MV/m and the temperatures were both at 20 and 100 °C. The measurement was performed with the heating rate of 3 °C/min. Both of the samples exhibited pyroelectric behaviors, but they depended differently on the temperature. As for the sample poled at 20 °C, the quantity of the signal was almost constant of $\beta \sim 3.5$ μC/m^2 K at the entire temperatures, although it exhibited a tiny decrease in the range 20–50 °C. On the other hand, the pyroelectric signal took a maximum value of $\beta \sim 21$ μC/m^2 K at 35 °C, above which it decreases gradually and reached the constant level of $\beta \sim 3.5$ μC/m^2 K. These results indicate that the two different polarization components are responsible for the pyroelectric signal of PHB. The first signal is induced, independent of the poling temperature, and it stably exists in the wide temperature range 20–120 °C. The second signal is induced only at higher temperatures and it stably exits at the temperature lower than 80 °C.

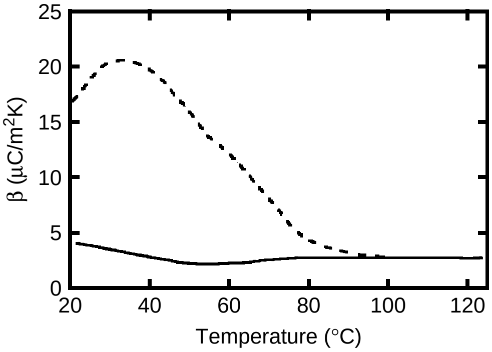

Fig. 4. Temperature dependence of pyroelectric coefficient of PHB. The samples were poled at 20 (solid curve) and 100 °C (dashed curve).

4. Discussion

The present experimental results of the *D–E* hysteresis loop and the pyroelectric signal indicate that the dipole ordered conformations could be formed in the PHB system after the poling procedure. The ester dipoles were oriented along the external field, and macroscopic polarization was brought about. The magnitude of the ester dipole is $\langle \mu \rangle \sim 2.4$ debye. Suppose that the ester dipoles in the entire monomer units are arranged along the field, the remanent polarization is reproduced with a following simple equation $D_r = \rho \langle \mu \rangle N_A / M$. The quantity is estimated to be $D_r = 61$ mC/m^2 under conditions of the weight density $\rho = 1.20$ g/cm^3 from a float and sink method, monomer molecular weight $M = 85$, and Avogadro number $N_A = 6.02 \times 10^{23}$. On the other hand, the remanent polarization determined by the *D–E* hysteresis loop was 5.3 mC/m^2 at 80 °C, 23 mC/m^2 at 90 °C, and 67 mC/m^2 at 100 °C. The experimentally-determined remanent polarization is almost comparable to the value estimated with the simple equation. Thus, it should be concluded that the ester dipoles are highly oriented in the PHB system. The remanent polarization at 100 °C is a little bit larger than the estimated value. The sample exhibited conductivity at the temperature. The motion of the ions may be accompanied with the polarization inversion and the quantity of the polarization became seemingly larger.

Relatively large remanent polarization might be caused by the ferroelectric ordering of the ester dipoles. The PHB system might form polar crystalline structure. However, a dielectric anomaly was not seen in the dielectric spectrum. Furthermore, the hysteresis behavior was observed only from the cast and dried samples with lower crystallinity, but not from the annealed samples with higher crystallinity. These evidences may indicate that the polar conformations were formed in the amorphous region of the chain system, and the dipole glass state, characterized by relatively short-range dipole ordering, is responsible for the formation of the polarization. This mechanism, however, cannot fully explain the electrical properties in the present PHB system from a following reason, either.

The glass transition of PHB was determined to be $T_g = 0$ °C from the DSC trace and the dielectric spectrum. On the contrary, the polarization inversion became active at the temperatures higher than 70 °C. Furthermore, the dielectric relaxation strength is as small as $\Delta\varepsilon = 1.5$. This value is the same order of magnitude as the dielectric relaxation strength that is estimated with Froehlich's free dipole rotation model [15]. The rotational motions of the dipoles progressed independently, and it was almost impossible for them to form the macroscopic polarization.

Fukada et al. studied the piezoelectric polarization in the elongated semicrystalline PHB sheets [3,16]. The piezoelectric polarization consisted of the two different components. The first piezoelectric polarization maintained a thermal stability in the range −150 to 150 °C and the magnitude of the piezoelectric constant was almost independent of the temperatures. The signal was resulted from instantaneous polarizations formed in the crystalline region. On the other hand, the magnitude of the second piezoelectric signal gradually decreased at the temperatures higher than the glass transition temperature. The signal was caused by the relaxational polarization formed in the oriented noncrystalline region, where structural ordering was not perfect. The relatively-ordered dipole conformations were formed in the intermediate region between the crystalline and noncrystalline phases. The temperature-dependent polarization, which was responsible for the present *D–E* hysteresis loop, is likely related to the second relaxational polarization formed in the intermediated phase.

The ester dipoles should be oriented in the directions perpendicular to the helical axis. In the α-helical polypeptides, such as poly(benzyl glutamate) or poly(methyl glutamate), the piezoelectric activities were resulted from the ordering of the amide(CO=NH) dipoles in the direction perpendicular to the helical axis [17]. In a single chain, the dipole elements in the direction perpendicular to the helical axis seem to be canceled out with one another because of the rotational symmetry around the helical axis. The symmetric structures, however, are easily broken by some external forces, such as shear or tensile stresses, and the ordering of the amide dipoles were brought about.

The dipole-ordered conformations are probably enhanced by the intrachain hydrogen bonding interactions. The infrared absorption spectroscopy and X-ray diffraction spectroscopy proved that week hydrogen bond interactions took place between the neighboring chains [18,19]; the oxygen atoms in C=O groups and one of the hydrogen atoms in CH_3 groups were attracted with each other. The study also demonstrated that the hydrogen bond strengths were gradually reduced as the temperature increased at the temperatures higher than the room temperatures. The polarization inversion was forbidden at the temperatures lower than 70 °C, the temperature much higher than $T_g = 0$ °C. This experimental result indicates that the hydrogen bonding interaction is too large and it prevented the coordinative rotational motions of the ester dipoles.

Finally, the polarizations responsible for the two kinds of pyroelectric signals are discussed. As seen in Fig. 4, the pyroelectric signal of the PHB consisted of two components with different poling temperature dependence. The first signal was induced only after the poling procedure at 80 °C, and it existed stably up to 80 °C. This pyroelectric signal was attributed to the modulation of the polarization associated with the *D–E* hysteresis. The polarization can be inversed at the temperatures higher than 80 °C. During the poling procedure at 80 °C, the dipoles were allowed to move in a coordinative manner, and the polar conformations were formed along the external field direction. The pyroelectric signal decreased gradually at the temperatures higher than 40 °C. It was because the interchain hydrogen bond interactions were reduced and accordingly the polar conformations were depolarized as the temperature increased, as mentioned above.

On the contrary, the second pyroelectric signal, which was observed at the temperatures 20–120 °C, was induced at both of the poling temperatures 20 and 80 °C. The second signal seems to be related to the short-range dipole ordering, namely, the dipole glass state, since it can be even generated after the poling procedure at as low as 20 °C, a little higher than the glass transition point T_g. However, the present pyroelectric signal cannot be fully explained with the framework of the dipole glass model. The thermal stability of the dipole glass is also related to the glass transition point, and the dipoles are depolarized at the temperatures higher than T_g. In the present case, the signal exists stably at the temperatures much higher than the glass transition point. As a probable mechanism, the dipoles took highly oriented conformations around the electrode, because of the metal surface orientation effect. In general, the effectively high electrostatic fields work around the metal-polymer surface. The short-range dipole ordering occurred at the poling temperature above T_g. The orientation of the dipoles was tightly kept because of the metal-polymer hetero-surface potential. Thus, the polarization remained even at the temperatures higher than T_g.

5. Conclusions

The present study reported the electrical response of the rigid rod-like polymer, PHB. The previous study exhibited that the PHB was active in the shear piezoelectricity. This study proved that the PHB system was rich in other electric functionalities, such as ferroelectric and pyroelectric behaviors, after the poling procedure. Our work opens a doorway for new potentials of the biodegrading polymers as electronic active polymers.

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