

Ferroelectric and Pyroelectric Behaviors in Poly(glycolic acid)

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ABSTRACT: Ferro and pyroelectric behavior was observed in poly(glycolic acid) (PGA) consisting of dipoles along the chain direction. The pyro- and piezoelectric (d_i) constants in poled sample ($T_p = 150^\circ\text{C}$; $t_p = 3$ min; $E_p = 50$ MV m $^{-1}$) were 32 $\mu\text{C m}^{-2} \text{K}^{-1}$ and 15 pC N $^{-1}$, respectively, at room temperature. Such large constants may be due to polar structure formed by poling. D - E hysteresis loop was observed above 100 $^\circ\text{C}$. Remanent polarization and coercive electric field were 70 mC m $^{-2}$ and 40 MV m $^{-1}$ at 120 $^\circ\text{C}$, respectively. It can be seen from IR, XRD, and polarizing microscope data that remanent polarization mainly results from the orientation in the amorphous chain by a high electric field.

KEY WORDS Polyesters / Poly(glycolic acid) / Ferroelectricity / Remanent Polarization / Pyroelectricity / Piezoelectricity /

The ferroelectricity of polymers has been extensively studied in the last decade as well as piezo- and pyroelectric behavior because of possible applications as new transducer materials. Typical examples are vinylidene fluoride copolymers and odd nylons^{1–3} which have polar ferroelectric crystals.

In recent years, however, ferroelectric behavior of several nonpolar crystalline polymers such as nylon 6,⁴ poly(β -propiolactone),⁵ and poly(L-lactic acid) (PLLA)⁶ has been reported. The crystal transformation has been suggested that nonpolar crystals may change to polar with the application of a higher electric field.

Poly(glycolic acid) (PGA) has been known to make low cost and tough fiber⁷ since 1954 and commercially available as the surgical suture Dexon since 1970.⁸ It has the shortest and simplest molecular repeating unit among polyester homologues as shown in Figure 1. The molecular chains in crystal have the planar zigzag conformation with adjacent C=O dipoles arranged opposite to form a nonpolar packing, suggested by Hirono *et al.*⁹ However, the molecular chain in PGA can make dipole moment along the chain. Therefore, as well as the case of other nonpolar crystalline polymers reported,^{4–6} PGA may also have the possibility of ferroelectric material upon application of a high electric field.

PGA with biodegradability has been noted as a low-load material to the environment, but application is limited only to the medical field as absorbable suture^{10,11} and drug-deliver for its biocompatibility. If ferroelectricity is available for biodegradable PGA, disposable electrets such as dust filters can be expected.

This paper discusses the field induced structural changes and pyroelectricity of PGA.

EXPERIMENTAL

PGA powder was supplied by Gunze Co., Ltd. Samples (10–20 μm thick) were prepared by melt-casting at 230 $^\circ\text{C}$ ($T_m = 219^\circ\text{C}$) and rapid quenching into liquid nitrogen. Aluminum was deposited on both sides of the films as electrodes for electrical measurements. Poling was carried out in the following two ways: (1) Ordinary poling carried

out at different temperatures and electric fields for 3 min using a dc power supply for measurements of piezo- and pyroelectric constants, and (2) Corona poling carried out at various temperatures (film thickness = 10 μm ; electric field = 6 kV) for 3 min for the measurements of XRD and IR. Both processes were followed by cooling to room temperature with the electric field applied. Nonpoled samples as references were annealed with the same condition as the poling.

Differential scanning calorimetric measurements were carried out with a MAC SCIENCE DSC 3100 with a heating rate of 10 $^\circ\text{C min}^{-1}$. Infrared (IR) spectroscopy measurements were carried out using a HORIBA FT 300. X-Ray diffraction (XRD) patterns were obtained with a RIGAKU-Rint 2100 diffractometer using Cu- K_α radiation. To obtain the information about molecular orientations, birefringence in the poled samples was observed by a polarizing optical microscope.

Displacement-field (D - E) curves were calculated from the I - V data obtained by measuring the current through the electrode area in response to a triangular voltage input with a frequency of 0.01 Hz. Thermally stimulated current (TSC) and reversible pyroelectric current were recorded simultaneously from the current through an electrode irradiated by a pulsed semiconductor laser (670 nm, 3 mW, 10 Hz) at a heating rate of 3 $^\circ\text{C min}^{-1}$. The absolute value of pyroelectric constant was calculated from reversible TSC with heating and cooling near room temperature. Piezoelectric constant (d_i) was obtained from the thickness strain (Laser Doppler Vibrometer ONO SOKKI LV3100) induced by the AC field (1 kHz).

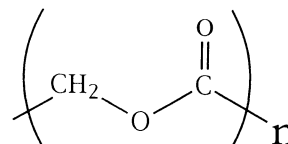


Figure 1. Chemical structure of PGA.

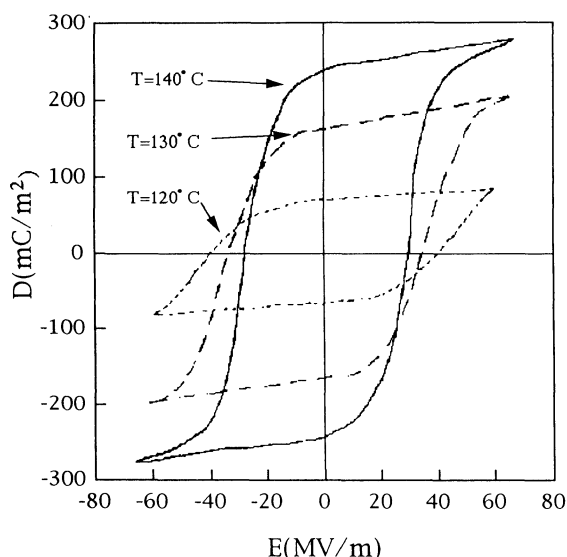


Figure 2. D - E hysteresis loops for PGA at different temperatures, and 0.03 Hz.

RESULTS AND DISCUSSION

Ferroelectric Hysteresis

According to our DSC data of a quenched PGA, there were three transitions up to 250°C: the glass transition at 30°C, crystallization from 50°C and melting at 219°C, in agreement with the experimental data reported.¹² This quenched sample is almost amorphous at room temperature from X-ray measurement.

We observed no D - E hysteresis below 100°C. D - E hysteresis was observed above 100°C, after crystallization.

Figure 2 shows the D - E hysteresis loops at 120°C, 130°C, and 140°C obtained from the current density-electric field curve in which the contribution of conduction current is excluded. The remanent polarization of PGA increases with temperature, similar to PLLA.⁶ Remanent polarization was 70 mC m⁻² at 120°C, but P_r increases to 230 mC m⁻² at 140°C. If it is possible for ester dipoles to orient in the direction of an applied field, the ultimate polarization (the number of C=O dipoles per unit volume (N) times the diole moment (μ)) can be estimated as 50–70 mC m⁻². The large remanent polarization may include bulk (crystal and amorphous) polarization and ionic impurity polarization. Only a part of the polarization reversal is probably due to a polar structure formed by electric field at high temperatures.

Structural Change of PGA by Poling

If crystals in PGA show ferroelectric D - E hysteresis characteristics, it will be necessary to change to a polar form from the original non-polar structure.

Figure 3 shows the X-ray diffraction patterns for PGA samples. There are two broad peaks at 8° and 20° for the quenched sample (a). This should be of a typical amorphous phase. In contrast, the sample annealed at 150°C (b) exhibits two crystal peaks at 21.7 and 28.8° as well as an amorphous pattern around 8°. Crystal peaks for the sample annealed and poled at 150°C (c) show evident shift to the low angle side of 21.4 and 28.4°,

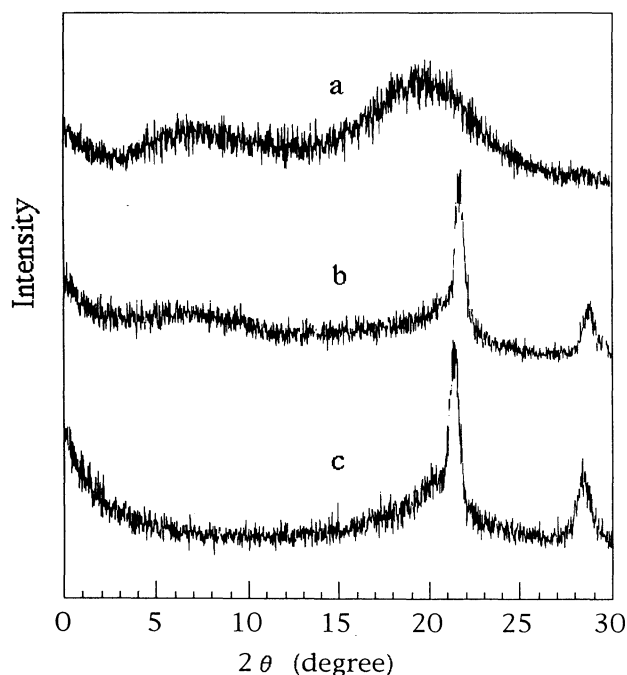


Figure 3. X-Ray diffraction patterns for PGA samples (a) quenched (b) annealed at 150°C and (c) annealed and poled at 150°C.

Table I. Changes of IR absorbance for PGA samples

Sample	C=O stretching (1751 cm ⁻¹)	CH ₂ bending (1419 cm ⁻¹)
Annealed at 150°C	1.54	0.84
Poled at 40°C	1.52	0.89
Annealed and poled at 150°C	1.46	0.81

respectively, suggesting a little change of crystal structure. The amorphous pattern at 8° disappears by poling at 150°C and a new broad peak appears at 20°. The crystallinity of these samples is below 50%. The amorphous structure of PGA seems to be appreciably changed by poling.

The rotation of dipoles can be detected by IR spectral measurement. If dipoles align in the direction of the poling field from their randomly oriented state, the absorption of C=O stretching vibration in the poled sample should be smaller than that in the non-poled one because the vibration mode does not agree with the direction of the electric vector of the IR-beam. As shown in Table I, absorbance of C=O stretching in poled samples is smaller than that in nonpoled sample. This suggests that the dipoles in crystal and amorphous regions may align normal to the film surface to form the remanent polarization by poling. The CH₂ bending mode shows small change. These indicate the selective orientation of -CH₂. Therefore, the polarization reversal possibly originates from the C=O dipole orientation.

According to the observation of polarizing optical microscope, the samples poled above 150°C had a large birefringence especially between the electrodes, as shown in Figure 4. Non-poled samples obtained by the same procedure have no macroscopic birefringence, except for that form spherulites (crystals). The macroscopic birefringence may come from PGA chain orientation. There

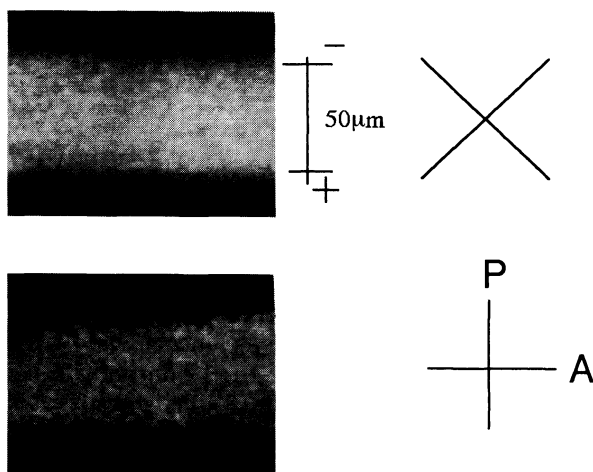


Figure 4. Polarizing optical micrographs of PGA film (10 μm thick) poled between parallel electrodes located on the glass substrate (poled at 180°C 20 MV m^{-1}): P, polarizer; A, analyzer.

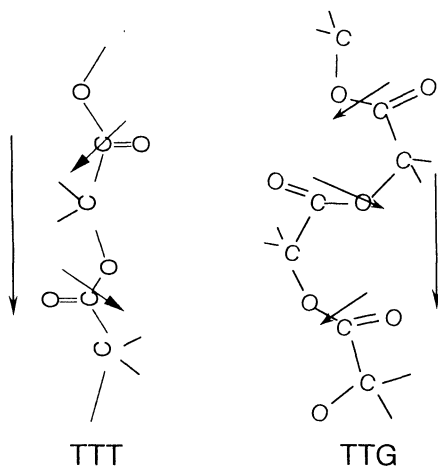


Figure 5. Dipoles and directions in PGA.

are two possible orientation, the chain normal to the electrode surface and the chain parallel to the electrode. C=O dipoles in the polymer chain can be rotated by an electric field near the glass transition, but the chain cannot move toward the electrode. By poling at higher temperatures, amorphous chains can easily orient so as to make a chain dipole orientation normal to the electrode surface. We observed randomly oriented crystals as spherulites in poled and non-poled samples. Therefore, field induced molecular orientation may occur mainly in amorphous phase at the higher temperatures.

The conformation of PGA in crystal is basically TTT (all *trans* or planer zigzag). It is very difficult to form a polar structure in which C=O dipoles orient in the direction normal to the molecular chain. However, this TTT structure has a large dipole moment along the chain because of the specific arrangement on chemical compositions. The TTG (*trans-trans-gauche*) helical conformation possible in crystal and amorphous phases induces a large dipole moment along the chain direction. Figure 5 shows these structures.

If TTT chains of PGA form a polar crystal like PLLA,¹³ XRD data should considerably change only in the intensity with poling. In practice, not only the peak position but the intensity of crystal diffraction was

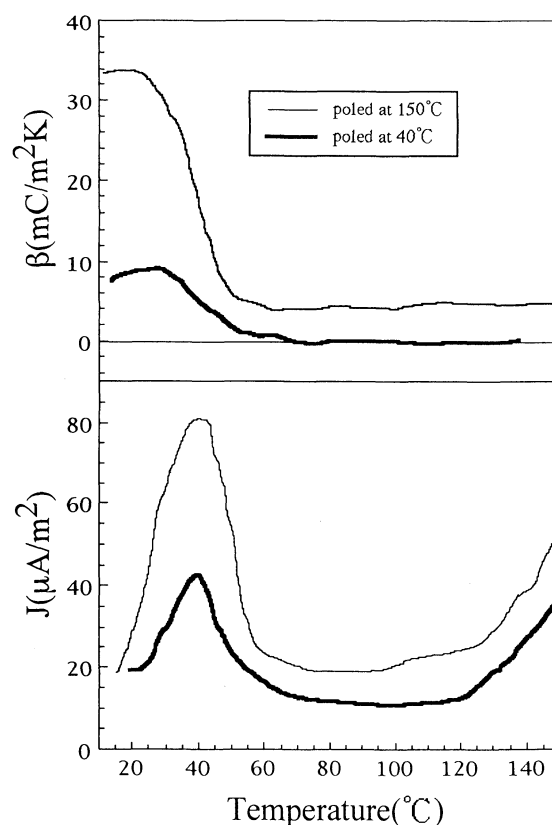


Figure 6. Temperature dependence of pyroelectric constants and thermally stimulated depolarization current (TSDC) curves for PGA samples ($E_p = 50 \text{ MV m}^{-1}$).

little changed by poling, and only the amorphous halo was significantly changed. These changes can be mainly explained by the formation of polar structures by field induced conformational change or by chain directional change in amorphous region.

Consequently, the poling process of PGA may be due to the rotation of C=O dipoles accompanying the chain orientation.

Pyroelectric Response of PGA

When C=O dipoles align normal to the film surface, the sample is expected to show pyro- and piezoelectric behavior. In general, pyroelectric response is strongly affected by the thermal transitions of samples. According to the DSC data, the crystallization of the sample occurs at 50°C, so that poling at high temperatures is performed for a crystallized sample. Therefore, we selected poling temperatures of 40°C, higher than T_g (30°C) but lower than the crystallization temperature to see the polarization in the amorphous phase, and 150°C, under the melting temperature but higher than the crystallization temperature to see the polarization in amorphous and crystal phases.

Figure 6 shows the temperature dependence of the pyroelectric constant and TSC curves for samples poled at 150°C and 40°C (50 MV m^{-1}), respectively. The pyroelectric constant at room temperature is about $8.5 \mu\text{C m}^{-2} \text{K}^{-1}$ for the sample poled at 40°C. It decreases continuously from the glass transition temperature and becomes zero at about 60°C. Even when the sample was poled at 80°C, the pyroelectric constant

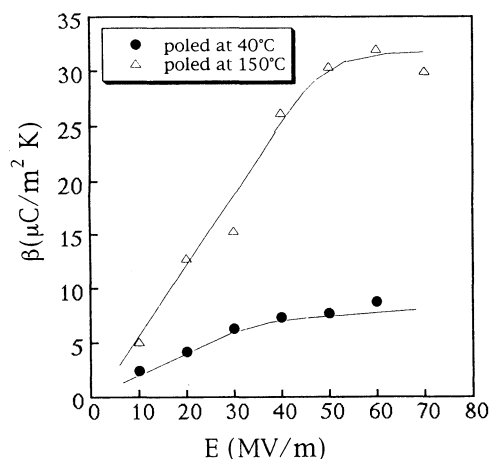


Figure 7. Poling electric field dependence of pyroelectric constant at 20°C for PGA.

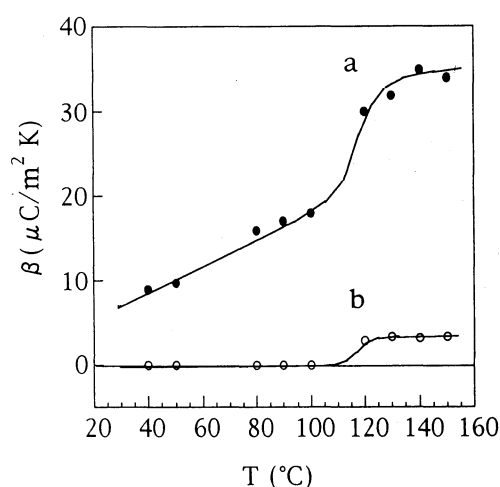


Figure 8. Poling temperature dependence of pyroelectric constant at 20°C for PGA ($E_p = 50 \text{ MV m}^{-1}$).

($15 \mu\text{C m}^{-2} \text{K}^{-1}$ at room temperature) decreased from T_g to become zero at 60°C. In contrast, the pyroelectric constant ($32 \mu\text{C m}^{-2} \text{K}^{-1}$) for the sample poled at 150°C decreases from 30°C and becomes constant to $3 \mu\text{C m}^{-2} \text{K}^{-1}$, remains stable up to 160°C, indicating the stable polarization formed by poling above 120°C.

Figure 7 shows the poling field dependence of pyroelectric constant at 20°C for the samples poled at 40°C and 150°C. The pyroelectric constant of the samples increases rapidly with poling field, and saturates from 50 MV m^{-1} . It reaches $32 \mu\text{C m}^{-2} \text{K}^{-1}$ in the sample poled at 150°C, close to that of poly(vinylidene fluoride) (PVDF).¹⁴ This indicates that a larger residual polarization is formed above the crystallization temperature.

Figure 8 shows the poling temperature dependence of pyroelectric constant measured (a) at 20°C and (b) at 50°C (after depolarization of amorphous dipoles) ($E_p = 50 \text{ MV m}^{-1}$). A small pyroelectric constant is obtained when the poling temperature is lower than 50°C, under which the sample is amorphous. After crystallization and poling above 80°C, it increases slowly and suddenly jumps to $32 \mu\text{C m}^{-2} \text{K}^{-1}$ at 120°C. As shown in (b) measured at 50°C, the pyroelectric constant becomes zero when the poling temperature is lower than 120°C. This means no stable polarization in the crystal

region. In contrast, the pyroelectric constant for sample poled above 120°C is stable even above T_g . This suggests that a small polarization possibly exists in a part of crystal or ordered amorphous.

We found an interesting phenomenon in poling process. When poled at 150°C and then depolarized at 160°C, this sample shows no pyroelectricity. This sample can be easily repoled nearby T_g to get a large pyroelectric constant, for example, $32 \mu\text{C m}^{-2} \text{K}^{-1}$. However, the sample only annealed at 150°C cannot have such a large value by poling near T_g . This indicates structural change of amorphous region by poling at higher temperatures, which is related to the amorphous chain orientation as discussed in the preceding section.

Piezoelectricity in poled polymers is known to have a close relation with pyroelectricity.¹⁴ The piezoelectric constants d_i for samples poled at 150°C and 40°C (50 MV m^{-1}) were 15 and 0.4 pC N^{-1} at room temperature, respectively, showing a similar temperature dependence with that of the pyroelectric constants in Figure 6.

Remanent Polarization of PGA

When an amorphous sample is poled at 40°C (even above T_g (30°C)), only a small pyroelectric response is observed. In a simultaneously annealed and poled sample at higher temperatures (above 120°C), a large pyroelectric constant is observed, which implies the remanent polarization in both amorphous and crystal phases. Our experimental data suggest that the contribution of the amorphous chains to the pyroelectricity is predominant.

The molecular chain of PGA has a macro-dipole along the chain for asymmetric arrangement of chemical composition. Therefore, the polarization reversal would involve rotation of the whole chain. If all the polar chains align in the same direction, the sample holding a polar state should have a stable remanent polarization even in amorphous region. However, this polar state can be considerably broken by $T_g + 30^\circ\text{C}$. The conformational change or the C=O dipole rotation above T_g , namely micro-dipoles, may lead to the depolarization of the macro-dipoles. It is necessary to consider the interaction between the micro-dipole of C=O and the macro-dipole of PGA chain.

There is a question why PGA shows the D - E hysteresis only at high temperatures. We observed the same kind of phenomenon in PLLA.⁶ If the polarization reversal is incident to the chain orientation along the electric field, the polarization reversal should be very slow even at a high temperature. This type of dipole rotation is quite different from that in vinylidene fluoride (VDF) copolymers.¹

The crystallinity of PGA annealed is less than 40% from density measurement. Therefore the molecular motion of the amorphous phase is important if the reorientation of PGA chain macro-dipoles results in the D - E hysteresis. We must consider amorphous molecular motions above T_g . In glassy polymer, T_u molecular level transition-relaxation associated with the thermal disruption of segment-segment contact, "segment melting".¹⁵ The relationship between T_g and T_u is about $T_u/T_g = 1.20 \pm 0.05$, depending on both stiffness and polarity of main chains. T_u for the amorphous PGA is estimated

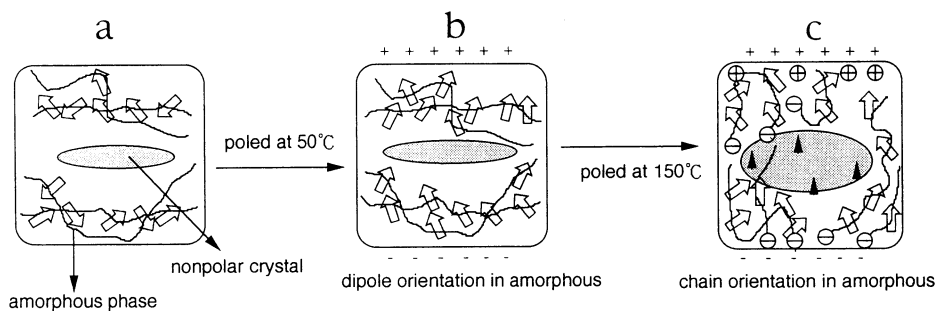


Figure 9. Remanent polarization model for PGA.

as about 100°C.

This temperature region is in agreement with the observation temperature of $D-E$ hysteresis. We think that the orientation of macro-dipoles along a main chain is accompanied by the large molecular motion like "segment melting".

Synthesized polyesters contain small amounts of ion as impurities and terminal groups. Especially, the chain ends of polyesters are carbonic acid strongly bound by counter cations. They can easily move and be polarized to make polymer ions (PGA anions) by electric field. The ions are moved to the surface of film by poling at higher temperatures. This ionic effect increases the remanent polarization measured at higher temperatures, especially above the T_{li} .

Consequently, to form the remanent polarization at higher temperature, not only the molecular chain dipole of PGA but also PGA anions and counter cations need to be oriented along the external electric field. We summarize the formation of the remanent polarization of PGA in Figure 9. There are mainly two remanent polarizations in the amorphous region: one from C=O dipole orientation below 100°C, and the other from macro-dipole chain orientation above 100°C.

CONCLUSIONS

The dipoles of PGA can be oriented by poling at high

temperatures (120–170°C) to form a polar structure mainly in amorphous phase and showed ferroelectric behavior and large pyroelectric activity.

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