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Direct proof of chain rotation on polarization reversal of amorphous poly(nonamethylene thiourea) by X-ray anomalous scattering

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Amorphous poly(nonamethylene thiourea) (polythiourea 9) (–$(CH_2)_9$–NH–CS–NH–$)_n$, under an electric field was examined below the glass transition temperature ($T_g = 48$°C) by X-rays. First, a structural change on poling was observed; the average inter-chain distance in the direction of the electric field increased by 0.3%, suggesting the parallel alignment of dipoles of the polymer chain with the direction of the applied electric field. Second, on the reversal of the applied electric field at 40°C a change in intensity profile of the amorphous halo was observed with CuK_α and CrK_α radiation; the change agrees well with that calculated taking into account the anomalous scattering, on the basis of the model of 180°-rotation of a polythiourea 9 chain around the chain axis. Polythiourea 9 is, therefore, proved to be an amorphous ferroelectric. © 1997 Elsevier Science Ltd.

(Keywords: amorphous; ferroelectric; X-ray anomalous scattering)

INTRODUCTION

Several amorphous materials have recently been reported to be piezo- and pyroelectric[1], and some of them were found to be ferroelectric through D–E hysteresis[2,3]. However, polymeric materials include some inhomogeneities such as impurities, foreign particles, and their interfaces, and hence macroscopic polarization could come from these inhomogeneities. Thus an X-ray investigation is required to examine their microscopic structures under an electric field.

Amorphous poly(nonamethylene thiourea) (polythiourea 9), (–$(CH_2)_9$–NH–CS–NH–$)_n$, has a glass transition temperature of 48°C. Ferroelectric behaviour in aliphatic polythioureas has been reported[3]; and the remanent polarization and pyroelectric constant measured. In this paper, the structural change on poling by an electric field is investigated for polythiourea 9 making use of X-ray scattering. Furthermore, in order to confirm the polythiourea 9 to be ferroelectric, a change in X-ray scattered intensity due to anomalous dispersion is observed on the reversal of direction of the electric field, and is analysed on the basis of a model in which 180°-rotation of the chain around the chain axis occurs on the reversal. Crystalline ferroelectric polymers such as PVDF were successfully examined by this method[4], but no amorphous material has been examined.

EXPERIMENTAL

Polythiourea 9 was synthesized by polycondensation of nonamethylenediamine and carbon disulfide. A dimethylacetamide solution was cast on a reflection-free quartz substrate on which aluminium was evaporated. A film 10–20 μm thick was obtained and dried in a vacuum oven at 110°C for 10 h. The polythiourea 9 film on the quartz substrate was mounted in a specimen holder kept at 40°C on a diffractometer. Scattered X-rays were measured in a scattering angle range of 20° using a one-dimensional position-sensitive proportional counter, PSPC (PSPC10, Rigaku Corporation, Japan); the intensity profile of the amorphous halo of this polymer could be obtained at a given time. With the aluminium electrode grounded, an electric field was applied by a corona discharge method with a needle at a distance of 1 cm apart from the specimen surface, the needle voltage being either plus or minus 5.5 kV; thus the direction of the applied electric field was almost perpendicular to the film surface. During the X-ray measurement, the electric field was applied to the specimen. X-Rays used were nickel-filtered CuK_α and vanadium-filtered CrK_α radiations. In order to eliminate the instability in X-ray generation, a scintillation probe was utilized for monitoring the intensity of incident X-ray. The probe was directed to a cobalt (for CuK_α) or titanium (for CrK_α) thin film evaporated on a thin polyethylene terephthalate film to detect the fluorescent X-ray excited by the incident characteristic

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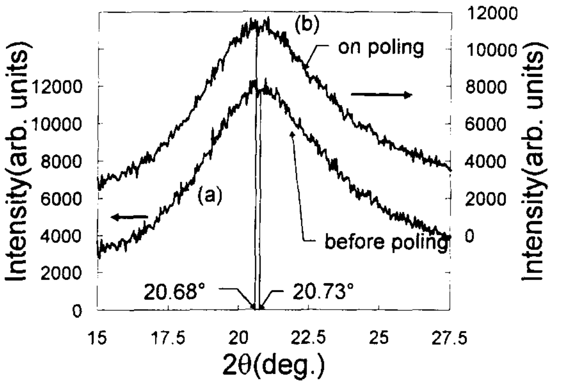

Figure 1 X-Ray scattering profiles (CuK_α radiation) of polythiourea 9 around the amorphous halo: (a) before poling; (b) on poling. A peak position for each case decided by fitting with a parabola is indicated by arrows

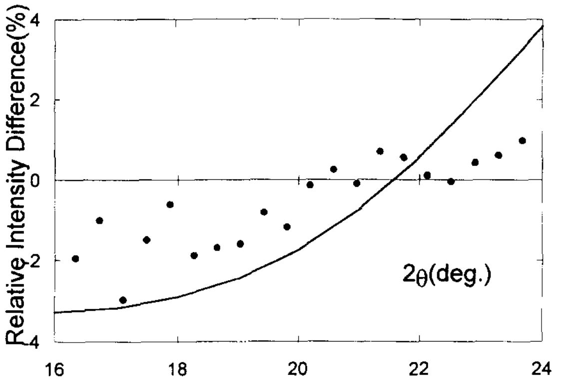

Figure 2 Relative intensity difference, $2(I_p - I_m)/(I_p + I_m)$, around the amorphous halo for CuK_α radiation. The solid line shows calculated values

X-ray. The metal film was put just behind the divergence slit. When the value of total count of the fluorescent X-ray in the scintillation counter system reach to a preset value, the PSPC system was gated to stop counting. The scattering from a polymer-free substrate was subtracted as a background to obtain the net scattering from the polymer specimen.

RESULTS

Effect of poling

The amorphous halo changed on poling (*Figure 1*). After poling, the peak position of the amorphous halo shifted to a lower angle from 20.73° to 20.68°. Since the amorphous halo corresponds to the correlation between chains, the inter-chain distance in the direction of the electric field increases on poling.

Scattered X-ray intensity difference on the reversal of applied field

Figure 2 shows the difference in the intensities around the amorphous halo under plus and minus electric fields for CuK_α radiation. The plus electric field is taken in the reverse direction to the scattering vector; namely, the needle for corona discharge is connected to the plus terminal of a high-voltage supplier. The intensity under a plus field is denoted by I_p and that at a minus field by I_m. Thus the value of $2(I_p - I_m)/(I_p + I_m)$ in *Figure 2* corresponds to the Bijvoet's ratio, if all the electric dipoles reverse direction with the reversal of the electric field. The difference changes from a minus to a plus value crossing zero around 20° with scattering angle. *Figure 3* shows a series of the intensities at three scattering angles of 17.5°, 22.9° and 28.6°, normalized by the average intensity for the first (plus) and the second (minus) poled states with the discharge voltage of +5.5 or −5.5 kV applied alternately; odd numbers in the abscissa are for the plus field, even numbers for the minus field. The intensities at 17.5° and 28.6° change jaggedly with the sequence of measurement, while that at 22.9° decreases monotonically. This behaviour of the intensities can be explained by the result in *Figure 2*; the 'Bijvoet's ratio' changes its sign around 20° with scattering angle. The gradual decrease in the intensities is due to the degradation of the specimen by corona discharge; in fact the film turned from semi-transparent to opaque.

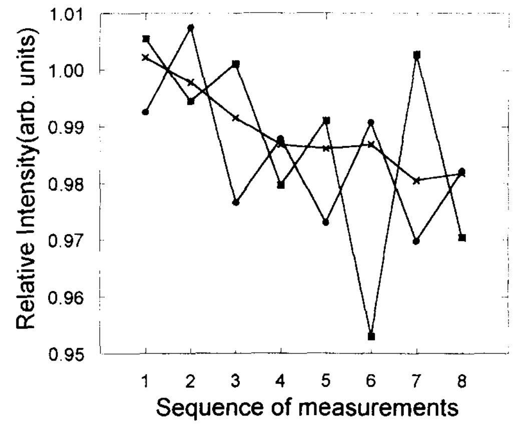

Figure 3 Series of the normalized intensities at three scattering angles, 17.5° (■), 22.9° (×) and 28.6° (●), when the discharge voltage of +5.5 or −5.5 kV is applied alternately. Odd numbers in the abscissa are for the plus electric field and even numbers for the minus

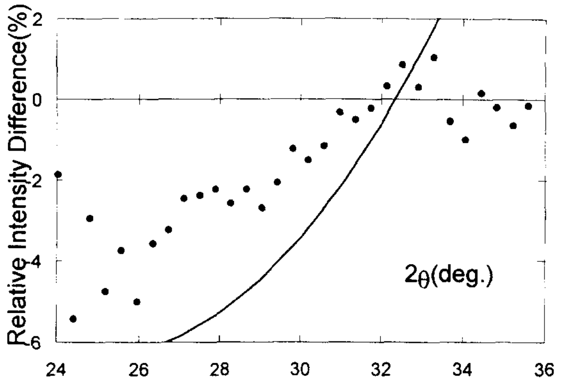

Figure 4 Relative intensity difference, $2(I_p - I_m)/(I_p + I_m)$, around the amorphous halo for CrK_α radiation. The solid line shows the calculated values

Figure 4 shows the data for CrK_α radiation. With a longer wavelength, larger effects of anomalous dispersion are to be observed for polythiourea 9 consisting of the rather light elements, H, C, N and S. The 'Bijvoet's ratio', $2(I_p - I_m)/(I_p + I_m)$, around the amorphous halo is similar to that for CuK_α, and increases from a minus to a plus value, crossing zero around 30° with scattering angle.

DISCUSSION

Structural change on poling

As mentioned in the previous section, inter-chain distance of polythiourea 9 in the direction of the electric

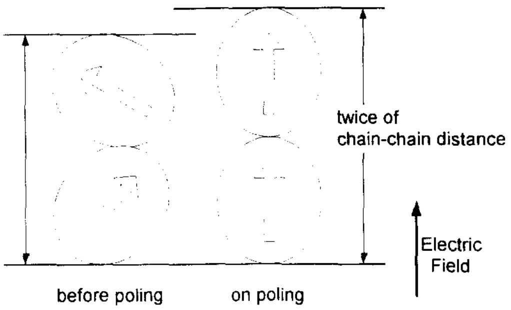

Figure 5 Schematic representation of the structural change on poling. An oval represents a cross-section of a chain of polythiourea 9, and a wide arrow represents a dipole moment. The dimension of the cross-section along the dipole moment is larger than that normal to the dipole moment for polythiourea 9, with the zigzag conformation

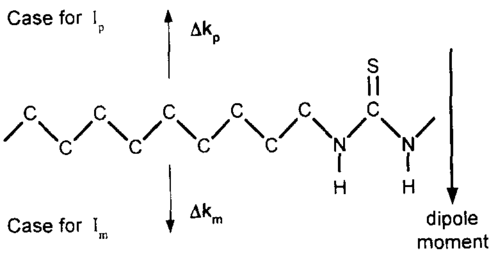

Figure 6 Monomer unit of polythiourea 9 with zigzag conformation. Scattering vectors $\Delta \mathbf{k}_p$ for I_p and $\Delta \mathbf{k}_m$ for I_m are shown

field increases on poling. The dipole moment of polythiourea 9 is perpendicular to the chain axis and parallel to the zigzag plane made of carbons and nitrogens in the main chain. We assume this zigzag conformation, namely all *trans* conformation, locally in the amorphous state. The parallel arrangement of the dipole moments along the electric field gives rise to an increase in the inter-chain distance along the direction (*Figure 5*), since the dimension along the dipole moment is larger in the cross-section of the chain than that perpendicular to it. A similar experiment has been carried out using a piezoelectric copolymer, poly(vinylidene cyanide/vinyl acetate), and has shown that the distribution of inter-chain distances become narrower[5].

Determination of polarization

In order to evaluate the relative intensity difference, $2(I_p - I_m)/(I_p + I_m)$, we calculate the scattering intensity of a monomer unit of polythiourea 9, taking account of the anomalous atomic scattering factors of carbon, nitrogen and sulfur[6,7]. It was assumed that all atoms in the monomer except H atoms are in a plane, which nine carbons in the methylene groups make in the planar zigzag conformation (*Figure 6*). The calculation was done for two cases of the scattering vector parallel to and anti-parallel to the dipole moment (*Figure 6*); the parallel case corresponds to I_m and the anti-parallel to I_p. Coordinates of the atoms used for the calculation are listed in *Table 1*; only the position along the dipole moment is relevant to the intensity for the present calculation[8,9].

The intensity differences calculated for CuK_α and CrK_α radiations are shown in *Figure 7*. In the scattering angle range of the amorphous halo, the intensity difference increases from a minus to a plus value with increasing scattering angle. This difference agrees well with the one observed (*Figures 2* and *4*). A measurement in i.r. spectrum for the N–H stretching mode under similar conditions showed that the polarization reached up to 60% of perfect polarization. Consequently, it is concluded that the chain of polythiourea 9 rotates by an angle of 180° around the chain axis on reversal of an applied electric field; amorphous polythiourea is thus a ferroelectric.

Table 1 Coordinate of each atom in the direction of the dipole moment[8,9]

Element	Coordinate (nm)
C[a]	0.0000
C[b]	0.0076
C[b]	−0.0804
S	0.1681
N	−0.0711
H[c]	−0.1720
H[b]	0.0708
H[b]	−0.1436

[a] Bonding to S and N; settled as an origin
[b] CH_2 groups
[c] Bonding to N

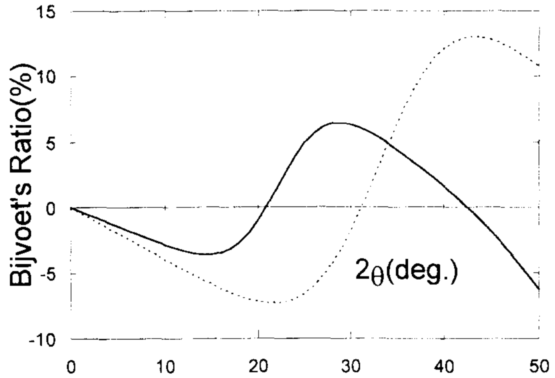

Figure 7 Bijvoet's ratio, $2(I_p - I_m)/(I_p + I_m)$, calculated for CuK_α radiation (solid line) and CrK_α radiation (dotted line)

In the calculation we have assumed the chain axis to be perpendicular to the scattering vector (*Figure 5*), and hence neglected the effect of the random orientation of the chain axis in the amorphous material. However, it should be noted that the intensity concerned is that of the amorphous halo around 22° or 30° for CuK_α or CrK_α radiation, respectively. This halo corresponds to the inter-chain correlation as discussed in the Results section; thus only the chains almost perpendicular to the scattering vector, namely parallel to the film surface, can contribute to the intensity observed at the scattering angle range in the present study.

CONCLUSION

On poling, a structural change associated with the dipole alignment along the poling field was observed for amorphous polythiourea 9; the inter-chain distances increased. The intensity of the amorphous halo changed with reversal of the applied electric field; the intensity difference agreed well with the calculated one based on a model that a polythiourea 9 chain rotates around the chain axis by an angle of 180° on reversal of the electric field. Thus we have confirmed that poly(nonamethylene thiourea) is an amorphous ferroelectric polymer on the basis of the structure at the molecular level.

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