SHORT COMMUNICATIONS

Ferroelectric Polarization Reversal Stabilized by Hydrogen Bonding in *N*-Phenylated Aromatic Polyurea

Shigeru TASAKA, Kazuya OHISHI, Hari Singh NALWA,*
Toshiyuki WATANABE,** and Seizo MIYATA**

*Faculty of Engineering, Shizuoka University, 3–5–1, Johoku,
Hamamatsu 432, Japan*

** Hitachi Reserch Laboratory, Hitachi Ltd., 7–1–1 Ohmika-cho,
Hitachi 319–12, Japan*

*** Faculty of Technology, Tokyo University of Agriculture and
Technology, Koganei, Tokyo 184, Japan*

(Received October 12, 1993)

KEY WORDS Polyurea / Ferroelectricity / Hydrogen Bonding / Remanent Polarization / Pyroelectricity /

Recently, Polyureas are attracting much attention in the fields of electronics and photonics. Polyureas with large dipole moments (4.5D) of —NHCONH— show strong pyroelectric¹ and ferroelectric behavior.² The molecules in most polyureas are generally aggregated by a strong hydrogen bonding of $\text{NH} \cdots \text{O}=\text{C}$ to induce unusual properties. It is of great interest to study the roles of hydrogen bonding in connection with electrical properties.

The *N*-phenylated aromatic polyurea used in this study, synthesized by reacting an equimolar mixture of diamino-*p*-xylene with 4,4'-diphenylmethane diisocyanate, forms flexible and transparent films and exhibits a large second-order nonlinear optical coefficient after poling.^{3,4} These properties seem to arise from the chemical structures of polymers. The lower density of hydrogen bonding introduced by *N*-substituted structure and bulky main chain are responsible for an amorphous structure. Though it is easy to form polar structures of polymers with hydrogen bonding, not to realize a ferroelectric structure. However, if one polymer chain can obtain a polar chain

structure without an strong aggregate moiety such as hydrogen bonding, the resulting bulk structure would be ferroelectrics by controlling the external electric field.

This communication discusses the possibility of amorphous ferroelectrics for polyurea systems having a small amount of hydrogen bonding.

Polyurea prepared by the method as described earlier³ was cast into thin film (5 μm) from a chloroform solution at room temperature. Thin film samples metalized by aluminum evaporation on both sides were subjected to the polarization reversal measurement. Dielectric measurements were carried out under vacuum with a HP 4285 LCR meter. Displacement–field (*D*–*E*) curves were generated 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 depolarization current (TSC) for poled samples was recorded at a heating rate of 4°C min^{–1}. IR spectra for the polyurea film were recorded on a JASCO FT/IR3 spectrometer.

Dielectric measurement performed on thin

Figure 1. Relationship between polarization current density and external field for *N*-phenylated aromatic polyurea at 120°C.

polyurea films showed two relaxation processes: first with a small relaxation strength at 100–120°C, probably due to processes such as a local motion, and second at 160–170°C, due to glass transition. The dc conduction above 160°C increased drastically and this restricted measurement under high electric fields. As a consequence, we measured the polarization reversal at 120°C, below the glass transition temperature of polyurea.

Figure 1 shows the electric field dependence of polarization current of the sample at 120°C. This type of measurement using triangular waves should give a rectangular shape in lower fields, and the height of the rectangle should be proportional to a linear dielectric constant. However, upper and middle curves in Figure 1 seems to consist of a superposition of two different rectangles indicating two dielectric constants corresponding to the lower and the higher fields. Inclination of the rectangle stands the magnitude of dc conduction based on ionic impurities. On lower fields, dipoles in the polyurea are aligned by an external field in order to have a large dielectric polarization. In the high electric fields, the orientation polarization may reach saturation and simultaneously

Figure 2. Current-field curve excluding dc conduction current and D-E hysteresis curve of *N*-phenylated aromatic polyurea at 120°C.

form hydrogen bonds between C=O and N-H in the polyurea. At this stage, the oriented dipoles reversibly change to the pristine unoriented state after removing the field. Consequently, the dielectric constant decreases with increasing the field.

Applying a higher electric field induces conformational change to a metastable structure with dipole orientation. The dipole polarization is restricted by hydrogen bonding formed by the external electric field. This may be field-induced structural change. Finally, hydrogen bonding may form a remanent polarization (P_r) and a D-E hysteresis curve was observed as shown in Figure 2. The polarization current curve which excludes the dc conduction current of the sample is also shown.

The remanent polarization obtained from the figure was found to be about 3 mC m^{-2} , which is smaller than the estimated value of $10\text{--}20 \text{ mC m}^{-2}$ assuming a reasonable con-

Figure 3. IR spectrum of *N*-phenylated aromatic polyurea.

formation of the polyurea chain. The sample with P_r gives a large pyroelectric constant ($3 \times 10^{-6} \text{ C m}^{-2} \text{ K}$), that seems stable, at least, up to the glass transition temperature. The X-ray diffraction spectrum showed that this polymer is typically amorphous so that the remanent polarization should be in amorphous region.

Polar polymers such as poly(vinyl chloride) exhibit remanent polarization for a poled sample. It is very difficult to saturate the polarization of such polymers by external electric field because the cooperativity of dipoles is low and mobility is frozen below T_g . Therefore, similar phenomena would not be observed except for hydrogen bonded polymers.

IR spectra give information on hydrogen bonding of amorphous polyurea. Usually, polyureas, polyamides or polyurethanes which form hydrogen bonding show more than the two of stretching bands of C=O or N-H. For example, N-H stretching mode in these polymer is observed at 3445 cm^{-1} (non-hydrogen bonded) and 3300 cm^{-1} (hydrogen bonded) near 3000 cm^{-1} region.⁵ The apparent absorptivity coefficient of the hydrogen bonded modes in the polymers is very strong.

Figure 3 shows the IR spectrum of polyurea, and in this *N*-phenylated polyurea,

the stretching modes are at 3423 cm^{-1} and 3345 cm^{-1} . C=O stretching occurs at 1673 cm^{-1} . The intensity of hydrogen bonded band is lower than that of the non-hydrogen bonded one, and its wavenumber shifts to lower energy, compared with that in other hydrogen bonded polymers. These points suggest weak hydrogen bonding and low cooperativity of the dipoles in this polyurea. Consequently, hydrogen bonding from the "free" N-H moiety and reconstruction of hydrogen bonded N-H are possible in polyurea systems under high electric fields.

In conclusion, we observed for the first time ferroelectric behavior in *N*-phenylated polyurea after applying a high electric field. Electric field treatment produces hydrogen bonding from the "free" or "hydrogen bonded" HNCO group in amorphous polyurea.

REFERENCES

1. Y. Tasakahashi, M. Iijima, and E. Fukada, *Jpn. J. Appl. Phys.*, **28**, L2245 (1989).
2. S. Tasaka, T. Shouko, and N. Inagaki, *Jpn. J. Appl. Phys.*, **31**, L1086 (1992).
3. H. S. Nalwa, T. Watanabe, A. Kakuta, A. Mukoh, and S. Miyata, *Polymer*, **34**, 657 (1993).
4. H. S. Nalwa, T. Watanabe, A. Kakuta, A. Mukoh, and S. Miyata, *Appl. Phys. Lett.*, **62**, 3223 (1993).
5. D. J. Skrovanok, P. C. Painter, and M. M. Coleman, *Macromolecules*, **19**, 699 (1986).