PII: S0032-3861(97)00289-9

*Polymer* Vol. 39 No. 2, pp. 455–458, 1998
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0032-3861/97/$17.00+0.00

# Annealing effects on crystal structure and ferroelectric properties in aromatic polyurethane

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*(Received 22 May 1996; revised 14 March 1997)*

Annealing effects on ferroelectric properties of an aromatic polyurethane (*m*-xylene nonamethylene dicarbamate, PUMX-9) were studied. X-ray diffractometry showed that the crystallinity of PUMX-9 increased during annealing. Both quenched and annealed polyurethane samples showed a similar electric displacement (*D*) versus electric field (*E*) hysteresis loop. Furthermore, the remanent polarization obtained from the *D–E* loop was slightly changed by annealing. The experimental results suggest that the ferroelectric properties of this polyurethane arise not in the crystal phase but in a well-hydrogen-bonded amorphous phase which behaves like crystals with large numbers of defects. © 1997 Elsevier Science Ltd.

**(Keywords: polyurethanes; ferroelectric properties; crystal structure)**

## INTRODUCTION

Investigations of the ferro- and pyroelectric properties of hydrogen-bonded polymers such as polyamides and polyureas have increased recently[1–5]. Polyurethanes also from hydrogen bonds between the adjacent molecular chains which contain the characteristic carbamate group (-NHCOO–). It has been reported that the ferroelectric and pyroelectric behaviour of odd–odd and odd–even linear aliphatic polyurethanes originates from urethane dipole rotation in the crystals[3,4]. Recently, ferroelectric behaviour in amorphous polyamides was reported only below the glass transition temperature, and this property was attributed to the dipole polarization of amide groups in the amorphous phase[2].

Annealing is one of the most common techniques used for increasing both quality and quantity of crystals in polymeric materials. The annealing process strongly affects the ferroelectric properties of drawn PVDF[6], P(VDF–TFE) copolymers[7] and drawn nylon 7 and nylon 11[8]. The remanent polarization of copolymers of P(VDF–TFE) is increased by the increase in crystallinity[7]. In P(VDF–TFE) copolymer of higher crystallinity, the dipole rotation is enhanced by the expansion of intermolecular distance and the decrease in the number of folds at defects in the crystals. On the other hand, the 'odd' nylons exhibit different behaviour after annealing: their remanent polarization disappears after annealing. Similar results have been reported for aromatic polyamides[2,9]. These types of behaviour of aromatic polyamides are related to the stabilization of hydrogen bonds by crystallization. In the present study, thermally annealed polyurethane was investigated to establish a clear relation between the structure and ferroelectricity.

## EXPERIMENTAL

An aromatic polyurethane (PUMX-9) was synthesized using approximately equal amounts of *m*-xylene diisocyanate and nonamethylene diol. Polyaddition reaction was carried out at 90–110°C for 2 h in anisole. The product obtained was well purified with water and methanol and then dried in a vacuum oven. The films were prepared by melt-casting and quenching to room temperature. The thickness of the films used in this study was in the range 10–15 $\mu$m. To measure the electrical properties, both sides of film samples were metallized with aluminium by vacuum evaporation. The samples were annealed at 80, 100 and 120°C for 2 h and denoted A80, A100 and A120 respectively. A sample was annealed at 75°C for 10 min to obtain similar annealing conditions as in the case of *D–E* measurements, and was denoted A75.

Differential scanning calorimetry (d.s.c.) was carried out using a MAC SCIENCE DSC 3100 with a heating rate of 10°C min$^{-1}$. Infrared (i.r.) spectroscopy was performed using a HORIBA FT 300. X-ray diffraction (XRD) spectra of samples were obtained with a RIGAKU-RAD B diffractometer (25 kV, 15 mA). The *D* versus *E* (*D–E*) hysteresis characteristics were obtained by applying a triangular voltage with a frequency of 0.03 Hz. Dielectric measurements were carried out with a LCR meter (HP4285) under vacuum conditions.

## RESULTS AND DISCUSSION

*Figure 1* shows the d.s.c. curves of PUMX-9 samples that were quenched and annealed at different temperatures. The quenched sample shows three transitions in the measured temperature region. The first step-like transition around 12°C is due to the glass transition, and the second exothermic peak is attributed to the crystallization of amorphous phase. The third broad endothermic peak at 137°C corresponds to the melting of crystals.

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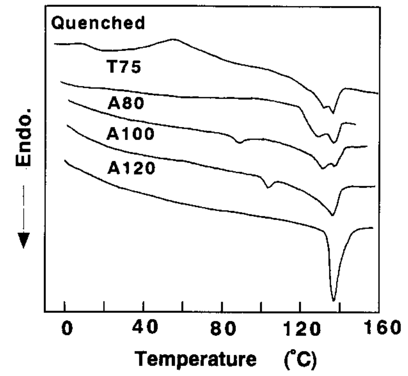

**Figure 1** D.s.c. curves of quenched and annealed PUMX-9 samples

**Table 1** I.r. data for quenched and annealed samples

| Sample condition | N–H stretching band position ($cm^{-1}$) | C=O stretching band position ($cm^{-1}$) |
|---|---|---|
| Quenched | 3315 | 1695 |
| A75 | 3316 | 1695 |
| A80 | 3311 | 1691 |
| A100 | 3311 | 1691 |
| A120 | 3309 | 1689 |

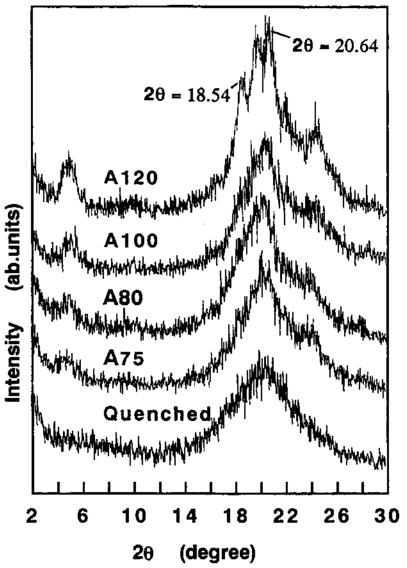

**Figure 2** XRD spectra of quenched and annealed PUMX-9 samples

**Table 2** Heat of fusion ($\Delta H_m$) obtained from d.s.c. and density of quenched and annealed PUMX-9 samples

| Sample condition | Density, 20°C ($g\,cm^{-3}$) | Heat of fusion, $\Delta H_m$ ($J\,g^{-1}$) |
|---|---|---|
| Quenched | 1.179 | — |
| A75 | 1.179 | 31.8 |
| A80 | 1.180 | 32.0 |
| A100 | 1.181 | 33.8 |
| A120 | 1.182 | 40.4 |

The melting peak of PUMX-9 is much broader than that of aliphatic polyurethanes[3], suggesting that the quality of the crystal is lower, even in annealed PUMX-9 samples. No crystallization peak is observed for annealed samples, but annealed samples show new small endothermic peaks due to the melting of metastable phase or premelting. This endothermic peak shifts to a higher temperature, and the heat of fusion of annealed samples increases with increasing annealing temperature. However, the melting temperatures of annealed and quenched samples are approximately the same.

In general, the interchains of polyamides, polyurethanes and polyurea are bound by hydrogen bonds between the adjacent N–H and C=O groups, and the strength of these hydrogen bonds depends on the polymer structure. The hydrogen-bonded N–H stretching vibration band of polyurethane occurs at ~3300 $cm^{-1}$ [10]. For PUMX-9, the hydrogen-bonded N–H stretching occurs at 3315 $cm^{-1}$, while the free N–H stretching and the hydrogen-bonded C=O stretching vibrations are respectively at 3400 and 1695 $cm^{-1}$. These results suggest that the hydrogen bonds in PUMX-9 are not stronger. Furthermore, the positions of the hydrogen-bonded N–H stretching and C=O stretching vibration bands are shifted to slightly higher wavenumbers in the annealing process. According to the i.r. data for quenched and annealed samples given in *Table 1*, the annealing process results in small changes in the hydrogen-bonded regions in the polyurethane. Skrovanek *et al.*[11] attributed the broad N–H stretching vibration bands to the ordered hydrogen bonds in the crystalline phase and the disordered hydrogen bonds in the amorphous phase for nylon 11 and polyurethane. In the present study, the differences between the i.r. spectra of quenched and annealed samples were negligible. Therefore very stable hydrogen bonds should exist in the crystalline and amorphous phases of PUMX-9.

*Figure 2* shows the XRD spectra of quenched and annealed PUMX-9 samples. Quenched PUMX-9 shows only a broad main peak at $2\theta = 20.4°$. The XRD spectrum of sample A75 is similar to that of the quenched sample. The quenched sample, which is in an almost amorphous state, starts to crystallize around 40°C according to the exothermic heat flow in d.s.c.. However, after annealing at 75°C (A75), it has a low degree of crystallinity according to XRD. As can be seen in the XRD spectra, the crystallinity of these samples increases only slightly even on high-temperature annealing: the volume fraction of the crystal phase of annealed samples (calculated from the ratio of the XRD peak corresponding to the crystalline part to the area of the peak in the $2\theta = 14–26°$ region) was $< 30\%$.

*Table 2* lists the heats of fusion ($\Delta H_m$) obtained from the d.s.c. measurements together with the densities of the annealed samples. It can be seen that the heat of fusion of annealed samples increases with annealing temperature. The density was measured by the float–sink method using a mixture of carbon tetrachloride and ethanol at 20°C. However, the increase in density on annealing is small. These results indicate that the difference in density (chain packing) between the amorphous and crystal phases is small, and the present polymer contains a large amount of hydrogen bonds.

*Figure 3* shows the temperature dependence of the dielectric constant ($\varepsilon'$) for sample A75 at three different frequencies. It can be seen that the dielectric constant starts to increase above the glass transition, and then gradually increases in the measured temperature region. This dielectric relaxation is attributed to the dipoles in the amorphous phase. *Figure 4* shows the dielectric strength ($\Delta\varepsilon$) of annealed PUMX-9 samples, obtained from Cole–Cole plots. This dielectric strength decreases slightly in the annealing process due to the increase in crystallinity.

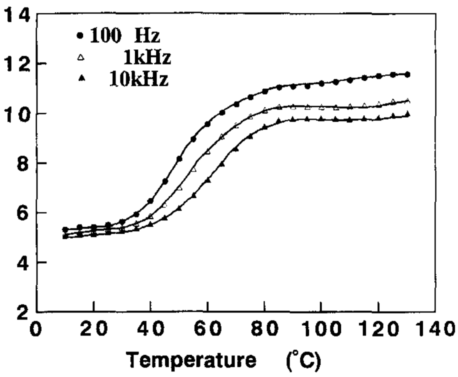

**Figure 3** Temperature dependence of dielectric constant (ε') for A75 sample

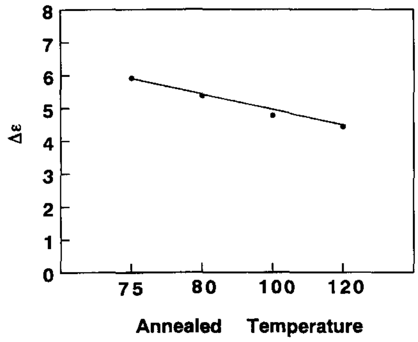

**Figure 4** Dielectric strength (Δε) measured at 80°C for annealed PUMX-9 samples

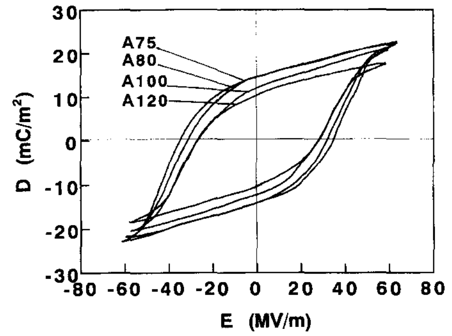

**Figure 5** *D–E* hysteresis loops for PUMX-9 quenched and annealed samples measured at 75°C

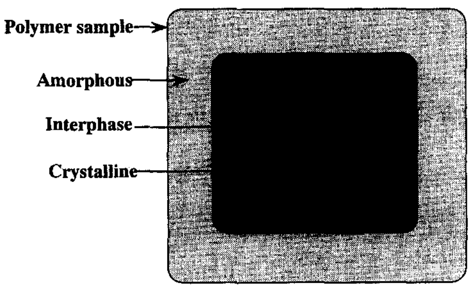

**Figure 6** Schematic diagram of model structure in PUMX-9 sample

However, the typical amorphous phase is not changed significantly by annealing.

*Figure 5* shows the electric displacement (*D*) *versus* electric field (*E*) hysteresis loops for quenched and annealed PUMX-9 samples measured at 75°C. These *D–E* hysteresis loops were obtained by integration of the current density (*J*) with respect to time. The remanent polarization values obtained from the *D–E* hysteresis loops are 14, 14, 12 and 10 mC m$^{-2}$ for the quenched and 80, 100 and 120°C annealed samples, respectively. It can be seen that the remanent polarization decreases slightly when the annealing temperature is increased above 100°C. This phenomenon occurs because the ferroelectric behaviour depends on the dipoles in the unstable crystals or well-hydrogen-bonded amorphous phase but not in the stable crystals.

Aromatic polyamides synthesized using similar monomers to that for PUMX-9 have shown ferroelectric properties below the glass transition temperature, due to the polarization of the amide dipole in the amorphous phase[2]. In this case, the pyroelectric current also disappeared at the glass transition temperature. In our study, PUMX-9 exhibits pyroelectric activity up to 105°C for poled samples. Furthermore, d.c. conduction for this sample was very low even at higher temperatures. Therefore this ferroelectric polarization was not affected by the impurity or ionic polarization. According to the observed pyroelectric activity above the glass transition temperature, no remanent polarization is formed by the dipoles in the typical amorphous phase. It has been reported[12] that undrawn specimens of vinylidene fluoride and trifluoroethylene copolymer contain an intimate mixture of two disordered crystalline phases, and both of these phases undergo a large increase in lattice at 65–70°C. Furthermore, Moreira *et al.*[13] have proposed the existence of an intermediate crystalline phase for poly(vinylidene fluoride–trifluoroethylene) copolymers. Therefore it is considered that the ferroelectric polarization of this polyurethane is formed by the urethane dipoles in the interphase between the amorphous and crystalline regions (see *Figure 6*).

The spontaneous polarization was estimated from the number of polarized dipoles in the molecules per unit volume. The equation used to calculate the spontaneous polarization is given by[14]:

$$P_{sc} = N\mu < \cos\phi > /v \qquad (1)$$

where $N$ is the number of dipoles in crystal volume $v$, and $\phi$ is the angle of the dipole moment with respect to the polarization axis. The dipole moment of the urethane group is 2.8 D and the repeat unit has two dipoles. Therefore the estimated value of the spontaneous polarization by the urethane dipole orientation of the PUMX-9 sample is 37 mC m$^{-2}$, assuming $< \cos\phi > = 1$. A dipole in a crystal is subjected to the Lorentz factor and instantaneous dielectric constant surrounding dipoles in the crystal and therefore an additional polarization is generated in the crystals. The measured remanent polarization (14 mC m$^{-2}$) is as small as half the estimated spontaneous polarization. This ferroelectric behaviour is seen only between the glass transition temperature and 105°C. It is reasonable to consider that the amorphous phase shows dielectric relaxation but the stable crystal phase cannot exhibit ferroelectric behaviour. These results suggest that this polymer possesses another phase, such as unstable crystals with a large amount of defects or well-hydrogen-bonded amorphous matrices.

The remanent polarization may be attributed to the dipoles in the interphase of amorphous and crystalline regions. This interphase should have stable hydrogen bonds, similar to those in the crystals. So the amount of hydrogen bonds in the interface cannot be changed by annealing, polarization reversal taking place even for a well-annealed sample. This behaviour is extremely different from that of annealed polyamide samples[2,8].

It is reasonable to consider that the number of defects in polyurethane molecular chains is larger than in polyamides. These defects may have been formed during the preparation of the samples. Although the polyurethane was synthesized under specified conditions, a small amount of diisocyanate may have participated in side reactions producing some defects, because of its high reactivity. Furthermore, a small amount of cross-linked structures can be formed by the linear polyurethane chains. These defects may prevent the formation of perfect crystals and further packing of crystals in the annealed samples. According to the i.r. data (see *Table 1*) and the XRD spectra of samples annealed above 100°C, the crystallinity is improved, and the strength of hydrogen bonds between the polyurethane chains is slightly increased. Therefore the polarization reversal is little hindered by partial crystallization or rearrangement of the hydrogen bonds.

## CONCLUSIONS

A linear aromatic polyurethane was synthesized using *m*-xylene diisocyanate and nonamethylene diol. According to XRD and d.s.c. measurements, the crystallinity and thermal stability of polyurethane increased with increasing annealing temperature. A typical $D$–$E$ hysteresis loop was observed for the quenched and annealed polyurethane samples. The dipoles in interphases such as well-hydrogen-bonded amorphous matrices or crystallites with a large number of defects are responsible for the ferroelectric behaviour of annealed polyurethane.

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