

Ferroelectric Behavior In Fluorinated Aliphatic Polyurethanes

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ABSTRACT: Ferroelectric behavior was investigated for fluorinated polyurethanes with odd-odd or odd-even numbers of C atoms; poly(hexafluoro-1,5-pentane-heptamethylene dicarbamate) (5F,7 polyurethane) and poly(hexafluoro-1,5-pentane-hexamethylene dicarbamate) (5F,6 polyurethane). Remanent polarization and coercive field estimated from D-E hysteresis loops were $25\text{--}35\text{ mC m}^{-2}$ and $20\text{--}30\text{ MV m}^{-1}$, respectively.

KEY WORDS Fluorinated Polyurethane / Ferroelectric / Pyroelectric / Polarization / Amorphous / Hydrogen Bonding /

The investigation of ferroelectric behavior in polymer materials has received a great deal of attention from applied and fundamental point of view.¹⁻⁷ Ferroelectric behavior was first found in poly(vinylidene fluoride) (PVF₂ or PVDF) and its copolymers.^{2,3} Recently, this property was found in Nylon 7 and Nylon 11^{4,5} for melt-quenched and cold-drawn samples. In polyamides with an even number of CH₂ groups, namely odd nylons, the arrangement of molecular chains has been considered to result from close-packing of paraffinic chains and N-H...O hydrogen bonds. Ferroelectric polarization reversal in polyureas with odd numbers of CH₂ groups has also been demonstrated.⁶ A ferroelectric crystal is likely to form in aliphatic polyurethanes having odd-odd and even-odd numbers of CH₂ groups.⁷ Polyurethane with NH...O hydrogen bonds are considered to have the same behavior as polyamides or polyureas. According to X-ray diffraction measurements, the crystal structure of polyurethanes is similar to that of polyamides.⁸ Infrared measurements show that all the hydrogen bondings are occurred for linear polyurethanes.⁹

Nylon 7 and Nylon 11 show no polarization reversal after annealing, suggesting the formation of strong hydrogen bonding in crystals. Polyureas and normal aliphatic polyurethanes (odd-even) do not show ferroelectric behavior after annealing.^{6,7} Therefore, polymers which have weak cohesive energy are desirable for ferroelectric polarization reversal. Fluorinated polymers generally have important features such as a) low cohesive energy, b) solubility in polar solvent, and c) chemical stability, which are favorable for the dipole rotation by electric field and the suppression of direct current (dc) conductivity. The significance of fluorinated polyurethanes compared with normal polyamides, polyureas or polyurethanes is that the hydrogen bonding of the polyurethanes can be weakened by the substitution of fluorine atoms. Hence, dipoles can be easily rotated toward the direction of electric field, even after annealing.

This paper reports the ferroelectric behavior of fluorinated polyurethanes. The formula of polyurethanes studied is $[-\text{OCH}_2(\text{CF}_2)_3\text{CH}_2\text{-OCONH}(\text{CH}_2)_n\text{-NHCO-}]_p$ where n is an integer and represents the number of CH₂ groups of diisocyanate. The polymers are

named as 5F,*n*-polyurethane because fluorine is included in the polymers.

EXPERIMENTAL

Polyurethanes were synthesized by condensation of diol and diisocyanate as reported by Iwakura and Koyama.¹⁰ For instance 5F,6 polyurethane was prepared as follows. Approximately equal amounts of hexamethylene diisocyanate and hexafluoro 1,5 pentanediol in anisole were heated stepwise to 140°C for 3 h. The reaction was gradually stopped by adding ethanol. 5F,7 polyurethane was also synthesized by the same method using heptamethylene diisocyanate synthesized by Siefken's method.¹¹ The chemical structures of polymers obtained are given in Figure 1. Melt-cast films were obtained on conductive glass plates (ITO) by quenching in an ice bath. Aluminum electrodes was made on the surface of the cast films by vacuum evaporation. These films were subjected to electrical property measurements.

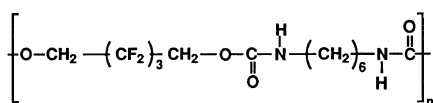
Infrared spectra were obtained with a HORIBA FT 300 with the resolution of 4 cm⁻¹. Differential scanning calorimeter (DSC) measurements were carried out with a MAC SCIENCE DSC 3100 with a heating rate of 10°C min⁻¹. X-Ray diffraction patterns were obtained with a RIGAKU RAD-B diffractometer using CuK_α radiation. Dielectric measurements were performed in vacuum with a HP 4285 LCR meter. *D* versus *E* hysteresis

characteristics were measured by applying a triangular electric field with a frequency of 0.03 Hz. Reversible pyroelectric current and thermally stimulated depolarization current (TSC) for poled samples were obtained simultaneously from the current through the electrode irradiated by a pulsed semiconductor laser (670 nm, 3 mW, 10 Hz) during heating (3°C min⁻¹).

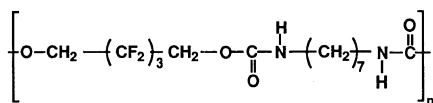
RESULTS AND DISCUSSION

Thermal properties of polyurethanes are given in Table I, obtained from DSC measurements. The melting and glass transition temperatures in fluorinated polyurethanes were lower than those of normal aliphatic polyurethanes.⁷ This may be attributed to weakened hydrogen bonding with expansion of crystal lattice containing fluorine atoms with large van der Waals radius. The transition temperatures strongly depend on thermal history. For example, the crystallization peak and glass transition are not observed in slowly-cooled samples.

Figure 2 shows the FTIR spectra of 5F,7 polyurethane. This spectra gives bands corresponding to all bonds of 5F,7 polyurethane. There are two peaks at 3450 and 3342 cm⁻¹ due to the N–H bonds. A free N–H stretching vibration band (3447 cm⁻¹) and hydrogen bonded N–H band (near 3300 cm⁻¹) appear in the range of the stretching vibration N–H groups for aliphatic polyurethane.⁹ The band at 3450 cm⁻¹ may be a free N–H stretching band and the hydrogen bonded N–H band



5F,6 polyurethane



5F,7 polyurethane

Figure 1. Chemical structures of fluorinated polyurethanes.

Table I. Thermal properties of fluorinated polyurethanes obtained from DSC at a heating rate of 10°C min⁻¹ ^a

Sample	<i>T_g</i> /°C	<i>T_c</i> /°C	<i>T_m</i> /°C
5F,6 Polyurethane	12	70	92
5F,7 Polyurethane	-5	—	63

^a *T_g*, glass transition temperature; *T_c*, crystallization temperature; *T_m*, melting temperature.

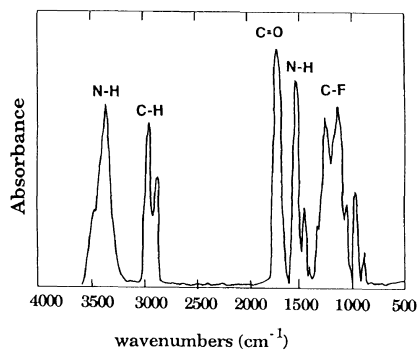


Figure 2. FTIR spectra for a quenched sample of 5F,7 polyurethane.

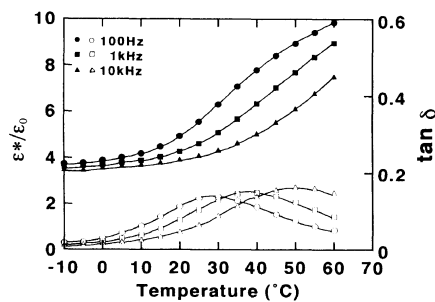


Figure 3. Temperature dependence of dielectric constant and dissipation factor for quenched samples in 5F,7 polyurethane.

around 3342 cm^{-1} is attributed to ordered and disordered hydrogen bonding in polyurethane.¹² The wavenumber of the hydrogen bonded N–H band in fluorinated polyurethane is higher than that of normal aliphatic polyurethanes. It is corresponded to weakening of hydrogen bonding by substitution of fluorine atoms in CH_2 groups.

Figure 3 shows the temperature dependence of the dielectric constant (ϵ^*/ϵ_0) and dissipation factor ($\tan \delta$) of 5F,7 polyurethane in the temperature range from -10 to 60°C at three different frequencies. The dielectric constant (ϵ^*/ϵ_0) starts to rise gradually from the glass transition temperature (-5°C). The crystallinity of the measured sample is probably low. However the sample participates in aggregation of the inter-chain hydrogen bonding. Temperature dependence of dielectric relaxation

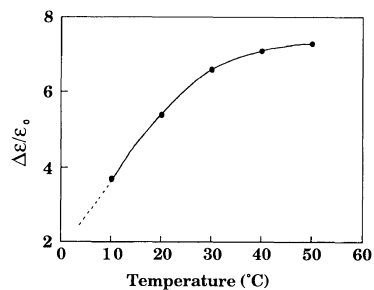


Figure 4. Temperature dependence of dielectric relaxation strength obtained by Cole–Cole plots in 5F,7 polyurethane.

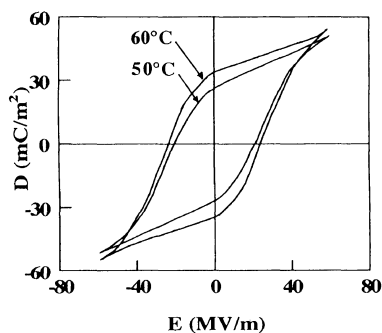


Figure 5. D–E hysteresis curves of a) 5F,6 polyurethane at 50 and 60°C b) 5F,7 polyurethane at 50°C with the frequency of 0.03 Hz.

strength obtained from Cole–Cole plots for 5F,7 polyurethane is shown in Figure 4. The dielectric relaxation strength increases with temperature from the glass transition temperature and saturates near the melting point ($\Delta\epsilon/\epsilon_0 = 7.3$ at 50°C). The dielectric increment of this sample due to free rotation of dipoles calculated from Onsager's equation was $\Delta\epsilon/\epsilon_0 = 7\text{--}8$. Therefore, the dipoles of polyurethanes at least behave as a free rotation model near the melting temperature. The dielectric relaxation of these samples is possibly due to the micro-brownian like motion having a wide relaxation time distribution from hydrogen bondings.

D *versus* E hysteresis is obtained by integrating the corrected current density with respect to time. Figure 5 shows D–E hysteresis loops for 5F,6 polyurethane and 5F,7 polyurethane above the glass transition temperature at 60°C

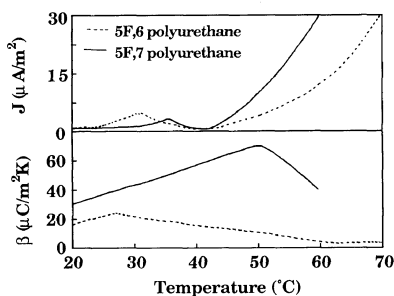


Figure 6. Thermally stimulated current (TSC) and pyroelectric constant (10 Hz) for 5F,6 and 5F,7 polyurethanes.

and 50°C. In the case of 5F,6 polyurethane, the value of the remanent polarization (P_r) determined from the intercept of each loops with the D-axis are 35 and 28 mC/m^{-2} for the temperatures of 60 and 50°C, respectively. These curves are essentially the same as those of PVDF or odd nylons. Reproducibility of P_r depended on the thermal history, crystallinity and molecular orientation of samples. Remanent polarization and coercive field estimated from D-E hysteresis loops of 5F,7 polyurethane were 32 mC/m^{-2} and 29 MV m^{-1} at 50°C. These hysteresis loops were observed even after annealing.

The dipole moment of the urethane group is about 2.8 Debye, smaller than those of the amide group (3.7 Debye) or urea group (4.9 Debye).^{4,6} Remanent polarization by the dipole orientation of the fluorinated polyurethane groups was estimated about 30–35 mC/m^{-2} in these polymers. This value agrees with the remanent polarization obtained from this experiment.

Figure 6 shows the temperature dependence of the TSC curve and pyroelectric constant (β) for both polymers. Both polymer samples were poled under a field of 40 MV m^{-1} at 45°C which is higher than the glass transition temperature of the polymers. For 5F,6 polyurethane, the TSC curve shows a peak at about 31°C, and increases above 40°C. The pyroelectric activity gradually decreases above 28°C. Therefore, pyroelectric activity is un-

stable above the glass transition temperature (12°C) but does not diminish to zero at the glass transition temperature. From these results, it may be considered that pyroelectric activity may originate from the remanent polarizations in the crystal region. The TSC curve of 5F,7 polyurethane shows a small peak at 36°C, which increases above 40°C. The pyroelectric constant increases gradually with temperature close to the melting temperature. Pyroelectric activity in 5F,7 polyurethane is also due to remanent polarization in crystalline phases but the pyroelectric activity of 5F,7 polyurethane is more stable than that of 5F,6 polyurethane. Remanent polarization in fluorinated polyurethanes may be not only from the crystallization phase, but also from the amorphous phase with hydrogen bonded dipoles, stable above the glass transition temperature.

X-Ray diffraction patterns of quenched samples of 5F,6 polyurethane and 5F,7 polyurethane are quite similar. Both polyurethanes show main broad peaks around $2\theta = 20^\circ$ and, another peak around $2\theta = 5^\circ$. The latter corresponds to fiber axis periodicity. The melt cast samples probably have disordered crystal structures. Saito *et al.* reported⁸ on the structures of aliphatic polyurethanes that crystal packing of odd-even and even-even polyurethanes is non polar and similar to that of polyamides. However, structural data of crystal in the fluorinated polyurethanes are not available at present. From analogy of odd nylons,¹³ odd-polyurethanes such as 5F,7 polyurethane may consist of parallel packing of polar chains. Although 5F,6 polyurethane have non-polar chains in trans conformation, it has possibly polar crystals by applying a high electric field because of weaker hydrogen bonding. Smectic structure of nylon 11 and consequent weakening of the interchain amide hydrogen bond are induced by quenching.¹⁴ Ferroelectric properties exist in other metastable phases of the odd nylons and possibly in amorphous regions. The strength of hydro-

gen bonding of the polyurethanes can be weakened by the ether group in polyurethanes and substitution of fluorine atoms. Therefore, the possible origin of the ferroelectricity in fluorinated polyurethanes is likely related to the polar structure formed by hydrogen bonding and an external electric field.

Further electrical and structural data are necessary to elucidate the origin of ferroelectricity in fluorinated polyurethanes.

CONCLUSIONS

We prepared two fluorinated linear (5F,6 and 5F,7) polyurethanes. These polyurethanes having odd-odd and odd-even number of carbon atoms showed ferroelectric D-E hysteresis loops. Ferroelectric behavior is possibly due to various hydrogen bonds in crystal and amorphous regions.

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