Effects of Impurity Ions on Electrical Properties of Poly(vinylidene fluoride)

Yoshio OKA and Naokazu KOIZUMI

*Institute for Chemical Research, Kyoto University,
Uji, Kyoto 611, Japan*

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ABSTRACT: Impurity ions in poly(vinylidene fluoride) were successfully removed by electro dialysis in water and removal was confirmed by the reduction of dc conductivity. A comparison of electrical properties before and after electro dialysis showed the effects of the impurity ions. TSC and low-frequency dielectric measurement were made to study impurity ion effects on both stretched and unstretched samples. From the TSC study, the α relaxation in the crystalline α phase was found to give a clear peak following electro dialysis while the β relaxation in the amorphous phase was not affected. Also, impurity ions become mobile above 260 K and are responsible for the peak above the polarization temperature. From low-frequency dielectric measurements, similar results to those in TSC was obtained with respect to the α relaxation at 27°C. At 88°C, the ionic contribution to the increment of dielectric constants was pronounced and ionic polarization rather than ionic conduction was found to be dominant in the dielectric behavior in the frequency range of 0.01 to 10 Hz.

KEY WORDS Poly(vinylidene fluoride) / Impurity Ion / Electro dialysis / Thermally Stimulated Currents / Low-Frequency Dielectric Behavior / Space Charge /

Electrical properties of polar polymers are strongly influenced by impurity ions. The effects are observed particularly in dc conductivity, low-frequency dielectric behavior and breakdown phenomenon. Dc conductivity at elevated temperatures is well governed by the Arrhenius-type equation with activation energy of ion migration. Also, the pressure dependence of dc conductivity in polar polymers is consistent with the concept of ionic conduction; that is, the higher the pressure, the lower the dc conductivity in accordance to the Arrhenius-type equation with activation volume.¹ Dielectric constants, particularly their imaginary parts, increase greatly with decreasing frequency and increasing temperature as a result of ionic polarization and conduction.² However, an exact mechanism for impurity ion effects on electrical properties remains unclear because of the difficulty in determining the ionic species involved and the contribution of impurity ions alone.

The origin of impurity ions in polymers is considered to be catalysts, plastisizers and the decom-

position products of the polymer chain. Ionic species of trace contaminants were examined by Sacher on polyimide and it was suggested that Na, Al, and Si were major contributors to ionic conduction.³ Also, from the electrical conduction study of poly(vinyl fluoride) by Kosaki *et al.*, fluorine ions were considered to be the likely main charge carriers.⁴ Osaki *et al.* pointed out that Na, Ca, Al, S, and Cl were present in poly(vinylidene fluoride) as trace impurities.⁵ So far, the major species of impurity ions have been found to be inorganic and consequently are expected to be released from polymer film into water by electro dialysis. In the present work, a rather simple setup for electro dialysis of polymer film in water was employed and the amount of impurity ions was significantly reduced. Since electrical properties can be measured on the same polymer film before and after electro dialysis or removal of impurity ions, the contribution of impurity ions can be determined separately.

Thermally stimulated current (TSC) technique is

a powerful means recently developed for studying dipole relaxation and space charge motion in insulating materials.⁶ In this method, frozen-in polarization induces nonisothermal currents by heating at a constant rate and the current profiles at lower temperatures provide information about dipole relaxation and at higher temperatures about space charge motion.

The purpose of the present work is to clarify the behavior of impurity ions in a semicrystalline polymer of poly(vinylidene fluoride) with crystal forms of antipolar α phase and polar β phase.⁷ The effects of impurity ions were investigated by TSC, low-frequency dielectric measurement and dc conductivity measurement for samples before and after electro dialysis in water in order to determine the ionic contribution.

EXPERIMENTAL

Poly(vinylidene fluoride) (PVDF) was provided by Daikin Kogyo Co., Ltd. Japan. Powder samples were heat pressed into films. Some of the films were uniaxially stretched to a draw ratio of 4:1 at 80 and 150°C so as to obtain oriented α and β type crystalline phases. The thickness of the film was 50 to 80 μm with a diameter of about 3 cm. An aluminum electrode was evaporated onto both surfaces of the film so as to make electrical measurement.

Electrodialysis was performed using the apparatus shown in Figure 1. The film was placed between platinum electrodes and distilled water was used as the liquid electrode. A dc voltage of 1000 V was applied and the electrode water was heated to 60°C so as to accelerate the release of ions. The period of electro dialysis was from one to two days. In this setup, cationic impurities were released into cathode water and anionic impurities into anode water. The electro dialyzed sample was heated in a short circuit to 100°C before the electrical measurements in order to avoid any electret effects during electro dialysis.

Dc resistivity was determined from the leakage current for one hour after application of 24 V at 25°C. TSC measurements were carried out using the TSC cell shown in Figure 2 as follows. First, a sample was kept at a constant polarization temperature (T_p) of 50°C and then a polarization field (E_p) of $2.1 \times 10^7 \text{ V m}^{-1}$ was applied for 1 h followed by

Figure 1. Apparatus for electro dialysis.

Figure 2. Sample cell for TSC measurement: (1) sample, (2) electrode, (3) high voltage lead, (4) low voltage lead (Type RG179/U coaxial cable), (5) spring, (6) platinum resistance temperature sensor for temperature control, (7) copper vs. constantan thermocouple, (8) sheathed heater, and (9) Macor glass-ceramic.

rapid quenching to the temperature of liquid N_2 . After removal of the dc bias, the sample was heated at a linear rate of 3 K min^{-1} to 90°C and current was measured by a Keithley Electrometer Model 610C. A sample cell was filled with helium gas at atmospheric pressure for better heat conduction. Low-frequency dielectric measurements were made with a three terminal cell over a frequency range of 0.01 to 10 Hz by an operational amplifier bridge at 27 and 88°C.

The fractions of the α and β phase in the total crystalline region of stretched samples were de-

terminated from the intensities of (002) reflection for the α phase and (001) for β phase in an X-ray diffraction pattern with proper orientation between the incident beam and stretching axis. X-Rays of high intensities of 40 kV and 200 mA were used for higher resolution.

RESULTS

The samples used were designated as follows: sample 1, 2 and 3 for unstretched, stretched at 150°C and stretched at 80°C, respectively and a, b, and c for X-ray, TSC and low-frequency dielectric measurement, respectively. For example, sample 1a represents the unstretched film used in X-ray diffraction measurements.

X-ray diffraction profiles of PVDF films and the setting of the films are illustrated in Figure 3. Enhanced diffraction peaks of (002) (α phase) and (001) (β phase) due to uniaxial stretching were observed in the stretched films, while the same peak was extremely small in unstretched film. From the peak intensities, the α and β phase fractions in crystalline region were estimated, taking into ac-

count the structure factors, as listed in Table I. Consequently, the samples used in the present study could be classified as sample 1 for the unoriented α phase, sample 2 for the oriented α phase and sample 3 for the oriented β phase. Also, the X-ray diffraction profiles show that the stretched films were almost completely oriented.

Dc resistivities at 25°C before and after electro-dialysis for samples used in TSC and low-frequency dielectric measurements are listed in Table II. Dc resistivity increased approximately by a factor of ten after electro-dialysis, indicating a reduction of impurity ions.

TSC spectra for samples before and after electro-dialysis are shown in Figure 4. In the temperature region of 200 to 350 K, two definite peaks were observed at 233 K ($\sim T_g$) and above the polarization temperature T_p ($=323$ K). The peak at 233 K was assigned to the β relaxation in amorphous region, which was invariant even after electro-dialysis. The effects of electro-dialysis were pronounced in the temperature range above T_g . The first effect could be observed in the peak around 260 K for samples 1 and 2. This peak was assigned to the α relaxation in the crystalline α phase⁹ and hence is missing in sample 3 of the β phase. The effects can be observed in detail in Figure 5. In untreated samples, the peak is fairly small (sample 1) or hardly observable

Figure 3. X-Ray diffraction profiles for sample 1a, 2a, and 3a and setting of film against X-ray beam.

Table I. α and β phase fractions in crystalline region

	α Phase β Phase		
Sample 1a	1.00	0	Unstretched
Sample 2a	0.72	0.28	Stretched at 150°C
Sample 3a	0.06	0.94	Stretched at 80°C

Table II. Dc resistivity of samples for TSC and low-frequency dielectric measurements at 25°C before and after electro-dialysis

	Untreated	Electro-dialyzed
Sample 1b	$7.35 \times 10^{12} \Omega\text{m}$	$3.93 \times 10^{14} \Omega\text{m}$
Sample 2b	$2.13 \times 10^{13} \Omega\text{m}$	$1.77 \times 10^{14} \Omega\text{m}$
Sample 3b	$2.43 \times 10^{13} \Omega\text{m}$	$1.77 \times 10^{14} \Omega\text{m}$
Sample 1c	$1.74 \times 10^{13} \Omega\text{m}$	$1.74 \times 10^{14} \Omega\text{m}$
Sample 2c	$1.16 \times 10^{13} \Omega\text{m}$	$1.06 \times 10^{14} \Omega\text{m}$
Sample 3c	$2.49 \times 10^{13} \Omega\text{m}$	$1.24 \times 10^{14} \Omega\text{m}$

Figure 4(c)

Figure 4(a), (b)

(sample 2), whereas in electrolyzed samples, it becomes large and clear in sample 1 and even in sample 2 in which the α relaxation should be suppressed according to Miyamoto *et al.*¹⁰ The peak temperature for sample 2 was 264 K which is slightly higher than that of 257 K for sample 1. For the second effect, it was quite evident that depolarization currents in untreated samples become considerably larger than those in electrolyzed

Figure 4. TSC spectra for various PVDF samples untreated and electrolyzed: (a) sample 1b, (b) sample 2b, and (c) sample 3b.

Figure 5. Enlarged TSC spectra in the temperature region of the α relaxation for samples 1b and 2b.

samples above 260 K. This effect was found to be common to all sample types, thus implying that impurity ions become mobile above 260 K. Concomitantly, the peak above T_p moved to a slightly higher temperature after electrolysis.

Figure 6. Frequency dependence of dielectric constant and loss for samples 1c, 2c, and 3c untreated and electrodialyzed at 27°C (a) and 88°C (b).

In Figure 6, low-frequency dielectric constants at 27 and 88°C before and after electro dialysis are

shown in the frequency range of 0.01 to 10 Hz. At a lower temperature of 27°C, as described below, the α relaxation could be observed in the frequency range employed and at a higher temperature of 88°C the ionic contribution on the dielectric behavior was expected to be enhanced. At 27°C (Figure 6a), the effect of electro dialysis was not so prominent in the real parts of the dielectric constants (ϵ'), while the imaginary parts (ϵ'') exhibited an obvious change after electro dialysis. A comparison of the curves of ϵ'' for untreated and electro dialyzed show that the effect of ion removal is remarkable in the frequency range below 1 Hz at this temperature. At this point, a dielectric dispersion around 1 Hz corresponds to the α relaxation in the crystalline α phase.² It is of interest that in electro dialyzed samples 1 and 2, the α relaxation becomes clearer probably as a result of reduced ionic polarization or conduction effects on the lower frequency side. This is consistent with the first effect of the TSC study previously described. A slight shift of the peak position of ϵ'' to a lower frequency in untreated sample 1c compared with that electro lyzed can be attributed to the superposition of the relaxation peak and the increase in ϵ'' due to ionic contribution toward the lower frequency side. The reason for the gradual decrease in ϵ'' with decreasing frequency in sample 3 is not clear since no relaxation has been reported for crystalline β phase in this region. At an elevated temperature of 88°C, the ionic contribution is pronounced as evident from Figure 6b in which the increments of ϵ' and ϵ'' for untreated samples in the lower frequency side are considerably greater than those for electro dialyzed samples. The substantial decrease in ϵ' and ϵ'' in electro dialyzed samples compared with those untreated is also a good indication of ion removal.

DISCUSSION

Impurity ions in PVDF were substantially removed by the simple method of electro dialysis in water on sample film. Field cleaning is a conventional method for reducing the ionic contribution. In this method, however, after removal of dc bias the displaced ions gradually diffuse back into the bulk.⁵ The present method has the considerable advantage that ions are swept away into the water, thus leaving the sample essentially clean.

Figure 7. TSC spectra obtained by subtracting currents in electrodyalized samples from those in untreated samples in Figure 4 for sample 1b, 2b, and 3b.

Figure 8. Dependence of peak temperature and peak current on dc resistivity at 25°C for the peak above T_p in unstretched and stretched samples.

Direct evidence for ion removal was found by dc resistivity measurements in which electrodyalized samples became less conductive regardless of sam-

ple type. The contribution of impurity ions can be appropriately determined by the subtracting depolarization currents of electrodyalized samples from those of untreated samples in TSC profiles. Current profiles thus obtained are exhibited in Figure 7. It is noted that the peak above T_p still remains in the subtracted current profiles in the vicinity of the original peak temperature. The origin of the peak is thus considered to be ionic. For the further analysis of the peak above T_p , peak temperature and peak current in original TSC are plotted against dc resistivity at 25°C in Figure 8. Although peak temperatures vary from sample to sample, peak temperatures are prone to increase with decreasing dc resistivity. This corresponds to the fact that the higher peak temperature originating from a space charge is related to a smaller conductivity in ionic crystals.¹¹ It is even more obvious that the peak current decreases with increasing dc resistivity, corresponding to the second effect of the present TSC study in which overall currents above 260 K were substantially reduced following electrodyalisis. As seen from Figure 8, a linear relation between peak current and dc resistivity was approximately obtained in a log-log plot and stretched samples gave somewhat higher peak current than the unstretched samples. This peak was observable for all sample types in the same temperature region; the nature of the peak was dependent on dc conductivity. Therefore, it is suggested that the peak is due to a drift or diffusion of displaced ions in the amorphous phase. Ieda *et al.*^{12,13} also consider the origin of the peak to be ionic, attributing this to interfacial polarization between the amorphous and crystalline phases. The possibility of the interfacial polarization may not be ruled out in the present study.

Adopting the initial rise method¹⁴ in subtracted current profiles in Figure 7, activation energies for ion drifting motion was estimated as 60.8 kJ mol⁻¹ for sample 1, 60.3 kJ mol⁻¹ for sample 2 and 53.6 kJ mol⁻¹ for sample 3. The activation energies had about the same value of 60 kJ mol⁻¹ for all samples. This value is smaller than 142 kJ mol⁻¹ for the ionic diffusion obtained from low-frequency dielectric measurements by Uemura,² but is in good agreement with that from TSC around 300 K by Yamada *et al.*¹³ Compared with the dielectric measurements, TSC often gives smaller activation energy values.¹⁵

Treatment similar to that in the TSC study

Figure 9. Frequency dependence of subtracted dielectric constant and loss at 88°C for sample 1c, 2c, and 3c in Figure 6b:

$$\Delta\epsilon' = \epsilon'_{\text{untreated}} - \epsilon'_{\text{electrodialyzed}} ;$$

$$\Delta\epsilon'' = \epsilon''_{\text{untreated}} - \epsilon''_{\text{electrodialyzed}} .$$

described above was employed on low-frequency dielectric constants at 88°C to eliminate the ionic contribution toward dielectric properties. Curves of subtracted dielectric constants and loss, $\Delta\epsilon'$ ($=\epsilon'_{\text{untreated}} - \epsilon'_{\text{electrodialyzed}}$) and $\Delta\epsilon''$ ($=\epsilon''_{\text{untreated}} - \epsilon''_{\text{electrodialyzed}}$) are represented in Figure 9. As for variation in $\Delta\epsilon''$ with frequency f , the f^{-n} dependence of $\Delta\epsilon''$ with $n < 1$ was observed in the frequency region above 0.01 Hz and the f^{-1} dependence due to ionic contribution was finally determined at the lowest frequencies used. It is thus suggested that ionic polarization rather than ionic conduction prevails in the frequency range observed. Frequency dependence of $\Delta\epsilon'$ shows interesting behavior; that is, $\Delta\epsilon'$ first increases by lowering the frequency and tends to level off on the lower frequency side. This behavior is inconsistent with the $f^{-(3/2)}$ dependence proposed by Uemura¹⁶ based on the diffusion of ions under dc bias and possibly implies the dispersion of ionic polarization instead. It should be noted that impurity ions cannot be completely removed by electro dialysis and mono-

valent ions such as alkali and halogen ions are expected to be removed preferentially. Thus, such ions are responsible for the dielectric dispersion observed in Figure 8.

The findings in the present study regarding the effect of impurity ions on α relaxation in the crystalline α phase are of interest (the first effect in the TSC study). From Figure 5, α relaxation is clearly observable in electro dialyzed samples in TSC spectra. This is also the case for low-frequency dielectric behavior at 27°C in Figure 6a. From the above results, it is considered that the relaxation is masked or hindered by impurity ions. Although the exact mechanism for this effect remains unknown, it may be concluded that impurity ions play some role in obscuring the α relaxation but have no influence on the β relaxation. Particularly in stretched samples, α relaxation is hardly observable without electro dialysis.

In conclusion, impurity ions have a significant effect on the electrical properties of PVDF. These ions become mobile above 260 K which is slightly higher than T_g and mask the α relaxation in the crystalline α phase. The peak observed in TSC above T_p may be attributed to the drifting motion of ions. Ionic polarization rather than ionic conduction contributes largely to low-frequency dielectric behavior. The electro dialysis method employed in the present study is excellent for removing impurity ions and such treatment is useful in the investigation of the electrical properties of polar polymers.

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