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Dielectric Hysteresis and Nonlinearity in a 52/48 mol % Copolymer of Vinylidene Fluoride and Trifluoroethylene

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ABSTRACT: The electric displacement D and the dielectric constant ϵ in the presence of a strong electric field E have been simultaneously measured for a ferroelectric copolymer containing 52 mol % vinylidene fluoride and 48 mol % trifluoroethylene. Below the transition temperature T_c, the D–E loop shows square-like hysteresis and the ϵ–E loop is of butterfly shape. Above T_c, these loops lose hysteresis and reflect only nonlinearity. The combination of D–E and ϵ–E loops allows the separation of the high-field-induced polarization into the remanent, switch-back, and reversible components. The remanent polarization P_r rapidly decreases with increasing temperature. Near T_c, most of the induced polarization disappears by reversible randomization and irreversible switching back of dipoles when the field is removed. The largest remanent polarization is created at room temperature rather than at elevated temperature. The transition temperature is markedly influenced by the electric field. The presence of 50 MV/m results in the shift of T_c from 68 to 74 °C. The complete poling at 20 °C shifts the T_c to 80 °C. The analysis of the ϵ–E loop at 70 °C suggests a double-hysteresis nature in the D–E loop. The shift of T_c and the double hysteresis are an indication that the phase transition of this copolymer is of the first order.

Introduction

Copolymers of vinylidene fluoride and trifluoroethylene have attracted considerable attention recently, because they undergo a ferroelectric-to-paraelectric transition.[2–5] In previous papers,[6,7] we have investigated the crystalline forms of the copolymer containing 52 mol % vinylidene fluoride below and above the transition temperature T_c, located near 70 °C. At room temperature, the unpoled sample has been shown[6] to contain two disordered crystalline phases: one is essentially trans planar and the other consists of irregular TG, T$\bar{\text{G}}$, and TT sequences akin to the 3/1 helical structure of atactic poly(trifluoroethylene).[8] Poling or drawing transforms such disordered phases into a well-ordered all-trans phase. Both unpoled and poled samples undergo a transition to a single disordered phase analogous to atactic poly(trifluoroethylene) as they are heated. The transition temperature of poled samples is 10 °C higher than that of unpoled samples. The ferroelectric-to-paraelectric transition of this copolymer has been attributable primarily to molecular changes from the polar all-trans conformation to its nonpolar disordered counterpart, as well as to the onset of dipolar motions leading to the dielectric anomaly.

In this paper, we investigate the ferroelectric nature of the 52/48 copolymer in detail on the basis of nonlinear dielectric measurements. In addition to the conventional D–E hysteresis, we have measured the ϵ–E hysteresis below and above T_c. The electric displacement D is connected with the orientation of dipoles, while the dielectric constant ϵ reflects their motions; the two are not independent, however, but influence each other. As a result, we have obtained detailed information about the ferroelectric polarization and the nature of the phase transition of this copolymer.

Experimental Section

The sample used was a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene, the same as used in the previous studies[6,7] and had been supplied by Daikin Kogyo Co., Ltd., Japan. Its thickness was 20 μm. Vacuum-deposited gold was used as electrodes.

Figure 1 shows a schematic diagram of the apparatus used for the measurements. Both dc high-field E and ac low-field E_ω were simultaneously applied to a sample via a high-voltage operational amplifier. The ac field was provided at a frequency of 100 Hz with an amplitude of 50 kV/m. The dc field up to 100 MV/m was actually applied as a triangular or sinusoidal wave form at very low frequencies from 1 to 300^{-1} Hz. The charge responses from the sample were detected by a charge amplifier. The ac and dc components in the charge responses were separated by a band-pass amplifier and a low-pass filter, respectively. As a result, we obtained the dielectric constant $\epsilon = D_\omega/\epsilon_0 E_\omega$ (ϵ_0 is the dielectric constant of free space) together with the electric displacement D as a function of E.

Results

A. *D*–*E* Hysteresis.

A ferroelectric reverses its spontaneous polarization when a suitable electric field is applied. This process is known as switching and is accompanied by hysteresis. The D–E hysteresis of this copolymer has been observed by Furukawa et al.[2] and Yamada et al.[4] Here we examine such hysteresis in detail below and above T_c.

As described in the previous papers,[6,7] unpoled samples of 52/48 copolymer consist of a mixture of polar and nonpolar phases, and poling causes a transformation of such phases into a single all-trans polar phase. Therefore unpoled samples are subject to crystalline transformation during D–E hysteresis measurement.

Figure 2 shows D–E hysteresis loops of 52/48 copolymer measured at 20 °C. The electric field was applied up to 100 MV/m at a frequency of 300^{-1} Hz. Open circles indicate the results at the first and second cycles and filled circles indicate the sixth cycle. When E is applied to an unpoled sample, D increases linearly except near 60 MV/m. An abrupt rise near 60 MV/m indicates that the dipoles originally oriented along the direction antiparallel to E are reversed. Reversed dipoles retain their new orientation and create a remanent polarization of ca. 60 mC/m^2. When E is reversed, D is reversed in two steps near 30 and 45 MV/m. The first and second steps are considered to be associated with the reorientation of dipoles that have been reversed and unreversed, respectively, in the first half cycle. As E is cycled, the D–E loop becomes more symmetrical and square, which indicates the progress of the crystalline transformation into a single all-trans phase. Such evolution of the D–E hysteresis loop with number of cycles can also be due to the gradual progress of the polar-axis orientation in all-trans phases, which has been suggested by Broadhurst and Davis on the basis of a six-site model.[9] After several cycles, the loop becomes stationary and gives a remanent polarization of

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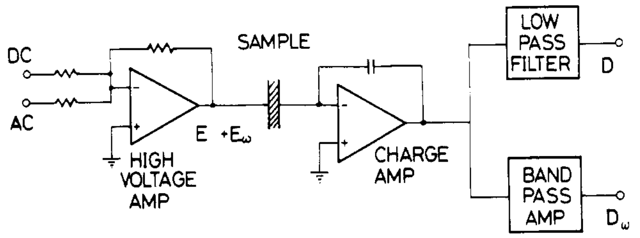

Figure 1. Schematic diagram of an apparatus for simultaneous measurement of D–E and ϵ–E hysteresis loops.

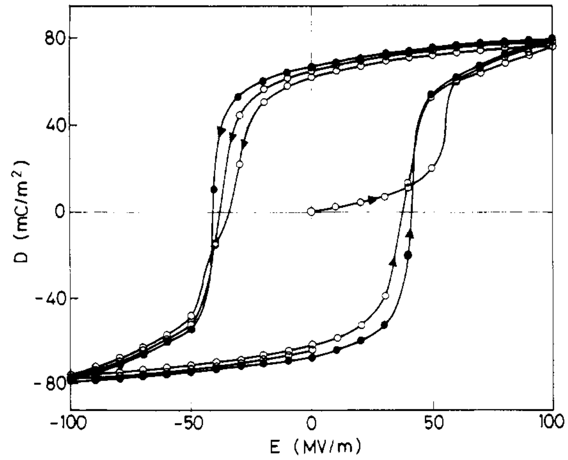

Figure 2. Change in D–E hysteresis loops for the 52/48 copolymer during repeated applications of the electric field. Open circles indicate the first and second cycles and filled circles indicate the sixth cycle.

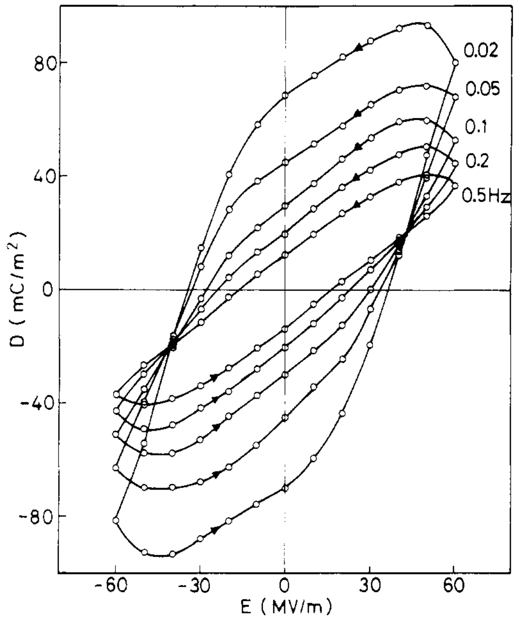

Figure 3. Dependence of D–E loops on the frequency of the applied electric field at 70 °C.

70 mC/m^2 and a coercive field of 40 MV/m at 20 °C.

We have performed such hysteresis measurements at various temperatures up to 100 °C. Prior to the measurement at each temperature, the sample had been heat treated at 120 °C for 30 min to be depoled. At high temperatures, especially above the transition point, the dc conduction becomes higher and results in rounded D–E hysteresis loops. This causes a recording of higher P_r and E_c values. In order to obtain the true remanent polarization, we measured D–E hysteresis loops at various frequencies. Figure 3 shows an example of results obtained at 70 °C. Here the frequency of applied field has been varied from 0.5 to 0.02 Hz. It is seen that the loop becomes narrower as the frequency is increased because the contribution from dc conduction is roughly proportional to the period.

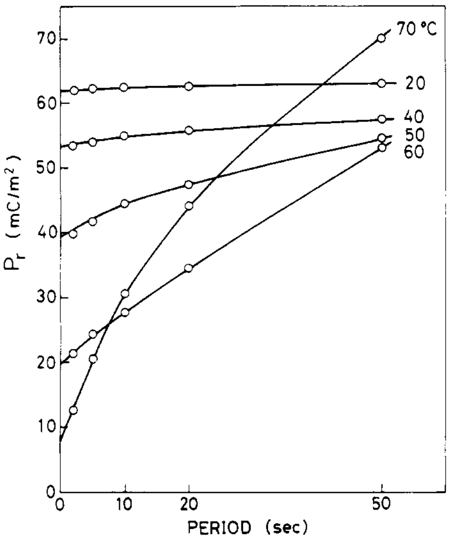

Figure 4. Dependence of remanent polarization P_r on the period of the applied electric field at various temperatures for the 52/48 copolymer.

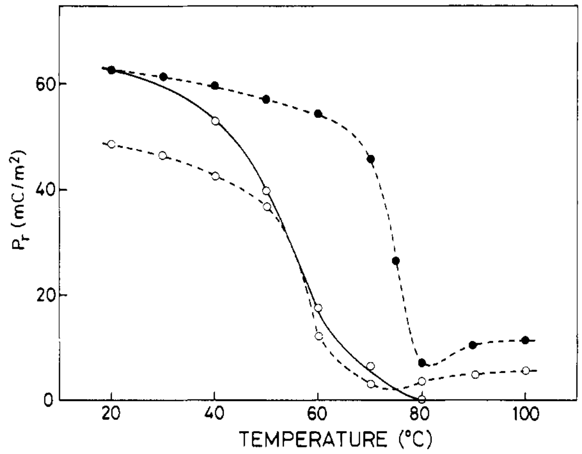

Figure 5. Temperature dependence of remanent polarization P_r for the 52/48 copolymer. Solid line indicates zero-period P_r estimated from D–E loops at each temperature. Dashed line with filled circles indicates the decay of P_r induced to the sample by poling at 20 °C under a maximum field of 100 MV/m for six cycles, and dashed line with open circles indicates similar data for a sample poled under a maximum field of 50 MV/m for one cycle.

In Figure 4, we show the dependence of P_r on the period of applied field. Extrapolation to zero period allows evaluation of the true P_r value. It is noted here that we have decreased the amplitude of applied field as the temperature is increased from 100 MV/m at 20 °C to 50 MV/m at 100 °C in order to prevent samples from electrical breakdown. We believe, however, that this has not caused significant errors in evaluating the true P_r, because the amplitude of the applied field has been larger than twice that of the coercive field. It is also noted that the period of the applied field on the order of seconds is much larger than the switching time, which is the time necessary to reverse the polarization of a ferroelectric. The switching time has been reported to be on the order of milliseconds to microseconds in poly(vinylidene fluoride).[10]

B. Temperature Dependence of Remanent Polarization. The solid line in Figure 5 shows the temperature dependence of the true P_r obtained from Figure 4. It is found that the remanent polarization induced in unpoled

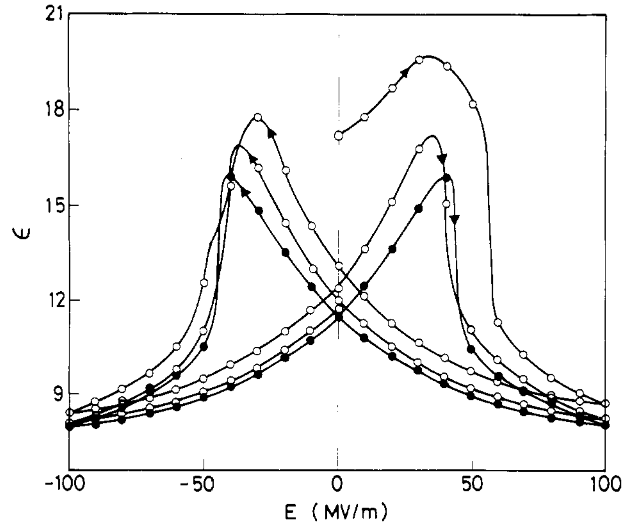

Figure 6. ϵ–E hysteresis loops obtained at the same time as D–E loops in Figure 2.

samples decreases as the temperature approaches the transition point and completely disappears above 80 °C. In other words, the largest polarization is created at room temperature. In the same figure, we also plot the decay of the remanent polarization of the sample poled at 20 °C. Dashed lines with open and filled circles show the results when the sample has been subjected to an electric field of 100 MV/m for six cycles and 50 MV/m for one cycle, respectively. After poling, a change in the remanent polarization was measured during heating at a rate of 1 °C/min. It is seen that the higher the applied field is and the more the field is cycled, the more stable is the induced remanent polarization. After showing a significant decrease, P_r increases slightly with increasing temperature. This may be ascribed to release of space charges that had been trapped near crystalline regions.

The application of 100 MV/m for six cycles induces almost complete crystalline transformation of this copolymer from a disordered mixture into the well-ordered all-trans phase. This phase is stable up to 80 °C. If the applied field is low and the transformation is incomplete, the shift of the transition temperature is small.

C. ϵ–E Hysteresis. Field-induced phase changes in the 52/48 copolymer are accompanied by a considerable decrease in the low-field dielectric constant ϵ. The progress of crystalline transformation is also observed during ϵ–E hysteresis measurement on unpoled samples. As shown in Figure 6, which is obtained at the same time as Figure 2, ϵ starts from 17 and exhibits a peak near 30 MV/m. When E exceeds 55 MV/m and just before D in Figure 2 shows a sharp rise, ϵ falls abruptly followed by a milder decrease to reach 8 at 100 MV/m. When E returns to zero, we find a drastic decrease of ϵ from the initial value, indicating that a considerable crystalline transformation has taken place in the first half cycle. During the next half cycle, ϵ shows a peak at 30 MV/m and a shoulder at 45 MV/m, corresponding to the two-step changes observed in the D–E loop of Figure 2. As the field is cycled, the ϵ–E loop becomes gradually lower and more symmetrical. After six cycles, the loop is stationary in the shape of an upside-down butterfly; such a hysteresis loop has been observed in poly(vinylidene fluoride) by Takahashi et al.[11]

Comparison of Figure 6 with Figure 2 allows us to infer that the ϵ–E loop corresponds to the gradient of the D–E loop. When the polarization reverses and D changes sharply, ϵ shows a peak. However, such correspondence is not quantitatively correct, as will be discussed later.

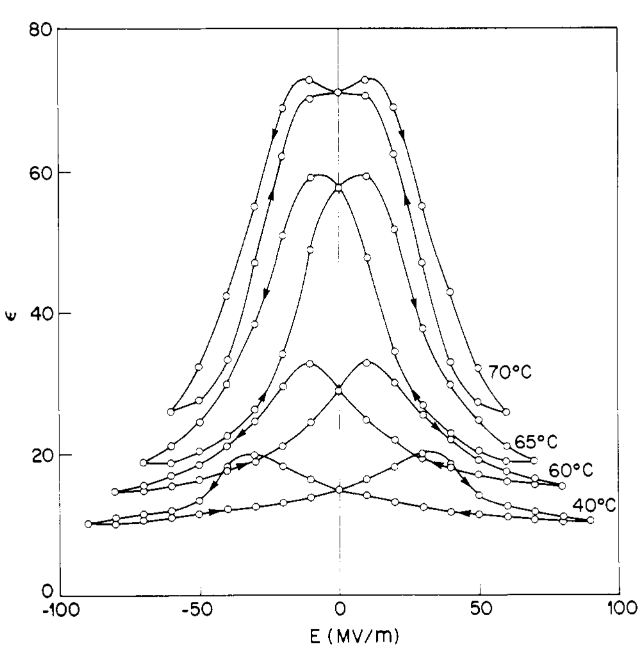

Figure 7. Temperature dependence of ϵ–E loops below the transition temperature of the 52/48 copolymer.

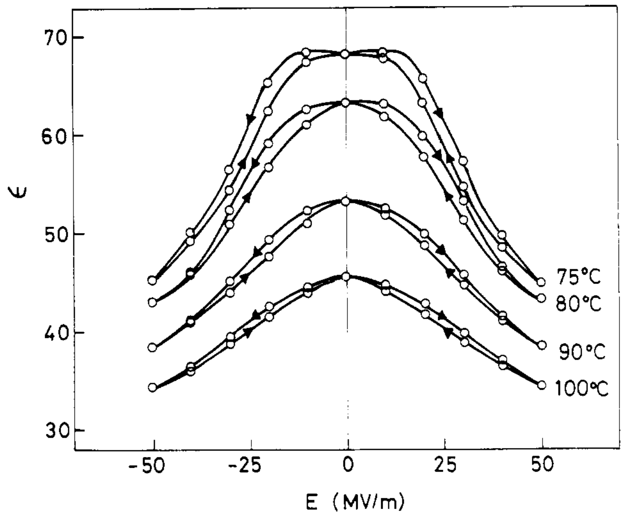

Figure 8. Temperature dependence of ϵ–E loops above the transition temperature.

As the temperature is increased and approaches the transition point, ϵ at $E = 0$ significantly increases and that at high field becomes much smaller, showing a strong nonlinearity as indicated in Figure 7. Near the transition point, crystalline dipoles begin thermal motions, resulting in a dielectric anomaly. The strong nonlinearity indicates that dipoles are forced to align rather cooperatively along the field direction but that they are thermally randomized if the field is removed. When the temperature exceeds the transition point, ϵ at $E = 0$ decreases and nonlinearity becomes weaker as shown in Figure 8. In contrast to the D–E loop, the ϵ–E loop is less affected by the dc conduction because the frequency for measuring ϵ is much higher than that for E.

D. Temperature Dependence of Dielectric Constants. Figure 9 shows plots of various dielectric constants as functions of temperature. The dashed line connecting open circles indicates data obtained from an unpoled sample and the dashed line connecting filled circles was obtained at $E = 0$ at each temperature after poling at a maximum of $E = 100$ MV/m at 20 °C for six cycles at 300^{-1} Hz. Solid lines indicate ϵ obtained from stabilized hys-

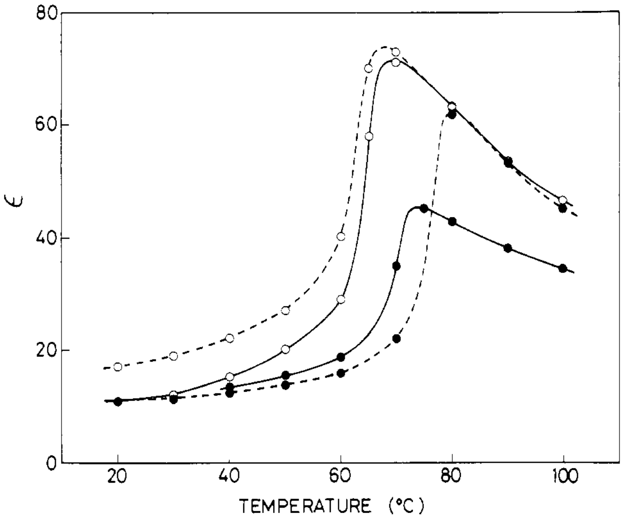

Figure 9. Temperature dependence of various dielectric constants. Dashed line with open circles indicates the data from the unpoled copolymer, and dashed line with filled circles from the sample poled at 20 °C under a field of 100 MV/m for six cycles. Solid lines with open and filled circles are the ϵ at $E = 0$ and 50 MV/m, respectively.

teresis loops at each temperature, where the filled circles refer to values at a field of 50 MV/m and the open circles refer to values obtained when the field had returned to zero.

The peak of ϵ corresponds to the dielectric anomaly caused by the onset of dipolar motions as well as conformational changes of molecules in the crystalline regions. The peak temperature defines the transition point T_c from the ferroelectric to the paraelectric phase. The T_c of poled and unpoled samples are determined to be 68 and 80 °C, respectively. The zero-field ϵ near T_c is close to ϵ of unpoled samples. This is consistent with the fact that the copolymer cannot be poled near the transition point. The line depicting ϵ at 50 MV/m in the ϵ–E hysteresis loops shown that the transition is shifted from 68 to 74 °C by the electric field. This means that the electric field suppresses the onset of the phase transition.

Discussion

The electric displacement D expresses the orientation or the long-range ordering of dipoles. On the other hand, the dielectric constant ϵ expresses the change of dipolar orientation caused by the change of electric field and reflects the fluctuation of the short-range correlation of dipoles. They are related with each other by definition

$$\epsilon = \frac{1}{\epsilon_0}\frac{\partial D}{\partial E} \tag{1}$$

which implies that the gradient of the D–E loop gives ϵ at E. This is qualitatively in agreement with our experimental results. However, there is a quantitative discrepancy because D at high field changes irreversibly in ferroelectrics.

Figure 10 compares D–E and ϵ–E hysteresis loops obtained at 20 °C. In general,[12] branch PQ(P′Q′) in the D–E loop refers to an absolutely stable state, while branch QR(Q′R′) refers to a metastable state. Transition from a metastable branch to an absolutely stable branch occurs when the electric field exceeds a specific value, the coercive field. Such transition is called switching and is known to occur not in a uniform fashion but successively via nucleation of antiparallel domains and subsequent growth. In the absolutely stable states, change of D is basically reversible. One of the origins of reversible polarization is associated with linear dielectric responses such as electronic and ionic polarizations. Rotation of noncrystalline dipoles is also responsible for them. Furthermore, the ferroelectric polarization in the crystalline regions can change its magnitude reversibly because the long-range order of dipoles is a function of electric field. These changes of D in the absolutely stable branch contrast to the switching process in the metastable state, bacause the former is reversible while the other is irreversible. Switched dipoles do not return to their previous position until the field is reversed.

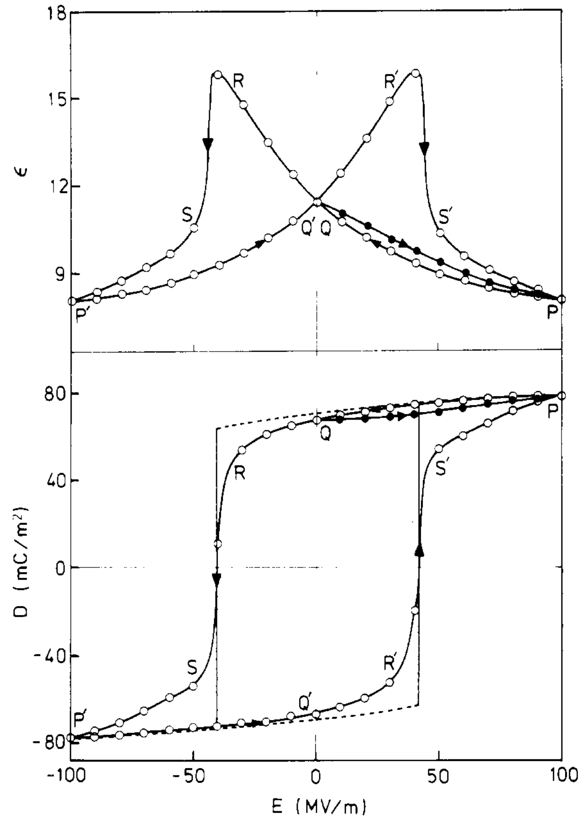

Figure 10. Comparison of D–E and ϵ–E hysteresis loops. PQ-(P′Q′) refers to an absolutely stable branch, QR(Q′R′) a metastable branch, and RS(R′S′) a transition branch. Filled circles are the data when the electric field is increased from Q in the same direction. Dashed line is a result of calculation via eq 2.

If change of D is reversible, the gradient of the D–E loop should quantitatively coincide with the value of ϵ at a given electric field E, because ϵ reflects only a reversible change of polarization. In order to examine the reversibility of the absolutely stable branch, we calculated the electric displacement at a given electric field according to the equation

$$D(E) = D_m - \epsilon_0 \int_{E_m}^{E} \epsilon(E)\,dE \tag{2}$$

Here, D_m is the electric displacement at the maximum field E_m. In this case, E_m is ±100 MV/m. Changes in D from its value at the extremes of E as calculated from eq 2 are shown by dashed lines in Figure 10. Irreversible switching of dipoles between the two branches is indicated by vertical lines drawn at values of E for which $\partial D/\partial E$ is a maximum. It is found that branch PQ(P′Q′) reflects almost reversible change of polarization but contains a small amount of irreversible switching of dipoles. Some of the dipoles near the surface or defects of crystalline lamellae might switch back before the field is reversed. Such switching is experimentally confirmed by increasing the field in the same direction at point Q. As shown by filled circles in Figure

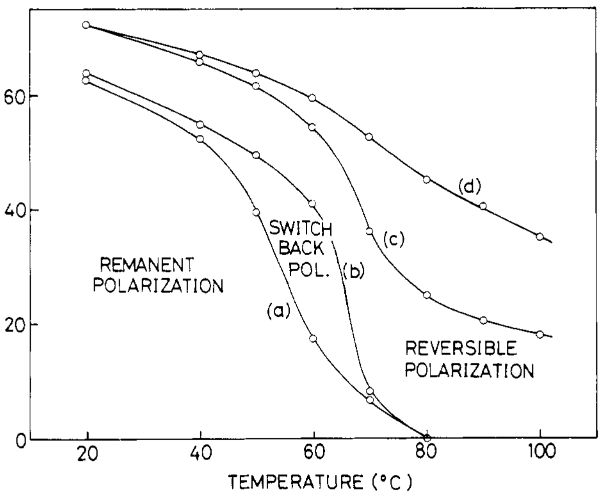

Figure 11. Temperature dependence of various polarizations in the 52/48 copolymer. Curve a indicates the remanent polarization and curve b the polarization at $E = 0$ calculated from eq 2. Curve c indicates the polarization at a maximum field E_m, which has been decreased from 100 to 50 MV/m with increasing temperature. Curve d indicates estimated polarizations on an assumption that the maximum field is 100 MV/m at all temperatures.

10, the electric displacement returns from Q to P, showing a small hysteresis. In the metastable branches, the observed curve significantly deviates from the calculated one, which indicates that certain dipoles start switching before the coercive field is reached. After most dipoles finish switching in the transition branch R′S′(RS), there still remains a considerable number of unreversed dipoles that need higher fields to undergo switching.

From hysteresis measurements, we have obtained the true P_r as a function of temperature by utilizing the frequency dependence of D–E loops. We also obtained the maximum-field polarization D_m in a similar manner. In Figure 11, we show P_r and D_m by curves a and c. Curve b shows the value of D at $E = 0$ calculated via eq 2. In the experiment, the maximum field was decreased with increasing temperature in order to avoid electrical breakdown. This has caused the large drop of curve c near T_c. If an applied field is assumed to be 100 MV/m at all temperatures, we obtain curve d, which exhibits rather mild temperature dependence. In the calculation, we used eq 2 with an assumption that ϵ did not change above E_m.

Measurements of both D–E and ϵ–E loops enable us to separate induced polarizations into three components: remanent, switch-back, and reversible, as shown in Figure 11. Near room temperature, most of the induced polarization remains after removal of the electric field to create large remanent polarization. As the temperature increases, the switch-back component becomes significant. Just below the transition temperature of 70 °C, the induced polarization consists of equal amount of reversible, switch-back, and remanent polarizations. Above 80 °C, the reversible polarization takes over the total induced polarization and no polarization remains after removal of the electric field.

The piezoelectric and pyroelectric properties originate from the remanent polarization: the larger the remanent polarization, the stronger these activities. In order to maximize the remanent polarization in the 52/48 copolymer, the best poling condition is to apply the electric field at room temperature rather than at elevated temperatures as have been traditionally used in poly(vinylidene fluoride).[13] It is also recommended to cycle the field for several times in order to complete the crystalline transformation and to obtain stable polarization.

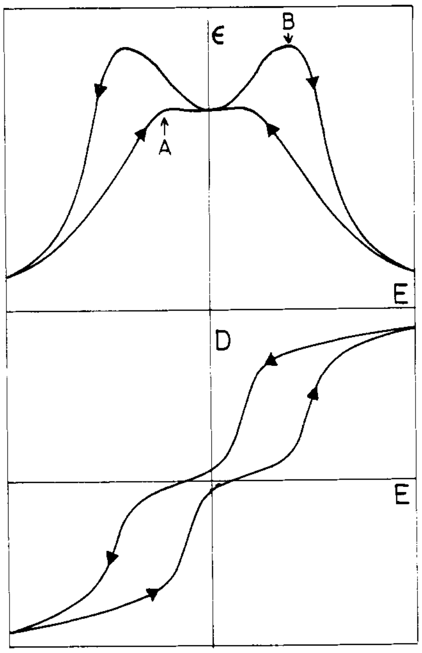

Figure 12. Schematic drawing of double-hysteresis loops suggested from the ϵ–E data at 70 °C.

Measurement of ϵ–E hysteresis loops provides important information to extend our earlier conclusions[7] on the nature of the transition in this copolymer. At 70 °C, which is just above the transition temperature, we have observed a particular shape of hysteresis loop, which is drawn in Figure 12 with some exaggeration. When the electric field reverses its direction, ϵ shows a shoulder A and a peak B, indicating the occurrence of dipole reorientation in *two* steps. To be more specific, dipoles are randomized at shoulder A and are aligned to their new direction at peak B. This implies that the D–E loop must also have a double-hysteresis nature as depicted schematically in Figure 12. While such double hysteresis is not clearly observable in Figure 3 because of distortion by dc conduction, its existence is proven by the shape of the ϵ–E loop.

It is important but sometimes difficult to determine from experimental results whether a particular transition is of the first or second order, although such order is clearly defined thermodynamically. In the case of the 52/48 copolymer, observed quantities such as remanent polarization and the dielectric constant show rather mild temperature dependence near the transition point, which obscures the order of this transition. However, the double-hysteresis nature derived from the ϵ–E hysteresis loop strongly suggests that the transition is of the first order. It is also confirmed by the electric-field-induced shift of the transition point to higher temperature as shown in Figure 9 and as was also found by X-ray diffraction in our earlier work.[7] These results imply that both polar and nonpolar phases are stable near the transition point and that the electric field forces transformation to the polar phase, characteristically of a first-order transition.

Conclusions

Simultaneous measurements of D–E and ϵ–E loops have revealed hysteresis and nonlinear behavior for a 52/48 mol % copolymer of vinylidene fluoride and trifluoroethylene and provided us with information about its ferroelectric polarization and phase transition.

(1) A cyclic repetition of sufficiently high electric field at room temperature induces rather complete crystalline transformation into the all-trans phase and results in the

largest remanent polarization.

(2) The true P_r obtained by frequency-dependent measurement rapidly decreases with increasing temperature.

(3) Although considerably high polarization is induced near T_c, most of it disappears through reversible randomization and irreversible switching-back of dipoles when the field is removed.

(4) The presence of an electric field results in a shift of T_c to higher temperature. The poled sample also exhibits a higher T_c than the unpoled one.

(5) Near T_c, the ϵ–E loop suggests a double-hysteresis nature.

(6) The shift of T_c and the double hysteresis indicate that the phase transition of this copolymer is of the first order.

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Nitroxide Spin Labeling of Epoxy Resins

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ABSTRACT: A description is given of the electron spin resonance results obtained from experiments dealing with the spin labeling of an uncured bifunctional and an uncured tetrafunctional epoxy resin. The labels were attached at the oxirane ring following an opening of the ring by primary, secondary, and tertiary amine nitroxides. Both neutral and zwitterion spin labels were identified. The former were either end labels or bridging-group labels; the latter formed a series of quaternary bases. Some of these quaternary bases can undergo a Hofmann elimination reaction to release a nitroxide spin probe.

Introduction

The spin label technique has been widely used with biological polymers but to a lesser extent with synthetic polymers.[1-5] This technique involves the use of electron spin resonance (ESR) spectroscopy to monitor a paramagnetic molecule, such as a nitroxide, that is bound at a known site in the polymer and serves as a probe of its environment. We are applying the spin label technique to amine-cured epoxy systems, a class of thermoset polymers employed as the matrix phase in fiber-reinforced composites. This paper describes one aspect of this work, the experiments dealing with spin labeling the uncured resins. Some of the results were briefly discussed in an earlier communication.[5]

The epoxy resins investigated were the diglycidyl ether of bisphenol A (DGEBA) in the form of the commercial resin DER332[6] and tetraglycidyl diaminodiphenylmethane (TGDDM) in the form of the commercial resin MY720.[7] These resins were spin labeled with the nitroxide amines 4-(methylamino)-2,2,6,6-tetramethylpiperidinyl-1-oxy (METAMIN), 4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy (TAMIN), 4-(dimethylamino)-2,2,6,6-tetramethylpiperidinyl-1-oxy (DIMETAMIN), and 3-(*N*-methyl-*N*-(6-(methylamino)hexyl)carbamoyl)-2,2,5,5-tetramethylpyrrolinyl-1-oxy (PYRODDH). The molecular structures of the resins and the nitroxides are shown in Figure 1.

Sample Preparation

The resins were heated at ~340 K for 1 h prior to use to melt any crystals that had formed (DGEBA) and to reduce the viscosity sufficiently to allow dissolution of the added nitroxide. The nitroxide amines METAMIN, TAMIN, and DIMETAMIN were obtained from a commercial source[8] and were used as received. The PYRODDH was synthesized in this laboratory in the following manner. First, the imidazole derivative of 3-carboxy-2,2,5,5-tetramethylpyrrolinyl-1-oxy (CPNO) was prepared as an intermediate product. This intermediate (IPNO) was made from CPNO and carbonyldiimidazole (CD) as follows: With stirring, 13.6 mequiv of CPNO was added to a solution of 26.1 mequiv of CD in 100 mL of chloroform. After additional stirring in a dry nitrogen atmosphere for 1 h, the mixture was extracted with water, dried with molecular sieves, and filtered. Following evaporation of solvent, the solid residue was recrystallized twice from methylcyclohexane to yield long, yellow needles, which were dried under vacuum.

PYRODDH was prepared from the IPNO intermediate using the reaction shown in Figure 2. A solution of 3 mequiv of IPNO in chloroform was added to 6 mequiv of *N*,*N*′-dimethyl-1,6-diaminohexane (DDH), and the mixture was stirred overnight to yield a product solution that contained approximately 50% PYRODDH, 25% PYRODDH biradical, and 25% unreacted DDH. The PYRODDH and DDH were separated from the solution by extraction with dilute aqueous HCl followed by addition of a NaOH solution to the aqueous layer and extraction with chloroform. The ESR spectrum of this chloroform layer revealed that no biradical contaminant was present. Evaporation of the chloroform yielded the mixture of PYRODDH and DDH that was used as the spin label.

Spin-Labeling Reactions of DGEBA with Nitroxide Amines

Following addition of a nitroxide amine to DGEBA, a sequence of ESR spectra was observed, each spectrum

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