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Ferroelectricity of Poly(Vinylidene Fluoride): Transition Temperature

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Temperature dependence of polarization of poly(vinylidene fluoride) (PVF₂) has been measured under ac fields of 100–400 kV/cm at 50 Hz at temperatures ranging from 22 to 150 °C. It is found that PVF₂ is a ferroelectric with its transition temperature at ~ 140 °C. Above this temperature, which is about 30 °C below the melting point, no remnant polarization can be measured.

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Since the discovery of large piezoelectricity and pyroelectricity in poly(vinylidene fluoride) (PVF₂) films, there have been intense investigations on this polymer during the last ten years.¹ These investigations are mostly concerned with origin and characteristics of piezoelectricity and pyroelectricity of PVF₂. Recently, on the basis of ferroelectriclike hysteresis loops of polarization^{2,3} and dipole orientation,⁴ it has been suggested that PVF₂ is a ferroelectric rather than an electret as it is commonly known.¹ However, the transition temperature, which is an important characteristic of ferroelectric materials, has not been observed so far for PVF₂. The purpose of this Letter is to present the first results on the temperature dependence of polarization of PVF₂, which show the presence of a transition temperature above which remnant polarization is not observed.

PVF₂ samples used in these studies are capaci-

tor-grade films of 6 μm in thickness obtained from Kureha Chemical Corporation. These films are biaxially oriented and contain both α - and β -phase crystalline regions of approximately equal amount.⁴ These films were first annealed at 150 °C for about half an hour under slight tension in order to prevent shrinkage and structural changes that may occur at high temperatures. Film surfaces were then cleaned with acetone and aluminum electrodes were evaporated on both sides.

Electrical displacement D , electric field E , polarization P , and residual polarization P_r are related by the following well-known equations:

$$D = \epsilon_0 E + P, \quad (1)$$

$$P = \epsilon_0 \chi' E + P_r(E), \quad (2)$$

where ϵ_0 is the free permittivity, and χ' is the susceptibility at low field. In this paper, we are

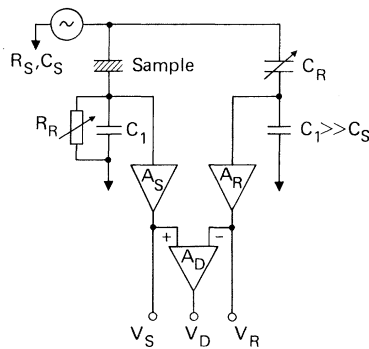
mainly concerned with the hysteresis loops of residual polarization $P_r(E)$ and the remnant polarization, i.e., $P_r(E=0)$.

The electrical circuit used to measure the residual polarization is shown schematically in Fig. 1. It is a bridge system with the sample in one branch and adjustable impedances in the other. Through two amplifiers (A_S and A_R) and one differential amplifier (A_D), the net balance of the bridge can be recorded. A small field is first applied to the sample and adjustable impedances are chosen to equilibrate the bridge. These matching conditions are

$$C_R = C_S \text{ and } R_R/R_S = C_S/C_1, \tag{3}$$

where C_S and R_S represent the capacitance and resistance of the sample, C_R and R_R are adjustable capacitance and resistance, respectively, and $C_1 (\gg C_S)$ is the measuring capacitance (see Fig. 1). Physically, this means that the R_R - C_1 branch cancels the dielectric loss, whereas the adjustable (air) capacitor C_R represents the capacitance of the sample at low field. Hence, the residual polarization $P_r(E)$ can be obtained by recording the differential output V_D as a function of the source voltage [for example, see Fig. 2(a)]. Measurements were made usually with a continuous sweep of the ac source. However, when the conductivity of the sample becomes large at high temperatures ($\geq 80^\circ\text{C}$), a single pulse of the ac source was used in order to avoid the change of sample temperature due to excessive dielectric loss during measurements. Absolute calibration is carried out by equating the output V_R from air capacitor C_R to $\epsilon'\epsilon_0 E$, i.e.,

$$P_r(E) = (V_D/V_R)\epsilon'\epsilon_0 E, \tag{4}$$



$C_1 = 10^5 \text{ pF}$
 $C_S \leq 200 \text{ pF}$

FIG. 1. Schematic diagram of the circuit to measure polarization under ac field.

where ϵ' is the relative permittivity at low field. The source and circuit were designed to supply voltages of maximum 1500 V (peak to peak) in the frequency range of 10 Hz to 20 kHz, and use of amplifiers enabled measurements of P_r as small as 0.5 nC/cm^2 . The frequency and field dependence of polarization hysteresis of PVF_2 will be published elsewhere.⁵

The residual polarization $P_r(E)$ has been measured at temperatures ranging from 22 to 150°C . At lower temperatures, typical ferroelectric hysteresis loops such as the one shown in Fig. 2(a) are observed. At temperatures higher than $\sim 140^\circ\text{C}$, however, a double hysteresis loop with negligible remnant polarization $P_r(0)$ appears [see Fig. 2(b)]. The double hysteresis loops look similar to those reported for conventional ferroelectrics, e.g., barium titanate⁶ and ferric ammonium sulfate alum,⁷ at temperatures above their Curie temperatures.

The temperature dependence of the remnant polarization $P_r(0)$ measured at 50 Hz is shown in Fig. 3 for applied fields ranging from 100 to 400 kV/cm in amplitude. Remnant polarization is found to increase with temperature to reach a maximum at $\sim 120^\circ\text{C}$ and then to fall down rapidly with further temperature increase to almost zero at $\sim 140^\circ\text{C}$. Beyond this temperature, no remnant polarization can be measured. Upon cooling down from 150°C , the polarization maximum is reproduced, indicating that this temperature dependence of the polarization is reversible. Thus, these results show that PVF_2 undergoes a ferroelectric-to-nonferroelectric transition at $\sim 140^\circ\text{C}$

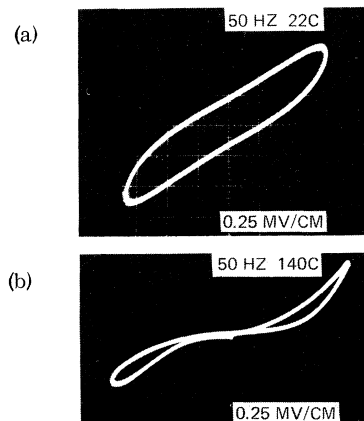


FIG. 2. Oscilloscope picture of residual polarization hysteresis of PVF_2 under ac field of 250 kV/cm in amplitude at 50 Hz: (a) At 22°C ; (b) at 140°C (single sweep).

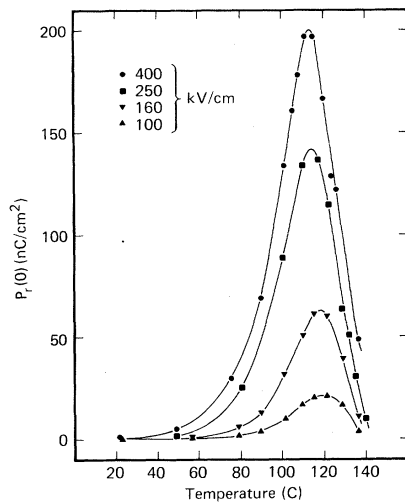


FIG. 3. Temperature dependence of remnant polarization $P_r(0)$ of PVF_2 under ac field of 50 Hz. The amplitude of the field is indicated for each curve in the figure.

whereby it can no longer maintain its remnant polarization. This temperature is found to be about 30°C below its melting point.

The rapid increase of remnant polarization with temperature observed for PVF_2 at temperatures lower than $\sim 120^\circ\text{C}$ (see Fig. 3) is rather unique when compared with conventional ferroelectrics.⁸ For these materials remnant polarization usually remains constant or decreases slowly before falling abruptly to zero at the transition temperature. It is believed that this difference may arise from the much higher coercive field of PVF_2 compared to other ferroelectrics, ~ 100 kV/cm versus ~ 1 kV/cm.² That is, with the electric field used in these measurements, the condition of saturation is not reached. Under these conditions, the remnant polarization is likely to be determined by the dynamics of chain rotations under the influence of oscillating electric field. As temperature increases, the rate of chain rotation (orientation) increases, possibly because of increases in kink (defect) generation and propagation.⁹ Hence, this will result in increasing remnant polarization with temperature. However, at higher temperatures, the crystal lattice energy becomes insufficient to contain the chain motions and, hence, to freeze the orientation of chain dipoles achieved

under the applied field. Then, the remnant polarization would vanish. It seems that the temperature dependence of the remnant polarization and the mechanism of ferroelectric-to-nonferroelectric transition of PVF_2 are intimately related to the molecular motions in polymer crystallites.

In summary, it is demonstrated that PVF_2 is a ferroelectric with its transition temperature located at $\sim 140^\circ\text{C}$, beyond which no remnant polarization can be measured. This temperature is found to be about 30°C below the melting point. The detailed mechanism of this transition with regard to molecular motions in polymer crystallites has yet to be understood.

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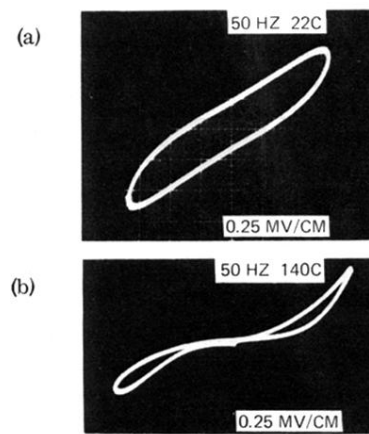


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