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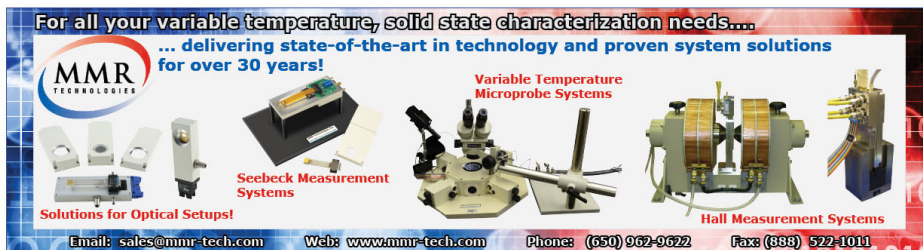
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Measuring hysteresis loops of ferroelectric polymers using the constant charging current corona triode

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A novel method is proposed for measuring the hysteresis loops of ferroelectric polymers. The samples need to have only one electrode and are poled by corona discharge in a constant current corona triode. It is shown how the sample surface potential and the charging current are related to the remanent polarization and coercive field, so that the hysteresis loops can be obtained. An illustrative example is given for samples of β-PVDF for which the hysteresis cycles were remarkably close to those obtained with the traditional Sawyer–Tower circuit. Values of 80 MV/m and 70 mC/m^2 were estimated for the coercive field and remanent polarization, respectively.

I. INTRODUCTION

Ferroelectric materials are usually identified by possessing permanent polarization denoted in their dielectric hysteresis loops in plots of electric displacement D versus electric field E. There are a number of experimental setups aimed at measuring these loops, with the Sawyer–Tower[1,2] circuit being one of the most traditional. In the Sawyer–Tower circuit, a sinusoidal or triangular voltage is applied to one of the electrodes of the sample, and the charge Q generated in the sample is detected by a charge amplifier connected to the other electrode. The electric displacement is calculated from the measured charge Q while the electric field is determined by the ratio of the bias voltage and the sample thickness.

In this article, we present a novel method for measuring the hysteresis loops in which samples of ferroelectric polymers need to have only one electrode. In this method, the samples are poled by corona discharge in a constant current corona triode,[3-5] and their surface potential is monitored during the whole charging process. It is shown how the surface potential and the charging currents can be related to the remanent polarization and coercive field, so that the hysteresis loops can be obtained.

II. EXPERIMENTAL PROCEDURES

The constant current corona triode, shown schematically in Fig. 1, has been described in detail elsewhere,[5] so only a brief description is given here. The triode consists basically of a corona tip P, a metallic grid, and a sample holder with a guard ring. The corona discharge is produced at the tip which is connected to a voltage supply V_c, and the charging current is controlled by biasing the grid with a voltage supply V_g. Both supplies V_g and V_c are operated in the constant current mode. To make the deposition of corona ions over the sample more uniform, the tip is placed in the center of a metallic cylinder biased by a voltage supply V_{ci}. The sample S stretched between two metallic rings is mounted on the sample holder and the distance d between the grid and the holder was adjusted to 3 mm. One surface of the sample is uncoated, and the other is covered by evaporated aluminum. The guard ring G is connected to the ground and is aimed at preventing surface currents from reaching the measuring electrode E which is connected to the feedback current input of the controlled supply V_g. A battery operated electrometer I_s (Keithley 602) and an ammeter I_c are used for monitoring the sample charging current I_0 and the corona current I_c, respectively. I_0 is kept constant by controlling the grid voltage V_g. During charging the potential difference between the grid and the sample has a constant value V_ρ, and therefore the surface potential of the sample, $V_s(t)$, can be inferred from measuring the output voltage V_g using the recorder R [$V_s(t) = V_g(t) - V_\rho$]. The polarity of all supplies can be reversed so that samples can be charged with currents of either positive or negative polarity.

The system described above allows the evolution of the surface potential during the charging process to be monitored. To obtain the whole hysteresis cycle it is necessary to invert the corona polarity as soon as the charging process is completed, and then submit the sample to an inverted constant charging current $-I_0$. The sample is then discharged and recharged with the reverse polarity. In the original version of this triode (represented in Fig. 1), the surface potential could not be measured during the discharge, for the V_g supply feedback system only works when V_g and I_0 have the same polarity and during the discharge V_g would still have its previous polarity. This was overcome by connecting an extra voltage supply V_a to the grid (not shown in the figure). V_a was set at approximately the same potential as V_s at the end of the charging process. V_g and V_c could then be biased with the inverted polarity and varied to give the constant current I_0. The grid voltage from which V_s is calculated was therefore given by $V_g - V_a$. The whole procedure of switching V_a on and inverting the polarity of the V_g supply takes around 50 s,
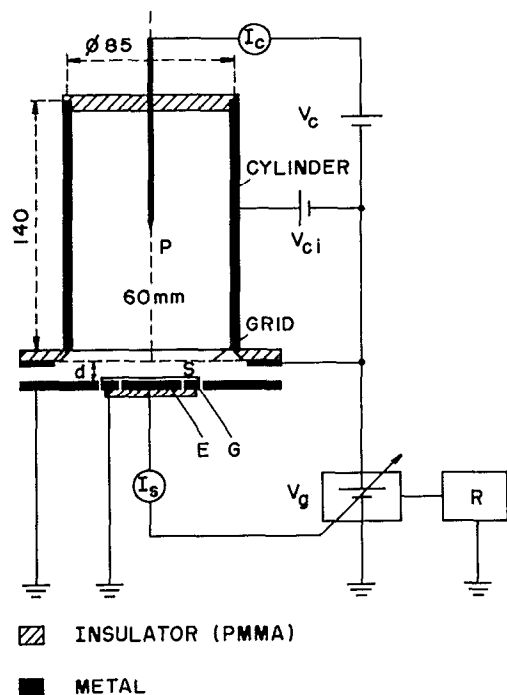
FIG. 1. Schematic diagram of the corona triode system. V_c and V_g are controlled power supplies; V_{Cl} a voltage supply; I_c and I_s are ammeters; R a pen recorder; S the sample; G is the guard ring; and E the measuring electrode. All dimensions are in millimeters and d is the distance between the grid and the sample.

and obviously no information can be obtained during this period. This does not represent a great loss since there is very little change in potential in this period.

The samples used in this work were 10-μm-thick β-PVDF samples stretched at 90 °C to four times their initial length. Aluminum electrodes (2.27 cm^2) were evaporated onto one side of the polymer foils. All measurements were carried out under room conditions, $T = 25$ °C and relative humidity of 50%–60%.

III. THE HYSTERESIS LOOPS

In order to illustrate how hysteresis loops can be obtained from surface potential measurements with the corona triode we show a hypothetical case of a sample with no conductivity submitted to charging currents of $I_0 = \pm 100$ nA. We also assume that there is a unique coercive field, E_c, at which all dipoles reorientate cooperatively (leading to a square hysteresis). Using typical values for the sample thickness, $L = 10$ μm, coercive field, $E_c = 70$ MV/m, remanent polarization, $P_r = 70$ mC/m^2, and a relative dielectric constant $\epsilon_r = 13$, one obtains the surface potential versus time curves as shown in Fig. 2. The surface potentials were calculated using the equation for the total current:

$$J_0 = \frac{\partial D(x,t)}{\partial t} = \epsilon \frac{\partial E(x,t)}{\partial t} + \frac{\partial P(x,t)}{\partial t}, \quad (1)$$
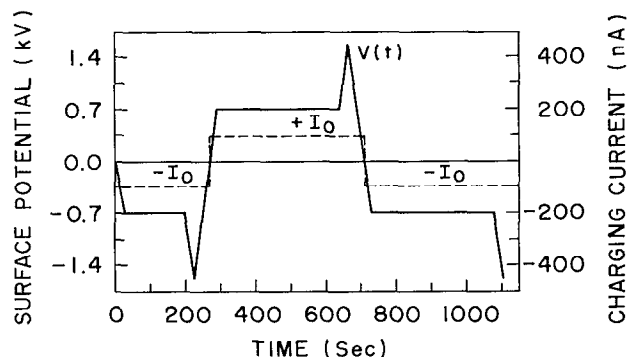

FIG. 2. Calculated surface potential build up for three charging-discharging cycles. The potentials were obtained from Eq. (1) using currents of ± 100 nA, $\epsilon = 13$, $E_c = 70$ MV/m, and $P_r = 70$ mC/m^2. In each cycle, three distinct regions can be identified: (1) a steep increase in $V_s(t)$ due to the capacitive behavior of the sample; (2) a plateau when the dipoles are being oriented but there is no change in the electric field; (3) another region where $V_s(t)$ increases linearly with time since all dipoles have already been oriented. The plateau in the second and third cycles is twice as long as in the first cycle because in the last two cycles the dipoles suffered a 180° rotation whereas in the beginning of the first cycle the dipoles were randomly oriented.

where J_0 is the total current density, D the electric displacement, ϵ the dielectric constant of the sample, E the electric field, P the polarization, and t time.

The results of the simulation for three cycles are shown in Fig. 2. In the first cycle a virgin sample (no net charge or polarization) was supposed to be charged with a constant current of -100 nA and then discharged and recharged with a current of $+100$ nA. The second and third cycles were identical but inverted, with the sample being positively and then negatively charged. In each cycle, three distinct regions can be identified: (1) a steep increase in the sample surface potential, $V_s(t)$, in the beginning of the charging process due to the capacitive behavior of the sample until a critical field (the coercive field) is reached. In this region no polarization occurs and therefore $\partial P/\partial t = 0$; (2) a plateau when the dipoles are being oriented but there is no change in the electric field; (3) another region where $V_s(t)$ increases linearly with time since all dipoles have already been oriented. The only difference between the first and the subsequent cycles is in the period of time (t_p) in which the plateau region is observed: t_p in the second and third cycles was twice the value of the first cycle because in the last two cycles the dipoles suffered a 180° rotation whereas in the beginning of the first cycle the dipoles were assumed to be randomly oriented.

The plateau at $V_s(t) = E_c L$ (L = sample thickness) appears because when the electric field reaches the coercive field, E_c, all the charge deposited onto the sample is compensated by the reorientation of the dipoles, and therefore V_s remains unchanged.[5] The charge impinged onto the sample during the period of time in which the plateau is observed (t_p) is then used to calculate the remanent polarization $2P_r = J_0 t_p$. The factor 2 appears because the sample was initially polarized with the opposite polarity. Hence, the results presented schematically in either the second or
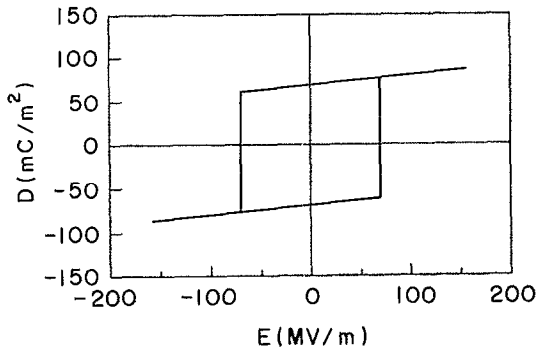
FIG. 3. Hysteresis loops obtained from the calculated surface potential curves shown in either the second or the third cycle in Fig. 2.

FIG. 4. Experimental surface potential curves for a 10-μm-thick β-PVDF sample, submitted to currents I_0 of $\pm$ 100 nA which are also shown in the figure. The value of t_p was estimated as indicated by the arrows in the figure. The coercive E_c is determined by the ratio of the mean value of the potentials indicated by the arrows and the sample thickness.

the third cycle in Fig. 2 can be converted into a hysteresis loop by remembering that, as the current is constant, the axis of time can be transformed into electrical displacement D. Integration of Eq. (1) gives

$$D(t) = I_0 t / A, \tag{2}$$

where I_0 is the charging current and A is the area of the electrode and

$$D(t) = \frac{1}{L} \int_0^L D(x,t) dx.$$

The electric field $E(t)$, on the other hand, is calculated as $V_s(t)/L$. In this conversion, the time for the second poling process is counted from the end of the first charging process. Also, the zero of the electrical displacement D is shifted to the middle of the plateau region in Fig. 2, when $P = 0$. The results are shown in Fig. 3 which displays a square hysteresis loop, as it had been anticipated since a unique value for the coercive field was assumed.

IV. RESULTS

The experimental results obtained in two charging-discharging cycles for a (previously poled) 10-μm-thick β-PVDF sample submitted to constant currents of $\pm$ 100 nA are now shown in Fig. 4. The main features presented in the second and third cycles of Fig. 2 can be identified, with two important exceptions. First, the plateau region is not so well defined as it was in the case of the theoretical curves in Fig. 2. Therefore, to estimate t_p and E_c it is necessary to extrapolate the linear parts of the curves[4] as illustrated in Fig. 4. Second, the slope of increase of the surface potential is not the same for the two linear portions in each cycle. This point will be further discussed in the next section. As shown in Sec. III, the coercive field E_c and the remanent polarization P_r can be obtained directly from the surface potential curve. The values estimated for E_c and P_r were 80 MV/m and 70 mC/m^2, respectively.

The hysteresis loops obtained from the results in Fig. 4 are shown in Fig. 5, where curves are also shown for a sample submitted to currents of 50 nA. The cycles were completed in 1000 and 2000 s, which would correspond in traditional hysteresis loops to frequencies of 1 and 0.5
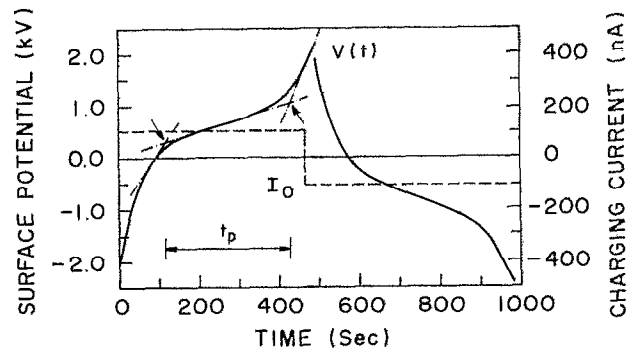
mHz, respectively. The values estimated for E_c and P_r were 70 MV/m and 70 mC/m^2, respectively. The value for the coercive field differs from the 80 MV/m calculated directly from the surface potential measurements because of the slight asymmetry around the D axis not considered in the estimation of E_c. The values for E_c and P_r were found to be practically independent of the charging current in the range between 50 and 150 nA, in agreement with the suggestion of Refs. 6 and 7 that the hysteresis loops of β-PVDF samples are independent of the frequency used in the range of 10^{-3} to 10^{-4} Hz. For lower currents, however, the conduction current is no longer negligible and a departure in the values of E_c and P_r is observed. For $I_0 = 25$ nA, for instance, $E_c = 90$ MV/m and $P_r = 100$ mC/m^2.
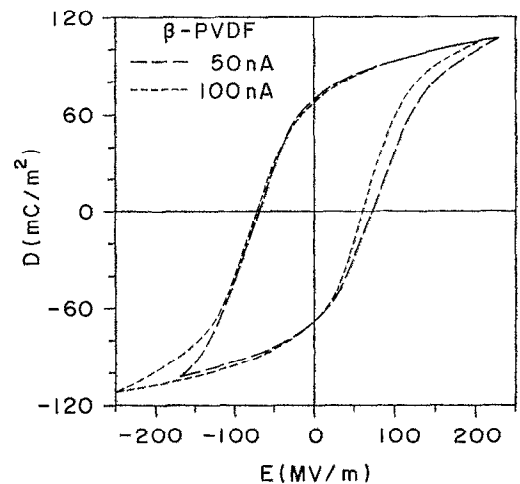

FIG. 5. Hysteresis loop obtained from the experimental surface potential curves shown in Fig. 4. Also shown in a loop for a charging-discharging cycle where I_0 was 50 nA. The values estimated for E_c and P_r were 70 MV/cm and 70 mC/m^2, respectively.

V. DISCUSSION

A novel method to obtain the hysteresis loop of ferroelectric polymers has been presented. The samples are charged at constant current and their potential buildup is measured in a corona triode—a technique that has already proven to be an excellent tool for the study of charge transport in highly insulating polymers.[8-11] Two fundamental assumptions had to be made in order to convert the surface potential measurements into D vs E hysteresis loops: (i) the conduction currents through the sample and the accumulated space charge are negligible; (ii) the polarization is given by a step function of the electric field, i.e., a mean value for the coercive field is assumed at which all dipoles reorientate cooperatively.

From the cycles presented in Fig. 5 it can be seen that the hypothesis of a unique coercive field certainly does not hold as the hysteresis is not of a square nature. The cycles are, nevertheless, very close to those published in the literature[4,6,7,12,13] for samples of β-PVDF, with E_c and P_r within 10% of the published value. This probably means that although a step function is not accurate for describing the polarization, the approximation of using a mean coercive field does give reasonable results. It has been shown[10] that the hysteresis cycles for biaxially stretched PVDF and VDF-TrFE copolymers depart less from the square cycle than the ones presented here. Therefore, the assumption of a mean value for the coercive field is likely to give even better results for those polymers. We have confirmed this expectation in some preliminary experiments which we shall report in the near future. The slight asymmetry observed in Fig. 5 could, in principle, be related to the fact that the sample possesses only one electrode and ions of different polarity are known to behave differently on the sample surface.[14] However, asymmetric behavior for the hysteresis loops of PVDF samples has also been observed by Wang et al.[13] using the traditional method for measuring D vs E curves. The effects of assumption (i), on the other hand, can be felt by analyzing the results with low charging currents ($\leqslant 25$ nA) when the remanent polarization and coercive field depart from the expected values. One should indeed expect that the value of the remanent polarization would be overestimated since a fraction of the total current is lost as conduction current (not considered in the calculations) and does not contribute to P_r. However, for currents between 50 and 150 nA the values estimated do agree with the literature which supports the hypothesis of a negligible conduction current under these conditions.

A remaining problem is concerned not with the hysteresis cycle itself but with the fact that in the V_s vs t curves in Fig. 4 different slopes were obtained for the two linear parts in each curve. This could be caused by conduction currents in the sample, but the effects from these currents on the slope would only appear if the conductivity was of the order of 10^{-10} $\Omega^{-1}m^{-1}$ which would make the calculation of the remanent polarization invalid. This has been shown not to be the case. Other possible explanations may lie in the fact that the conductivity and the dielectric constant of the sample could be both dependent on the electric field,[15-17] but the data presented here do not suffice for a definitive conclusion to be reached.

One of the advantages of this method may be that if one uses very low currents, the corresponding frequencies would also be very low. To obtain reliable results the conduction processes in the material must be known though, and there will probably exist a lower limit for the charging current below which the sample cannot be polarized because all the current impinging onto the sample would be lost through conduction. Another possible advantage is that the method requires only one electrode to be deposited onto the sample which may be an interesting feature in some specific applications.

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