DISCUSSION

Piezo and Pyroelectricity in Electrets

Caused by Charges, Dipoles, or Both?

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The very lively and stimulating discussion on the last day of the 7th International Symposium on Electrets was transcribed and edited from an audio tape in order to obtain a readable text. It was, however, attempted to preserve at least some of the original flavor of the discussion by not polishing the more colloquial style of the statements too much and by not eliminating all redundancies. If the results of this experiment are not totally satisfactory the editor (and not the discussion panelists or participants) is to be blamed.

1. INTRODUCTION

By Gerhard M. Sessler (Institute for Electroacoustics, Technical University of Darmstadt, Germany)

THE topic of this session has been discussed for the past twenty or thirty years, but the discussion got more intense during the past ten years or so. Let me first make a few general comments on the question of piezo and pyroelectricity in electrets; later on the panelists will, of course, discuss these things in more detail.

In a homogeneous medium space charges cannot cause piezo or pyroelectricity. If stressed, there will be affine geometrical changes throughout the medium, and therefore the induction charges on the electrodes will remain the same, and piezoelectricity cannot be generated. However, if dipoles are present in such a homogeneous dielectric, then piezoelectricity is possible. Take for example

quartz: If one compresses the medium then the dipoles will somehow be subjected to a different degree of strain, — let's discuss it on a very elementary basis — and for this reason the induction charges on the electrodes can change and there is piezoelectricity. In an inhomogeneous medium such as a semicrystalline polymer, charges and dipoles can cause piezoelectricity. If you have, for instance, a semicrystalline polymer then the crystalline and the amorphous parts are, upon compression, subjected to different degrees of deformation; and for this reason, a piezoelectric effect can be generated.

So the fundamental situation is that, in order for space charges to cause an effect, one needs an inhomogeneous medium. Now the experiments tell us that the space charge really plays an important role in the piezoelectric properties of polymers, in particular in the piezo and pyroelectric properties of polyvinylidene fluoride (PVDF) and its copolymers. There were early experiments in the 1970s, and all these experiments indicated that charge in-

jection has an effect on the piezo and pyroelectric properties. In these experiments, injecting and blocking electrodes were used; and with blocking electrodes, usually the piezoelectric effect generated during the poling process was much smaller. So there was a strong indication that space charges or injected charges had an effect on the piezoelectric properties. If charge is injected during the poling process it will diminish the field in certain regions and strengthen the field in other parts of the samples. It was shown that in the vicinity of the positive electrode of PVDF such a strengthening of the field was achieved due to charge injection and that therefore the piezoelectric activity in this region was larger than in the other regions of such samples.

These effects were extensively discussed around 1980, and it was concluded at that time that charges play an important role in establishing piezoelectric properties in PVDF and its copolymers. By that time also the ferroelectric nature of the polarization was firmly established by hysteresis and other measurements, and it was believed that the behavior of this material was — at least as far as the piezo and pyroelectric effects are concerned — basically understood.

But in the past decade, this picture has been significantly supplemented by experiments that involve again poling or polarization reversal and also by studies of the polarization distribution, experiments that were carried out for a large part by the panelists who are here with us today. At least some of these experiments indicated that the injected charge played a much more important role than just changing the electric field in the dielectric. I will not go into more detail because these findings will be discussed by the panelists.

Let me therefore close my remarks at this point and just say that we are assembled here to discuss these new results that were found over the past ten years or so and to discuss their meaning for the piezo and pyroelectric effects in PVDF. I would like to ask the panelists now to start the discussion with short statements about the work which they have done and about the explanations they have concerning the piezo and pyroelectric effects in electrets.

2. THE ORIGIN OF FERROELECTRICITY IN PVDF AND VDF-TrFE POLYMERS

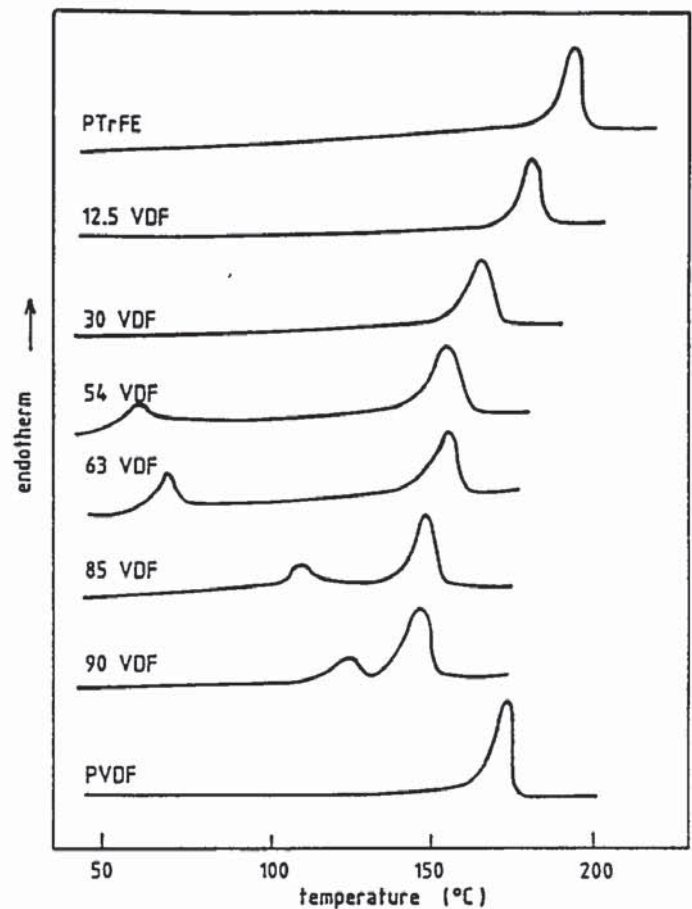*Opening Statement by Dilip K. Das-Gupta (School of*

Figure 1.

Ferroelectric transition and melting behavior of the VDF-TrFE copolymer system as measured by differential scanning calorimetry (DSC) [1].

Electronic Engineering Science, University of Wales, Bangor, Gwynedd, UK)

PVDF and its copolymers are ferroelectric. As you can see in Figure 1 based on data by Yagi and his co-workers [1], if you take the top part, which is the phase transition of trifluoroethylene (TrFE), and if you increase the amount of vinylidene fluoride (VDF) in the copolymer you introduce disorder and reduce the phase-transition temperature. And around 54% VDF, you see the Curie temperature there at ~ 60°C; as you increase gradually the percentage of the VDF, the second phase transition moves towards a higher temperature; and in PVDF, we do not really see it because the polymer reaches its melting point. But this is a good proof of its ferroelectric behavior as has been demonstrated.

As Furukawa will show some of his own data, I will not show them here. But in Figure 2, there are three basic models: The first one is due to Broadhurst and his co-workers in the United States [2], the second one is due to Wada in Japan [3], and the third one is due to Purvis

	d_P (%)			p (%)		
	model 1	model 2*	model 3	model 1	model 2	model 3
Electrostriction	34	22	45	27	0	76
Dipole libration	10	--	--	23	--	--
Dimensional changes of samples	56	78	55	50	47	24
Dimensional changes in crystal	--	--	--	--	53	--

* e_{31} coefficient

Figure 2. A summary of calculated contributions in electroactivity from different models [2–4].

and Taylor in the US [4]. And these are the contributions: Electrostriction, dipole libration, dimensional changes of the whole sample, and dimensional changes in the crystallites. Those are the four components, which these models prophesy as origins of the piezo and the pyroelectricity. There is a wide discrepancy and difference in opinion; so we are not yet sure which is the real originator of the piezo and pyroelectricity in semicrystalline polymers. But all these models agree on one thing namely that the maximum contribution probably comes from the dimensional changes in this material, that means the changing dipole density when the dimension changes.

As Sessler has said, that if space charges should be the originator of the electroactivity in this polymer then the material has to be heterogeneous in the sense that the thermal-expansion coefficient and the temperature derivative of the permittivity must be heterogeneous in the thickness direction for pyroelectricity; and similarly, the elastic modulus and the electrostriction coefficient must also be heterogeneous in the thickness direction for piezoelectricity. And there are no theories in those areas.

You can look at hysteresis loops and polarization reversal of a ferroelectric material by means of several techniques, one is the normal cyclic field; if you operate the cyclic field at a very low frequency such as 0.01 Hz then it is quasistatic, and the hysteresis loop is practically independent of frequency. Alternatively, you can use a step-voltage input, which will be shown by Furukawa; but if you do that you can also show that the hysteresis behavior is field-dependent. You can switch the polarization in a millisecond or less if the field is 100 MV/m, but if it is 50 MV/m switching could take as long as a second; and the coercive field is nearly 50 MV/m.

At Bangor, we applied a slightly different technique [5], which is due to Wang [6]; and in Figure 3 you see that we have a power supply with a very high resistance and a
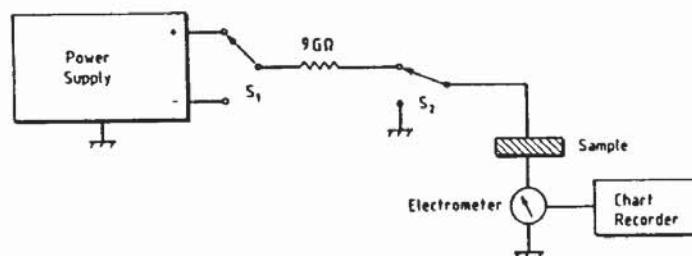

Figure 3.

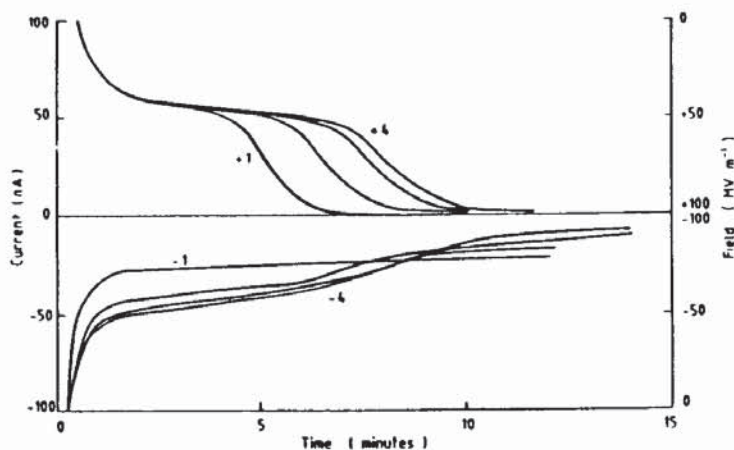Circuit used to observe polarization-reversal currents in a VDF-TrFE copolymer [5].

Figure 4.

Polarization-reversal currents at 20°C in a 9μm thick copolymer film poled at high temperature [7].

switch. If we keep reversing the applied field and record the current that flows we can show space-charge injection and space-charge removal on the sample as such. If we do the experiment repeatedly (−1, +1, −2, +2, and so on in that order) with such a technique [7] then we can see some asymmetry (Figure 4): You have a capacitive component, where the dipoles in the amorphous phase are changing; and then you have a big shoulder, where the dipoles in the

crystalline lamellae are very, very slowly switching in the field, which is then followed by another capacitive component. So that part has been demonstrated as well for PVDF; but the negative part, which is quite asymmetric to the positive part, is of interest: You can see that for −1 there is no shoulder like that until the field reaches something like 75 MV/m. And then you have the three components again: initial capacitive discharge, followed by a big, big shoulder when the dipoles start to switch in the space-charge field, and then a long tail following the second period.
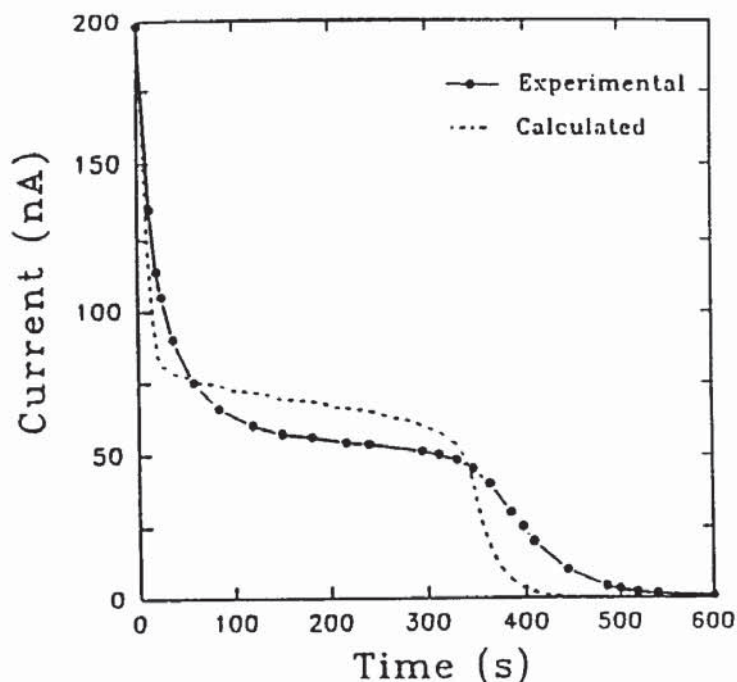

Figure 5.

A typical experimental current (dots and solid line) and the corresponding calculated current (dashed line) [7].

The analysis of this could be done in the same way as in the model due to Ikeda, Fukada, and Wada [8]: You have two components, the capacitive components and the polarization component, and if you use the following three equations

$$I = I_c + I_p \qquad (1)$$

$$\frac{dP}{dt} = \frac{P_s - P}{\tau} \qquad (2)$$

$$E = \frac{V - IR}{d} \qquad (3)$$

you can then find an equation to work out the field. Using the switching time of ∼ 1 ns as given by Furukawa and the activation field of ∼ 1 GV/m again from Furukawa's data, we computed what the current should be [7]; the result is shown in Figure 5. The full line represents the experimental data, and the dashed line the theoretical ones. There are differences between the two, and we think

these are due to the fact that we have used a model with two parallel elements, but it may not be as simple as that, and secondly that there is a field component of the permittivity as well, which we did not consider here.

So, basically we are saying that space charge does affect the polarization reversal of the crystalline dipoles. What happens is that if you pole the material at high temperature then the space charges will be moving towards the field direction and enhance the dipolar field; and until you remove the space charge, the dipoles are somewhat restricted to move and they take time to move. And if we integrate the area under the curve for the negative polarity we can calculate the total space charge; similarly, if we then integrate the previous area and the new one we find that the space charges released in both cases equate quite well. The coercive field of this material is ∼ 50 MV/m, the space-charge field we worked out as ∼ 30 MV/m, and the activation energy of the space charge we calculated to be ∼ 0.2 eV. So once you move the space charge away, the dipoles are free to move.

Therefore, for all it is worth, my view is that the space-charge contribution in the piezo and pyroelectricity is there, but if I have to guess I would say that the relative amount of this contribution is only about 5 to 10% and no more.

3. CHARGE AND POLARIZATION SIGNATURES AND THEIR RELATION TO MICROSCOPIC MODELS OF POLARIZED MEDIA

Opening Statement by Aimé S. DeReggi (National Institute of Standards and Technology, Gaithersburg, Maryland, USA)

I am going to address the subject of this discussion from a phenomenological point of view which is tied to my own experience with thermal-pulse measurements. The first thing I would like to do is to look at the problem of space charge and polarization using some very simple models, in order to see if we can make some general predictions in support of what Sessler has already said. Let us take a look for a moment at the sketch on the top of Figure 6, which is a planar capacitor geometry with a layer of space charge right smack in the middle of it. Now the induced charges on the plates are going to be determined by Gauss' law and the line integral of the field across the thickness. You are going to have the sum of
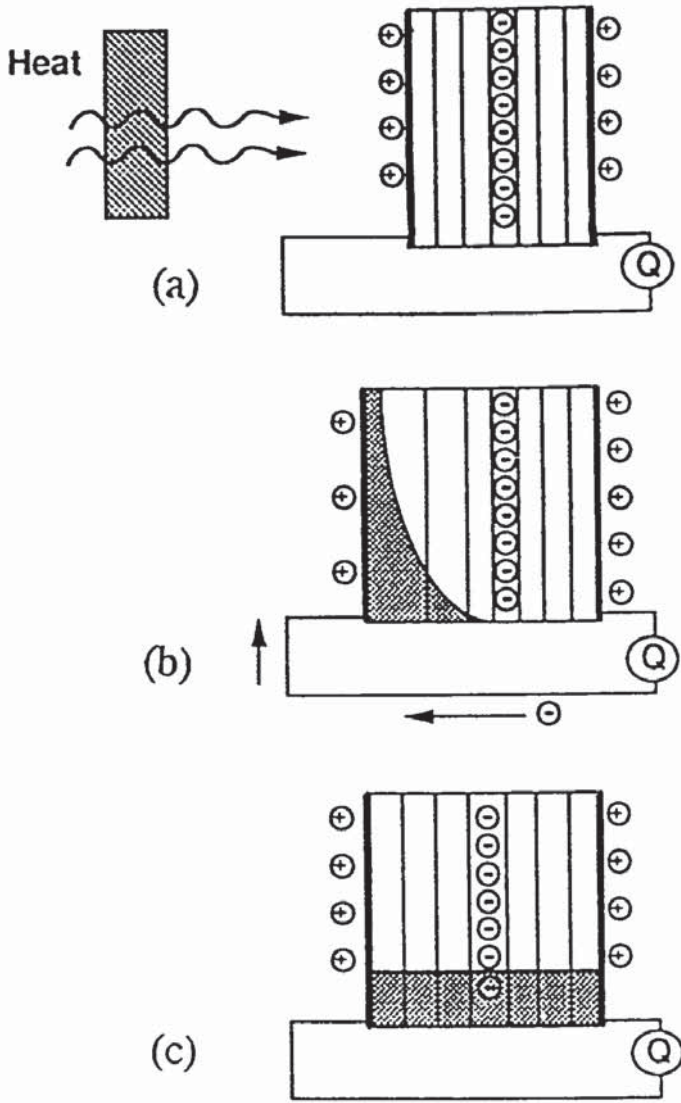
(a)

(b)

(c)

Figure 6.

Thermal pulse measurement on dielectric sample containing charge layer, at different times t in relation to the diffusion-controlled thermal relaxation time τ: (a) $t < 0$, (b) $0 < t < \tau$, and (c) $t \gg \tau$ [9].

the charges on the electrodes equal to the charge in the material, and the charge on each electrode is going to depend inversely on the distance from the charge to that electrode. Here, from symmetry, the induced charges are equal. You can generalize this for an arbitrary charge distribution by saying that the induced charge on one electrode is proportional to the first moment of the embedded charge about the other electrode.

The response we measure is the change in the induced charges, which is manifested by a charge flow from one electrode to the other through the charge meter. In the case where you have some stress applied, either a temperature or a pressure distribution, you are going to have

some deformation of the sample. If the deformation produces a change in the ratio of the charge-to-electrode distances, you get a response, as in Figure 6(b), where the symmetry is broken. So the basic idea here is that in order for the response to be non-zero, you need to have an inhomogeneous deformation of the sample. So, if you have a homogeneous material and you homogeneously stress it, either by raising its temperature uniformly, or by applying a constant pressure to it, the distance ratios are not changed and you will get no response, as Sessler said earlier.

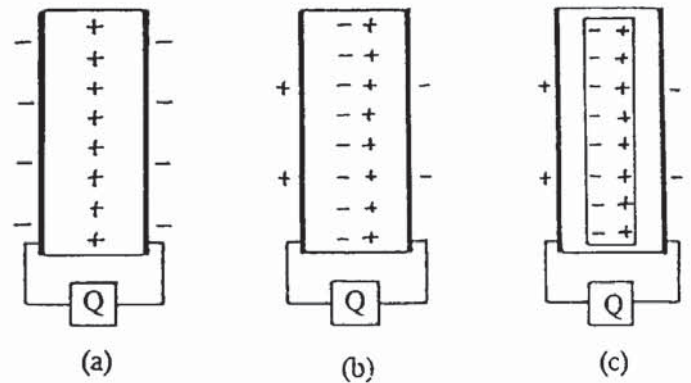(a)   (b)   (c)

Figure 7.

Theoretical models: (a) and (b), space charge layers; (c) polarization charge layers representing layer of dipoles [10].

Suppose you have two layers of charge, one positive and the other negative, as in Figure 7(b) and (c). In (b), the charge layers are separately attached to the medium and do not interact with each other. In (c), the charge layers are bound to each other more strongly than each is bound to the medium. Those charges are like the positive and the negative charges of dipoles — they are not independent of each other, but they are coupled. Usually a dipole has a strong chemical bond such as a covalent bond. And so, the charge layers in Figure 7(c) are physically different from the charge layers in (b) and in (a). And we can see how this difference comes about by simply thinking through what the response should be. Suppose you deform the material in the second case. Well, the distance ratios for the charge layers are going to change only if the deformation is inhomogeneous. You get no change in the ratios if the deformation is homogeneous. You can apply superposition in analyzing the response from the positive and the negative charges and conclude that the two charge layers in (b), like the single layer in (a), also give no response for homogeneous stress and strain.

Now, we know that we have a pyroelectric response and a piezoelectric response when the material has dipoles in it. So what is it that makes this situation different? Well, if you were to apply a homogeneous stress to the sample

shown in Figure 7(c), you have — as I said a moment ago — some constraints on the deformation. And the constraints are making the system deform inhomogeneously at the molecular level. So, if you were for example to heat the sample homogeneously, the thickness of the sample will change, but — if the covalent bond is strong enough — it could be that the distance between the dipolar charges does not change proportionally as much as the thickness. And so, you have an inhomogeneous deformation even if your stress is homogeneous. That is essentially the source of your pyroelectric or piezoelectric response.

So I think, having these models in mind, we can give a direct answer to the question of what contributes, space charge, dipoles, or both. And basically, the conclusion is that if you have a homogeneous sample, you must have an inhomogeneous stress in order for the deformation to be inhomogeneous and to get a response. And if you have a homogeneous stress, you can get a response if the sample itself has inhomogeneous properties. The properties I am talking about are the thermal-expansion coefficient, the temperature coefficient of the permittivity, and the temperature coefficient of the polarization. Now those coefficients can all be lumped together into the temperature coefficient, *i.e.* the logarithmic derivative, of the capacitance. So, essentially, if you have an inhomogeneous thermal stress you will get a response proportional to the temperature coefficient of the capacitance. Similarly, if the stress is mechanical, you will get a response proportional to the appropriate pressure coefficient of the capacitance. And, if the temperature or pressure coefficient happens not to be homogeneous then you will get a response whether or not the stress is homogeneous. Now in the case of dipoles, we said a moment ago, that you always expect an inhomogeneous deformation and hence a response. You could think of a case where there is no response: that is the case where the average polarization is zero.

Keeping in mind the simple models we have just discussed, we can now look at thermal-pulse data. The thermal-pulse method produces automatically both inhomogeneous stress at short times and homogeneous stress (uniform temperature) at long times as Figure 6 showed. Short and long are in reference to the diffusion-controlled thermal relaxation time. Figure 8 shows data [11] for nominally uniform distributions of polarization (a) and space charge (b). The data in (b) are typical of polyethylene and polyethylene-like materials that are fairly thin (10 to 100μm) and that have been charged under an applied voltage for several hours at 70°C. The main thing I want to illustrate is that the response in (b) goes to zero at long times, which is typical of nonpolar polymers and is the signature of response coming from space charge.
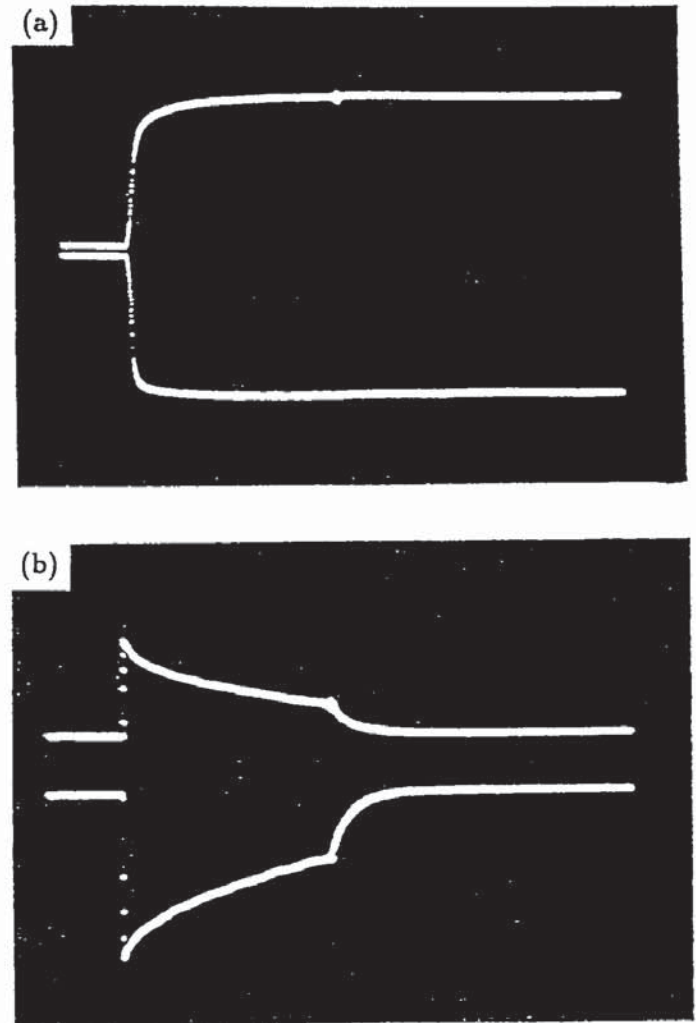

Figure 8.

Thermal pulse signals (charge *vs.* time) for: (a) nominally well poled PVDF (nearly uniform polarization distribution), and (b) polyethylene in charging steady state (nearly uniform space charge distribution). In (a) and (b), upper transients obtained with thermal pulse applied to side that was positive during poling, lower transients obtained with thermal pulse applied to opposite side. Polarity of lower transient in (a) is reversed for clarity [11].

Next look at Figure 9 which is for a nonuniformly poled copolymer of vinylidene fluoride and tetrafluoroethylene. Note that the response goes to a non-zero constant value at long times. This is the signature of response coming from polarization. The long-time response is proportional to the mean polarization. Of course, there is no guarantee that the response at short times comes entirely from polarization. In other words, a mixed contribution is admissible at short times.

The size of the response also tells us something. Thermal-pulse measurements on nonpolar polymers give peak signals that are systematically a few hundred times
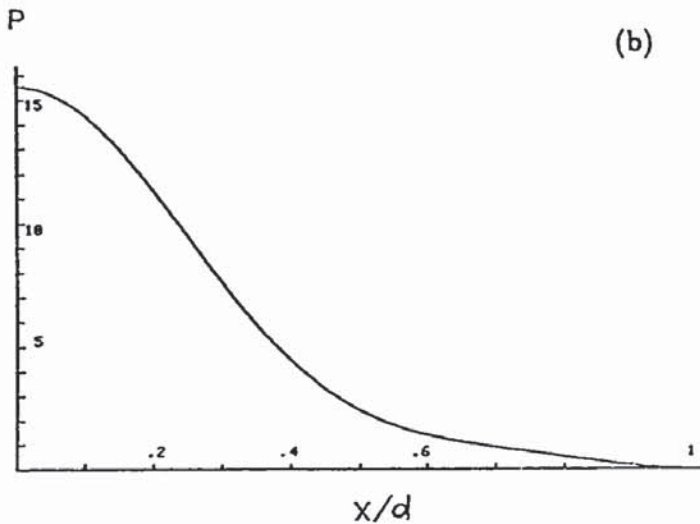
P

(b)

X/d

Figure 9.

(a) Thermal pulse signals (charge *vs.* time) and (b) polarization distribution, for inhomogeneously poled P(VDF- TFE) copolymer. In (a), upper and lower transients obtained by applying thermal pulses to sides that were positive and negative respectively, during poling. In (a), polarity of lower transient is reversed for clarity [11].

weaker than peak signals from ferroelectric polymers. Non-ferroelectric, polar polymers like polyvinyl chloride give peak signals of intermediate strength. Of course, we cannot relate the size of the response directly to the space-charge and polarization-charge densities, because we have to consider the prefactor of the response equation

$$\frac{Q(t)}{A} = \frac{\alpha_c}{d} \int P(x)T(x,t)dx, \qquad (4)$$

where $\alpha_c = (1/C)dC/dT$.

In a medium without permanent dipoles, $P = \int \rho(x)dx$ where $\rho(x)$ is the space charge distribution, and $C = \varepsilon A/d$. So, we expect contributions to $(1/C)dC/dT$ that

correspond to dimensional changes and to dielectric permittivity changes. In a medium with dipoles, C has to be rewritten as Q/V where Q includes the induction due to dipoles. Anyhow, we expect an additional term in α_c that involves $(1/P)dP/dT$ corresponding to polarization changes. From the large difference in signal strengths between nonpolar and ferroelectric samples, it would appear that the temperature coefficient of the polarization $(1/P)dP/dT$ is the dominant contribution to $(1/C)dC/dT$ in a ferroelectric. In addition, in the fully charge-compensated ferroelectric, $(1/C)dC/dT$ theoretically goes to $(1/P)dP/dT$.
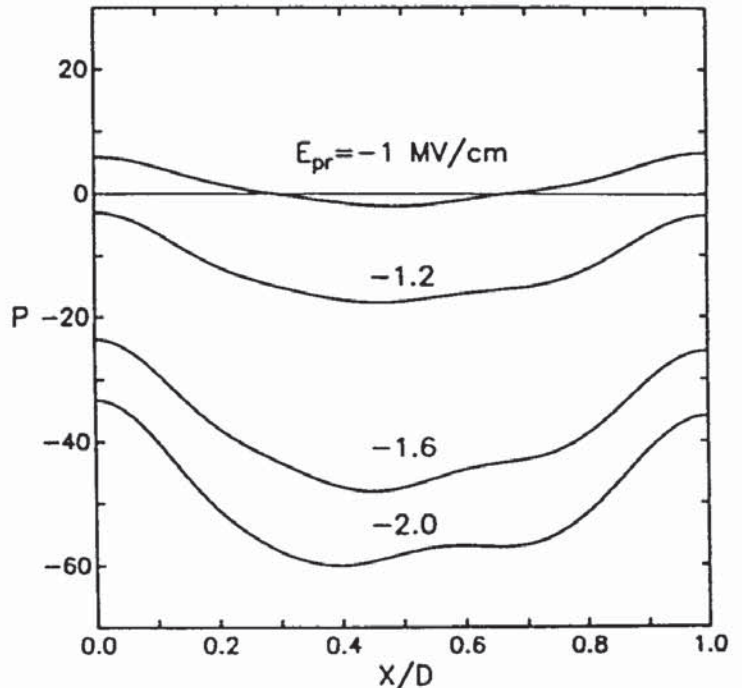

Figure 10.

Polarization distribution for PVDF poled at 2 MV/cm and subsequently reverse-poled using reverse poling fields E_{pr} indicated on Figure. Poling time at each stage was 10 min [12].

The point I want to make is that, in a medium with space charges and dipoles under inhomogeneous stress, the space-charge contribution to the response may be small compared to the dipolar contribution, but the amount of space charge is not necessarily small compared to the amount of dipolar charge. This is an important point because it explains the apparently contradictory observations of large ferroelectric signals on one hand (that indicate negligible space-charge contribution) and other observations we have made that indicate strong space-charge effects, as for example, the evolution of the polarization distribution during poling and reverse poling in polyvinylidene fluoride [12] as shown in Figure 10, and the thermally induced coercive-field increases in copolymers of vinylidene fluoride and tetrafluoroethylene, which

strongly stabilize the polarization. So, in our discussions we have to be careful about whether we are talking about the space-charge contribution to a signal or about the amount of space charge that is present.

As for the source of the space charge, internal generation should probably be considered in addition to injection. Injection is very likely in samples with poling electrodes based on the observation of an injection-limited charging steady state in many types of polyethylenes [13]. Internal generation cannot be dismissed however. In recent work [14], we have observed poling-induced color changes in the vinylidene fluoride-trifluoroethylene copolymer containing the dye dimethylaminonitrostilbene that are similar to the color changes that occur when a solution of the same dye is acidified. In this material, we believe that poling field-driven electrochemistry is implicated in the generation of H-F which dissociates and liberates mobile H^+ ions.

Finally, I want to mention briefly a new idea that I am working on that is pertinent to the topic of this discussion. Specifically, I am looking into the possibility of determining the relative contributions from dipoles and space charge in a medium containing both, by performing thermal-pulse measurements as a function of voltage applied to the sample during the measurement. Ideally, the applied voltage should change the internal field, but not permanently alter the electrical state of the sample. Mathematically, the idea appears promising. However, preliminary experiments on PVDF show time effects which complicate the comparison of theory and experiment. I hope to have more to say on this in the months to come.

In summary, space charge and polarization have different signatures. Space charge gives no response to homogeneous stress (temperature or pressure changes) unless the material is inhomogeneous. Polarization gives a response to homogeneous as well as to inhomogeneous stress because a sample with dipoles has microscopically inhomogeneous properties and deforms inhomogeneously (dipoles deform differently from the rest of the medium). Space charge and polarization have different response coefficients, the former being much smaller than the latter. The signatures are such that we can tell if we have space charge only, but we cannot tell if we have polarization only. In the mixed case, we cannot determine the relative amounts of space charge and dipolar charge from a single response measurement. Measurements under applied voltages may help resolve this question in the future.

4. EXPERIMENTS INDICATING THAT PIEZOELECTRICITY IN PVDF IS BASED ON THE COUPLING BETWEEN DIPOLES AND TRAPPED CHARGES

Opening Statement by Wolfgang Eisenmenger (Institute of Physics, University of Stuttgart, Germany)

Now what is the experimental evidence? First, we know from X-ray analysis that piezoelectricity and pyroelectricity are connected with dipole orientation. We also know that if materials such as PVDF are stretched (that means we obtain the β conformation) they become spontaneously polarized; so we have crystallites which show spontaneous polarization [15] as evidenced by X-ray diffraction. This is sufficient for saying that the material is ferroelectric. But X-ray analysis does not answer the question whether the domain or Bloch walls [16] within these crystallites — which indicate the dipolar orientation boundaries of the polymer chains — are moving freely or are pinned very strongly. So one of the questions in having permanent piezoelectricity or pyroelectricity is: By which mechanism are the domain walls (or the polarization) in the crystallites made permanent or fixed so that they cannot move?

In this respect, one of the experiments is to look what happens when you charge a sample. And we did this using the piezoelectrically generated pressure-step (PPS) method [17, 18] as shown in Figure 11. We can generate a pressure step, let it propagate into a polymer film, and detect the sample response with a wide-band oscilloscope. Since we have a pressure step and not a pulse, we directly see a signal which is proportional to the polarization or to the integral over the charge density. In the lower part of Figure 11 we find the arrangement [18] for studying how PVDF is polarized: We have a PVDF sample, an electrode in the center, a voltage supply (symbolized by a battery) — the voltage can be either continuously increased or switched on — and a polyethylene (PE) thin-film capacitor.

Figure 12 shows what is observed when we pole β-PVDF with 40 MV/m. In the first moment, when the field is switched on, we see a rectangular distribution which indicates that there are charges at the surfaces and that the material is homogeneously polarized [19] inside; and there is also a uniform distribution of the dielectric permittivity ϵ. But if we wait for 5 min we see that the
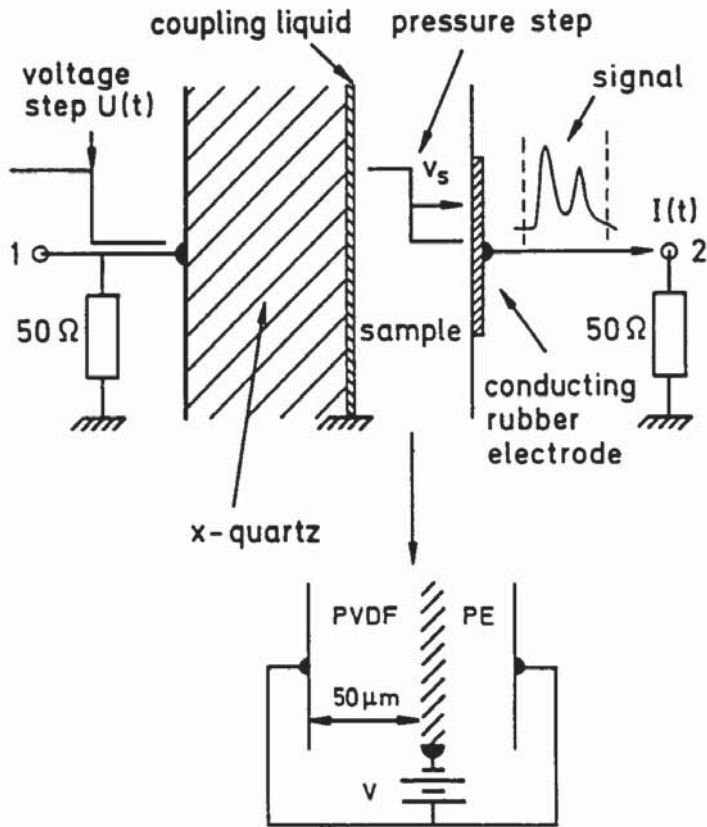
Figure 11.

Schematic representation of the experimental technique; (1) connection to voltage-pulse generator, (2) connection to wide-band preamplifier and oscilloscope [17, 18]; the lower part shows a two-layer sample used for studying the poling of PVDF.

Figure 12.

Polarization evolution in a 50 μm thick PVDF film at a field strength of 40 MV/m [19].

shape of the polarization profile rounds off, which indicates charge injection. So charges migrate from the electrodes to the center. After 30 min, the charges are already accumulating left and right of the center, and there is a buildup of polarization in the center. After 75 min, the distribution in a 50 μm thick PVDF film becomes stable. So if you continue to apply the field for hours or so the profile does not change anymore. And this means that the charges are stopped; they are first injected and then after some time, say an hour or so, at least part of the charges are trapped very efficiently.

Now the question is: What is the mechanism for this charge trapping, which did not exist before? And looking at the distributions, we came to the idea or the conclusion [18] that the charges are trapped by the polarized crystallites — maybe at the crystallite surfaces. If the charges are trapped there perhaps they also have some influence on the polarized crystallites; so maybe they have something to do with the stabilization of the polarization. One can see these internal poling zones again and again in β-PVDF if there is a sufficiently high content of β phase.
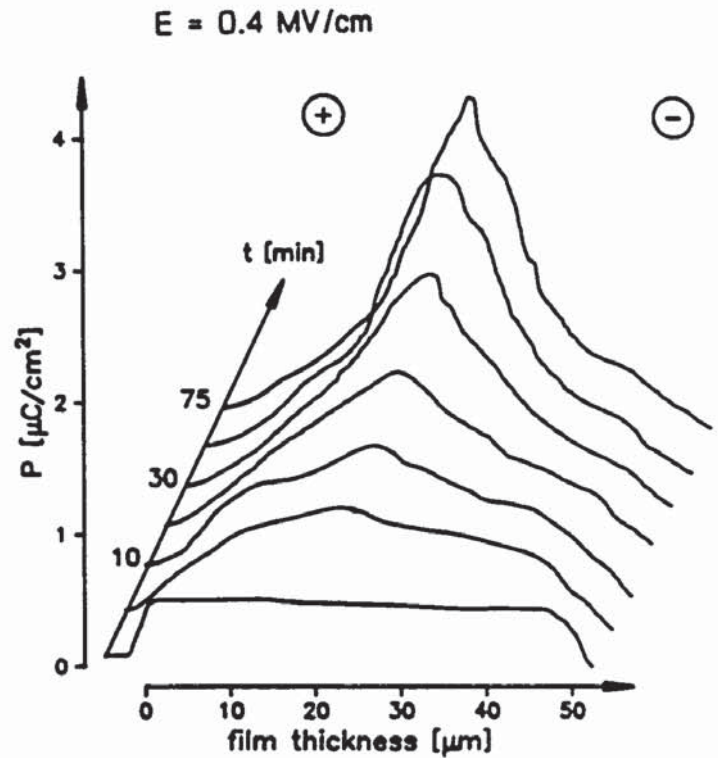
In α-PVDF, one sees the polarization [20] at the positive side; but I will not discuss the α material here.

If the field strength is increased to 80 MV/m we find almost the same behavior in the beginning, but the polarization extends further from the center as shown in Figure 13. And we still see a polarization-free boundary zone. So the charges are again trapped at the boundary of the polarization zone, but this zone has now become wider [19] because the charges were trapped earlier after injection. That is just the interpretation of what you see in Figure 13. If you now short the sample [19] you see how the charges partly move out again as depicted in Figure 14. The distribution relaxes, but the permanent polarization zone in the center remains stable.

If the dipoles are oriented by the injected and trapped charges and if this trapping is also responsible for the stabilization of the polarization, then one should be able to see this simply by the fact that you polarize and then wait for some time and look how strong the permanent polarization gets. As shown in Figure 15, we used an apparatus [21] with which we could apply a voltage to the sample via switch S1. For measuring the charge that flows into the sample, we have a capacitor C, an amplifier, and an oscilloscope. To short-circuit the sample after a certain time (e.g. if we applied a pulse), we use the
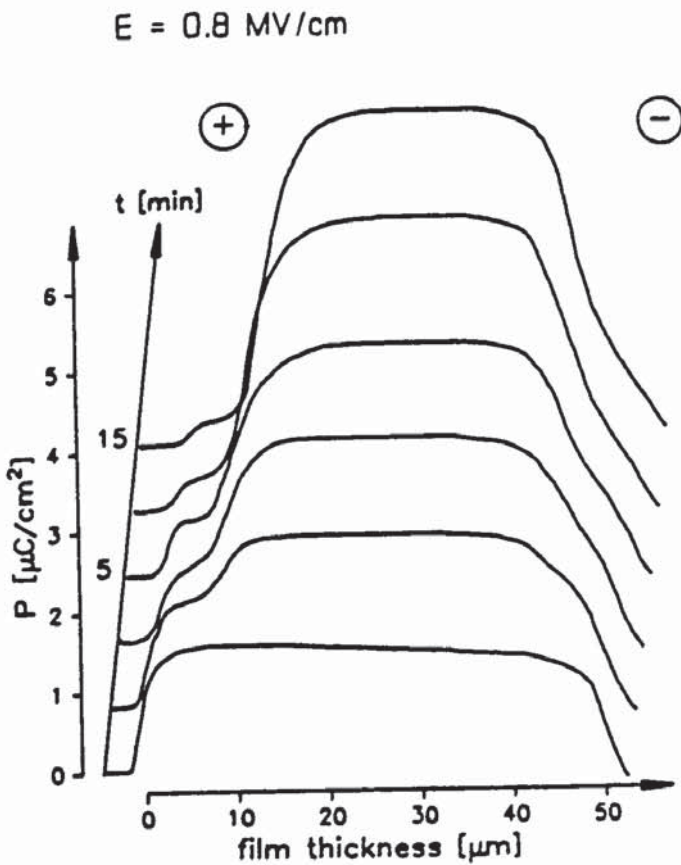
E = 0.8 MV/cm

PPS−signal   E = 0.8 MV/cm

Figure 13.

Polarization evolution in a 50 μm thick PVDF
film at a field strength of 80 MV/m [19].

Figure 14.

Relaxation of the polarization in PVDF after pol-
ing at 80 MV/m and short-circuiting [19].

switch S2. After this we look for the polarization, which
is stabilized in the sample.

In Figure 16, you see how this setup [21] basically
works. You switch on, and the charge in the sample in-
creases until you short-circuit the sample. The final po-
larization value gives you the maximum (momentary) di-
electric displacement, and after switching off you wait for
some time and measure the remanent polarization that is
left in the sample.

Now, in Figure 17, you can see the result [21] of this
experiment for PVDF: You see in the upper curve the
momentary displacement or polarization under field and
in the lower curve the permanent polarization, which is
stabilized in the sample after short-circuiting. As shown
in this double-logarithmic plot, we find a momentary po-
larization of about 3 μC/cm^2 already at 10^{-5} s, but the
permanent polarization is still way down. And you have
to wait roughly until 10^{-1} s for the permanent polariza-
tion to keep up with the momentary polarization.

This effect is also shown in Figure 18 for the polar-
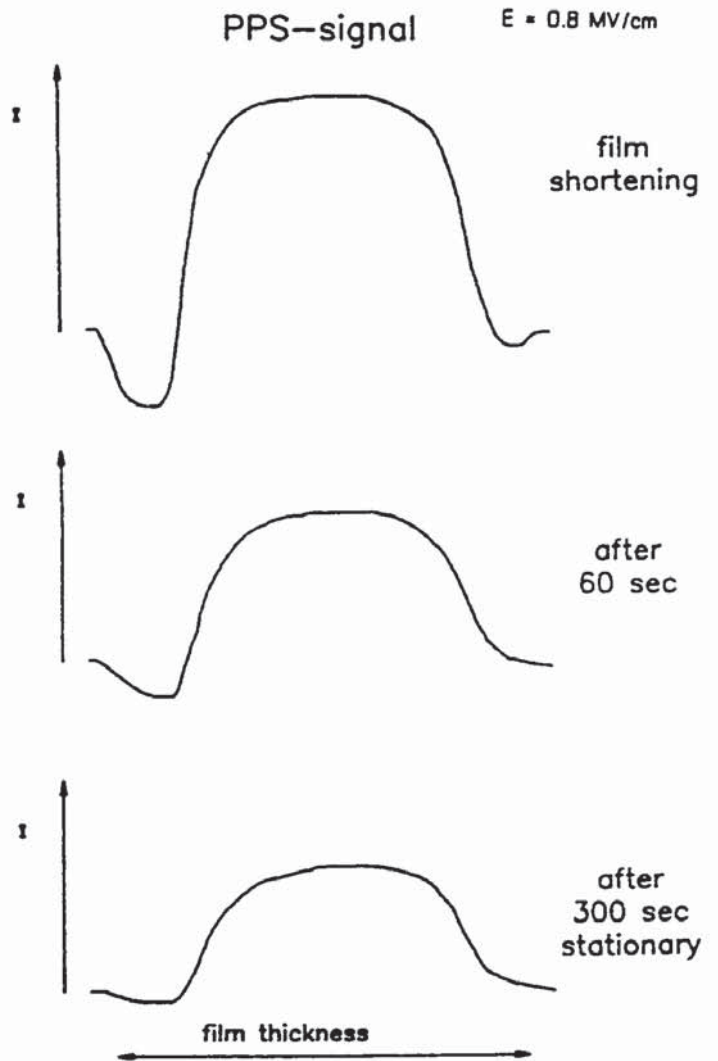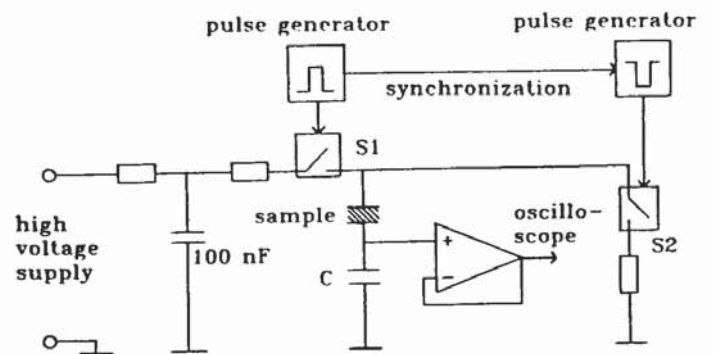ization reversal [21] in PVDF, where the polarization

Figure 15.

Block diagram of the HV pulse generator used for
poling [21].

reversal is delayed by one order of magnitude in time.
We thought the situation might by different in the 75/25
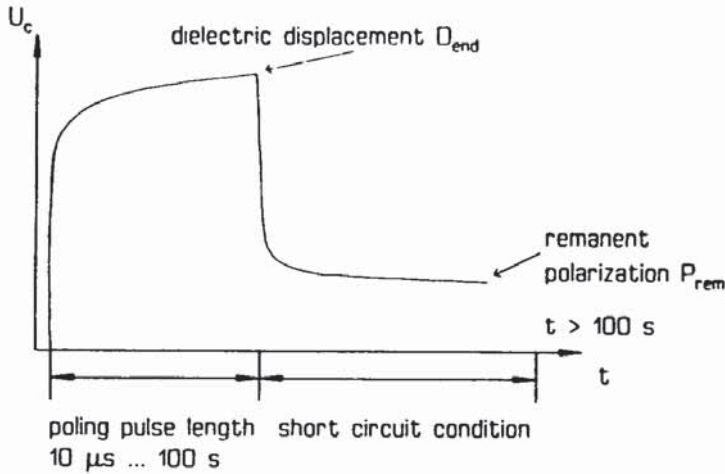P(VDF-TrFE) copolymer, which reacts faster. In Fig-

Figure 16.
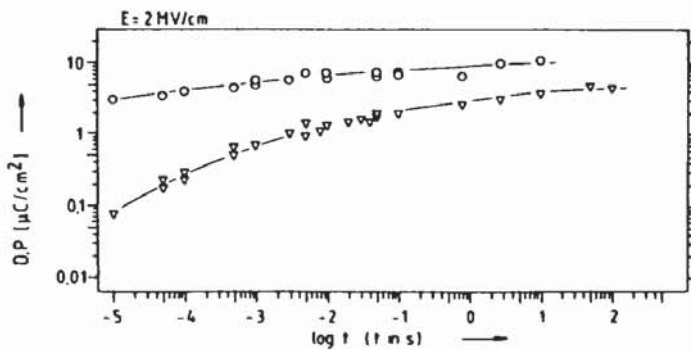Voltage at capacitor C for a typical pulse experiment [21].

Figure 17.

Development of the displacement D_{end} (○) and the remanent polarization P_{rem} (▽) for unpolarized Kureha PVDF samples at a field of 200 MV/m [21].

ures 19 and 20, you can see [22] how the copolymer behaves: There is also a delay in polarization, if you compare the upper part of Figure 19 depicting the momentary polarization and its lower part illustrating the permanent polarization. Figure 20 shows a polarization reversal that is also delayed. Here, you find a time factor of 2 to 3 for the delay if you look properly.

We think that this delay time can be — at least qualitatively — explained by the fact that the stabilizing mechanism is mediated by charges, which are trapped at the crystallite surfaces. And the picture, which can perhaps be used in these cases, involves crystallites and charges bound in Coulomb traps at the ends of the polymer chains [21] as shown in Figure 21. There are also crystallites in the center which have no charges at their surfaces, and it remains an open question whether this is possible. A safer situation [23] would be the one shown in Figure 22, where you have polymer chains and just monopolar charges at their ends in Coulomb traps. Now the question is: What
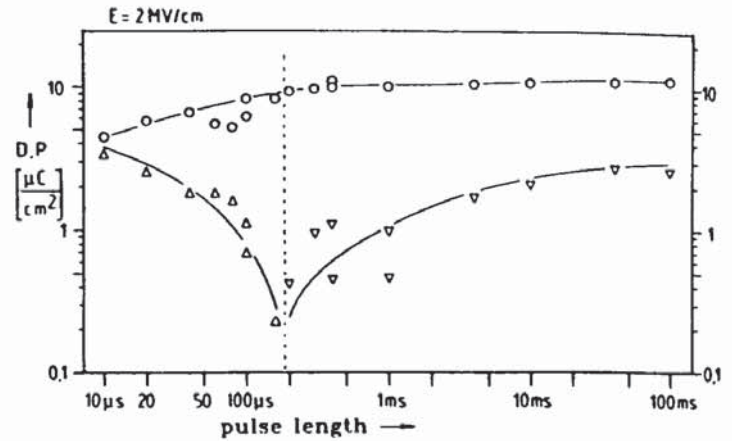

Figure 18.

Reversal of the remanent polarization in prepolarized samples at a field strength of 200 MV/m; displacement D_{end} (○), remanent polarization P_{rem} in the original (△) and the reversed (▽) directions [21].

kind of charges are these? We think they are ions [20–22] because ions are much more strongly bound in the Coulomb traps than electrons or holes.

As Sessler already mentioned, the final check on whether these charges can really be the origin of the permanent polarization is doing blocking experiments, but you must do these blocking experiments very carefully. I leave out the pulse experiments, perhaps in the discussion we can talk a little bit about pulse experiments.

At the end of my statement, I now discuss the blocking experiments, a typical result [23] of which is shown in Figure 23: In order to do these experiments carefully, we also use the switching equipment shown in Figure 15 above, but in one case we have just metal electrodes and in the other case we have electrodes with highly insulating material on their surfaces. The best material we found for this purpose was polyethyleneterephthalate (PETP) (Mylar or Hostaphan). It also turned out that in order to have reliable conditions it is necessary to use not PVDF, but the copolymer as sample material because the threshold field for polarizing the copolymer is lower. And we have to make sure that the Maxwell time constant (the dielectric relaxation time) is longer than the time during which we apply the voltage pulse. In Figure 24, you can see the equivalent circuit [23] of the setup with an insulator (PETP), the sample (PVDF or better P(VDF-TrFE) copolymer), another identical insulator (PETP), and an additional capacitor (C_m). We have to measure all these time constants very carefully and have to make sure that the field inside the sample does not decay within the time of polarization.
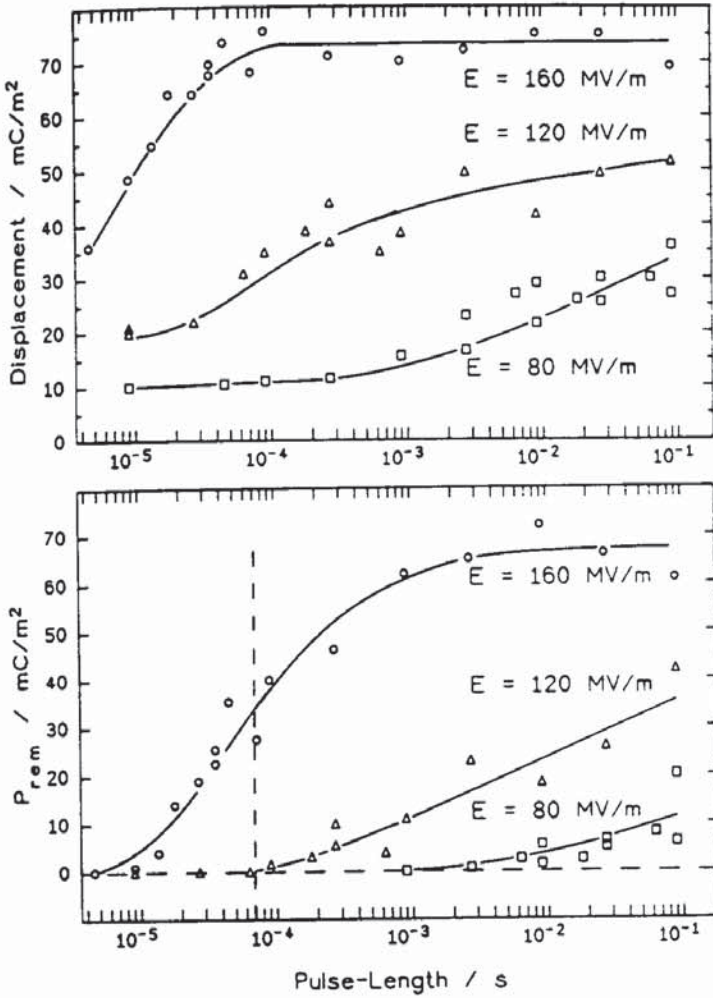
Figure 19.

Time development of the displacement under field (top) and the remanent polarization (bottom) for unpolarized 75/25 P(VDF-TrFE) copolymer at different field strengths as indicated [22].
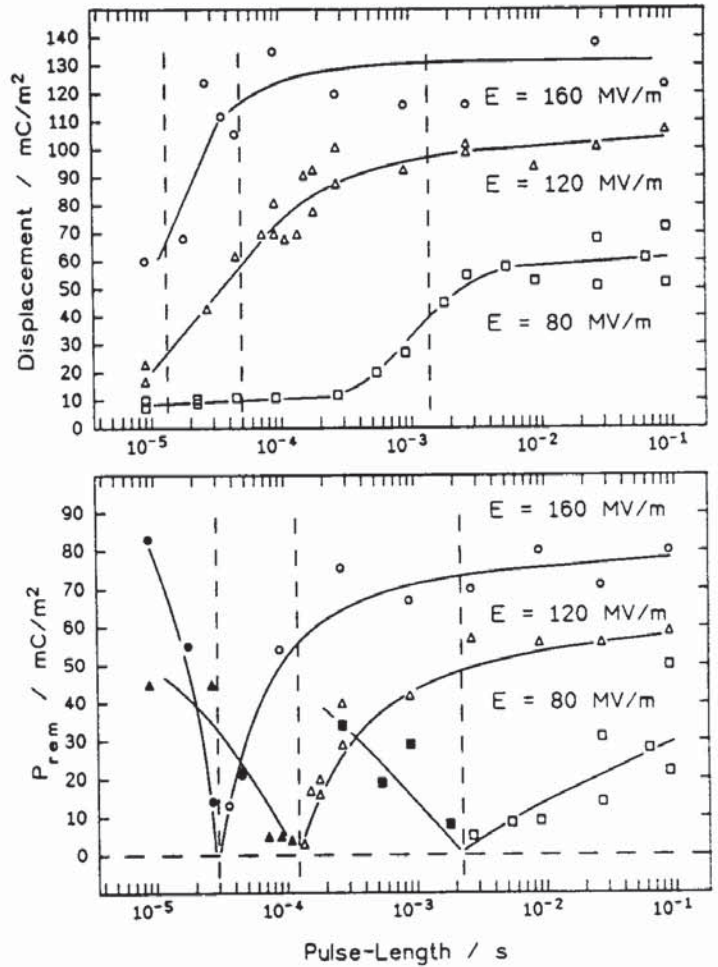

Figure 20.

Reversal of the displacement under field (top) and the remanent polarization (bottom) for prepolarized 75/25 P(VDF-TrFE) copolymer at different applied fields as indicated [22].

The result of such an experiment is shown in Figure 25, where we see polarization profiles [23] in the P(VDF-TrFE) copolymer at 135°C with blocking as well as with conducting electrodes. It is really difficult to find the proper conditions under which you can do this experiment reliably. But I think when you do it once you find convincing evidence that the permanent polarization depends on trapped charges.

To conclude, I would just like to show you how mobile the domain or Bloch walls in crystallites are. And we thought we have to try to see these domain walls. Just by chance, playing around with a scanning tunneling microscope (STM), we managed to produce a monomolecular layer [27] of the copolymer. We were quite surprised to find not only crystalline domains, but also dark stripes within them, which seem to indicate that there are domain walls in the two-dimensional system of this monomolecular layer. Even though this is not the re-

al three-dimensional system, we see (in the video shown during the Discussion) that these domain walls are really moving very fast under thermal influence and that one has to pin them in some way, in order to obtain a permanent polarization.

A single frame of the video tape [27] was selected for Figure 26. In this STM experiment, the base electrode was graphite. You see the polymer molecules which lie aligned in parallel and are oriented in the direction prescribed by the graphite substrate. The dark areas, which cut through the straight molecular chains, are interpreted as domain walls (kink aggregates) inside crystallites. At different temperatures, these dark areas move with different speed. Domain walls perpendicular to PVDF chains have been recently discussed theoretically [28].
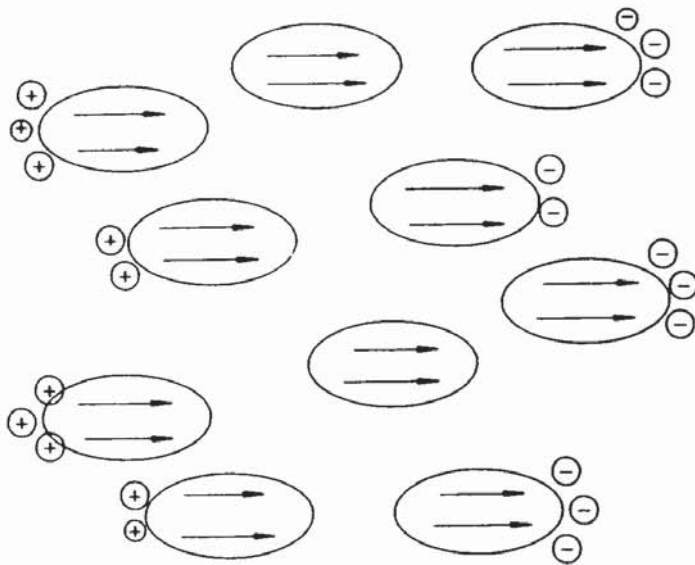
Figure 21.

Charge-trapping model: The charges are trapped at the surfaces of crystallites at the boundaries of the polarization zone and *vice versa* stabilizing the oriented crystalline dipole moments [21].
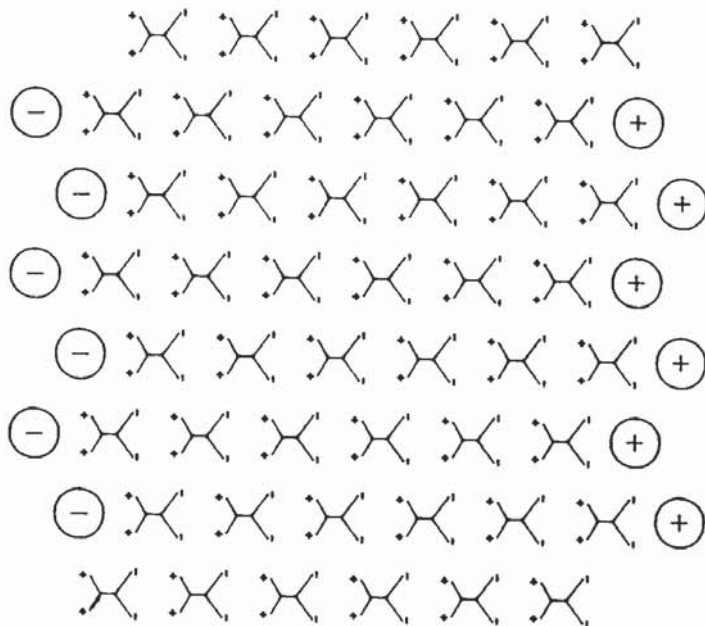

Figure 22.
Charge trapping at crystallite surface [23].

5. PIEZO AND PYROELECTRICITY ORIGINATING FROM ORIENTED DIPOLES

Opening Statement by Takeo Furukawa (The Institute of Physical and Chemical Research, Wako, Saitama,
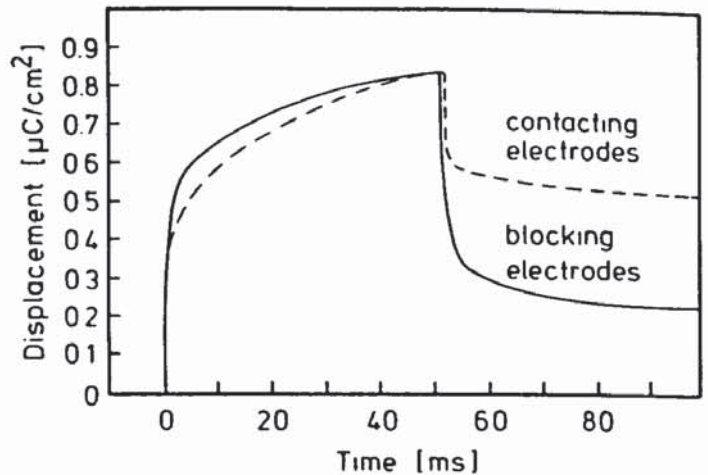

Figure 23.
Dielectric displacement in P(VDF-TrFE) annealed at 135°C after poling with (solid line) and without (dashed line) blocking electrodes [23].
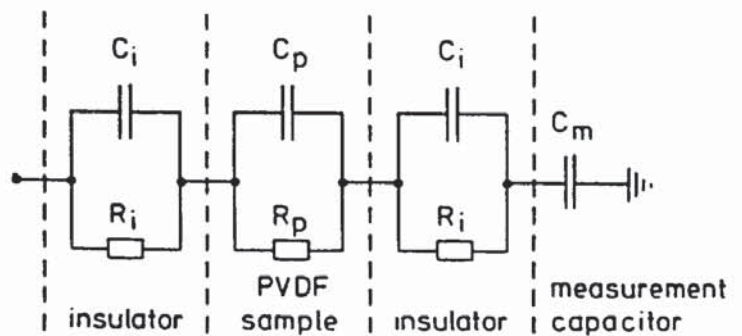

Figure 24.
Equivalent circuit of the poling setup with two blocking layers and an additional capacitor [23].

Japan)[1]

OUR work done in recent years stresses the importance of dipoles in PVDF and its copolymers. So my opinion would be that most of the behavior (maybe more than 90%) could be interpreted or understood if you think only about dipoles. The theme of this discussion is the origin of piezo and pyroelectricity which arise from the ferroelectric nature of PVDF and its copolymers. So what we did first was to show that ferroelectric polymer materials exhibit ferroelectric switching behavior and that the switching probably arises from the rotation of dipoles and is accomplished by the rotation of chain molecules. This behavior is just along the line of usual ferroelectrics, and it was shown that the switching time τ_s of the dipoles depends upon the applied field E according to the so-called exponential law ($\tau_s = \tau_{s0} \exp(E_a/E)$).

We also observe that the switching part of the polarization, which is the remanent polarization P_r, can
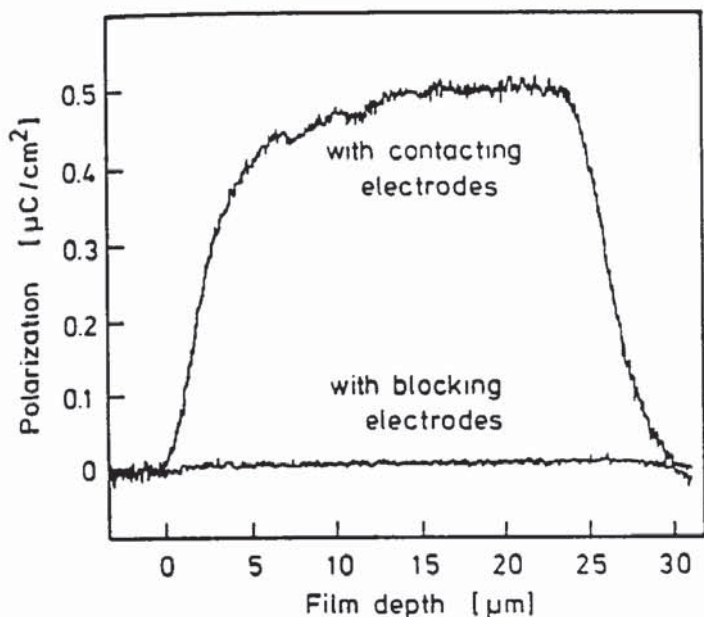
Figure 25.

Permanent-polarization profile after poling of P(VDF-TrFE) annealed at 135°C after poling with and without blocking electrodes [23].

Figure 26.

Single frame of an STM video depicting a P(VDF-TrFE) copolymer monolayer on graphite; the dark zones, which show thermal movement, are interpreted as domain walls (kink aggregates) [27].

be written as the product of the crystallinity χ_c and the spontaneous polarization P_s of the crystalline region ($P_r = \chi_c P_s$); and we can show that the spontaneous polarization of the crystalline region is just the simple sum of molecular dipoles ($P_s = \sum \mu_t$). We constantly find

this relation observed. Once we show that the switching behavior mostly arises from dipoles, then if we can show that this polarization is strongly related to its piezo and pyroelectricity we could say that piezo and pyroelectricity arise from oriented dipoles.

Also, according to conventional phenomenology, there is a quantitative relationship between piezoelectricity and strain $x = \kappa P^2$ in the sample, which is in turn related to the square of the polarization P via the electrostriction coefficient κ. This equation leads to an expression of the piezoelectric coefficient g as the product of the electrostriction coefficient κ and the remanent polarization P_r (given by the switching of dipoles in the sample under an applied field) ($g = 2\kappa P_r$). Near the end of my statement, I will also talk about space-charge effects.

First I show some of our data published several years ago. In Figure 27, we find the typical hysteresis behavior of PVDF and its copolymer. PVDF has quite a low crystallinity, something like 50%; so it exhibits a rounded hysteresis loop. But if you use copolymer with quite high crystallinity (80 or 90%) and apply fields > 100 MV/m, the square-shaped hysteresis loops become independent of field. This means that all dipoles in the crystalline regions switch their directions either from positive to negative or from negative to positive.

If we make time-domain measurements we see complete reversal of the polarization very clearly. The curves of Figure 28 show the time dependence of the polarization or the electric displacement and its derivative during application of a square electric field. If we change the field strength we can see that the only difference is the switching time and that the change in polarization is nearly independent of the applied field. After the polarization reversal is completed there is no change in the electric displacement. But if you apply the field longer (e.g. for 100 or 1000 s) then you see some increase of the electric displacement due to induced charges or conductivity changes. So the time behavior mostly arises from the orientation of dipoles. These results may confirm that dipoles play a most important role in ferroelectric switching phenomena in polymers.

As you pole by applying an electric field you have remanent polarization; and as shown in Figure 29, the piezoelectric activity is completely proportional to the remanent polarization. As the remanent polarization arises from dipole orientation, piezoelectricity also mostly arises from oriented dipoles. We have obtained similar data for pyroelectric and other coefficients; an example is found in Figure 30.

POLYVINYLIDENE FLUORIDE
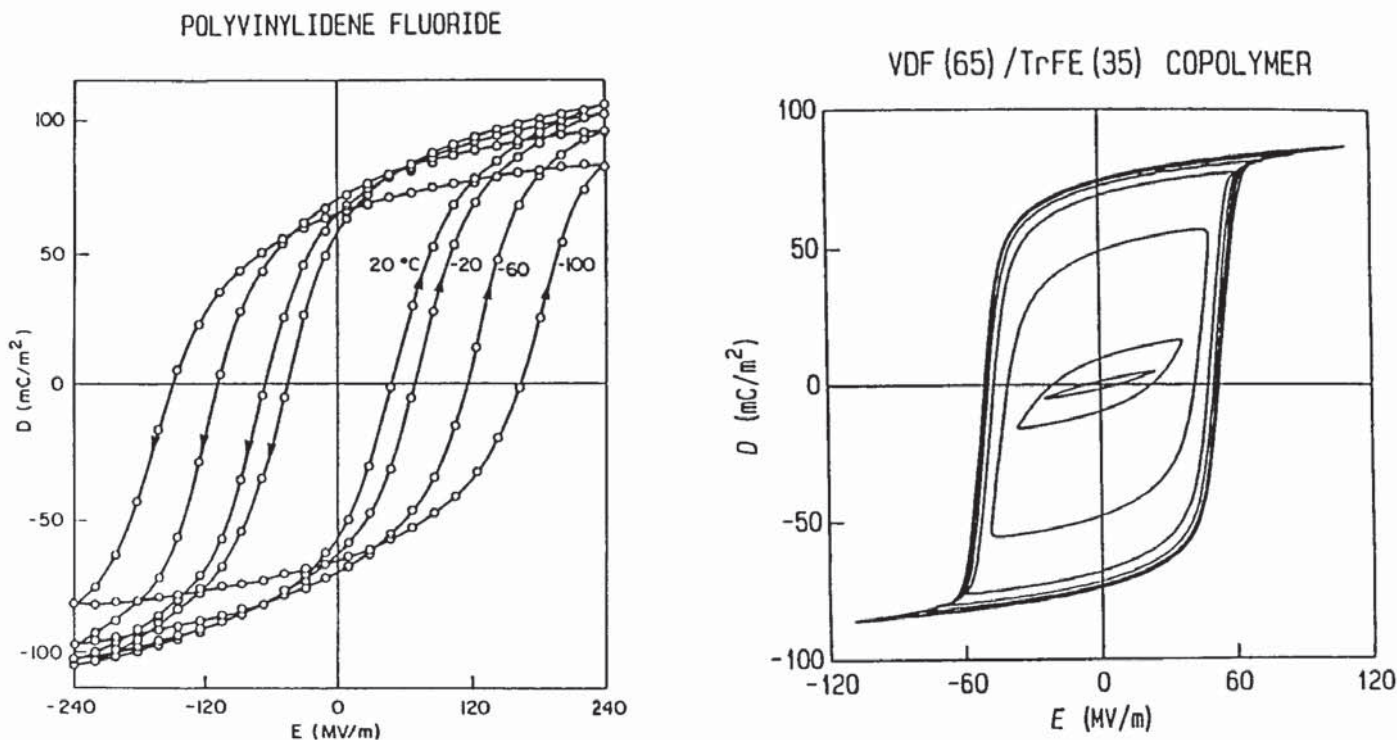
VDF (65) /TrFE (35) COPOLYMER

Figure 27.

$D - E$ hysteresis loops for PVDF (left) and 65/35 P(VDF-TrFE) copolymer (right) after electrical excitation [29].

Figure 31 shows electron micrographs taken by Kimura and Ohigashi in Japan [32]. As you anneal copolymer samples very well, you get very high crystallinity. In Figure 31, you see a surface and a side view of a 60 μm thick film, and in the side view you find very well grown lamellae; the lattice seems to be very well aligned perpendicular to the film surface. In this situation we can speculate that a complete alignment of dipoles could have taken place. Here the crystallinity could be as high as 90%, and we can expect very good alignment of the dipoles.

Actually there exists space charge in the sample, and space charge could affect some of the behavior especially if the sample has low crystallinity or if you are interested in the behavior at long times or lower electric fields. As Eisenmenger told us, space charges could reduce or compensate the internal field. If we have a structure with confined crystallites there is a very strong internal field inside the sample, and this field could be compensated by space charges. The internal electric field could be $\sim$ 1 GV/m and should be compensated somehow.

Also redistribution of space charge takes place over quite a long time; its time constant could be calculated from the ratio of the permittivity ϵ and the conductivity σ and is usually $\sim$ 100 s. So if you look at the very-short-time high-field behavior most of it must be attributed to dipoles.

Suppose there is a severe discontinuity in the electric field between the crystalline and the amorphous region, which has no remanent polarization, then the field in the amorphous region becomes very high. The electric field in the crystalline region is given by the product of the spontaneous polarization and the permittivity in the crystalline region and the volume ratio of crystalline and amorphous phase. If the amorphous region is quite small (like 1 or 10% of the volume) the internal field in the crystalline region will be decreased, and even though the amorphous region is very small, it is very important for the alignment of the dipoles in one direction. The electric displacement in the amorphous region is determined by the spontaneous polarization and the amorphous-to-crystalline volume ratio. If the amorphous region is very small then all dipoles should be aligned in one direction, the polarization in the crystalline region is not affected, and the total polarization should be close to the crystalline polarization. Maybe I am stressing this too much, but I would like to say that dipoles are most important in this system.

6. FERROELECTRIC POLARIZATION IN CORONA-CHARGED SAMPLES

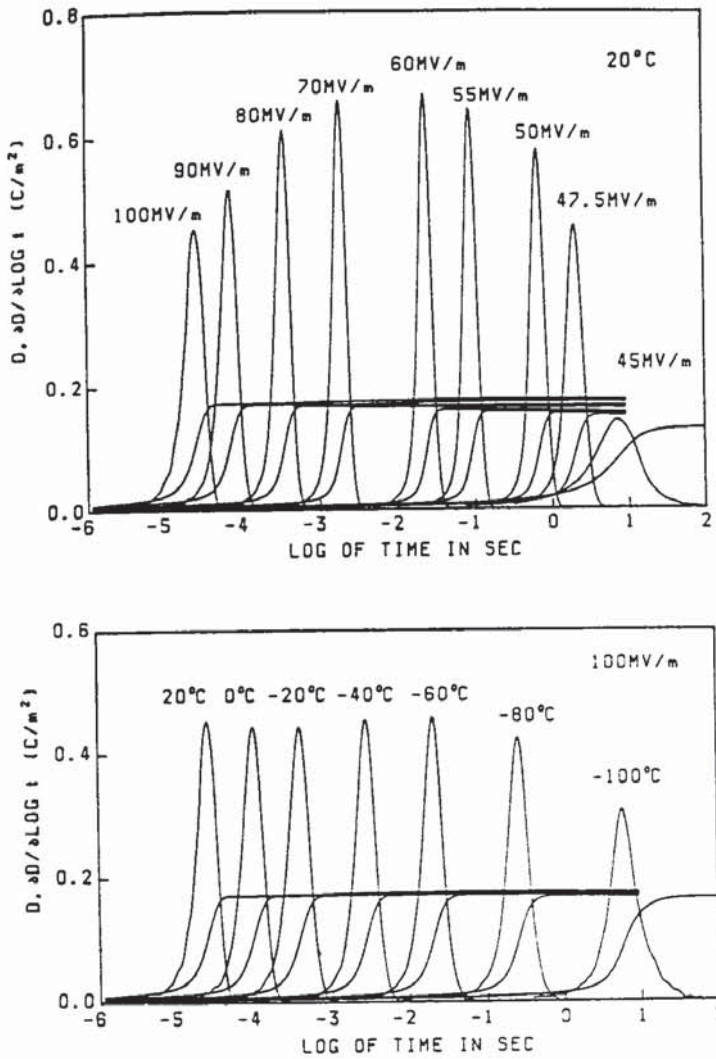*Opening Statement by José A. Giacometti (Institute*

Figure 28.

Switching characteristics of 65/35 P(VDF-TrFE) copolymer at different fields (top) and temperatures (bottom) [30].

Figure 29.

Apparent piezoelectric constants e_{31}^a of several ferroelectric polymers as a function of the remanent polarization P_r [31].
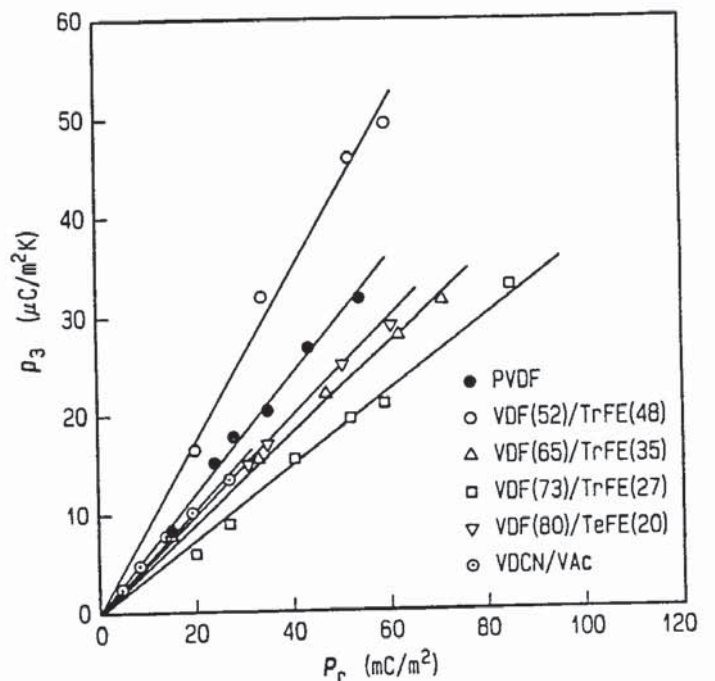
Figure 30.

Pyroelectric constants p_3 of several ferroelectric polymers as a function of the remanent polarization P_r [31].

of Physics and Chemistry, University of Sao Paulo, Sao Carlos, Sao Paulo, Brazil)

IN this statement, I shall try to give some results and discuss some ideas about using corona charging with a constant current. The main idea was to charge samples with a constant current using the corona triode and to measure the surface-potential buildup in these samples. We will see that the potential-buildup curves could be explained if we assume phenomenological models that take into account the ferroelectric polarization. In order to show this, we use several different techniques: Constant-current corona charging, piezoelectric-coefficient measurements, and polarization-distribution measurements with the thermal-pulse method.

First we show in Figure 32 what happens in a ferroelectric sample that has no conductivity and no inhomo-geneities; and we assume that we have a unique coercive field in the sample. At the beginning of charging,
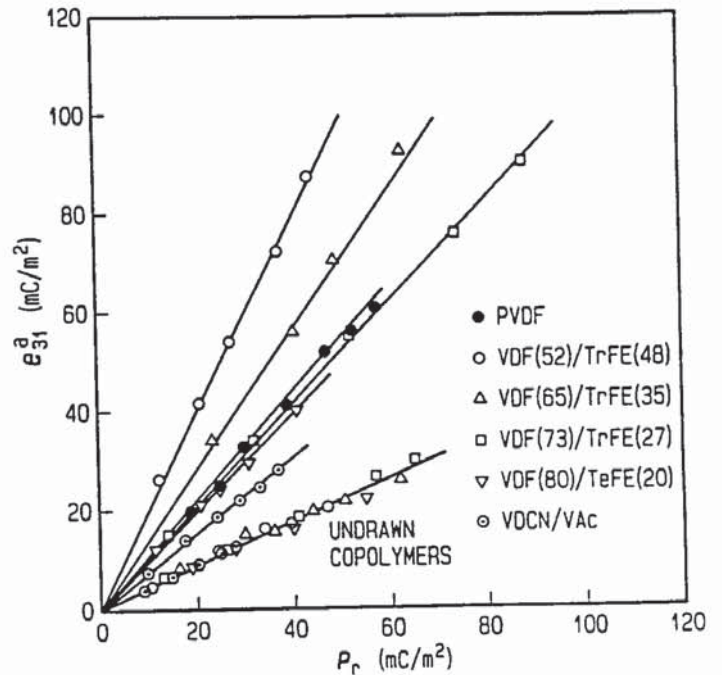
Figure 31.

SEM images of the surface (top) and a cross section (bottom) of a 60 μm thick P(VDF-TrFE) film [32].
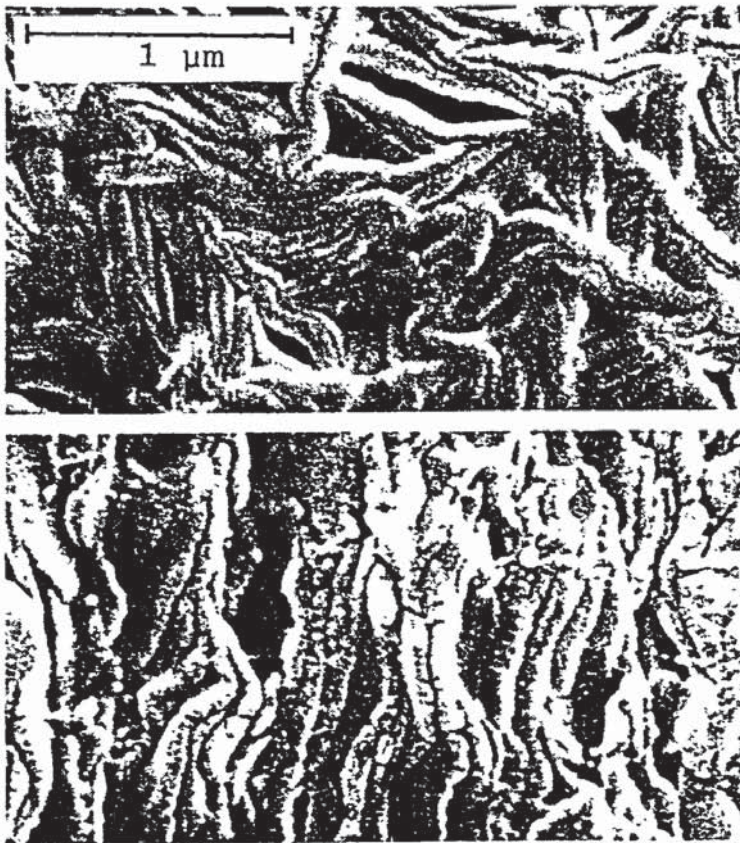
you have only a displacement current; so the potential increases at a constant rate until we reach the coercive field. Then the dipoles start to orient inside the sample thus neutralizing the charges delivered by the corona ions. When this process is completed the potential will increase again at a constant rate. And now we look what happens with the polarization: If we started with a sample that was previously poled with a negative corona then we start to charge the sample positively. You see that if the corona-deposited charge is neutralized by dipole rotation the polarization must increase also at a constant rate with time. And if the piezoelectric coefficient is proportional to the polarization we must see the same behavior as a function of time. The x axes in Figure 32 denote the time, but also the charge delivered to the sample, since the charging current is constant. These are the results that we expect from our measurements.

Figure 33(a) shows potential-buildup curves obtained for the P(VDF-TrFE) copolymer at different charging currents. For lower currents we find a larger plateau than for higher currents. If we normalize these curves by plotting charge instead of time we get a master curve as shown in Figure 33(b). The behavior of PVDF samples is very
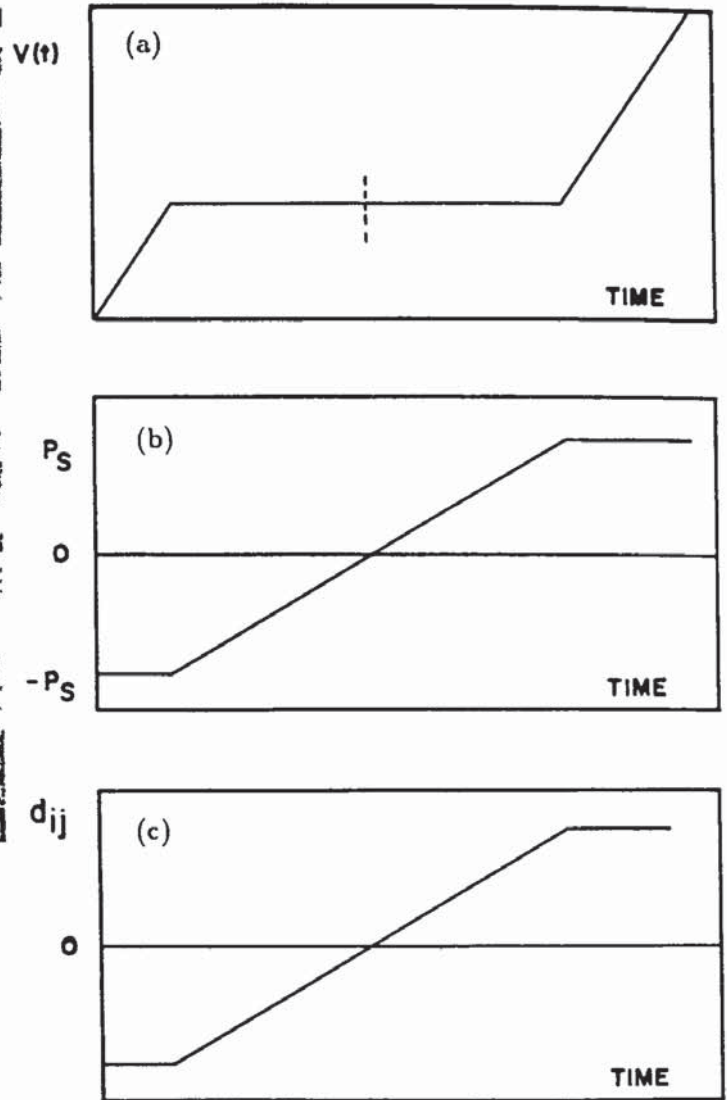

Figure 32.

Constant-current charging of an ideal ferroelectric sample (no conductivity and a unique coercive field): (a) Surface-potential buildup showing a plateau (top), (b) ferroelectric polarization during charging (center), and (c) piezoelectric coefficient during charging (bottom).

similar; the only difference is that the plateau is not so well defined with PVDF as with the copolymer.

In Figure 34 you see the thermal-pulse responses (not the polarization distributions) of PVDF samples. In the beginning the sample was poled with a positive corona. Then we start to pole our sample with a negative corona. If the poling process is stopped at different times for identical samples we see in Figure 35 that the thermal-pulse response decreases at first until it becomes almost zero and then changes into a negative signal corresponding to a negative polarization. The same behavior is found for the piezoelectric coefficient as shown in Figure 36.
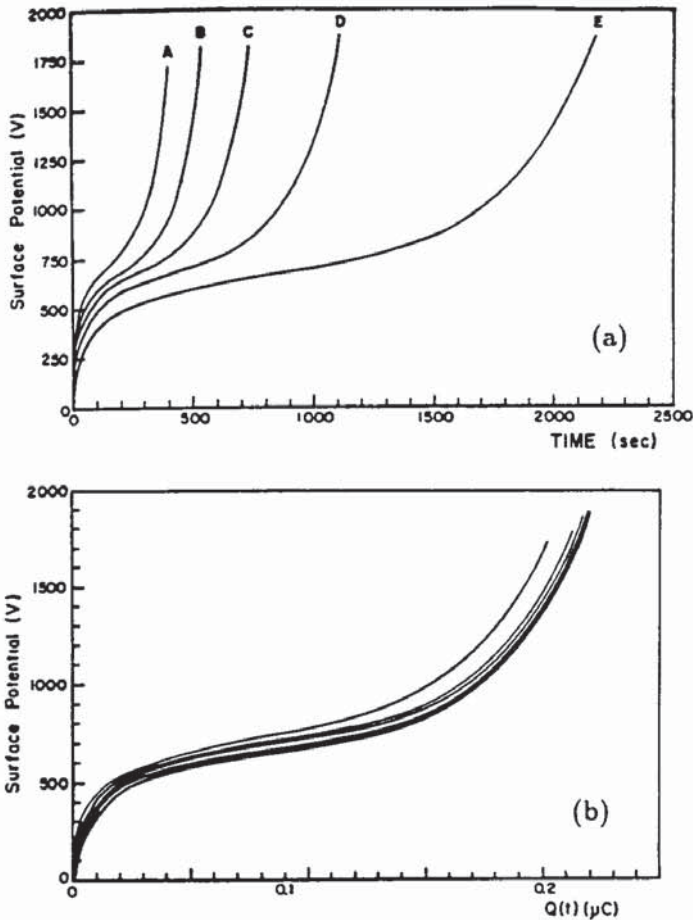
Figure 33.

(a) Surface-potential buildup of a $12.5\mu m$ thick 60/30 P(VDF-TrFE) copolymer sample for charging currents I_0 of (A) 50 nA, (B) 40 nA, (C) 30 nA, (D) 20 nA, and (E) 10 nA; (b) the same curves plotted as a function of the total charge $Q(t) = I_0 t$ deposited on the sample.
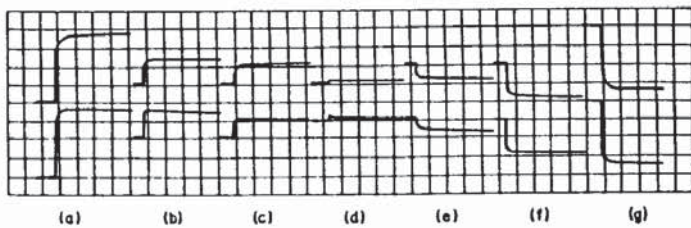

Figure 34.

Thermal-pulse signals obtained during the charging process and the reversal of the ferroelectric polarization: (a) prior to charging, (b)–(g) during short interruptions of the charging process; curve (d) corresponds to a charging time in the middle of the plateau region in Figure 33(a).

We can explain the potential buildup shown in Figure 33 on the basis of a very simple model. The polarization is assumed to be fast because the time scale of the experiment is very large compared to the switching times
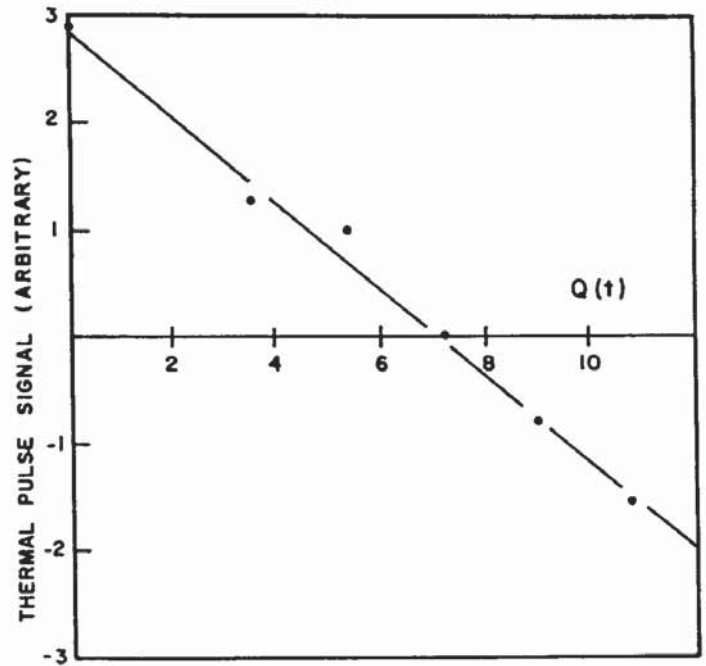
Figure 35.

Step height of the thermal-pulse signals of Figure 34 plotted as a function of the charge $Q(t)$ deposited on the sample.
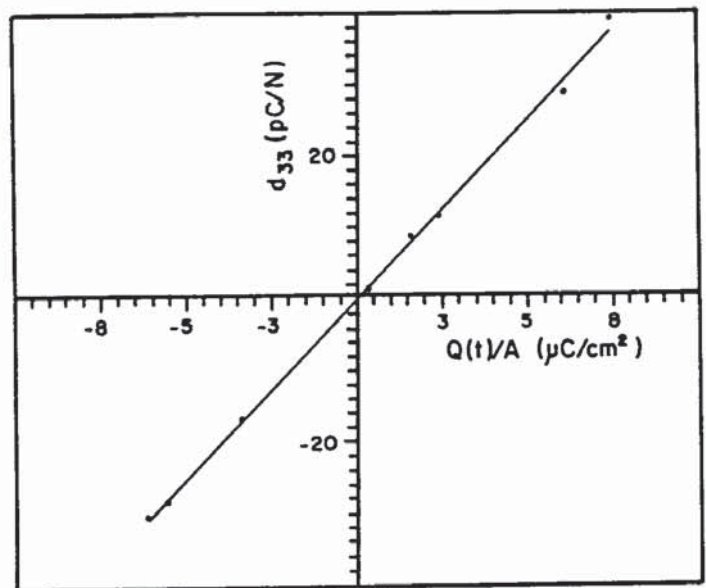
Figure 36.

Dependence of the piezoelectric coefficient d_{33} on the charge per unit area $Q(t)/A$, where A is the sample area, during poling with a constant-current corona triode; the measurements were taken during interruptions of the charging process.

obtained by Furukawa. So we assume that the polarization rotation happens instantaneously. Then we put the polarization into the equation for the total current tak-

ing into account space-charge injection and obtain more or less good agreement with the experimentally observed potential buildup.

In conclusion it can be stated that

1. the potential-buildup curves show a shape, which seems to be determined by ferroelectric dipole switching,

2. the theoretical analysis of the experimental curves with models including ferroelectric polarization give a qualitatively correct description of the experimental results,

3. the observed piezoelectric activity and the polarization reversal obtained from thermal-pulse measurements are in qualitative agreement with the model, and

4. pure space-charge models cannot explain the experimental results; the space charge only decreases the polarization in the sample bulk.

In our experiments, it is clear that the space charge is only decreasing the electric field at the injecting surface of the sample. Of course, this was shown by several groups using corona poling and coming to the same conclusions.

7. DISCUSSION

Gerhard M. Sessler: I think there is general agreement here that dipoles and space charge have something to do with the piezoelectricity, but the amount to which space charge really is involved is under debate. The most diverse statements were made by Eisenmenger on the one side and perhaps Furukawa and Giacometti on the other side. The importance of the space charge in these models is really very different. I think we on the panel have talked enough, the floor is now open for discussion.

Roberto M. Faria (Institute of Physics and Chemistry, University of Sao Paulo, Sao Carlos, Sao Paulo, Brazil): I would like to add some data on space charge (Figure 37). I have carried out thermally stimulated discharge (TSD) measurements on PVDF samples under a small electric field of ~ 10 MV/m and I observed a TSD current peak at $\sim 80^{\circ}$C in a first measurement (curve I). In a second measurement under the same conditions (curve II), the peak disappeared completely. But in a further measurement with the electric field inverted, I observed another current peak shifted to higher temperature (dashed curve). If I repeated the experiment again and again, each time inverting the field, I always observed the same peak. I realized that this peak is connected with space charge that is not removed from the sample, but rather had remained trapped on the surface. In the second TSD measurement, I did obviously not observe the same peak because the charges were already in one of the electrodes. But with
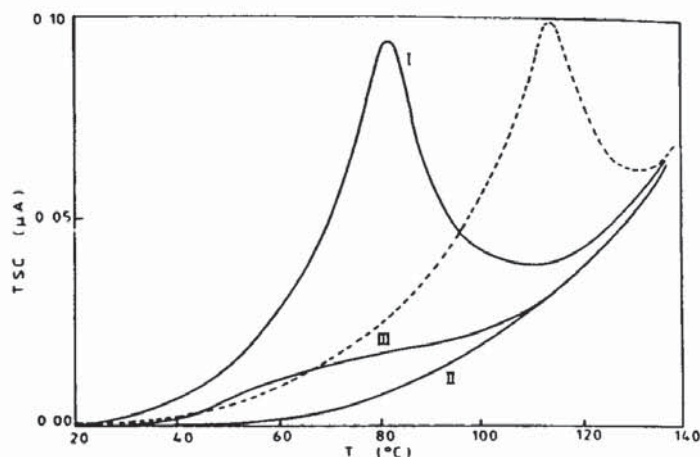
Figure 37.

TSC thermograms of a 12 μm thick PVDF sample under an applied electric field of $E = 10$ MV/m for (I) a fresh sample, (II) the 2nd TSC run after the sample had been cooled under the applied field, and (III) the 3rd TSC run after the sample had been cooled under short circuit; the 4th TSC run with an inverted electric field (dashed curve) is also shown.

an inverted field, the charges returned to the bulk of the material stopping at the other surface. Why did I suspect that this phenomenon is caused by space charge? Because when I irradiated the sample with X-rays this TSD peak increased strongly. It means that the irradiation generated some charges, which are also trapped in the bulk of the material, and so the amount of charge in the TSD measurement could increase.

And I have another series of not yet completed measurements which indicate that moisture is apparently an important parameter for the space charge. We find that the amount of charge increases if the moisture of the ambient in the experiment is higher and it decreases if the moisture is very low. Koizumi made measurements on copolymer samples with different amounts of impurity ions and found a strange peak in the polarization current. I observed the same effect. Also I observed that if you dry the sample, the peak disappears completely. So I think that it is very interesting to discuss the origin of the space charge in PVDF.

Wolfgang Eisenmenger: I would like to say something about the influence of moisture and other substances in PVDF and other materials. We have noticed that there is an influence of moisture in PVDF, but mostly on the conductivity as I remember. And there is a very strong influence on the conductivity and on the permanence of the polarization if you have some solvents such as acetone in the sample. If it is not very strongly polarized you can destroy the polarization in PVDF by just exposing it to

acetone. Only if it is very strongly polarized this is not possible. These results will be published soon. So one has to be very careful at least with ionic solvents. The fact that water penetrates to a certain (but small) extent into PVDF is correct. So there is an influence (on conductivity), but so far, at least in our experiments, the qualitative behavior of charges going into the material is not influenced by moisture; the behavior in PVDF and its copolymers is more or less the same. But there are other polymers where the charge-injection behavior is tremendously influenced by exposure to moisture.

Takeo Furukawa: I would like to make another point and explain the behavior of the Curie-transition temperature. There are no big arguments about the Curie temperature which — as you know — depends strongly upon crystallite size and defects. In certain pure copolymer samples we find the Curie point at 70°C; and if we pole we get very sharp X-ray diffraction peaks, and the Curie temperature is 20°C higher. Crystallinity and Curie point strongly depend on defects and ordering in the sample.

Gerhard M. Sessler: Here, I would particularly like to encourage comments that relate to the heart of the matter, namely the question: Are space charges really essential for holding the polarization in place or are they just something that is in there to compensate the field?

Sergei N. Fedosov (Department of Physics, Odessa Technological Institute, Odessa, Ukraine): We measured the pyroelectricity of unpolarized and polarized PVDF films with a dynamic method and got results like the ones shown in Figure 38. So you can see the changes of the pyroelectric coefficient with cyclic increase and decrease of temperature and increasing final temperature of the cycle. We found that in general the pyroelectric coefficient decreased with increasing temperature. The experiments shown in Figure 39 were carried out on unpoled samples at different temperatures with a bias voltage changing from +300 to −300V. I think that these experimental results can be taken as a proof of the correlation between space charge and internal polarization. So I was impressed especially by the video tape presented by Eisenmenger where we could see the moving boundaries of poled zones. And I want to add that if samples are not poled completely (*e.g.* under a field of only 40 MV/m) one can see waves of polarization moving from one electrode to the other. This can be considered as a proof of the importance of the coupling between space charge and polarization. We also observed that if PVDF samples were poled the conductivity as measured by means of the potential decay decreased tremendously, presumably because of deep trapping of charge carriers at the boundaries of the polarized crystallites.
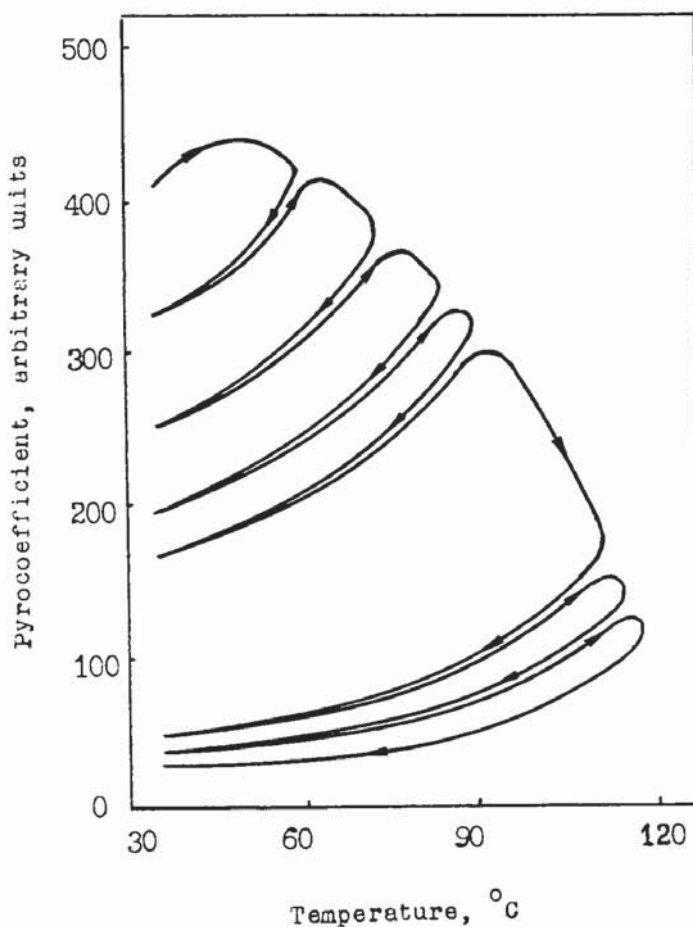

Figure 38.

Temperature dependence of the pyroelectric coefficient in PVDF poled at 100°C under an electric field of 130 MV/m [33].

Ludwig Brehmer (Thin Organic Films Research Group at the University of Potsdam, Germany): I think it is not possible to explain the piezoelectricity and other electrical properties of polymers without taking into consideration both the dipole processes and the charge-carrier transport processes. For the explanation of the long-term stability of the pyroelectricity it is necessary to take into account the rearrangement of the space charges. And I think it is possible in principle to improve the long-term stability of the pyroelectricity by including special deep traps in order to catch the charge carriers. Also I want to draw your attention to my proposal to improve the long-term stability of partially crystalline samples by introducing deep levels into the sample (of course this is not so simple) in order to trap the charge carriers.

Aimé S. DeReggi: I have results I must show that relate to the stabilization of polarization. These are for a layered sample prepared by G. T. Davis at NIST with P(VDF-TrFE) copolymers of different compositions to get different Curie temperatures. The sample consists of one layer of 80% VDF + 20% TrFE material with a Curie
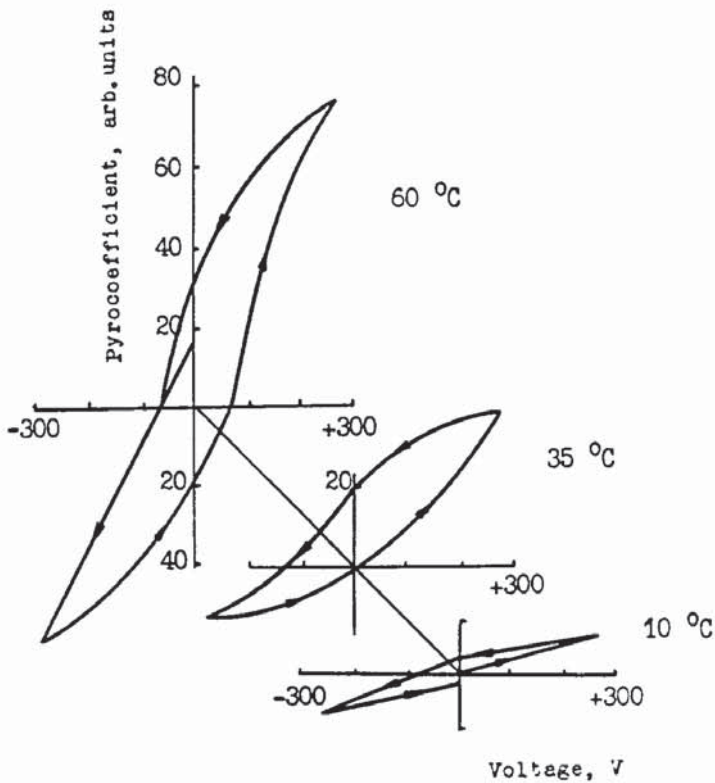
Figure 39.

Hysteresis loops of the pyroelectricity in unpoled
PVDF at three different temperatures.

temperature > 100˚C and another layer of 60% VDF +
40% TrFE material with a Curie temperature < 100˚C.
Having made the bilayer, we first polarize it in one di-
rection with an applied field, and you see in Figure 40(a)
that a thermal pulse from one side or the other gives
roughly unit steps (with some differences initially). So,
this means that the entire system is now polarized in one
direction.

Now suppose we heat the sample to about 100°C (in
between the two Curie transitions). The side which has
the lower Curie temperature becomes depolarized, where-
as the other side is annealed below its Curie temperature,
which promotes stabilization of the polarization. We see
this in Figure 40(b). When the thermal pulse is applied
to the high-T_C side, we see a step response immediately
followed by decay to half the initial value, showing the
polarization to be strong on the high-T_C side; but the
low-T_c side has in fact a near-zero polarization as shown
by the initial zero response when the thermal pulse is
applied to the low-T_C side.

What is really remarkable is shown in Figure 40(c).
When you apply a reverse field, you can reverse pole the
unpoled side, as noted by the reversed (negative) polar-
ization as compared to the initial, but the originally poled
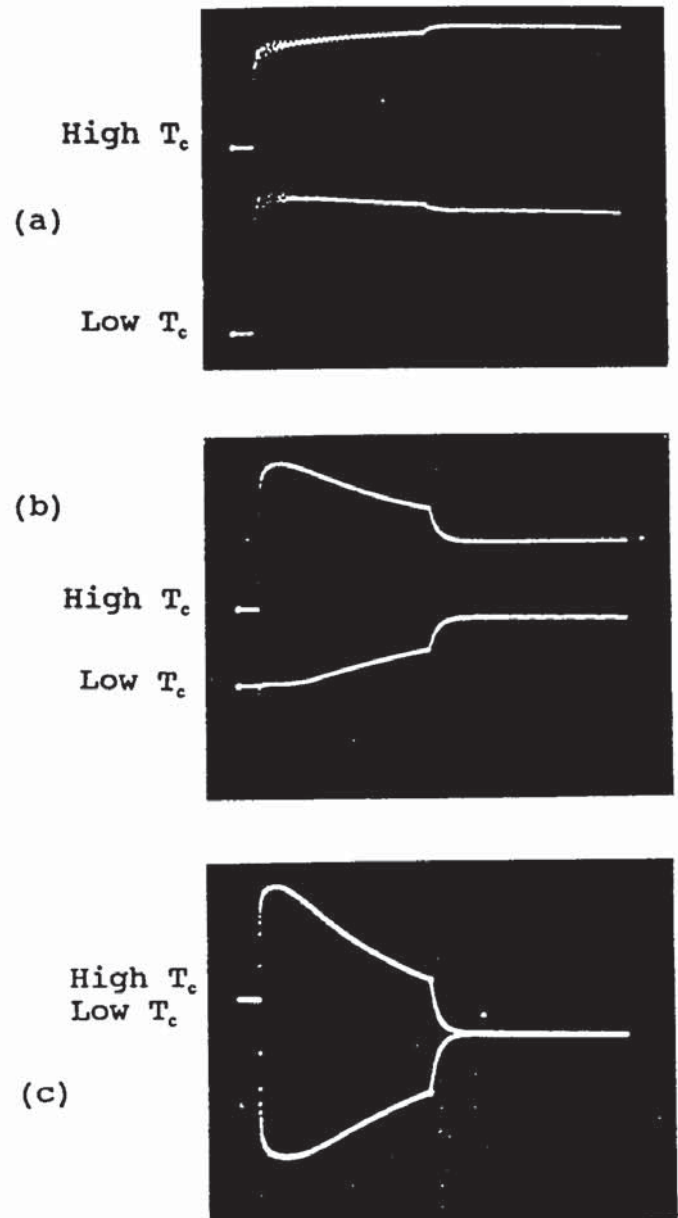
Figure 40.

Thermal pulse signals (charge vs. time) for bilayer
of copolymers $P(VDF_{0.6}TrFE_{0.4})$ with $T_c \approx 70$˚C
and $P(VDF_{0.8}TrFE_{0.2})$ with $T_c \approx 140$˚C, with
nominally equal thicknesses: (a) after poling as
a composite (both layers are seen to be poled in
same direction); (b) after heat treating at 100˚C,
(high T_c layer is seen to have retained its polar-
ization while low T_c layer is seen to have lost it);
and (c) after applying reverse poling field (no fer-
roelectric switching is seen to have occured in high
T_c layer due to increase of coercive field induced
by thermal treatment described in (b) [34].

side with the high Curie transition has been so strongly
stabilized that you cannot reverse its polarization. So,

only one half can be switched, the other half remains unswitched!

(a)

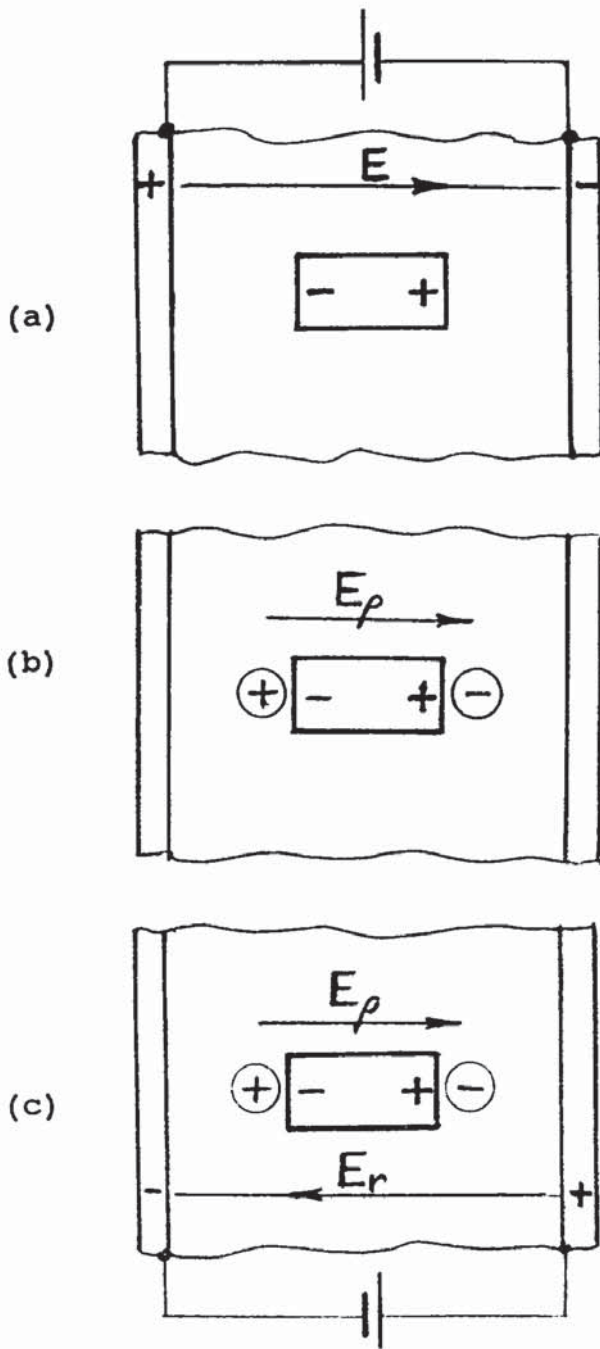**(b)**

(c)

Figure 41.

Space-charge stabilization model: (a) crystallite dipole aligned by poling field E; (b) dipolar charges at crystallite-amorphous interfaces compensated by space charges, after extended poling time and/or thermal treatment (remanent space charge and remanent polarization are mutually stabilized); and (c) reverse poling field E_r opposed by space-charge field E_ρ (coercive field appears doubled).

The same behavior can be observed if you have a copolymer, which is simply stored at ambient temperature or at reasonably high temperatures, but not above the Curie temperature, for a long time. You find that you cannot change the polarization state of that sample (even if the polarization is zero) because the coercive field is anomalously high. So, we think that these phenomena may be related to space charge, particularly when you cannot reverse the polarization. A space-charge model predicts an increase of the coercive field by a factor of two as shown in Figure 41. So this is just as in the models that Eisenmenger was mentioning where you have space-charge stabilization of dipoles.
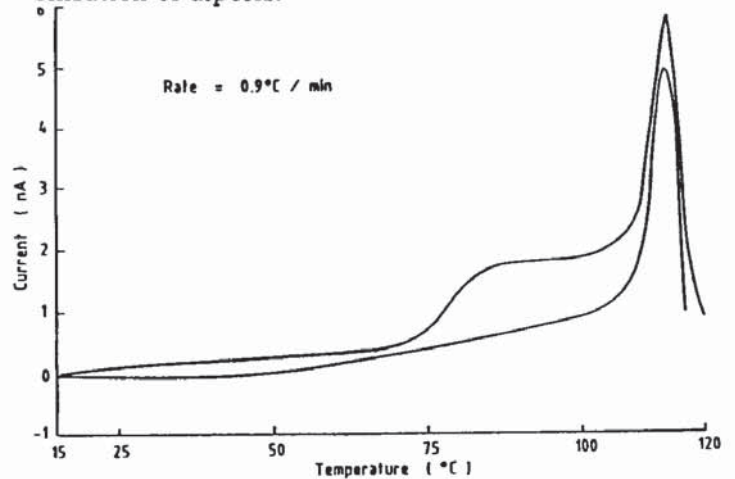

Figure 42.

TSDC obtained from two copolymer samples poled at 80°C (upper curve) and first poled at 80°C, then reverse poled at 20°C for 10 minutes (lower curve) [7].

Dilip K. Das-Gupta: We have to disagree with what has just been said. I apologize to Aimé for showing this. The top part of Figure 42 was taken after poling the copolymer at 80 MV/m at 80°C; and then a thermally stimulated discharge was performed. So you can see a peak you would normally expect near the poling temperature followed by the phase transition at 116°C. We then applied a reversed field of 10 MV/m for 10 min and repeated the TSD measurement. The peak at the lower temperature is most affected by the reverse field. The most noticeable change we see is probably because we got two kinds of dipoles, one kind of dipole which is affected very seriously by space charge, and another different type. So I am saying that the space charges are there, but they cannot be very deep. That is the difference we have with Aimé's suggestion.

Bożena Hilczer (Institute of Molecular Physics, Polish Academy of Sciences, Poznań, Poland): I have to deal with the maximum value of the internal bias due to the space charge as proposed by Furukawa. This model can explain the asymmetry in charge increase shown by Das-Gupta to be a time-dependent property in the field. It is only hard for me to ascribe the relaxation time of 100 s

just to the internal bias, since in my opinion this relaxation time should be determined by the interaction of the space charge and the dipolar polarization. So it is very sensitive to the value of the dipolar polarization, and different dynamics cannot be just expected as dependent on the speed.

Takeo Furukawa: 100 s is not the relaxation time.

Bożena Hilczer: You proposed it as a relaxation time just calculated from the conductivity.

Takeo Furukawa: This is the time constant of some behavior related to charge transport or charge movement, not the relaxation time of the dipoles.

Juliusz Sworakowski (Institute of Organic and Physical Chemistry, Technical University of Wrocław, Poland): I want to just turn your attention to one fact: Most of you assume readily that pure PVDF and copolymer behave in the same way and that the polarization has exactly the same nature. Now, from the point of view of thermodynamics if you look at the manner of preparation of the samples you see that pure PVDF has an unpolar phase that is thermodynamically stable. To stabilize the polar phase, you probably need something, some kind of preparation. Maybe these charges should be there and exert a stabilizing effect. On the other hand, in the copolymer the polar phase can be obtained as a thermodynamically stable phase as some DSC experiments have shown. Probably there the presence of charges helps, but is not necessary to obtain a long-term stability.

M. Wübbenhorst (Plastics and Rubber Research Institute, TNO, Delft, The Netherlands): I think that it is a good proof for the amount of space charges at the surfaces of the crystallites in PVDF — and I am only talking about PVDF — to estimate the internal field which exists between the crystalline and the amorphous phase. If we would have a high internal field then this should contribute significantly to the total pyroelectric response.

I performed some LIMM (laser-intensity modulation method) experiments where I have investigated a well prepolarized PVDF film; and in addition, I applied a bias field, which was relatively small compared with normal poling fields, one order of magnitude less than the coercive field strength. And I found that the change in total pyroelectric response was one order of magnitude higher than expected if I compare the spontaneous polarization inside the crystallites with the polarization induced by the external bias. And I think that I can explain this high pyroelectric efficiency in the amorphous phase by assuming a high temperature coefficient of the capacitance as

reported by DeReggi. That means we can really measure the thermal expansion coefficient of the capacitance, and this is in good agreement with the observed induced pyroelectric coefficient. But at least if we assume a low degree of space-charge compensation at the surfaces of the crystallites I would expect a much higher total pyroelectric efficiency of PVDF than normally measured. So I must conclude that the degree of charge compensation is > 80% of the amount necessary to stabilize or fully compensate the crystallites.

Wolfgang Eisenmenger: I would just like to make a short comment on the copolymer. Now, it may be that between different copolymers there are also differences in the behavior, but what we found is just that in the copolymer we tried for the blocking experiment we cannot have stable polarization under these conditions of blocking as opposed to the case where we inject charges under otherwise identical conditions. So the injection and trapping of charges really stabilizes the polarization even in this copolymer.

Yao Xi (Electronic Materials Research Laboratory, Xi'an Jiaotong University, Xi'an, China): I think the importance of dipoles for the piezo and pyroelectricity is widely accepted. The question is about the role of the space charges. Is there any evidence for the space charge developing during times of several minutes in comparison with the evolution of the piezo and pyroelectricity with time? Is there any information about the time dependence of piezo and pyroelectricity compared with poling times and space-charge effects? I think this is a critical point.

Wolfgang Eisenmenger: What I would like to say is the following: If you measure the poling time which is necessary to have a permanent polarization then you can compare this with the time you need to inject charges by observing the time development of the field distribution.

Yao Xi: If you are using vibrating electrodes you are able to make passive measurements without any injection of charges. If you make pyroelectricity measurements by other methods it is also connected with the injection of charges.

Wolfgang Eisenmenger: I pointed out that it is very difficult experimentally just to suppress charge transport through an insulator. For one case, we are very sure and we did it very carefully to avoid charge injection, and this was the case I showed to you. So for this case, we are sure that if we do not inject charges under otherwise identical conditions we will not have permanent polarization. And if you inject charges with the same total polarization current then you have permanent polarization. And so we

think this is the only situation where we so far are really sure that we did not make any mistakes. So in a certain sense I think that what you wish is much too difficult to do carefully at the moment.

James E. West (Acoustics Research Department, AT& T Bell Laboratories, Murray Hill, New Jersey, USA): The copolymers — usually the component that is added — are known to have good charge-storage capabilities. And we also know that the Curie temperature decreases with the relative amount of the added component. In view of these points, does anyone on the panel care to speculate on the real role of the copolymer in this case from the standpoint of charge storage?

Dilip K. Das-Gupta: Well, the copolymer contains a monomer in addition to VDF that leads to a crystalline phase, in which the dipoles of neighboring macromolecular chains are aligned in parallel, not antiparallel. But, unfortunately, it also produces lots of grain boundaries when you introduce that. And then you have a considerable amount of trap sites present. So when you pole that sample then you fill those traps up — probably to a fairly low value, that's the only thing I don't know. But when you inject space charge some of the space charges would be located near the surface of a crystallite. And its field would be in the same direction as that of the dipoles thus enhancing the local field. And this is probably what Eisenmenger sees: that you cannot have stabilization without space charge. So you have an enhancement of the crystalline field by the presence of space charge in the crystalline area. But in the amorphous area, of course, the story is different.

Gerhard M. Sessler: Let me ask a last question: In the opening statements, we heard different views about the role of space charge. And I would like to ask the defenders of the minor role of the space charge: You have seen the experiments of Eisenmenger where he found the discrepancy between the electric displacement and the permanent or remanent polarization — the time delay between the two. Does this convince you that space charge has more of an effect than just compensating or diminishing internal fields — that it has a stabilizing effect as far as the polarization is concerned? Or are you unconvinced of this more important role of the space charge?

José A. Giacometti: I have no comment, but I think what I would like to be considered is the new idea proposed by Faria that you can have not only charge injection, but also another mechanism that makes the charge move inside the sample. There is another point that I would like to make: We should consider the amount of charge that we need to neutralize or to stabilize the dipoles.

Takeo Furukawa: As I told you, if you end up in very highly crystalline samples and look at their high-field behavior you do not have to think about space charge. All the dipoles are already stable even if there is no space charge. But if you look at very slow or low-field behavior on the order of seconds then space charge does compensate or stabilize the polarization especially if the crystallinity is low.

Aimé S. DeReggi: I wonder if we are using the right term here because we talk about stabilization in the sense of increasing the reluctance to switching when a field is applied, whereas Sworakowski was speaking about stability in the thermodynamic sense. I think we agree that the ferroelectric state is a stable state. So, the way I looked at stabilizing the polarization by space charge is in terms of raising the coercive field rather than in terms of raising the Curie temperature. In other words, it becomes more difficult to switch, but it does not have much to do with the thermodynamic stability which is accepted by all of us, I believe. So I think we should be careful when we talk about stability. Is the space charge contributing to the response? Well, I think it is probably not contributing much. I am going out on a limb by saying that, but that is my feeling. However, it has a very strong role in determining what the coercive field is.

Wolfgang Eisenmenger: I think that is also my opinion. And the basic mechanism of piezoelectricity, if you have a stable orientation of dipoles of any sort, is clear. You can just either say you have a change of dipolar density or you can say you have a movement of compensation charges; that gives you even quantitatively the same answer if the mechanics of the system is the same. The point really is: What is the mechanism of stabilizing the dipoles. And in principle, you have to add something to the thermodynamic ferroelectric state in order to make it stable. You have to say whether it is a soft ferroelectric or a hard ferroelectric. It is the same thing in magnetism: If you have iron for a transformer it is a soft ferromagnetic, and if you have a magnet to hold something it is a hard ferromagnetic. And the point is that for the hard ferromagnetic you need some agent by which the magnetism is stabilized; you need — so to speak — traps or defects which pin the Bloch or domain walls to prevent them from moving or to keep the dipoles in place by anisotropy. This is the mechanism. And what we are trying to say is: We think that in the ferroelectric situation and especially in PVDF and in the copolymer you need this additional stabilizing mechanism; and we think the charges trapped at the surfaces of crystallites are doing this.

Gerhard M. Sessler: I would like to close the discussion session by first thanking the organizers again for making

this session possible, second thanking the panelists for their opening statements and their contributions during the discussion, and then of course thanking all the discussants from the floor for their questions and comments.

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