

Investigation of Poling Dynamics For Multi-layer Polymer Electro-optic Materials

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ABSTRACT

An analysis is presented of the charge dynamics involved in the poling of electro-optic polymer multi-layer materials. Specifically addressed are the electrical properties of the cladding layers in comparison to those of the active core layer which lead to the largest protection against premature dielectric breakdown during poling, the largest fraction of the applied DC poling field falling across the core during poling, and the largest fraction of the applied AC field during modulation. Also presented is an in-depth analysis of the voltage-divider effect and the relative merits of conductive versus regular claddings for achieving efficient poling and minimal optical loss.

1. INTRODUCTION

Poling – i.e. the use of very high static electric fields – is the only practical and available means for producing second-order nonlinear optical polymer materials. In practice, a thin film (on the order of 1 to 2 micron thick) of electro-optic polymer material is sandwiched between two electrodes, the film is raised to its glass transition temperature T_g , and a large voltage of over 100 volts is applied across the film. The voltage is held there for a few minutes at T_g , and the temperature is then allowed to fall back to room temperature with the voltage still maintained. At room temperature, the voltage across the sample is then removed. The film is then subjected to measurements of its electro-optic(EO) activity, such as the method of Teng & Man or second harmonic generation (SHG), to determine how successful the poling procedure has been. A diagram of the poling geometry is shown in Fig.1 .

As simple as it is to describe poling in an operational sense, it is also very simple to describe the process of poling in a conceptual sense. The EO-active material contains chromophore molecules which possess permanent electric dipole moments, μ . At the high temperature of T_g , the polymer becomes softened, allowing the permanent dipoles to rotate and to align themselves parallel to the applied electric field $E = V/d$, where V is the applied voltage and d is the thickness of the film and the distance between the electrodes. Because of random thermal motion at the poling temperature T_g , the alignment of the permanent dipole moments is not expected to be perfect. Instead, a measure of the alignment is given theoretically by the formula¹

$$\langle \cos^3 \theta \rangle = \frac{f_o \mu E}{5kT_g} \quad (1)$$

where θ is the angle between the direction of the electric field E and the dipole axis, the $\langle \rangle$ brackets indicate an ensemble average over all dipoles in the material, f_o is the local field factor (giving the effective electric field inside the material based upon its intrinsic dielectric properties) and k is Boltzmann's constant. In practice, the value of this alignment factor is typically about 0.3, giving a value of about 45° for the alignment angle of the average chromophore dipole.

One practical complication in using poling to obtain EO polymer materials is that since these materials are to be employed as elements of an optical waveguide network, the active EO material must be sandwiched between two cladding materials. Hence, it is this triple-stack of thin layer films which now must be sandwiched between the poling electrodes. In principle, this is not a significant complication, since this primarily means that the power supply which is providing the DC poling voltage must be cranked up to a larger value than that needed for poling a single layer. And, if one knows the electrical resistance of each

layer in the triple stack, one can presumably calculate the voltage applied to the active center or core layer using simple ohmic circuit formulas. That is,

$$V_{\text{core}} = V_{\text{app}} (R_{\text{core}}/R_{\text{tot}}) \quad (2)$$

and one is left with a standard resistance voltage divider.

While it is true that it is necessary to pole a triple stack in order to fabricate an actual waveguide device, in the preliminary stages when new materials are being explored, one is usually poling only the EO polymer core material sandwiched between the electrodes. During the poling process one typically also measures the conductivity/resistivity of the material as a function of time and temperature. One can also do in-situ measurements of the EO coefficient, r_{33} or d_{33} , during the poling, or measure them after the poling has been completed. Thus, these single-layer poling exercises allow one to determine two of the most important properties of the material: its EO activity and its electrical conductivity.

The above discussion assumes that the poling is being carried out as contact poling, where the thin film to be poled is sandwiched between conductive electrodes. Typically, one electrode is a metal such as gold or aluminum, with the other being a transparent conductor such as ITO (indium tin oxide), since this arrangement is the most suitable for measuring the post-poling EO activity using the Teng & Man² procedure. Another version of poling sometimes employed is corona poling, in which the thin film is placed on a conducting substrate which serves as the grounding electrode. A few cm above the film is placed a needle-shaped conductor which is then raised to several kilovolts above ground potential. The process is conducted in air or other suitable atmosphere (N_2 or Ar) and a corona discharge takes place between the needle and the exposed surface of the film being poled. The accumulation of charged ions from the gaseous corona on the surface of the film then establishes a high voltage across the film, which produces the poling.

Corona poling has one significant advantage and two major disadvantages over contact poling. The advantage is that the chances of catastrophic dielectric breakdown are significantly reduced, since the exposed surface of the film is a very low conductivity surface, and gives a much smaller opportunity for destructive shorts to propagate through the film. The disadvantages are 1) that the crashing of the corona ions on the exposed surface of the film can cause significant damage to this surface, and 2) that it is difficult to know exactly the precise value of the poling field E that is produced in the film. Overall, these two disadvantages outweigh the one advantage, and contact poling has been the preferred method employed by most researchers in recent years. Thus, we will restrict the remainder of our discussion to the technique of contact poling.

2. A CLOSER LOOK

Not everything associated with the poling of EO polymers is as straight forward and blissfully simple as described above. The nature of the poling process and the intrinsic properties of the materials considerably complicate both the poling process and a simple theoretical understanding of it. We now list some of these known complications.

a. In order to obtain reasonably high EO coefficients, one must use very large poling fields on the order of $100 \text{ V}/\mu\text{m}$ (10^8 V/m) or larger. This translates into high probabilities of dielectric breakdown of the materials, especially in the case of poling single-layer materials. Frequently this results in catastrophic electrical shorts through the sample, and the sample must be discarded.

b. Because one is operating on the threshold of dielectric breakdown, the simplest models of conduction do not apply in most respects.

c. A further complication is that the polymer materials involved are highly resistive materials, and attempts to explain their conductive properties, even well below dielectric breakdown, are more complicated than the standard models used to explain conduction in metals or semiconductors.

d. Adding to the complications is that conduction in these materials is in general mediated by four types of carriers: electrons, holes, and + and – ions, with the possibility that ionic carriers might be the majority carriers in typical situations.

e. The number of charge carriers is constantly changing in response to the changing experimental conditions.

i) as one takes the material from room temperature to poling temperature at T_g , the number of thermally generated carriers can change by over and order of magnitude

ii) as one takes the material from zero volts to the large poling voltage, large numbers of carriers can be generated by the applied field itself

iii) the open structure of polymers allows for many charge traps inside the material, allowing charges to be trapped and de-trapped with changes in temperature and applied field

iv) ionic and/or electronic charges that move through the bulk of the material can accumulate at interfaces (either between the polymer and the electrodes, or between the core and clad layers in triple stacks), causing distortions of the electrical field inside the materials

v) because of non-ohmic effects at the electrode-polymer interfaces, electron or hole injection can take place at these interfaces, further distorting the internal electric fields.

3. SCIENTIFIC UNDERSTANDING VS. WHAT WORKS

During the past 15 years a number of informative studies aimed at an in-depth understanding of the poling mechanism have appeared in the scientific literature. We will refer to some of these later in our discussion. Overall, these studies have greatly added to our understanding of the electrical conduction phenomena involved in poling EO polymers. However, in our opinion, with the exception of those studies aimed at reducing the chances of dielectric breakdown and those validating the voltage divider effect, these studies have had little impact on the practical realities of poling of EO polymers and of achieving greater EO activity through the poling process.

That is, the two major objectives of the poling process – avoiding dielectric breakdown and achieving the highest EO activity – have not required thus far an in-depth understanding of the intricate and complicated conduction mechanisms involved in the poling process. That is, using only a practical understanding of the differences in poling single and multiple layer materials and of the resistive voltage divider mechanism, one can achieve both a significant reduction in the occurrence of catastrophic dielectric breakdown and a significant enhancement of the poling efficiency.

A. Poling of Two-layer Stacks

In order to demonstrate the enhancement of the ability to avoid early dielectric breakdown during poling, a few studies have systematically approached the issue by poling a double stack: an active core layer and a single cladding layer sandwiched between two electrodes. The success of this approach does not depend on whether the additional cladding or buffer layer is more or less conductive than the active polymer layer. Eich and coworkers³ showed that the addition of a resistive siloxane buffer layer substantially reduced the number of dielectric breakdown incidents during poling, and thus extended the effective poling range from 180 to 230 V/ μm in polymer samples of DR1 dispersed in PMMA as a side chain pendant. This resulted in an EO activity some 20% larger than that obtained when poling single layer films without a buffer layer.

On the other hand, Drummond⁴ also demonstrated a significant decrease in dielectric breakdown tendency and an extension of the poling region from 160 to 225 V/ μm in DR1/PMMA guest-host samples when

combined with a more conductive Baytron P layer. (The Baytron P employed had a conductivity some 5 orders of magnitude greater than that of the active layer.)

The simplest explanation of this behavior is illustrated in Figs. 2 and 3. When a single-layer polymer sample is sandwiched between two conducting electrodes for poling, the contact surfaces of the electrodes with the polymer are very high-conductivity, charge-rich surfaces, as depicted in Fig. 2. Typically, at poling conditions, the active core layer will have a resistivity of around 10^{10} ohm-cm, and the metal electrodes in the vicinity of 10^{-5} ohm-cm. Thus, the difference in the conductivities of the metallic electrodes and the active polymer is greater than 15 orders of magnitude. Consequently, when an incipient short begins to start within the high-resistance core material at one of its weak points, the short is quickly fed by the high-conductivity electrodes on either side of the active polymer. This results in a cascading, catastrophic breakdown current through the sample, rendering it useless for further study.

The case of the poling of a two-layer sample, active polymer plus cladding layer, is illustrated in Fig. 3. The major change from the previous case is that the internal interface between the polymer and cladding layer is now a much lower conductivity interface, by many orders of magnitude than that between the core-electrode interface in a single layer configuration. One can assume that the effective charge mobility at the polymer-cladding interface is also orders of magnitude smaller than that which exists at the polymer-electrode interface. Hence, an incipient short starting in either the polymer or buffer layers does not have access to a rich source/sink of mobile charges at both ends. Thus, the chances that a catastrophic short will propagate through the sample are significantly reduced.

B. Poling of Triple Stacks

It has been noted above that the poling of active waveguide devices necessitates the poling of a triple stack: the active EO layer sandwiched between two cladding layers. At first, it appears that this practical requirement imposes an unfortunate complication on the whole process of poling. But, as we have just seen directly above, there is a distinct advantage to poling the active layer when it is combined with a buffer layer. If we now just substitute the term "cladding layer" for "buffer layer," we see that the requirement of poling a triple stack is really a blessing in disguise, rather than an inordinate complication. In fact, this complication-turned-to-advantage, now bestows even more of an advantage than that discussed in the two-layer results discussed above.

Fig. 4 shows a typical triple-stack waveguide structure. With the active core material now sandwiched between two cladding layers, the active core material now has a low-conductivity interface on each side of it. For a catastrophic short to propagate between the electrodes in this structure, it must pass through three separate layers and two low-conductivity interfaces. The chances for a catastrophic breakdown through this structure should be decreased by at least several orders of magnitude compared to the two-layer case discussed above, which itself represents a decrease of several orders of magnitude compared to the case of poling a single layer between two electrodes.

Hence, the chances of catastrophic dielectric breakdown during poling is significantly reduced by this triple-stack structure. This implies that much higher poling voltages can be employed, resulting in higher EO coefficients.

Before leaving this part of the discussion, we wish to note that an extension of the range of poling voltage does not necessarily translate into a proportional increase in the EO coefficient obtained. That is, the linear relationship between the poled-in order, $\langle \cos^3 \theta \rangle$ and the applied field E as given by Eq. 1 is only a first-order approximation. As the poling field E is increased, eventually this linear relationship begins to fall off and the linear curve bends over, so that the same percentage increase in the applied field leads to smaller percentage increases in the effective EO activity.

C. The Voltage Divider Effect

As discussed above, the voltage divider effect assumes that when either two or three layers of materials are poled as a stack, the simplest representation is that of applying a voltage across two or three resistors in series. If these materials obey standard ohmic circuit rules, then the fraction of the total applied voltage which appears across any layer is the same as the fraction of the resistance of that layer to the total resistance of the stack. This was previously given as Eq. 2. In particular, the fraction of the total applied voltage which appears across the active core layer should then be proportional to the ratio of its resistance to the total resistance of the stack.

Inherent in this interpretation are two assumptions: The first is that it is assumed that we are dealing with a steady-state, non-time-varying current which has been established through the stack. It may take some time for such a current to be established once the voltage connection has been made. Exactly how much time we will look at in more detail below. Suffice it to say that each layer can be looked at as a parallel combination of a resistor and capacitor, and that the three-layer stack consists of a series connection of the layers. As such, there will be an RC-time constant associated with the transition of the stack from a capacitive voltage divider at $t = 0^+$, just after the voltage is connected, to a resistive voltage divider at some longer time. The second assumption is that each material in the stack behaves ohmically – i.e. that the voltage and current for each layer are directly proportional in accordance with ohm's law: $V_i = I R_i$, where the index i stands for a particular cladding layer or the core layer. Such an assumption is not likely to be absolutely true, and the exceptions will be discussed below in Section 4.

Starting in the early 1990s, a number of investigators began to pole EO polymer materials in either double or triple stacks in anticipation of their being employed as optical waveguide devices. In general, their results appeared to demonstrate the validity of the voltage divider effect during poling.

Ling et. al.⁵ measured the net resistivity of double layers of polymer core and clad materials and found that their results were in fairly good agreement with the values predicted by the ohmic series addition of resistances, a result nearly equivalent to the voltage divider effect. However, they performed only resistance measurements and did not attempt measurements of the EO activity.

Gulotty⁶ performed poling experiments on both double and triple stacks of core and cladding materials. In the triple-stack poling studies, the measured values of the EO activity were only about 20% lower than those predicted by the voltage divider formula when using an average poling field of 50 V/ μm . When the average poling voltage was raised to 200 V/ μm , the measured EO activity dropped to only 37% of the predicted value.

Drummond⁴ poled double stacks consisting of an active layer (DR1 in PMMA) along with cladding layers of varying conductivity. When the cladding layer was the conductive material Baytron P, the measured EO activities were nearly the same as for poling a single layer of the same material. Since Baytron P has a conductivity some 5 orders of magnitude greater than the core material under poling conditions, the results are consistent with the voltage divider interpretation that more than 99% of the applied poling voltage was falling across the core material. Likewise, when a resistive cladding of polyimide material with a conductivity an order of magnitude smaller than the core was used, very low EO activity was measured, indicating that very little of the applied voltage was actually falling across the core material, again in agreement with the voltage divider predictions. Thus, in this study, the voltage divider effect gave good predictions at opposite ends of the conduction spectrum, when the core was combined with both much higher and lower conductivity cladding materials.

Thus, in one study, the voltage divider effect appears to be valid, and in the other only partly valid. In addition to the Gulotty data noted above in which the predicted EO activity falls far short of that predicted as the poling voltage is increased, recent research at our own laboratory has also shown mixed and confusing data whereby occasionally the measured EO activity of a double stack is much higher than that predicted by the voltage divider formula when a high-resistance cladding is employed. Clearly, something

more complex is taking place in the poling of multi-layer stacks of materials. A further, more general discussion of this matter is attempted in Section 4 below.

In closing this section on “What Works”, we conclude that the poling of multi-layer stacks has been shown to offer inherent protection against early dielectric breakdown of samples during poling and also allows the extension of poling fields to higher values than those possible while poling single layers, with an attendant increase in the EO activity of the active core layer. The use of the voltage divider effect in order to predict the effective EO activity of a multi-layer stack, however, has shown mixed results regarding its validity. However, when it does work for a certain set of materials, it does simplify the preparation and testing procedure for multi-layer samples.

In the next section we consider another type of voltage divider which is involved in the operation of these devices.

4. OTHER CONSIDERATIONS

A. Modulation Efficiency

Although the focus of this article is on the dynamics of poling and how this effects the performance of an EO polymer device, eventually one must deal with another dynamic which has a crucial impact on device performance – EO modulation efficiency.

That is, when a poled, triple-stack device is placed into an optical waveguide circuit, it is often used as a modulator for the purpose of transforming a high-bandwidth electrical signal into an optical one. Typically this is done by constructing a Mach-Zhender modulator. In practice, this means impressing a high-frequency electrical signal on the triple-stack structure using the same electrodes that were employed in the poling operation. In order to determine what fraction of the applied modulation voltage amplitude is applied to the poled core material, one can do a standard AC circuit analysis. Here the triple stack is represented as a series combination of three elements, each of which is a parallel combination of a resistor and capacitor. One then solves this equivalent circuit for the effective impedance as a function of applied frequency.

The result one finally obtains from this analysis is that for frequencies beyond the range of a few tens of Hz, the ratio of the AC voltage amplitude across the core to the amplitude of the applied voltage, V_2/V_{tot} , is given by⁷

$$\frac{V_2}{V_{tot}} = \frac{1}{1 + \frac{2\epsilon_2}{\epsilon_{13}}} \quad (3)$$

where ϵ_2 and ϵ_{13} represent the permittivities (or dielectric constants) of the core and cladding layers, respectively, and it is assumed that the thickness of all layers is the same. This now represents the case of a capacitive voltage divider in analogy to the resistive voltage divider for the poling process as given above in Eq. (1). Thus, if the core and clad layers have the same dielectric constants, only one-third of the applied AC voltage signal falls across the core. In order to get a larger fraction of the applied voltage across the core, one needs cladding layers with dielectric constants greater than that of the core. For the case of $\epsilon_{13} = 10 \times \epsilon_2$, the percent of the voltage across the core rises to 83% .

Thus, besides serving as a buffer layer and a resistive voltage divider for poling, the cladding layers could also be chosen to ensure the maximum modulation efficiency. In the case of poling, one gets the maximum benefit of the resistive voltage divider if one uses claddings that are substantially more conductive than the core. This also allows one to use lower applied voltages for poling, which may have other advantages in the

construction of a multi-layer waveguide device (e.g. the prevention of spurious arcing during poling to other parts of the device structure).

It was originally thought that the choice of conductive claddings would also have immediate benefits for increasing modulation efficiency. That is, in the previously-cited study by Grote and coworkers, the use of the conductive cladding material Baytron P not only gives a conductivity some 10^5 times larger than that of a typical core material, but at frequencies close to DC, it also gives a dielectric constant over a 1,000 times larger than that of a typical core material such as DR1 in PMMA. This would mean that over 99.9% of the modulation voltage would fall across the core and give a second incentive for using conductive claddings.

However, further investigation of Baytron P as a function of frequency by Subramanyam et. al.⁸ shows that the dielectric constant quickly falls off as the frequency is increased. At a frequency of 100 KHz, it is down to about only 10 times greater than that of the core, and at a frequency of around 10 GHz, it is nearly equal to that of the core. But, one of the primary reasons for developing EO polymer materials is because of their enhanced performance compared to conventional materials such as lithium niobate at frequencies above 20GHz. So, in this case, while Baytron P does serve well as a resistive voltage divider for efficient poling, it offers little in the way of producing efficient modulation in this targeted high frequency region.

Such is likely to be the case with claddings other than Baytron P, be they conductive or not, since the real part of the dielectric constant of essentially all materials cascades monotonically downward as one goes to higher frequencies. It is not likely that one can easily find a cladding material in the frequency range above a MHz that is more than a factor of 2 or 3 greater than that of a typical polymer core material. Thus, the net advantage of conductive claddings is to gain efficiency in the poling process, with little or no effect in modulation efficiency, except at low modulation frequencies.

B. Cladding Layer Requirements

Finally, one must not lose sight of the original purpose of cladding layers: to help guide the optical wave with minimum loss and to keep it primarily confined to the core layer. In order to do this efficiently, a cladding layer must have two characteristics: 1) its refractive index must be less than that of the core; and 2) it should contribute as little optical propagation loss as possible.

Let us look in particular at the second requirement. In the discussion above it was pointed out how conductive claddings such as Baytron P do an excellent job of permitting nearly 100% of the poling voltage to be applied across the core in a triple-stack structure. However, this increased poling efficiency comes with an associated optical propagation loss. Typically, waveguide propagation losses for claddings are considered marginally acceptable if they are no larger than about 5 dB/cm. (Acceptable losses for cladding layers are considerably higher than those for the core layer, around 1.0 dB maximum, since only a small fraction of the guided wave is propagating in the cladding layer in the ideal case.) However, the losses for Baytron P as a cladding were measured by Drummond⁴ and shown to be on the order of 10.0 dB/cm or greater. This leaves Baytron P as a poor choice for a cladding layer when considering optical loss.

C. Summary of “What Works” Approach

For our discussion above it is clear that the single most important thing that one can do to improve the poling efficiency of EO polymer materials is to pole them as a triple stack – core layer sandwiched between two cladding layers. Such an arrangement significantly reduces the likelihood of catastrophic dielectric breakdown in these materials and allows the use of higher poling voltages, which should lead to higher EO coefficients.

Also, taking into account the resistive voltage divider effect, one can attempt to find cladding materials which are more conductive than the active core layer in order to reduce the total applied poling voltage and the possible effects of spurious voltage discharges within the extended poling apparatus. However, in principal, one can still get protection against catastrophic breakdown in the sample by using claddings with

conductivities of about the same value as those of the core material simply by raising the applied voltage, assuming that this does not lead to other spurious voltage discharges within the poling apparatus.

Finally, the use of conductive claddings appears to offer no real advantages in the modulation efficiency of these materials in the desired high-frequency region of greater than 20 GHz, and very conductive clads can significantly contribute to increased and unacceptable optical loss.

5. APPROACHING A DETAILED ANALYSIS: THE VOLTAGE DIVIDER

In concluding our analysis of the voltage divider effect in Section 3, it became apparent that the voltage divider phenomena is not truly a “What Works” approach, but more aptly a “What Works Sometimes” approach. That is, an approach based on the simple and straightforward ohmic division of voltages in a series stack does not appear to provide a consistent explanation of the actual poling voltage which is applied to a core layer when it is sandwiched between cladding layers. That is, we are now faced with the second approach: a detailed and more sophisticated analysis of the electrical conduction dynamics in these high-resistance polymer materials – the messy science alternative.

In trying to determine why the voltage divider effect appears to work well at times and not so well at other times, there are several issues that can be investigated. The first is whether the two specific assumptions made in applying this formula are fulfilled: i.e., that a steady-state current has been established through the sample and that the individual layers exhibit ohmic behavior. A second issue is whether the formula is being applied properly, i.e. whether proper values of the resistances of each layer are being inserted into the formula.

The determination of whether a steady-state current has been established through the sample is an easy one to establish. It is now standard practice to monitor the poling current through the sample using sensitive electrometers which can measure currents down to the level of picoamperes. Various investigators^{3,4,5,6,9,10} report that if the sample is poled from the strictest initial conditions (the sample at poling temperature and the maximum voltage applied instantaneously) then it takes somewhere between 15 and 30 minutes for the current to stabilize. In practice, however, most investigators have found that more controlled poling is done (and fewer samples are destroyed) by gradually raising the both the sample’s temperature and voltage in increments until the ultimate temperature and voltage are reached. In that case, one usually finds that poling currents stabilize in about 5 minutes or less once the final temperature and voltage are reached. All of the above results are those reported for the poling of single-layer samples. However, the author has seen very little published data for the time evolution of poling currents when two- or three- layer samples are being poled. One is left to assume that the time evolution for multi-layer samples would not differ drastically from that of the single layers. In any case, it is just as simple to follow the time evolution of the current of a multi-layer sample as for a single layer. In addition, it is relatively simple to measure the EO activity of the sample during poling using *in situ* measurements of either the second harmonic signal (SHG) or the method of Teng and Man to determine r_{33} . These measurements are most easily done when measuring single layers, but become more difficult when the optical beam must travel through multiple layers. However, in most cases one can be reasonably confident that both the poling current and the EO activity have been stabilized when the poling has been completed.

We will deal next with both of the two remaining issues together - the ohmic/nonohmic behavior of the materials and the insertion of the proper values of resistance into the divider formula. The voltage divider formula for a two-layer stack is given by

$$\frac{V_1}{V_{tot}} = \frac{R_1}{R_1 + R_2} \quad (8)$$

where the index 1 represents the core layer and index 2 the cladding layer. (For mathematical simplicity, a two-layer stack is investigated; all of the arguments apply in principle to a three-layer stack.) The issue then becomes one of inserting the correct values of R_1 and R_2 into the formula corresponding to the specific poling conditions. We briefly recall that poling is performed at a temperature in the vicinity of the material's glass transition temperature T_g and using applied voltages which produce very large electric fields in the sample, on the order of $100 \text{ V}/\mu\text{m}$ (or 10^8 V/m). With regard to the first criterion, the variation of a polymer's resistance with temperature in the range from room temperature to its T_g is a well known and well studied phenomena.^{4,5,6,9,10} In general, such studies show that polymer's resistance falls dramatically and uniformly from its value at room temperature to that at its T_g , typically by 1 to 3 orders of magnitude. Thus, all investigators have been quite careful to use the known resistance of the polymer in the vicinity of its T_g in applying this formula.

The case of the second criterion, the proper value of the resistance at a certain poling voltage, is more problematic. Many investigators have demonstrated that when applying the high voltages typical of poling to these materials, that their overall behavior is nonohmic. That is, when one plots the current through the sample as a function of the voltage, one generally does not get linear behavior; i.e. the ohmic relationship $I = (1/R) V$ does not hold. This is illustrated in Fig. 5, where the I-V relationship for a polyimide guest-host core layer as measured in our lab is depicted. (The material was synthesized and supplied to us by Lockheed Martin.) It is instructive to plot this same data on a logarithmic current scale as shown in Fig. 6. Here one does get a linear relationship, indicating that the current varies exponentially with the applied voltage; i.e. $I \approx \exp(cV)$, a relation which is consistent with standard models for polymer conduction.⁶

In the same figure, the values of the specific resistance (calculated as the ratio of V to I) of this material at two particular points at each end of the data are also displayed. We see that the resistance at 20 volts is nearly 5 times its value at 150 volts. So now the question becomes: if this material is used as one layer in a double or triple stack, what value of resistance R_1 should be used in Eq. 8 to represent this material? One cannot immediately say, since one does not know exactly what final voltage it will be subjected to as part of this stack. Exactly the same thing can be said for the correct value R_2 of the other material, assuming that it also has a nonohmic behavior. That is, one cannot *a priori* predict the final voltage across each layer when both layers exhibit nonohmic behavior. In only two cases can one have confidence in predicting the final voltage distribution across the layers. One case is when both layers are of the same material, but this is trivial and hardly of any practical interest. (No one is interested in a situation where the core and the claddings are the exact same material.) The other case is when the conductivities of the materials differ by a great amount –by orders of magnitude.

This is exactly the case for the conductive clad Baytron P used by Drummond et. al.⁴ in their studies, where this cladding layer's conductivity is some 5 orders of magnitude greater than the active core layer. As long as one had previously determined the conductivity of each layer in a voltage region reasonably close to the actual final applied voltage, one can easily predict that more than 99% of the applied voltage will fall across the high resistance-low conductivity core layer. This assumption is confirmed by measuring the r_{33} coefficient when this double layer is poled: two-layer samples in which Baytron P served as the cladding layer yielded r_{33} coefficients that are essentially the same as those for poled single-layer samples, indicating that essentially all of the applied voltage in the two-layer stack fell across the higher resistance core layer.

For the general case, one need not resort to a guessing game. If analytical expressions can be found for the I-V relation of each layer [i.e. $I_1 = f(V_1)$, $I_2 = g(V_2)$], one can then solve the system of equations that apply for a steady-state solution for V_1 and V_2 :

$$V(\text{total}) = V_1 + V_2 ; \quad \text{and} \quad I_1 = f(V_1) = I_2 = g(V_2) \quad (5)$$

Otherwise, in the absence of analytical expressions for I as $I(V)$, one can always do a numerical solution using the known I-V data of each material. When one is dealing with a true triple stack, where each layer is a different material with its own unique I-V relation, the steady-state relations become

$$V(\text{total}) = V_1 + V_2 + V_3 ; \text{ and } I_1 = f(V_1) = I_2 = g(V_2) = I_3 = h(V_3), \quad (6)$$

and an analytical solution is still possible, as is a numerical one.

We are now in a position to propose that a possible reason for the voltage divider failing to predict the correct fraction of the total applied voltage which falls across the active core layer is that in some cases the correct values of the resistances of the individual layers were not inserted into the voltage divider formula. In particular, we previously mentioned the data of Gulotty,⁶ who poled triple stacks but got increasingly lower values of the measured EO activity compared to those predicted by the voltage divider formula as the applied poling voltage was increased. When the applied average poling field was around 50 V/μm, the measured d_{33} was about 80% of that predicted by the formula. By the time that the applied average field reached 200 V/μm, the measured d_{33} was only about 35% of the predicted value. There is now a possible consistent interpretation of these results employing the analysis used above.

That is, if the core material behaved in a manner similar to that depicted in Fig. 4, and if one chose a value of the core resistance by measuring it at one point close to the 50 V/μm of applied voltage, this value would overestimate the true value of the core's resistance at higher poling voltages. This in turn would overestimate the fraction of the applied voltage being dropped across the core at higher voltages, with the degree of overestimation increasing as the applied voltage was set progressively higher. However, this explanation is merely a plausible one. (Gulotty himself hinted at such an explanation in his report.) In order to establish that it is indeed a valid one, much more research on the poling of double and triple stacks – where careful attention is paid to the specific nature of the I-V behavior of each material throughout the range of poling voltages – is needed.

6. SUMMARY AND CONCLUSIONS

In concluding, we note that the suggested reasons for the failure of the voltage divider effect only begin to scratch the surface of the complicated conduction phenomena which can occur during poling of these materials. These other issues could have a significant impact on the use of the voltage divider formula as a valid predictor of the effective poling voltage for multi-layer stacks. For example, the effect of the migration of charges to interfacial surfaces during poling has not been discussed here at all. These interfacial charge layers could have a significant effect on the final voltage distribution across the layers -- or they could have very little effect. That is, the ohmic voltage divider effect in fact requires that an interfacial charge layer be established at the interface between two layers of differing conductivity when a steady-state current flows through the sample. (As depicted in Fig. 3, in steady-state, a discontinuity in the electric field occurs across the interfacial layer between the core and clad material requires that a surface charge layer must be present at the interface.) The questions that should be answered are how long does it take for this layer to be established and is it established by more mobile electronic charges or less mobile ionic ones? Moreover, one should also look at how such charge layers affect the electric field distribution within the core layer itself, and what effects this might have on poling efficiency. Various investigators^{3,9,10} have studied these issues for the past decade or more, but as of yet these studies have not yielded information as to how to achieve better results in the poling process.

Likewise, our above analysis of the voltage divider did not really delve in any detail into the nature of the nonohmic behavior of these materials. Clearly, as was pointed out in the introduction, these polymeric materials possess rather complicated electrical conductivity properties in comparison to metals and semiconductors. This was demonstrated above in showing both the significant changes in effective resistance with temperature and with voltage. Part of this behavior can be attributed to the nature of the largely amorphous structure of these materials. Another is that it is very difficult to mate these materials with electrodes such that their interfaces exhibit ohmic behavior because of the extremely high conductivity mismatch of these different materials.

Likewise, we did not discuss another potentially important “What Works” approach – the establishment of an efficient poling protocol. That is, it is up to the investigator to determine if more efficient poling can be

obtained by choosing to approach the final poling conditions in a particular manner. For example, one can choose to raise the sample up to poling temperature without any voltage being applied, then gradually raise the voltage in increments until the final poling voltage is reached. Or, one can do the opposite and raise the applied voltage to near its final value while the sample is still at room temperature and then gradually increase the sample's temperature until the final poling temperature is reached. We have just started such investigations in our own laboratory, but no definitive results have been obtained thus far.

However, for the time being, we are stuck with these materials and their complicated electrical conduction properties. Hopefully, further research will develop ways in which a more detailed understanding of their properties will yield techniques for more efficient and reliable poling of these materials.

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Contact Poling

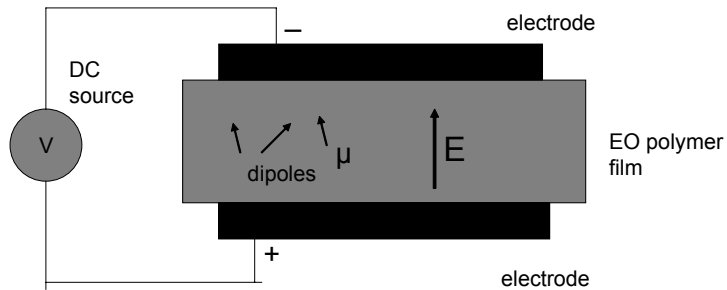


Fig. 1. Diagram of contact poling for single layer polymer film.

Single Stack

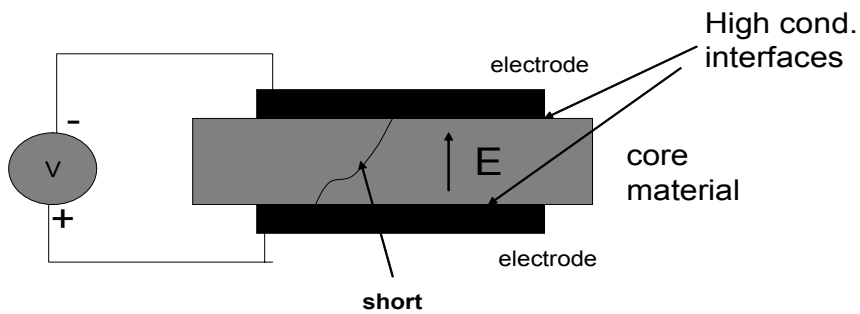


Fig. 2. Electrode-polymer interfaces for single layer poling

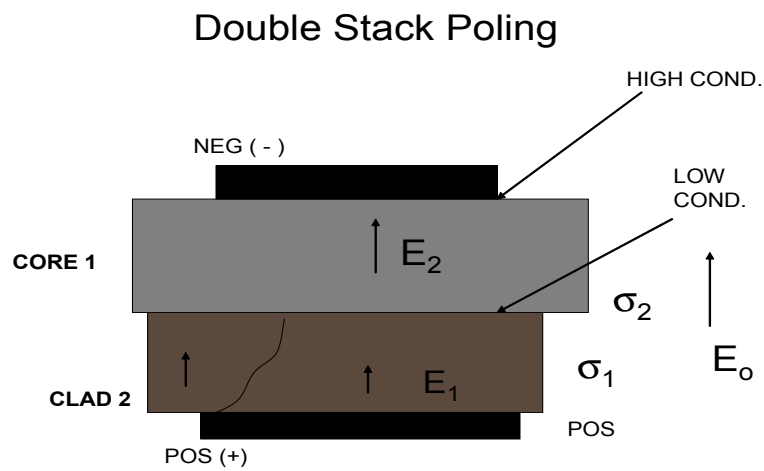


Fig. 3. Layer interfaces for double-stack poling

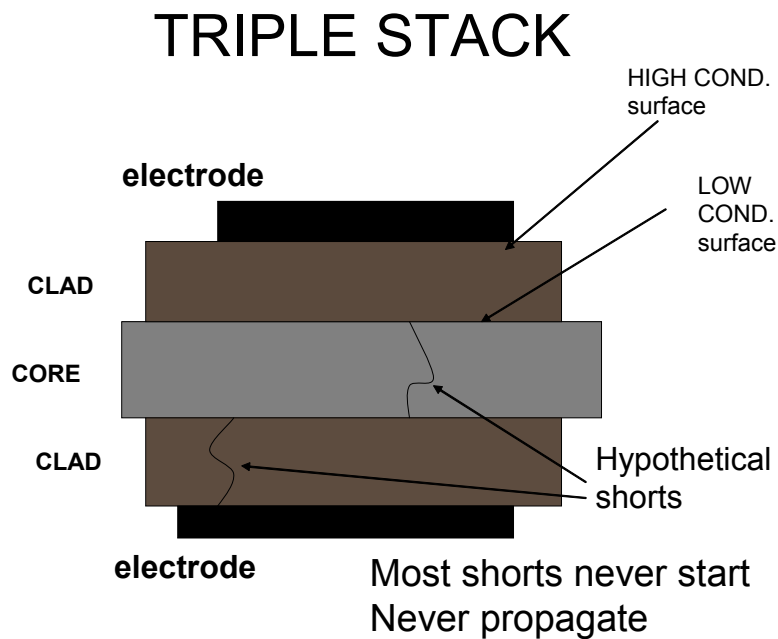


Fig. 4. Layer interfaces for triple-stack poling.

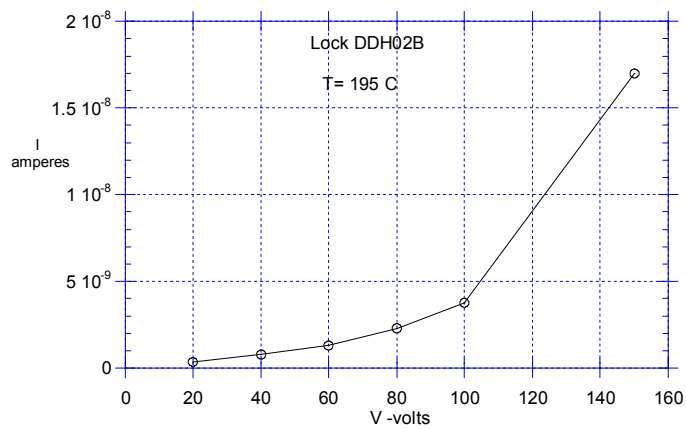


Fig. 5. Current-voltage relationship for guest-host polyimide material.

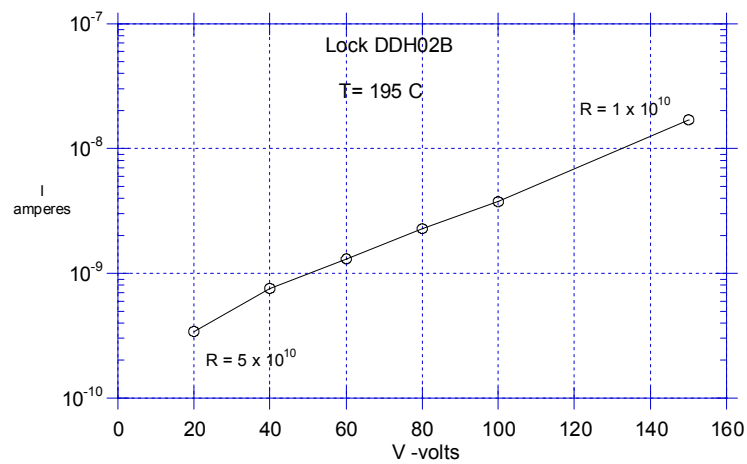


Fig. 6. Current-voltage relationship plotted on a logarithmic scale.