

# Poling Dynamics and Investigation into the Behavior of Trapped Charges in Poled Polymer Films for Nonlinear Optical Applications

H.W. Guan, M.A. Pauley and C.H. Wang\*

Department of Chemistry, University of Nebraska - Lincoln, Lincoln, Nebraska, 68588-0304

## Abstract

The behavior of surface and trapped charges that originate during contact electric-field poling of a model guest-host nonlinearly active polymer has been investigated. Charge effects in thin films of *para*-nitroaniline doped polymethylmethacrylate were studied during and after the poling process by simultaneous measurement of the current through the poling circuit and the SHG signal from the polymer system. The poling current present in a fresh sample is found to differ in both magnitude and temporal dependence to that observed in the sample during subsequent polings. These effects are interpreted by the initial presence of ionic impurities in the sample and the injection of charge into the polymer matrix during poling. The magnitude of the steady-state current eventually reached during the poling process is found to depend on temperature and is related to the mobility of charges. A sharp drop-off in SHG signal intensity that occurs when the poling electrodes are grounded is shown to result from the removal of surface charge that orients chromophore dipoles near the surface of the film; the decay in the macroscopic polarization that then occurs is prolonged by charges trapped in the polymer matrix. The build-up of trapped charge explains a memory effect in which the SHG

---

\* To Whom Correspondence Should Be Addressed

signal relaxation time gradually increases as the polymer is subjected to multiple polings until a steady-state value is reached. Finally, it is demonstrated that the charges trapped in the polymer matrix are released only after the polymer is heated to high above its temperature of glass transition and the SHG signal has completely decayed away.

Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By _____	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

## Introduction

Over the past decade much effort has been directed towards the study of polymers combined with nonlinear optical chromophores for possible applications in the developing technology of photonics.<sup>1,2,3</sup> These systems are of interest due to qualities that distinguish them from currently-available, inorganic NLO materials, the most important being low dielectric constants, high intrinsic nonlinearity, high damage threshold, fast response time and ease of processability.<sup>4,5</sup>

In order for second-order nonlinear optical and first-order electro-optical processes, e.g. second-harmonic generation (SHG) and the Pockels effect, to propagate in such systems, they must lack center of inversion symmetry (be noncentrosymmetric). Since the polymer systems used are, by nature, amorphous, some process must be applied in order to generate polar orientation of the incorporated dipolar nonlinear optical species. One of the most commonly used methods to do this has been electric-field (E-field) poling, both the contact type<sup>6,7</sup> and corona-discharge type.<sup>8,9</sup> In contact poling, the polymer is sandwiched between two electrodes to which a potential difference is applied. When corona poling is used, the polymer is placed on a conducting surface which is grounded and separated by an air gap from a metallic point source. Gas ions, formed by the application of an intense field to the point source, are deposited on the bare surface giving rise to an electric field in the film.

Many studies in this area have focused either on the magnitude of the second-order response from NLO chromophore/polymer systems and its temporal

stability<sup>2,3,10,11,12</sup> or on the physics of the orientation and relaxation processes that occur during poling and after the poling field has been removed.<sup>13,14,15,16</sup> However, little direct attention has been paid to the poling process itself, specifically to the complications that may arise from the presence of the charges that produce the poling electric fields.

The presence of surface charges on poled NLO films has been discussed somewhat in the literature, particularly with regards to corona poling.<sup>17,18,19,20</sup> (Here we describe as *surface* charges those charges which reside at the interface between the polymer film and the conducting substrate) The presence of surface charges can complicate the interpretation of temporal stability results obtained when corona poling is used since the charges deposited on the films are hard to remove and can remain for extended periods.<sup>20</sup> These persistent charges maintain a potential gradient in the film which helps to keep the chromophores oriented. It is believed that the use of contact poling avoids the complications that result from surface charges since they are easily removed by grounding.<sup>21,22</sup>

As is well known, charge can not only reside on the surface of polymer films, but can also be forced into the bulk.<sup>23</sup> This charge (*trapped* or *injected* charge) is more permanent than surface charge since it is not removed from the polymer by grounding. Although the class of materials known as electrets (in which charge is permanently injected into a polymer by the application of a poling voltage<sup>24</sup> or low-energy electron beam<sup>23</sup>) is well known in the literature<sup>25,26</sup> and has been used in several commercial applications (e.g. the electret microphone), the possible effects that injected charges have on the NLO behavior of these polymers have not been completely determined. In this

paper we present the results of a detailed study on the behavior of surface and injected charges in NLO polymer films and demonstrate some of the effects that these charges have on the NLO behavior of the materials. The results presented in this paper will be of interest to those working with polymer films subjected to a poling field.

In previous works we have suggested that the presence of trapped charge can affect the performance of nonlinear optical polymers in several ways. We have indicated that trapped charge is responsible for the "memory effect" in which the relaxation time of a poled polymer film increases with the number of poling cycles performed.<sup>27,28</sup> The presence of trapped charge has also been suggested as a possible reason for the great difference in the orientational relaxation times in a polymer as measured by the techniques of second harmonic generation and dielectric relaxation.<sup>29,30</sup> Finally, the presence of trapped charge has been used as an explanation for the effect that the magnitude of the poling field has on the relaxation time of the polymer.<sup>31</sup>

The NLO system with which we chose to examine these charge effects is *para*-nitroaniline (*p*NA) doped, to varying degrees, into polymethylmethacrylate (PMMA). This system was chosen not for its second-harmonic conversion efficiency, but as a model for demonstration because of its simplicity. In this study, thin films of *p*NA/PMMA were spin-coated onto conducting substrates that then served as the electrodes used in poling the samples. Surface and trapped charges were studied by simultaneous monitoring of the current in the poling circuit (using a very sensitive and stable electrometer) and the SHG signal from the polymer. As will be demonstrated, we have found that the charging of a polymer has both time and temperature dependencies.

In addition, it was found that the poling current observed in a fresh sample has a different time dependence than that obtained during subsequent polings. In addition, trapped charge is not released from the sample until it is heated far above the temperature of glass transition ( $T_g$ ) of the sample, after the SHG signal has fully decayed away.

The current that we measured in this study is similar, but not identical to, that measured in depolarization current studies of the molecular motions in polymers.<sup>32,33,34,35</sup> In the present case we measured the current from surface and trapped charges that originated with the electric poling field whereas depolarization currents result from the motion of an anisotropic arrangement of molecular dipoles. Although a depolarization current would also have been present in our samples, its contribution was completely dominated by that of the surface and trapped charges.

## Experiment

For this study thin PMMA films doped with 10 and 20 mole percent *p*NA were used. PMMA (weight average molecular weight 25,000 with a polydispersity index of 1.54 as measured in our laboratory by gel permeation chromatography) was obtained from Aldrich (catalog no. 18.223-0); *p*NA (purity 99+%) was also purchased from Aldrich (catalog no. 18,531-0). Both substances were used without further purification. Fig. 1 shows the chemical structures of the materials used. Glass transition temperatures of the polymer films were measured using differential scanning calorimetry (Perkin-Elmer Delta Series DSC 7, heating rate 20 °C/min) and were found to be 115 °C for the

10 mole % *p*NA/PMMA polymer and 110 °C for the 20 mole % polymer. The presence of *p*NA does not appear to depress the  $T_g$  of the pure polymer very much.

Thin films of the mixtures were prepared in the following manner. Appropriate amounts of *p*NA and PMMA were first combined in two clean sample vials. Enough chloroform ( $\text{CHCl}_3$ ) was then added to dissolve the *p*NA and PMMA to form slightly viscous solutions. To ensure complete dissolution of polymer and chromophore, the samples were mixed overnight in the capped vials. Afterwards the solutions were filtered into fresh, clean sample vials using 0.2  $\mu\text{m}$  syringe filters (Watterman) and disposable syringes in order to remove any undissolved particulates. In the final stage of solution preparation, a clean piece of lens tissue was placed over the open mouth of the sample vials and solvent was allowed to evaporate until the solutions were viscous enough to form good quality films of the correct thickness.

Clean glass slides (approximately 3 cm  $\times$  1.5 cm  $\times$  0.1 cm) coated with a thin conducting layer of indium-tin oxide (ITO) were used as sample substrates. Before polymer films were applied, all slides were cleaned by refluxing in trichloroethane and then isopropanol (approximately 2 hours in each). *p*NA/PMMA films were cast onto the substrates using a spin-coating apparatus (Headway Research, Inc.). When the films were spun, enough of the *p*NA/PMMA/chloroform solution was applied to completely cover the ITO side of the slides which were then spun at 1000 rpm for approximately 1 minute. Films (approximately 1-2  $\mu\text{m}$  in thickness) of good optical quality resulted. To remove any residual solvent, all spun films were immediately placed into a vacuum oven heated to 75 °C (above the boiling temperature of chloroform but below the  $T_g$  of the polymer);

films were kept overnight without a vacuum applied and then for another 24 hours under vacuum. Each sample that was used during the current measurement experiments was made by placing two slides in contact (film sides together). A small weight (approximately 1000 g) was then placed on top of each pair of slides to insure good physical contact between the films. The sandwiched films were kept in the vacuum oven at 75 °C until they were needed.

The optical setup used to record the SHG signal relaxations during this study was similar to that previously described.<sup>36</sup> Basically, it consisted of a Spectra-Physics GCR-11 Nd:YAG operating at 10 Hz and the associated optics. The sandwiched thin films were housed in a temperature-programmable sample oven ( $\pm 0.1$  °C) equipped with glass windows that were transparent to both the 1064 nm (fundamental) and 532 nm (second-harmonic) radiation. The second-harmonic radiation was detected with a photomultiplier tube (Hamamatsu model 960) biased at 900 V and the resulting signal was processed by a boxcar integrator (EG&G 4400, 4402) which was interfaced to a personal computer.

Fig. 2 is a schematic of the equivalent circuit used in detecting the charging/discharging current of the sandwiched polymer films. The current was detected using a Keithley model 6512 electrometer which has a maximum resolution of 100 aA ( $a = \text{atto} = 10^{-18}$ ). For all of the current measurements made in this study the electrometer was kept in its 200 nA range where the resolution is 10 pA. In order to record the current during experimentation, the analog output from the electrometer was interfaced to a personal computer using a data acquisition board. Continuous monitoring of the current was performed using software written under LabVIEW™ (National Instruments). The

program allowed the output from the electrometer to be sampled at a high rate (50 Hz); depending on the resolution desired, differing number of samples were averaged by the computer to form one data point. In order to isolate the electrometer from any possible electromagnetic noise generated by the laser flashlamps, the electrometer was powered by an electric circuit isolated from that of the laser. In addition, as suggested by the manufacturer, the electrometer was allowed to warm up for over two hours before it was used to make measurements.

For reasons described below, we used the contact electrode poling method instead of the corona discharge technique to pole our polymer films. In addition to the complication of the difficulty in removing surface charges, corona discharge in air results in the production of highly reactive nitrogen oxides which can damage the polymer.<sup>37</sup> Dao, et. al. have also reported that the application of a corona discharge in ambient air caused oxidation on the surface of the NLO polymer that they were using.<sup>38</sup> Another problem that is aggravated by corona poling is the rapid diffusion of chromophore out of the polymer matrix. Since during experimentation the polymer sample is heated to above the glass transition temperature and because one of the polymer surfaces is exposed to air when corona poling is used, chromophores can diffuse out of the sample through the uncovered side. Shown in Fig. 3 are results obtained by monitoring the concentration of *p*NA in a 20% *p*NA/PMMA polymer film via ultraviolet/visible (UV/Vis) spectroscopy (the absorption at  $\lambda_{\text{max}}$  was measured while a corona field was applied to the polymer at 114 °C, slightly above the  $T_g$  of the polymer). Although some of the decrease in signal would have been due to the orientation of chromophores in the polymer (relaxation of

electrochromism<sup>39</sup>), this would happen rather quickly (within the first 100 sec); the decrease in signal at times longer than 100 sec is due to the loss of chromophore from the sample. The loss of NLO chromophore could be mistaken for orientational relaxation which causes the SHG signal decay. As can be seen from the figure, the loss is fairly rapid with only about 50% of the original UV/Vis signal remaining after 1300 sec (approximately 20 min). Although the dimensions of *p*NA molecules are small compared to many NLO chromophores and thus diffusion of *p*NA might occur more rapidly than these larger molecules, this diffusion effect should be present to some extent in all doped NLO systems (We have observed the same effect with another, larger NLO chromophore also doped into PMMA<sup>40</sup>). Thus, in interpreting the orientational relaxation data at high temperature for films subject to corona poling one must consider the chromophore sublimation effect in order for the results to be meaningful. We also monitored (via UV/Vis) the concentration of the *p*NA chromophore in one of our sandwiched samples. In this case, the absorption at  $\lambda_{\max}$  remained constant with time with a poling field applied at 114 °C. The contact poling method thus minimizes the effect of chromophore sublimation and is suitable for a quantitative poling dynamics study.

Three types of experiments were performed in this study. In the first type, the sample was maintained at a fixed temperature (e.g. 100 °C). While at this temperature, the sample was poled by applying a large poling voltage across the ITO electrodes (480 V for a field of approximately 3 MVolt/cm). The SHG signal was monitored and once it maintained a steady-state plateau level, the voltage was removed by grounding the electrodes. (Grounding the electrodes served to remove the charges from the

electrode/polymer interface) The SHG signal was then monitored as it decayed away due to chromophore reorientation and polymer relaxation. During this isothermal processing, the current passing through the polymer was also measured. After the SHG signal decayed away completely, some time was allowed to elapse and the process was repeated. The second type of experiment was similar to the first except that in this case temperature was used as a parameter instead of elapsed time (i.e. isothermal poling/relaxation trials were performed at a number of temperatures with the thermal history of the polymer being erased between each trial). The third type of experiment performed in this study was the simultaneous measurement of the current and SHG signal as the temperature of a poled sample was ramped from room temperature to above the temperature of glass transition. To prepare the sample for this type of measurement a poling voltage was applied to the sample above  $T_g$ . The sample was then allowed to cool to room temperature with the poling field still applied; once there, the poling field was removed by grounding the electrodes. The sample was then reheated at a constant rate to high above the glass transition temperature of the polymer system. During this heating process both the SHG signal and the current were monitored. The results from all three types of experiments are reported below.

## Results and Discussion

Fig. 4 shows the current observed in a fresh 10 mole % sample as it was subjected to a poling voltage of 480 V at 100 °C and also the current present in the same sample the second and third times it was poled under identical conditions. In this experiment, the

poling voltage applied to the sample was ramped from 0 V to the maximum applied value of 480 V in 20 V increments at the rate of approximately one 20 V increment every 3 seconds. (High voltage can also be suddenly applied to a sample but increasing the voltage by ramping is a superior method as the former can often result in dielectric breakdown) During this time, the current was found to incrementally increase (following the voltage ramp) from a zero value to the value corresponding to the maximum applied voltage (beginning of each trace in Fig. 4). When the SHG signal (which was being monitored simultaneously) reached a steady-state value, poling was terminated by grounding the electrodes (the end of each trace) and the SHG signal then gradually decayed to the background level. The sample was then repoled under the same conditions and the relaxation procedure was repeated. There are several interesting aspects to this data. First, the maximum current observed in the fresh sample is much larger than that present after the sample has been previously poled. Second, after the sample has been poled once, the current reaches a steady-state value much more quickly than in the fresh sample. Third, the SHG relaxation times become longer after successive polings until a plateau level was reached (data shown in Fig. 7). Finally, the current behavior observed in the sample during the second and third polings (and all additional ones although they are not shown) is nearly identical.

The current behavior shown in Fig. 4 can be interpreted as follows. Although considerable care was taken to keep our samples clean during preparation, ionic impurities would still be present in the fresh sample and would be distributed randomly throughout it. When a poling field is applied to a fresh sample, these impurities migrate

towards the oppositely charged electrode where they are neutralized. At the same time, charge from the electrodes is being injected into the polymer. (Since the mass of an electron is much smaller than that of a positive charge, electrons are thus more easily injected and will therefore be the dominant type of charge in the polymer matrix) The initial current through the fresh sample will thus be very large since there are contributions from ionic impurities and charge injection effects. However, as the sample is poled the ionic impurities migrate out of the sample and thus the current resulting from this source will gradually decrease. Moreover, some of the electrons injected into the polymer will become trapped by the electronegative methacrylate groups of PMMA. As more electrons become embedded in the polymer, the electrons already present begin to impede the intake of additional electrons and current from this source also decreases as the poling field remains applied. The current in the fresh sample reaches a steady-state value only after the sample has been "cleansed" of ionic impurities and the flow of injected charges into and out of the sample reaches an equilibrium level.

After the fresh sample has been electrically "cleansed" of ionic impurities, it acquires an intrinsic resistivity characteristic of the sample at that temperature. The poling current observed during the second and third polings are that of the cleansed sample and is proportional to the characteristic electric resistivity of the polymer film. This explains the observation of a small constant steady-state poling current after the initial trial. The approach to the steady-state poling current is short after the first poling because no electrolysis takes place after the ionic impurities have been removed and injected charge already exists in the polymer matrix.

During the time between the first and second polings of the sample (and between the second and third, etc.), some of the charge that had become imbedded during the previous poling(s) would have slowly diffused out of the sample. The mean time for charge to diffuse out of a material is given by the expression<sup>23</sup>

$$\tau \propto \epsilon_0 \epsilon \rho(T). \quad (1)$$

Here,  $\tau$  is the relaxation time for decay of charge,  $\epsilon_0$  is permittivity of vacuum,  $\epsilon$  is the dielectric constant of the polymer system (together  $\epsilon_0 \epsilon$  describe the material's inherent charge-storage capacity) and  $\rho$  is the bulk resistivity of the polymer which is a function of temperature,  $T$ , as indicated. Since the resistivity of a cleansed polymer is high, this equation indicates that the relaxation time for charge diffusion in the polymer will be long. Thus, not much charge would have been able to diffuse out of our samples in the time (on the order of hours) between polings. When a poling voltage was applied to the sample again, it took only a short time for the charge that had diffused out of the polymer to be replaced. For the data shown in Fig. 4 approximately one-half hour separated the end of first poling from the beginning of the second and approximately one hour separated the end of the second from the beginning of the third. As can be seen in both cases, it takes only a few minutes for the current to reach a constant value after the poling voltage reaches its maximum level.

The effect of the temperature dependence of  $\rho(T)$  on the mobility of charge in the polymer is demonstrated in Fig. 5. This figure shows the current that was observed in a 10 mole % *p*N<sub>A</sub>/PMMA polymer film as a function of time at several temperatures.

The sample used in this experiment had been cleansed of ionic impurities as discussed above. For the poling current measurements at the various temperatures, the sample was heated to above its  $T_g$  (at a rate of 0.5 °C/min) and remained at that temperature for approximately twenty minutes before it was cooled down (again at 0.5 °C/min) to the temperature of interest. One notes that the magnitude of the initial poling current increases with increasing temperature. Moreover, the poling current of each trace starts out at a high level and then decreases to a steady-state value. This behavior is characteristic of the polymer charging process as described above. The steady-state current is also higher at higher temperatures. These results are consistent with Eq. 1 which shows that the charge diffusion time decreases with increasing temperature as the resistivity of the polymer decreases with increasing temperature.

As mentioned above, both surface and trapped charges are able to retard the decay of the SHG signal. Removing the surface charges by grounding the electrodes allows the dipoles near the surface to quickly reorient, resulting in a rapid drop-off in the SHG signal. As shown in our previous work,<sup>27-29,39,41</sup> macroscopic polarization in the bulk can be induced by using a high poling field (comparable in magnitude to the one used in the present study). The SHG intensity arising from the bulk polarization decays very slowly and is strongly affected by the charges trapped in the interior of the polymer that are not removed by grounding.

Fig. 6 shows the decay behavior of the SHG signal for a 10 mole % *p*NA/PMMA sample at 100 °C before, during and after the electrodes were grounded. The SHG signal intensity and current flowing through the sample immediately before and after the poling

electrodes were grounded are also shown in the inset. As can clearly be seen, before the electrodes were grounded the SHG signal and current are both at constant levels (with some fluctuations in the SHG signal intensity). At the time when the electrodes were grounded, a spike is observed in the current trace during which the current reverses polarity and then decreases rapidly to zero; at the same time, the SHG signal also takes a step drop-off but does so at a slower rate. After removal of the surface charges, trapped charges within the polymer will diffuse out, but they diffuse at such a slow rate that the diffusion current is practically not detectable.

The rate at which surface charges are able to leave the sample is clearly a function of the resistance present in the electric circuit leading to ground. In the present case, no additional resistance was added to the circuit and the surface charges were able to leave very quickly (hence the presence of the large spike in the figure). If, however, the resistance in the wires had been increased (e.g. by adding an external variable resistor), the rate at which the surface charges departed from the surface of the film could have been controlled; this, in turn, would have affected the rate of the SHG signal decay. The effect that the magnitude of an external resistance has on the decay of the SHG signal film has been demonstrated in a previous work.<sup>28</sup>

One notes in Fig. 6 that the magnitude of the SHG signal immediately following the removal of the surface charge is almost half of that present before the electrodes were grounded. This suggests that the dipoles near the surface which are oriented by the surface charges contribute significantly to the SHG intensity. As the surface charges are removed, rapid reorientation of the surface dipoles occurs and a rapid decrease in the

SHG intensity results. Moreover, the SHG signal due to the third-order effect associated with the second hyperpolarizability also diminishes as the surface charges are removed. These two effects contribute to the rapid drop-off of the SHG signal. After the rapid drop-off, the remaining SHG signal decays slowly to the background value. The slow SHG decay is associated with the reorientational relaxation of the oriented dipoles in the bulk, which, as shown below, is strongly affected by the trapped charge.

Similar to results report previously by our laboratory<sup>27,28,29</sup> we have observed an interesting memory effect associated with the establishment of the NLO macroscopic polarization in our *p*N<sub>A</sub>/PMMA polymer films. Listed in Table I and plotted in Fig. 7 are the average relaxation times of one of our 10 mole % *p*N<sub>A</sub>/PMMA polymer films, kept at a constant 100 °C, as a function of elapsed time,  $t_{elp}$  ( $t_{elp}$  is defined as the amount of time elapsed since the beginning of the first poling/decay cycle). Since the SHG signal decay was not single exponential, we have fitted the time dependence of the signal to the Kohlrausch-Williams-Watts (KWW) stretched exponential equation (Eq. 2).

$$\chi^{(2)} \propto \sqrt{I_{SHG}} = ae^{-\left(\frac{t}{\tau}\right)^\gamma} \quad (2)$$

The average relaxation time,  $\langle \tau \rangle$ , was calculated according to the equation

$$\langle \tau \rangle = \int_0^{\infty} \exp\left(-\left(\frac{t}{\tau}\right)^\gamma\right) dt = \frac{\tau \Gamma\left(\frac{1}{\gamma}\right)}{\gamma}. \quad (3)$$

The KWW equation is commonly used to describe the relaxations occurring in complex systems.<sup>42,43,44</sup> Here  $\tau$  is the characteristic relaxation time of the SHG signal decay,  $a$  is the signal amplitude,  $\gamma$  is the width parameter (often interpreted as describing a distribution of relaxation times) whose value is  $0 < \gamma \leq 1$  and  $\Gamma$  is the gamma function. The measured intensity of the second-harmonic light,  $I_{\text{SHG}}$ , is directly proportional to  $|\chi^{(2)}|^2$  where  $\chi^{(2)}$  is the nonlinear susceptibility of the polymer system.<sup>45</sup> As can be seen from the table and figure, the average relaxation time depends strongly on the number of poling cycles performed and reaches a steady-state value only after many poling/decay cycles. Notice also from the table that the average relaxation time from the initial poling of the sample is much larger than the average relaxation times of the subsequent polings and that only after multiple polings does  $\langle \tau \rangle$  approach that obtained initially. This is a demonstration of the strong effect that the initial presence of ionic impurities had on the physical properties of the polymer.

The results shown in Fig. 7 can be understood in terms of the charge injection effect that occurs during the poling process. The presence of trapped charges in the polymer matrix is expected to retard chromophore reorientation. Those charges trapped near the surface of the polymer will create an electric field inside the polymer which will orient the dipoles in the same direction as the poling field. Charge trapped in the interior of the polymer can correlate the motion of chromophore dipoles, thereby stabilizing the dipolar reorientation. Since the rate of diffusion of the trapped charges out of the polymer is slow compared with the relaxation of the SHG signal,<sup>46</sup> the effects of the

trapped charges will be present throughout the entire SHG signal decay. It follows from the above that the greater the density of charge in the polymer, the slower the relaxation rate will be. As was discussed in relation to Fig. 4, it takes many poling cycles (or very long poling times) for the polymer to become saturated with charge. Thus, the reorientational relaxation rate of the chromophores will be retarded gradually until the concentration of charge in the polymer reaches a maximum level; once this charge concentration has reached its maximum level the rate of SHG signal decay should then remain at a near constant value. However, if the polymer is allowed to remain at a constant temperature for an extended period of time, charges will gradually diffuse out of the polymer (at a rate which will depend on the temperature) and the relaxation rate will increase. Note in the table and figure that the great increase in the average relaxation time between poling trials 8 and 9 is consistent with a very long poling time and that the decrease by a factor of two in the average relaxation time between trials 10 and 11 is consistent with a decrease in trapped charge that occurred when the polymer was allowed to remain for a long period. However, at room temperature the relaxation time of charge diffusion is much longer than the time of the experiment; for practical purposes one may consider the lifetime of trapped charges to be infinite at room temperature.

Fig. 8 shows the measurement of the SHG signal and the current associated with the release of trapped charges for a 10 mole % *p*NA/PMMA polymer sample. In this experiment, the sample was first heated to above its glass transition temperature. A poling voltage of 480 V was then (incrementally) applied to polarize the sample. After achieving a steady-state SHG signal the sample was allowed to cool, with the poling field

still applied, to room temperature at a rate of 0.5 °C/min. Once the sample reached room temperature, the poling field was removed by grounding the poling electrodes. The sample was then heated (again at a rate of 0.5 °C/min) to above its glass transition temperature (160 °C in this case). During heating, both the current flowing through the sample and the SHG signal were continuously monitored. As can be seen from the figure, the current corresponding to the charge diffusion remains practically zero up to  $T_g$ . The SHG signal has an initial drop-off that occurs from 35 °C to approximately 45 °C. This initial drop-off is apparently associated with the  $\beta$  relaxation process of the PMMA.<sup>47</sup> After the initial drop-off, the SHG intensity only decreases slightly until the glass transition region begins. Above the glass transition region, the SHG signal decreases rapidly to zero within a span of approximately 10 °C. This is a result of the movement of the backbone of the polymer chains that begins in the vicinity of  $T_g$  ( $\alpha$  relaxation<sup>47</sup>). Since the motion of the NLO dipoles is coupled to the movement of the polymer chains, this movement randomizes the NLO chromophore dipole orientation. Once the SHG signal has decayed completely away, the current flowing through the sample begins to dramatically increase. This increased current at higher temperatures is due apparently to the release of trapped charges. The mobility of the charges is clearly coupled to the mobility of the polymer chains. One notes that the current resulting from the diffusion of trapped charges reaches a maximum at about 160 °C. Above this high temperature the sample began to decompose and the measurement had to be stopped. However, if special care had been taken to conduct the experiment in an inert atmosphere to avoid oxidation of the polymer, one would expect the current to have gone through a

maximum as the temperature was raised further and as more of the charge trapped in the polymer was released. However, as the instrumentation necessary to perform this experiment is rather elaborate, it was not carried out during the present study.

## Conclusions

To summarize, we have carried out a detailed investigation into the behavior of surface and trapped charges in thin films of a guest-host nonlinearly active polymer. We have shown a clear correlation of the SHG intensity with the poling current. We have shown that as a polymer sample is poled for the first time the current through the sample is very large but gradually decreases to a plateau level. When the sample is poled again after its initial, first poling, the current through the sample starts out at a much lower level and more quickly reaches the plateau level. We have attributed these results to ionic impurities initially present in the sample and to the accumulation of charges which are injected into the sample. Furthermore, we have confirmed the gradual lengthening of the SHG signal relaxation time as the polymer film is successively poled and have provided evidence to associate this "memory" effect with the poling current and retardation of relaxation time. We have attributed this lengthening to the accumulation of trapped charges in the polymer.

By studying the current through the samples during the poling process, we have found that the plateau current is found to depend on temperature and is related to the mobility of the charges. By simultaneously monitoring the current through the sample and the SHG signal from the sample, we have been able to show that the drop-off of the

SHG signal is strongly correlated to the removal of surface charges. We have attributed the sharp decrease in the SHG signal to the reorientation of NLO chromophores near the surface of the sample. The slow decay of the remaining SHG signal has been associated with the relaxation of the chromophore dipoles oriented in the interior of the sample. The reorientation of these chromophores has been shown to be greatly retarded by the presence of trapped charges. Finally, we have shown the trapped charges are released only when the sample is heated to above its glass transition temperature and after the SHG signal has decayed completely away.

### Acknowledgments

This supported by the Office of Naval Research, the National Science Foundation (DMR 912933) and the Center for Materials Research and Analysis at the University of Nebraska - Lincoln.

## References

---

- <sup>1</sup>D.J. Williams, Ed., *Nonlinear Optical Properties of Organic and Polymeric Materials*, ACS Symposium Series 233, American Chemical Society: Washington, D.C., 1982.
- <sup>2</sup>D.S. Chemla, J. Zyss, Eds., *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press: New York, 1987; Vols. 1, 2.
- <sup>3</sup>D.M. Burland, R.D. Miller and C.A. Walsh, *Chem. Rev.*, **94**, 31 (1994).
- <sup>4</sup>K.D. Singer, M.G. Kuzyk and J.E. Sohn in *Nonlinear Optical and Electroactive Polymers*, Plenum: New York, 1987 p. 189-204.
- <sup>5</sup>P.N. Prasad and D.J. Williams, *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, John Wiley & Sons, Inc.: New York, 1991.
- <sup>6</sup>K. Singer, J. Sohn and S. Lalama, *Appl. Phys. Lett.*, **49**, 248 (1986).
- <sup>7</sup>M. Eich, A. Sen, H. Looser, G.C. Bjorklund, J.D. Swalen T. Tweig and D.Y. Yoon, *J. Appl. Phys.*, **66**, 2559 (1989).
- <sup>8</sup>M. Eich, A. Sen, H. Looser, G.C. Bjorklund, J.D. Swalen, R. Twieg and Y.D. Yoon, *J. Appl. Phys.*, **66**, 2559 (1989)
- <sup>9</sup>M. Mortazavi, A. Knoesen, S. Kowel, B. Higgins, and A. Dienes, *J. Opt. Soc. Am. B.*, **6**, 733, (1989).
- <sup>10</sup>H. Katz, K. Singer, J. Sohn, C. Dirk, L. King and H. Gordon, *J. Am. Chem. Soc.*, **109**, 6561 (1987).
- <sup>11</sup>Y. Shi, W. Steier, L. Yu, M. Chen and L. Dalton, *Appl. Phys. Lett.*, **58**, 1131 (1991).
- <sup>12</sup>S. Yitzchaik, G. Berkovic and V. Krongaus, *Opt. Lett.*, **15**, 1120 (1990).

- 
- <sup>13</sup>S.S. Gong, T. Goodson III, H.W. Guan and C.H. Wang, *Nonlinear Optics*, **6**, 92 (1993).
- <sup>14</sup>T. Goodson III, S.S. Gong and C.H. Wang, *Macromolecules*, **27**, 4278 (1994).
- <sup>15</sup>G. Boyd, C. Francis, J. Trend and D.J. Ender, *J. Opt. Soc. Am. B*, **8**, 887 (1991).
- <sup>16</sup>M. Stahlein, C.A. Walsh, D.M. Burland, R.D. Miller, R.J. Twieg and W. Volksen, *J. Appl. Phys.*, **73**, 8471 (1993).
- <sup>17</sup>S. Yitzchaik, G. Berkovic and V. Krongaus, *J. Appl. Phys.*, **70**, 225 (1991).
- <sup>18</sup>H. Hampsch, J. Torkelson, S. Bethke and S. Grubb, *J. Appl. Phys.*, **67**, 1037 (1990).
- <sup>19</sup>K.M. White, C.V. Francis and A.J. Isackson, *Macromolecules*, **27**, 3619 (1994).
- <sup>20</sup>H.L. Hampsch, J. Yang, G.K. Wong and J.M. Torkelson, *Macromolecules*, **23**, 3640 (1990).
- <sup>21</sup>J. Zyss, ed., *Molecular Optoelectronics: Materials, Physics and Devices*, Academic Press: New York, 1993.
- <sup>22</sup>K.D. Singer and L.A. King, *J. Appl. Phys.*, **70**, 3251 (1991).
- <sup>23</sup>A.R. Blythe, *Electrical Properties of Polymers*, Cambridge University Press: Cambridge, 1979.
- <sup>24</sup>J. van Turnhout, *Polymer J.*, **2**, 173 (1971).
- <sup>25</sup>G.M. Sessler, Ed., *Electrets*, Springer-Verlag: Berlin, 1980.
- <sup>26</sup>J. van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets*, Elsevier: Amsterdam, 1975.
- <sup>27</sup>C.H. Wang, H.W. Guan and S.H. Gu, *J. Non-Crystal. Solid*, **172**, 705 (1993).
- <sup>28</sup>H.W. Guan, C.H. Wang and S.H. Gu, *J. Chem. Phys.*, **100**, 8454 (1994).

- 
- <sup>29</sup>H.W. Guan, M.A. Pauley, T. Brett and C.H. Wang, *J. Polym. Sci., Part B, Polym. Phys.*, (1994).
- <sup>30</sup>H.W. Guan, M.A. Pauley and C.H. Wang, *Bulletin of Amer. Phys. Soc.*, **40**, 158 (c'32 10) (1995).
- <sup>31</sup>C. Ye, N. Minami, T.J. Marks, J. Yang, and G.K. Wong, *Macromolecules*, **21**, 2899 (1988).
- <sup>32</sup>A. Bernes, R.F. Boyer, D. Chatain, C. Lacabanne and J.P. Ibar in *Order in the Amorphous State of Polymers* (Ed. S.E. Keinath), Plenum Press, London, 1987.
- <sup>33</sup>B.B. Sauer and P. Avakian, *Polymer*, **33**, 5128 (1992).
- <sup>34</sup>K. Zimmerman, F. Ghebremichael, M.G. Kuzyk and C.W. Dirk, *J. Appl. Phys.*, **75**, 1267 (1994)
- <sup>35</sup>M. Topic and K. Katovic, *Polymer*, **35**, 5536 (1994).
- <sup>36</sup>H.W. Guan and C.H. Wang, *J. Chem. Phys.*, **98**, 3463 (1993).
- <sup>37</sup>D.S. Weiss, *J. Imag. Sci.*, **434**, 132 (1990).
- <sup>38</sup>P.T. Dao and D.J. Williams; W.P. McKenna, K. Goppert-Berarducci, *J. Appl. Phys.*, **73**, 2043 (1993).
- <sup>39</sup>O.K. Song, H.W. Guan and C.H. Wang, *J. Phys. Chem.*, **99**, 3540 (1995).
- <sup>40</sup>M.A. Pauley, C.H. Wang and A. K.-Y. Jen (*manuscript in preparation*).
- <sup>41</sup>C.H. Wang, S.H. Gu and H.W. Guan, *J. Chem. Phys.*, **99**, 5597 1993.
- <sup>42</sup>C. Lindsey and G.J. Patterson, *J. Chem. Phys.*, **73**, 3348, (1980).
- <sup>43</sup>C.H. Wang, G. Fytas, D. Lilge and Th. Dorfmueller, *Macromolecules*, **14**, 1363 (1981).

---

<sup>44</sup>I. Teraoka, D. Jungbauer, B. Reck, D. Yoon, R. Twieg and C. Willson, *J. Appl. Phys.*, **69**, 2568 (1991).

<sup>45</sup> Shen, Y.R., *Principles of Nonlinear Optics*, Wiley: New York, 1984.

<sup>46</sup>W. Köhler, D.R. Robello, P.T. Dao, C.S. Willand and D.J. Williams, *J. Chem. Phys.*, **93**, 9157 (1990).

<sup>47</sup> N.G. McCrum, B.E. Read and G. Williams, *Anelastic and Dielectric Effects in Polymer Solids*, John Wiley & Sons: New York, 1967.

Table

Table I - Change in the average relaxation time of the SHG signal decay and width parameter as a function of elapsed time and poling duration.

Trial	Elapsed Time (hr)	Poling Time (min)	$\langle\tau\rangle$ sec	$\gamma$
1	0	83.6	1907.85	0.4546
2	1:14	35.1	513.85	0.7517
3	3:18	34.5	567.08	0.8440
4	21:46	85.2	765.18	0.7727
5	23:25	58.4	881.18	0.7622
6	27:59	42.5	940.94	0.7569
7	30:01	27.3	858.66	0.8501
8	31:54	36.3	954.78	0.8074
9	48:05	960.0	1842.10	0.8140
10	50:20	14.7	1927.16	0.7364
11	68:10	22.5	1081.56	0.6476
12	70:18	24.1	1420.98	0.8085
13	73:41	24.2	1409.32	0.8726

## Figure Captions

Figure 1- Chemical structures of the materials used in during the course of this study.

Figure 2 - Equivalent circuit of the electrical setup used to measure current through the samples.

Figure 3 - A plot of  $\lambda_{\max}$  vs. time for a 20 mole % *p*NA/PMMA sample being subjected to corona poling with a 2.5 kV positive voltage applied to the metallic point source. Notice the rate at which the UV/Vis signal decreases (it has decreased by almost 50% in approximately 20 minutes). The solid line is a plot of the equation  $I_{abs} = I_a e^{-(t/\tau)} + I_b$  with the fitted parameters  $I_a = 2.19$ ,  $I_b = 1.95$  and  $\tau = 5202.81$  sec.

Figure 4 - Current through a fresh 10 mole % *p*NA/PMMA polymer sample during its first three polings. The large current through the sample during its first poling is the result of contributions from both ionic impurities and injected charge.

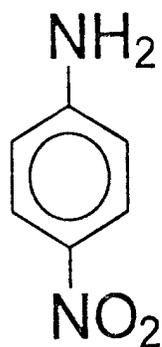
Figure 5 - Current through a 10 mole % *p*NA/PMMA polymer sample (not fresh) as a function of temperature. In-between polings the sample was heated to above its glass transition temperature where it remained for approximately 20 minutes before being cooled down to the temperature of interest.

Figure 6 - Average SHG signal relaxation time plotted vs. elapsed time for a 10 mole % *p*NA/PMMA sample (quantities defined in the text).

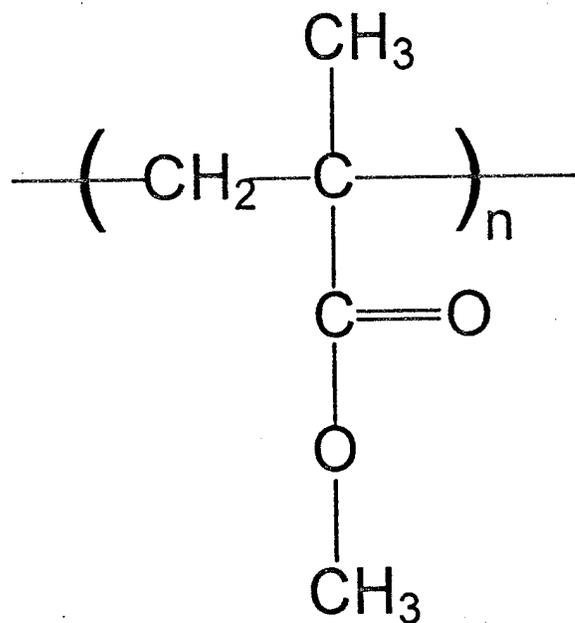
Figure 7 - SHG signal from a 10 mole % *p*NA/PMMA sample before, during and after the grounding of the electrodes. Note that more than 50 % of the SHG signal disappears after the electrodes are grounded. Inset - Expansion of the data in main trace

around the time that the poling electrodes were grounded and the current through the sample at this time.

Figure 8 - The thermal discharge of charge from a 10 mole % *p*NA/PMMA sample. Both the SHG signal (O) and the current (•) are shown.



*para*-nitroaniline (*p*NA)



polymethylmethacrylate (PMMA)

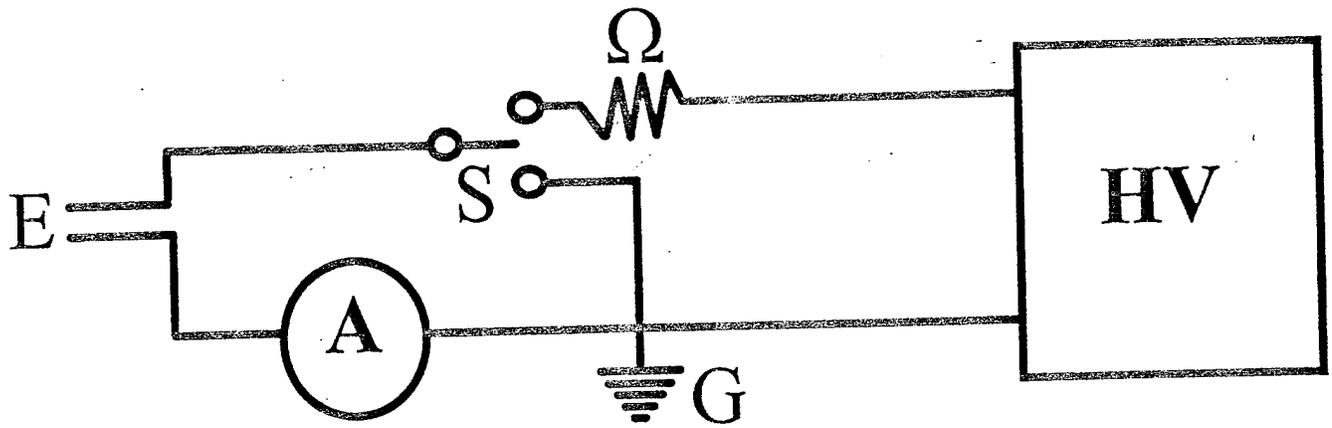


Fig 2

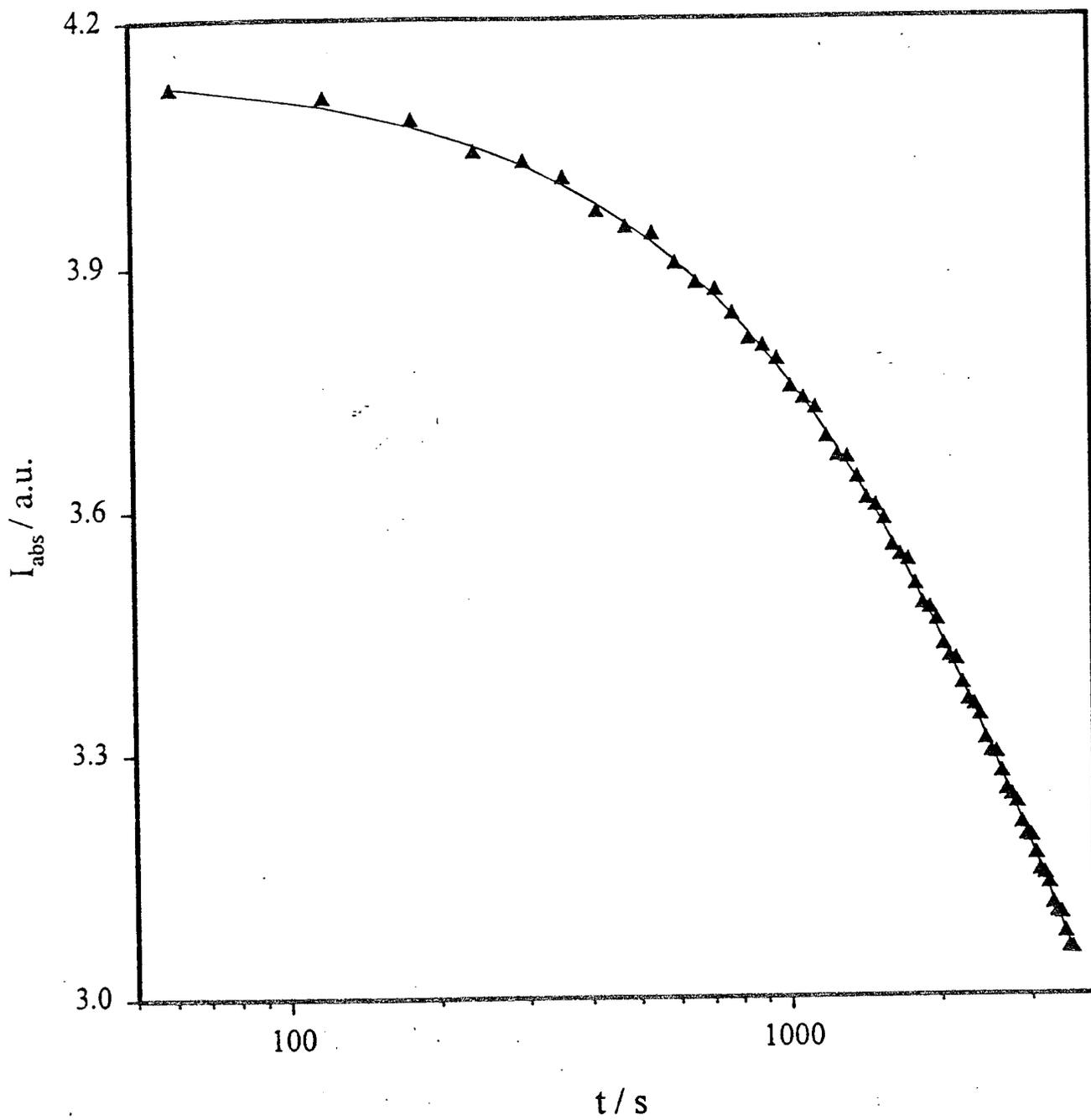


Fig 3

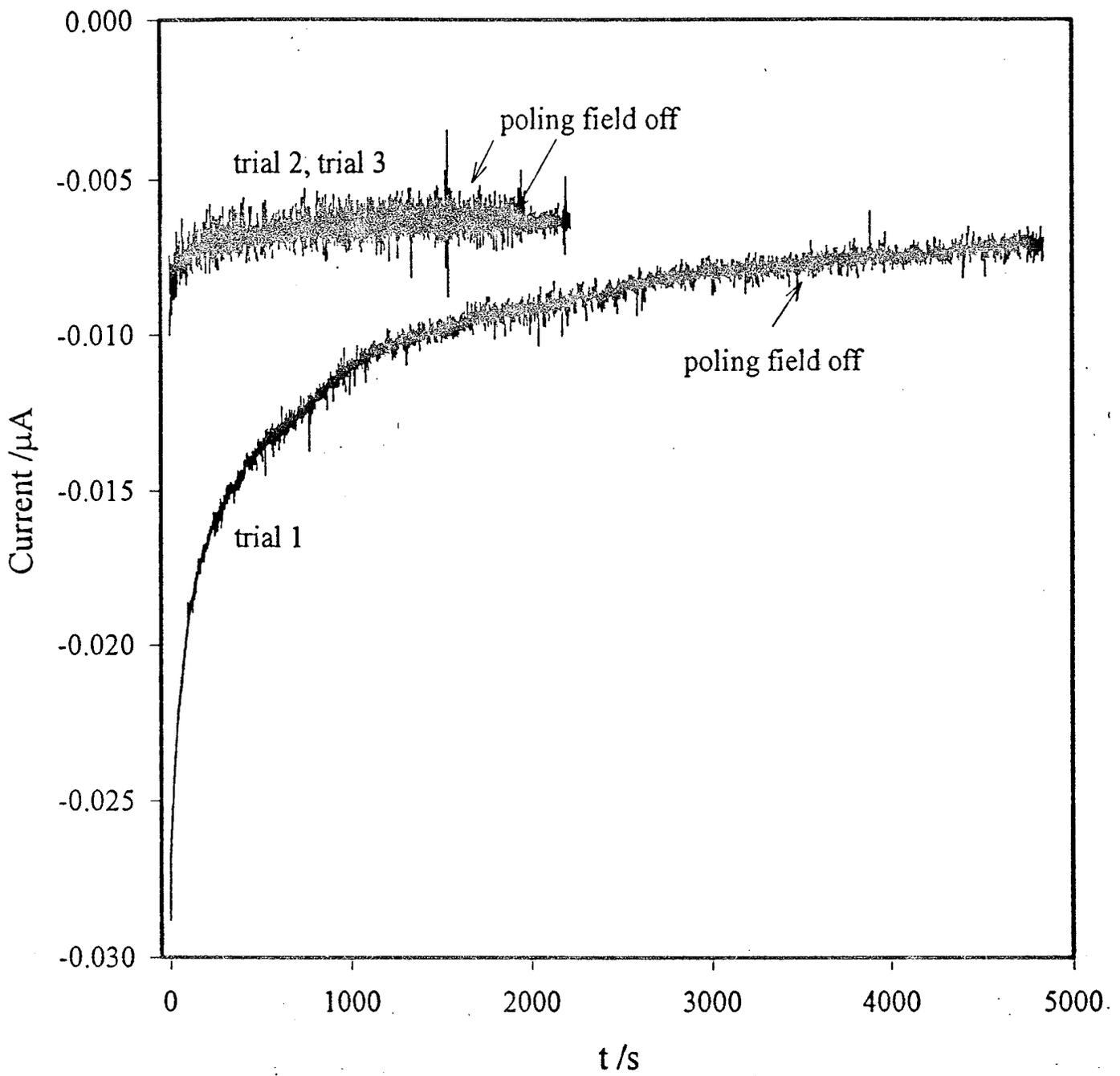
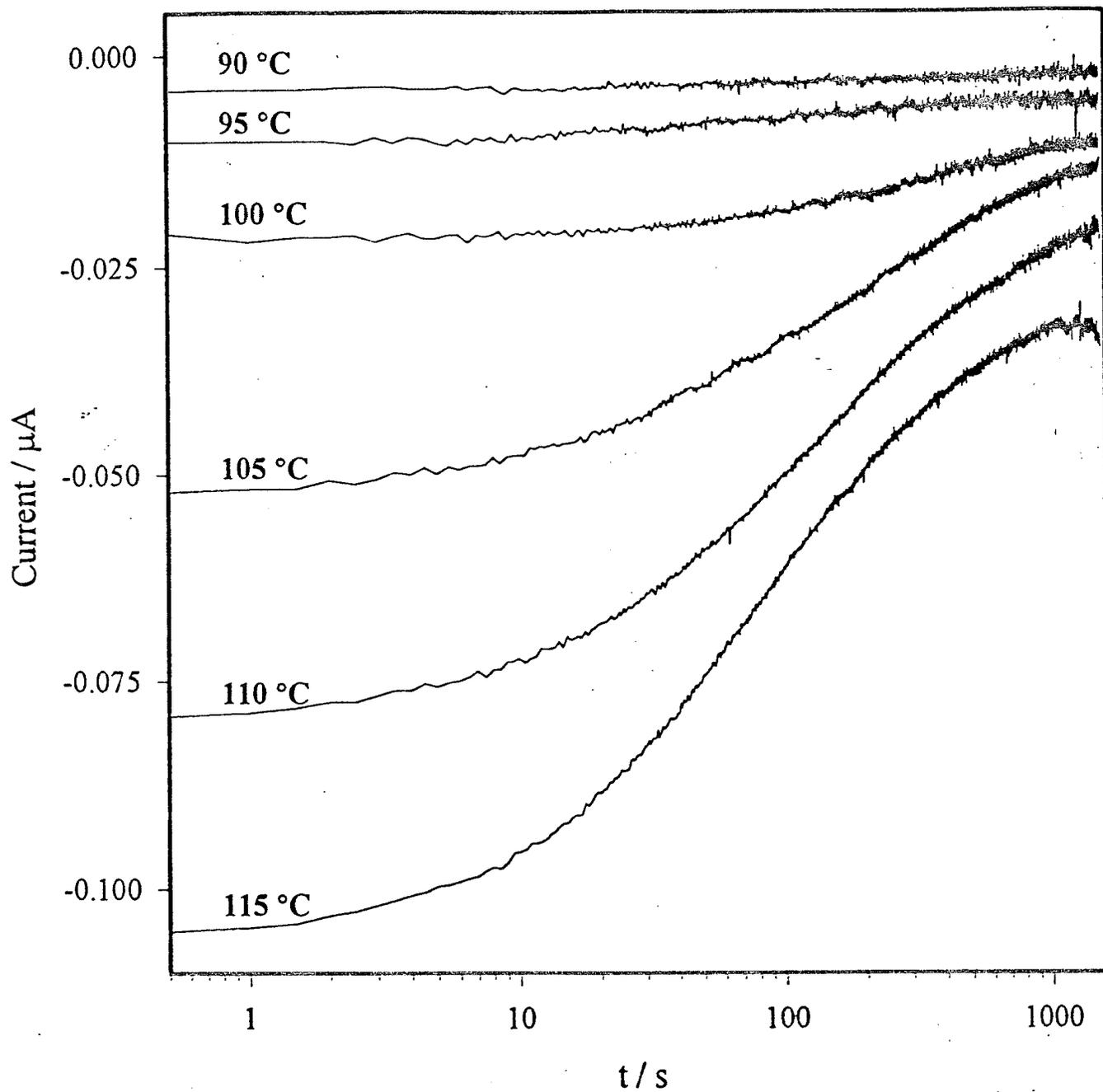


Fig 4



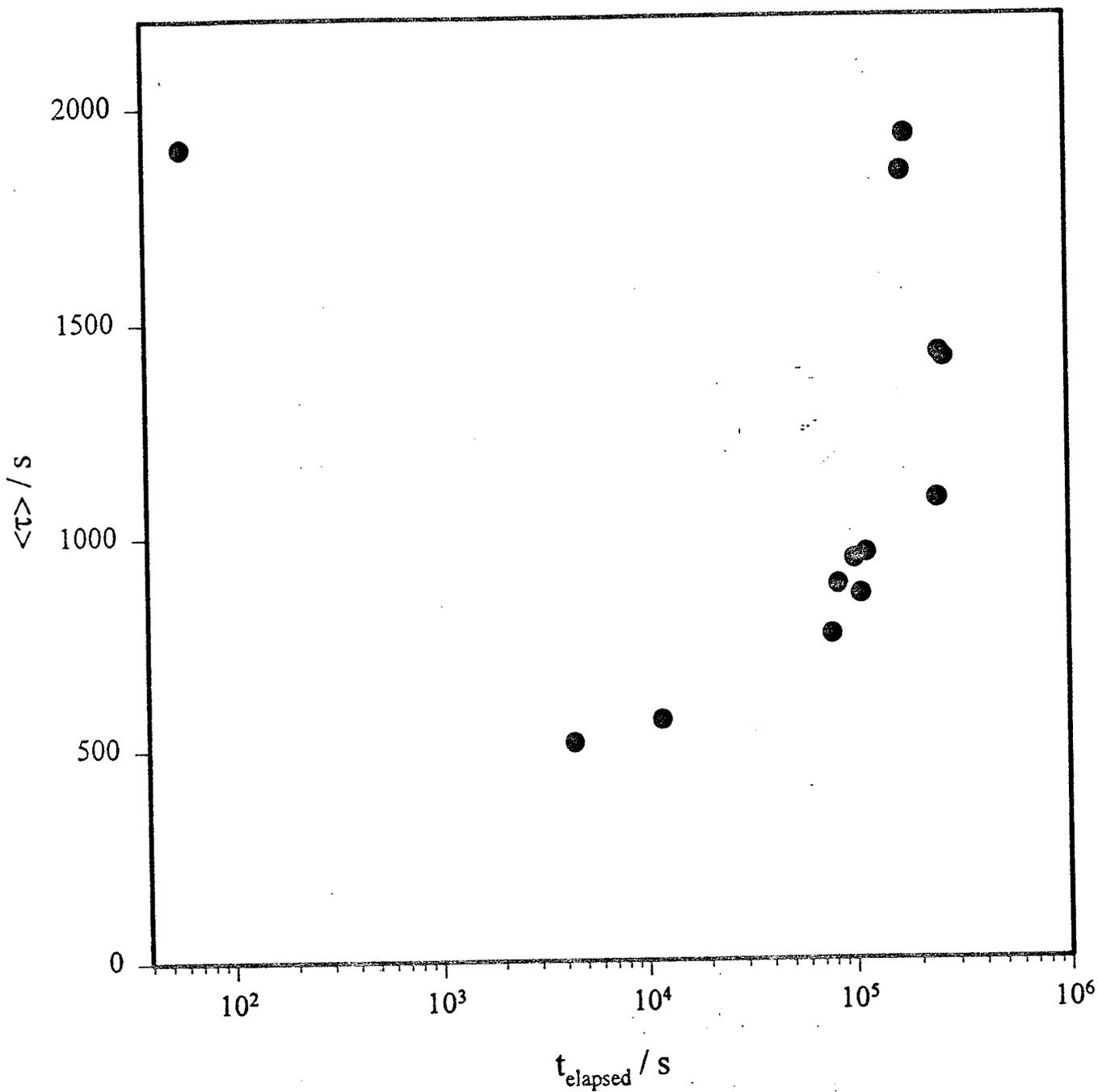


Fig 6

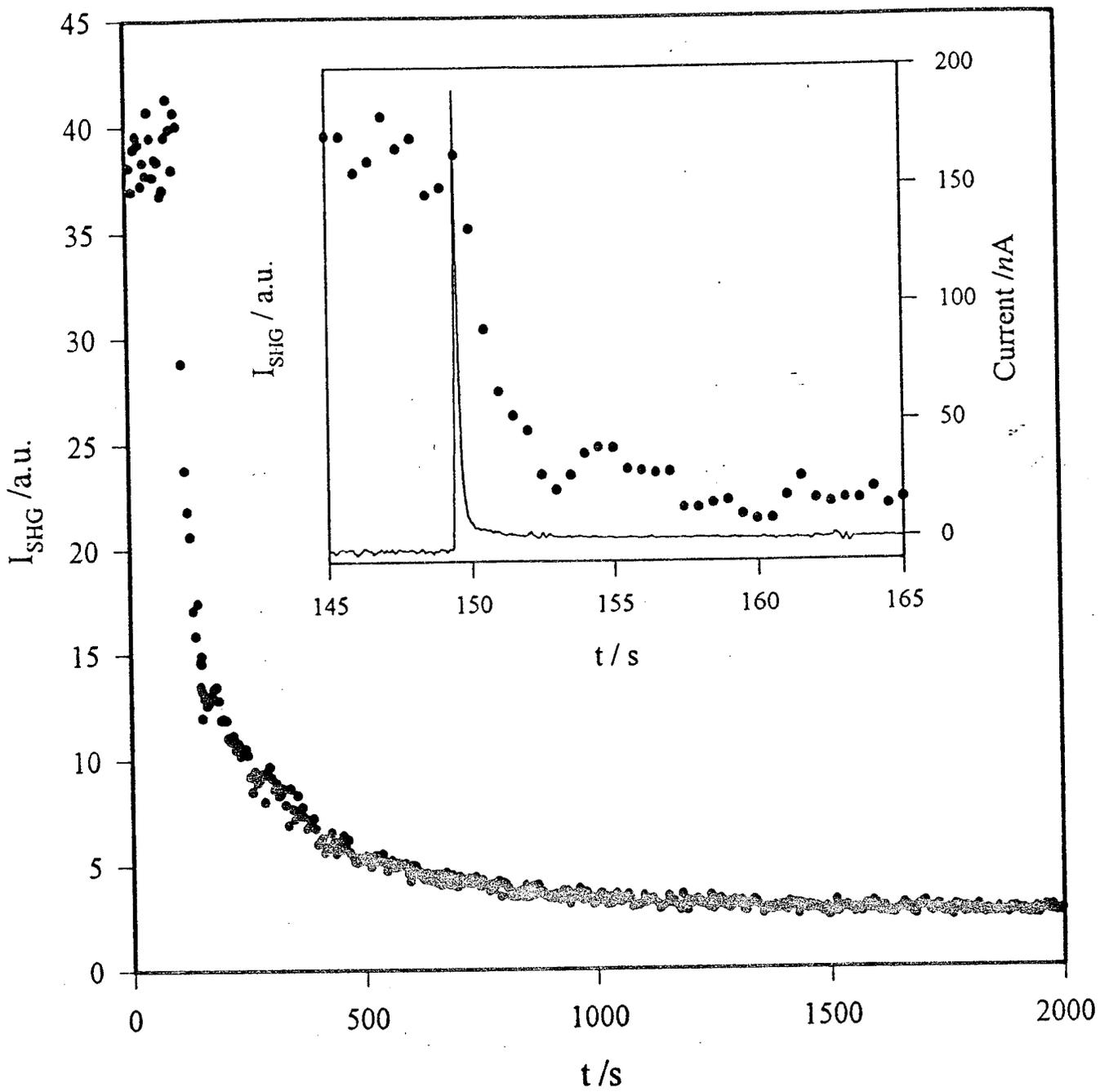
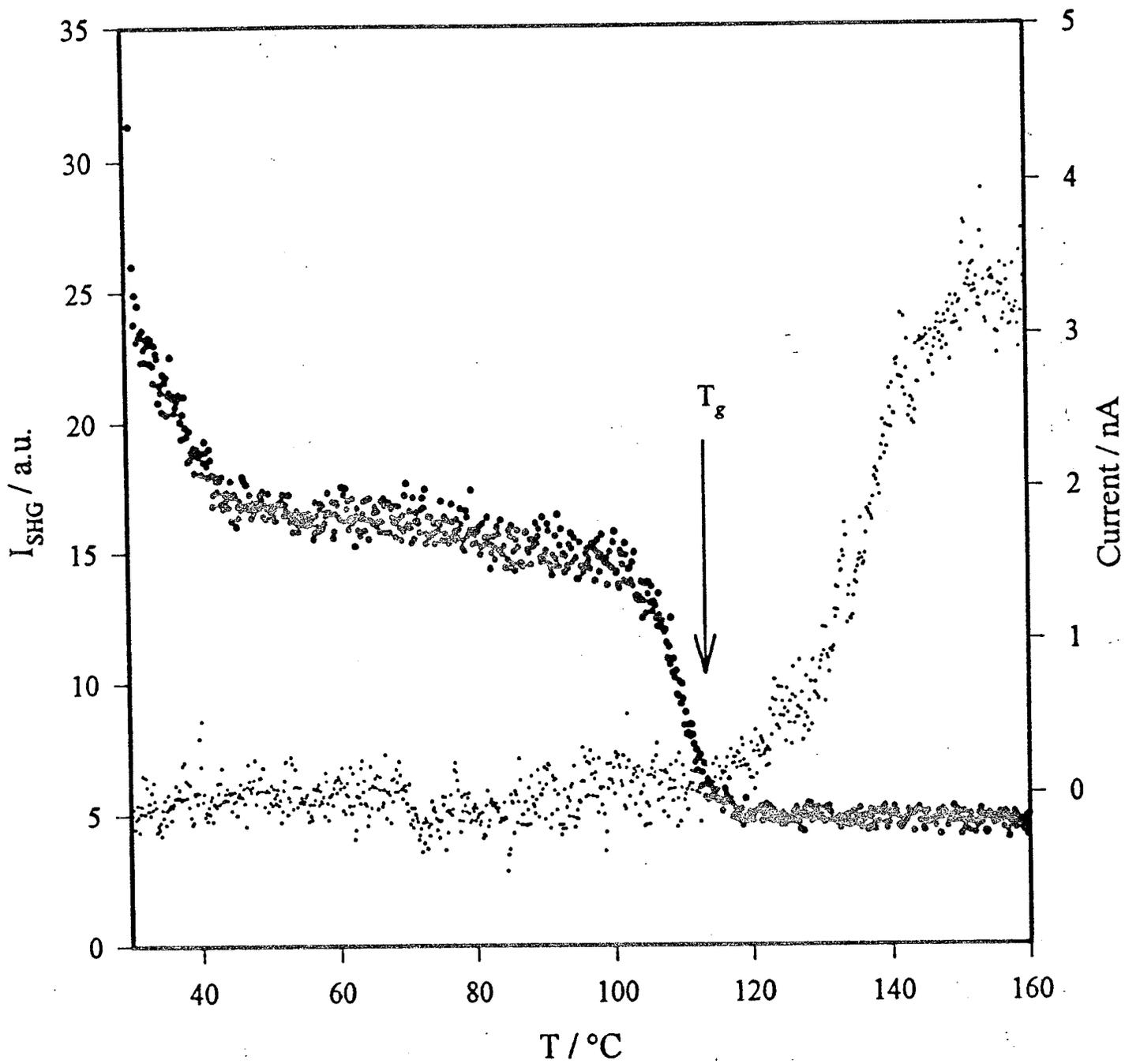


Fig 7



# REPORT DOCUMENTATION PAGE

Form Approved  
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE <b>June 20, 1995</b>	3. REPORT TYPE AND DATES COVERED <b>Technical</b>	
4. TITLE AND SUBTITLE <b>Poling Dynamics and Investigation into the Behavior of Trapped Charges in Poled Polymer Films for Nonlinear Optical Applications</b>			5. FUNDING NUMBERS <b>#313H030 Kenneth J. Wynne</b>	
6. AUTHOR(S) <b>M.A. Pauley, H.W. Guan and C.H. Wang</b>				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>632 Hamilton Hall Department of Chemistry University of Nebraska-Lincoln Lincoln, NE 68588-0304</b>			8. PERFORMING ORGANIZATION REPORT NUMBER <b>35</b>	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) <b>Office of Naval Research 800 N. Quincy Street Arlington, VA 22217-5000</b>			10. SPONSORING/ MONITORING AGENCY REPORT NUMBER <b>Office of Naval Research</b>	
11. SUPPLEMENTARY NOTES <b>Journal of Applied Physics, submitted</b>				
12a. DISTRIBUTION/AVAILABILITY STATEMENT <b>Distribution Unlimited</b>			12b. DISTRIBUTION CODE <b>Unlimited</b>	
13. ABSTRACT (Maximum 200 words) <p>The behaviour of surface and trapped charges that originate during contact electric-field poling of a model guest-host nonlinearly active polymer has been investigated. Charge effects in this films of <i>para</i>-nitroaniline doped polymethylmethacrylate were studied during and after the poling process by simultaneous measurement of the current through the poling circuit and the SHG signal from the polymer system. The poling current present in a fresh sample is found to differ in both magnitude and temporal dependence to that observed in the sample during subsequent polings. These effects are interpreted by the initial presence of ionic impurities in the sample and the injection of charge into the polymer matrix during poling. The magnitude of the steady-state current eventually reached during the poling process is found to depend on temperature and is related to the mobility of charges. A sharp drop-off in SHG signal intensity that occurs when the poling electrodes are grounded is shown to result from the removal of surface charge that orients chromophore dipoles near the surface of the film; the decay in the macroscopic polarization that then occurs is prolonged by charges trapped in the polymer matrix. The build-up of trapped charge explains a memory effect in which the SHG signal relaxation time gradually increases as the polymer is subjected to multiple polings until a steady-state value is reached. Finally, it is demonstrated that the charges trapped in the polymer matrix are released only after the polymer is heated to high above its temperature of glass transition and the SHG signal has completely decayed away.</p>				
14. SUBJECT TERMS			15. NUMBER OF PAGES <b>29</b>	
17. SECURITY CLASSIFICATION OF REPORT <b>Unclassified</b>			16. PRICE CODE	
18. SECURITY CLASSIFICATION OF THIS PAGE <b>Unclassified</b>		19. SECURITY CLASSIFICATION OF ABSTRACT <b>Unclassified</b>		20. LIMITATION OF ABSTRACT <b>Unlimited</b>

