Dopant Orientation Dynamics in Doped Second-Order Nonlinear Optical Amorphous Polymers. 2. Effects of Physical Aging on Poled Films

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ABSTRACT: Polymer relaxation and physical aging phenomena at temperatures well below the glass transition have been examined in corona- and contact-poled, doped poly(methyl methacrylate) (PMMA), polystyrene, and bisphenol A polycarbonate films using in situ second harmonic generation (SHG). The local polymer microenvironment has been studied by examining dopant orientation and disorientation in samples physically aged before or during poling as a function of aging time and temperature. The dopant orientation, related to the observed SHG intensity, is sensitive to the surrounding local mobility and free volume. Films aged before corona poling showed decreased SHG intensities upon application of the electric field, due to decreased mobility and local free volume reducing rotational mobility of the dopant in the matrix. No SHG intensity could be observed in doped PMMA films aged for 100 h at 25 °C before poling, indicating that the regions of local free volume and mobility sufficiently large to allow mobility of the dopant are removed. Samples aged during corona and contact poling showed improved temporal stability of the SHG intensity after the electric field was removed, indicating changes in free volume and chain mobility surrounding the dopant. The effect of the corona poling used to orient the dopants on the measured intensity is discussed in terms of a field-induced surface/space charge region within the polymer film.

Introduction

Polymer mobility and relaxation phenomena can be studied at temperatures well below the glass transition temperature (T_g) using nonlinear optical (NLO) methods such as second harmonic generation (SHG).[2-5] Amorphous polymers doped with NLO chromophores are examined using in situ SHG to provide the sensitivity to study the relaxation of the polymer segments and local free volume around the dopants. By examining modifications to the doped systems, including dopant size and physical aging,[3-5] it has been shown that information can be obtained on basic physical properties and relaxation behavior of the polymers. Secondary properties such as mechanical and chemical stability are important in the practical consideration of these materials[6] and will be affected by physical aging.[7-13]

The physical behavior of the polymer matrix is affected by sample history. Physical aging,[8-22] or sub-T_g annealing, changes segmental relaxation times and is characterized by a slow densification of the matrix, with a decrease in the amount[12] and redistribution[14] of the local free volume, here designated as the space not occupied by the packed polymer chains. Aging has been examined by a variety of experimental techniques, including differential scanning calorimetry (DSC),[7,8] dilatometry,[9] dielectric relaxation,[10] and mechanical[11,12] and thermal[13] testing. Molecular sensitivity to physical aging has been investigated by photochromic,[14,15] X-ray scattering,[16] NMR,[17] and forced Rayleigh scattering[18] techniques. Photochromic studies[14] have shown that the amount and distribution of free volume both change during aging, with larger pockets of free volume decreasing in size more rapidly than smaller pockets in polystyrene (PS) and poly(methyl methacrylate) (PMMA). The polymer chains pack more efficiently during this temperature-dependent densification, slowing chain relaxations and decreasing the cooperativity of the motions, thereby decreasing chain mobility. Both phenomenological and kinetic and thermodynamic models have been examined in considering glassy behavior. The phenomenologial models[10,13,19,20] involve multiordering parameter equations, all containing a distribution of structurally dependent characteristic relaxation times.[13] Statistical thermodynamics has been used to develop molecular models[22,23] that relate T_g to molecular and composition parameters but do not predict the temporal dependence of thermodynamic properties.[19f]

In this work, physical aging is examined in poled amorphous polymers doped with NLO dyes using in situ SHG to give a sensitive measure of dopant orientation in the amorphous polymer matrix. (Since 4 wt % dye is doped into the matrix, this test may not probe pure homopolymer relaxations.[4c]) It has been shown that physical aging during contact poling improves the short-term stability of dopant orientation and that increasing the dopant size increases the temporal stability of dopant orientation in the matrix. This paper further considers in situ experiments where the polymers are aged before and during poling and explores the effect of aging time and temperature on dopant orientation. The amorphous polymers studied include PS, PMMA, and bisphenol A polycarbonate (PC) doped with well-characterized NLO dyes such as 4-(dimethylamino)-4′-nitrostilbene (DANS) and 4-amino-4′-nitroazobenzene (disperse orange 3, DO3).[3,4] This work should give insights on the dynamics of dopant orientation in the amorphous matrix and the changes induced by modifying the local microenvironment surrounding the dopant by physical aging.

Experimental Section

The NLO dopants have been previously characterized.[3,4] DO3 (Aldrich) is purified by Soxhlet extraction with spectroscopic grade acetone to isolate the dye. Films (1.5–2.5 μm thick, 4 wt % dye) are prepared as previously described.[3,4] Dopant aggregation is

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not observed spectroscopically.[4c] T_g's for the doped materials are measured (Perkin-Elmer DSC-2, 10 °C/min heating rate) as ca. 85 °C for PMMA, 88 °C for PS, and 95 °C for PC (M_n = 17 300, M_w = 28 000). Immediately prior to testing, the thermal history of each samples is erased by heating the film to 110 °C for a minimum of 3 h. Samples are quenched to room temperature (25 °C) over a 1–3-min period following this treatment. If the sample is to be aged before poling, aging is immediately initiated in an oven ex situ (outside of the beam path). The sample is then poled in situ.[4c] Samples aged during poling are placed in the beam path following the erasure of thermal history, and poling followed by aging is immediately started. Quenched samples are poled immediately following thermal history erasure. Poling times are arbitrarily chosen to allow sufficient dopant orientation to obtain high signal-to-noise ratios.

Aging times and temperatures were chosen based on photochromic[14] and dilatometric[9] studies. Films are aged at 60, 40, or 25 °C. Several aging times are examined in order to select conditions that are both sufficiently long to affect measurably the polymer system yet short enough to be experimentally practical, particularly for samples aged in the beam path. Aging times of up to 100 h in samples aged before poling are examined, with the majority of the films annealed for 0, 1, 3.2, or 10 h before poling. Films aged during corona poling are annealed in situ for 3.2 h. The films aged during contact poling are annealed ex situ for 10 h at 25 °C. Corona-poled films are poled at either 60 °C for 30 min or 25 °C for 40 min, and contact-poled films are treated at 100 °C for 1 h. The corona discharge experiment and the SHG test apparatus have been described.[4c] The square root of the SHG intensity is proportional to the magnitude of the second harmonic coefficient d_{333} (referred to as d) and related to the angle between the applied field and the axis of the dopant parallel to the molecular dipole moment.[4c]

Sample-to-sample variation can be significant, particularly in samples aged for short duration (1–3 h) at 25 °C before corona poling at 25 °C. In these films the SHG intensity can vary up to ±10%. The sample-to-sample variation in films aged during poling is slightly lower. Error limits for each film are equal to or smaller than the size of the symbols in the figures.

Results and Discussion

Aging is performed before and during poling for several temperatures and times to obtain a relative measure of the physical behavior. Changes in the SHG intensity growth or decay with time are related to differences in the ability of the NLO dopant to rotate freely in the polymer matrix.[3-5] Variations in the local microenvironment surrounding the dopant can be studied as a function of aging history.

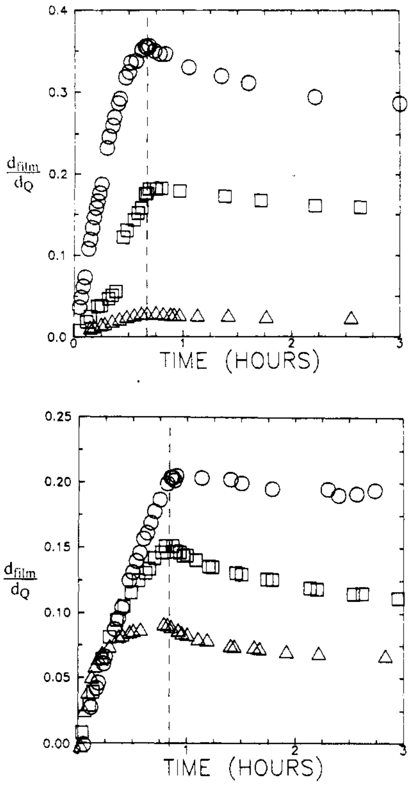

Figure 1. Effect of physical aging at 25 °C before corona poling in (a) (top) PMMA + 4% DANS (4-(dimethylamino)-4′-nitrostilbene) (poled at 25 °C, 40 min) and (b) (bottom) PS + 4% DANS (poled at 25 °C, 50 min). Films are quenched (○) or aged for 1 h (□) or 10 h (△) before poling. Dashed line indicates time when electric field is removed. $d_{\rm film}$ is the second harmonic coefficient of the doped film and is related to the angle between electric field lines and the dopant molecular axis. $d_{\rm film}/d_Q$ (where d_Q is the second harmonic coefficient of a quartz reference) is proportional to $[I_{\rm film}/I_Q]^{1/2}$, where $I_{\rm film}$ and I_Q are the SHG intensities of the sample and the quartz reference, respectively.

Aging before Poling: Investigation of Local Free Volume Surrounding the Dopant. Samples that are aged before poling are annealed in an oven prior to application of the orienting field in situ. Figure 1 examines the effect of physical aging for 0, 1, and 10 h at 25 °C before poling in PMMA and PS + 4 wt % DANS films corona poled at 25 °C. Figure 1a illustrates the dependence of $d_{\rm film}/d_Q$[4c] with time for PMMA + 4 wt % DANS films aged before poling (poled for 40 min at 25 °C). The corona discharge applied at zero time creates an electric field gradient across the film capable of orienting the polar dopants in regions of sufficient local free volume in the field direction that generates the increased SHG intensity. The shape of the normalized growth rates of $d_{\rm film}/d_Q$ during poling is similar for the three aging times. This indicates that the dopant rotation mechanism during poling does not change substantially with aging before poling, but the decreased magnitudes indicate that the amount of free volume available of sufficient size for the dopants to be able to rotate is decreased. For films aged for 1 h at 25 °C before poling, $d_{\rm film}/d_Q$ (≈0.18) is ca. half the value of the quenched film value (≈0.35) at the time the electric field is removed. After 10 h of aging at 25 °C before poling, $d_{\rm film}/d_Q$ (≈0.03) when the field is removed is ca. an order of magnitude lower than that achieved in the quenched film. Thus, significant changes in the ability of the dopant to be oriented can be observed after only a short time of aging at 25 °C.

After the applied electric field is removed, the second harmonic coefficient decays as dopants in areas of sufficient free volume are able to rotate out of their poling-induced alignment and can no longer contribute to the net SHG intensity. The shapes of the decay curves are similar upon normalization, indicating that the time dependence of the decay is not a function of aging before poling. This implies that the dopants that reside in regions of sufficient mobility or local free volume rotate in a similar fashion independent of the number of dopants able to rotate. As aging proceeds, the segmental mobility and local free volume decrease, reducing the number of dopants in regions of sufficient local free volume able to rotate into orientation (decreasing $d_{\rm film}/d_Q$). The values of $d_{\rm film}/d_Q$ following the removal of the applied corona field are relatively stable, with 20–30% of the initial signal lost over the first 3 h. At longer times the signal continues to decay.

In addition to the films aged for 0, 1, and 10 h studied in Figure 1a, films aged for 3.2, 32, and 100 h before corona poling (poled at 25 °C for 40 min) were also examined. As the aging time before poling increases, the shapes (although not magnitudes) of normalized growth and decay curves are similar. As the aging time before poling increases from 0, 1, 3.2, 10, to 32 h, $d_{\rm film}/d_Q$ decreases from 0.35, 0.18, 0.11, 0.03, to 0.02, respectively, at the time the field is removed. No SHG intensity could be measured for a sample aged for 100 h before poling, indicating that no or very few regions of local free volume large enough for the dopants to rotate into orientation at room temperature are available. Thus, physically aging PMMA for 100 h at 25 °C can remove almost all of the regions of free volume in the size range capable of allowing motion of the DANS dopant. (The size of the DANS molecule is ≈200 Å^3.[3,5,14]) This supports the case that the dopant orientation and disorientation relate to the polymer relaxation behavior.

Similar conclusions about the role of physical aging were reached in photochromic studies[14c,d] in PS and PMMA films. In the case of the PMMA studies,[14d] it was determined that physically aging PMMA at 60 °C for 100 h could result in the virtually total loss of regions of local free volume or mobility that are sufficient in size to allow diphenylstilbene to isomerize. Furthermore, these studies[14c,d] revealed that the effects of physical aging were most significant at shorter times, in agreement with the results of this study.

When the dopant orientation and disorientation are examined, both polymer physics and corona-induced surface/space charge effects must be considered.[4] There should be no significant difference in the effect of charge decay in samples aged before poling since the corona field is applied for the same length of time at the same temperature. Preliminary studies of surface voltage (SV) on films aged before poling indicate no measurable differences in the magnitude and rate of the SV decay in films quenched or those aged for 1 or 10 h at 25 °C before poling at 25 °C for 40 min.[4c] The SV remains constant for about 15 min and then decreases almost linearly, so that 2.5 h after the corona field is removed, the SV is ca. 45 V. The significance of the small magnitude of the SV and its persistence to the observed temporal stability of dopant orientation has been discussed.[4c] Since the SV effects are similar for all three thermal histories, the change in magnitude of d_{film}/d_Q is primarily due to polymer characteristics associated with the changes caused by the physical aging and should be independent of space charge effects.

Figure 1b illustrates the dependence of d_{film}/d_Q with time for PS + 4 wt % DANS films aged at 25 °C before corona poling at 25 °C for 50 min. As seen previously in the doped PMMA films, increasing the aging time before poling decreases the number of dopants that can rotate, decreasing the maximum signal. In terms of shape (but not magnitude), upon normalization the PS data also show similar growth rates during poling. The rate of dopant orientation into alignment occurs more slowly in PS than in PMMA. In all cases, the number of dopants able to orient in PS is fewer than those able to rotate in PMMA as indicated by the smaller magnitudes of the SHG signals for each aging condition (d_{film}/d_Q for quenched films ≈0.35 in PMMA but ≈0.2 in PS at the time the field is removed). This has also been observed in contact- and corona-poled, doped polymer films.[3,4] These results suggest that on the size scale required for the dopant orientation, PMMA is a more mobile matrix than PS, in agreement with conclusions reached with photochromic probes.[14] Solvatochromic effects may also contribute to differences in the observed magnitudes of d_{film}/d_Q

It is interesting to note that the aging process affects the dopant rotation in the PMMA matrix more significantly than it does in the PS matrix. When comparing the quenched films to those aged for 10 h before corona poling at 25 °C, we find that d_{film}/d_Q at the time the field is removed for the aged films drops to 9% and 40% of that obtained by the quenched films in PMMA and PS, respectively. The temporal stability of the dopant rotation after the electric field is removed is greater in PS than in PMMA. These results indicate that a greater number of regions of local free volume or mobility large enough to allow the DANS to rotate exist in the PMMA matrix than in the PS matrix or, alternately, that the mobility in PMMA is greater than that in the PS matrix at 25 °C. Thus, dopant orientation and disorientation results are consistent with results obtained by photochromic and other techniques and can be directly related to the polymer matrix relaxation behavior. Greiner and Schwarzl[9] found relaxation rates in homopolymer PMMA and PS to be similar at room temperature. However, their study examined aging times of 12 days (as opposed to a few hours), measuring bulk effects of the homopolymers via dilatometry.

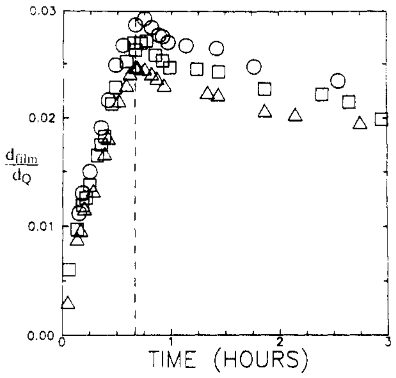

Figure 2. Effect of aging temperature on the dependence of d_{film}/d_Q versus time for PMMA + 4% DANS films physically aged before corona poling (poled at 25 °C, 40 min). Aging temperatures of 25 (○), 40 (□), and 60 °C (△) are examined. Dashed line indicates time when electric field is removed.

The experiments illustrated in Figure 1 indicate that the in situ SHG technique is sensitive to physical aging over short time scales. Significant changes in SHG intensity, related to dopant orientation, are seen within 1 h of physical aging at room temperature, well below T_g. This illustrates the sensitivity of this technique at temperatures and under conditions that would be impractical to study by many other techniques. Most dilatometric studies see significant aging effects only after time scales of hours or days.[9] Changes in the specific volume of PS of <0.001 cm^3/g over aging times of 10^6 s at 25 °C and ≈0.001 cm^3/g over aging times of ≈10^3–10^4 s at 95 °C are observed.[9] In enthalpy relaxation studies on PMMA,[9a] annealing temperatures of $T_g - 25$ °C to T_g were used, with annealing times of 0–1000 min. At these temperatures, measurable changes in some enthalpy recovery curves were seen over short time scales (1.67 h). DSC studies of PS aged at 92 °C showed significant changes in enthalpy relaxation after 3 h.[8b,c]

The effect of aging temperature on PMMA + 4% DANS films aged before poling at 25 °C is illustrated in Figure 2. Samples are aged at 25, 40, or 60 °C for 10 h before corona poling at 25 °C for 40 min. As the aging temperature increases, the maximum magnitude of d_{film}/d_Q decreases slightly (from 0.03 to 0.023 at the time the field is removed), indicating that the number of dopants able to orient with the field is a weak function of aging temperature. This implies that aging at 60 °C anneals out the greatest number of regions of local free volume or mobility with the requisite space for the NLO dopants to rotate and that the most efficient aging is thus achieved by the samples aged at 60 °C. The normalized growth

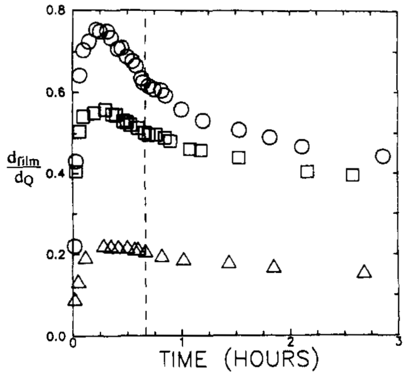

Figure 3. Effect of physical aging at 25 °C before corona poling on the dependence of d_{film}/d_Q versus time in PMMA + 4% DANS (poled at 60 °C, 30 min). Films are quenched (○) or aged for 1 h (□) or 10 h (△) before poling. Dashed line indicates time when electric field is removed.

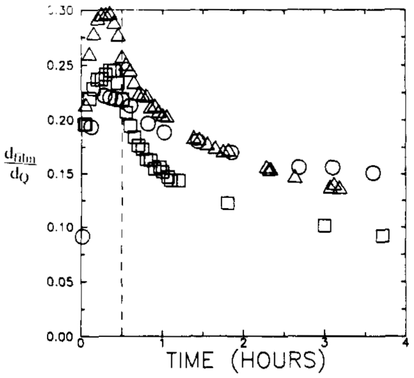

Figure 4. Effect of aging temperature on the dependence of d_{film}/d_Q versus time for PMMA + 4% DANS films physically aged before corona poling (poled at 60 °C, 30 min). Aging temperatures of 25 (○), 40 (□), and 60 °C (△) are examined. Dashed line indicates time when applied electric field is removed.

curves during poling are independent of aging temperature for aging before poling at 25 °C. The shapes of the normalized growth and decay curves are similar, as with the samples aged before poling discussed above. In all cases, d_{film}/d_Q is small. This is due to the difficulty for the dopants to rotate into alignment at 25 °C in the films aged for 10 h before corona poling. The effect of aging temperature has also been examined by photochromic techniques. Victor et al.[14] found that in PMMA most of the loss of the local free volume fraction between 280 and 600 Å^3 during aging occurred within a few hours (when compared to a 200-h time frame) and also found that aging proceeded more efficiently at 60 °C than at 25 °C in films with much smaller dopant concentrations than those used here. This is in contrast to dilatometric studies[9] of homopolymer PMMA aged for 12 days that indicate the maximum relaxation rate occurs at temperatures near 30 °C. However, the photochromic and SHG studies examine local as opposed to bulk properties and have been applied in these studies at much shorter aging time scales.

Poling temperature will also affect the dynamics of dopant orientation. Figure 3 illustrates the dependence of d_{film}/d_Q with aging time for PMMA + 4 wt % DANS films aged at 25 °C for 0, 1, or 10 h before corona poling at 60 °C for 30 min. The growth rate is much faster in these films than in films corona poled at 25 °C, with a sharp initial rise in signal intensity followed by a leveling off within 10–15 min. Poling at higher temperatures allows more dopant orientation due to greater segmental mobility, generating larger SHG intensities than in films poled at 25 °C. d_{film}/d_Q at the time the field is removed decreases from ≈0.8 to ≈0.22 with increasing aging times. The growth of the intensity occurs more rapidly at 60 °C than at 25 °C due to the improved freedom for the dopants to rotate along the field vector associated with increased local free volume and segmental mobility. When the data are normalized, the shape of the intensity growth curves during poling is similar for all three aging times. After reaching a maximum, d_{film}/d_Q decreases even with the electric field still applied. This is due to space charge effects within the film.[4] The rate of decay of the SHG intensity after the applied field is removed is greater in the samples poled at 60 °C than in those poled at 25 °C. The d_{film}/d_Q data are fit conveniently (with no implied physical significance for the parameters[4c]) with a biexponential function of the form[4c]

$$y = \theta_1 \exp(-t/\tau_1) + \theta_2 \exp(-t/\tau_2) \qquad (1)$$

When fitting the decays in Figure 3a using eq 1, $\theta_1 \approx 0.16$ for all three conditions, and τ_1 increases from ≈0.28 to ≈0.85 h while τ_2 increases from about 10 to 20 h with increasing aging times. These results imply that heating the films, even below T_g, creates larger size regions of local free volume or, alternately, allows greater mobility and increases the dopant disorientation dynamics.

Studies were also performed examining the SHG intensity with time for PS + 4 wt % DANS corona poled at 60 °C after aging at 25 °C for 0, 1, or 10 h. The films poled at 60 °C show a more rapid growth and greater magnitude of d_{film}/d_Q during poling than those PS films poled at 25 °C for each aging condition. The growth of the SHG intensity was somewhat slower in the PS films than in the PMMA films poled at 60 °C, and the intensity magnitudes were smaller. d_{film}/d_Q at the time the field is removed decreases from ≈0.42 to ≈0.16 with increasing aging times. Once the electric field is removed, the decay of the SHG intensity occurs more slowly with time in PS films than in PMMA films. However, the decay after the field is removed is similar in the PS films poled at 60 °C and at 25 °C. As with the systems poled at 25 °C, at 60 °C the PMMA matrix has greater mobility than the PS matrix.

The effect of aging temperature before poling has also been examined in films poled at higher temperatures. Figure 4 shows the dependence of d_{film}/d_Q with time for PMMA + 4% DANS aged at 25, 40, or 60 °C for 10 h before poling for 30 min at 60 °C. It is interesting to note that the films corona poled at 60 °C show increasing d_{film}/d_Q magnitudes as the aging temperature increases (from 0.22 to 0.25 at the time the field is removed). This is the opposite of the trend observed in films poled at 25 °C and aged before poling at higher temperatures. For the films aged for 10 h at 25 and 40 °C and then poled at 60 °C, this may be due to a memory effect[13] involved in the temperature jumps from the 110 °C erasure of thermal history to the aging temperatures well below T_g to the rapid increase to the poling temperature (60 °C). The greater restriction in mobility on the dopant orientation implied by the smaller magnitude of d_{film}/d_Q may be due to the longer time scale components of the relaxations induced by the aging at the lower temperatures. The film temperature is reduced from 110 °C to much lower temperatures after the erasure of thermal history, and the chain segments approach an equilibrium with time. When the temperature is increased a second time, segments that had reached equilibrium must reach a new equilibrium, while those that had not achieved equilibrium continue to relax until equilibrium is achieved at the poling temperature.[13e] Since the poling time is only 30 min, the systems aged at lower temperatures do not have the time

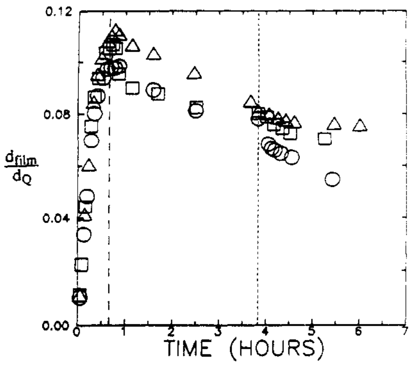

Figure 5. Effect of aging temperature on the dependence of d_{film}/d_Q versus time for PMMA + 4% DANS films physically aged during corona poling (poled at 40 min, 25 °C). Aging temperatures of 25 (○), 40 (□), and 60 °C (△) are examined. The long-dashed line indicates the end of the 25 °C pole and the short-dashed line indicates when the electric field is removed after the aging at the different temperatures.

to recover to the expected mobilities. The film aged at 25 °C shows slightly greater temporal stability of dopant orientation than the other films after the field is removed.

Upon examining the SHG intensity of doped glassy films physically aged before corona poling, one can obtain information on the local microenvironment surrounding the dopant. The rate of the growth and decay of the SHG intensity relative to the aging conditions is a measure of the characteristic dynamics of the dopant rotation in the matrix. Normalized shapes of intensity growth and decay are relatively independent of aging before poling, implying that the mechanism of dopant rotation is unaffected by aging. The magnitude of the SHG intensity indicates a relative measure of the number of dopants able to rotate along the electric field vector, thus supplying a measure of the regions of local free volume and the effect of aging on the distribution of these regions. Since the corona poling, aging time, and poling temperature are the same within each set of experiments, there should be little difference between the films due to space charge effects, so data within a set can be compared in terms of polymer relaxation behavior. It is more difficult to compare experiments where corona poling was performed at 25 °C to those where corona poling was performed at 60 °C due to the temperature dependence of the charge effects.[4c]

Aging during Poling: Investigation of Orientational Disordering of Dopants. Experiments are performed to examine the effect of physically aging the glassy polymer matrix during poling. These experiments are performed with the film poled for a given time at a given temperature and then aged for set time and temperature with the electric field maintained. The field is maintained during aging so that the dopants do not rotate out of alignment during the aging process. After the film has been aged, it is cooled to 25 °C (if aged at a higher temperature), and the electric field is removed. The SHG intensity is measured throughout the experiment.

Figure 5 indicates the effect of aging temperature on d_{film}/d_Q for PMMA + 4 wt % DANS films aged during corona poling (poled at 25 °C for 40 min). Aging temperatures of 25, 40, and 60 °C are examined for an aging time of 3.2 hr. Films are cooled to 25 °C before the applied corona field is removed. Since all three films have similar thermal histories and are poled under the same conditions, they should show similar intensity behavior with time during poling. After corona poling at 25 °C, the sample is either maintained at 25 °C or heated to 40 or 60 °C over a 5-min period and aged with the applied field maintained. For samples aged above 25 °C, as the temperature increases, d_{film}/d_Q initially increases and then levels and starts to decrease within the first 5–10 min. As the temperature increases during poling, the magnitude of the SHG intensity should increase due to greater local mobility allowing more dopants the freedom to rotate into orientation. d_{film}/d_Q of the film aged at 25 °C maintains its magnitude for about 15 min and then begins to decay. During the physical aging, the d_{film}/d_Q values of films aged at 40 °C decrease most rapidly initially following the temperature jump, but the overall greatest decrease in d_{film}/d_Q values occurs with films aged at 60 °C, followed by films aged at 40 °C and at 25 °C. This decrease in signal with the electric field still applied is due to real charge effects built up in the polymer film and on the surface due to the corona discharge.[4c] The greatest temporal stability after the applied field is removed is achieved in samples aged at 60 and 40 °C. This implies that the segmental mobility or local free volume surrounding the NLO dopants decreases to a greater extent in films aged during corona poling at the higher temperatures since the dopants have less freedom to rotate out of alignment. This is consistent with the results shown in Figure 2 of the films aged before poling at 25 °C.

Similar results are obtained when examining the dependence on the aging temperature for films aged during poling when the poling temperature is increased to 60 °C. PMMA + 4% DANS films are poled at 60 °C for 30 min and then aged for 3.2 h at 25, 40, and 60 °C with the electric field still applied. Films were cooled to 25 °C following aging before the field was removed. The magnitude of the maximum intensity and the amount of decay during poling were greater than in films poled at 25 °C (maximum values of d_{film}/d_Q between 0.18 and 0.32 when poled at 60 °C but between 0.10 and 0.12 when poled at 25 °C). d_{film}/d_Q continued to decay during aging, with the rate of decay similar in the films aged at 25 and 40 °C (d_{film}/d_Q decreases $\approx$25%) and a slower rate in the film aged at 60 °C (d_{film}/d_Q decreases $\approx$15%). For data normalized to the time of aging begins, d_{film}/d_Q at the end of the aging process decreases for samples aged at 60 to 40 to 25 °C. When the applied field is removed, the sample aged at 25 °C shows the greatest signal ($d_{film}/d_Q \approx 0.21$). The greatest temporal stability of d_{film}/d_Q is seen in the sample aged at 40 °C, followed by samples aged at 25 °C and then at 60 °C. As the films aged at 40 °C have the greatest temporal stability, the most efficient aging takes place under these conditions at this temperature. These results are consistent with the dilatometric studies of homopolymer PMMA, with the greatest relaxation rates observed at 30–40 °C.[9]

These results are also consistent with the temperature dependence of the real charges in and on the polymer film during the poling and aging.[4c] Since films poled at 25 and 60 °C were aged during corona poling for similar lengths of time at different temperatures, it is reasonable to attempt to identify differences in intensity decay behavior during poling due to the thermal dependence of surface and space charge effects as well as temperature-related differences in polymer relaxation behavior when comparing data from a range of samples.

Contact-poled films physically aged during poling have also been examined. Figure 6 illustrates aging behavior of contact-poled PC doped with 4 wt % DO3 over longer time scales. Films were poled at 100 °C for 1 h at a field of 0.5 MV/cm and then cooled to 25 °C with the field still applied. Since contact poling generates a lower field than corona poling, longer poling times and higher poling

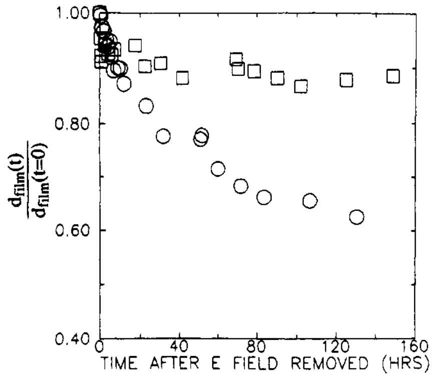

Figure 6. Effect of physical aging during contact poling on the dependence of $d_{film}(t)/d_{film}(t=0)$ versus time over long time scales. Measurement at time equals zero represents sample about 5 min after removal of the electric field. Contact-poled PC + 4% DO3 quenched (○) and aged 10 h at 25 °C (□).

temperatures are required to obtain reasonable SHG intensities. Contact poling is not performed in the beam path. Data in Figure 6 represent the time dependence of $d_{film}(t)/d_{film}(t=0)$ ($t = 0$ is 5 min after the applied field is removed) for films that were either quenched or aged 10 h at 25 °C with the field still applied. After ca. 150 h following removal of the field, d_{film} for the quenched samples decreases ca. 40%. d_{film} for samples aged during contact poling decays only 10% after 150 h; this decay occurs after 5 h in the quenched sample. The greatly improved temporal stability in this system is also related to the ability of the DO3 to hydrogen bond to the polymer matrix, an important effect currently under examination.[5] A large number of dopants have been examined in PC, PMMA, and PS matrices, and similar improvements in temporal stability with aging during poling have been seen in varying degrees.[3-5] This effect should be common to all amorphous polymers.

The effect of surface charge persistance in the contact-poled films is negligible, since there is no charge layer deposited on the film surface during poling. However, space charge effects must still be considered but are likely to be smaller in magnitude than in the corona-poled films. In addition, the space charge effect is not likely to persist over the longer experimental time scales used in the study illustrated in Figure 6.

Aging during poling is thus seen to affect the temporal stability of the SHG intensity decay and the optical properties of the material after the electric field is removed. This yields information about the dynamics of the dopant disorientation, which in turn gives information about the local segmental mobility and free volume environment surrounding the dopant.

This technique will allow the measurement of dopant rotation in the amorphous matrix with relative experimental ease. In an attempt to measure independently dopant orientation, various spectroscopic methods were tried, including absorbance, fluorescence, and FTIR-ATR dichroism. It was found when using conventional equipment that the films were too thin and the number of oriented dopants too low to measure accurately orientation coefficients and net angles of orientation. From SHG measurements it has been determined that roughly 10% of the available dopants orient in the field direction during contact poling above T_g.[6,24]

The polymer relaxations and corona discharge induced surface/space charges both affect the measured temporal stability of dopant orientation. The kinetic aspects of these effects are intimately interrelated and may prove difficult to separate. There may be an interaction between the highly polar dopants and the polar group in the PMMA side chain that would affect relaxation. No sophisticated theory has been developed for amorphous relaxation behavior at temperatures well below the glass transition. Corona poling effects must also be considered. The corona discharge generated surface voltage persists over a relatively long time scale following removal of the applied field, resulting in a driving force capable of maintaining a degree of dopant orientation over longer time scales. It has been shown that the growth and decay as well as the magnitude of the SHG intensity of doped films are a function of corona polarity. The corona discharge characteristics also depend on relative humidity and ambient atmosphere.[4] This makes interpretation of the SHG behavior based solely on polymer relaxations difficult.

Summary

In situ SHG is sensitive for probing amorphous polymer physics at temperatures well below T_g and has been used to examine the effect of physical aging in doped PMMA and PS films. The SHG technique is sensitive to small changes in dopant orientation relating to the local microenvironment surrounding the NLO dopants, and the stability of the dopant orientation depends strongly on the microenvironment surrounding the dopant, including segmental mobility and local free volume.

Aging the materials before poling decreases the amount of free volume in the system and in particular decreases the number of larger regions of local free volume or mobility required for the dopants to rotate. This decreases the number of dopants able to rotate into alignment when poling is subsequently performed below T_g, where the mobility is relatively low. Changes in the observed dopant orientation, related to SHG intensity and d_{film}, due to physical aging effects are observed even at short aging time scales (after 1 h at room temperature). Aging a PMMA + 4 wt % DANS film for 100 h at 25 °C before poling annealed out the mobility sufficient in size to allow dopant disorientation, with no SHG signal observed upon corona poling. Aging the material during poling allows the matrix to densify around the oriented dopants, decreasing their ability to rotate out of alignment once the electric field is removed and improving the temporal stability of d_{film}.

Poling at higher temperatures increases the magnitude of d_{film} at early poling times, with the greater segmental mobility allowing larger numbers of dopants to orient during poling. As the temperature is decreased from a higher poling temperature to a lower one or during long-time higher temperature poling, the SHG signal decays even with the electric field still applied. This is caused by space charge effects due to the corona-generated ions deposited on the film surface. The implications of the interaction between the corona-induced electric field and the polymer matrix are particularly significant when examining the kinetics of the dopant orientation processes in amorphous matrices.

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