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Effects of Chromophore Functionalization and Physical Aging during Poling on Chromophore Orientational Dynamics in Poly(arylene ether)s for Second-Order Nonlinear Optics

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ABSTRACT: The structure/property relationships including the effects of chromophore functionalization and physical aging during poling on the chromophore orientational dynamics and intermolecular cooperativity in a class of poly(arylene ether)s are discussed. Second-order nonlinear optics is used to examine the thermal and temporal stability of chromophore orientation in the poled polymer films as a function of processing.

Introduction

One major obstacle to the development of nonlinear optical (NLO) polymers for device applications[1] is that the chromophores doped or covalently bonded to the backbones disorient following electric field poling, decreasing the NLO signal with time.[2] Little information is available concerning the mechanism behind the decay, as the loss of signal is related to several complex phenomena. Although several synthetic approaches have been employed to optimize polymer structures and glass transition temperatures, T_g's, in order to maximize stability,[3] the studies of the physics governing the relaxation behavior of these materials are still incomplete. Better understanding of the relaxation characteristics is important so that the materials can be better tailored for specific end-use applications. The structure/property relationships including the effects of polymer backbone structures, molecular weight, and chromophore/polymer interactions on the dopant orientational dynamics and intermolecular cooperativity in a class of high-T_g poly(arylene ether)s have been reported.[4,5] In this report, the effects of chromophore functionalization, physical aging during poling, and the chromophore orientational dynamics are discussed. We are not concerned here with the most thermally and temporally stable polymers for device applications; rather, we are discussing methods for understanding the polymer dynamics governing stability and trying to generalize these methods for similar classes of polymers to be developed that will be commercially attractive.

Second harmonic generation (SHG), a second-order NLO effect, and dielectric relaxation studies were employed to examine the relaxation behavior of these polymers. The principles and theories of these techniques can be found elsewhere.[5,6] Corona poling[7] was used to orient the NLO chromophores into the noncentrosymmetric orientation required to observe a second-order nonlinear effect. Because the residual charges persisting in the films following corona poling retard the randomization of chromophore orientation,[7b] polymer relaxations and residual charge effects influencing the dopant orientational dynamics must be examined and considered in combination. Typically, we measure surface voltage decay following corona poling using an electrostatic voltmeter. Because the electrostatic voltmeter probe currently being used cannot withstand temperatures greater than 50 °C,[8] surface voltage measurements could not be performed on these poly(arylene ether)s; consequently, it was not possible to quantitatively separate the electric effects from the observed decay of the second harmonic intensity. This work thus focuses on aspects and trends of polymer relaxations; the field effects in this case are not yet well understood and are currently extensively under study by others in our group.[9] The SHG data obtained, however, allow us to qualitatively interpret the trends of the chromophore orientational dynamics during and following poling as a function of processing. This report also shows that by employing SHG and dielectric relaxation, the local mobility and relaxation phenomena in these NLO polymers can be investigated.

Experimental Techniques

This section describes the experimental protocols employed to investigate the relaxation phenomena in the doped and side chain functionalized poly(arylene ether) polymers.

The structures (shown in Table 1) and properties of the homopolymers and side chain functionalized polymers, phenolphthalein−Bis A-poly(arylene ether) phosphine oxides (PP-PEPO), PP-PEPO derivatized with 10% *p*-nitrophenylhydrazine (PP-PEPO-pNPH), and PP-PEPO derivatized with 10% 2,4-dinitrophenylhydrazine (PP-PEPO-DNPH), investigated here have been reported elsewhere.[4,5] These polymers have number-average molecular weight, $\bar{M}_n$, of 15 000 and polydispersity indices of approximately 2 as determined by gel permeation chromatography. PP-PEPO with $\bar{M}_n$ of 41 000 and a polydispersity index of approximately 2 was also investigated. The T_g's of PP-PEPO ($\bar{M}_n \approx 15\,000$), PP-PEPO ($\bar{M}_n \approx 41\,000$), PP-PEPO-pNPH, and PP-PEPO-DNPH measured via differential scanning calorimetry (DSC) (10 °C/min heating rate) are 265, 267, 284, and 278 °C, respectively. The NLO chromophore used for this study is 4-(dimethylamino)-4′-nitrostilbene (DANS) (Kodak). The T_g of the 10 wt % DANS doped PP-PEPO ($\bar{M}_n \approx 15\,000$) is 185 °C.

The 10 wt % DANS doped PP-PEPO, PP-PEPO-pNPH, and PP-PEPO-DNPH were dissolved in chloroform to make up a solution that contained about 10 wt % solids. These solutions

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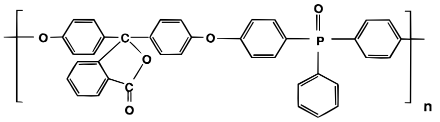
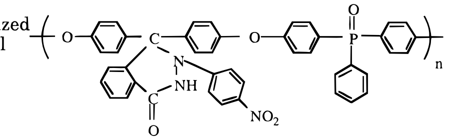
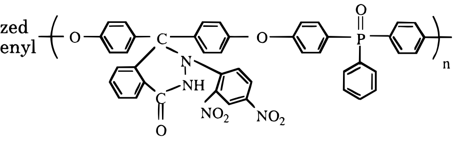
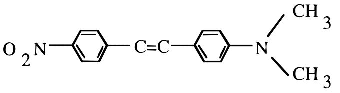
Table 1. Structures of the Polymers and Chromophore

Phenolphthalein/ PEPO (PP-PEPO)	
PP-PEPO derivatized with 4-nitrophenyl hydrazine PP-PEPO-pNPH	
PP-PEPO derivatized with 2,4-dinitrophenyl hydrazine PP-PEPO-DNPH	
DANS	

were well mixed, filtered through a 5 μm filter, and spin-coated onto indium tin oxide (ITO) coated glass slides for SHG experiments. The spun films were then dried to remove as much solvent as possible using the procedure described elsewhere.[5] Samples for dielectric relaxation measurements were prepared by spin-coating the solutions onto glass substrates with ITO covering 50% of the surface.[10] After careful drying, gold electrodes were then deposited on top of the films using an evaporator. Film thicknesses measured via profilometry ranged between 4 and 6 μm for SHG experiments and between 12 and 20 μm for dielectric relaxation measurements.

The detailed descriptions of the SHG and corona poling apparatus and experiments can be found elsewhere.[5,8] The laser light was generated by a Q-switched Nd-YAG laser (Continuum NY61-10; 10 Hz, 6−8 ns pulse width) at a fundamental wavelength of 1.064 μm. The beam was p-polarized and split so that the sample and quartz reference could be tested simultaneously. The $\chi^{(2)}$ values of the samples were ratioed to those of the quartz reference to minimize errors due to laser drifts and/or changes in the ambient environment and normalized to the point at which the applied voltage was turned off. The errors due to noise in these SHG measurements were less than or equal to twice the size of the symbols in the graphs in the figures.

The detailed descriptions of the dielectric relaxation apparatus and experiments have also been reported.[5] These experiments were performed using a RLC Digibridge (GenRad 1689), with a frequency range between 12 Hz and 100 kHz and a tolerance of 0.005%. A setting of 1 V peak-to-peak was used for all measurements.

Results and Discussion

Effect of Chromophore Functionalization. The effect of side chain functionalization on the chromophore orientational dynamics has been investigated, and improved temporal stability of chromophore orientation has been observed when compared to that of the guest−host doped systems.[11] Improved temporal stability of the chromophore orientation results from the stronger coupling between the covalently bonded chromophores and polymer backbone. These effects are examined in these stiffer backbone poly(arylene ether) polymers.

The normalized dielectric loss curves of PP-PEPO, PP-PEPO-pNPH, and PP-PEPO-DNPH at a temperature of approximately $T_g + 15$ °C have been reported.[5] They were broader on the low-frequency side for the two side chain functionalized systems, PP-PEPO-pNPH and PP-PEPO-DNPH, than the undoped PP-PEPO, indicating stronger intermolecular coupling between the covalently bonded chromophores and polymer. PP-PEPO-DNPH exhibited a narrower loss curve than that of PP-PEPO-pNPH, though the former polymer has an extra NO_2 group on each NLO-phore. This phenomenon was contrary to observations reported in the literature[12] and may be because the extra NO_2 groups could not pack as well in the PP-PEPO-DNPH matrix, resulting in greater local mobility and a lower T_g (as determined by DSC) and weaker intermolecular cooperativity (as reflected by a narrower loss curve) than PP-PEPO-pNPH.

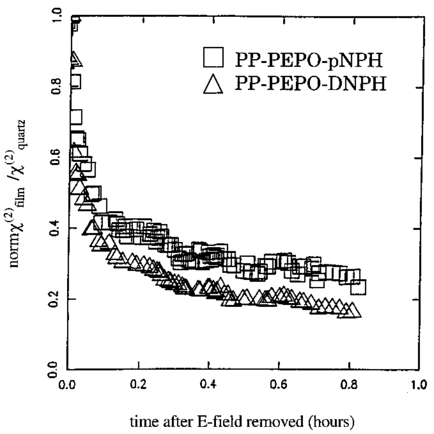


Figure 1. Temporal stability of dopant orientation in PP-PEPO-pNPH and PP-PEPO-DNPH poled at −3500 V, $T_g + 5$ °C; temperature at which chromophore disorientation was observed $\approx T_g - 250$ °C.

Second harmonic generation experiments were performed on the PP-PEPO-pNPH and PP-PEPO-DNPH polymers. The magnitudes of the second harmonic signal generated from these two side chain functionalized polymers were approximately 2 times smaller than those generated from the 10 wt % DANS doped or 10 wt % 4-amino-4′-nitroazobenzene (disperse orange 3, DO3) doped PP-PEPO systems. This may be because the chromophores covalently attached to the side chain of the PP-PEPO polymer backbone, *p*-nitrophenylhydrazine and 2,4-dinitrophenylhydrazine, had smaller dipole moments and molecular hyperpolarizability values than those of DANS and DO3. This was evident from the $\chi^{(2)}$ measurements.[13] In addition, the chromophores were directly bonded to the polymer backbone; i.e., no flexible spacer units were incorporated to connect the chromophores to the backbone.[10,11c] Thus the spacer units should aid the chromophores to align more easily with respect to the field. It might thus be more difficult to orient the chromophores, resulting in a smaller second harmonic signal. Furthermore, the signal decreased in the side chain functionalized polymers while it increased in the DANS and DO3 doped systems during the cooling period with the electric field still applied. This might be because as the system was cooled, the rigid polymer chains gradually relaxed, causing the covalently attached chromophores to rotate out of poling-induced orientation and thus decreasing the second harmonic signal even with the field applied. This phenomenon was also observed in some main chain functionalized systems.[14]

As shown in Figure 1, PP-PEPO-pNPH had better temporal stability of chromophore orientation at $T_g - 250$ °C following poling than PP-PEPO-DNPH. Because of the stronger intermolecular coupling of the PP-PEPO-pNPH chain segments, chromophore motions were more restricted, resulting in better temporal stability of second harmonic signal. This demonstrates that by combining dielectric relaxation and SHG, information concerning the extent of intermolecular coupling and chromophore orientational dynamics in these side chain functionalized polymer matrices can be obtained.

It should be pointed out that better temporal stability of $\chi^{(2)}$ in these two side chain functionalized systems at $T_g - 140$ °C following poling was not observed when compared to that of the 10 wt % DANS doped PP-PEPO ($\bar{M}_n \approx 16\,000$) system reported in our previous work.[5] This can be explained by the fact that the chromophores covalently bonded to the side chain of the PP-PEPO backbone are small. Furthermore, without the incorporation of the spacer units, the polymer chains, as they relaxed with time, might cause the covalently attached chromophores to rotate more rapidly out of the poling-induced orientation. Enhanced stability in these side chain functionalized systems therefore could not be observed. Other side chain functionalized systems with flexible spacer units and larger chromophores (such as DO3) are being synthesized. Further investigations and synthesis of related systems will be conducted in order to examine how these structural changes affect the chromophore orientational dynamics.

Effect of Physical Aging during Poling. Physical aging increases chain packing and decreases segmental mobility of the polymer chains, causing densification of the polymer glass.[15,16] Aging the material during poling allows the polymer matrix to densify around the oriented dopants, hindering them from rotating out of the poling-induced orientation after the applied voltage is turned off.[17−20]

To date, limited studies on the effect of physical aging during poling on the chromophore orientational dynamics in NLO polymer systems have been reported.[10,17−20] Here, aging during poling experiments were performed on the 10 wt % DANS doped PP-PEPO ($\bar{M}_n \approx 16\,000$ and $\bar{M}_n \approx 41\,000$) systems. Because the degree of the decrease in a local free volume fraction depends on the aging time and aging temperature,[15,21c] the effects of these parameters on the chromophore orientational dynamics were examined. After erasing the thermal history for an hour, the film was poled at $T_g + 5$ °C for 25 min and then aged at $T_g - 140$ °C or $T_g - 50$ °C with the electric field applied. The voltage was turned off at the end of the aging period, and the decay of the second harmonic signal was observed at $T_g - 140$ °C. For the sample that was aged at $T_g - 50$ °C, it was cooled to $T_g - 140$ °C at the end of the aging period before the voltage was turned off and the decay of $\chi^{(2)}$ was observed.

As shown in Figure 2a, better short-time temporal stability of $\chi^{(2)}$ for the DANS doped PP-PEPO ($\bar{M}_n \approx 16\,000$) system aged at $T_g - 140$ °C for 10 h was observed when compared to that of the unaged sample. However, the overall temporal stability remained similar. Better overall temporal stability of $\chi^{(2)}$ for the same system aged for 17 and 31 h was observed when compared to that of the unaged sample as shown in Figure 2b. In the short-time regime where the initial fast relaxation dominates, the aged samples showed a reduction in the relaxation rate, while in the long-time region, the relaxation rate remained virtually unaffected. This observation is consistent with that reported for the side chain functionalized copolymers, 25/75 and 50/50 (mol/mol) copolymers of ethyl methacrylate functionalized with DANS and butyl methacrylate.[18] In agreement with the conclusions made in the literature,[17,18] these data indicate that aging reduces the larger free volume elements responsible for the initial fast relaxation. Furthermore, the majority of the aging effect observed in the sample aged for 31 h was present in the one aged for 17 h. This result is consistent with those observed in the doped polystyrene (PS), poly(methyl methacrylate) (PMMA), and poly(isobutyl methacrylate) (PIBMA) systems using SHG[17,19] and the photochromic technique[21b,c] and agrees with the literature that the rate at which physical aging proceeds decreases with increasing aging time.[15]

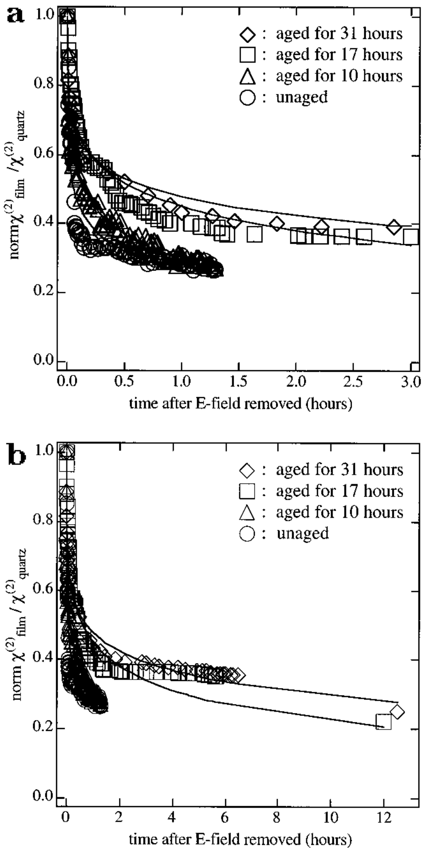


Figure 2. Effect of aging time on the temporal stability of chromophore orientation ((a) short-time scale and (b) long-time scale) in the 10 wt % DANS doped PP-PEPO system (T_g = 185 °C) poled at −3000 V, $T_g + 5$ °C; aging temperature ≈ $T_g - 140$ °C, temperature at which chromophore disorientation was observed ≈ $T_g - 140$ °C. The solid lines are the Kohlrausch−Williams−Watts equation fits.

Table 2. Values of the Kohlrausch−Williams−Watts Parameters, τ and β, as a Function of Aging Time for the 10 wt % DANS Doped PP-PEPO System (T_g = 185 °C) Aged at $T_g - 140$ °C

aging time (h)	τ (h)	β
0	0.27	0.17
10	0.49	0.29
17	2.28	0.27
31	4.06	0.22

The Kohlrausch−Williams−Watts (KWW) equation[22] has been extensively used to describe the relaxation phenomena observed using techniques such as dielectric relaxation,[23a,b] dynamic mechanical analysis,[23c−e] enthalpy relaxation,[23f] second harmonic generation,[17,19,23g] and nuclear magnetic resonance[23h] and has been shown to fit the decay data well. Here, this equation was also used to fit the decays of the normalized $\chi^{(2)}$. The values of the characteristic relaxation time, τ, and β, which reflects the distribution of relaxation times, as a function of aging time are tabulated in Table 2. The value of τ increased as the aging time increased, reflecting a decrease in local mobility in the polymer matrix. The

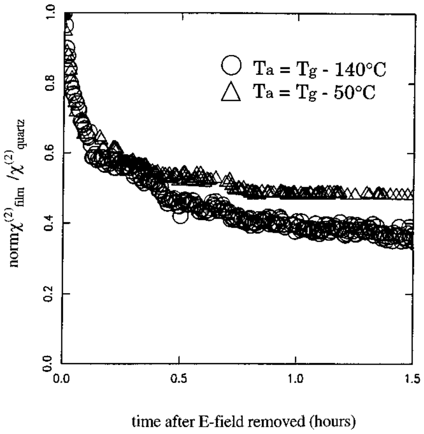


Figure 3. Effect of aging temperature on the temporal stability of chromophore orientation in the 10 wt % DANS doped PP-PEPO system ($T_g = 185$ °C) poled at -3000 V, $T_g + 5$ °C; aging time = 17 h, temperature at which chromophore disorientation was observed $\approx T_g - 140$ °C.

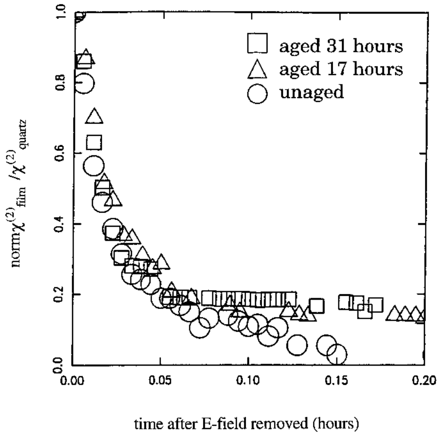


Figure 4. Effect of aging time on the temporal stability of chromophore orientation in the 10 wt % DANS doped PP-PEPO system ($T_g = 185$ °C) poled at -3000 V, $T_g + 5$ °C; aging temperature $\approx T_g - 80$ °C, temperature at which chromophore disorientation was observed $\approx T_g - 80$ °C.

β values for the aged samples were larger than the one for the unaged film, indicating a narrower distribution of relaxation times as a result of the loss of the short-time components of relaxation distribution. This was observed experimentally as a reduction in the initial fast relaxation rate (Figure 2a) and is consistent with those reported for the DANS doped PMMA and Bisphenol-A polycarbonate (BPA-PC) systems aged at 25 °C.[17a] Furthermore, using the photochromic technique, it was also found that upon physical aging in PMMA at 25 °C, larger pockets of local free volume decreased in number more than the smaller pockets, causing the size distribution of local free volume to narrow upon aging.[21c] However, it is interesting to note that for the 2 wt % DR1 doped PIBMA system aged at $T_g - 15$ °C, the value of β remained minimally affected upon aging.[19] The short-time components of the relaxation distribution were lost upon aging, but the relaxation distribution was shifted relatively intact to longer times. It was also pointed out that the relatively unchanged β value may be because the aging temperature used was not far below T_g.

It should be noted that the values of β for the samples aged for 17 and 31 h, though larger than the one for the unaged film, were smaller than the one for the sample aged for 10 h. This is because the equation could not fit as well for these two sets of decay data, particularly in the short-time regime, as for the relaxation data obtained for the unaged film and the film aged for 10 h. The discrepancy may very likely be due to the slower second harmonic signal decay observed in the two samples as a result of the loss of the short-time components of relaxation distribution. This result has also been reported in the DANS doped PMMA and BPA-PC systems aged during contact poling[17a] and in the poly(methyl methacrylate-*co*-coumaromethacrylate) aged prior to corona poling.[20b]

Different aging temperatures result in different aging rates for each polymer.[15,21c] When comparing the samples aged at $T_g - 140$ °C and $T_g - 50$ °C for 17 h, the one that was aged at $T_g - 50$ °C yielded slightly better temporal stability of $\chi^{(2)}$ following poling as shown in Figure 3. This implies that the local free volume surrounding the chromophores decreased to a greater extent in the sample aged at temperatures closer to T_g during poling so that the dopants had less freedom to rotate out of the poling-induced orientation after the voltage was turned off. This phenomenon is consistent with that observed in the DANS doped PMMA systems aged at different temperatures during poling[17b] and is also in agreement with the physical aging experiments conducted using dielectric relaxation,[24a] dynamic mechanical analysis,[24b] and the photochromic technique.[21b,d] It was reported from the dielectric relaxation and dynamic mechanical analysis experiments that aging proceeds more quickly at higher temperatures and is a nonlinear effect.[24] Furthermore, using the photochromic technique, it was observed that a maximum loss of local free volume occurred when PS was aged at temperatures approximately 20−25 °C below T_g, and the time required to reach equilibrium became longer as $T_g - T_a$ (aging temperature) became larger.[21b,d]

Figure 4 shows that when the samples were aged at $T_g - 80$ °C for 17 and 31 h and the chromophore orientational dynamics was observed at the same temperature, there was little improvement in the temporal stability of $\chi^{(2)}$ as compared to that of the unaged sample. This may be because the local free volume/local mobility, though reduced during the aging period, still remained sufficiently large at $T_g - 80$ °C to allow the chromophores to easily rotate out of the poling-induced orientation after the voltage was turned off, and thus enhanced stability of $\chi^{(2)}$ could not be observed.

Aging during poling at $T_g - 140$ °C for as long as 45 h did not result in an increase in the temporal stability of chromophore orientation in the DANS or DO3 doped PP-PEPO ($\bar{M}_n \approx 41\,000$) systems. This was very likely because the polymer was more rigid (i.e., there were fewer larger free volume elements) than the one with $\bar{M}_n \approx 16\,000$. Since physical aging results in a greater reduction in larger local free volume than smaller local free volume,[21a,c] the aging effect therefore could not be observed in this high-molecular-weight polymer matrix under the experimental conditions used. Longer aging times were also used in these systems; however, these polymer films could not be aged during corona poling for more than 2 days because the corona discharge would damage the films, and thus no second harmonic signal could be observed. Contact poling would be a better technique for these experiments because longer aging times are allowed without concerns about charge damage to the samples.[19]

Conclusions

By employing SHG and dielectric relaxation, the effects of chromophore functionalization and physical aging during poling on the chromophore orientational dynamics in these thermally stable NLO poly(arylene ether)s can be examined. In summary, physical aging during poling is a useful method for yielding better temporal stability of chromophore orientation. This result should be general for polymers with similar backbone structures. The effects of aging time and aging temperature on the dopant orientational dynamics were examined. Some results obtained for these thermally stable polymers are consistent with those reported for the polymers with lower T_g's and more flexible backbones. The aging studies on the thermally stable NLO polymers have not been performed and may have important implications for designing other classes of high temperature stable materials for device applications. The information obtained here is important for assisting the design and processing methods for other classes of high temperature stable materials used for second-order NLO applications.

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