Macromolecules 1994, *27*, 3619–3624 **3619**

Stability of Dipole Orientation and Second-Order Nonlinearity in Poled and Cross-Linked Polymer Films

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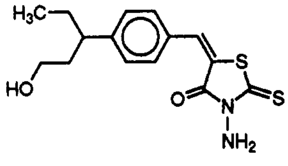
Received December 12, 1993; Revised Manuscript Received April 5, 1994[•]

ABSTRACT: Processes that generate decay of polarization in a cross-linked, nonlinear optical polymer have been studied, and their relationship to a corresponding change in second-order nonlinearity ($\chi^{(2)}$) has been determined. Measurements of second-harmonic generation, thermally stimulated discharge current, and UV–visible absorbance have been employed to identify polarization decay resulting from relaxation of oriented molecular dipoles, migration of space charge, and chemical degradation of chromophores. The effect of process parameters on $\chi^{(2)}$ stability in these materials is observed and explained.

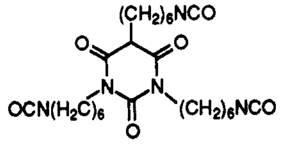
Introduction

The successful implementation of poled polymer films in electrooptic devices depends largely on the outcome of research aimed at developing materials in which dipole orientation will be retained over an extended period of time in the operating temperature range. An important element of this research comprises not only the determination of process and material factors that affect stability of polar order but also the mechanisms involved in relaxation which translate into loss of optical second-order nonlinearity ($\chi^{(2)}$) in the material. Investigations that have addressed these issues have made use of electrooptic (EO), second-harmonic generation (SHG), thermally stimulated current (TSC), and dielectric relaxation measurements to study guest–host, side-chain, and cross-linked polymer systems.[1–7] In several cases, films maintained at room temperature over several weeks have been shown to exhibit negligible decay in the second-order nonlinear response, but adequate stability for more than a few days at temperatures approaching 100 °C has seldom been reported.[5,8–10] Explanations for decay in $\chi^{(2)}$ at elevated temperatures have centered around orientational relaxation, making use of a number of different models which generally have employed biexponential or Kohlrausch–Williams–Watts (KWW) stretched exponential expressions to describe the time constants.[2,11,12] The temperature dependence of relaxation times has been analyzed by means of Arrhenius plots,[3,13] although some authors have observed better fits using formulas similar to the Williams–Landel–Ferry (WLF) expression.[2,14,15]

Significant advances have been made with regard to $\chi^{(2)}$ stability in cross-linked polymers in which the nonlinear optical (NLO) dye molecule is covalently attached to the network at more than one site. We recently reported[16] the incorporation of a novel bifunctional NLO molecule, 3-amino-5-[4′-[*N*-ethyl-*N*-(2″-hydroxyethyl)-amino]benzylidene]rhodanine (RA), into a poled, cross-linked polymer by means of a two-stage reaction with a trifunctional isocyanurate comonomer, tolonate HDT (HDT),made by trimerizing 1,6-hexamethylene diisocyanate. The NLO molecule was designed with two functionalities having different reactivities so that at one end of the molecule an amino group reacts in solution slightly above room temperature to allow coating of a smooth film of uniform thickness and at the other end a hydroxyl group reacts at elevated temperatures during poling to form a network intended to restrict orientational relaxation once the poling field is removed from the cooled film. Since the NLO molecule is not attached to a polymer backbone prior to the poling stage, it was anticipated that this process would assure greater mobility for alignment of dipoles under an applied electric field than might be observed should the molecule instead be incorporated in the polymer as side chains.



RA



HDT

Our initial studies of poled and cured RA–HDT films[16] produced evidence for the two-stage reaction used to process them and showed that the resulting films exhibited promising $\chi^{(2)}$ stability when maintained at 100 °C. Furthermore, in contrast to $\chi^{(2)}$ decay observed in poled polymers due to orientational relaxation, the long-term decay observed in RA–HDT films at this temperature was found to result from thermal degradation of the RA molecule itself. Consequently, it was felt that the cross-linked network existing in these materials might be sufficiently rigid for use in polymeric EO devices and therefore warranted further investigation.

In this paper, we examine more closely the poling and curing process used in preparing RA–HDT films and determine the effects that changes in process parameters have on physical properties of the cross-linked network and its resulting $\chi^{(2)}$ stability. By means of simultaneous SHG and TSC measurements on poled films, the respective contributions of orientational relaxation and chromophore degradation to the decay of second-order nonlinearity in these materials are identified. TSC data on aged and unaged films also reveal multiple space charges in poled samples, and their possible influence on alignment stability is considered.

Experimental Section

Procedures and instrumentation employed in synthesis of RA dye, film preparation and poling, and measurement of SHG and UV–visible spectra have been reported previously.[16] Tolonate HDT was obtained from Rhone-Poulenc and used as received in the amount of 10% equivalent excess relative to RA dye. RA–HDT films (2.2-μm typical thickness) were coated onto glass substrates having indium tin oxide (ITO) electrodes and were overcoated by thin (90 Å) gold electrodes via vapor deposition.

[•] Abstract published in *Advance ACS Abstracts*, May 15, 1994.

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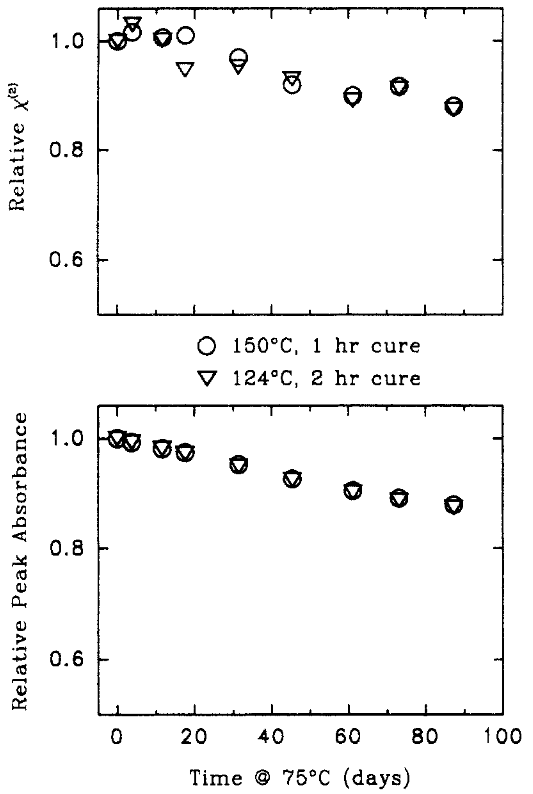

Figure 1. Decay of second-order susceptibility and peak absorbance in RA-HDT films maintained at 75 °C during a 3-month period. In the top plot, relative changes in $\chi^{(2)}$ were determined from SHG measurements, and in the bottom plot, relative changes in peak absorbance of the 474-nm band were determined from UV-visible spectroscopy.

The samples were poled under an applied field of 100 V/μm and simultaneously cured for either 1 h at 150 °C or 2 h at 124 °C in ambient atmosphere. Because conductivity of the films varied as a function of poling time and temperature, the effective field across the films ranged from 80 to 100 V/μm. The electric field was removed after cooling the samples to room temperature at a rate of 2–3 °C/min.

The poled and cured RA-HDT films were maintained at 75 °C in air, and $\chi^{(2)}$ stability was monitored by means of SHG measurements over a period of 3 months. Another set of films made thinner and cured as described above but not poled was also stored at 75 °C, and changes in film absorbance were followed by UV-visible spectroscopy.

A modification of the oven used in poling the samples permitted the electrodes to be short-circuited so that TSC data could be measured along with SHG while applying a computer-programmed linear temperature ramp from 30 to 180 °C at a rate of 2.5 °C/min. Current was measured by a Keithley 417 picoammeter.

Results and Discussion

A plot of $\chi^{(2)}$ stability of the poled and cured RA-HDT films maintained at 75 °C is shown in Figure 1. The data have been normalized to the $\chi^{(2)}$ values obtained for the respective films prior to storing them at elevated temperature. The rate of $\chi^{(2)}$ decay is independent of the conditions employed to cure the films, suggesting that the different procedures cross-link the films to nearly the same extent and that the oriented NLO dyes exist in very similar environments. Indeed, infrared (IR) measurements on comparable films cured along with the poled films in the poling oven showed that the fraction of isocyanate left unreacted after curing was on the order of 5% for the 2 h/124 °C procedure and less than 2% for the 1 h/150 °C procedure. Moreover, data from a previous study[16] indicated that $\chi^{(2)}$ stability in poled RA-HDT was nearly the same for films cured at 135 °C for 1 h or more. IR analysis of materials cross-linked under those conditions revealed that less than 7% of the isocyanate remained after curing.

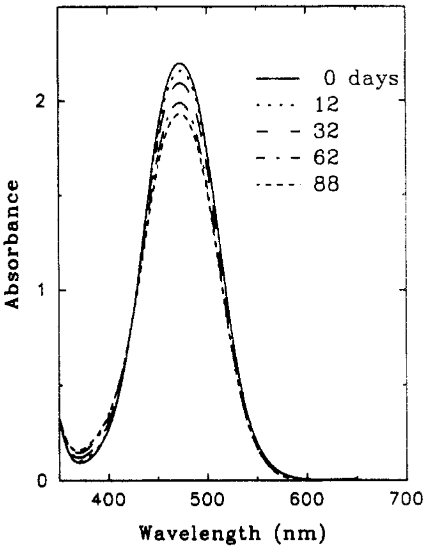

Figure 2. UV-visible absorption spectra of RA-HDT film manifesting alteration of the chromophore during the 3 months the film was maintained at 75 °C.

A graph of the change in peak absorbance of RA-HDT samples that were cured but not poled is also shown in Figure 1. Again, the data have been normalized to the peak absorbance values observed for the respective films after curing but prior to 75 °C storage. No difference is seen in the rate of change of peak absorbance for samples cured under different conditions; even the two sets of absolute absorption measurements themselves were nearly identical.

A comparison of the two plots displayed in Figure 1 indicates that the slopes generated from the two types of decay are identical and implies that the same mechanism is responsible for the instabilities. As both $\chi^{(2)}$ and absorbance are linearly dependent on the concentration of NLO dyes in the poled polymers, degradation or some other alteration of the chromophores is occurring when the films are stored at 75 °C in air. When similar tests were performed on RA-HDT films maintained at 100 °C, the $\chi^{(2)}$ and absorbance decay rates were also comparable during the time period following a more rapid drop-off of $\chi^{(2)}$ over the first several days.[16] An estimation of the energy of activation for this degradation process was made by fitting the 75 and 100 °C data—as well as a third set of absorbance data measured from samples stored at 140 °C—using a single-exponential expression. Plotting the resulting rates using an Arrhenius equation yielded E_a = 84 ± 40 kJ/mol and exhibited a temperature dependence that follows the general rule of thumb observed for organic chemical reactions.[17]

Analysis of degradation products of RA was attempted using various spectroscopic methods. The UV-visible spectra of RA-HDT films stored at 75 °C, shown in Figure 2, display a distinct isosbestic point. Thus, the dye is being converted into one or more products, of which only one is absorbing in the visible region of the spectrum. Isolation of this product from the RA-HDT films was thwarted by insolubility. Therefore, in an attempt to produce the species in a more tractable form, RA dye was refluxed in pyridine for 4 days and the products separated by liquid chromatography with UV detection. The visible spectrum of one prominent fraction contained an absorption band located in the wavelength region where absor-

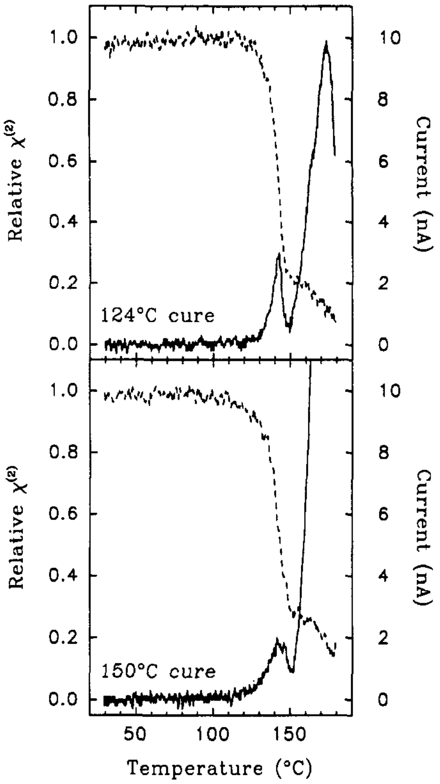

Figure 3. Relative $\chi^{(2)}$ (dashed line) and depolarization current (solid line) obtained via SHG and short-circuit TSC measurements, respectively, on RA-HDT films shortly after poling and curing. The heating rate was 2.5 °C/min.

bance increased during storage of RA-HDT at elevated temperature (see Figure 2). Mass spectroscopic analysis of this fraction suggested that it contained an oxidation product of RA in which a sulfur atom was replaced by oxygen.

Since $\chi^{(2)}$ stability of RA-HDT at elevated temperature over the long term is governed by changes to the NLO chromophore, such tests provided little information regarding orientational stability imparted to the poled dyes by the cross-linked network itself. Therefore, we turned to a short-term experiment, measuring SHG and TSC simultaneously while applying a linear temperature ramp, to determine whether there were any differences in physical properties pertaining to the polymers cured at 124 and 150 °C. At the heating rates and ranges employed in this experiment degradation of RA dye is insignificant, allowing dynamics of dipolar relaxation to be exhibited in the SHG and TSC data. UV-visible spectra of RA-HDT films heated for 2 h at 150 °C revealed only a 2% drop in the peak absorbance, while thermal gravimetric analysis (TGA) of the chromophore in powder form exhibited less than 1% weight loss up to 200 °C.

SHG and TSC traces of RA-HDT films poled and cured at 124 and 150 °C, respectively, are shown in Figure 3. SHG data are displayed as $\chi^{(2)}$ values normalized to values observed near the beginning of the temperature ramp. The current obtained from TSC measurement is the total current through an electrode area of approximately 0.8 cm^2. The location of the low-temperature bands in the TSC spectra at the point of steepest decline of $\chi^{(2)}$ identifies these bands as α bands which arise from image charge released during relaxation of molecular dipoles.[18] The area under the α band, which corresponds to the amount of charge released, is approximately the same for the two films. The depoling temperature T_d, arbitrarily defined as the temperature at which the α band peaks, is 142 °C for both samples. It is also seen that neither of the poled materials relaxes to a completely random state, as evidenced by a residual $\chi^{(2)}$ that decays slowly at temperatures above the position of the precipitous drop in SHG intensity. A similar response was recently reported in another cross-linked NLO polymer.[19] These results suggest that for both curing procedures the cross-linked networks obtained are equally poled and impart nearly equal stability to the oriented NLO dyes. Moreover, when the dyes do relax, they do so by means of a two-stage mechanism.

Closer inspection of the SHG and TSC curves, however, reveals differences between the two cured films. In the first place, the decrease in $\chi^{(2)}$ is found to begin at a lower temperature and progress more gradually in the film cured at 150 °C than in the one cured at 124 °C. This observation is confirmed by a broader α band in the corresponding TSC spectrum. The width of TSC bands depends on the breadth of the distribution of dipolar relaxation frequencies. For α relaxations, which require configurational rearrangement of molecular dipoles *and* the polymer chains to which they are attached, this distribution is attributed to differences in rotational masses of the relaxing segments.[20] Therefore, curing at a higher temperature appears to tie the RA dyes into the cross-linked network in a broader range of structures. One possible means by which this could occur is through secondary isocyanate reactions that form biurets and/or allophanates. Such reactions would result in the attachment of more than two cross-linking hexamethylene chains to some fraction of the RA molecules. At the same time, some dyes would be left bound to the network at only one end, owing to the depletion of available isocyanate.

A second variation is seen in the value of $\chi^{(2)}$ that persists after passing through the depoling temperature. The value is larger in the film cured at higher temperature, although the rate of $\chi^{(2)}$ decay thereafter appears to be equal in the two films. This result, together with the observation made above, implies that film cured at 150 °C provides a stiffer cross-linked network for the NLO dye than does the film cured at 124 °C.

This conclusion is supported by another experiment, in which the films were repoled after having been depoled during the TSC runs and quenched to room temperature. Concurrent monitoring of SHG during repoling disclosed that the steepest point of $\chi^{(2)}$ onset was at 122 °C for the film cured at 124 °C. This was also the temperature at which the current passing through the film rose rapidly. When the temperature was raised to 137 °C and the poling voltage removed, the SHG signal immediately dropped to near zero and then returned sharply to its original value once the voltage was reapplied. For the film cured at 150 °C, the steepest point of $\chi^{(2)}$ onset did not occur until the temperature reached 137 °C, where the current through this film rose rapidly.

These findings indicate that the two films have different effective glass transition temperatures when poled after quenching. In both cases the effective T_g lies *below* the temperature at which the respective films were cured. Such results are expected since as the T_g approaches the temperature at which the films are being cured, reduced mobility of reactants hinders cross-linking that would increase T_g further. On the other hand, when the films were cooled slowly after repoling, TSC runs on both samples again gave T_d near 142 °C, which is slightly higher than their effective T_g values. This result suggests that, regardless of curing temperature, slow cooling after poling allows densification of the polymer that produces equivalent environments in both films and provides enhanced

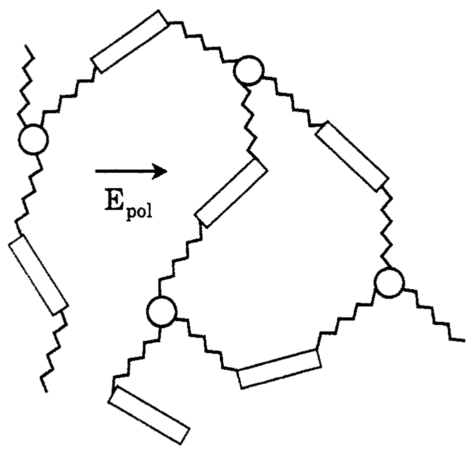

Figure 4. Pictorial representation of RA–HDT polymer network after poling and cross-linking showing why the RA dyes are restricted from complete dipolar relaxation when heated above T_d. Dye molecules are represented by rectangles and isocyanurate rings by circles.

stability over and above that of the cross-linked network alone.

The SHG/TSC data affirm that altering the curing temperature, which is the only difference in the procedures employed to cure the two RA–HDT films studied here, produces cross-linked networks which in some ways appear to be identical but in other ways are quite distinct. In Figure 4, we propose a model of the polymer structure that is consistent with these observations. The figure shows a cross-linked network in which the NLO dyes exhibit net polar order along the direction of the field used to pole the material. When the molecular dipoles relax during a TSC experiment, the temperature at which this occurs is influenced most by mobility imparted by the alkyl chains to which the dyes are attached. If some dyes are attached by more or less than the two chains shown, as was proposed to explain SHG/TSC data for the film cured at 150 °C, then this process will be stretched out over a broader temperature range.

Since attachment of the dyes to the alkyl chains was effected while the dyes were in an oriented state, the entire polymer network generated during curing also contributes to alignment stability. Consequently, some residual dipolar alignment persists above the depoling temperature because the dyes can only relax to the extent allowed them by the chains to which they are tethered. The stiffer network of the film cured at higher temperature maintains slightly greater polar order at this stage, and only when the entire network becomes rubbery at sufficiently high temperatures would complete relaxation of the dipoles in either film be enabled. The relative flexibility of the cross-linked polymer network also determines the effective T_g at which these depoled films can be repoled.

The TSC data can also be used to determine the activation energy for the dipolar relaxation process. We have employed two methods that have been described in the literature, the first based on the initial current rise of the α band[18] and the second on the half-width of the current peak.[20] Since both methods apply strictly to calculation of activation energy of dipoles with a single relaxation frequency, we used the α band corresponding to the film cured at 124 °C shown in the top plot in Figure 3, as it has the steepest current rise and is the narrowest. The broadening of the α band pertaining to the film cured at 150 °C exhibits a more gradual rise of the initial current, and it has been shown that, for distributed relaxation frequencies, an effective activation energy is derived from this procedure which is always lower than that corresponding to a single relaxation frequency.[18] Therefore, the value obtained from the film cured at 124 °C should represent a lower bound on the activation energy.

Activation energies from 260 to 450 kJ/mol were obtained for RA–HDT. These values are in the range of those obtained for other NLO polymers, such as the side-chain polymers reported by van der Vorst and van Rheede.[3] Moreover, they are far in excess of the activation energies determined from the long-term SHG and UV–visible stability measurements, confirming that one mechanism (namely, chromophore degradation) dominates $\chi^{(2)}$ decay at lower temperatures over long periods of time while another (dipolar relaxation) governs the decay at sufficiently high temperatures.

Turning from the current response in the TSC spectra that originates from dipolar relaxation, we now consider the current that appears at even higher temperatures, as observed in Figure 3. This current arises from the mobilization of space charges in the film and is labeled as the ρ band. Two types of charges have been described. Heterocharges are associated with ions and/or electrons in the polymer which are frequently found to originate from impurities in the sample.[20] During poling they migrate toward electrodes having opposite polarity and are restrained in the cooled polymer until the film is reheated above T_g. Homocharges are trapped in the film near electrodes having the same polarity as their respective charges and, for the case of poling with deposited electrodes, occur by means of charge injection at high fields.[21]

The sign of the current giving rise to the ρ bands in Figure 3 indicates that these bands are produced by relaxation of heterocharges in the RA–HDT films. The current observed from the sample cured at 150 °C exceeded 35 nA and had not yet peaked at the end of the TSC scan. The fact that it was several times larger than the corresponding current from the film cured at 124 °C is due to increased space charge mobility and/or concentration that occurs at higher curing temperatures. Indeed, the current observed during poling was substantially larger in the film cured at 150 °C.

The stability of the polarized heterocharges was investigated by running SHG/TSC on the RA–HDT films that had been maintained at 75 °C for 3 months. Plots of the spectra obtained are shown in Figure 5. The data are nearly identical to the results in Figure 3 except for two features: (1) the current at temperatures just above the point of dipolar relaxation is negative instead of positive, and (2) the current density in this temperature region is approximately of the same magnitude for the two samples. (The measured current in the TSC spectrum of the film cured at 150 °C is smaller because the area of the electrode had been reduced.) The change in sign of the current indicates that homocharges were flowing in the aged films. When the films were repoled and SHG/TSC run immediately thereafter, heterocharge current reappeared, as manifested by a positive sign for the high-temperature band.

For the case of homocharge injection when poling an NLO polymer under high field (~1 MV/cm) using deposited electrodes, the isolation of homocharge current in short-circuit TSC of by means of aging at elevated temperature has not been noted previously, to our knowledge. Some poled polymer studies have reported the coexistence of heterocharge and homocharge currents in short-circuit TSC,[7,22] but observation of homocharge current occurred after heterocharge relaxation (i.e., at higher temperatures) and did not depend on aging. The

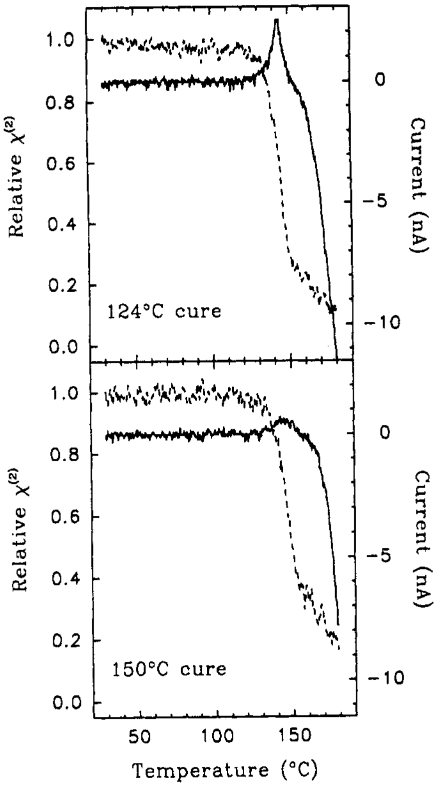

Figure 5. Relative $\chi^{(2)}$ (dashed line) and depolarization current (solid line) obtained via SHG and short-circuit TSC measurements, respectively, on RA-HDT films that had been maintained at 75 °C for 3 months after poling and curing. The heating rate was 2.5 °C/min. Note the large, negative homocharge current in place of the large, positive heterocharge current observed in Figure 3.

role of aging in the relaxation of heterocharge to leave only homocharge remaining has been demonstrated in other materials,[23-25] although these investigations involved homocharge produced at low poling fields by breakdown in an air gap between the film surface and a mechanically contacted electrode.

An explanation of our results derives from an understanding of the polarization and relative stability of hetero- and homocharges. During the time period shortly after poling, separation of heterocharges dominates the space charge polarization, as evidenced by the relatively large positive currents produced in the TSC. Homocharges are also present at this stage, but their concentration and/or mobility are too low to significantly oppose the heterocharge current. During the 75 °C aging period the heterocharges, which have been shown in other materials to decay more quickly[23,24] and at lower temperatures[7,22] than homocharges, acquire sufficient mobility to be neutralized via drift in the local electric field and by diffusion. As a result, when TSC is run on the aged samples, only homocharge current is observed in the region above the temperature of dipolar relaxation. The magnitude of the homocharge current density is nearly equal in the two films cured at different temperatures because charge injection is highly dependent on the poling field strength (which was nearly the same in both cases) but, in contrast to heterocharge polarization, is influenced little by the difference in curing temperatures employed here.[21]

The persistence of dipolar alignment in RA-HDT throughout the 75 °C aging period while heterocharges completely relax is not inconsistent with the fact that heterocharge current does not flow until after dipolar relaxation in the TSC. Relaxation of the oriented dyes typically occurs at temperatures where motion of the alkyl chains to which they are attached begins.[20] A substantial flow of heterocharges, on the other hand, is facilitated by heating the polymer to higher temperature where, in the case of ionic carriers, sufficient free volume has been created for the charges to drift and diffuse readily.[18,20] However, well below these temperatures the heterocharges still have a finite probability for migration since they are not bound to the surrounding network. As a result, given a sufficiently small activation energy the heterocharge may be neutralized even at relatively low temperatures. In contrast, relaxation of molecular dipoles in this temperature range is significantly restricted due to large activation energy (see above). Trapping of homocharges preserves their polarization throughout the temperature range.

The longevity of homocharge polarization accompanied by decay of heterocharge in these poled polymers may be beneficial in terms of $\chi^{(2)}$ stability. Since heterocharges are polarized in the same direction as the oriented molecular dyes, they would serve as a destabilizing factor to the NLO material by repelling like charges. Thus, it would be favorable for them to neutralize during aging. However, homocharges would tend to stabilize the alignment since they are polarized in the opposite direction and their persistence could help maintain the $\chi^{(2)}$ induced by poling. The effect they would have on field uniformity during EO device operation is unknown.

Conclusions

Long-term stability measurements employing SHG have shown that RA-HDT films which have been poled and cross-linked exhibit a slow decay in $\chi^{(2)}$ when maintained at 75 °C in air. Additional measurements by UV-visible spectroscopy displayed the same rate of decay in the peak absorbance of the films, implying degradation of the RA dye itself and not relaxation of dipolar alignment was the major cause of the decline of $\chi^{(2)}$. The significance of these results lies in the fact that despite the short-term stability at 150 °C demonstrated in UV-visible spectra and TGA measurements of the RA chromophore in film and powder, respectively, degradation of the dye and an accompanying 15% drop in $\chi^{(2)}$ occurred at 75 °C over the space of 3 months. When evaluating dye stability in NLO materials, long-term measurements of the chromophores *in the NLO polymer* should therefore be considered.

While long-term $\chi^{(2)}$ stability was unaffected by cross-linking poled RA-HDT film at either 124 °C for 2 h or 150 °C for 1 h, short-term SHG/TSC experiments revealed subtle differences in the resulting polymer networks. Curing at higher temperature produces a material that comprises a broader range of structures which secure the NLO dye in the oriented film. This material also maintains slightly greater residual alignment of the dyes after depoling by TSC and must be repoled at a higher temperature than is necessary for the film cured at lower temperature.

On the other hand, $\chi^{(2)}$ stability of RA-HDT as determined by TSC is quite similar for films cured at either temperature. Depoling occurs reproducibly at 142 °C and is influenced most by the alkyl chains immediately surrounding the NLO dyes, provided the films have been cooled slowly after poling. The activation energy of depoling is at least 260-450 kJ/mol, far exceeding the corresponding energy of RA dye degradation, 84 kJ/mol, obtained from long-term $\chi^{(2)}$ and UV-visible stability measurements. Thus, the cross-linked polymer should provide excellent alignment stability to an NLO dye that exhibits suitable thermal stability in a polymer film.

At the electric field strengths used to pole RA-HDT films (~1 MV/cm), substantial charge is injected into the films as revealed by homocharge current detected in TSC measurements. The homocharge current is only observable after the samples have been aged at elevated temperature, during which time space charges which have been polarized during poling are able to migrate and be neutralized. Homocharge, which persists throughout the aging time span, may also contribute to stability of oriented molecular dipoles.

Acknowledgment. We thank T. Lo for synthetic efforts, W. Stebbings, J. Miller, J. Schroepfer, D. Weil, and C. Jacoby for analytical measurements, and G. Boyd, R. Moshrefzadeh, D. Lin, and E. Cross for helpful discussions.

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