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Optical and Nonlinear Optical Characterization of Molecularly Doped Thermotropic Liquid Crystalline Polymers

Gerald R. Meredith, John G. VanDusen, and David J. Williams*

Webster Research Center, Webster, New York 14580. *Received January 26, 1982*

ABSTRACT: Films consisting of a thermotropic nematic liquid crystalline copolymer doped (2% by weight) with the pleochroic dye 4-(dimethylamino)-4′-nitrostilbene (DANS) were subjected to dc transverse electric fields and their linear and second-order nonlinear optical properties examined. Orthoscopic examination of the films established the nematic texture of the doped polymer and the ability to achieve dc field induced homogeneous alignment. From linear dichroism measurements in the films an order parameter of 0.3 was obtained. Second harmonic generation (SHG) measurements relative to quartz were made to establish the value of second-order nonlinear susceptibility $\chi_{111}^{(2)}$ and to probe the nature of the dc field induced alignment. The reduced dimensionality of the nematic environment enhanced the dc field induced statistical dipole alignment of the dopant molecule as predicted by the Ising model. Poling of the films below T_g leads to a second-order susceptibility $\chi_{111}^{(2)} \sim 3 \times 10^{-9}$ esu. Measurements of SHG at beam powers sufficient to provide local heating reveal relaxation mechanisms involving the DANS molecule or molecular aggregates and the polymer "cage" in which the molecules reside. Measurements of SHG under thermal equilibrium conditions reveal an unexpected decrease in SHG above T_g, which may be due to aggregation of the DANS molecules.

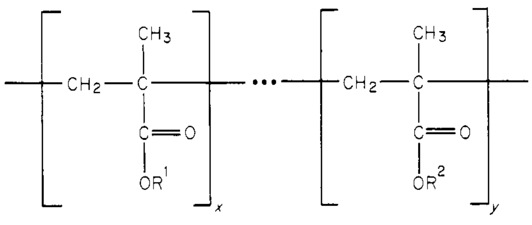
Introduction

The ease of orientation of nematic liquid crystalline materials in electric fields and the resulting anisotropic properties have been the source of numerous applications in display technologies.[1] It has recently been demonstrated that the properties of liquid crystals and polymers could be combined by attaching mesogenic units to polymers by flexible spacer groups that "decouple" the motions of the mesogenic units from those of the polymer backbone.[2] The new materials exhibit broad nematic regions above the glass transition temperature and exhibit many of the features of molecular liquid crystals. It has been shown that in certain uses electric field induced orientation of the nematic phase can be achieved, and the possibility of freezing in the induced orientation by cooling below the glass transition temperature T_g has been suggested.[3]

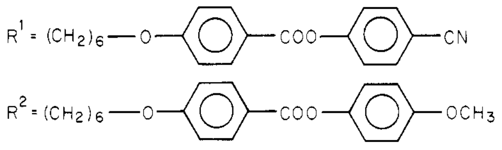
The use of pleochroic dyes to probe the structure of liquid crystals and to provide high-contrast electrooptic (Kerr type) effects has been investigated.[4] Finkelmann has probed a negative uniaxial liquid crystalline polymer (optic axis perpendicular to cover slides) with 4-(dimethylamino)-4′-nitrostilbene (DANS) and found that no macroscopic preferential alignment of the dye could be detected. Microscopic regions of the orientation were not ruled out and might explain birefringence and X-ray diffraction data. The possibility of guest-host alignment in these materials suggests the possibility of achieving homogeneous electric field induced alignment of a guest dye in a host polymer and maintaining that alignment below T_g.

In addition to acting as a probe for guest-host interactions, DANS is one of a class of organic molecules that exhibits an extremely large molecular hyperpolarizability $\beta = 4.5 \times 10^{-28}$ esu.[6] Third-rank tensorial properties such as second harmonic generation and the linear electrooptic (Pockels) effect require that the bulk phase must not possess either a real or orientational average inversion center. Several approaches for achieving noncentrosymmetric polar structures in organic crystals[7] and molecular aggregates[8] have been recently reported. Electric field induced dipolar alignment of a guest molecule in a host polymer followed by freezing this structure into the rigid state of the polymer is another way of destroying this center of inversion symmetry. This has been demonstrated to occur for numerous guest dyes in polymer hosts when electric fields were applied above the glass transition temperature.[9] Other alignment methods based on shear-induced orientation may provide uniaxial but not dipolar alignment.

In this study we have explored the possibility of guest-host interactions of DANS with thermotropic liquid crystalline copolymer I. We have also investigated the possibility of enhanced dipolar alignment (relative to that obtained in an amorphous polymer medium) of the DANS molecule in the polymer due to the nature of their cooperative interaction. Linear and nonlinear optical characterization were used to determine the electric field induced axial alignment of the copolymer and dye and the extent of polar alignment of the DANS molecule. The value of the second-order nonlinear coefficient $\chi^{(2)}$ of the film was measured. During the course of the nonlinear optical characterization some novel features of the guest-host interaction in the films were found.



I



$x = 0.5, y = 0.5$

Experimental Section

Monomer Synthesis. Methacrylate monomers possessing mesogenic side-chain structures as described by Finkelmann[2] were prepared by the procedure outlined in Figure 1. The monomers reported here consist of an *n*-hexyl spacer group coupled to either the 4-methoxyphenyl 4-oxybenzoate (I) or 4-cyanophenyl 4-oxybenzoate (II) unit. Structural identification was made by ^{1}H NMR, ^{13}C NMR, and infrared spectroscopy.

Polymerization. Random copolymers of I and II were obtained by solution polymerization in vacuum ampules with chlorobenzene solvent and azobis(isobutyronitrile) initiator. Purification by reprecipitation into methanol gave an 80% recovery of polymer for a 50/50 monomer charge ratio.

GPC. Gel permeation chromatography was carried out in chloroform with Styragel columns with narrow-distribution polystyrene standards. The molecular weight distribution of both

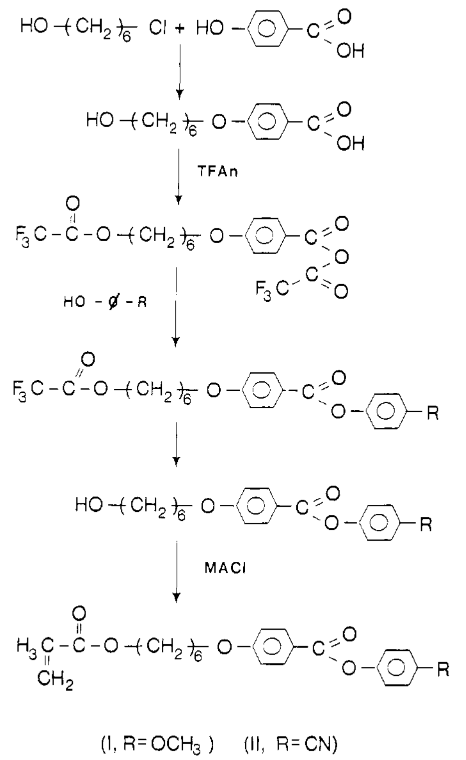


Figure 1. Synthesis of monomers.

the 50/50 copolymer and the homopolymer of I was approximately 3.4 with estimated $\bar{M}_n$ values of ~50 000.

Dopant. DANS [4-(dimethylamino)-4′-nitrostilbene] was used as received (Eastman).

Film Preparation. Films of the copolymers and their solid solutions with the pleochroic molecule (DANS) were cast from 10% (w/v) THF solution onto interdigital electrode patterns that were positioned on 1 in. × 3 in. × 0.06 in. glass substrates. The electrodes were 25 μm wide evaporated chrome via photolithographic delineation, having interdigital spacings of 200 and 1000 μm. Transverse electric field (dc) orientation of the film was achieved at field strengths of 0.6–1.0 V/μm as the nematic phase was heated at temperatures 2–4 °C below the isotropic clearing point and then cooled below the polymer glass transition.

Measurements. Optical characterization and thermotropic observations were made using transmission microscopy with a Mettler F-52 hot stage. Optical absorption measurements were performed on a Cary 17D spectrophotometer with a linear polarization fixture.

The apparatus employed for SHG measurements, schematically shown in Figure 2, was a Q-switched Nd^{3+}/YAG laser configured as an unstable resonator with polarization output coupling (Quantel Polarex). The laser was operated just above threshold, supplying 2–5 mJ per pulse of 1.06-μm light, which was focused to an approximately 400-μm spot at the sample. Variation of the laser polarization was accomplished with a double-quarter-wave rhomb rotator. Signal polarizations were checked with plastic polarizing sheet. The harmonic light was collected with $f/16$ optics, filtered from the fundamental, and passed through a 20-cm focal length grating monochromator with an 8-nm bandwidth. Detection was accomplished by an 11-stage amplified S-20 photomultiplier tube (EMI 9558). The computer-controlled gated electronic detection and digitization apparatus is described elsewhere.[10]

Results and Discussion

A. Electric Field Alignment and Characterization. If the structure of a dopant dye molecule is chemically similar to the mesogenic unit in a liquid crystalline material, the dye will tend to adopt the same anisotropic orientation as the liquid crystalline phase. If the transition moment is known relative to the principal axis of the dye molecule, information can be obtained on the local ordering in the system. For DANS the principal direction and polarization of the longest wavelength transitions are parallel.[11] Finkelmann and Day[5] used DANS to probe the structure of the liquid crystalline polymer II and found no apparent differences between absorbance in the isotropic and liquid crystalline phases.

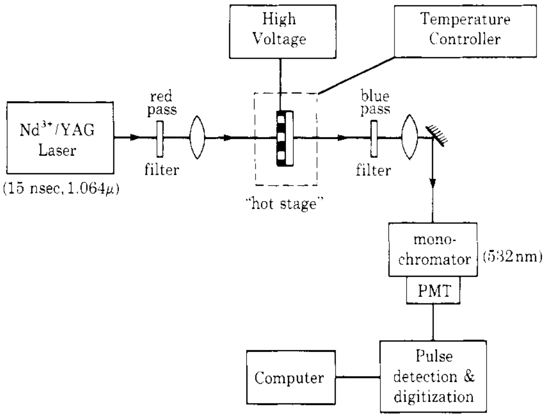
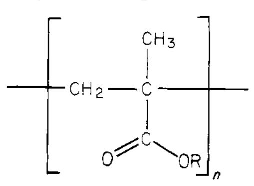
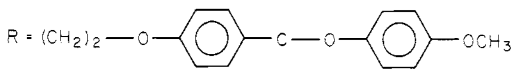


Figure 2. Schematic representation of experimental apparatus.



II



Described below are experiments to probe electric field induced homogeneous alignment of thin films of I doped with 2% DANS by weight.

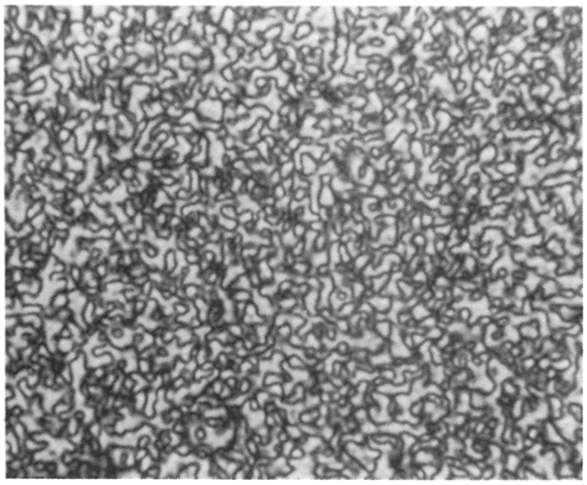
The thermal properties and phase transitions in the film were examined by DSC. A broad second-order transition characteristic of T_g was observed between approximately 300 and 320 K. An exotherm is observed at 374 K and is attributed to the nematic-to-isotropic melting point.

A thin film (~3 μm) of the mixture in THF was cast onto a glass slide with interdigital electrodes. The spacing between the electrodes was 200 μm. As the film was heated, the liquid crystalline state could be identified by its scattering texture and disinclination lines from polarization microscopy (Figure 3a). As the film was heated slowly through its clearing point (274 K), total extinction of light was observed through cross polarizers (Figure 3b). Below the clearing point the scattering texture reappeared. Application of a ~1 V/μm transverse electric field resulted in a nearly homogeneous birefringent film. When viewed perpendicular and then parallel to the applied field with a single polarizer, the homogeneous alignment of the film was evident and the dichroic contrast could be easily observed. From the optical absorption spectrum of the film (Figure 4) the order parameter, defined as

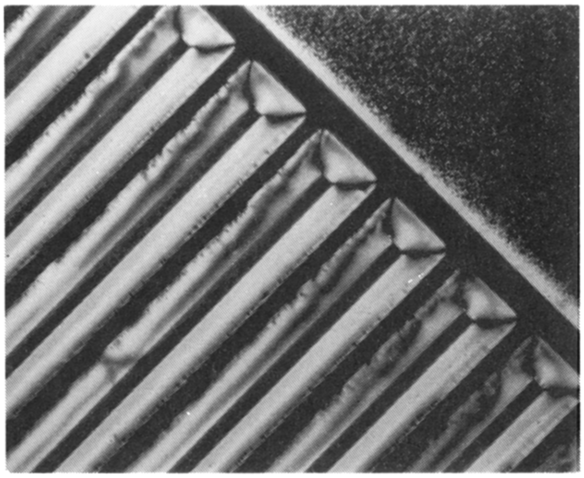
$$S = (A_{\parallel} - A_{\perp})/(2A_{\perp} + A_{\parallel})$$

where $A_{\parallel}$ and $A_{\perp}$ are the absorbances parallel and perpendicular to the field direction, was determined to be 0.3. These experiments are the first demonstration of homogeneous transverse alignment of a thermotropic liquid crystalline polymer, which is a necessary prerequisite for probing the second-order nonlinear optical properties of the films in transmission.

B. Second-Order Nonlinear Optical Susceptibility Measurements. The electric field induced second-order



a.) Optical texture of unaligned mesophase (orthoscopic veiw 500x)



b.) Electric field aligned mesophase (100x)

Figure 3. Orthoscopic view of (a) nematic texture viewed through crossed polarizers and (b) transverse homogeneous texture following application of a 1.3 kV/mm dc field.

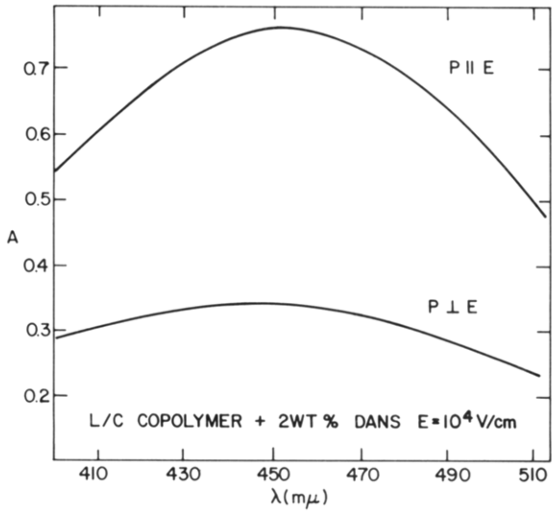


Figure 4. Optical absorption spectrum with polarizers perpendicular and parallel to the applied field.

nonlinear susceptibility $\chi_{111}^{(2)}$ for a 3-μm-thick 2% doped DANS film was estimated through measurements of SHG for fundamental and harmonic light polarized parallel to the alignment field (taken as direction 1). Numerous combinations of thermal and electric field histories were investigated. It was found that a large signal could be obtained when the film was poled with an applied field of 1.3 V/μm at 293 K for 6 h. When the maximum SHG was achieved under these conditions, the value of $\chi_{111}^{(2)}$ was determined relative to the known value of $\chi_{xxx}^{(2)}$ for quartz[12,13] according to the following procedure. A 2° y-cut quartz wedge compensated by a 2° x-cut quartz wedge was placed in the laser beam before the film. To avoid heterodyne beating of SHG from quartz and the film, which would occur since $\chi_{111}^{(2)}$ and $\chi_{xxx}^{(2)}$ quartz were comparable, the laser polarization and quartz wedges were rotated 90° relative to the direction of large nonlinearity in the film. The quartz wedges were translated relative to the beam to locate a position where the path length through the crystal is a proper multiple of the coherence length to ensure that the harmonic signal is maximum. The ratio of signals from film to quartz was then noted and subsequently corrected for two effects.

The first effect relates to the differences in harmonic generation due to differences in position of the quartz wedge and film relative to the focal point of the laser beam. In order to make this correction, the focal point of the beam was moved relative to the quartz wedge after the optical limitation of the interdigital electrode pattern was removed. This determined the SHG that would arise for a laser beam equivalent to that intercepted by the film. This resulted in a 20% increase for quartz and an appropriate correction in the ratio was made.

The second effect involves corrections for transmission of the harmonic light generated in quartz through the film. This correction was determined by placing the film at the focus of a harmonic beam generated in quartz at the input slit of the detection monochromator. The film was positioned to ensure passage between the electrodes. Transmission coefficients for $E^{2\omega}$, both parallel and perpendicular ($T_{\parallel}$ and $T_{\perp}$) to the alignment field, were measured. The SHG ratio was multiplied by $T_{\perp}$. Disregarding differences in the refractive indices of film and quartz, one can show that[14]

$$\chi_{111}^{(2)} = \chi_{xxx}^{(2)}[R]^{1/2} l_c^{q} / lF \tag{1}$$

where R is the corrected SHG intensity ratio, l_c^q is the coherence length of quartz (20.6 μm), l is the film thickness, and F is a factor defined as

$$F^2 = (l_c^2/2l^2)e^{-\alpha l/2}\{\cosh(\alpha l/2) - \cos(\pi l/l_c)\} \tag{2}$$

Here α is the absorption coefficient and l_c is the coherence length for fundamental and harmonic waves in the film. For the film

$$F^2 \approx (0.28 l_c^2/l^2)[1 - \cos(\pi l/l_c)] \tag{3}$$

for $l < lc/2$, which is applicable for the films, $F \sim 1.2$. From these considerations and using $\chi_{xxx}^{(2)} = 2.25 \times 10^{-9}$ esu, we obtain $\chi_{111}^{(2)} \sim 3 \times 10^{-9}$ esu for the film.

The measured value of $\chi_{111}^{(2)}$ is compared with what might be expected from a simple model below. The model deduces the second-order susceptibility expected for an "oriented gas" with statistical averaging of the molecular dipole moments. The second-order polarizability can be written as[15]

$$P^{2\omega} = \chi^{(2)}(E^{\omega})^2 \tag{4}$$

where

$$\chi_{xxx}^{(2)} = \frac{N}{V}\langle F\beta_z\rangle \approx \frac{N}{V}F\langle\beta_z\rangle \tag{5}$$

where N is the number of molecules, V is the volume, F is a local field factor, and β_z is the projection of the vector portion of the third-rank hyperpolarizability tensor component onto z, the long molecular dipole axis. For DANS it is expected that $\beta_z = \beta_{zzz}$, the major element of this term.[14] The brackets in (5) indicate orientational averaging and the approximation of replacing the average over F with an average value is made. The thermal average of β_z under our approximation and according to the Boltzmann distribution law can be written as[15]

$$\langle\beta_z\rangle = \beta\langle\cos^3\theta\rangle \tag{6}$$

where

$$\langle\cos^3\theta\rangle = [(6+\alpha^2)\coth\alpha - (6+3\alpha^2)/\alpha]/\alpha^2 \tag{7}$$

and

$$\alpha = \mu F_0 E/kT \tag{8}$$

with μ the permanent dipole moment, F_0 the local field factor, and E the applied dc field. In the high-temperature limit when $\mu F_0 E << kT$, eq 6 reduces to

$$\langle\beta_z\rangle \approx \beta_z\alpha/5 \tag{9}$$

The local field factors F_ω can be approximated by Onsager's equation[16]

$$F_\omega = (\epsilon_\omega^i + 2)/(2 + \epsilon_\infty^i/\epsilon_\omega) \tag{10}$$

where ϵ_∞^i is the high-frequency dielectric constant of species i, ϵ_ω^i is that at frequency ω, and ϵ_ω is that of the solution. For frequency doubling $F = F_\omega^2F_{2\omega}$[15] and typical values are $F_0 \approx 3$ and $F_\omega \approx F_{2\omega} \approx 2$.

An additional modification must be made to eq 5 to account for the correlation between the DANS molecule and the principal axis of the nematic liquid crystal. This favorable one-dimensional orientation enhances the statistical probability for alignment and, therefore, the value of $\langle\beta_z\rangle$ in eq 9. If we assume a simple Ising model, the enhancement would be a factor of 5. Substituting (9) and (8) into (5) and multiplying by the factor of 5 for the Ising model, we obtain

$$\chi_{xxx}^{(2)} = (N/V)F\beta_z(\mu F_0 E/kT) \tag{11}$$

For a 2% by weight doping of a polymer (specific gravity $\sim$1), $N/V \approx 4 \times 10^{19}/\text{cm}^3$, $F_0 \sim 3$, $F \sim 8$, $E = 43$ esu (1.3 kV/mm), $T = 293$ K, $\mu = 7.4$ D, and $\beta = 4.5 \times 10^{-28}$ esu,[6] we obtain $\chi_{xxx}^{(2)} \sim 3 \times 10^{-9}$ esu. Considering the level of approximation, this is in excellent agreement with the observed value of 3×10^{-9} esu. This coincidence shows on a gross scale the reasonableness of our interpretation that inversion symmetry could be partially removed by electronic field poling. Clearly, the crudity of the local field estimation, the neglect of a third-order parameter, which breaks down the Ising model, and disregard of the host nonlinearity prevent claims of a more than fortuitous agreement between the measured value of $\chi_{xxx}^{(2)}$ and that predicted by the model.

C. Thermal and Relaxation Effects. In the course of the nonlinear optical characterization it became apparent that at higher laser powers local heating of the film could occur and that rather complex local relaxation and reorientation behavior could be probed by SHG measurements. After the SHG signal reached its maximum value due to poling of the sample with an electric field of 1.3 kV/mm, the applied voltage was removed, with precautions taken to thermally regulate the film and substrate. At sufficiently low incident powers the SHG signal intensity was stable over many days. If the laser power was increased or thermal regulation not maintained, it was noticed that the SHG intensity began to decrease in the absence of the poling field.

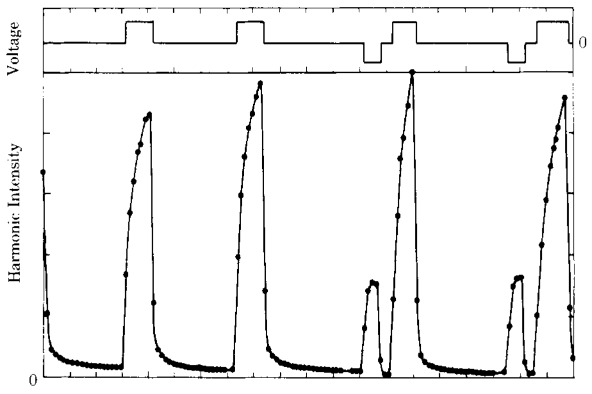


Figure 5. Second harmonic generation intensity following application of dc fields as indicated at the top of the diagram.

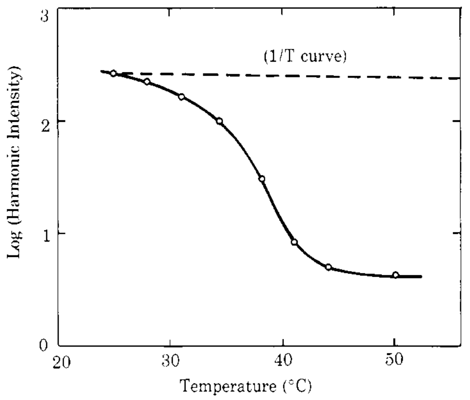


Figure 6. Logarithmic plot of second harmonic generation vs. temperature and $1/T$ curve from eq 11.

A time profile of the SHG intensity under various applied voltage conditions is shown in Figure 5. In preparation for this experiment the sample was poled for several hours. Upon zeroing of the applied voltage, the SHG underwent rapid decay ($\tau \sim 40$) followed by a much slower decaying component ($\tau \sim 23$ min). When the dc field was reapplied, the SHG recovered and exceeded the initial value by 30% after only 6 min. Continued cycling resulted in further increase in the SHG to a level 50% greater than the initial value and in the same fast and slow decay components. Each time the cycle was repeated the slow component decreased $\sim$20% relative to its value in the previous cycle. Reversing the dc bias produces a smaller SHG followed by rapid relaxation. Application of the original dc bias causes the signal to reappear. It is obvious that further combinations of field and local heating would reveal additional subtleties in behavior.

The results of a second experiment to probe the thermal behavior of the system are given in Figure 6. The data points represent the maximum dc-induced SHG intensity achievable at a given temperature. Since the same intensity is achieved by either lowering or increasing the temperature, it is presumed to represent the equilibrium condition for the sample. The dashed line represents the expected $1/T$ dependence of $\chi^{(2)}$ predicted by eq 11. It is clear (note the log scale) that the data represent a significant departure. It should also be noted that the main decrease occurs in the region of the broad T_g noted by DSC.

The data in Figures 5 and 6 represent two distinctly different modes of sample heating. The former were acquired under highly nonequilibrium conditions and the latter at equilibrium. In both cases the SHG of the DANS molecule acts as a highly sensitive probe of local structure and motion in the doped solid.

The decay and buildup of SHG intensity shown in Figure 5 can be attributed to two effects. The long relaxation tail appears to be associated with the polymeric "cage" in which the dopant molecule resides. As the polymer is heated it apparently deforms to accommodate dopant molecule. The rapid buildup and decay of SHG reflects the relative ease of turning the molecule within the cage. The asymmetric nature of the cage is clearly indicated by the much smaller SHG obtained when the dc bias is reversed. The increase is harmonic intensity on repeated cycling indicates that repeated attempts to align molecules increases the probability of circumventing local cage barriers, which hinder the rotations of some guests or associates.

The interpretation of the data obtained under equilibrium conditions (Figure 6) is less straightforward. Clearly, the relaxation phenomena occurring in the glass transition region have a profound effect on the ability of a dc field to sustain molecular alignment. Above T_g there is an increased possibility of translation diffusion of the DANS molecule and the establishment of a monomer–dimer or higher order aggregate equilibrium. Since it is likely the dimer would be of the head-to-tail centrosymmetric variety, we would expect the presence of dimers to significantly decrease SHG. Below T_g it may be possible to dissociate dimers by the action of the external field and achieve net dipolar orientation. The reestablishment of dimers or centrosymmetric aggregates might also account for the rapid relaxation of SHG under nonequilibrium heating conditions. Further detail on the nature of the alignment and thermal relaxation processes will be the subject of future work.

Conclusions

We have demonstrated that large second-order nonlinear optical coefficients can be obtained when molecules with large molecular hyperpolarizabilities are doped into a thermotropic nematic liquid crystalline polymer host. The SHG was considerably larger (100-fold) than could be obtained wih a 2% DANS doped poly(methyl methacrylate) sample. This result is interpreted as being, at least in part, due to the guest–host correlations that were characterized in the case of the liquid crystalline polymer. Excellent agreement was obtained between the experimentally measured value of $\chi^{(2)}$ and that predicted by a simple model based on statistical dipolar alignment of the guest in the oriented host.

The polar alignment was found to be stable for long periods of time in the absence of external fields as long as local nonequilibrium heating by the laser was avoided. The complex relaxation of the SHG can be interpreted with a molecule (dimer or aggregate) in a viscous hole model. The precipitous drop in SHG above T_g appears to be accounted for only if the establishment of a new equilibrium between a species not exhibiting SHG and an active one is invoked. A monomer–dimer or higher aggregate equilibrium would appear to account for this.

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