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Polar Order and Relaxation

of Second Order Nonlinear Optical Susceptibility

in an Electric Field Polarized Amorphous Polymer

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Abstract

The dependence of the second harmonic generation (SHG) signal of an amorphous polymer system containing nonlinear optical (NLO) chromophores on the polarizing electric field is investigated. It is shown that under a weak poling field condition, the SHG intensity is proportional to E_p^2, provided that the polarizing electric field E_p is greater than a threshold field, E_s. Above E_s, the macroscopic polar orientational order is established. The lengthening of the relaxation time for polar orientational order with increasing E_p is also observed. Theoretical analysis shows that the relaxation time is proportional to the polar order initially induced by the polarizing field. Experiments have been carried out to confirm the theoretical prediction.

Introduction

Amorphous polymers incorporated with chromophores having large second order hyperpolarizability have emerged as a new class of electro-optic materials. The nonlinear optical (NLO) effect responsible for the electro-optic response and second harmonic generation can be induced by an external electric field, by which the macroscopic center of inversion symmetry is destroyed. The external electric field polarizes the sample, and creates polar order in the amorphous polymer system. The electric field is usually applied at temperatures higher than the glass transition temperature (T_g) of the polymer, and removed at temperature below T_g when the induced polar order is frozen in.

Two types of polymeric second order NLO materials have been prepared:[1]
1) guest/host systems with NLO chromophores dispersed in the amorphous polymers;
2) NLO chromophores covalently linked to the polymer backbone. Due to chemical bonding, type 2 materials build in significant impediment to relaxation of the polar order induced by the electric field. Further stability in the orientational polar order can be accomplished through structure-enhancing hydrogen bonding or chemical cross-linking of the NLO chromophores to neighboring polymer chains.[2] However, due to ease in varying the relaxation rate and in changing continuously the NLO chromophore concentration before the phase separation sets in, type 1 materials provide as a useful system for investigating the relaxational dynamics of the second order NLO effect.

The effectiveness of poling will determine the subsequent electro-optical activity of the sample. To prepare a stable NLO polymeric material for device applications, one needs to understand effects associated with thermal annealing and electric field poling. Isothermal annealing has an effect on lengthening the relaxation time of the orientational polar order parameter (POP) and thereby stabilizing the second harmonic generation (SHG) response.[3]

The lengthening of the relaxation time is due to densification of the material below the glass transition temperature, in connection with physical ageing of the amorphous polymer in the nonequilibrium state. We are concerned in this paper with the effect of electric field poling. We have investigated the electric field dependence of the orientational relaxation time of the NLO chromophores under an isothermal condition. In addition, the SHG intensity is also measured as a function of the strength of the poling electric field. We show that both the intensity and the relaxation time increases with increasing the poling field strength. The increase in the relaxation time with increasing the poling field strength clearly indicates that the decay of the SHG response is closely associated with the induced orientational polar order, thereby suggesting that the decay of the second order NLO response can be impeded by poling the amorphous NLO polymer with a high electric field strength. We have provided a theoretical analysis to substantiate the electric field dependence effect.

Experimental

Appropriate amounts of NLO chromophores NAS (4-amino-4´-nitro-trans stilbene) and PMMA (polymethylmethacrylate) were dissolved in chloroform to form solutions with different NAS concentrations. After filtering each solution to remove undissolved particulates, polymer films were prepared by spin coating the solution on ITO (indium tin oxide) coated soda lime glass slides. The glass slides containing polymer films were first placed in a vacuum oven at 50°C for over 24 hours, and then baked for another 24 hrs. at higher temperature (slightly above T_g) to remove the solvent used in spin-coating. The concentration of the NAS chromophore was monitored by UV-visible absorption spectroscopy and appeared to suffer little decrease by the soft and hard baking processes. Two identical glass slides coated with NLO polymer films were then placed in the vacuum

oven at 120°C to fuse in a sandwich configuration for future contact electrode poling.

The second harmonic generation SHG intensity was measured by using a setup similar to that reported previously.[4] It consisted of a Nd:YAG laser (Spectra Physics GCR-11, λ = 1.06 μm, Q-switched at 10 Hz) used as an excitation source. The polymer film/electrode assembly was placed on a goniometer stage located inside a temperature controlled oven. The film temperature was accurate to ± 0.2°C, controlled by a temperature controller. The incidence angle of the fundamental beam at 1.06 μm was 60°; the transmitted SHG signal at 532 nm was selected by a monochromator and detected by a photomultiplier, followed by a preamplifier and averaged by a boxcar integrator.

The glass transition temperatures (T_g) of the NAS/PMMA samples were determined by using a DSC (Perkin Elmers, Delta series). Shown in Fig. 1 is the variation of T_g with the NAS concentration. Over the 0-10 wt % concentration, the glass transition temperature appears to decrease linearly with increasing NAS concentration. The refractive index and thickness of the polymer film were measured by using a prism coupler (Metricon). The prism coupler was operated in accordance with the optical waveguide principle where the polymer film serves as the propagation layer in the slab waveguide configuration.

Results and Discussion

1. SHG Intensity and Poling Field Strength

The SHG signal of the NLO film under the isothermal condition was measured as a function of the strength of the electric field employed to polarize (or pole) the sample. Shown in Fig. 2 is the plot of the amplitude of the SHG signal for the 5 wt% NAS in PMMA sample at 110°C as a function of the square of the poling field strength (E_p^2). One notes that there appears a threshold voltage of about 0.9×10^6 V/cm, below which the signal

only increases slightly with increasing poling field strength. Above this voltage, the SHG signal increases more rapidly and it clearly increases linearly with E_p^2.

The existence of the threshold poling field (E_s) has not heretofore noticed, and it indicates that the poling process proceeds in two separate stages. The poling field which provides surface charges first aligns the molecules adjacent to the electrodes, and the field from the aligned dipoles and additional surface charges further orient the remaining NLO chromophores. Because of thermal motion, the alignment takes place in competition with the intermolecular potentials that act among the NLO dipoles and between the dipoles with the polymer host. It appears that below E_s, the poling field provides only enough surface charges to align the molecules near the surface and very little macroscopic order is induced, hence giving rise to a small SHG intensity. Above E_s, the surface charges provided by the poling voltage as well as the oriented dipoles combine to overcome the orientation-randomizing molecular motion and induce macroscopic nonlinear polarization for SHG.

The SHG intensity is proportional to the square of the second order macroscopic susceptibility $\chi_{ijk}^{(2)}$ ($-2\omega; \omega, \omega$).[1] Here ω is the frequency of the fundamental laser beam (the frequency of the YAG laser oscillating at 1.06 μm in the present case). Two elements of $\chi^{(2)}$ are involved in the electric field poled amorphous NLO polymer. They are $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$, where z refers to the direction of the poling electric field, i.e. the direction perpendicular to the polymer film surface on the ITO substrate; the x direction is on the surface of the film. By using different polarizations of the exciting laser beam the values of $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$ can be determined.[4]

These $\chi^{(2)}$ elements are related to the orientational polar order parameters L_{33} and L_{31} by[5]

$$\chi_{zzz}^{(2)} \equiv \chi_{33}^{(2)} = \rho \, F \, L_{33} \qquad (1)$$

and

$$\chi_{zxx}^{(2)} \equiv \chi_{31}^{(2)} = \rho \; F \; L_{31} \tag{2}$$

where ρ is the number density of NLO chromophores; F is equal to $\beta \; f_\omega^2 \; f_{2\omega}$. Here f_ω and $f_{2\omega}$ are local field factors at frequency ω and 2ω, respectively. In the Lorentz model, the local field factors are given by $f_\nu = (n_\nu^2 + 2)/3$, where n_ν is the refractive index at frequency ν. β is the dominant component of the molecular second order hyperpolarizability tensor. In writing Eqs (1) and (2), one neglects the contribution from other minor components of the hyperpolarizability tensor.

The pertinent orientational polar order parameters (POP) L_{33} and L_{31} are given by[5]

$$L_{33} (t) = <\cos^3\theta_1 (t)>_E = \frac{1}{5} \; \{3<P_1 (\cos\theta_1(t))>_E + 2 <P_3(\cos\theta_1(t))>_E\} \tag{3}$$

$$L_{31} (t) = (<\cos\theta_1 (t)>_E - <\cos^3\theta(t)>_E)/2 =$$

$$\frac{1}{5} \; \{ <P_1 (\cos\theta_1(t))>_E - <P_3(\cos\theta_1(t))>_E\} \tag{4}$$

where θ_1 refers to the polar angle of the principal axis of representative NLO chromophore 1 with respect to the external poling field. Here $P_1(\cos \theta_1)$ and $P_3(\cos\theta_1)$ are the Legendre polymonial of order 1 and 3, respectively. The time dependence in L_{33} and L_{31} is caused by molecular reorientation which leads to relaxation of POP. The angular brackets with a subscript E indicated that the ensemble average is taken on the system in the presence of the poling field E.

As an approximation, POP parameters L_{33} and L_{31} are often described in terms of

Langevin functions of order 3 and 1.[6] Such a simplistic description is only valid at very low NLO chromophore concentration when the intermolecular interaction between dipoles can be neglected. In reality these are complex functions of the external poling field and the anisotropic (angular dependent) intermolecular interaction potential.[5] The dynamics of molecular motion renders the time dependence of order parameters and gives rise to the relaxation of L_{33} and L_{31}. However, as shown in ref. 5, under a weak poling field condition, $<P_3(\cos\theta_1)>$ is not excited. In the next section, we show by linear response theory that the time dependence of POP in the weak poling field condition is given by

$$L_{31}(t) = L_{33}(t)/3 = \frac{a}{5} \left[<\cos\theta_1(t) \cos\theta_1> + (N-1) <\cos\theta_1(t) \cos\theta_2> \right] \qquad (5)$$

where $a = f_o \mu E_p/kT$ is the poling constant. f_0 is the Onsager local field factor associated with the poling field, and μ is the ground state dipole moment of the chromophore. θ_1 and θ_2 correspond to polar angles for representative molecules 1 and 2, respectively. N is the total of number of NLO chromophores which have been polarized by the external field. The angular brackets without the subscript E in Eq. (5) correspond to an average over an equilibrium distribution function in the absence of the poling field.

For t = 0, Equation (5) reduces to the initially induced orientational order parameter, given by

$$L_{31}(0) = L_{33}(0)/3 = \frac{a}{5} \left[<\cos^2\theta_1> + (N-1) <\cos\theta_1 \cos\theta_2> \right]$$

$$= \frac{a}{15} g_K \qquad (6)$$

Equation (6) was obtained in ref. 5 by using the method of equilibrium statistical mechanics.

Here g_K is the Kirkwood g-factor given by

$$g_K = 1 + \frac{(N-1)\langle\cos\theta_1\cos\theta_2\rangle}{\langle\cos^2\theta_1\rangle} = 1 + \rho\, G_\Delta \qquad (7)$$

where G_Δ is the cluster integral defined previously.

As one sees in Eq. (6), the weak poling field condition the POP is proportional to the poling constant a, which is proportional to E_p; one thus expects that the SHG intensity is proportional to E_p^2, provided that the poling field is larger than the threshold field E_s, as shown in Fig. 2.

By increasing the temperature, we have found that the SHG intensity first decreases in accordance with the 1/T dependence in the poling constant a. However, as shown in Fig. 3, by keeping the same poling voltage, we have found that as time progresses, the lost SHG intensity recovers and maintains at the same level as before the temperature change. One notes that as the sample (5 wt% NAS) is heated gradually from 100 to 160°C (about 50°C above T_g), SHG intensity remains nearly constant, in contrast to the expected intensity decrease as the temperature increases. This intensity/temperature behavior differs from the result of Mortazavi et al,[7] who have reported a strong temperature dependence in the main chain polymer. The present result can be understood as due to electrodes attraction associated with the increase of the effective poling field strength. As the temperature increases above T_g, the compliance of the polymer increases and the more compliant polymer facilitates the electrodes separation to decrease. The decrease in the electrodes separation increases the effective poling field strength which probably compensates the $(1/T)^2$ temperature dependence factor provided that a sufficient amount of time is allowed

for the polymer compliance to change.

2.   Relaxation of Polar Order Parameter

Shown in Fig. 4A is the decay curve of the SHG intensity for the 5 wt% sample at
100°C after the poling field (= 217 V/μm) is removed. One notes the initial rapid intensity
decrease at short times, followed by a gradual decay at subsequent times in the SHG time
dependence curve. The nature of the initial rapid intensity decrease is not clearly
understood, despite the fact that it has been attributed to the third order nonlinear optical
effect[8] and to the relaxation of the oriented chromophores in the liquid-like region for the
polarized sample below T_g.[9] We have recently carried out detailed experiments, and have
found that the portion of the rapid SHG intensity decrease can be made to diminish if the
field higher than E_s is employed to pole the sample above T_g for a sufficiently long time.
In Fig. 4B, we show the decay curve for the sample poled at 121°C using the same poling
voltage for more than 24 hr.; one notes that there is only a negligible initial drop in the
SHG intensity in this case. The result of the comprehensive study of the poling dynamics will
be published elsewhere.[10]

The entire SHG relaxation curve, including the initial intensity drop, can be fit to a
KWW (Kahrausch-Williams-Watts) function: $Ae^{(-(t/\tau_0)^\beta}$, where τ_0 is the characteristic
relaxation time, and β is the parameter signifying the distribution of relaxation times. By
fitting to one KWW function, one obtains the stretch exponential parameter β about the
order of 0.3, which is consistent with the previous result.[11] However, recent work has shown
that the decay of the second order nonlinear susceptibility is better fit to a bi-exponential
form.[12,13] Using the birexponential fit, we write the SHG intensity relaxation curve as:

$$I_{SHG}(t) = (Ae^{-t/\tau_1} + Be^{-t/\tau_2})^2 \qquad (8)$$

where A and B are constants associated with the amplitudes of the initial and the second

long decay, respectively. As mentioned above, if a sufficiently high voltage is used to pole the sample above T_g for a long time, the amplitude of the initial decay becomes rather small. As a result, the long decay associated with the reorientation of the chromophores dipoles is found to be described by a single exponential given by

$$I_{SHG}(t) \sim B^2 \exp(-2t/\tau_2) \qquad (9)$$

The continuous curves shown in Fig. (4A) and (4B) are the single exponential fit to the experimental data. The fit to Fig. (4A) is carried out by removing the portion corresponding to the initial rapid intensity decrease. One notes that by excluding the initial intensity decrease, the single exponential function gives a good fit to the experimental data.

The decay of the SHG intensity corresponds to the relaxation of the polar order of the NLO chromophore dipoles. The relaxation of the orientational order parameter can in general be expressed in terms of time correlation functions, but to our knowledge, this connection has not yet been shown. We now use linear response theory to relate the relaxation of the order parameter associated with the decay of the SHG signal to the specific time correlation functions.

To apply linear response theory, we consider a collection of electric dipoles of NLO chromophores $\mu_1, \mu_2 \ldots, \mu_N$, each of these interacts with the external poling field $\underset{\sim}{E}_P(t)$ and also with the others. The poling field depends on time as it is switched off after the sample is polarized and the relaxation effect is to be probed. The Hamiltonian describing the interaction of the dipoles with the poling field is given by

$$H_{ext}(t) = - \sum_j \mu_j \cdot \underset{\sim}{E}_P(t) = - \mu E_P(t) \sum_j \cos\theta_j \qquad (10)$$

where θ_j is the polar angle of dipole j with respect to the poling field $\underset{\sim}{E}_P$. μ is the amplitude

of the electric dipole of the NLO chromophore. In addition to the external Hamiltonian, the material system is described by a Hamiltonian H_0 before the poling field is applied. Following a series of standard steps needed in linear response theory,[14] we find that

$$<\cos^n\theta_1(t)>_E = \int_{-\infty}^{t} \phi_n(t,t') E_P(t')dt' \tag{11}$$

where the response function $\phi(t,t')$ is given by (in terms of classical mechanics)

$$\phi_n(t,t') = \frac{\mu}{kT} \sum_j <\cos^n\theta_1(t) \frac{\partial}{\partial t'} \cos\theta_j(t')> \tag{12}$$

In accordance with Eqs. (3) and (4), we need $\phi_3(t,t')$ in order to calculate $L_{33}(t)$; to calculate $L_{31}(t)$ we need $\phi_3(t,t')$ and $\phi_1(t,t')$. To derive Eqs. (11) and (12), we have assumed that initially the system has no polar order. Polar order is induced after the external electric field is turned on. However, as previously shown, under the weak poling field conditions only the $<P_1(\cos\theta)>$ type of polar order is excited. The excitation of the $<P_3(\cos\theta>$ order requires a high poling field and cannot be calculated with linear response theory. We shall in another publication consider the high field case and consider here only the low poling field condition.

We now substitute Eq. (12) into Eq. (11) (with $n = 1$) and carry out the integration by part to reduce Eq. (11) to

$$\langle\cos\theta_1(t)\rangle_E = \frac{\mu}{kT} \sum_{j=1}^{N} \langle\cos\theta_1(t)\cos\theta_j(t)\rangle E_P(t)$$

$$- \frac{\mu}{kT} \sum_{j=1}^{N} \int_{-\infty}^{t} \langle\cos\theta_1(t)\cos\theta_j(t')\rangle \dot{E}_P(t')dt' \qquad (13)$$

where the dot above $E_P(t')$ designates taking the derivative with respect to t'.

We next consider the situation that after the NLO polymer material is poled for a sufficiently long time, the dipolar order has reached a steady state. At $t=0$, we turn off the poling field and begin to investigate the relaxation behavior of the established polar orientational order. The investigation is proceeded by observing the decay of the SHG signal at $t>0$. Namely, we set

$$E_P(t) = E_P\,\theta(t) \qquad (14)$$

where $\theta(t)$ equals 1 for $t\leq0$, and equals 0 for $t>0$. From Eq. (12), we obtain

$$\dot{E}_P(t) = -E_P\delta(t) \qquad (15)$$

where $\delta(t)$ is the Dirac delta function. Substituting Eqs. (14) and (15) into Eq. (13), we obtain for $t>0$

$$\langle\cos\theta_1(t)\rangle_E = (\frac{\mu E_P}{kT}) \sum_{j=1}^{N} \langle\cos\theta_1(t)\cos\theta_j(0)\rangle$$
$$= a\,[\langle\cos\theta_1(t)\cos\theta_1\rangle + (N-1)\langle\cos\theta_1(t)\cos\theta_2\rangle] \qquad (16)$$

where the angular brackets without the subscript E indicate that the ensemble average is taken without the poling field. The first term on the right hand side of Eq. (13) is absent for $t>0$ as the poling field is removed at $t=0$. In Eq. (16), we have succeeded in relating the decay of the polar order parameter to time correlation functions. One notes in Eq. (16) there are two types of time correlation functions, one corresponding to the self time

correlation and the other pair time correlation. In the previous work, only the analysis of the self time correlation function is considered.[15] We emphasize in this paper the importance of the pair correlation contribution to the decay of the SHG intensity. Without the pair correlation term, it would be impossible to understand the concentration dependence[16] and the present poling field dependence of the relaxation time.

3. Effect of Pair Correlation

In Eq. (16), we have established that the time dependence of the order parameter $<\cos\theta_1(t)>_E$ is related to the correlation functions $<\cos\theta_1(t) \; \cos\theta_1>$ and $<\cos\theta_1(t) \; \cos\theta_2>$. To show the importance of pair correlation contribution, we consider a model with two interacting dipoles immersed in the environment of the amorphous polymer above its glass transition temperature.

The dipoles are initially oriented by the poling field. After the poling field is removed, the dipoles undergo reorientational motion to randomize the orientational order established by the poling field. The reorientational dynamics of the dipoles can be described by the generalized Langevin equation.[17]

If we denote the state of dipoles by the dynamic variables Q_1 and Q_2, then the kinetic equation for the vector variable

$$\underset{\sim}{A} = \begin{pmatrix} Q_1 \\ Q_2 \end{pmatrix} \tag{17}$$

is given by the generalized Langevin equation[17] (in the Markov approximation) where the relaxation matrix is given by

$$\frac{\partial}{\partial t} \underset{\sim}{A}(t) = \underset{\approx}{\Gamma} \cdot \underset{\sim}{A}(t) + \underset{\sim}{F}(t) \tag{18}$$

$$\underset{\approx}{\Gamma} = \begin{pmatrix} K_{11} & K_{12} \\ K_{21} & K_{22} \end{pmatrix} \begin{pmatrix} <|Q_1|^2> & <Q_1 Q_2^*) \\ <Q_2 Q_1^*> & <|Q_2|^2> \end{pmatrix}^{-1} \tag{19}$$

Here K_{ij} are the Onsager kinetic coefficients associated with the random force $\underset{\sim}{F}(t)$. Since the two dipoles are assumed to be chemically equivalent, we set $K_{11} = K_{22} = d$, and $K_{12} = K_{21} = h$. Here d is associated with the decay rate of uncorrelated single dipole, and h represents dynamic correlation of the two dipoles. In addition, Q_1 and Q_2 are proportional to $\cos\theta_1$ and $\cos\theta_2$, respectively, we set $<|Q_1|^2> = <|Q_2|^2> = \alpha$ and $<Q_1 Q_2^*> = <Q_2 Q_1^*> = \beta$. Here β represents the static pair correlation between the two dipoles. Using Eq. (6), we can write for the case of two dipoles the initial orientational order parameter L_{31} before turning off the poling field is

$$\alpha + \beta = L_{31}(0) = \frac{a}{5} [<\cos^2\theta_1> + <\cos\theta_1 \cos\theta_2>] \tag{20}$$

Equation (20) will be used as the initial condition for the kinetic equation given by Eq. (18). Thus, in order to show that Eq. (18) can be used to describe the decay of the polar orientational order parameter after the poling field is turned off, we need to make connection of Eq. (18) to Eq. (16).

We take the time derivative on both sides of Eq. (16) and obtain after associating Q_i with $\cos\theta$, (i = 1 and 2):

$$\frac{\partial}{\partial t} <\cos\theta_1(t)>_E = \frac{a}{2} \frac{\partial}{\partial t} [<\cos\theta_1(t) \cos\theta_1> + <\cos\theta_1(t) \cos\theta_2>$$

$$+ <\cos\theta_2(t) \cos\theta_1> + <\cos\theta_2(t) \cos\theta_2>]$$

$$= \frac{1}{2} \frac{\partial}{\partial t} [<Q_1(t) Q_1> + <Q_1(t) Q_2> + <Q_2(t) Q_1> + <Q_2(t) Q_2>] \qquad (21)$$

where we have added two terms associated with the representative dipole 2 to exploit the symmetry of the problem. The initial condition for Eq (21) is given by Eq. (20).

The calculation of the sum of four correlation functions on the right hand side of Eq (21) is best proceeded by considering the correlation matrix

$$\underset{\approx}{C}(t) = \begin{pmatrix} <Q_1(t)Q_1> & <Q_1(t)Q_2> \\ <Q_2(t)Q_1> & <Q_2(t)Q_2> \end{pmatrix} \qquad (22)$$

The equation of motion for $\underset{\approx}{C}(t)$ is obtained from Eq (18) by multiplying the adjoin of $\underset{\sim}{A}$ to the right side of both equations and then taking the ensemble average:

$$\frac{\partial}{\partial t} \underset{\approx}{C}(t) = -\underset{\approx}{\Gamma} \cdot \underset{\approx}{C}(t) \qquad (23)$$

Unlike Eq. (18), the random force $\underset{\sim}{F}(t)$ is absent explicitly in Eq. (23) owing to the fact that the correlation between random force $\underset{\sim}{F}$ and dynamic variable $\underset{\sim}{A}$ vanishes.[17]

The sum of the diagonal elements of $\underset{\approx}{C}(t)$, $[<Q_1(t) Q_1> + <Q_2(t) Q_2>]$, and the sum of off-diagonal terms of $\underset{\approx}{C}(t)$, $[<Q_1(t) Q_2> + <Q_2(t) Q_1>]$, are known as the self-time correlation functions and the pair-time correlation functions, respectively. The orientational

order parameter can thus be obtained from the elements of the time correlation function matrix.

To calculate the time correlation function matrix, we take the Laplace transform of Eq (23) and convert it into an algebraic equation:

$$\hat{\underset{\approx}{C}}(z) = \left(\frac{1}{z\underset{\approx}{I} + \underset{\approx}{\Gamma}}\right)\underset{\approx}{C}(0) \tag{24}$$

where $\underset{\approx}{I}$ is a 2 by 2 unit matrix, and

$$\hat{\underset{\approx}{C}}(z) = \int_0^\infty dt\, e^{-zt}\, \underset{\approx}{C}(t) \tag{25}$$

$\underset{\approx}{C}(0)$ is $\underset{\approx}{C}(t)$ at $t = 0$. Using the definition of the $\underset{\approx}{\Gamma}$ matrix (Eq (19)), we have found after performing several straightforward matrix multiplication steps that

$$\hat{\underset{\approx}{C}}(z) = \frac{1}{(z+L)^2 - M^2} \begin{bmatrix} \alpha(z+L) - \beta M & \beta(z+L) - \alpha M \\ \beta(z+L) - \alpha M & \alpha(z+L) - \beta M \end{bmatrix} \tag{26}$$

where

$$L = \frac{1}{\alpha^2 \beta^2} (\alpha d - \beta h) \tag{27A}$$

$$M = \frac{1}{\alpha^2 \beta^2} (\alpha h - \beta d) \tag{27B}$$

The self- and pair correlation parts of Eq (26) are thus given by

$$\hat{C}_s(z) = \frac{2}{(z+L)^2 - M^2} \{\alpha(z+L) - \beta M\} \tag{28A}$$

$$\hat{C}_p(z) = \frac{2}{(z+L)^2 - M^2} \{\beta(z+L) - \alpha M\} \tag{28B}$$

One notes from Eq (16) that the Laplace transform of the order parameter $<\cos\theta_1(t)>_E$ is equal to one half of the sum of $C_s(z)$ and $C_p(z)$; i.e.,

$$<\cos\theta_1(z)>_E = \int_0^\infty dt\, e^{-zt} <\cos\theta_1(t)>_E = \frac{1}{2} [\hat{C}_s(z) + \hat{C}_p(z)]$$

$$= \frac{\alpha+\beta}{z+L+M} = \frac{(\alpha+\beta)}{z+(d+h)/(\alpha+\beta)} \tag{29}$$

Equation (29) can be reverted to time by taking the inverse Laplace transform. Thus, we have found that the decay of the POP to the polar orientational order parameter is given by

$$<\cos\theta_1(t)>_E = (\alpha+\beta)\, e^{-t/\tau} \tag{30}$$

where the relaxation τ is given by

$$\tau = \frac{(\alpha+\beta)}{(d+h)} \tag{31}$$

Equation (31) shows that the relaxation time τ for a two-coupled dipole system is proportional to $\alpha + \beta$, which in accordance with Eq (20), is equal to the order parameter $L_{31}(0)$. Thus, the relaxation time increases as the polar orientational order parameter increases. Both kinetic coefficients d and h also contribute to the relaxation time τ, but they do not depend on the order parameter. It is important to point out that if the pair correlation contribution (Eq. (28B)) is not included in the calculation, the decay of the POP will only be given by the self-part (Eq. (28A)), which does not have the simple form of Eq. (30).

   Although the above calculation is made on a two-coupled dipole model, we have

shown elsewhere,[18] that the above result is only slightly modified when the calculation is extended to a general N-coupled dipolar system. The modification corresponds to the replacement of β by $(N-1)\beta$, and h by $(N-1)$h.

To verify the prediction of Eq. (33), we have carried out the measurement of the SHG signal as a function of time using a sample (containing 5 wt% NAS) under an isothermal condition. The sample isothermally controlled at 115°C are repeatedly poled by an electric field of variable strengths. The shape of the decay curve at each poling field is fit to Eq. (9) to obtain the relaxation time τ. In Fig. 5, we plot the relaxation time τ versus the strength of the poling field E_p. One notes that τ increases with E_p, consistent with the prediction of Eq. (31). As $\alpha + \beta$ is equal to the order parameter $L_{31}(0)$, which increases with the poling field strength.

We have thus shown that the decay of the SHG signal can be impeded by increasing the poling field strength E_p. The increase in E_p results in a larger POP, which thus stabilizes the SHG signal.

In summary, we have investigated the electric field dependence of the SHG intensity and its stability using a guest/host polymer system. We have shown that under the low poling field condition the SHG intensity is proportional to E_p^2, provided that the poling field is greater than the threshold field E_s. Below the threshold field, only the dipoles near the electrodes are oriented. The macroscopic orientational polar order develops as the poling field exceeds E_s. The decay of the SHG signal is strongly affected by the pair orientational correlation which significantly contributes to the polar order. The lengthening of the orientational relaxation time by the increase of the poling field strength is observed. Theoretical analysis utilizing linear response theory shows that the relaxation time associated

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with the decay of polar order is proportional to the polar order parameter initially induced

in the sample. We have carried out experimental measurements and verified the prediction.

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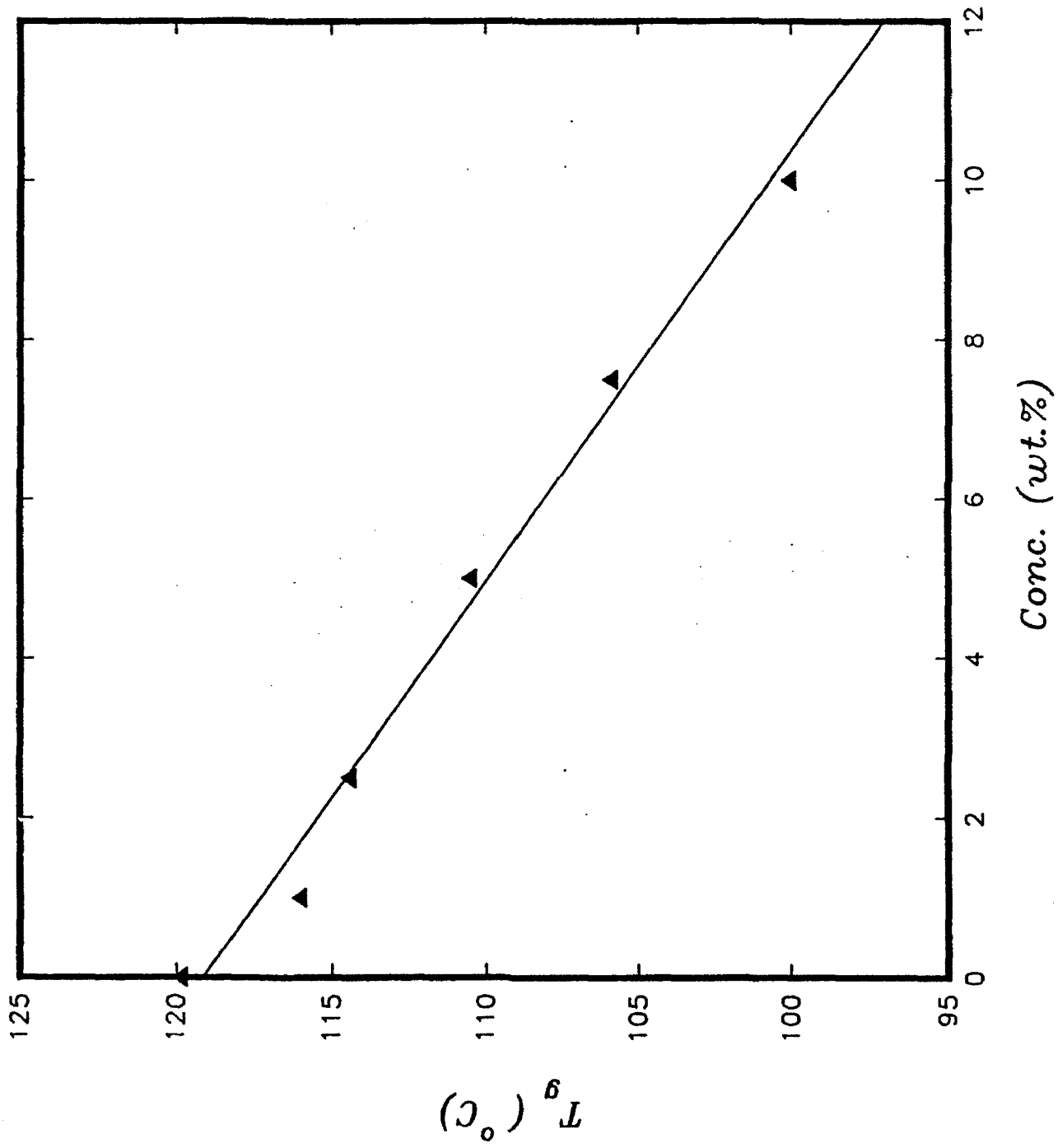
Figure Captions

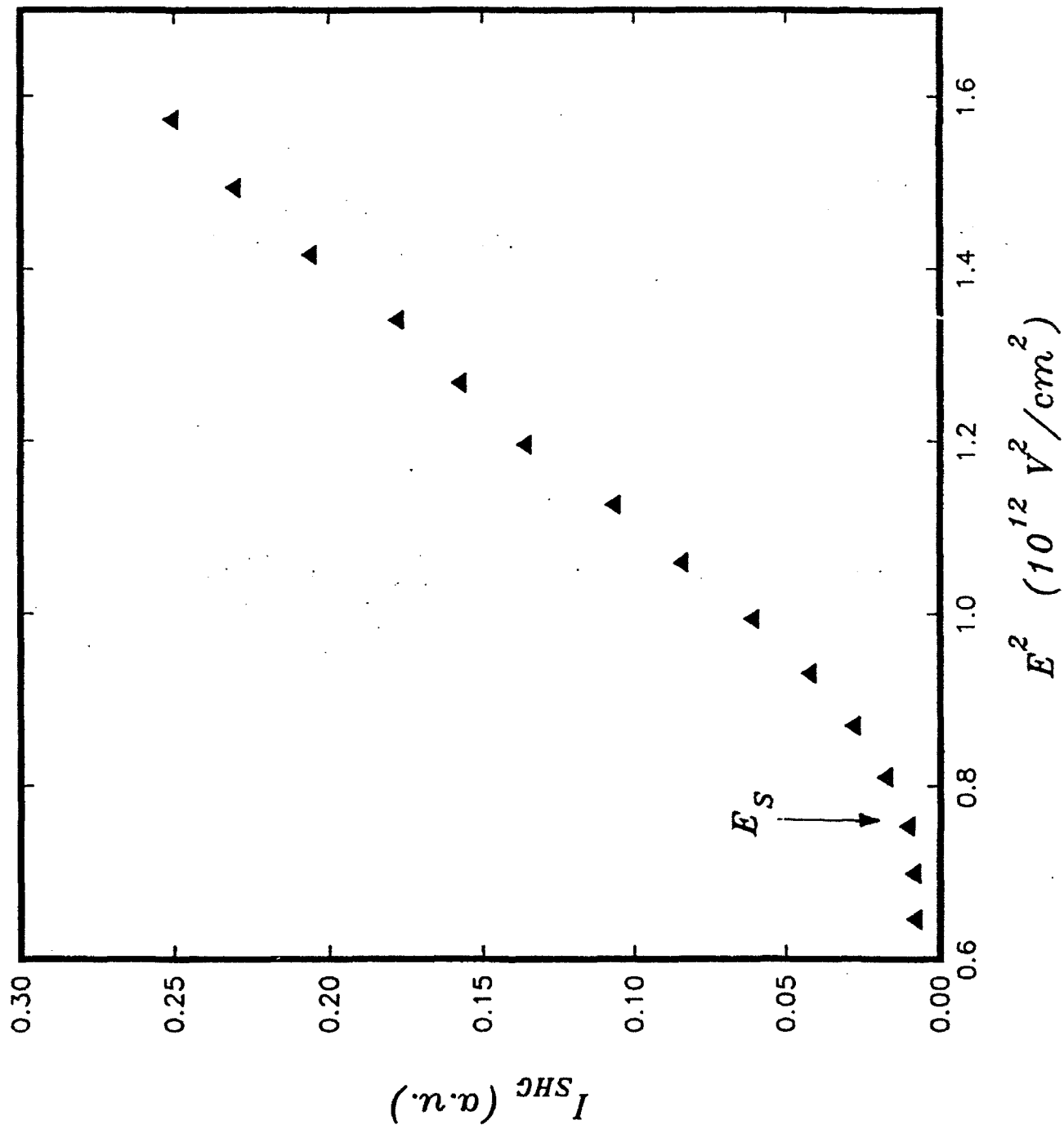Fig. 1 Variation of the glass transition temperature (T_g) of the NAS/PMMA system with the NAS concentration.

Fig. 2 Amplitude of the SHG signal for the 5 wt% NAS in the PMMA sample at 110°C plotted as a function of the square of the poling field strength (E_p^2).
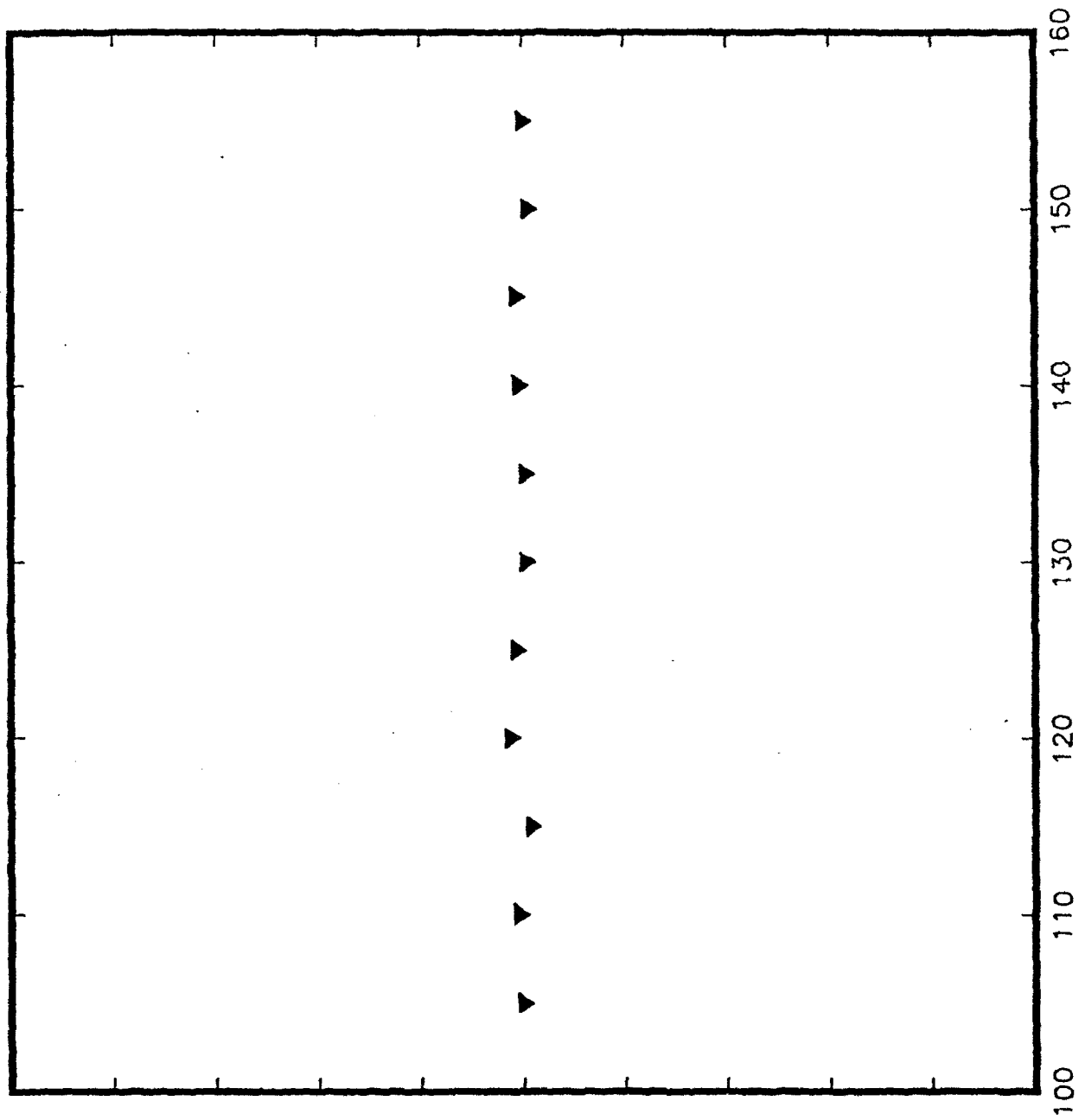
Fig. 3 Temperature dependence of the SHG intensity for the 5 wt% sample.

Fig. 4 The SHG decay data for the sample poled at two temperatures, at the same electric field. Note the disappearance of the initial intensity decrease in Curve B. The solid curves are the single exponential fit to the experimental data.

Fig. 5 Relaxation time constant τ associated with the decay of the polar order for the 5 wt% NAS sample isothermally controlled at 115°C plotted as a function of the strength of the poling field. The solid curve is drawn to indicate the trend.

T_g (^oC)

Conc. (wt.%)

T (sec.)

280

260

240

220

200

0.70   0.75   0.80   0.85   0.90   0.95

E_p $(10^6 \ V/cm)$