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Dipolar Orientational Relaxation in Guest/Host
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ABSTRACT

The decay of the second harmonic signal of a nonlinear optical chromophore dispersed in an amorphous polymer matrix is investigated. The decay curve can be fit either to the Kohrausch-Williams-Watts (KWW) stretched exponential function or to a bi-exponential function. The bi-exponential fit gives a better description of the decay of the second order nonlinear optical susceptibility of the contact electrode poled amorphous NLO polymer film. The fast decay component of the relaxation curve is attributed to the combined effect of reorientation of NLO dipole and the third order optical nonlinearity. The slow decay is due to the rotational diffusion of the NLO dipole. The temperature dependence of the rotational relaxation time is found to follow the Vogel-Fulcher-Tamman equation.

INTRODUCTION

Organic molecules, with a conjugated π electron system terminated by donor and acceptor groups, show a significantly high second order hyperpolarizability. Nonlinear optical (NLO) properties exhibited by amorphous polymers incorporated with these molecules are very promising for the development of electro-optical (EO) devices and second harmonic generation (SHG)¹. Since the isotropic amorphous polymer lacks the second order optical response, a common method to induce the NLO effect is to impart polar orientational order by poling the sample with an electric field. The polar orientational order parameters (POP) associated with SHG are $\langle P_1(\cos \theta) \rangle$ and $\langle P_3(\cos \theta) \rangle$.¹ Here θ is the angle between the dominant principal axis of the molecular hyperpolarizability tensor and the poling electric field; P_1 and P_3 are Legendre polynomials of order 1 and 3, respectively; the angular brackets denote an ensemble average in the presence of the electric field. The $\langle P_1 \rangle$ and $\langle P_3 \rangle$ can be determined by measuring the SHG signals using the incident fundamental wave successively in different polarizations; however, as shown recently, in the weak poling condition, $\langle P_3 \rangle$ is not excited,² and, in this case the decay of the SHG signal is expected to follow the relaxation behavior of $\langle P_1 \rangle$, which describes the dipolar orientational dynamics of the NLO molecules. The work of Eich et al.³ seems to support this result, as they have found a close similarity in the relaxation behavior of the SHG signal and the dipolar relaxation of the NLO chromophore, as measured by the dielectric relaxation technique.

The NLO sample polarized by using a corona discharge method exhibits a non-exponential time dependence.⁴⁻⁶ In corona poling, the dynamics of the charge deposition, the charge decay and the orientational dynamics of NLO chromophores are known to affect the time dependence of the SHG signal.⁶

Although the behavior of POP of the NLO molecules induced by the electric field poling

determines the characteristics of the SHG signal, the dynamics of the polymer chain motion also strongly affects the stability of the second order NLO response. The nature of the relaxational behavior of the SHG signal in regard to poling and polymer chain motion is not presently understood. A considerable amount of discrepancy concerning the analysis of the SHG decay data is present in the literature. Teraoka et al.⁷ reported that the decay of birefringence following the removal of the poling electric field in the corona poled film is better described by a single Kohlrausch Williams-Watts (KWW) stretched exponential given by⁸

$$g(t) = A \exp[-(t/\tau)^\beta] \quad (1)$$

where β is a value between 0 and 1 and is a measure of the deviation from the single exponential, and τ is a characteristic relaxation time. However, Hampsch et al.⁶ have found that the KWW function is inadequate to describe the relaxational behavior of the second order NLO susceptibility of corona-poled films of 4 wt% 4-dimethylamino-4'-nitrostilbene (DANS) dispersed in poly(methylmethacrylate) (PMMA) and in polystyrene (PS). They have found instead that a bi-exponential function better fits experimental result. The KWW stretched exponential function was also recently used by Singer and King to describe the decay of the second harmonic coefficient of the contact electrode poled film of Disperse Red (DR1) in PMMA.⁹ In the KWW fit, they have found a small β value about 0.25-0.4.⁹⁻¹⁰ Such a small β value means that the relaxation of the NLO chromophore has a very broad distribution of relaxation times. In addition, they have also found that over the temperature range of 300 to 350°K, the characteristic relaxation time τ shows an Arrhenius temperature dependence. Although the effect of surface charges on the orientation relaxation of DR1/PMMA is minimized in the experiment of Singer and King by the use of contact electrode poling followed by shorting of the electrodes right after turning off the poling voltage, these results are inconsistent with the present knowledge on the relaxation of electric dipoles in a complex system. For dipolar reorientation,

the broad relaxation time distribution is generally accompanied by a non-Arrhenius temperature dependence of the mean relaxation time¹¹.

Nevertheless, due to the persistence of surface charges resulting from the ions deposited on the film during corona poling, which tends to slow down the NLO chromophore reorientation after the removal of the poling field, the contact electrode poling technique is better suited for a quantitative study of the relaxation effect of the NLO chromophore in the polymer matrix. To help clarify the relaxation behavior, we have in this paper reported the relaxation behavior of the SHG intensity of a contact electrode poled film consisting of 3% DANS in PMMA. We have designed a precise temperature controlled oven housing the sample assembly to allow in situ measurements. In the present experimental set-up, the SHG signal increase during poling and the intensity decay after the field removal are monitored in real time. In addition, we have also carried out careful data analysis of the SHG decay signal using computer programs previously developed in this laboratory for the analysis of the shape of the photon correlation function measured by the dynamic light scattering technique.

EXPERIMENTAL

Appropriate amounts of DANS and PMMA were dissolved in chloroform to form a solution of 3 wt% chromophore concentration. After filtering solutions to remove undissolved particulates, films were prepared by spin coating the solution on the soda lime glass slides. These slides are pre-coated with 300Å SiO₂ and 250Å ITO layers. An identical ITO coated soda lime glass slide was then placed on top of the polymer/ITO glass slide to form a sandwich configuration for contact electrode poling. The slides were then placed in a vacuum oven at 50°C for more than 24 hours in order to remove any solvent that was used in spin coating. Measurements of the thickness and the refractive index of the samples were determined by a

prism coupler (Metricon). This prism coupler is operated in accordance with the optical waveguide principle where the polymer film serves as the propagation layer in the slab waveguide configuration.

The second harmonic generation (SHG) experimental set-up involving a ND:YAG laser (Spectra-Physics GCR-11, $\lambda = 1.06$ microns, Q-switched at 10 Hz, 250 mJ per pulse) was used to measure the second order nonlinear susceptibility of the poled DANS/PMMA film. The sample film was mounted on a computer controlled goniometer stage, which was placed inside a temperature controlled oven. The motion of the goniometer was controlled by a personal computer (PC). The oven temperature was controlled to within $\pm 0.1^\circ\text{C}$. The contact electrode poling technique was employed to orient the electric dipoles of NLO chromophores. The SHG signal, obtained in transmission, was selected by a monochromator and detected by a photomultiplier tube, followed by a preamplifier, and averaged by a boxcar integrator. The boxcar output was interfaced to a PC to facilitate subsequent signal processing and curve fittings.

For each isothermal decay of SHG intensity measurement, the sample was first heated and stabilized to a desired temperature for at least $\frac{1}{2}$ to one hour. The fundamental optical wave was then turned on and the background signal from the boxcar was detected and recorded. Afterward the poling field was applied, and the growth of the SHG signal was detected in real time. After the SHG intensity reached its constant maximum value, the poling field was turned off while simultaneously shorting the electrodes to bleed off any surface charges which might have built up during the poling stage. Experiments of this type were carried out at temperatures above and below the glass transition temperature in the range of 55 - 105°C . The glass transition temperature of the 3% DANS/PMMA samples was measured by using a DSC (Perkin Elmers, Delta series) to be $\sim 85^\circ\text{C}$. The refractive index and the sample thickness measured by the waveguide technique were equal to 1.4951 and 4.53 micrometers, respectively. Both the poling

and SHG decay measurements were made at the same temperature. The film at each temperature was poled at 350 volts.

RESULTS AND DISCUSSION

The SHG decay isotherms measured with incident radiation polarized in the plane of incidence (p polarization) at the temperatures above and below T_g are shown in Fig. 1. In each case the vertical axis is the square root of the intensity, and is thus proportional to the nonlinear optical polarization, or to the second harmonic coefficient. With the fundamental wave in the p-polarization with incident angle ϕ , the NLO polarization is given by

$$\vec{P}_{NL} = \begin{pmatrix} \chi_{31}^{(2)} \cos \phi' \sin \phi' \\ 0 \\ \frac{1}{2} \chi_{31}^{(2)} \cos^2 \phi' + \frac{1}{2} \chi_{33}^{(2)} \sin^2 \phi' \end{pmatrix} \quad (2)$$

where ϕ' is related to ϕ by Snell's law, and $\chi_{31}^{(2)}$ is proportional to the POP by¹

$$\chi_{31}^{(2)} = B (\langle \cos \theta \rangle - \langle \cos^3 \theta \rangle) / 2 = B/5 \{ \langle P_1 \rangle - \langle P_3 \rangle \} \quad (3)$$

and $\chi_{31}^{(2)}$ by

$$\chi_{33}^{(2)} = B \langle \cos^3 \theta \rangle = B/5 \{ 3 \langle P_1 \rangle + 2 \langle P_3 \rangle \} \quad (4)$$

here B is a quantity proportional to local field factors, second order hyperpolarizability and the number density of the chromophores. $\langle P_1 \rangle$ and $\langle P_3 \rangle$ are abbreviations for $\langle P_1 (\cos \theta) \rangle$ and $\langle P_3 (\cos \theta) \rangle$, respectively.

In the weak poling field condition, as applied to the present case, one has $\chi_{33}^{(2)} = 3 \chi_{31}^{(2)} \sim \langle P_1 (\cos \theta) \rangle$.² Thus, the SHG decay curve measured in the present contact poled film is essentially the chromophore dipolar relaxation curve arising from rotational diffusion.

As shown in Fig. 1, the decay curve at each temperature is not a single exponential but displays a "fast" decay at short times and a "slow" decay at long times. The present result differs from that reported by Dhinojwala et al.¹² on a similar sample. In ref. 12, it was reported that "as long as the decay is measured at the same temperature as used in poling the sample, regardless of being in the glassy state or rubbery state, the decay of $\chi^{(2)}$ upon the removal of the electric field is extremely rapid, resulting in total loss of SHG signal within 1.5 min." As clearly shown from Fig. 1, the SHG signal does not decay in 1.5 min for each isotherm. In addition to the rapid decay, there is a slow decay portion, which is extremely temperature dependent and it takes several minutes to relax. We do not know the cause for the discrepancy; the experimental result of reference 12 appears to miss the weaker slow component, possibly due to sample temperature inhomogeneity as well as the limited sensitivity of the detection scheme used.

While we have found that the rapid decay part of the relaxation curve depends somewhat on the degree of sample annealing, its presence is ubiquitous. The slow relaxation part of the relaxation curve appears to undergo a single exponential decay. However, we can force fit the whole decay curve to Eq. (1). By doing so, we obtain a very temperature dependent β parameter with a considerable deviation in the fit at short times. The β values obtained in a single KWW fit are 0.25 at 98°C and 0.42 at 62°C, consistent with the result obtained by Singer and King.^{9,10} However, considering the fact that the short time decay portion does not vary with temperature as strongly as the long time portion and, furthermore, the amplitude of the short time decay appears to depend also on the sample annealing time and the poling field, it is likely that different relaxation mechanisms are involved with the short and long time decays.

Since the single KWW function given by Eq. (1) implies only one single relaxation mechanism responsible for the decay, to associated different mechanisms with fast and slow

decays, we have adopted a function consisting of two double KWW stretched exponentials given by

$$g(t) = B \exp[-(t/\tau_1)^{\beta_1}] + C \exp[-(t/\tau_2)^{\beta_2}] \quad (5)$$

to fit the whole decay following the removal of the poling field. Using this function, we thus recognize two relaxation mechanisms characterizing the SHG intensity decay process. We choose to use the double KWW function to fit the decay curve simply to avoid imposition of any bias imposed on the nature of the multiplicity of relaxation times for each decay mechanism. We let the computer fitting program dictate the best fit to the experimental curve. Table I gives the values of β_1 and β_2 as well as the characteristic relaxation times τ_1 and τ_2 for curves measured at various temperatures. All best fits that have been obtained appear to give $\beta_1 \approx \beta_2 \approx 1$. In Figs. 2-4, we show the comparison of curves observed at 65°C, 82°C and 95°C with the curves calculated by using Eq. (5) with the parameters given in Table I.

Our result is similar to that reported by Hampsch et al.⁶ who, as mentioned above, have found that a bi-exponential function (i.e. setting $\beta_1 = \beta_2 = 1$ in Eq. (5)) rather than a single KWW stretched exponential, better fits the measured SHG decay curves of the corona-poled DANS/PMMA and DANS/PS films.⁶ However, as pointed out above, owing to the persistence of surface charges in the corona poled films which tend to prolong the decay, the present result, obtained by using the contact electrode poled film with the electrodes shorted out right after turning off the poling field, reveals more accurately the effect of polymer segmental motion on the orientational relaxation of the NLO chromophore.

While the characteristic relaxation time τ_1 is not sensitive to temperature variations, the value of τ_2 decreases rapidly as the temperature of the sample increases. Over the 55-105°C temperature range, τ_2 increases from 27s at 105°C to 4602 at 55°C. For measurements below T_g , the value of relaxation time τ_2 is also affected by physical aging of the polymer. The effect

of physical aging on τ_2 is in progress and will be reported elsewhere.¹³ In Fig. 5 the relaxation time τ_2 is plotted versus $1/T$. Clearly the temperature variation of τ_2 is not Arrhenius, in contrast to the Arrhenius dependence of the orientational decay of Dispersed Red (DRI) in PMMA reported by Singer and King.⁹ The Arrhenius temperature dependence reported for the DRI/PMMA system may be due to a result of a rather limited temperature range covered in their study. The temperature dependence of τ_2 for DANS/PMMA can be fitted to the Vogel-Fulcher-Tamman (VFT) equation given by¹⁴

$$\tau = \tau_{\infty} \exp\left(\frac{B}{T - T_0}\right) \quad (6)$$

where τ_{∞} is the high temperature asymptotic relaxation time; B and T_0 are constants equal to 1399 K and 65 K, respectively.

The VFT equation may be derived from free volume theory.¹⁴ The orientational relaxation of the NLO dipole in a polymer host is due to the mobility of dipole and the available local free volume that allows the dipole to undergo rotational diffusion. Above T_g , the α -motion of the polymer chain creates a large free volume fluctuation to facilitate the reorientation of the dipole. Below T_g , the α -motion is in general frozen; however, unless considerable time is allowed to anneal the sample to uniformly distribute the chromophores, because of the plasticization of the polymer matrix by the NLO chromophores (3 wt % in the present case), local free volume surrounding each chromophore is still sufficient to permit dipolar reorientation even at temperature below T_g . As a result, the glass transition of the amorphous guest/host system exerts little effect on τ_2 , and τ_2 undergoes a continuous change with temperature as T_g is transversed. This situation is similar to translational diffusion of photochromous chromophores in the plasticized polymer matrix in the vicinity of T_g ,¹⁵ in which no evidence of an abrupt change in the translational diffusion coefficient is discerned as T_g is traversed, in contrast to the

case of unplasticized polymer matrix.¹⁵

The relaxation time τ_1 is a combination of several effects. The fact that τ_1 is only slightly temperature dependent and that a near instantaneous drop in the SHG intensity is observed following the removal of the applied field suggests that the fast decay may be associated with the third order optical effect involving $\chi^{(3)}$. However, since the $\chi^{(3)}$ effect is nearly instantaneous, the long switching time (about 10 ms) of the poling field used in the present experiment cannot be used to separate this effect. However, as one notes τ_1 is the order of 50 s (Table I), the fast decay following the removal of the poling field may then be attributed to the combined effect of the NLO chromophore dipolar reorientation and the 3rd order $\chi^{(3)}$ nonlinearity.

In summary, we have studied the decay of the SHG signal of the DANS/PMMA system oriented by the contact electrode poling technique. The decay of the square root of the SHG signal which is proportional to the second order NLO susceptibility, can be fit either to a KWW and or a bi-exponential function. All evidence, however, suggests that the bi-exponential function fit describes better the relaxation of the SHG signal. The fast decay following the removal of the poling field is associated with a relatively temperature insensitive relaxation time τ_1 and the slow decay is characterized with a temperature dependent relaxation time τ_2 . The amplitude of the fast decay depends on the sample annealing time. The temperature dependence of the relaxation time τ_2 can be described by the Vogel-Fulcher-Tamman equation. The fast decay component is attributed to the combined effect of $\chi^{(3)}$ and orientational relaxation, and the slow decay is attributed to the rotational diffusion of the NLO dipole in the polymer matrix.

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Table I Parameters obtained by fitting the SHG decay curves at various temperatures to Eq. (5).

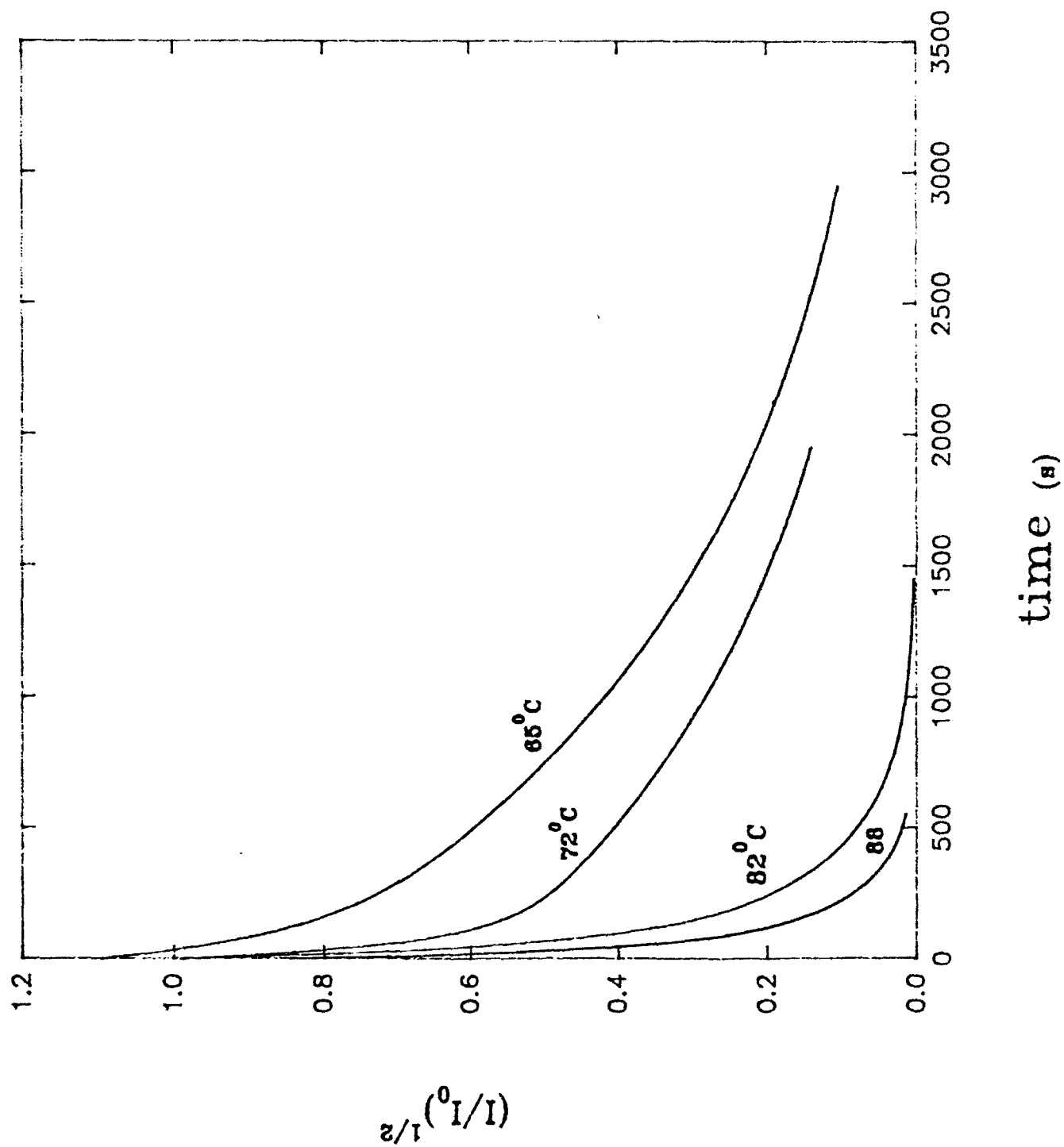
Temperature (° C)	τ_1 (± 7 s)	β_1 (± 0.06)	τ_2 (± 5s)	β_2 (± 0.06)
55	79	1.06	4602	1.08
62	69	1.03	3890	1.08
65	62	1.02	2486	1.08
72	59	1.02	1505	1.06
75	51	1.02	1301	1.06
78	47	1.01	851	1.06
82	50	1.01	302	1.06
85	52	1.05	172	1.05
88	50	1.01	113	1.04
98	41	1.02	83	1.04
105	36	1.01	27	1.04

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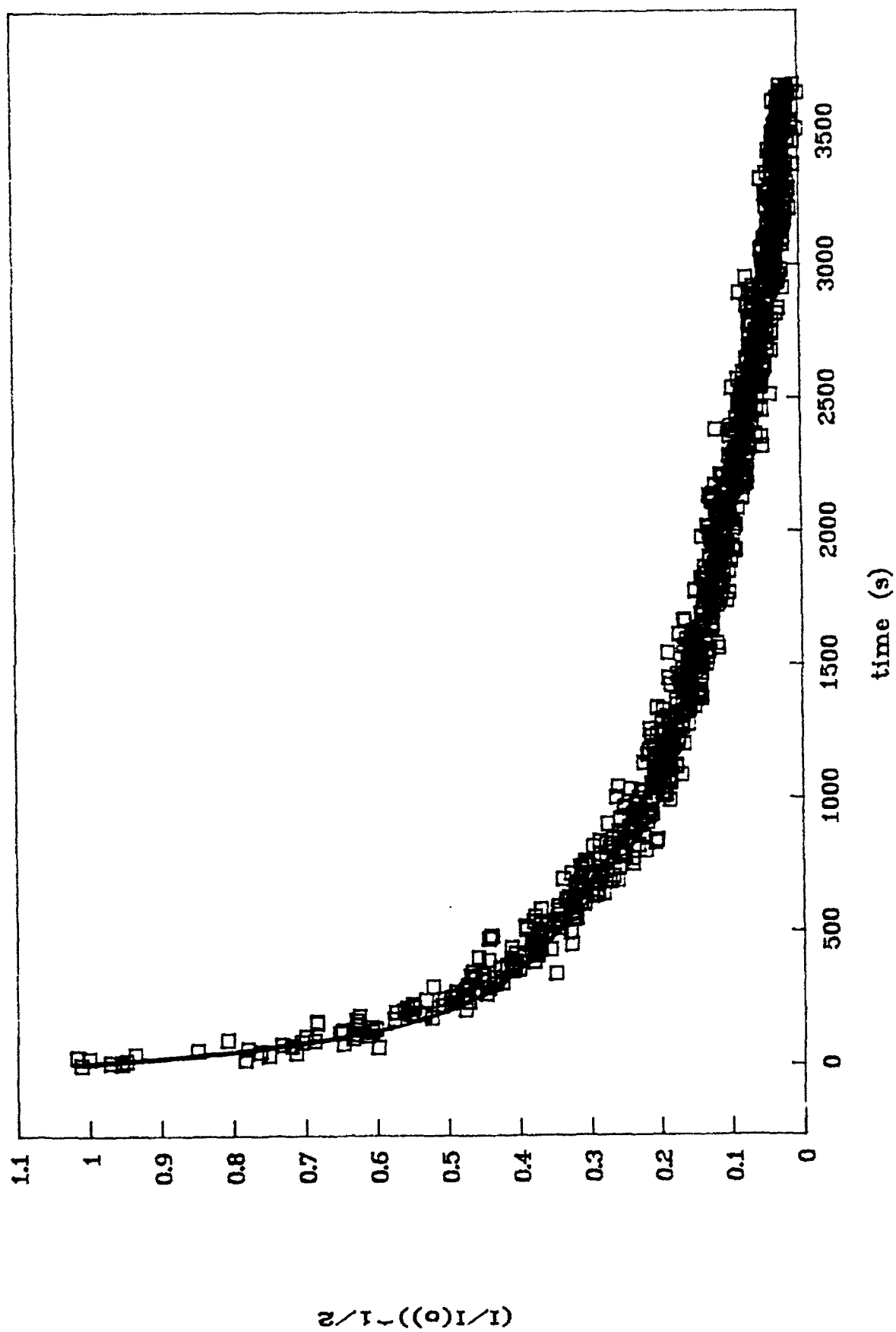
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FIGURE CAPTIONS

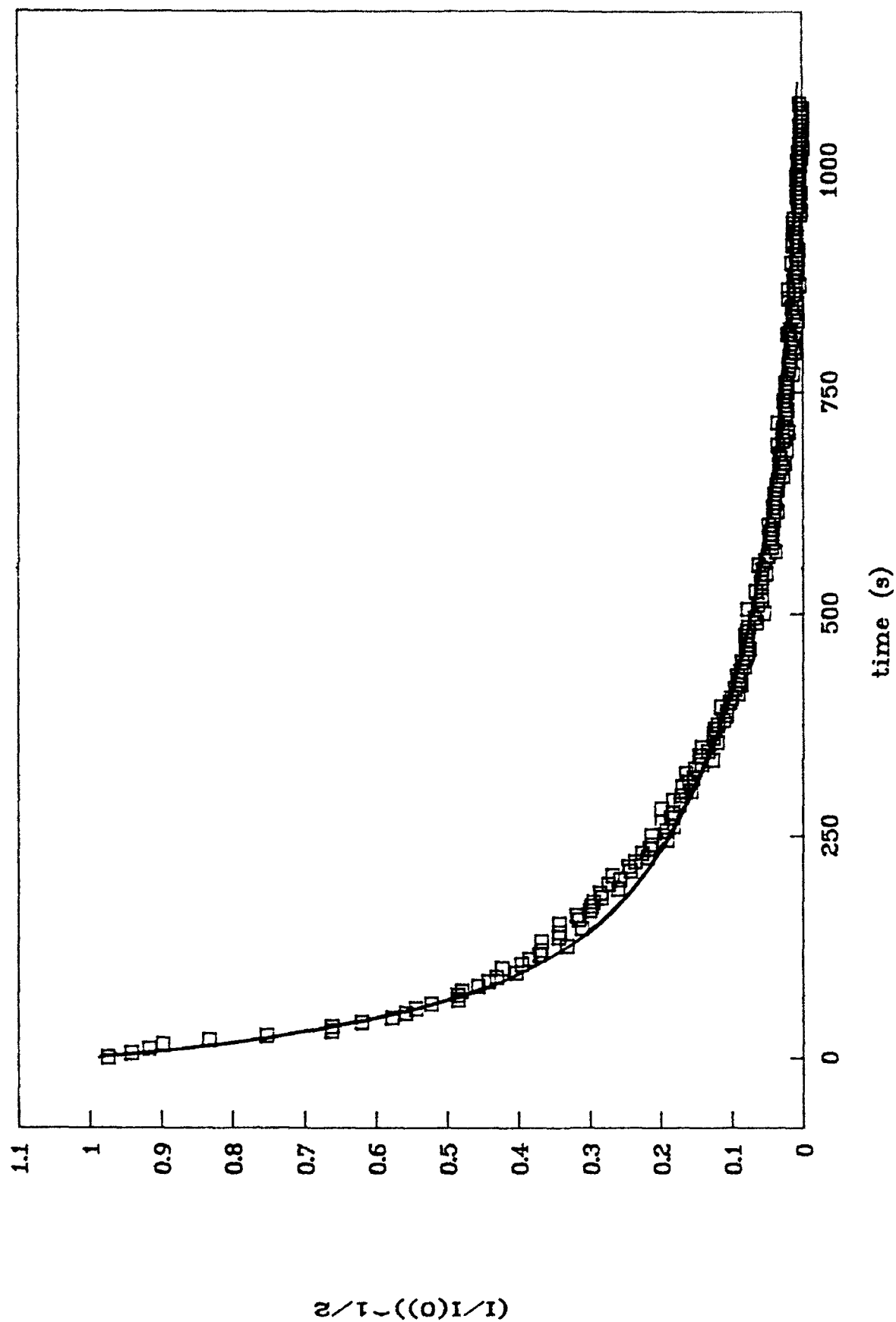
- Fig. 1** Decay curves of square root SHG signals at various temperature above and below T_g for 3 wt % DAN in PMMA.
- Fig. 2** Comparison of the measured curve at 65°C with that calculated by using Eq. (5) with the parameters given in Table I.
- Fig. 3** Comparison of the measured curve at 82°C with that calculated by using Eq. (5) with the parameters given in Table I.
- Fig. 4** Comparison of the measured curve at 95°C with that calculated by using Eq. (5) with the parameters given in Table I.
- Fig. 5** Relaxation time τ_2 plotted versus $1/T$. Different symbols denote data obtained at different times.



65 °C



82 °C



98 °C

