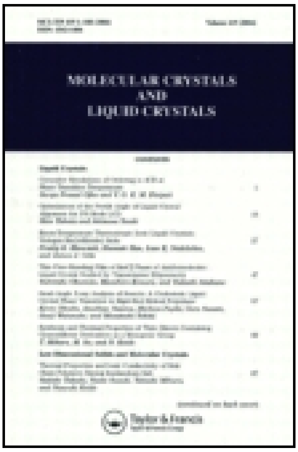

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Liming Wang, Yadong Zhang, Mieko Yamakado, Tatsuo Wada & Hiroyuki Sasabe (1994): Depoling Mechanism of Main-Chain Polyester Containing 3,6-Disubstituted Carbazole, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 255:1, 131-137

To link to this article: http://dx.doi.org/10.1080/10587259408029784

Mol. Cryst. Liq. Cryst. 1994, Vol. 255, pp. 131–137
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Printed in the United States of America

DEPOLING MECHANISM OF MAIN-CHAIN POLYESTER CONTAINING 3,6-DISUBSTITUTED CARBAZOLE

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Abstract Thermal relaxation properties of a poled polyester containing carbazole nonlinear optical chromophores in the main chain have been studied. The polymer has two acceptor groups in the 3- and 6- positions of carbazole ring, and the net dipole moment is perpendicular to the polymer backbone. The decays of second-harmonic intensities at different temperatures were monitored after the removal of electric field. The decay of second harmonic intensity consists of fast and slow processes. These two processes can be attributed to the small-scale local orientation of individual chromophores around the polymer backbone, and the large-scale gross orientation due to micro-Brownian motion of the main chains, respectively. The decay characteristics were well fitted to a relaxation function which consists of a stretched exponential and a single exponential functions.

INTRODUCTION

Polymeric systems which show second-order nonlinear optical responses have conjugated π-electron system terminated by electron-donor and -acceptor groups in a noncentrosymmetric array. The second-order nonlinear optical contributions of individual molecules cancel each other when the nonlinear optical (NLO) chromophores are randomly oriented or they have the center of symmetry. The bulk material has a large second-order NLO susceptibility only if the NLO chromophores were aligned in a polar orientation.[1] One of the most promising techniques is the incorporation of active NLO chromophores into a glassy polymer with subsequent alignment in a strong electric field.[2,3] The state of aligned dipoles is thermodynamically unstable in the absence of the electric field, and the noncentrosymmetry is thus sustained only by a high-energy barrier that prohibits rotation of dipoles towards the lower free energy of random orientation.

The dipole randomization can be well suppressed if the NLO chromophores are chemically attached to the polymers.[4-6] Two different situations arise, depending on whether the NLO chromophores are loosely attached to the polymers in the side chain (side-chain type polymers),[5,7-9] or they are incorporated in the main chain (main-chain type polymers).[6,10-14] The orientational relaxation of chromophores in the side-chain type polymers requires only local chain movements, whereas in main-chain type polymers, it is coupled to a large scale molecular motion of the main chain, leading to quite different relaxation processes according to their configurations of chromophores in the main chain.

The electric field induced alignment and relaxation behavior of these NLO polymers are of interest in terms of both fundamental polymer physics and future applications. In this paper, we discuss the relaxation behaviors of second harmonic intensity of the electric poled polyester containing 3, 6-disubstituted carbazole NLO chromophores in the main chain. The decays of second harmonic generation (SHG) signals at different temperatures were monitored after the removal of electric field in real time. We have carried out data analysis of the SHG decay using a coupled relaxation function.

EXPERIMENTAL

Sample

The structure of the polyester is shown in Figure 1. This polyester has carbazole moiety in the main chain through 3, 6-linkages. Two acceptor groups were introduced in 3- and 6-positions of carbazole ring and the net dipole moment vector is perpendicular to the polymer backbone. The glass transition temperature T_g is 82.1°C . The weight-averaged molecular weight M_w is 14,000 determined by GPC. Details of the synthesis were published elesewhere.[15,16] Films were prepared by spin coating or casting on ITO glass slides from chloroform solution.

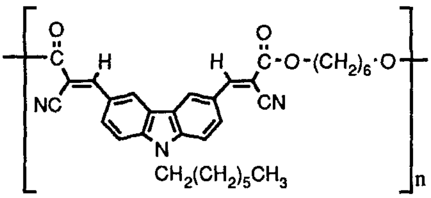

FIGURE 1 Structure of the carbazole main-chain type polymer.

Second Harmonic Generation Measurements

SHG measurements were performed in the transmission way using a Q-switched Nd:YAG laser.[17] In this experiment, the sample was fixed at 45° incident angle and the incident light was *p*-polarized. After the sample was heated at about 100°C, an electric field of 7.5kV/cm was applied for 5~10 min. (confirmed the steady state), and then let the sample cool down spontaneously to the room temperature, 40°C, 60°C and 80°C, respectively, with the electric field on (in less than 3 min., and then kept in the steady state. These temperatures are called 'poling sustained' temperatures hereafter). The temporal behavior of SHG signals was recorded immediately after the poling voltage was switched off.

RESULTS AND DISCUSSIONS

SHG Decay

The SHG decay isotherms are shown in Figure 2. The vertical axis is the square root of normalized intensity, which is proportional to the nonlinear optical polarization and the second-harmonic coefficient. The decay curve at each temperature is evidently governed by a "fast" decay component at shorter times and a "slow" one at longer times. Comparing with the guest/host polymer,[18] the fast decay component of this polymer is dominant, while the slow component shows much more stable behavior.

The nature of the relaxation behaviors of the SHG signal is not fully understood. There are some discrepancies in the analyses of the SHG decay data presented in the literatures. A single Kohlrausch-Williams-Watts (KWW) stretched exponential and a biexponential functions are often used to fit the data for both guest/host[18] and side-chain polymers.[5,19] For main-chain type polymers, the chromophores are tightly incorporated as a part of polymer backbone, so the relaxation behavior usually depends on the chemical structure of the polymer. This makes the analysis of decay data more complicated. The attempt to fit our experimental data with above two kinds of relaxation functions was failed as expectedly.

Depoling Mechanism

In general the potential field surrounding a molecular dipole of polymer unit is complicated; there are many local minima due to the polymer configuration and conformation, which governs the torsional oscillations of dipoles with different relaxational time constant (β-process). This wide distribution of relaxation times leads to the stretched exponential relaxation function $\varphi_\beta(t)$ as discussed later. On the other hand, the large scale molecular motion of polymer backbone such as micro-Brownian motion causes the gross motion of molecular dipoles, which corresponds to the free rotation of dipole in a viscous media governed by surrounding polymer chains (α-process). This leads to a Debye-type single exponential relaxation function $\varphi_\alpha(t)$.

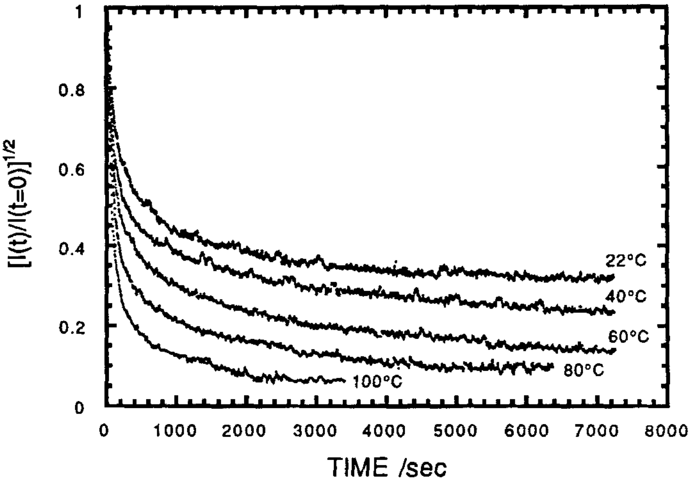

FIGURE 2 Decay curves of SHG signal at various poling sustained temperatures.

Now coming back to our poled polymer system, we will describe the depoling process of dipoles. After the poling voltage is switched off (t=0), the electric field induced dipole alignment is partially relaxed via the local motions of polymer backbone chain, characterized by the relaxation function of $\varphi_\beta(t)$, and the gross dipolar relaxation occurs via the micro-Brownian motion of the polymer, characterized by the relaxation function of $\varphi_\alpha(t)$. It follows that the total relaxation of the poled system can be characterized by the relaxation function $\phi(t)$ as

$$\phi(t) = [I(t)/I(0)]^{1/2} = \varphi_\alpha(t)[A+B\varphi_\beta(t)], \qquad (1)$$

where $A+B=1$, and A is the fraction of $\chi^{(2)}$ which is not relaxed by the β-process.

The α– and β-processes have been demonstrated by dielectric relaxation for many solid amorphous polymers which contain dipoles rigidly or loosely attached to the main chain,[20] and by SHG decay for Disperse Red 1 (DR1) doped in poly(methyl methacrylate) (PMMA).[21] The β-process is usually a weighted sum of elementary processes occurring in a variety of local environments, and described by a KWW stretched exponential[20]

$$\varphi_\beta(t) = \exp[-(t/\tau_2)^\beta], \qquad (2)$$

where β is a constant between 0 and 1 and a measure of distribution of relaxation times.[22] The α-process is described by a single exponential

$$\varphi_\alpha(t) = \exp[-(t/\tau_1)]. \qquad (3)$$

Using these relaxation functions Eqs.(1)-(3), we fitted the dacay isotherms for the main-chain polymer. The two dashed lines in Figure 3 represent the component functions. Evidently the second term of Eq.(1), $B\varphi_\alpha(t)\varphi_\beta(t) \approx B\varphi_\beta(t)$, corresponds to the short scale behavior, and the first term $A\varphi_\alpha(t)$ to the long scale one. Table I gives the values of A , β and the characteristic relaxation times τ_1 and τ_2 for the decay curves obtained at various poling sustained temperatures. The long scale characteristic relaxation time τ_1 decreases from 3.7×10^4 to 2.4×10^3 seconds over the 22~100°C range. These relaxation times are much longer than the corresponding long scale relaxation in DANS/PMMA system,[18] especially at high temperature range. It is worth noting that T_g of the present polymer is 82.1°C, which is almost the same as that of 3% DANS/ PMMA sample (T_g=85°C).[18]

TABLE I Parameters obtained by fitting SHG decay curves at various poling sustained temperatures to Eqs. (1)-(3).

temperature (°C)	τ_1 (sec)	τ_2 (sec)	A (%)	β
22	37000	167	37.7	0.5
40	15000	84	37.1	0.5
60	7100	57	35.5	0.5
80	3100	46	24.2	0.5
100	2400	32	18.2	0.5

The effect associated with the third-order nonlinear optical effect may contribute to the fast drop in the SHG intensity observed after the removal of applied field. In order to determine whether the effect is a primary contribution to the fast decay or not, we carried out another SHG decay measurement on poled carbazole monomer/PMMA system (~10% concentration by weight). This carbazole monomer has the same 3, 6-disubstituted chromophore with that of the main-chain type polymer used in this study. The decay curve at room temperature showed that the fast decay process contributes in much less fraction of $\chi^{(2)}$ value for monomer/PMMA than that for the polymer. It indicates that the third-order nonlinear optical effect is not dominant.

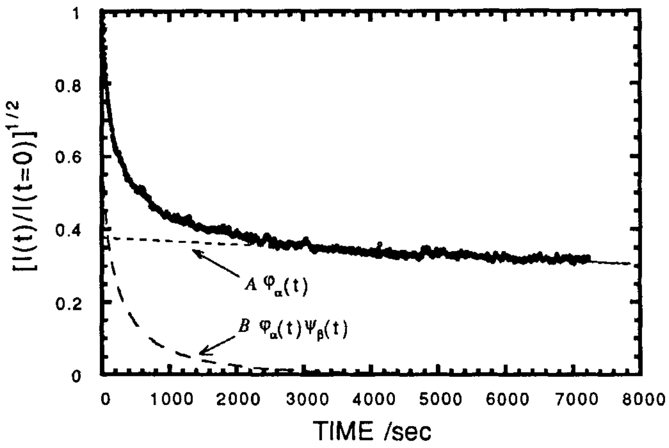

FIGURE 3 Comparison of the observed curve with that calculated by Eqs.(1)-(3) using the parameters given in Table I. The dashed lines represent the component functions.

CONCLUSIONS

We have studied the thermal relaxation properties of a novel poled main-chain type polymer containing carbazole NLO moieties in the polymer backbone. SHG decay of this polymer shows that the decay consists of two processes: a fast process corresponding to a small-scale local orientation of individual chromophores around the polymer backbone and a slow one corresponding to the large-scale gross orientation due to micro-Brownian motion of the main chain. The decay curves were well fitted to a two-stage relaxation function consisted of a stretched exponential with β=0.5 and a single exponential functions. When the poling sustained temperature is higher than T_g, the micro-Brownian motion of main chains leads to a remarkable decrease in the contribution of slow decay process to $\chi^{(2)}$.

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