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Photoinduced Optical Functionalism of Branched Azophenylcarbazoles in Molecular Glass Matrices

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A new guest-host composition of 3-(4-nitrophenyl)azo-9-(2-ethyl)hexyl-2-(2-ethyl) hexyloxycarbazole as chromophore and 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl}propane (molecular glass) as host for all-optical poling application was developed and investigated. A comparison between molecular glass and commonly used bisphenol Z polycarbonate as host showed a slightly better ability for the molecular glass to keep the azophenylcarbazole molecules oriented. Erasure while reading the non-centrosymmetry created is demonstrated and explained. Using an adopted model orientational diffusion coefficient, lifetime of cis isomer and probabilities of redistribution were evaluated.

1. Introduction

Nonlinear optical (NLO) materials attract much attention because of their possible applications in various fields of opto-electronics such as holographic memories, functional surfaces, optical networks as modulators, switches, frequency converters and other photonic tunable devices. Usually NLO materials are used in the form of solid film, where the dye is physically dispersed or chemically bound to the matrix polymer. The most common structure developed is a thin film made of guest-host system consisting of polymer matrix and aromatic azo chromophore composed dye, so that it can be easily fabricated at low cost. Extensive studies have been made on photochromic polymers, where low molecular-weight photochromic compounds were dispersed in polymer binders [1]. In the majority, authors chose one of thermoplastic polymers such as polyacrylates [2] or polycarbonates (PC) for the matrix [3,4].

In the 80's we have started to synthesize well defined low-molar-mass photoconductive compounds, which are able to form amorphous films on substrates including flexible ones for the application in opto-electronic devices [5,6]. Low-molar-mass compounds capable of existing in amorphous state have been later named as molecular glasses or amorphous molecular materials [7]. We prepare the molecular glasses in reactions of oxiranes containing carbazolyl groups with different bifunctional compounds such as aromatic diols, dimercapto compounds, and derivatives of aniline. In contrast to functional polymers used,

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they have an advantage of a well-defined molecular structure, no molecular weight distribution, and no undefined endgroups. They can be highly purified with established methods of organic chemistry such as absorption chromatography or recrystallization.

To achieve high second order nonlinearity in polymers, namely, to create noncentrosymmetry inside the material, special techniques such as Corona or all-optical poling are required. All-optical poling appears as a promising tool for optical manipulation of nano/micro particles and molecules. The method does not need to use electrodes or discharge and it automatically produces quasi-phase-matched $\chi^{(2)}$ micro-pattern providing condition for second harmonic generation.

In this work we demonstrate a new guest-host composition, where branched azophenylcarbazole-based dye is dispersed in a molecular glass matrix possessing carbazolyl chromophores. Molecular orientation properties in the system are investigated by all-optical poling technique, features of the new host are analyzed and compared with commonly used polycarbonate ones.

2. Experimental

2.1 Samples

The three-step synthesis route to 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl}propane (**BCCPP**), possessing four carbazolyl moieties and two hydroxyl groups in the flexible bridge, is shown in Fig. 1. First step was by the nucleophilic opening of the oxirane ring of 2-(carbazol-9-yl)ethanol glicydyl ether (**1**) with carbazole in the presence of KOH to give 1,6-di(carbazol-9-yl)-4-oxa-2-hexanol (**2**). 1,6-Di(carbazol-9-yl)-4-oxa-2-hexanol glycidyl ether (**3**) was prepared in the second

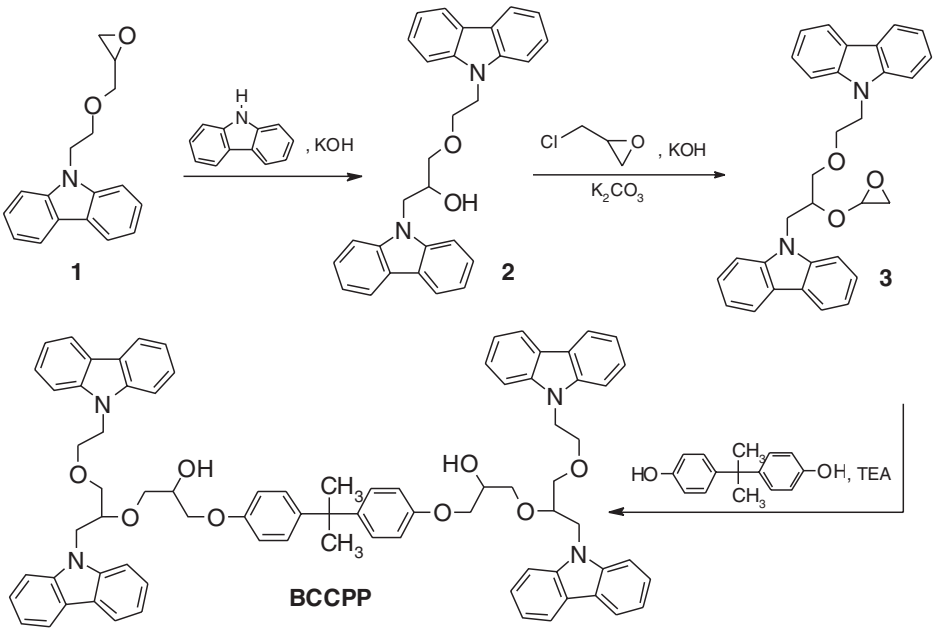

Figure 1. Synthesis route to the branched carbazolyl-based host material **BCCPP**.

step by interaction **2** with epichlorohydrin in the presence of KOH and anhydrous K_2CO_3. And finally, two molecules of glycidyl ether **3** were linked by the nucleophilic opening of the oxirane cycle with 2,2-bis(4-hydroxyphenyl)propane (molar ratio 2:1) in the presence of catalyst TEA at 90–95°C in to goal product **BCCPP**. The branched carbazolyl-based **BCCPP** was isolated by column chromatography with the following precipitation in a great excess of hexane. Isolated by such a procedure **BCCPP** is amorphous compound. All our attempts to crystallise it were unsuccessful. X-ray diffraction patterns of this compound show only broad halos. Such high morphological stability of this glass can apparently be explained by existance of several diastereoisomers, the possibility of intermolecular hydrogen bonding and flexibility of aliphatic linking chains. The glass transition temperature (T_g) of **BCCPP** established by a differential scaning calorimetric method (DSC) is 74°C. **BCCPP** is low molecular glass and exhibit glass-transition phenomena usually associated with polymers. In contrast to amorphous polymers the obtained branched compound is pure material with well-defined molecular structure and definite molecular weight without any distribution.

All reagents were purchased from *Aldrich Chemical Co.* and were used without purification. All solvents were purified using standard procedures. 2-(carbazol-9-yl)ethanol glicydyl ether (**1**) was synthesized according to known procedure [8].

1,6-Di(carbazol-9-yl)-4-oxa-2-hexanol (2). 40.1 g (0.15 mol) of 1,6-di(carbazol-9-yl)-1-oxa-2-hexanol glycidyl ether (**1**) and 25.1 g (0.15 mol) of carbazole were dissolved in 200 mL of butanone. After the cooling the solution to the room temperature 19.6 g (0.35 mol) of 85% powdered KOH were added and the mixture was stirred at room temperature. After completion of the reaction (Silufol UV-254, eluent – *n*-hexane-diethyl ethyl ether, 1:3). After termination of the reaction butanone was removed and the residue was treated with 10 mL of mixture of toluene and ethanol (1:1). The obtained crystals were filtered off and washed with the same mixture. Yield 44.3 g (68%); mp: 62–63°C (toluene). IR, $\bar{\nu}$/cm^{-1}: 3600–3300 (OH); 3057, 3030 (CH_{arom}); 2945, 2880 (CH_{aliph}); 1633, 1600 (C=C); 1152, 1136, 1125, 1090 (C−O−C); 754, 730 (=CH of no substituted Ht). ^{1}H NMR ($CDCl_3$,δ, ppm): 7.98 (m, 4H, 4-H, 5-H Ht); 7.18 (m, 12H, Ht); 4.40 (t, 2H, $NC\underline{H}_2CH_2$); 3.90 (m, 3H, NCH_2CH); 3.65 (m, 2H, $NCH_2C\underline{H}_2$); 3.07 (m, 2H, $OC\underline{H}_2CH$); 1.86 (m, 1H, OH). Found,%: C 79.91; H 6.00; N 6.29. $C_{29}H_{26}N_2O_2$; Calculated,%: C 80.16; H 6.03; N 6.45.

1,6-Di(carbazol-9-yl)-4-oxa-2-hexanol Glycidyl Ether (3). To the solution of compound **2** (43.4 g, 0.1 mol) in 50 mL butanone 64.8 g (0.7 mol) of epichlorohydrin, 16.8 g (0.3 mol) of 85% powdered KOH and 10 g (0.07 mol) of anhydrous K_2CO_3 were added. The mixture was stirred at 25–30°C temperature until **1** was completely consumed. After termination of the reaction (Silufol UV-254, eluent – diethyl ether-hexane, 3:1), the mixture was treated with toluene and water. The organic layer was washed with distilled water until the wash water was neutral, dried over anhydrous Mg_2SO_4, treated with activated charcoal and filtered off. Toluene was removed and the residue was treated with 10 mL of mixture of toluene and ethanol (1:1). The crystals formed upon standing were filtered off and washed with ethanol. The yield was 28.0 g (57.1%); mp: 98.5–99.0°C (toluene). IR, $\bar{\nu}$/cm^{-1}: 3060, 3030 (CH_{arom}); 2940, 2900, 2879, 2824 (CH_{aliph}); 1632, 1600, 1580 (C=C, C−N); 1254, 978, 832 (cycle of oxirane); 768, 731 (=CH of no substituted Ht). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.0 (m, 4H, 4-H, 5-H Ht); 7.75–6.75 (m, 12H, Ht); 4.42 (m, 2H, $NC\underline{H}_2CH_2$); 4.08 (m, 2H, $NC\underline{H}_2CH$); 3.68 (m, 2H, $NCH_2C\underline{H}_2$); 3.37–2.87 (m, 4H, $C\underline{H}_2OCH$, $CH_2OC\underline{H}_2CH$); 2.62 (m, 1H, CH of oxirane); 2.37 (m, 1H, one of CH_2 of oxirane); 2.03 (m, 1H, other of CH_2 of

oxirane). Found,%: C 78.51; H 6.10; N 5.8. $C_{32}H_{30}N_2O_3$; Calculated,%: C 78.34; H 6.16; N 5.71.

2,2-Bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl} propane (BCCPP). The mixture of compound **3** (24.5 g, 0.05 mol), 2,2-bis(4-hydroxyphenyl)propane (4.6 g, 0.02 mol) and 1 mL of triethylamine was stirred at 90°C in 10 ml of chlorobenzene 28 h. After termination of the product was purified by column chromatography using acetone-hexane (1:4) as the eluent. Fraction containing resulting product was collected and the eluent was evaporated. Then the 20% solution of the resulting product in toluene was prepared and poured with intensive stirring into a 20-fold excess of hexane. The product was filtered off and washed with hexane to yield 17.0 g (70.3%) of amorphous **3**. IR, $\bar{\nu}/cm^{-1}$: 3600–3300 (OH); 3050, 3020 (CH_{arom}); 2970, 2933, 2880 (CH_{aliph}); 1620, 1595, (C=C, C–N); 1120 (C—O—C); 832 (=CH of 1,4-disubstituted benzene); 755, 725 (=CH of no substituted Ht). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.83 (m, 8H, 4-H, 5-H Ht); 7.5 5–6.66 (m, 28H, Ht and *p*-Ph); 6.43 (m, 4H, *p*-Ph); 4.18 (m, 4H, NCH_2CH_2);3.87 (m, 4H, NCH_2CH); 3.47 (m, 12H, $NCH_2CH_2OCH_2CHOCH_2CHCH_2O$); 3,07 (m, 8H, $NCH_2CH_2OCH_2CHOCH_2CH$); 2.0 (m, 2H, OH); 1.47 (s, 6H, CH_3). Found,%: C 78.51; H 6.5 0; N 4.71. $C_{79}H_{76}N_4O_8$; Calculated,%: C 78.45; H 6.33; N 4.63.

Branched 3-(4-nitrophenyl)azo-9-(2-ethyl)hexyl-2-(2-ethyl)hexyloxycarbazole [4] molecules dispersed in **BCCPP** and in polycarbonate (PC-Z, *Iupilon Z-200*, $T_g = 189$°C) (Fig. 2) matrix for optical poling experiments were prepared by spin-coating technique. It concerned 500 cycles per min. for the first 6 seconds followed up by 2000 for the next 20 seconds. Silica glass plates used as substrates were degreased in ethanol, washed in distilled water and dried.

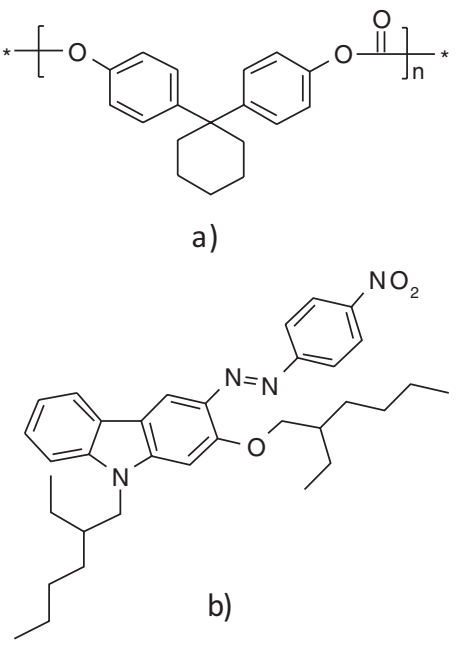

Figure 2. Molecular structures of polycarbonate (a) and azophenylcarbazole-based dye (b).

In order to avoid aggregation, the loading density of chromophores in all samples was chosen to 10% (wt%). Drying via two steps (25 min. at room temperature followed up by 45 min. at 80°C) was performed for finishing.

2.2 Technique

The ^{1}H NMR spectra were recorded in deuterochloroform ($CDCl_3$) using a HITACHI R-22 (90 MHz) spectrometer, the chemical shifts are expressed in ppm, downfield from tetramethylsilane (TMS), used as internal standard. The symbols d, m, t, s were respectively used for doublet, multiplet, triplet and singlet. The IR spectra were taken for samples in KBr pellets on a Specord M80 spectrometer. X-ray diffraction was recorded using DRON-6 diffractometer. The course of the reactions was monitored by TLC on Silufol UV-254 plates and development with I_2 or UV light. Silica gel (grade 62, 60–200 mesh, 150 Å, Aldrich) was used for column chromatography. The differential scanning calorimetry (DSC) measurements were recorded on a Mettler DSC 30 calorimeter at a scan rate of 10 K/min.

The all-optical poling technique permits polar orientation of molecules. If material with the initial centrosymmetric structure irradiated with fundamental ω and its second harmonic 2ω beams is able to absorb these beams, quantum interference between two photons of fundamental and one photon of the second harmonic to the same energy level can be achieved. The coherent pumping of the NLO polymer film results in an orientational hole burning [3,9], which leads to a net permanent molecular polar order. The induced molecular orientation breaks the initial centrosymmetry inside material creating a quasi-phase-matched grating of nonlinear second order susceptibility $\chi^{(2)}$ applicable to the second harmonic generation.

We used a two-branch type of experimental setup [3]. The light source was a Nd:YAG laser operating at wavelength 1064 nm. Pulse width and repetition rate at the output from the laser were ∼30 ns and 50 Hz, respectively. The polarized source beam was split into two branches by a beam splitter. One branch was frequency doubled by the KDP crystal (2ω beam) and served as one of the seeding beams, the ω beam served as the second seeding beam. These two beams of Gaussian profile were focused on the sample at the same spot of about 330 μm diameter. A pair of shutters was used to alter the seeding and reading processes. Optically-induced second order susceptibility of the sample was measured via second harmonic generation. The signal was detected by a photomultiplier tube. No photothermal heating of samples was observed, because of low loading density of chromophores and relatively high glass transition temperature for the polymer matrix used. The decay of second harmonic generation was measured by probing with a few single laser shots only, thus, having minimal influence on the decay process from the reading beam ("dark" regime).

3. Results and Analysis

3.1 Theoretical Background

The physical origin of all-optical poling is attributed to orientational hole burning and molecular re-orientation of azo-dye chromophores in polymer host matrix. This process can be described by two coupled orientational diffusion equations for photoexcitation and

re-orientation of azo-dye molecules in *trans* and *cis* states [10–12]:

$$\begin{aligned}\frac{\partial n_t(\Omega)}{\partial t} &= -\xi I(\theta) n_t(\Omega) + \phi \iint \Phi(\Omega' \to \Omega) I(\theta') n_c(\Omega') d\Omega' \\ &\quad + \frac{1}{\tau_c} \iint G(\Omega' \to \Omega) n_c(\Omega') d\Omega' + D_t \nabla^2 n_t(\Omega) \\ \frac{\partial n_c(\Omega)}{\partial t} &= -\phi I(\theta) n_c(\Omega) + \xi \iint Q(\Omega' \to \Omega) I(\theta') n_t(\Omega') d\Omega' \\ &\quad - \frac{1}{\tau_c} n_c(\Omega) + D_c \nabla^2 n_c(\Omega) \end{aligned} \tag{1}$$

where $n_t(\Omega)$ and $n_c(\Omega)$ are the molecular density of *trans* and *cis* isomers, respectively, with dipole momentum direction in the solid angle $\Omega(\theta, \varphi)$. ξ and ϕ are the quantum efficiency of *trans*-to-*cis* and *cis*-to-*trans* photoisomerization, respectively. τ_c represents the lifetime of *cis* isomer defined by thermal relaxation rate. $G(\Omega' \to \Omega)$ is probability for molecules to rotate from Ω' to Ω in the process of *cis*-to-*trans* thermal recovery. $Q(\Omega' \to \Omega)$ and $\Phi(\Omega' \to \Omega)$ are probabilities of *trans*-to-*cis* and *cis*-to-*trans* optical transition, respectively. D_t and D_c are thermal-induced orientational diffusion constants for *trans* and *cis* isomers, respectively.

The first term in Eq. (1) (upper) and the second term in Eq. (1) (lower) define isomerization of *trans* to *cis* state under photo excitation. Isomerization of *cis* to *trans* state describe the first term in Eq. (1) (lower) and the second term in (Eq. (1) (upper). The third and the forth terms stand for thermal-induced relaxation of *cis* isomer back to *trans* state and for molecular orientational diffusion, respectively. Further, we neglect the term $I(\theta)n_c(\Omega)$ by setting $\phi = 0$, because the orientational hole burning mechanism for ball-like *cis* isomer molecules is less important [13]. Thus, Eq. (1) simplifies into:

$$\begin{aligned}\frac{\partial n_t(\Omega)}{\partial t} &= -\xi I(\theta) n_t(\Omega) + \frac{1}{\tau_c} \iint G(\Omega' \to \Omega) n_c(\Omega') d\Omega' + D_t \nabla^2 n_t(\Omega) \\ \frac{\partial n_c(\Omega)}{\partial t} &= \xi \iint Q(\Omega' \to \Omega) I(\theta') n_t(\Omega') d\Omega' - \frac{1}{\tau_c} n_c(\Omega) + D_c \nabla^2 n_c(\Omega) \end{aligned} \tag{2}$$

The orientational hole burning mechanism for *trans* isomer in all-optical poling is represented by the term $I(\theta)n_t(\Omega)$, where $I(\theta)$ is azo-dye excitation rate:

$$I(\Theta) = I_1 \cos^2 \Theta + I_2 \cos^4 \Theta + I_3 \cos^3 \Theta \tag{3}$$

with

$$\begin{aligned} I_1 &\propto \mu_{01}^2 \left| E_{2\omega}^2 \right|, \\ I_2 &\propto \frac{\mu_{01}^2 \Delta\mu^2}{(2\hbar\omega)^2} \left| E_{\omega}^4 \right| \\ I_3 &\propto \frac{\mu_{01}^2 \Delta\mu}{\hbar\omega} \left| E_{\omega}^2 E_{2\omega}^* \cos(\Delta\phi + \Delta kz) \right| \end{aligned}$$

where μ_{01} is the transition dipole moment and $\Delta\mu = \mu_1 - \mu_0$ is the difference between the dipole moments in the excited and ground state for two-level molecule approximation of rod-like azo-dye chromophore [2]. Parameters I_1, I_2, I_3 correspond respectively to excitation terms of one-photon absorption at frequency 2ω (field amplitude $E_{2\omega}$), two-photon

absorption at frequency ω (field amplitude E_ω) and the interference between these two terms. $\Delta\phi$ corresponds to the phase difference between two beams on the incident surface of the sample. $(\Delta\phi+\Delta kz)$ is the relative phase between two beams after propagation over distance z. The term containing $I_3 cos^3\theta$ bears polarity, which is the origin of photoinduced polar orientation [2,14].

3.2 Results and Discussion

The investigated new composition of guest-host materials – azophenylcarbazole molecules dispersed in **BCCPP** – featured relative good molecular orientation property. The ability to get the system poled were predicted by measuring absorption spectra, which showed appropriate absorption at 532 nm wavelength (Fig. 3). The spectra appeared quite similar to spectra for polycarbonate as a host. Poling performed with azophenylcarbazole molecules in **BCCPP** proceeded within 20 minutes till saturation indicating some balance between orientation and re-orientation of the molecules was reached (Fig. 4). It is defined that read-out of poled structure by high intensity fundamental wave induces additional decay of recorded micro-pattern [15]. The physics behind rests on different excitation condition while seeding or reading. At the time of reading, the photoinduced hole burning no more affects entirely molecules that have their transition dipole moment parallel to the direction of poled electric field since the ω beam has alternating electric field orientation, what finally results into photoinduced erasure of the poled situation via hole burning of oriented molecules as well. Theoretically it originates from the second term in Eq. (3). To prove that experimentally reading beam of different fluence was applied (Fig. 4). Phenylazocarbazole dispersed in **BCCPP** showed that the read-out fluence determines faster decay of the second harmonic signal, i.e., effective "washing-out" of the orientation alignment of molecules.

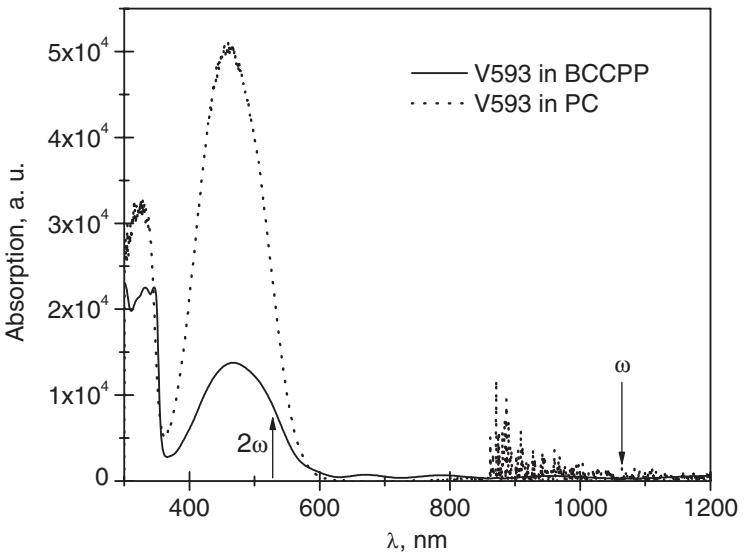

Figure 3. Spectral dependence of absorption coefficient for azophenylcarbazole samples in 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl}propane (**BCCPP**) and polycarbonate (**PC**). Arrow indicates quantum energy for the first (1.17 eV) and second (2.34 eV) harmonic light.

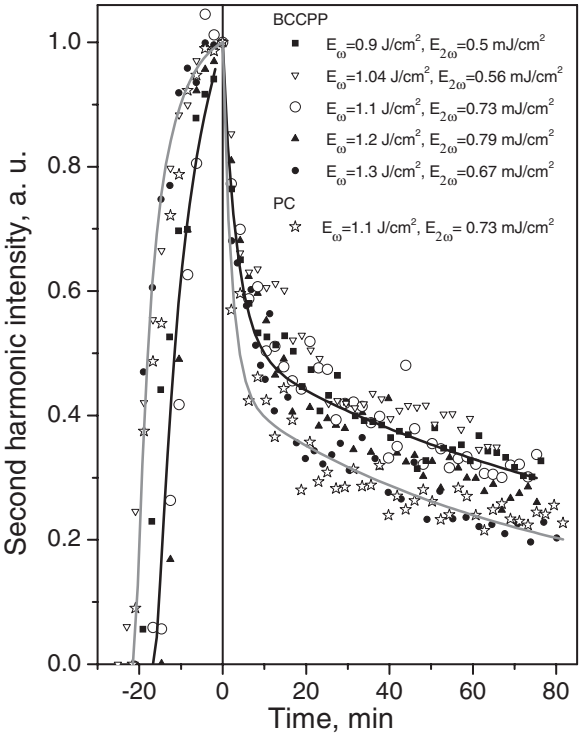

Figure 4. Optical poling and decay of generated second harmonic signal in optical poled azophenylcarbazole dispersed in 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl}propane (**BCCPP**) and polycarbonate (open stars) at different fluence of seeding and reading for one time per point reading in "dark" regime (reading fluence same as for seeding). Lines are modeling results according Eq. (2) (for parameters see Table 1) for azophenylcarbazole chromophores dispersed in BCCPP (black) and polycarbonate (grey) (seeding beam: I_ω – 1.1 J/cm^2, $I_{2\omega}$ – 0.73 mJ/cm^2; reading beam: I_ω – 1.1 J/cm^2).

Same effect appeared, when more frequent reading was applied. This slowed dawn the total speed of poling and prolonged the rising part of the kinetic to about 40 minutes (Fig. 5). Surprisingly, it was not as pronounced for the decaying part.

The adhesion with matrix and it's influence on motion of phenylcarbazole molecules was proved by comparing the **BCCPP** host with the polycarbonate. From the faster decaying kinetic measured at "dark" regime relative lower adhesion with the polycarbonate should be considered, though, weakly expressed (Fig. 4). To confirm that measurement with higher repetition reading was performed giving same tendency for the kinetic (Fig. 6). The more branched architecture of **BCCPP** provides less freedom for phenylcarbazole molecules in orientation motion, what results in relative longer decay. From the optical point of view relative higher absorption at 2ω quantum energy observed for polycarbonate approves the faster decay, since higher photoinduced erasure of the poled situation via hole burning of oriented molecules could be expected (Fig. 3).

The theoretical modeling (Eq. (2)) disclose polar order relaxation kinetics of azophenylcarbazoles roughly split into two time periods, short and long. The long term period (over 30 min.) is fully characterized by only *trans* isomer orientational diffusion coefficient D_t and this coincides well with previous data [2–4,10]. For the short time period (up

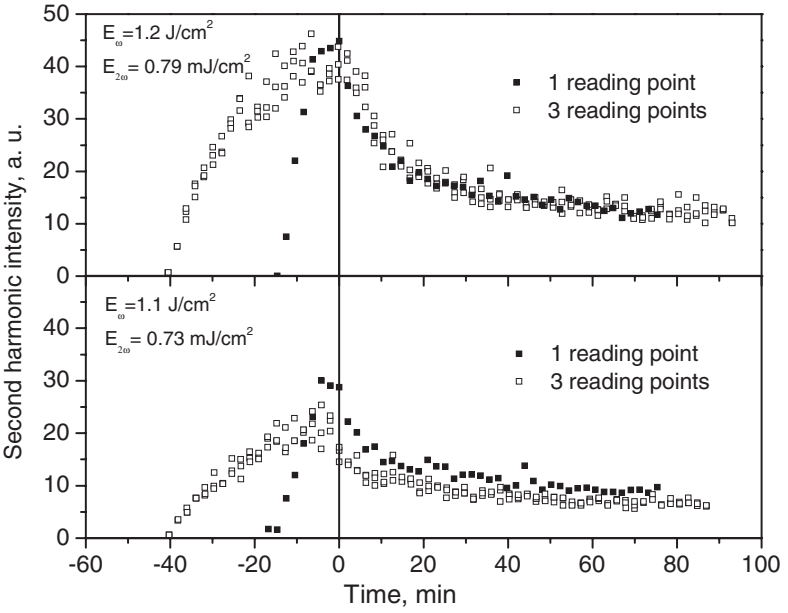

Figure 5. Optical poling and decay of generated second harmonic signal in optical poled azophenylcarbazole dispersed in 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl}propane at different fluence of seeding and reading for one (full square) and three (open square) time per point reading in "dark" regime (reading fluence same as for seeding).

to 30 min.) the relaxation kinetics of polar order is defined by many parameters of the azo-polymer system. First of all, the importance of the parameters G_m and Q_k standing for probabilities of redistribution process, which was mainly not noted in previous works. In Ref. [2], it was assumed that $G(\Omega' \to \Omega) = 1/4\pi$ and $G_0 = 1$, $G_1 = G_2 = G_3 = G_4 = 0$.

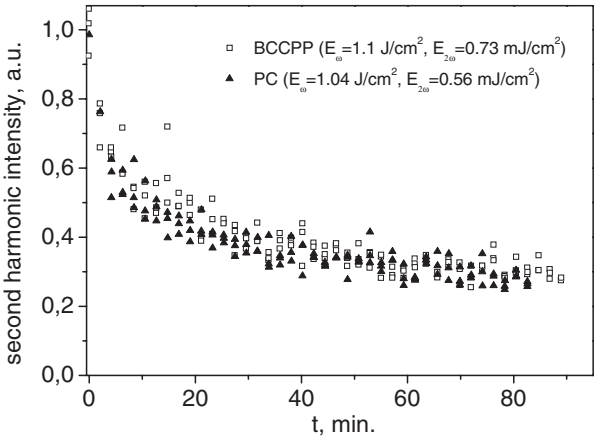

Figure 6. Decay of generated second harmonic signal in optical poled azophenylcarbazole dispersed in 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy] phenyl}propane (open squares) and polycarbonate (full triangles) for three time per point reading in "dark" regime (reading fluence same as for seeding).

Table 1. Parameters used for modeling (according Eq. (2)) of experimental optical poling kinetics for "dark" reading regime (see Fig. 4) (seeding beam: I_ω – 1.1 J/cm^2, $I_{2\omega}$ – 0.73 mJ/cm^2; reading beam: I_ω – 1.1 J/cm^2) of azophenylcarbazole chromophores dispersed in polycarbonate and 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy] phenyl}propane

Azophenyl carbazole	Regime	I_1 (s^{-1})	I_2 (s^{-1})	G_1	D_t (s^{-1})	D_c (s^{-1})	τ_c (s)
PC	"Dark"	$0.4{\cdot}10^{-4}$	$1.8{\cdot}10^{-3}$	0.94	$2.2{\cdot}10^{-5}$	$2.2{\cdot}10^{-5}$	143
BCCPP	"Dark"	$0.4{\cdot}10^{-4}$	$1.7{\cdot}10^{-3}$	0.85	$2.0{\cdot}10^{-5}$	$2.0{\cdot}10^{-5}$	222.2

This implies that after excitation, each chromophore may rotate from its initial direction by any angle in any azimuthal direction and with the same probability. In Refs. [10,12], it was assumed that $G_1 \times Q_1 << 1$ and all expansion coefficients are small and does not influence the relaxation kinetics. Rather strong influence on the fitting procedure for the short time scale was observed, when the finite values of G_m and Q_k were taken into account. Thus, the G_m values obtained demonstrate the *trans*-to-*cis* thermal recovery input in orientational rotation. Slightly less orientational diffusion coefficient $D_t \approx 2{\cdot}10^{-5}$ s^{-1} and longer lifetime of cis isomer $\tau_c \approx 222$ s extracted from the quantitative analysis indicate relative less flexibility for azophenylcarbazole molecules in **BCCPP** as in polycarbonate (see Table 1).

To evaluate the macroscopic second-order optical non-linearity of the material a comparison of second-order non-linear susceptibility $\chi^{(2)}$ between azophenylcarbazole and z-cut quartz plate was performed using equation [16]:

$$\frac{\chi^{(2)}}{\chi_q^{(2)}} = \frac{2}{\pi} \cdot \frac{l_{c,d}}{d} \cdot \sqrt{\frac{I^{2\omega}}{I_q^{2\omega}}} \tag{4}$$

where the coherence length $l_{c,q} = \lambda_\omega/(4(n_{q(2\omega)} - n_{q(\omega)}))$ and the refractive index n are parameters for quartz and d is the thickness of the azophenylcarbazole film. $I^{2\omega}$ and $I_q^{2\omega}$ are the second harmonic intensities measured from azophenylcarbazole film and quartz plate, respectively. The values of $\chi_q^{(2)}$ for quartz measured over the past two decades had a wide range from 1.0 to 0.6 pm/V [17]. The latter value claimed as more accurate was used in our calculation for z-cut quartz plate. For our **BCCPP** film with azophenylcarbazole of thickness 1.2–1.5 μm measured using a profilometer the obtained $\chi^{(2)} = 0.72$ pm/V is only slightly higher than that of z-cut quartz. Our value is far from the susceptibility 150 pm/V which could be induced in PMMA–DR1, however, substantially larger than 0.001 pm/V measured for PMMA-PNA [18].

4. Conclusions

A new guest-host system composed of 3-(4-nitrophenyl)azo-9-(2-ethyl)hexyl-2-(2-ethyl)hexyloxycarbazole as chromophore and 2,2-bis{4-[2-hydroxy-9-(carbazol-9-yl)-5-(carbazol-9-methyl)-4,7-dioxanonyloxy]phenyl}propane as host for all-optical poling application was developed and investigated. It revealed better features for keeping the chromophore molecules oriented as compared with polycarbonate as host. From modeling the experimental results orientational diffusion coefficient $D_t \approx 2{\cdot}10^{-5}$ s^{-1} and longer lifetime

of cis isomer $\tau_c \approx 222$ s for azophenylcarbazole in **BCCPP** were extracted. Reading of the created non-centrosymmetry showed increased erasure effect.

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