

Thermally Stimulated Current and Electro-Optic Responses in a Main- and Side-Chain Photorefractive Polymer

Tetsuya AOYAMA,^{*,**} Tatsuo WADA,^{*,†} Ya-Dong ZHANG,^{*} Yuji MORITSUKI,^{*}
Yuriko YONECHI,^{*} Hiroyuki SASABE,^{***} and Yasuhiro KOIKE^{**}

^{*}Supramolecular Science Laboratory,
RIKEN (The Institute of Physical and Chemical Research),
2-1 Hirosawa, Wako, Saitama 351-0198, Japan

^{**}Department of Material Sciences, Faculty of Science and Technology, Keio University,
3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

^{***}Faculty of Photonics Science and Technology, Chitose Institute of Science & Technology (CIST),
758-65 Bibi, Chitose, Hokkaido 066-8655, Japan

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ABSTRACT: The polarization and depolarization behavior of electric field-induced polar alignment in a side- and main-chain photorefractive polymer was measured by thermally stimulated current (TSC) and electro-optic (EO) modulation experiments. A relaxation peak was observed around the glass transition temperature (T_g) for the poled photorefractive polymer in a TSC experiment. The apparent TSC was not observed at room temperature. The polarization calculated from the relaxation peak linearly increased with the strength of the poling electric field. This result was consistent with the EO behavior which showed the linear dependence of the EO coefficients on the poling electric field. The main- and side-chain photorefractive polymer could be aligned by the electric field at an elevated temperature, and the polar alignment was stable at room temperature, which could lead to the long-term stability of the photorefractive responses without an external applied electric field.

KEY WORDS Thermally Stimulated Current (TSC) / Electro-Optic (EO) Response / Photorefractive Effect / Multifunctional Carbazole Polymer /

Recently organic photorefractive materials have attracted a lot of attention both from the point of view of fundamental science and practical applications.¹ Most of the reported photorefractive polymers consist of multi-components: electro-optic (EO) chromophore, plasticizer, sensitizer, and photoconductive polymer.²⁻⁴ Although these multi-component polymeric systems have film-forming properties and large photoinduced index changes,⁵ they are not stable material systems due to the phase separation or crystallization.⁶ In order to improve the physical properties of multi-component polymeric systems, our group has developed the main-chain carbazole polymer in which single component exhibits all the necessary responses for photorefractive. This monolithic photorefractive polymer showed net two-beam coupling gain.⁷⁻¹⁰ In order to enhance the photorefractive properties, we have introduced additional functional groups into the main-chain photorefractive polymer. This new photorefractive polymer (Figure 1) contains an additional EO chromophore in the side chain besides a carbazole moiety with two acceptor groups in the main chain, and showed large net two-beam coupling gain of 103 cm^{-1} without an external applied electric field.¹¹

Photorefractive responses are very sensitive to the

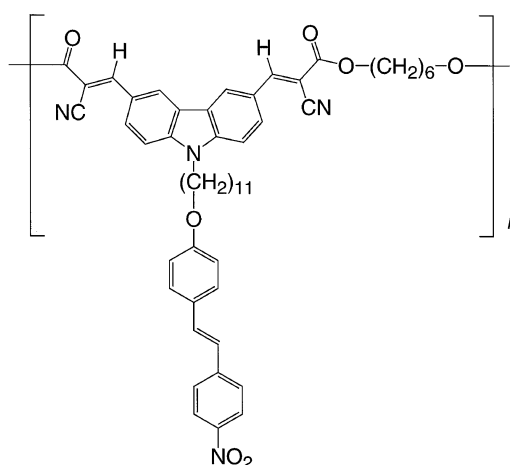


Figure 1. Chemical structure of a main- and side-chain photorefractive polymer.

molecular orientation because EO responses are necessary process for the photorefractive and molecular re-orientation by the space-charge field¹² provides large changes of refractive index. Therefore, the polarization and depolarization of multifunctional polymers are of fundamental interest for development of the effi-

[†]To whom correspondence should be addressed (Tel: +81-48-467-9378, E-mail: tatsuw@postman.riken.go.jp).

cient photorefractive materials. Although a spectroscopic technique is widely used to monitor the optical anisotropy, it is not so sensitive that small orientation in photorefractive polymers could not be observed. In addition, when the electronic transition dipole moment is not parallel to the ground-state dipole moment, it is difficult to discuss the polarization based on the change of the absorbance. Two-dimensional charge-transfer (CT) molecules show complicated absorbance change by the polarization or depolarization. Their absorbance coming from CT band doesn't change so much or decrease by poling while the absorbance of conventional one-dimensional CT molecules increase by depoling.^{13–15}

Thermally stimulated current (TSC) experiment is a useful tool to investigate the polarization and depolarization behavior with a high resolution because TSC directly results from depolarization of polar orientation.¹⁶ This polarization can be confirmed by measuring the EO modulation which comes from the polar orientation of the second order nonlinear optical (NLO) chromophores.

In this paper, we describe the polarization and depolarization behavior of the main- and side-chain photorefractive polymer in terms of TSC and EO responses. The combination of the TSC and the second harmonic generation (SHG) experiments has been reported.¹⁷ However, the intensity of a laser beam must be controlled carefully to avoid the damage of electrodes. In addition, the photorefractive effect requires the EO responses. Therefore we carried out the TSC and the EO experiments which provide the important aspect for the design of photorefractive polymers.

EXPERIMENTAL

The glass transition temperature (T_g) was found to be 87°C by the differential scanning calorimetric (DSC) analysis (DSC-7, Perkin–Elmer). The film was prepared by spin-coating from a chloroform solution onto an ITO substrate, and dried overnight at 50°C under vacuum. The thicknesses of the films were 3.9 μm for TSC measurements and 3.1 μm for EO measurements. A gold electrode (1.2 cm² area for TSC measurements) was made onto the film surface by vacuum-deposition. The samples were set into a temperature controlled hot stage (FP90/82HT, METTLER) with an optical window. Contact poling was performed to align dipole moments at 90°C slightly above T_g . After heating up to 90°C, a DC electric field was applied to the sample for 1 h, then the sample was cooled to room temperature with the electric field.

For TSC measurements, the poled polymer samples were heated at a constant heating rate of 3.0°C min⁻¹.

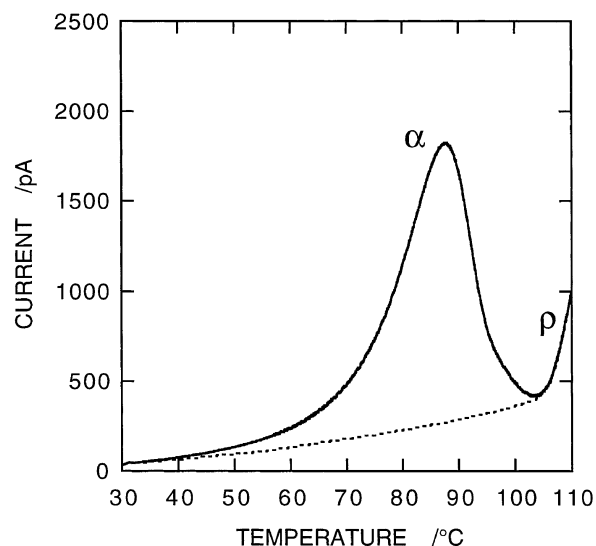


Figure 2. The TSC curve of the photorefractive polymer poled at a temperature of 90°C and with an electric field of 40 Vμm⁻¹. The solid curve is the experimental data, and the dashed curve corresponds to the ρ peak.

The resulting depolarization current was measured using a Keithley 6512 electrometer.

The EO response of the poled polymer was measured by the reflection method^{18,19} at a wavelength of 532 nm (frequency doubled Nd:YAG laser). It should be mentioned that our optical configuration for the measurement was a little different from the reflection method, *i.e.*, a laser beam was transmitted through the sample. An AC voltage of 10 V rms at a frequency of 2.3 kHz was applied to the sample to observe EO modulation. In order to measure the EO coefficients, after contact poling we took out the sample from the hot stage and set to a holder at an incident angle of 45°.

RESULTS AND DISCUSSION

Figure 2 shows the TSC curve of the main- and side-chain polymer poled at an electric field of 40 Vμm⁻¹. We observed two different processes labeled α and ρ . An α relaxation peak was observed around the T_g . This result is explained by the depolarization of the electric field-induced polar alignment. The ρ peak located above 110°C in Figure 2 is associated with the motion of the space charges induced during the poling process. In addition, we could confirm that TSC experiment was more sensitive rather than measuring the absorbance change caused by molecular relaxation. Order parameter for the contact-poled polymers is usually very small. For example, if we assume dipole moment μ to be 6 D, poling factor $a = \mu f^0 E_p / k T_p$ would be 0.27 in our condition, which result in order parameter of 0.0048, where f is the local field factor at the designated frequency, E_p is the poling electric field, k is the Boltzmann constant,

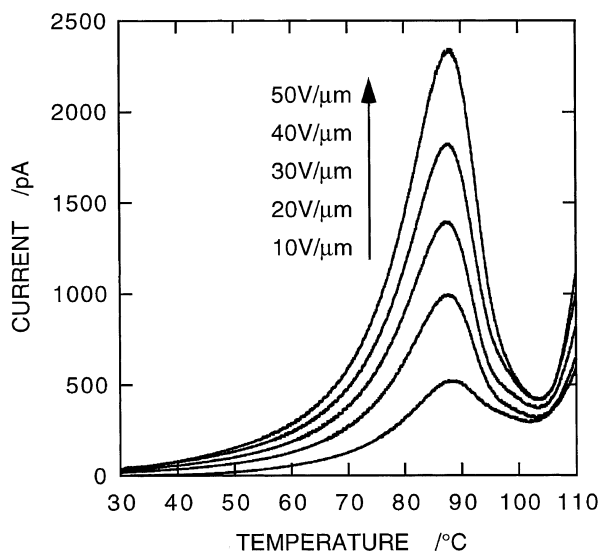


Figure 3. The poling electric field dependence of the TSC curves.

and T_p is the poling temperature. This means the absorbance would decrease by 0.48% caused by contact poling. It is very difficult to detect such a small absorbance change. On the other hand, we could clearly observe the depolarization behavior by the TSC experiment.

Figure 3 shows TSC curves obtained at various the poling electric fields. All α relaxation peaks were observed around the T_g . This result indicated that the depolarization behavior is independent on the poling electric field of 10–50 $V\mu m^{-1}$. The value of TSC increased with the poling electric field. The TSC density $j(T)$ is given by

$$j(T) = -q \frac{dP(T)}{dT} \quad (1)$$

where q is a constant heating rate ($q = dT/dt$), P is polarization, and T is temperature. Therefore we can calculate the frozen-in polarization P_0 from the TSC curves by integrating over the only α peak through the following equation:

$$P_0 = \frac{1}{q} \int_{T_1}^{T_{fin}} j_\alpha(T') dT' \quad (2)$$

T_1 and T_{fin} are the temperature at the start and the end of the scan, and $j_\alpha(T)$ is TSC density corresponding to the α peak. Figure 4 shows the poling electric field dependence of the polarization calculated from the α relaxation peak through the eq 2. The frozen-in polarization linearly increased with the poling electric field. By the thermodynamic models of poling, the polarization is expressed by²⁰

$$P_0 = N f^0 \mu \frac{f^0 \mu E_p}{3 k T_p} \quad (3)$$

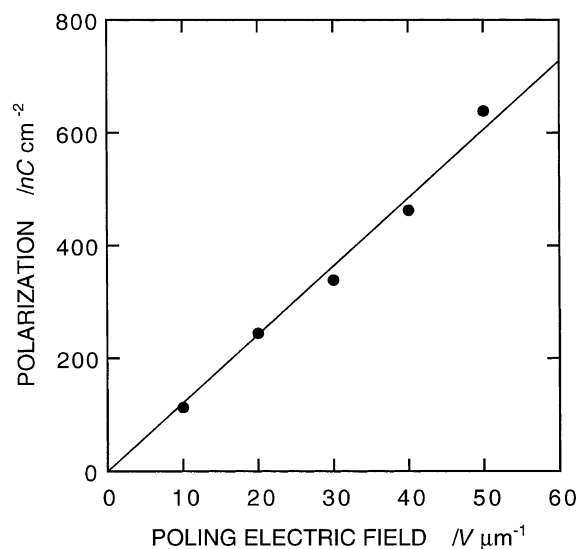


Figure 4. The poling electric field dependence of the frozen-in polarization calculated from the α relaxation peak. The solid line is a fit to the eq 3.

where N is the number of density of polar molecules. This equation indicates the polarization is linearly proportional to the poling electric field. The linear dependence of the calculated polarization on the poling electric field agrees with the thermodynamic models. This result means the α peak is associated with the depolarization of the polar orientation, and we could discuss the polarization in the photorefractive polymer by TSC experiments.

The TSC corresponding to the relaxation at room temperature was so small as shown in Figures 2 and 3. This result indicates that the depolarization is restricted at room temperature due to the high T_g , which could lead to the long-term stability of the photorefractive responses without an external applied electric field.¹¹

In order to confirm the orientation of the polar molecules, we examined EO responses. EO coefficient r_{33} is linearly proportional to the poling electric field according to the thermodynamic models²¹

$$r_{33}(-\omega; \omega, 0) = \frac{2N f^\omega f^\omega f^0}{n_3^4(\omega)} \beta_{zzz}(-\omega; \omega, 0) \frac{f^0 \mu E_p}{5 k T_p} \quad (4)$$

where n is the refractive index, β is the molecular hyperpolarizability. Figure 5 shows the poling electric field dependence of r_{33} at a wavelength of 532 nm and a linear dependence was obtained. Where, in order to calculate the r_{33} we measured refractive index by the m-line method and the value was determined to be 1.75. This result confirms that noncentrosymmetric alignment of the acceptor-substituted carbazole moiety and second order NLO chromophores was achieved.

From the results of the poling electric field dependence of the polarization and the r_{33} , we could find that the r_{33} linearly increased with the polarization calcu-

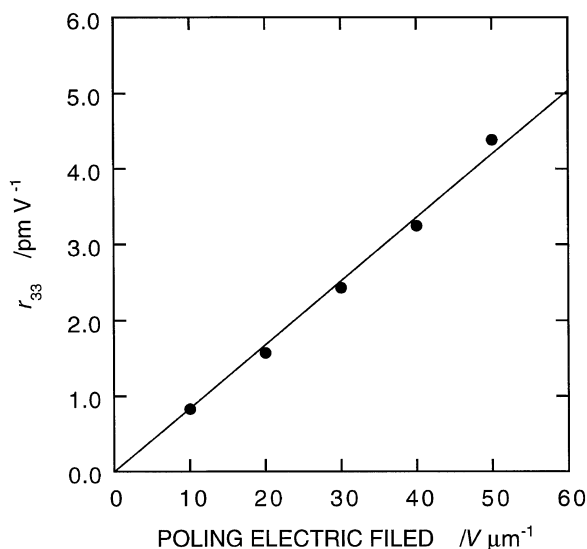


Figure 5. The poling electric field dependence of the EO coefficient at a wavelength of 532 nm. The solid line is a fit to the eq 4.

lated from the results of TSC experiments. Comparing the eq 3 with the eq 4, we find the following relationship,

$$P_0 \propto r_{33} \propto E_p \quad (5)$$

Therefore, the linear dependence of r_{33} on the polarization agrees with the thermodynamic models, and the results of the TSC and the EO experiments are in good agreement.

As mentioned above, the polar orientation of the electric-field induced alignment could be obtained by the contact poling at an elevated temperature, and these of depolarization was restricted at room temperature. These results distinguish the photorefractive properties of the main- and side-chain polymer from those of the multi-component photorefractive polymers which show low T_g and the orientational enhancement effect.¹² For photorefractive polymers with orientational enhancement effect, molecular reorientation caused by the space-charge field induces the modulation of the anisotropy of the first-order optical polarizability and the hyperpolarizability, and contributes to the refractive index change. Although, these polymers showed large photorefractive responses,⁴ an external electric field must be applied to induce the photorefractive responses. On the other hand, the polar alignment of the main- and side-chain polymer could be frozen, and the depolarization was restricted at room temperature as shown in Figure 2, which could lead to the photorefractive response without an external applied electric field and the long-term stability.¹¹

CONCLUSION

The polarization and the depolarization behavior of the main- and side-chain photorefractive polymer was measured by TSC and EO experiments. The EO coefficient linearly increased with the polarization calculated from the α relaxation peak in TSC curves. The TSC corresponding to the relaxation was not observed at room temperature. These results suggest that the origin of the refractive index change for the main- and side-chain polymer in the photorefractive responses is not the orientational enhancement but the pure EO.

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