

Electro-optic Properties of a Guest-Host System Containing a Phenothiazine-based Chromophore: Effect of the Chromophore Density on the Macroscopic Optical Nonlinearity

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Abstract: We have prepared a phenothiazine-based nonlinear optical (NLO) chromophore that displays a fairly high microscopic nonlinearity through intramolecular charge transfer. The phenothiazine unit plays important roles of contributing its high electron donating ability and connecting the resonance pathway through a conjugative effect in the cyclized ring adjacent to the aromatic ring. Theoretical calculations and an absorption spectroscopic study provided useful information concerning the microscopic nonlinearity of the chromophores. We investigated the electro-optic (EO) properties of the guest-host systems in amorphous polycarbonate containing the synthesized chromophores at different concentrations under different poling temperatures. A real-time pole and probe method provided a much greater amount of information regarding how the EO properties can arise and how they can be optimized.

Keywords: phenothiazine, nonlinear optical chromophore, electro-optic effect, effect of chromophore concentration.

Introduction

Organic nonlinear optical (NLO) materials provide strong potential advantages for second harmonic generation and electro-optic applications and are considered as most promising candidates for application in electro-optic and photonic devices.¹⁻⁶

A high NLO susceptibility, fast response time, low dielectric constant, small dispersion in the refractive index, structural flexibility, and ease of material processing are advantageous in organic NLO materials systems and can lead to apply them to various photonic devices such as high speed electro-optic modulators, and switches. To achieve good device functionality, the NLO chromophore has to possess high microscopic molecular nonlinearity ($\mu\beta$), good thermal stability, good photostability, low absorption, and particularly weak molecular electrostatic interaction in the polymer matrix simultaneously.

Much effort was made to develop the highly functional chromophore with high molecular hyperpolarizability, β and to improve the thermal/photo-stability. Some electron-deficient heterocyclic compounds have been known as strong acceptors for nonlinear optical materials. Particularly, 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran

(TCF) was well adopted as a strong electron acceptor to induce significantly high dipole moment (μ), first-order molecular hyperpolarizability (β), and their product ($\mu\beta$).⁷⁻¹¹

Since acentric ordering of dipolar chromophores is required to exhibit second-order nonlinearity, usually electrical poling is employed to the NLO sample film. Among many kinds of host amorphous polymer, polycarbonate (APC, poly(bis-phenol A carbonate-co-4,4'-(3,3,5-trimethylcyclohexylidene)diphenol, $T_g=202^\circ\text{C}$) behaves as a quite rigid polymer binder to retard the dipolar relaxation after poling process.^{12,13}

In this report, we selected a phenothiazine-based chromophore to be synthesized. Phenothiazine was used as an electron donor in PTZ-TCF (see Figure 1). 2-Cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was employed as a strong electron acceptor to induce charge transfer complex.⁷⁻¹¹

In order to investigate the macroscopic nonlinearity of the chromophores, we introduced the chromophore into the amorphous polycarbonate with various doping concentrations. The samples were poled to measure the electro-optic coefficient at 1300 nm. Poling conditions were fully optimized to enhance the electro-optic effect of the samples without any information from thermal analysis such as DSC, DTA, etc. Real time poled and probe technique permits us to monitor the electro-optic signal of the material. The effect of the chromophore density was investigated on the temperature dependence of the electrical and the electro-optic properties.

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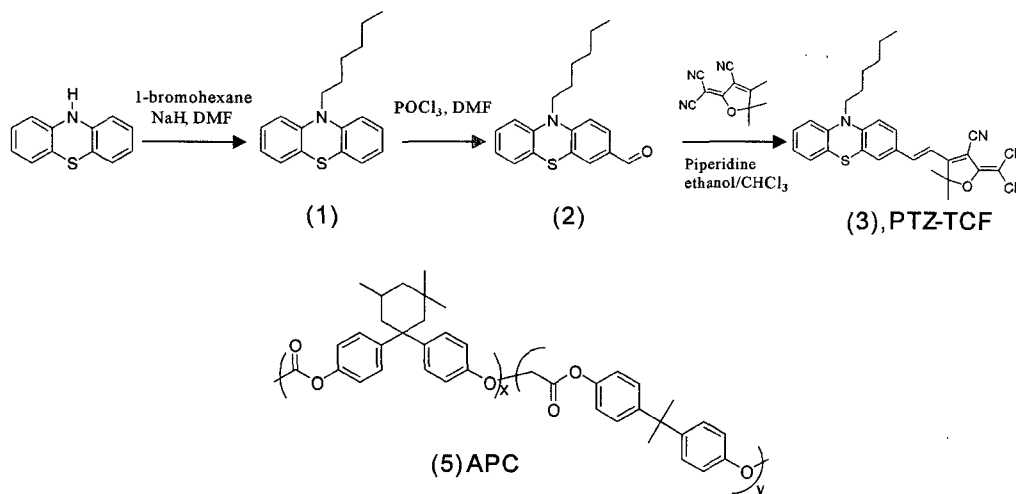


Figure 1. Synthesis of phenothiazine-based nonlinear optical chromophore and the structure of amorphous polycarbonate used as a host material.

Experimental

Materials. Phenothiazine, phosphorous oxychloride (POCl₃), and 1-bromohexane were purchased from ACROS Co. and used after purification. All solvents used in this study were freshly dried under distillation method. The synthesis of 2-cyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (TCF) was synthesized following the known procedure.¹¹

Synthesis of 10-hexyl-10H-phenothiazine (1): Sodium hydride (14.4 g, 0.36 mol) was dissolved in dried dimethylformamide (DMF, 200 mL) at 0°C. Phenothiazine (59.7 g, 0.3 mol) in DMF (100 mL) was added dropwise into the mother solution and stirred for one hour. Then, 1-bromohexane (59.4 g, 0.36 mol) in DMF (50 mL) was also added dropwise over 30 min and the reaction mixture was kept stirring at room temperature for 12 hrs. After completion of the reaction, the solution was neutralized with dilute HCl aqueous solution. The mixture was extracted with ethylacetate/water and the organic layer was dried under MgSO₄. The dried solution was concentrated. The resulting crude oily product was purified by silica gel column chromatography (ethylacetate: hexane = 1 : 10 vol%) to yield 59.5 g (70%) of colorless oil.

¹H NMR (300 MHz, CDCl₃): δ 7.14 (t, 2H), 7.12 (d, 2H), 6.90(t, 2H), 6.77(d, 2H), 3.85(t, 2H), 1.80(m, 2H), 1.43(m, 2H), 1.31(m, 4H), 0.87(t, 3H).

Synthesis of 10-hexyl-10H-phenothiazine-3-carbaldehyde (2): An oven dried 500 mL, round bottom flask was charged with a solution of DMF (29.2 g, 0.4 mole) and 1,2-dichloroethane (50 mL) at 0°C. POCl₃ (38.2 g, 0.25 mole) was slowly added to the mixture for 30 min. Then, 10-hexyl-10H-phenothiazine (56.6 g, 0.2 mole) in 1,2-dichloroethane (50 mL) was added dropwise over 30 min. The mixture was allowed to stir for 12 hrs at 90°C. It was poured

into ice-water, 300 mL and neutralized with NaHCO₃ aqueous solution. The reaction mixture was extracted with chloroform. The organic layer was dried over MgSO₄ and the solvent was removed in vacuo after filtration. The resulting product was purified by silica gel column chromatography (ethylacetate: hexane = 1 : 5 vol%) to yield 46 g (74%) of yellow solid.

¹H NMR (300 MHz, CDCl₃): δ 9.76 (s, 1H), 7.61(d, 1H), 7.55(s, 1H), 7.15(t, 1H), 7.08(d, 1H), 6.94(t, 1H), 6.86(d, 2H), 3.85(t, 2H), 1.79(m, 2H), 1.42(m, 2H), 1.29(m, 4H), 0.86(t, 3H).

Synthesis of 2-[3-cyano-4-(2-(10-henyl-10H-phenothiazin-3-yl)vinyl)-5,5-dimethyl-5H-furan-2-ylidene]malonitrile (3): In a dried 250 mL, round bottom flask, 10-henyl-10H-phenothiazine-3-carbaldehyde (3.11 g, 0.01 mole) and TCF (1.99 g, 0.01 mole) were dissolved in ethanol/chloroform(4 : 1, 50 mL) under argon. After heating the solution at 70°C, a trace amount of piperidine was added dropwise. After 3 hr reaction, the solvent was evaporated to obtain a dark solid. The resulting product was purified by silica gel column chromatography (ethylacetate: hexane = 1 : 10 vol%) to yield 2.31 g (47%) of dark violet solid.

¹H NMR (300 MHz, CDCl₃): δ 7.53(d, 1H), 7.41(d, 1H), 7.34(s, 1H), 7.18(t, 1H), 6.98(t, 1H), 6.89(d, 1H), 6.85(d, 1H), 6.82(d, 1H), 3.88(t, 2H), 1.81(m, 2H), 1.76(s, 6H), 1.44(m, 2H), 1.31(m, 4H), 0.88(t, 3H).

Anal.: C₃₀H₂₈N₄O₅ (492.20) Calcd. C 73.14, H 5.73, N 11.37; Found C 73.10, H 5.56, N 10.75

Instrument. Proton NMR was recorded with JEOL 300 NMR spectrometer. Deuterated chloroform (CDCl₃) was used as a solvent for recording the spectra. The UV-VIS absorption spectra of the chromophore solution (solvent: chloroform, conc. 1 × 10⁻⁴ mole/L) and the film samples were recorded with an UV-VIS spectrophotometer (HP 8453, photodiode array type 190-1,100 nm). Thermal decom-

position temperature was measured by Perkin Elmer 7 TGA under nitrogen (rate of temperature: 5 °C).

Spectroscopic ellipsometry measurement to determine the refractive indices at various wavelengths was performed on the thin films with incidence angles of 65, 70, 75 degrees using a Woollam VASE model with autoretarder in the spectral range of 264-1,550 nm (0.8-4.7 eV).

Material Processing for Electro-optic Study. The mixed solution (8 wt%) of chromophore and APC were prepared in cyclopentanone/cyclohexanone (1:1 vol%). 25, 35, and 45 wt% chromophore were doped in every APC sample. For studying electro-optic effect, thin films (thickness: 2.2-2.5 μm) were fabricated on indium tin oxide (ITO) precoated glass with a filtered solution. For linear electro-optic coefficient measurement, we deposited the gold electrode on top of the film (thickness: 100 nm) to fabricate sandwiched samples. The thickness of the film sample was measured by using Surface Profilometer (KOSAKA, ET-3000).

Measurement of dc Current through the Sample Film with the Temperature. The dc current profile of the APC polymer film played an important role to obtain very useful information for the poling temperature and the dielectric breakdown behavior. We measured the current using Keithley 2400 sourcemeter under applying the poling voltage ($E_p = 35 \text{ V}/\mu\text{m}$) and monitored the sample temperature of the sample with Keithley Digital Multimeter 2000 (k-couple), instantaneously. Computer with the uniform time interval instantaneously integrated all current data.

Real Time Poled and Probe Measurement for Electro-optic Effect. Firstly, we measured the linear electro-optic signal (I_m/I_c) of the samples by way of reflection technique after poling the sample following the conventional way.¹⁴ The a.c. voltage (10 V_{rms} at 1 kHz) was applied to each sample for observing the modulated signal (I_m). The linear electro-optic coefficient, " r_{33} " of the poled APC film was calculated by the following equation. The r_{33} value is directly proportional to I_m/I_c in eq. (1).

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2 \theta)^{1/2}}{\sin^2 \theta} \sim I_m/I_c \quad (1)$$

where n is the refractive index at 1,300 nm and I_m is the amplitude of electro-optic modulation. V_m is the a.c. voltage applied to the sample and I_c is the intensity of incident light where phase retardation is 90° between TE and TM mode.

For *in-situ* EO study, the sample was placed on the heater to apply the voltage combined with d.c. and a.c. component, which is represented as follows (see Figure 2).

$$V(t) = V_{d.c.} + V_o \sin \omega t \quad (2)$$

An a.c. voltage ($V_o \sin \omega t$) was added to the d.c. voltage ($V_{d.c.}$) for poling and probing the electro-optic signal (I_m/I_c) simultaneously. EO signal could be monitored during poling

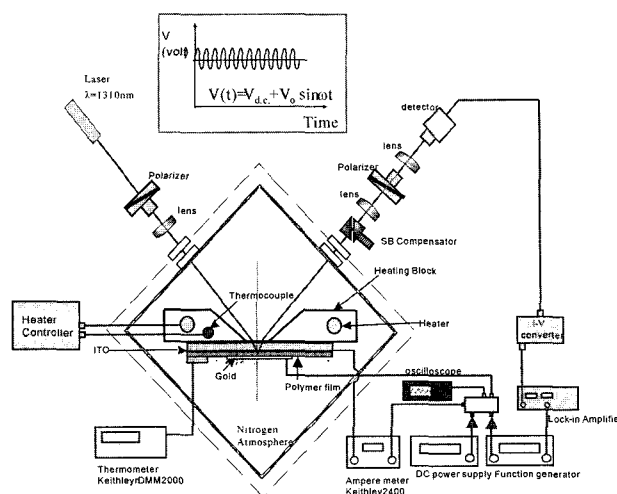


Figure 2. Optic measurement setup for electro-optic effect.

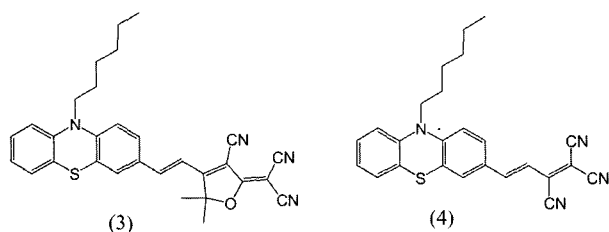
with increase of the sample temperature. The flowing current was measured by using Keithley 2400 sourcemeter without applying the input voltage.^{15,16}

Results and Discussion

Material Consideration. The synthesis of the NLO chromophore and the structure of amorphous polycarbonate were illustrated in Figure 1. The chromophore molecule forming Donor-Acceptor (D-A) was obtained and the structure may result in the requisite ground-state charge symmetry, whereas π -conjugation or conjugative effect through the heterocyclic center bridge provides a pathway for the redistribution of electric charges under influence of the electric field. Incorporation of heterocyclic donor to the molecular backbone and the use of strong electron accepting tricyano acceptor moiety can be expected to lead high molecular nonlinear optical property. Regarding the microscopic nonlinear optical properties of the chromophore, we did molecular orbital calculation to determine quantum mechanical parameters. The geometry of the chromophore was optimized for chromophore by means of the MOPAC 2002 (CACH version 5.04, PM3-Hamiltonian). The PM3 program was used for calculating the dipole moment (μ), polarizability (α), and molecular hyperpolarizability (β) in the ground state under the method of time-dependent Hartree-Fock (TDHF).

In Table I, the product of the dipole moment (μ) and the molecular hyperpolarizability (β) of the chromophore were shown. In order to evaluate the microscopic property of the phenothiazine-chromophore, we designed the other chromophore (4) having tricyanovinyl acceptor. The calculated results showed clear difference in the microscopic origin (see Table I). The TCF acceptor induce enhancement of ground state dipole moment and microscopic nonlinearity significantly. The closed furan ring exhibited higher electron withdrawing property although three cyano groups exist in the two chro-

mophores commonly.



Thermal stability is an important requirement for the incorporation of the chromophores in poled-polymer systems. The chromophore synthesized in this study showed very good thermal stability as confirmed by the decomposition temperature (T_d) shown in Table II.

Absorption Spectral Analysis. The absorption spectra of the chromophore both in solution state (CHCl_3) and film state were shown in Figure 3A. The film sample was made in amorphous polycarbonate after doping the chromophore. The spectrum of chloroform solution was taken from 420 to 850 nm range at room temperature. The phenothiazine-based chromophores showed λ_{max} around 570 nm in APC film and 578 nm in the chloroform solution, respectively.

The refractive index is very important information for studying the electro-optic property. Using the ellipsometry with the wavelength, we could obtain the real part and imaginary part of the refractive index in Figure 3B. We could observe the clear inflection point in the real part of the index (n) and the maximum point in k , which are all consistent with the λ_{max} of the chromophore in APC.

Electrical Property of the APC NLO Sample with the Temperature. We investigated the dc current of the polymer films with the change of the temperature (see Figure 4). In three APC polymers, the current started to increase from 90-120°C approximately and the abruptly increased around 105-130°C in heating cycle. Therefore, we could observe "transition temperature" at which the current is largely changed. The transition temperature of each sample was selected as a poling temperature, which can be in the vicinity of the glass transition temperature of the doped polymer.

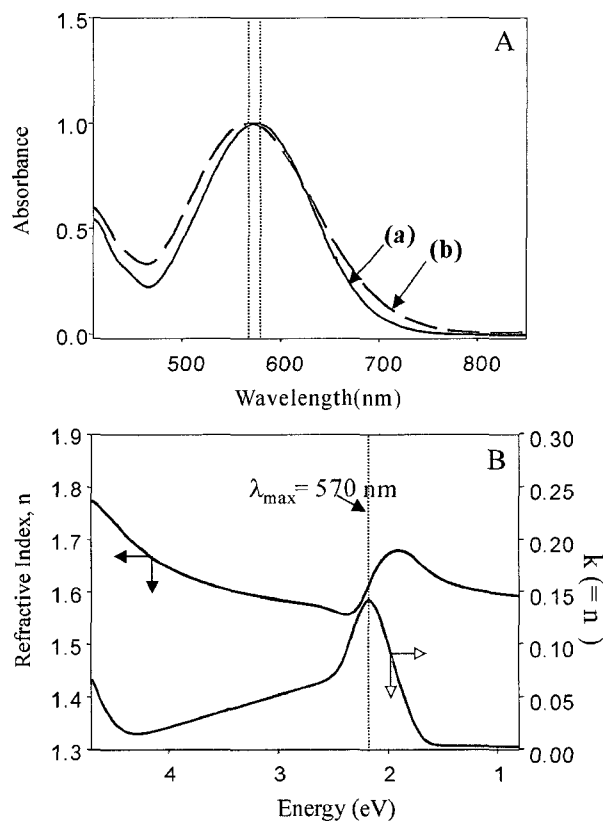


Figure 3. A: UV-Vis absorption spectra of PTZ-TCF chromophores. (a): solution in chloroform, (b): APC film. B: Refractive index profile of the APC film bearing PTZ-TCF with the wavelength.

The sample bearing higher concentration of the chromophore showed lower transition temperature since the higher plasticizing effect exists. The results from this experiment were quite informative to select the optimum poling temperature for electro-optic coefficient measurement.

Electro-optic Properties of the APC samples. We investigated the electro-optic properties of amorphous polycarbonate samples doped with different concentrations (25, 35, and 45 wt%). We dissolved the chromophores in amorphous

Table I. Comparison of the Microscopic Nonlinearity between the Chromophore (3) and (4)

| | μ ($\times 10^{18}$ esu) | α_{xx} ($\times 10^{23}$ esu) | $\Delta\alpha$ ($\times 10^{23}$ esu) | $\beta(0)$ ($\times 10^{30}$ esu) | $\mu\beta(0)$ ($\times 10^{48}$ esu) |
|-------------|----------------------------------|--|---|---------------------------------------|--|
| PTZ-TCF (3) | 10.00 | 588.26 | 347.84 | 50.78 | 507.80 |
| PTZ-TCV (4) | 6.38 | 427.10 | 221.17 | 32.00 | 204.16 |

Table II. Material Properties and Determined Electro-optic Properties of the Chromophores

| | λ_{max} (nm) | | T_d (°C) | $\mu\beta(0)$ ($\times 10^{48}$ esu) | r_{33} (pm/V) | | | Rate Constant (k_i) | | |
|---------|-----------------------------|------|---------------|--|-----------------|-------|------|-------------------------|-------|-------|
| | Solution | Film | | | 25% | 35% | 45% | 25% | 35% | 45% |
| PTZ-TCF | 578 | 570 | 321 | 592.6 | 7.92 | 11.64 | 9.66 | 2.071 | 1.929 | 0.879 |

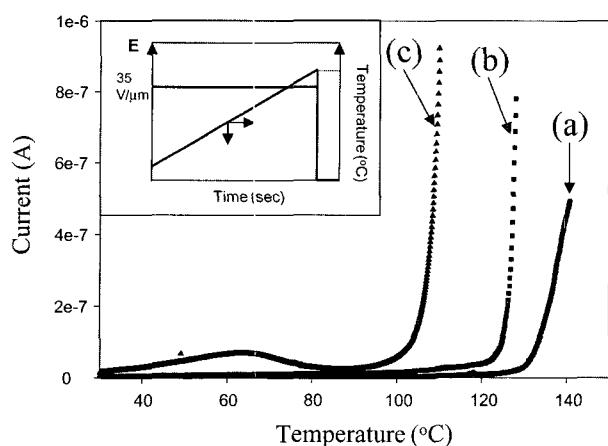


Figure 4. Temperature dependence of the d.c. current in the APC samples. Loading density: (a) 25%, (b) 35%, and (c) 45%.

polycarbonate to form composite materials. In the poling process, thin film samples of the guest-host system were poled using a parallel electrode configuration at a poling temperature under applying dc electric field of $70 \text{ V}/\mu\text{m}$. The poling temperature was selected according to the transition temperature from the dc measurement.

The electro-optic coefficient, r_{33} was obtained using the simple reflection technique.¹⁴ For measuring the electro-optic modulation signal, reflection technique was widely used for many researchers, which was proposed earlier. Although there is some problems due to the multiple reflection between each boundary, contribution of induced piezoelectric & electrostrictive effect and imposition of the third order NLO effect, the approximate linear electro-optic coefficient was measured much more simple and easier than using prism coupling methods. All samples possess very little absorbance at the measured wavelength so that we did not consider the absorption induced resonance enhancement at $1,300 \text{ nm}$.

In order to observe the maximum EO signal, we performed real-time pole and probe method to observe the maximum EO effect from each samples used above. In this experiment, we applied the electric field ($70 \text{ V}/\mu\text{m}$) to the sample and no dielectric breakdown occurs during measurement. We applied the $V(t) [=V_{d.c.} + V_o \sin \omega t]$ to the samples for measuring the EO signal during heating the sample. The EO signal was recorded from room temperature to the temperature that was 20°C higher than the transition temperature from the dc current measurement in the presence of the electric field, $V(t)$ (see Figure 5). As soon as we applied the electric field, $V(t)$ to the sample at room temperature, the signal was raised suddenly to a certain level and saturated. After the signal was stabilized at a certain value, we started to increase the temperature of the sample. The asymptotical value of the signal is mostly attributed to d.c. electric field induced Kerr effect and Pockels effect, which was already discussed.^{15,16} The EO signal, (I_m/I_c) increased slowly as the

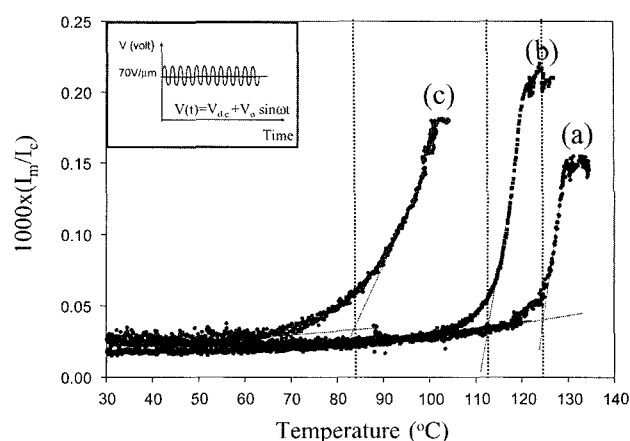


Figure 5. Temperature dependence of EO signal, I_m/I_c . Loading density: (a) 25%, (b) 35%, and (c) 45% ($E_p=70 \text{ V}/\mu\text{m}$).

temperature was raised. The rising rate of the temperature was set to be $5^\circ\text{C}/\text{min}$. From the saturated value of I_m/I_c , we calculated the EO coefficient, r_{33} of each sample.

Recently, electro-optic effect was suggested to increase linearly or nonlinearly with chromophore concentration at a low chromophore density, where the intermolecular dipolar interactions are relatively weak.⁹ As the intermolecular electrostatic interaction is higher than the interaction between the chromophore dipole and poling field, we could observe the decreasing behavior over certain high chromophore density

When comparing the electro-optic properties of three samples, we could observe that the samples with highest density (45%) of the chromophore molecules showed lower EO coefficient than the sample with 35 wt% chromophore. Therefore, we can conjecture occurrence of higher electrostatic interaction between the chromophores in the sample with 45 wt% chromophore (see Table II).

The rising curve of the electro-optic signal was well fitted to the single exponential growth function to determine the rate constant, k_i (see Figure 5). In the case of the samples with 25% and 30% PTZ-TCF, the increasing rate of the EO signal were determined around 2.071 and 1.929. Although the transition temperatures have some difference, the rising rates in two samples are almost similar. However, in the sample with 45 wt%, the rate constant was determined around 0.879 away of the previous rate constant. The rising behavior was much more retarded, which is strongly attributed to the higher molecular electrostatic interaction to require the higher energy to induce same extent of acentric ordering.

Conclusions

We employed phenothiazine-based chromophore and investigated the effect of the chromophore density in the host polymer. Phenothiazine donor was confirmed to be a strong

donor in terms of absorption spectroscopy and theoretical calculation. Real time pole and probe method provided us to measure the maximum electro-optic coefficient rather than the static poling and measurement effectively. The sample bearing 35 wt% PTZ-TCF exhibited much higher electro-optic coefficient around 11.64 pm/V than the sample with 45% of the chromophore and we can expect much higher EO coefficient under poling at a higher field.

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