

Temporal stability of the electro-optic effect in poled polymethacrylate and polynaphthalate bearing methylsulfonyl benzothiazolyl azo dyes below the glass transition temperature

Dong Hoon Choi*, Ju Sik Kang, Hyeon Taik Hong

College of Environment and Applied Chemistry, Institute of Material Science & Technology, I.L.R.I., Kyung Hee University, Kyungki 449-701, South Korea

Received 27 December 1999; received in revised form 6 March 2000; accepted 10 April 2000

Abstract

We synthesized second-order nonlinear optical (NLO) polymers for studying the structural effect on the electro-optic (E/O) properties. A heterocyclic azo chromophore was synthesized to be tethered to the methacrylate and naphthalate polymer backbones. Particularly, 2-amino-6-methylsulfonylbenzothiazole was employed to prepare the NLO azo chromophore. The real time pole and probe method was employed to investigate the change of the poled order during poling. The increasing rates of the E/O effect were considered in two polymer systems during poling. The decaying behaviors of the electro-optic signal were observed at different temperatures below the glass transition temperature. The decaying rates of the E/O effect were compared and the effect of structural difference was investigated. © 2000 Published by Elsevier Science Ltd.

Keywords: Structural effect; Heterocyclic chromophore; Electro-optic

1. Introduction

Nonlinear optics is an important field of photonics whose technology includes acquisition, storage, process, and transmission of photons instead of electrons in signal processing. Organic nonlinear optical (NLO) materials provide strong potential advantages for the second harmonic generation and electro-optic (E/O) applications [1–3].

Particularly, poled polymeric systems have attracted remarkable interest in recent years as promising candidates for application in E/O and photonic devices [4–7]. Useful measurement techniques were developed for the determination of the NLO response of polymeric materials. Time resolved techniques have been developed, which permit monitoring either the relaxation dynamics of the NLO effect following previous poling of the material or the growth dynamics during poling [8–10]. Such time resolved techniques facilitate the study of the physics of electro-optics in detail and provide a promising method for improving the NLO properties by optimizing the poling conditions.

The poled order relaxation is important from practical points of view. The second-order NLO polymeric devices

require that the poled order be quite stable. The study of orientational relaxation processes in poled NLO polymers below the glass transition temperature can be utilized as an important method for investigating polar molecular dynamics over a long period of time. The poled order relaxation process can be related to the relaxation processes measured in polymers using other experimental technique such as dynamic mechanical analysis, dielectric relaxation spectroscopy, piezoelectric relaxation spectroscopy. In these analyses, we can observe two kinds of major transitions for the molecular relaxation process [11–13]. α -Relaxations are usually identified with the glass transition and involve relative motions of the polymer main chains. β -Relaxations are frequently associated with the local motions of the side groups in the polymer chain, which can be observed below the glass transition temperature (T_g). Usually the α -transition can appear at the temperature much higher than that of the β -transition. Poled order that is strongly related to the second-order NLO property can be relaxed both above and below the T_g . Therefore, the molecular relaxation process can be explained by two temperature regimes. The relaxation behavior of the poled polymer can be described using the William–Landel–Ferry equation above the T_g . Below the T_g , the relaxation behavior can be described using an Arrhenius-like behavior.

We report, herein, the results of the in situ measurement

* Corresponding author. Tel.: +82-331-201-2921; fax: +82-331-202-9484.

E-mail address: dhchoi@khu.ac.kr (D.H. Choi).

concerning the isothermal relaxation dynamics of the E/O signal of poled polymer films made up of polymethacrylate and polynaphthalate by means of a modified reflection technique. In an attempt to investigate the rate of molecular relaxation in the chromophore after poling, we designed two NLO active polymers. One is composed of a relatively long repeating unit with a short side chain group. The other consists of relatively short repeating groups with a long side chain group. Using two polymers, we performed the in situ E/O measurement and traced the relaxation behavior of the signal at temperatures lower than the glass transition temperature. The relaxation dynamics of two different polymers were studied below the glass transition temperature after analyzing the decaying curve of the E/O signal. The structural difference in the two polymers was considered to deduce how it could affect the E/O properties and their relaxation dynamics.

2. Experimental section

2.1. Materials

2-Amino-6-methylsulfonylbenzothiazole, 3-chloro-1-propanol, and diisopropyl azodicarboxylate (DIAD) were purchased from Aldrich Chem. Co. and used without further purification. *N*-phenyldiethanolamine purchased from Aldrich Chem. Co. was used after recrystallization from ethanol. Methacryloyl chloride and *N*-methylaniline were purchased from Acros Chem. Co. and the latter was purified by vacuum distillation. 1,4-Hydroquinone, triethylamine, and triphenylphosphine were purchased from Kanto Chem. Co. Dimethylformamide (DMF) was purified by vacuum distillation just before polymerization. Azobisisobutyronitrile (AIBN, Wako Pure Chemical Co.) was recrystallized from acetone. Naphthalene-2,6-dicarboxylic acid (NDA) was made of naphthalene-2,6-dicarboxylate (NDC) supplied by Kolon Co. Ltd.

2.2. Synthesis of monomers and polymers

2.2.1. Synthesis of 2-methyl-acrylic acid 3-methyl-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amine-propyl ester [M I]

2.2.1.1. Synthesis of 3-(methyl-phenyl-amino)-propan-1-ol. 3-(Methyl-phenyl-amino)-propan-1-ol was prepared following the literature method [14]. Yield 71%, b.p. 134°C (0.11 mmHg). $^1\text{H NMR}$ (DMSO- d_6) δ (ppm) 1.65 (m, 2H), 2.1 (s, 3H), 3.47 (m, 4H), 4.59 (t, 1H), 6.69 (m, 3H), 7.19 (t, 2H).

2.2.1.2. Synthesis of 3-methyl-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amino-propan-1-ol. 2-Amino-6-methylsulfonylbenzothiazole (5.7 g, 0.025 mol) was dissolved in H_2SO_4 (125 g) at 90°C and the solution was cooled to -10°C . Then, sodium nitrite (1.75 g,

0.025 mol) in H_2SO_4 (12.5 g) was added dropwise in the mother solution while maintaining the cold temperature. It was stored at -10°C for 75 min. 3-(Methyl-phenyl-amino)-propan-1-ol (4.05 g, 0.025 mol) was dissolved in H_2O (112.5 g) and H_2SO_4 (12.5 g) and the solution was cooled to -4°C . In this solution, the prepared solution containing the diazonium salt was added slowly under vigorous stirring. The coupling reaction continued for 30 min and the resulting mixture was poured into H_2O (600 ml) to collect the solid. The solid was washed with water thoroughly. The product was dissolved in tetrahydrofuran and the solution was dried with sodium sulfate. The concentrated solution was added to hexane to obtain the violet solid. The solid was dried in vacuo. Yield 71%, m.p. 148°C. $^1\text{H NMR}$ (DMSO- d_6) δ (ppm) 1.73 (m, 2H), 3.13 (s, 3H), 3.28 (s, 3H), 3.44 (t, 2H), 3.59 (t, 2H), 4.68 (t, 1H), 6.93 (d, 2H), 7.84 (d, 2H), 7.94 (d, 1H), 8.13 (d, 1H), 8.62 (d, 1H). Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{N}_4\text{O}_3\text{S}_2$: C, 52.56; H, 5.18; N, 14.42; S, 16.51. Found: C, 53.87; H, 5.86; N, 14.04; S, 16.25.

2.2.1.3. Synthesis of 2-methyl-acrylic acid 3-methyl-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amine-propyl ester [M I]. 3-Methyl-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amino-propan-1-ol (5 g, 0.012 mol), triethylamine (1.045 ml, 0.008 mol), and a trace amount of 1,4-hydroquinone were dissolved in methylene chloride (200 ml) at 35°C under nitrogen purging. Methacryloyl chloride (2.442 ml) was added dropwise and the reaction mixture was kept aside for 4 h. Another portion of methacryloyl chloride (2.442 ml) was added to the mixture. The solution was stirred at 35°C for another 20 h. The resulting solution was washed twice with water. The extracted solution was diluted in methylene chloride and dried with sodium sulfate. The solid was collected after precipitation into hexane and the solid was dried in vacuo. Yield 52%, m.p. 155°C. $^1\text{H NMR}$ (DMSO- d_6) δ (ppm) 1.88 (s, 3H), 1.95 (m, 2H), 3.14 (s, 3H), 3.28 (s, 3H), 3.66 (t, 2H), 4.14 (t, 2H), 5.70 (s, 1H), 6.05 (s, 1H), 6.95 (d, 2H), 7.85 (d, 2H), 7.95 (d, 1H), 8.14 (d, 1H), 8.62 (s, 1H). Anal. Calcd for $\text{C}_{22}\text{H}_{24}\text{N}_4\text{O}_4\text{S}_2$: C, 64.67; H, 5.92; N, 13.71; S, 15.70. Found: C, 63.97; H, 5.83; N, 13.45; S, 15.58.

2.2.1.4. Synthesis of 2-(2-hydroxy-ethyl)-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amino-ethanol [M II]. 2-Amino-6-methylsulfonylbenzothiazole (5.7 g, 0.025 mol) was dissolved in a mixture of H_2O (62.5 g) and H_2SO_4 (62.5 g) at 60°C. The solution was cooled to -10°C and sodium nitrite (1.75 g, 0.025 mol) in H_2SO_4 (12.5 g) was added. Maintaining the solution temperature at -5°C , diazotization was continued for 75 min. *N*-phenyldiethanolamine (4.4 g, 0.025 mol) was dissolved in H_2O (112.5 g) and H_2SO_4 (12.5 g). The solution was added dropwise into the diazotized solution to facilitate the coupling reaction. The coupling reaction was continued for 30 min. The floating

solid was collected and stirred in water (600 ml) for 30 min. Then, the solid was filtered again. The given solid product was dissolved in THF and dried with sodium sulfate. It was concentrated and poured into hexane to make a precipitation. The obtained violet solid was dried in vacuo. The crude product was recrystallized from ethanol/THF (4:1 v/v). Yield 63%, m.p. 145°C. ¹H NMR (DMSO-d₆) δ (ppm) 3.21 (t, 4H), 3.40 (s, 3H), 3.62 (d, 4H), 4.95 (t, 2H), 6.99 (d, 2H), 7.84 (d, 2H), 7.96 (d, 1H), 8.14 (d, 1H), 8.62 (s, 1H). Anal. Calcd for C₁₈H₂₀N₄O₄S₂: C, 49.90; H, 4.94; N, 13.72; S, 15.70. Found: C, 50.26; H, 5.32; N, 13.30; S, 15.54.

2.2.1.5. Copolymer of 2-methyl-acrylic acid 3-methyl-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amine-propyl ester [M I] and methylmethacrylate (MMA) [MSA]. 2-Methyl-acrylic acid 3-methyl-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-phenyl]-amine-propyl ester (2 g, 0.004 mol), purified MMA (0.42 g, 0.004 mol), and AIBN (0.069 g, 0.42 mmol) were dissolved in distilled DMF (24.2 ml). The solution was poured into an ampoule and dried under vacuum-freeze-thaw technique. The solution was kept aside at 75°C for 48 h. After cooling the solution was poured into ethanol. The solid was collected and reprecipitated into ethanol repeatedly. Yield 84%, *T_g* 130.8°C. ¹H NMR (DMSO-d₆) δ (ppm) 0.90–3.5 (14H, –CH₂–C(CH₃)–, –N(CH₃)–, –(CH₂)₃– in M I; 8H, –CH₂–C(CH₃)–, –COOCH₃ in MMA), 4.02 (3H, –SO₂CH₃ in M I), 6.62–8.39 (7H in M I). Anal. Calcd for *m*(C₅H₈O₂), *n*(C₂₂H₂₄N₄O₄S₂); Found: C, 56.78; H, 6.98; N, 7.40; S, 7.40. *m/n* = 4.5:1.

2.2.2. Polymerization of 2-(2-hydroxy-ethyl)-[4-(6-methylsulfonyl-benzothiazol-2-ylazo)-yl]-amino-ethanol (M II) and naphthalene-2,6-dicarboxylic acid [MSC]

Naphthalene-2,6-dicarboxylic acid (NDA, 1.0283 g, 5 mmol) and M II (2 g, 5 mmol) were dissolved in DMF (27 ml) in the presence of triphenyl phosphine (2.745 g, 0.011 mol) at 50°C. After complete dissolution, diisopropyl azodicarboxylate (2.116 g, 0.011 mol) in DMF (3.3 ml) was added into the solution and the reaction was continued for 48 h. The resulting solution was poured into ethanol to facilitate precipitation. The crude product was redissolved in DMF and reprecipitated into ethanol. Yield 76%, *T_g* 137°C. ¹H NMR (DMSO-d₆) δ (ppm) 1.20–4.10 (8H (= 2 × 4H), –(CH₂)₂– in M II), 4.50 (3H, –SO₂CH₃ in M II), 6.40–8.62 (13H, aromatic protons in M II and NDA). Anal. Calcd for C₂₉H₂₄N₄O₆S₂: C, 59.17; H, 4.11; N, 9.52; S, 10.89. Found: C, 58.42; H, 4.81; N, 10.04; S, 10.70.

2.3. Material processing

Polymethacrylate was dissolved in tetrachloroethane/methylene chloride (5:1) with a 15% proportion in weight. Polynaphthalate was also dissolved in dimethylacetamide/

tetrahydrofuran (1:5). These solutions were filtered before spin coating with a 0.2 μm filter. The films were spun at about 1000 rpm onto ITO pre-coated glass. After deposition, the films were dried in a vacuum oven at 150°C for 72 h. The prepared films were approximately 1.2–1.5 μm thick. The thickness was measured using a surface profilometer (Tencor P10). Gold was deposited on the surface of the film fabricating a sandwich sample.

2.4. In situ measurement of electro-optic effect

We measured the linear E/O signal (*I_m/I_c*) of the polymer samples using the reflection technique [8–11]. An ac voltage was applied to each sample for observing the modulated signal (*I_m*). The linear E/O coefficient, “*r₃₃*” of the poled film can be calculated from the following equation. The *r₃₃* 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 of the polymer film, *I_m* the amplitude of the E/O modulation, *V_m* the ac voltage applied to the sample and *I_c* the intensity of incident light where phase retardation is 90° between the TE and TM modes.

The pulse poling method was employed to monitor the variation of the E/O signal. Poling, *t₁*, and probing time, *t₂*, were controlled by a programmable device to give any combination of the time period. We can either decide to investigate the poling dynamics under pulse poling conditions or observe an isothermal relaxation of the E/O signal (*I_m/I_c*).

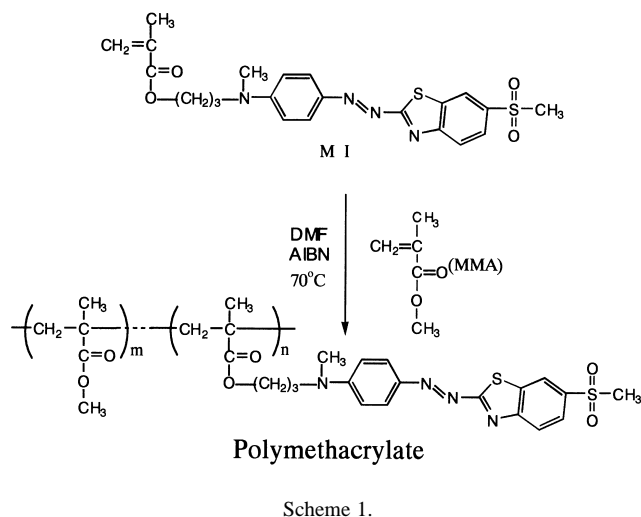
2.5. Measurement of thermally stimulated current (TSC)

For this experiment, we used the same type of the sample that was used in the E/O signal measurement. The dc current that flows between the two electrodes was measured with an electrometer (Keithley 8517A). The current was measured with increasing and decreasing sample temperature.

3. Results and discussion

3.1. Synthetic consideration

The present work describes the second-order NLO properties of active polymers with a simple structure and a chromophore for attaining high NLO activity, and the relaxation of molecular alignment after poling. The synthetic procedures for the new polymers are illustrated in Schemes 1 and 2 (synthetic procedures for polymethacrylate and polynaphthalate, respectively). The NLO active methacrylate monomer was synthesized to prepare the copolymer with methylmethacrylate. The molar composition of the copolymer was determined to be 4.5:1 (MMA/NLO monomer, M I) by virtue of elemental analysis. Polynaphthalate was prepared with naphthalene



dicarboxylic acid (NDA) and a chromophoric diol compound via the Mitsunobu reaction. At low temperature the polymers were successfully prepared without the decomposition of the chromophore.

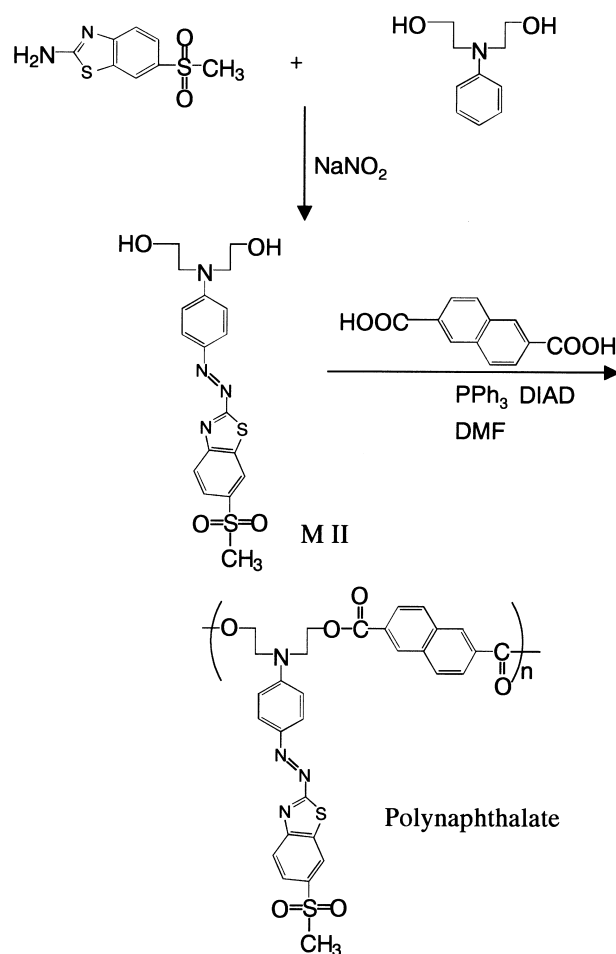
The glass transition temperatures of two polymers were obtained from DSC thermograms. The glass transition temperatures of polynaphthalate and polymethacrylate were found to be 137 and 130.8°C, respectively, which are close to each other.

3.2. Linear E/O effects of poled polymers

For measuring the E/O modulation signal during poling, a reflection technique widely used by many researchers was used [10]. Although there are some problems due to the multiple reflection between each boundary, contribution of induced piezoelectric and electrostrictive effect, and the imposition of third order NLO effect, the linear E/O coefficient was measured by the reflection method being much simpler and easier than the prism coupling methods. Recently this setup was modified for investigating the molecular dynamics during poling.

We fabricated the sandwiched samples with two polymers between ITO and gold electrode. We can switch the applied voltage between a poling dc voltage, V_p , and an ac voltage of amplitude, V_m , in a periodic manner and study the time and temperature dependence of $[I_m/I_c](t, T)$. Using the computerized switching device of applying voltage, any selection of poling (t_1) and probing (t_2) times can be adjusted ($3 s < t_1, t_2 < \infty$).

The sample was mounted on a heating plate whose temperature can be varied from room temperature up to 180°C with a precision of 0.5°C. We applied 20 V/ μm of the poling dc field to the sample for poling at room temperature. The temperature was programmed to increase at a rate of 10°C/min and to decrease at a rate of 15°C/min approximately. We set t_1 and t_2 to be identical at 5 s. For every 5 s,



we poled and integrated the E/O signal of the sample at an instant temperature.

In both polymers, we could not observe a large increment of the E/O effect at room temperature during the application of the pulse electric field. The E/O signal (I_m/I_c) increased slowly as the sample temperature was raised. In the case of polymethacrylate, the signal increased faster at around 115–120°C. Then, the signal increased continuously until the temperature reached 143°C (see Fig. 1A). The temperature (115–120°C) at which the E/O signal starts to increase coincides with the temperature at which the specific heat has a discontinuity in the DSC thermogram (onset temperature of T_g). We also measured the dc current through the sample after applying the poling voltage with the sample temperature (Fig. 2A). The tunneling dc current increased rapidly from about 120°C. Therefore, the maximum poling temperature should be selected to be around 140–145°C.

In the case of polynaphthalate, the transition temperature of the E/O signal was observed at around 123°C, i.e. 5–10°C higher than that of polymethacrylate (see Fig. 1B). This temperature is consistent with that at which the glass transition starts to appear in the DSC thermogram. We also measured the thermally stimulated dc current of the sample

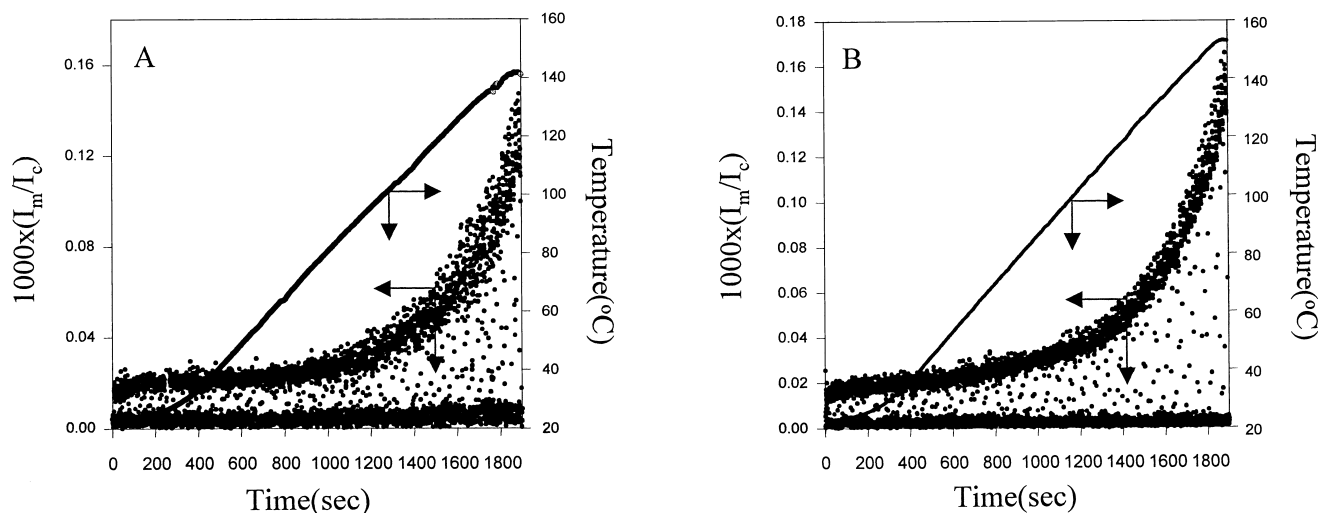


Fig. 1. Temperature dependence of the E/O signal, I_m/I_c : (A) polymethacrylate; (B) polynaphthalate.

after applying the poling voltage. The change of the measured current is quite reversible in the heating and cooling cycle (Fig. 2B). As can be seen, the tunneling current increased rapidly from about 140°C. Therefore, the maximum poling temperature can be selected to be around 145–150°C in polynaphthalate.

As shown in Fig. 1A and B, the temperature dependence of the E/O signal appeared. The E/O signal started to increase slowly from 45 to 50°C, which is far below the T_g . As the temperature increased, the E/O signal, I_m/I_c , also increased constantly. This indicates that the origin of the E/O effect can be attributable to the segmental motion in the polar molecule. The motion of polar molecule will be, of course, much enhanced in the vicinity of the T_g . However, the small segmental motion at some nodes can provide a

change of the transition dipole moments because there is a flexible bond in the side chain of this polymer. The origin of the E/O effect can be considered from the polar side group itself. Once the environmental condition gives some degree of freedom to the polar molecules, the applied field can generate the change of the dipole moment during poling. This can provide some extent of electron delocalization to induce the enhancement of dipole moment at an instant.

From the above experiments, we could optimize the poling temperature to induce the maximum E/O signal in a short poling time.

We also observed the increasing rate of the E/O signal below the T_g under the same temperature rate (see Fig. 3). The slope of the E/O signal in polynaphthalate is slightly

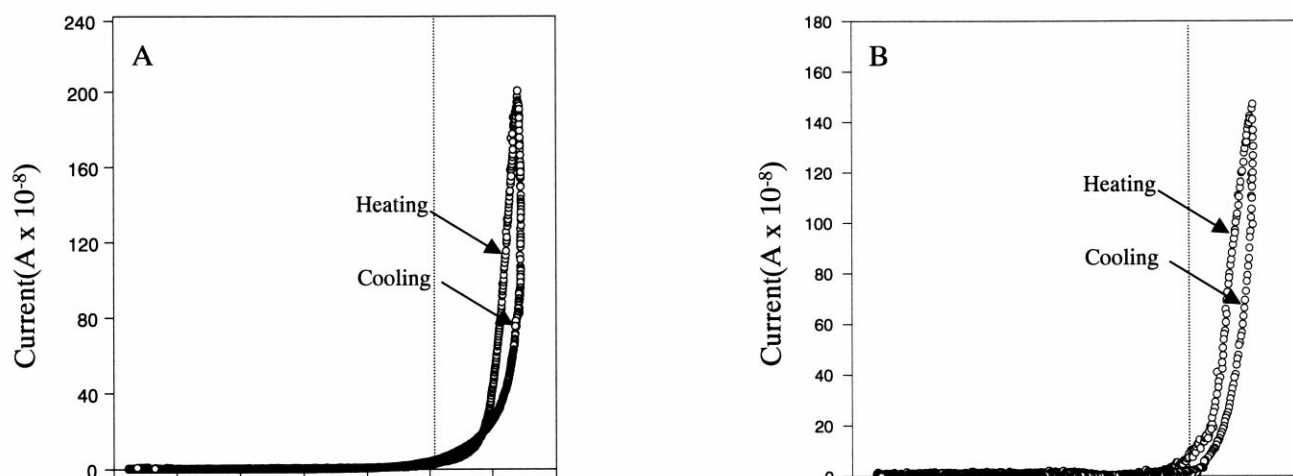


Fig. 2. Temperature dependence of the tunneling current during heating. Applied dc field, 20 V/μm: (A) polymethacrylate; (B) polynaphthalate.

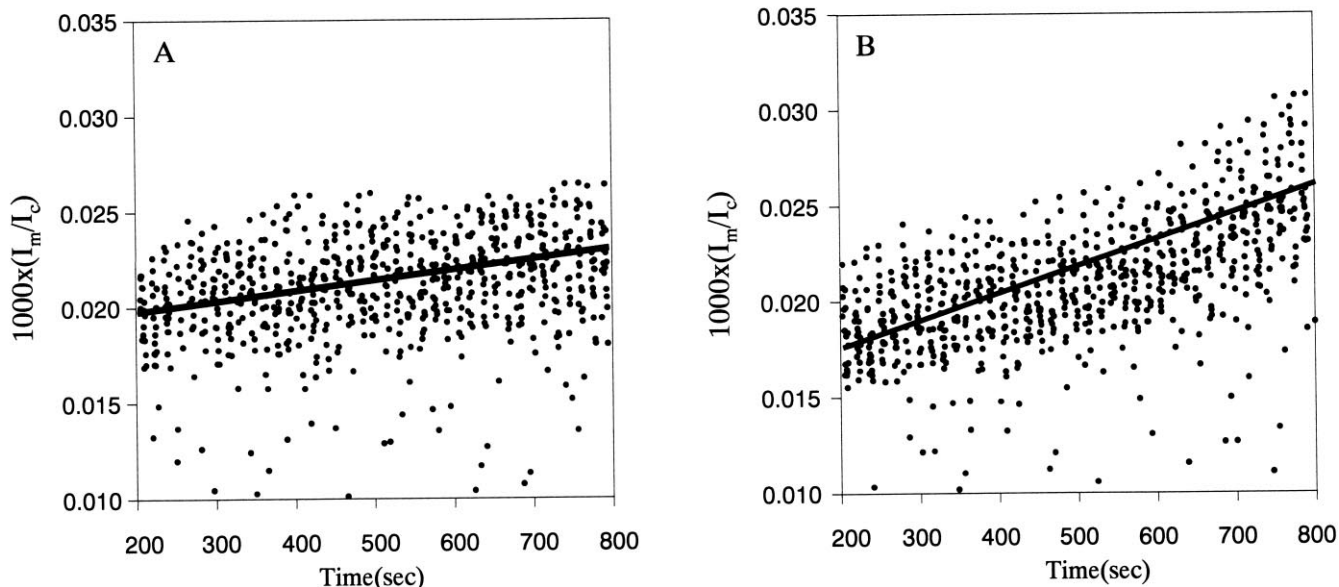


Fig. 3. Growth of the E/O signal, I_m/I_c , below the glass transition temperature: (A) polymethacrylate; (B) polynaphthalate.

larger than that in polymethacrylate, which implies the smaller effect of geometrical hindrance of the chromophores. The chromophores in polynaphthalate are much easier to move due to less hindrance in their positions.

3.3. Isothermal relaxation behavior of the E/O signal

In order to compare the temporal stability of the two polymers, we traced the decaying behaviors of the E/O signal without poling field at certain temperatures. In order to investigate and compare the relaxation behaviors of the E/O signal, we selected a reduced temperature (T_{red}). The reduced temperature (T_{red}) was calculated dividing the measuring temperature, T (K), by the glass transition temperature, T_g (K). We selected six annealing temperatures including the T_g . In order to investigate the decaying

behavior of (I_m/I_c) and prevent the relaxation of molecular alignment, we applied the poling dc electric field and raised the temperature to T_g . After the temperature reached T_g and the sample was stored for 10 min for thermal equilibrium, we decrease the temperature to the desired level and stored the sample for another 10 min. Then, the dc voltage was switched off and the ac voltage starts to be applied for recording the E/O signal. The normalized decaying data of polymethacrylate and polynaphthalate at each temperature are plotted in Figs. 4 and 5. The decaying curves were analyzed using a stretched single exponential function (Eq. (2)):

$$(I_m/I_c)_t = (I_m/I_c)_\infty + \Delta(I_m/I_c) \exp(-(t/\tau)^\beta). \quad (2)$$

Using the above equation, we could determine the relaxation time, τ , and a stretching parameter, β . Using these two parameters, we finally calculated the average

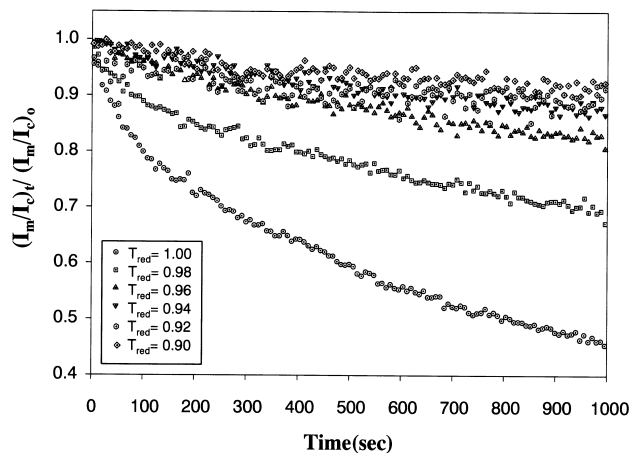


Fig. 4. Relaxation behaviors of the measured E/O signal, I_m/I_c , for six temperatures (*sample: polymethacrylate).

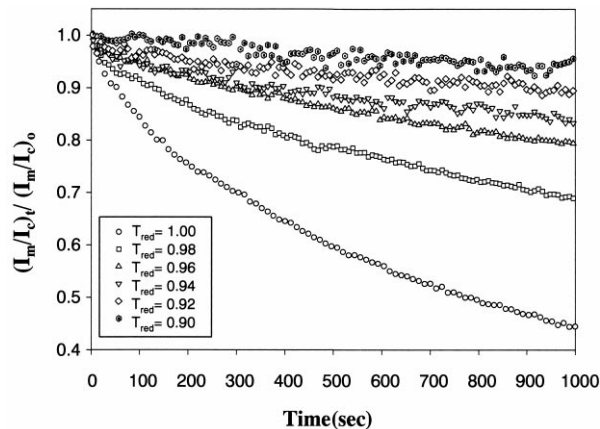


Fig. 5. Relaxation behaviors of the measured E/O signal, I_m/I_c , for six temperatures (*sample: polynaphthalate).

Table 1
Selected and calculated parameters in polymethacrylate and polynaphthalate

$T_{\text{red}} (= T/T_g)$	Polymethacrylate					Polynaphthalate				
	T (K)	$1000 \times 1/T$	$\langle \tau \rangle$	$\ln \langle \tau \rangle$	β	T (K)	$1000 \times 1/T$	$\langle \tau \rangle$	$\ln \langle \tau \rangle$	β
1.00	404	2.48	2.43×10^3	7.80	0.58	410	2.43	1.78×10^3	7.49	0.67
0.98	396	2.53	1.12×10^4	9.33	0.55	402	2.49	7.81×10^3	8.96	0.60
0.96	388	2.58	5.06×10^4	10.83	0.47	394	2.54	1.85×10^4	9.82	0.58
0.94	380	2.63	1.35×10^5	11.81	0.46	385	2.60	7.25×10^4	11.19	0.49
0.92	372	2.68	1.31×10^6	14.08	0.36	377	2.65	9.51×10^4	11.46	0.47
0.90	364	2.73	8.10×10^7	18.21	0.28	369	2.71	3.97×10^6	15.19	0.34

time constant $\langle \tau \rangle$ and β at each annealing temperature (see Table 1). The β value increased with temperature, which is consistent with the results in the literature [3,7]. As the β value is smaller, the distribution of relaxation times is broader. It will accompany the apparent Arrhenius behavior that is characteristic of a local dipolar relaxation and the relaxation of the backbone molecules was excluded in this behavior due to the large segmental motion. The increase in β with the temperature implies that the distribution of relaxation times would be narrow and the polymer approaches a highly viscous phase close to the glass transition temperature.

The relationship between the reduced temperature, T_{red} , and the average time constant, $\langle \tau \rangle$, is illustrated in Fig. 6. Since the difference of $\langle \tau \rangle$ is ambiguous between 0.94 and 1.00 of T_{red} , the expanded plot is illustrated as an insert figure. We could find that the rate of relaxation of the E/O signal in polymethacrylate is much smaller than that in polynaphthalate. Below the T_g , the poled order in polynaphthalate was randomized much faster. The NLO chromophores were tethered partly in the backbone of polynaphthalate. Therefore, it is difficult to reach a complete

equilibrium state of poling alignment. The oriented dipolar molecules were trapped in a strained conformation during poling below the T_g . The effect of residual strain on thermal backward isomerization kinetics has already been shown for the photoisomerized azobenzene chromophore in polymer solids [15]. According to the literature, it can be explained that the existence of residual strain from the equilibrium state during poling provided more degrees of freedom for rapid relaxation from the oriented dipolar alignment than the case in polymethacrylate where the NLO chromophore is attached more flexibly in the side chain.

In Table 1, the temperature dependence of the average time constant $\langle \tau \rangle$ is shown. Below the T_g , the decaying curve exhibits an Arrhenius temperature dependence. In Fig. 7, we can observe the linear relationship between $\ln \langle \tau \rangle$ and the inverse sample temperature, ($1000 \times 1/T$). The curves are well fitted to the Arrhenius relationship with activation energies of 72.89 and 48.58 kcal/mol in polymethacrylate and polynaphthalate, respectively. This indicates a better stability of the orientation of the chromophore in polymethacrylate. Briefly, the temporal stability of NLO effect in poled polymer is strongly dependent on the geometrical environment of

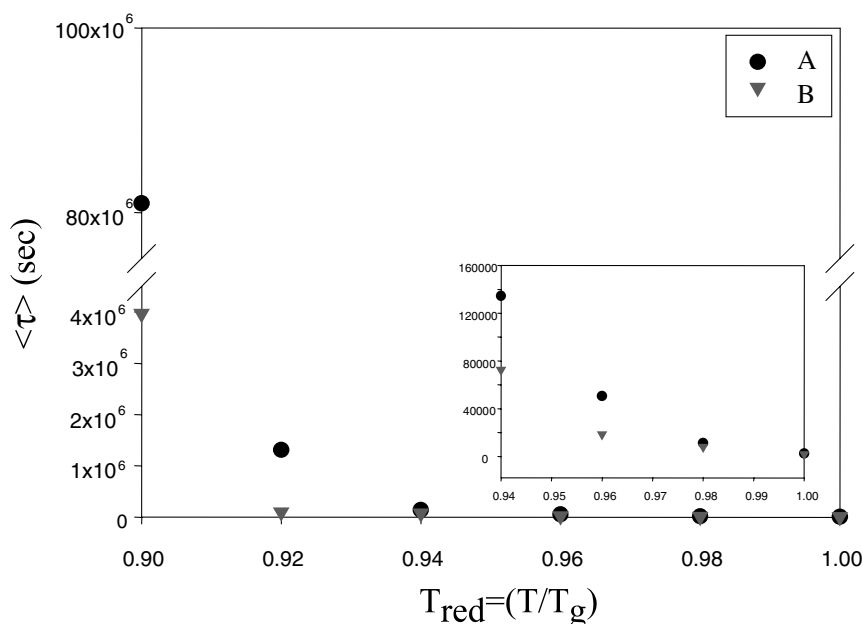


Fig. 6. Relationship between the average relaxation time constant, $\langle \tau \rangle$, and the reduced temperatures: (A) polymethacrylate; (B) polynaphthalate.

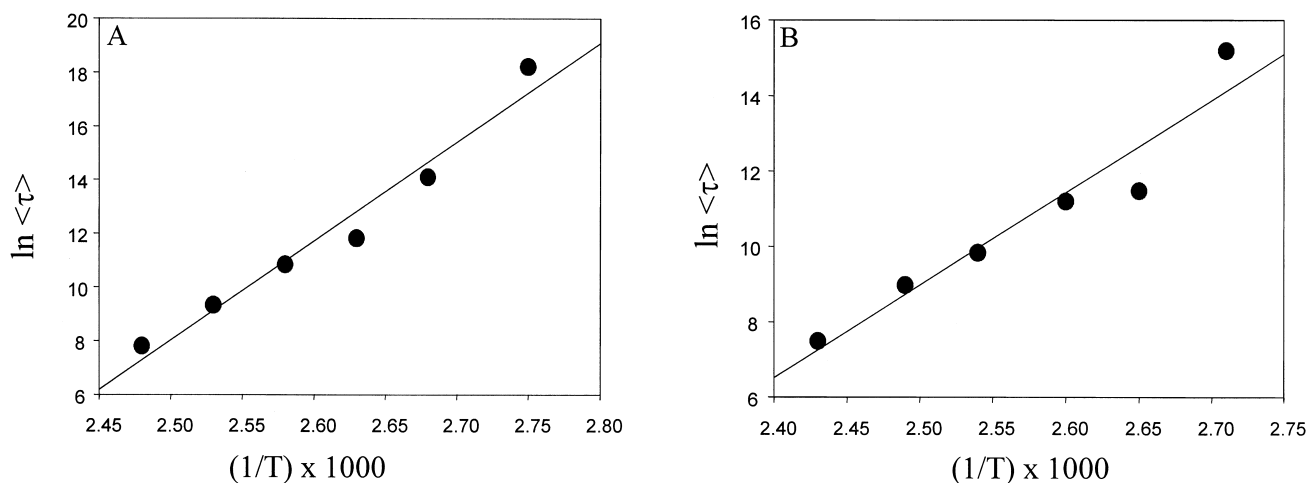


Fig. 7. Relationship between $\ln \langle \tau \rangle$ and the inverse sample temperature, $(1000 \times 1/T)$: (A) polymethacrylate; (B) polynaphthalate.

the side chain in a wide range of the temperatures below the T_g .

4. Conclusions

Polymethacrylate and polynaphthalate bearing a methylsulfonyl benzothiazolyl azo chromophore were synthesized to study the relaxation dynamics of poled E/O polymer films via a modified reflection technique. The pulse poling method led to an increase in the rate of the E/O signal during heating. The increasing rate of the E/O signal in polynaphthalate is relatively larger than that in polymethacrylate.

In the two different polymer systems, we found that isothermal relaxation of the E/O signal can be described by the KWW stretched exponential function with temperature dependent average relaxation time constant, $\langle \tau \rangle$, and the stretching parameter, β . The temperature dependence of the decay constant, $\langle \tau \rangle$, is Arrhenius-like below the T_g . We compared the activation energies of the two polymer systems. Compared to polynaphthalate, polymethacrylate has higher activation energy, E_a , so that it can show a better orientational stability of dipolar alignment in poled polymer system below the T_g .

Acknowledgements

This work was supported by grant no. (981-1109-047-2) from the Basic Research Program of the Korea Science & Engineering Foundation.

References

- [1] Dhinojwala A, Wong GK, Torkelson JM. J Opt Soc Am B 1994;11:1549.
- [2] Ghebremichael F, Kuzyk MG. J Appl Phys 1995;77:2896.
- [3] Singer KD, King LA. J Appl Phys 1991;70:3251.
- [4] White KM, Cross EM. J Appl Phys 1994;77:833.
- [5] Shuto Y, Amano M. J Appl Phys 1995;77:91.
- [6] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31.
- [7] Michelotti F, Toussare E, Levenson R, Liang J, Zyss J. Appl Phys Lett 1995;67(19):2765.
- [8] Trollsas M, Orrenius F, Sahlen F, Gedde UW, Norin T, Hult A, Hermann D, Rudquist P, Komitov L, Lagerwall ST, Jindstrom J. J Am Chem Soc 1996;118:8542.
- [9] Choi DH. Polymer 1999;40:1709.
- [10] Teng CC, Man HT. Appl Phys Lett 1990;56:30.
- [11] Dhinojwala A, Wong GK, Torkelson JM. J Chem Phys 1994; 100:6046.
- [12] Goodson III T, Wang CH. Macromolecules 1993;26:1837.
- [13] Kaatz P, Pretre P, Meier U, Stalder U, Bosshard C, Günter P, Zyset B, Stahelin M, Ahlheim M, Lehr F. Macromolecules 1996;29:1666.
- [14] Robello D. J Polym Sci A 1990;28:1.
- [15] Mita I, Horie K, Hirao K. Macromolecules 1989;22:558.