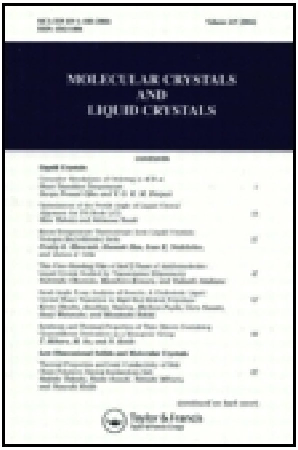

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Synthesis of Photocrosslinkable Non-Linear Optic Polyimides and Electro-Optic Properties

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Synthesis of Photocrosslinkable Non-Linear Optic Polyimides and Electro-Optic Properties

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Photocrosslinkable polyimide-type non-linear optical (NLO) polymers were obtained by multi-step reactions. Polyimide substrate polymer (P05) made from 3,3′-diamino-4,4′-dihydroxybiphenyl (HAB) and aromatic dianhydride (6FDA) had higher molecular weight than other polyimides due to the high nucleophilicity of the amine group in HAB compared to the one in 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane(Bis-AP-AF) with the electron-withdrawing group. The introduction of DR-1 chromophore into the polyimide substrate polymers depended on the steric factor between the bulky DR-1 chromophore and the substrate polyimide in the polymer reaction via the Mitsunobu reaction. In the DR-1 substituted NLO polyimides, Tg decreased with the increasing amount of DR-1 chromophore. Photocrosslinkable NLO polyimide (P05-DR-cin) was obtained by the introduction of the photoreactive cinnamoyl group into the DR-1 substituted polyimides. The electro-optic coefficient (r_{33}) of the NLO polymer was determined with an experimental set-up capable of real-time measurement by varying both the poling field and temperature. The electro-optic coefficient (r_{33}) of the linear NLO polymer (P05-DR) started to show a decrease of the r_{33}value from about 80°C. The photocrosslinked NLO polymer (P05-DR-cin), however, maintained a high r_{33} value up to 150°C due to chromophores locked in the polymer matrix with a network structure.

Keywords: photocrosslinkable nonlinear optical polymer; polyimide-type NLO polymer; electro-optic property; photocrosslinkable polyimide

INTRODUCTION

Compared to inorganic crystals, nonlinear optical NLO polymers offer such advantages as low intrinsic dielectric constant, ease of processing into thin films,

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and good compatibility with the microelectronics process[1–6]. Important properties of NLO polymers required for the photonic application include; (a) large optical nonlinearity, (b) temperature stability of oriented dipole and (c) low optical loss.

One main problem of the NLO polymer material is the thermal instability of the poling-induced alignment of chromophore, which relaxes partially even below the glass transition temperature (Tg) of NLO polymers. To realize a stable dipole alignment, chromophores were covalently attached to high Tg polymers such as polyimides[7,8,9] or the NLO polymer matrix was crosslinked[10,11] to lock in the dipole orientation after poling.

In this study, we first synthesized polyimide substrate polymers with high Tg and good solubility in a common organic solvent, and then introduced the chromophore and photosensitive groups together into the substrate polymer utilizing the polymer reaction. Detailed studies of the synthesis, characterization and nonlinear optical properties are discussed.

EXPERIMENTAL

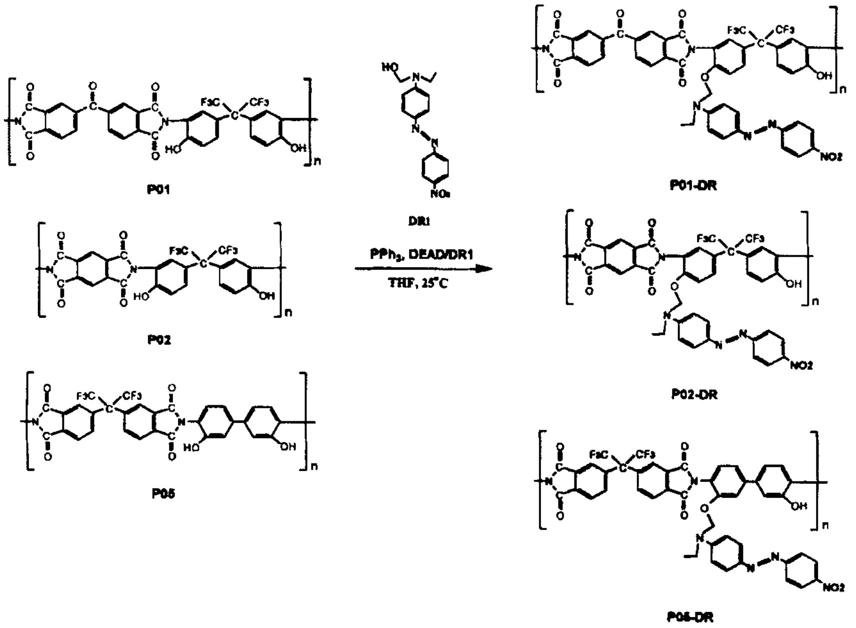
Materials

3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA), 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane(Bis-AP-AF), pyromellitic dianhydride (PMDA), 3,3′-diamino-4,4′-dihydroxybiphenyl (HAB) and 4,4′-(hexafluoro isopropylidene)diphthalic anhydride (6FDA) from Tokyo Kasei Co. were used as received without further purification. N,N-dimethyl acetamide (DMAc) and xylene were refluxed with CaH_2 and distilled under reduced pressure before use. Triphenylphosphine (PPh_3) and diethylazodicarboxylate (DEAD) used in the Mitsunobu reaction were purchased from Tokyo Kasei Co. and used as received. 2-[4-(4-nitrophenyl azo)-N-ethylphenyl amino]ethanol (Dispese Red 1, DR1) from Aldrich Chemical Co. was also used without further purification.

Synthesis of NLO polymers

Photocrosslinkable polyimide-type non-linear optical (NLO) polymers were obtained by multi-step reactions. First, polyimide substrate polymers with good solubility in a common organic solvent were prepared according to the reported process by two-step reactions[12]. Aromatic diamines with two hydroxy groups were dissolved in DMAc in a three-necked flask at 0 °C. Stoichiometric amounts of three different dianhydrides were then added to the dissolved diamines. The polymerizations were carried out in a dry nitrogen-flushed flask at room temperature with a concentration of 15% solid in DMAc. Each mixture solution was warmed to room temperature and magnetically stirred for 12h to form corresponding poly(amic acid). The poly(amic acid) was fully imidized by removing water in the azeotropic mixture of DMAc and xylene at 160 °C for 5h. The resulting solutions were then precipitated into a mixture solution of methanol/2N HCl (50:1, v/v) to give three different polyimides as shown in Scheme 1.

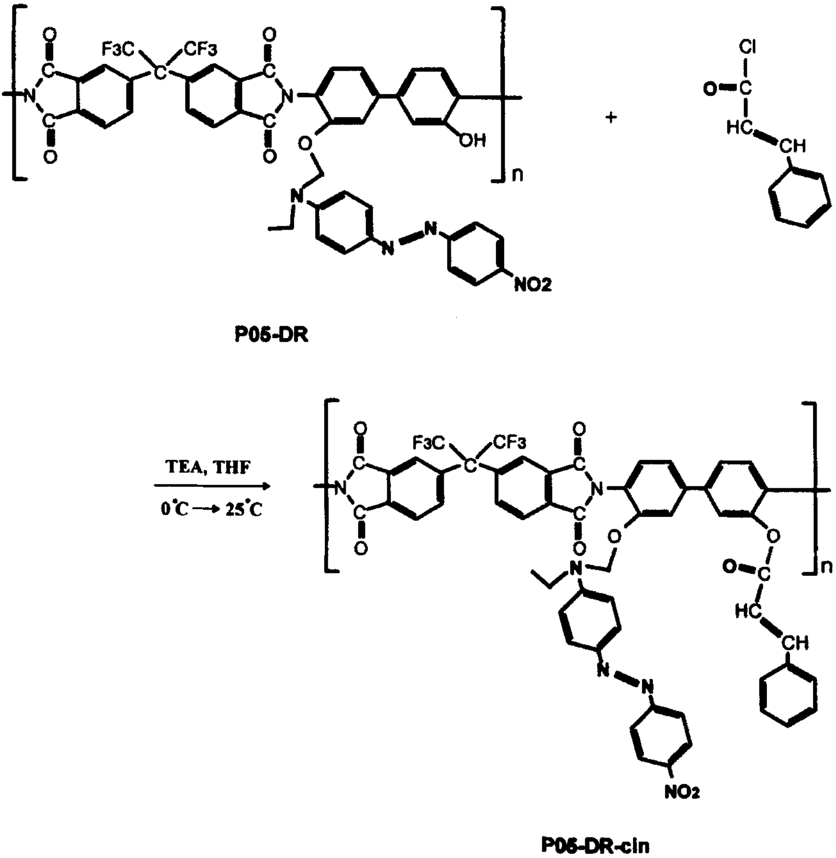
The second step was the introduction of chromophore (DR1) into the polyimides by using the Mitsunobu reaction. A polyimide substrate polymer (1 eq., repeat unit basis), Disperse Red1 (DR1) (1.5 eq.) and triphenylphosphine (PPh_3) (1.5 eq.) were dissolved in dry THF. Diethyl azodicarboxylate (DEAD) (1.5 eq.) was added dropwise into the solution. The solution was stirred at room temperature under nitrogen for 24h and then poured into methanol. The resulting NLO polyimide was washed with methanol, filtered and dried under vacuum at 80 °C for 48h.



SCHEME 1 Synthesis of NLO polyimides by the Mitsunobu reaction

The third step was the synthesis of photocrosslinkable NLO polymers by polymer reaction. A typical example is shown in Scheme 2 for the synthesis of

P05-DR-cin. P05-DR (lg, 1.60mmol) was dissolved in THF in a nitrogen-flushed flask. Triethylamine (TEA) (0.32g, 3.20mmol) was added to the solution, and was stirred for 20min. Cinnamoyl chloride (0.53g, 3.20mmol) was then added dropwise to the solution at 0°C, and stirred at room temperature for 24h. After filtering the byproduct, TEA salt, the solution was poured into methanol to give the photocrosslinkable NLO polymer, P05-DR-cin. This polymer after purification by reprecipitating in methanol was dried at 20°C under vacuum for 48h.



SCHEME 2 Synthesis of photocrosslinkable polyimide-type NLO polymer (P05-DR-cin)

Instrumental Analysis and Electro-Optic Measurement

For the identification of intermediates and NLO polymers, FT-IR (Jasco 620V), UV-Vis (Shimadzu UV-2100) and ^{1}H-NMR (Bruker AM300) spectrometric analyses were performed. The glass transition temperatures were measured with a DuPont TA2000 differential scanning calorimeter (DSC). A thermogravimetric analyzer (DuPont 951) was used to examine the thermal degradation properties of polymer samples with a heating rate of 30°C /min up to 1000°C.

The dipole alignment (poling) and measurement of electro-optic coefficient (r_{33}) were conducted with a previously reported apparatus which had the capability of measuring r_{33} under a different poling field and temperature successively, i.e. real time measurement[13]. Procedures for the poling and measurment of r_{33} are as follows. NLO polymers were dissolved in a cyclohexanone solvent at a concentration of about 10 wt% and filtered with a syringe filter. This solution was spin-coated onto ITO glass at 300 rpm for 5 sec followed by 1500 rpm for 60sec. The NLO polymer film was dried at 100°C for 24hr to remove the residual solvent. An aluminium electrode (about 1μm) was deposited on top of the NLO polymer film with a thermal evaporator. Poling was performed by applying DC voltage between the Al and ITO electrode while varying the temperature of the NLO polymer sample. The electro-optic coefficient (r_{33}) of the poled film was measured with an experimental set-up similar to that described by Teng et al.[6] at 632.8nm

RESULTS AND DISCUSSION

Charaterization and Thermal Properties of NLO polymers

Polyimide substrate polymers obtained through poly(amic acid)s exhibited good solubility in such common organic solvents as THF, DMAc, dimethylformamide and cyclohexanone. The molecular weight of the polyimide substrate polymer was obtained by GPC with THF as eluent (Table I). The molecular weight of polyimide substrate depends on both the reactivity of aromatic diamine and dianhydride monomer. When same diamine, 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane (Bis-AP-AF), was used, polyimide P2 which employed dianhydride with high electron affinity (PMDA, Ea = 1.90) exhibited higher molecular weight than polyimide P01 in which BTDA (Ea = 1.55) was used as dianhydride[14]. Polyimide P05 made from 3,3′-diamino-4,4′-dihydroxybiphenyl (HAB) and 4,4′-(hexafluoro-isopropylidene)diphthalic anhydride (6FDA) had higher molecular weight than the other two polyimides (P01 and P02). This may be explained by the high nucleophilicity of the amine group in HAB compared to the one in 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (Bis-AP-AF) which has an electron-withdrawing hexafluoropropane group.

TABLE I Chracterization of substrate and NLO polymers

Polymer	*Mw/Mn ($\times 10^4$g/mole)*	*Tg (°C)*	*Ti (°C)*	*Content of Chromophore*[a] *(mole%)*	n^b
P01	12.99/4.2	>350	549.5	–	1.418
P01-DR	–	221.1	342.2	23.54	1.472
P02	17.44/8.14	350	533.9	–	1.417
P02-DR	–	231.8	334.6	12.27	1.470
P05	21.32/9.73	>350	540.4	–	1.412
P05-DR	–	200.5	348.3	54.82	1.474
P05-DR-cin[c]	–	191	342.6	54.82	1.494
P05-DR-cin[d]	–	212.3	351.2	54.82	–

a. Determined by UV spectroscopy
b. Determined by Abbe refractometer in solution (calibrated with test piece, n=1.5162)
c. Determined before UV irradiation
d. Determined after UV irradiation

The introduction of DR-1 chromophore into the polyimide substrate polymers by the Mitsunobu reaction gave NLO polyimides (P01, P02, P05-DR). The degree of substitution was determined by UV spectroscopy using the calibration curve obtained in the previous report[13]. The content of DR-1 substituted in the NLO polymers increased in the following order: P02-DR (12.3 mole%), P01-DR (23.5 mole%), P05-DR (54.8 mole%) as shown in Table I. The high degree of substitution of DR-1 into P05-DR compared to the other two NLO polymers may be due to the steric factor between the bulky DR-1 chromophore and the substrate polyimide in the polymer reaction via the Mitsunobu reaction.

Synthesis of NLO polymers were checked by FT-IR spectrometric analysis. In Figure 1(a), the FT-IR spectrum of the polyimide substrate (P05) exhibited characteristic aromatic polyimide peaks from C=O at 1,780cm^{-1} (asymmetric), 1,720 cm^{-1} (symmetric), and 725 cm^{-1} (bending) together with the CN peak at 1,380 cm^{-1} (stretching). The absence of peaks at 1,710 cm^{-1} (COOH) 1,660 cm^{-1} (CONH), and 1,550 cm^{-1} (CONH) confirmed that poly(amic acid) was fully converted to polyimide. The introduction of DR-1 chromophore into polyimide could be seen from Figure 1(b) by the characteristic NO_2 peak at 1,514 cm^{-1} (asymmetric) and 1,336 cm^{-1} (symmetric). The synthesis of photocrosslinkable NLO polyimides was confirmed by the -C=C- peak of the cinnamoyl group at 1,636 cm^{-1} as shown in Figure 1(c). It was also noted that the broad peak at 3,200–3,650 cm^{-1} due to the hydroxy group almost disappeared after the introduction of cinnamoyl groups.

The thermal properties of the substrate and NLO polyimides were checked by DSC and thermogravimetric analysis (TGA). In Figure 2 are shown the DSC

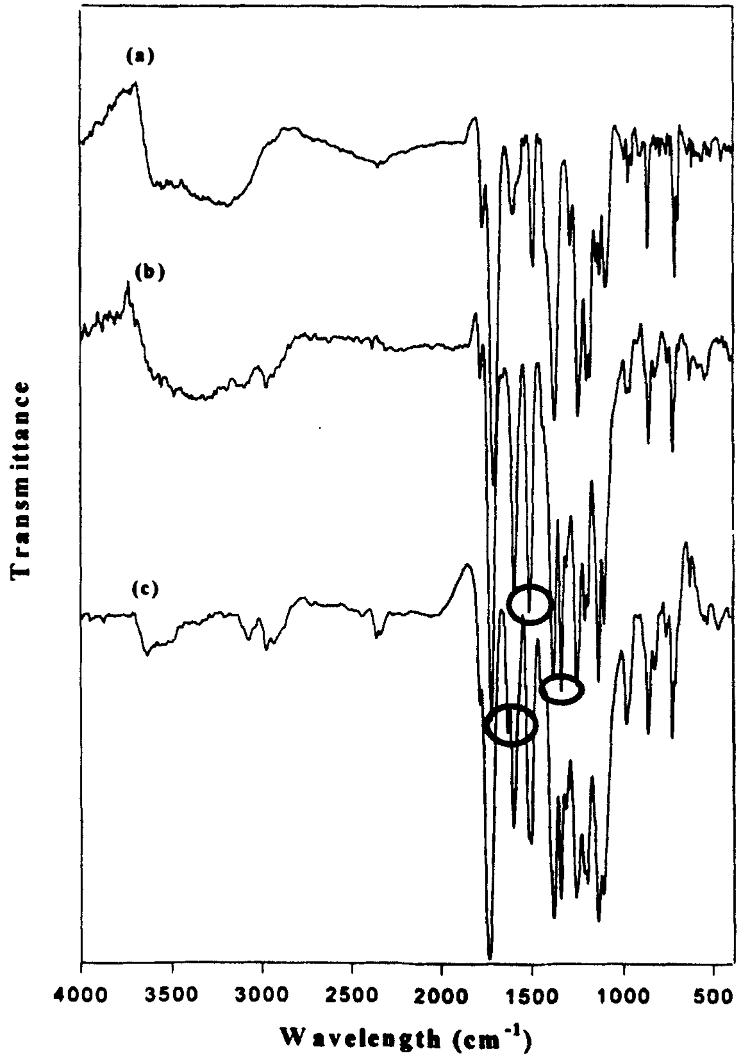


FIGURE 1 FT-IR spectra of (a) P05, (b) P05-DR, and (c) P05-DR-cin polymers

thermograms of P05-DR (a), P05-DR-cin before UV irradiation (b), and P05-DR-cin after UV irradiation (c) as a typical example. From the DSC analysis the polyimide substrates all exhibited Tg's above 350°C as shown in Table I. In the DR-1-substituted NLO polyimides, Tg decreased with the increasing amount of DR-1 chromophore in the following order: P02-DR (231.8°C), P01-DR (221.1°C), and P05-DR (178.5°C). TGA thermograms of P05, P05-DR and P05-DR-cin samples are shown in Figure 3. The loss of weight was high in the order P05 < P05-DR < P05-DR < P05-DR-cin with the increasing temperature after the initial thermal decomposition. It was noted, however, that photo-crosslinkable NLO polymer (P05-DR-cin) exhibited about the same initial thermal decomposition temperature as P05-DR and the P05 substrate polymer. The introduction of DR-1 chromophore also increased the refractive index value from about 1.42 to 1.49 as shown in Table I.

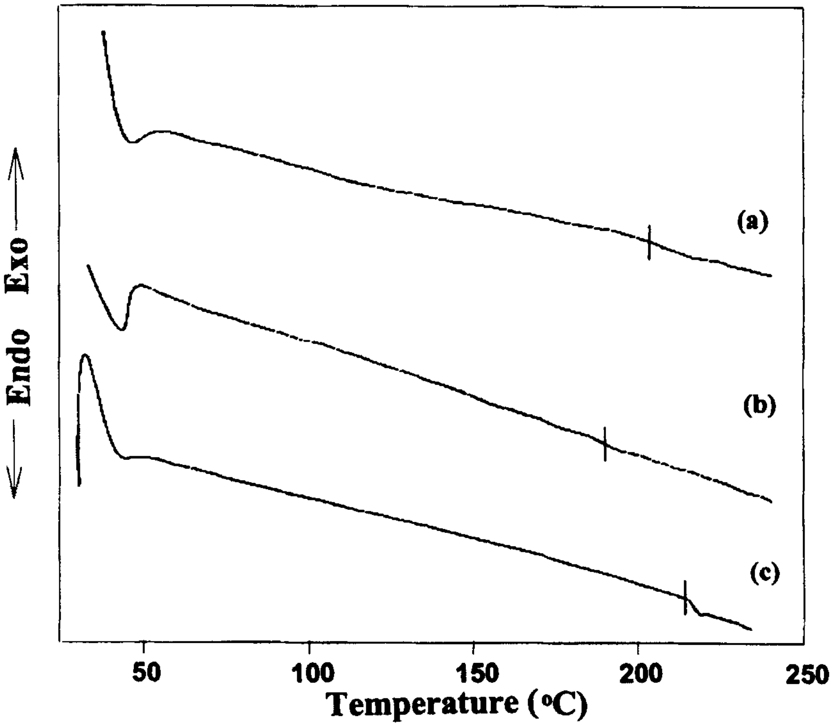


FIGURE 2 DSC thermograms of (a) P05-DR, (b) P05-DR-cin (before UV irradiation), and (c)P05-DR-cin (after UV irradiation)

Dipole Alignment and Electro-optic Properties

In order to exhibit electro-optic properties, the chromophores in the NLO polymer must be oriented in a non-centerosymmetric geometry. Such orientation can be achieved by the electric poling of chromophores at a temperature close to the

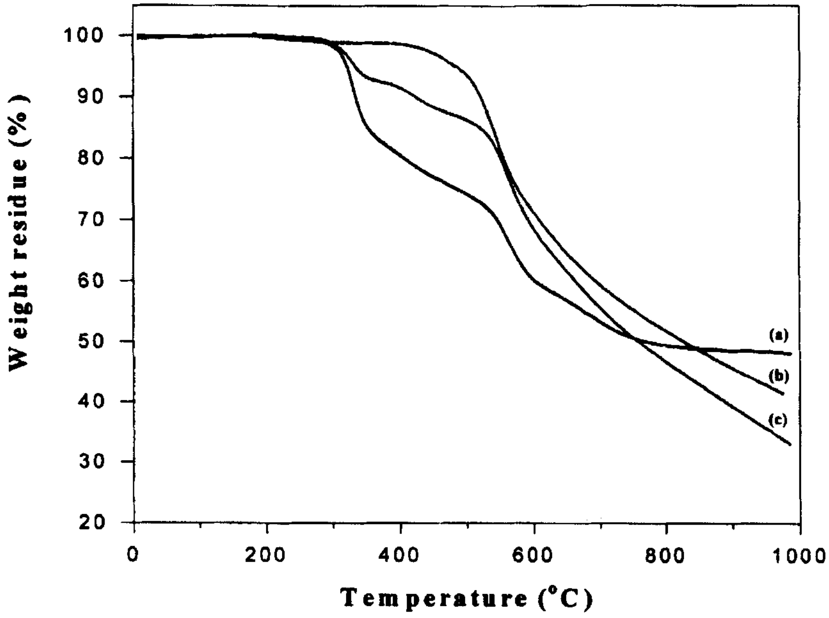


FIGURE 3 TGA thermograms of (a) P05-DR-cin, (b) P05, and (c) P05-DR

glass transition temperature of the NLO polymer. The effect of poling on the orientation of chromophore was checked by UV spectrometry[15]. NLO polymer P05-DR exhibited a shifted absorption maximum (b) at 473nm from the unpoled P05-DR (a) at 481nm after poling with the accompanying reduction of absorption peak. This is known to be due to the birefringence occurring in the poled NLO polymer film with oriented chromophores. It was also noted in Figure 4 that the absorptions at 293nm due to phenylene groups in the polyimide substrate are not changed. These changes of UV absorption suggest that the relatively stiff polyimide chain was not affected, but the flexible chromophores were moved by the poling field. The dipole alignment and the electro-optic coefficient (r_{33}) measurement were conducted with an experimental set-up reported previously[13] with the capability of measuring r_{33} while increasing the temperature and poling field successively.

In Figure 5 are shown the r_{33} vs. poling-field plots for P01-DR and P05-DR NLO polymers. Here the poling field was applied to the electrodes for 5 min at 150 °C and a modulating signal was applied for 5 sec to the NLO polymer film. The electro-optic effect reached the saturation state within 5min and the modulated optical power could be detected within 5sec. The thickness of the NLO polymer film was measured with a surface profiler. The r_{33} value increased with the poling field up to 140MV/m above which electrical breakage occurred. The NLO polymer, P05-DR exhibited higher r_{33} values than P01-DR due to the increased substitution of the DR1 chromophores.

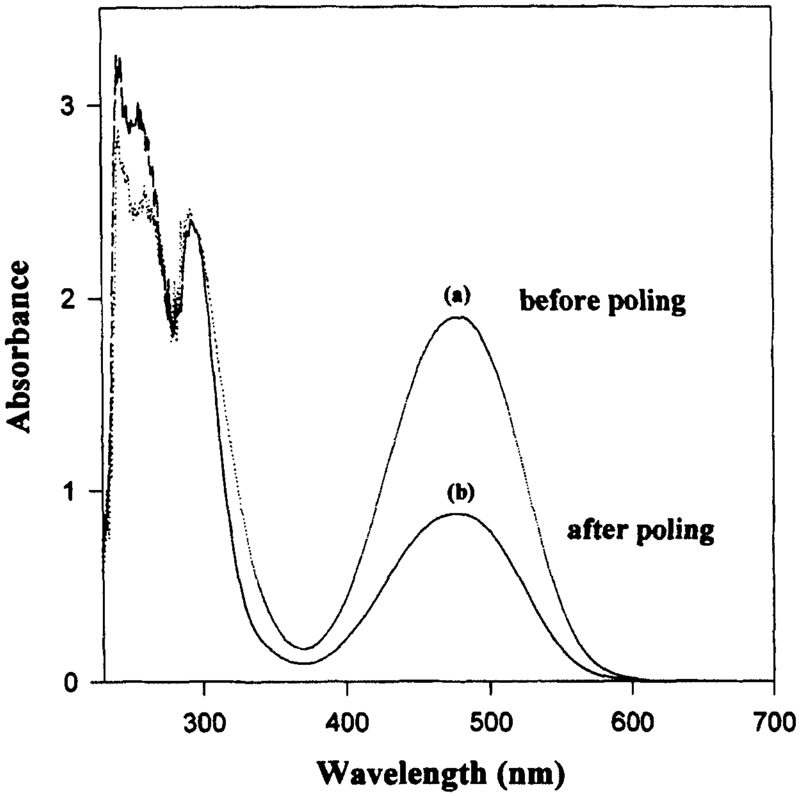
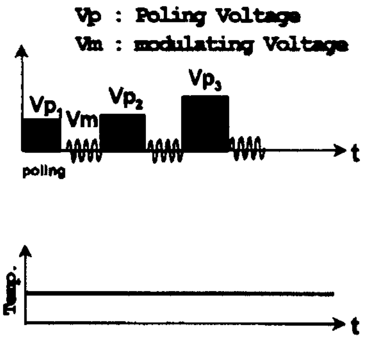


FIGURE 4 UV-visible spectra of the P05-DR before and after poling

In Figure 6 are shown the r_{33} of P05-DR measured with the increasing temperature at the rate of 10°C /3min under the constant poling field of 70MV/m. The r_{33} value started to increase rapidly at about 180°C and reached a maximum r_{33} value of 67pm/V at about 210°C and then decreased. From this result, we could know that poling could be effectively performed at a temperature just below Tg (Table I). The decrease of r_{33} at a temperature higher than Tg may be due to rapid segmental motions of both chromophores and the substrate polymer chain.



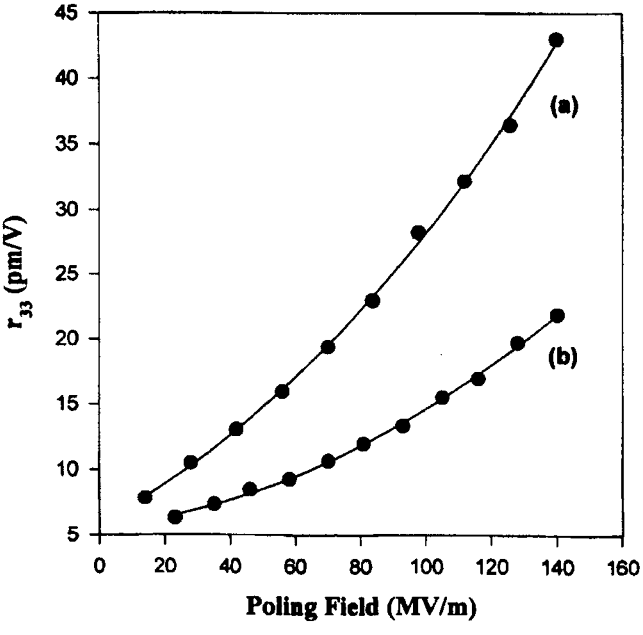


FIGURE 5 Change of r_{33} in (a) P05-DR and (b) P01-DR with poling electric field (150°C)

The photosensitivity of P05-DR-cin sample was checked by UV spectrometry in THF solution. As shown in Figure 7 the peak at 280 nm due to -C=C- bond of cinnamoyl group decreased continuously upon UV (high pressure Hg lamp) irradiation through the photodimerization reaction. The effect of crosslinking of

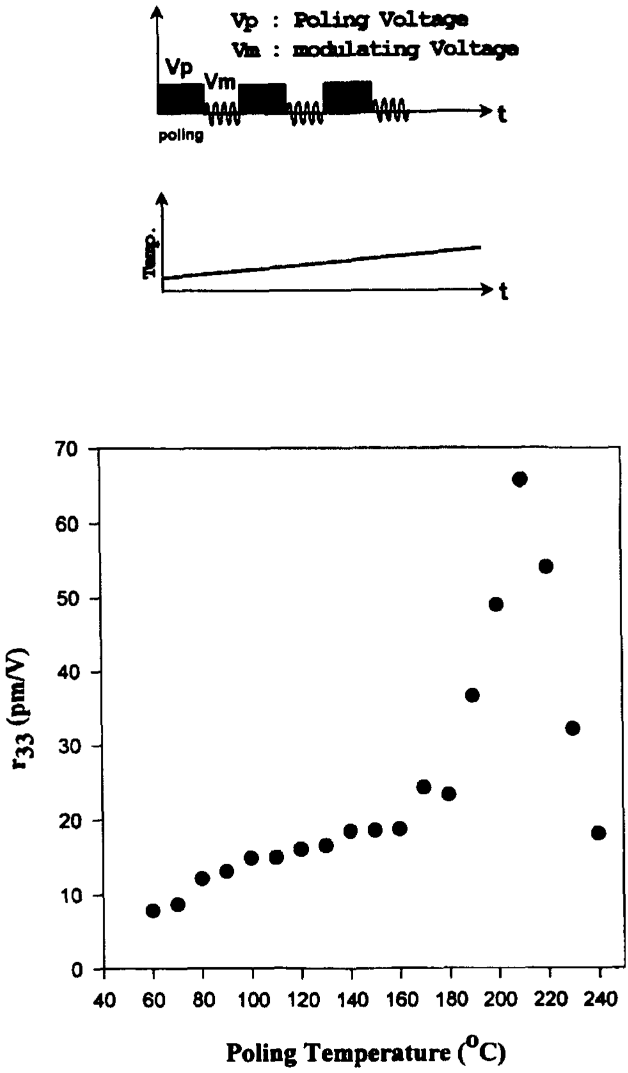


FIGURE 6 Change of r_{33} in P05-DR with poling temperature under constant poling field (70MV/m)

NLO polymers after poling on the change of r_{33} with temperature is shown in Figure 8. The NLO polymer films (P05-DR and P05-DR-cin) were heated to 150°C, and poling was conducted at 70MV/m for 10min. and then the films were cooled to 25°C. The P05-DR-cin film was irradiated with UV at 9mW/cm^2 for

1min to crosslink the polymer chains with the cinnamoyl groups. The r_{33} values of both P05-DR and UV-irradiated P05-DR-cin films were measured with the increasing temperature at a rate of 10°C /3min. The electro-optic coefficients (r_{33}) of both linear NLO polymer (P05-DR) and P05-DR-cin before UV irradiation started to decrease the r_{33} value from about 80°C. The photocrosslinked NLO polymer (P05-DR-cin), however, maintained a high r_{33} value up to 150°C due to chromophores locked in the network structure.

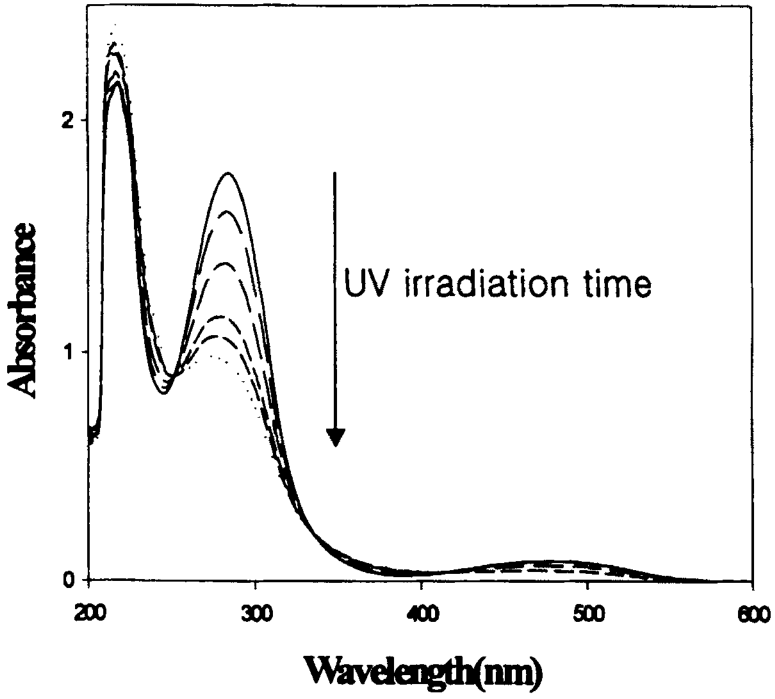


FIGURE 7 Change of the ultraviolet spectrum of P05-DR-cin in THF upon UV irradiation

SUMMARY

Photocrosslinkable NLO polyimides could be synthesized by polymer reaction utilizing the Mitsunobu reaction. The degree of substitution of DR-1 chromophore into the polyimide substrate was strongly dependent on the steric factor during the polymer reaction. In the DR-1 substituted NLO polyimides, Tg decreased with the increasing amount of DR- chromophore in the following

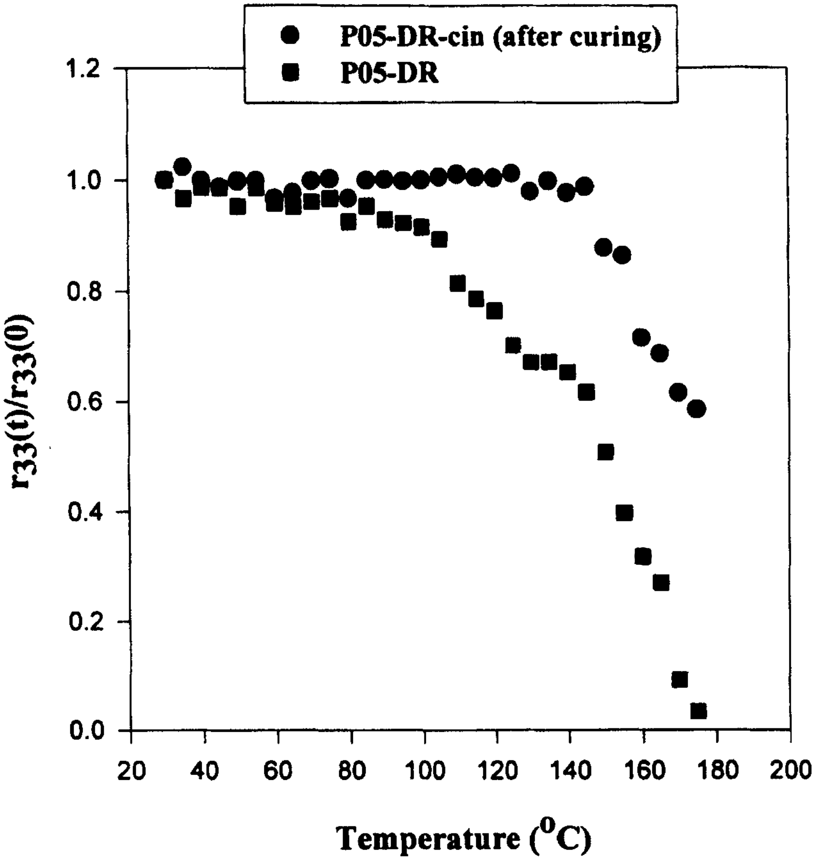


FIGURE 8 Relaxation of r_{33} in poled P05-DR and P05-DR-cin film with temperature

order: P02-DR (231.8°C), P01-DR (221.1°C), and P05-DR (178.5°C). The NLO polymer, P05-DR exhibited higher r_{33} values than P01-DR due to the increased substitution of the DR1 chromophores. The r_{33} values of both P05-DR and UV-irradiated P05-DR-cin films were measured with the increasing temperature at a rate of 10°C /3min. The electro-optic coefficient (r_{33}) of linear NLO polymer (P05-DR) started to decrease from about 80°C. The photocrosslinked NLO polymer (P05-DR-cin), however, maintained a high r_{33} value up to 150°C due to chromophores locked in the polymer matrix with a network structure.

Acknowledgements

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