ELSEVIER

Polymer 41 (2000) 5237–5245

polymer

Synthesis and characterization of a novel polyimide-based second-order nonlinear optical material

T.-D. Kim[a], K.-S. Lee[a,*], G.U. Lee[b], O.-K. Kim[b]

[a]*Department of Macromolecular Science, Hannam University, Taejon 306-791, South Korea*
[b]*Chemistry Division, Naval Research Laboratory, Washington, DC, USA*

Received 23 March 1999; received in revised form 27 August 1999; accepted 22 September 1999

Abstract

A processable polyimide having azo-chromophore functionalized with cyanosulfonyl group (PI-SOT) was prepared for nonlinear optics applications. To introduce a highly nonlinear optical active chromophore on the polyimide matrix, we first synthesized monomers 4-[*N*,*N*-bis(hydroxyethyl)amino]-4′-(2,5-dioxolane)azobenzene (AZO-OH2) and 4,4′-(hexafluoroisopropylidene)diphthalimide (6F-DI). After the polymerization reaction between AZO-OH2 and 6F-DI by using the Mitsunobu reaction, the dioxolane group of the resulting polymer PI-PRO was deprotected from the polymer PI-DEP having aldehyde group, and this polymer was further reacted with methanesulfonylacetonitrile to produce the final polymer PI-SOT. The molecular weight of PI-SOT was determined to be $M_n = 5650$ ($M_w/M_n = 1.4$). From DSC and TGA thermograms a glass transition temperature of ca. 186°C and an initial decomposition temperature of ca. 201°C were observed. PI-SOT dissolved in cyclohexanone could be easily processed into high optical quality films. The optical nonlinearity was determined to be $d_{31} = 50\ \text{pm V}^{-1}$ and $d_{33} \cong 150\ \text{pm V}^{-1}$ (nonresonant $d_{33}(\infty)$ value: $47\ \text{pm V}^{-1}$) by the second harmonic generation method in in-situ condition at a fundamental wavelength of 1064 nm and its value showed good thermal stability up to 150°C. By using the simple reflection measurement technique, a large electro-optic coefficient of $r_{33} = 28\ \text{pm V}^{-1}$ at 633 nm wavelength was obtained. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyimide; Second-order nonlinearity; Mitsunobu reaction

1. Introduction

Nonlinear optics are expected to play a major role in the fields of optical information processing, optical sensing, and telecommunications [1]. Nonlinear optical (NLO) materials include inorganic and organic crystals, polymers, organic–inorganic hybrids, and Langmuir–Blodgett compounds. Of these, polymers are considered the most promising materials because of their ease of processability, excellent thermal stability, environmental resistance, good mechanical strength and flexibility in molecular designs [2–5]. Because of these advantages, some polymers have been extensively investigated for photonic devices such as optical switches, optical fibers for use in communications, and frequency modulators [6–9].

For the practical application of second-order NLO polymeric materials, high NLO activities plus its temporal and thermal stability are particularly required. Electric poling, a common technique for achieving noncentrosymmetric chromophore-ordering in NLO polymers, is thermodynamically unstable, especially at higher temperatures [10–14]. Various approaches, including a cross-linking method and the use of high glass transition temperature (T_g) polymers, have been used to prevent the relaxation of chromophores caused by the thermal motion of polymer chains [15–22]. In particular, the use of polyimides has been considered to be one of the best NLO matrix methods for stabilizing poled chromophores [23–30].

Polyimides are commonly synthesized by the reaction of dianhydrides with diamines to provide poly(amic acid) precursor polymers, followed by a high-temperature imidization process to produce the desired polyimides. However, this two-step reaction method makes it difficult to obtain the quantitative transformation from amic acid form to imide ring, and limits the choice of NLO chromophores because of the high temperature reaction required.

We report here on a new synthetic method for making NLO-active polyimides by a one-step reaction of diol with diimide. This reaction is known as the Mitsunobu reaction, and it does not need the imidization process at high temperatures. We also discuss the physicochemical properties,

---

* Corresponding author. Tel.: +82-42-629-7394; fax: +82-42-626-8841.
E-mail address: kslee@eve.hannam.ac.kr (K.-S. Lee).

PII: S0032-3861(99)00723-5

including details of the optical second-order nonlinearity and the thermal stability of the aligned dipoles in this polyimide system.

2. Experimental

2.1. Reagents

Tetrahydrofuran (THF) (Junsei) was purified by refluxing, distilling from calcium hydride, and drying on 4 Å molecular sieves. 4-Nitrotoluene (Lancaster) and *N*-phenyldiethanolamine (Aldrich) were purified by recrystallization in ethanol/water. 4-Aminobenzaldehyde was synthesized according to the procedure in Ref. [31]. All other solvents and reagents, of analytical-grade quality, were commercial products and used as received.

2.2. Monomer synthesis

2.2.1. 4-[N,N-bis(hydroxyethyl)amino]-4′-formylazobenzene

To a solution of 6.0 g (0.05 mol) of 4-aminobenzaldehyde in 100 ml of water was added 12.5 ml (0.15 mol) of concentrated HCl. The solution was mechanically stirred for 30 min and cooled to 0°C in an ice bath. A solution of 3.5 g (0.05 mol) of sodium nitrite in 10 ml water was then added drop-wise to the resulting solution and stirred for another 30 min to yield a clear orange solution. The temperature was maintained between 0 and 5°C, 9.0 g (0.05 mol) of *N*,*N*-bis(2-hydroxyethyl)aminobenzene was added with vigorous stirring, and the color changed to dark red. This solution was stirred for 24 h, and the temperature was slowly raised to ambient. It was poured into a saturated aqueous sodium carbonate solution and a reddish brown solid resulted. The product was separated by filtration, washed several times with water, and dried under vacuum at 60°C for 6 h. Yield: 8.77 g (56.40%); m.p. 153°C. ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.03 (s, 2H, OH), 3.74 (t, $J = 5$ Hz, 4H, NCH_2CH_2OH) 3.96 (t, $J = 5$ Hz, 4H, NCH_2CH_2OH), 6.78 (d, $J = 9$ Hz, 2H, Ar-CH), 7.74 (d, $J = 9$ Hz, 2H, Ar-CH), 7.98(m, 4H, Ar-CH), 10.06 (s, 1H, CHO). FT–IR (KBr pellet, cm^{-1}): 3600–3100 (OH), 3300–3200 (Ar-CH), 1725 (CHO), 1600 (C=C), 1375–1300 (C–N), 1200–1100 (C–O).

2.2.2. 4-[N,N-bis(hydroxyethyl)amino]-4′-(2,5-dioxolane)azobenzene

Ethylene glycol (15.0 g of 0.2 mol) and 0.2 g (0.8 mmol) of *p*-toluenesulfonic acid monohydrate were added to a solution of 5.0 g (15.9 mmol) 4-[*N*,*N*-bis(hydroxyethyl)amino]-4′-formylazobenzene (AZO-OH1) in 500 ml of benzene. The mixture was stirred for 24 h at 120°C. After cooling the solution to room temperature, it was poured with vigorous stirring into a 250 ml solution of 10% aqueous potassium carbonate in 250 ml of saturated aqueous sodium chloride. The organic layer was dried with anhydrous sodium sulfate and filtered. Removing the solvent by rotary evaporation at 25–35°C produced a bright red color solid. This crude product was recrystallized from an isopropyl alcohol/hexane mixture. Yield: 3.2 g (55%); m.p. 180°C. ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.17 (s, 2H, OH), 3.72 (t, $J = 5$ Hz, 4H, NCH_2CH_2OH), 3.94 (t, $J = 5$ Hz, 4H, NCH_2CH_2OH), 4.12 (s, 4H, OCH_2CH_2O), 5.87 (s, 1H, *t*-CH), 6.78 (d, $J = 9$ Hz, 2H, Ar-CH), 7.58 (d, $J = 9$ Hz, 2H, Ar-CH), 7.87 (m, 4H, Ar-CH). FT–IR (KBr pellet, cm^{-1}): 3600–3100 (OH), 3300–3200 (Ar-CH), 1600 (C=C), 1375–1300 (C–N), 1200–1100 (C–O).

2.2.3. 4,4′-(Hexafluoroisopropylidene)diphthalimide

Urea (1.0 g of 17.2 mmol) was added to 5.0 g (11.2 mmol) of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride in a 250 ml two-neck round-bottom flask. The mixture was reacted at 200°C for 2 h and then cooled to room temperature. The resulting solid was crushed into a fine powder and further reacted at 200°C for 1 h. The crude product was washed with water, dried in a vacuum oven, and the product recrystallized from ethanol. Yield: 4.7 g (95%); m.p. 360°C. ^{1}H NMR (DMSO-d_6): δ(ppm) = 7.63 (s, 2H, Ar-CH), 7.81 (d, $J = 8$ Hz, 2H, Ar-CH), 7.98 (d, $J = 8$ Hz, 2H, Ar-CH), 11.62 (s, 2H, NH). FT–IR (KBr pellet, cm^{-1}): 3400–3200 (NH), 1790 and 1750 (C=O), 1450 (C–N), 1400–1100 (C–F).

2.3. Polymer synthesis

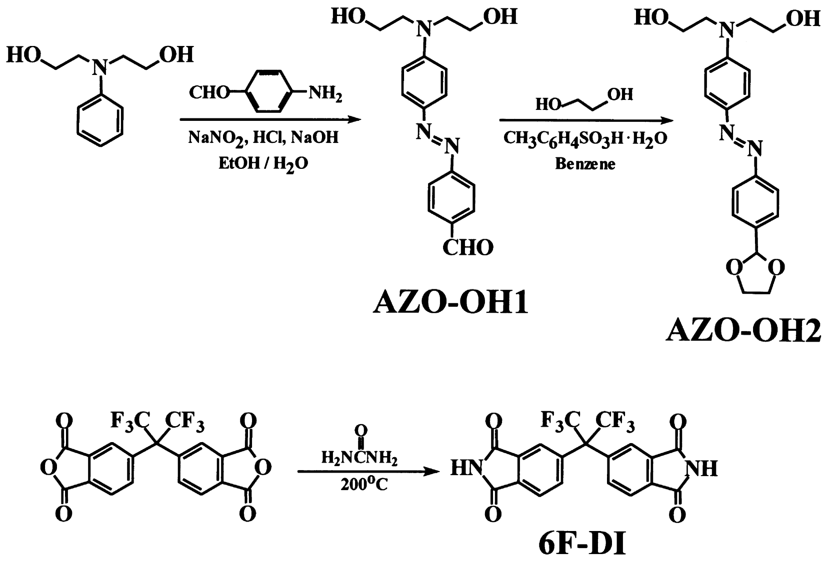
2.3.1. Polymer PI-PRO

4,4′-(Hexafluoroisopropylidene)diphthalimide (6F-DI) (3.0 g of 6.75 mmol), 2.5 g (6.75 mmol) of 4-[*N*,*N*-bis(hydroxyethyl)amino]-4′-(2,5-dioxolane)azobenzene (AZO-OH2), and 5.3 g (20.30 mmol) of triphenylphosphine were added to 50 ml of anhydrous THF in a 100 ml three-neck round bottom flask connected to a condenser. The reaction mixture was purged with nitrogen gas and dissolved by mixing. 3.5 g (20.30 mmol) of diethyl azodicarboxylate (DEAD) in 5 ml of anhydrous THF was added drop-wise to this reaction mixture. The solution was stirred for 2 days at room temperature and then crystallized in an excess amount of methanol (500 ml). The polymer of orange-colored solid was collected by filtration and then washed in a Soxhlet extractor with methanol for 3 days. Yield: 3.2 g (60%). ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.73–3.89 (br, 8H, NCH_2CH_2N), 3.93–4.09 (br, 4H, OCH_2CH_2O), 5.82 (s, 1H, *t*-CH), 6.78–6.89 (br, 2H, Ar-CH), 7.61–7.89 (br, 12H, Ar-CH). FT–IR (KBr pellet, cm^{-1}): 3300–3200 (Ar-CH), 1785 and 1730 (C=O), 1600 (C=C), 1400–1200 (C–F), 1375–1300 (C–N), 1200–1100 (C–O). UV–vis (THF): $\lambda_{max} = 409$ nm.

Anal. calcd for $C_{38}H_{27}N_5O_6F_6$ (763.65): C, 59.81%; H, 3.61%; N, 9.19%. Found: C, 59.79%; H, 3.45%; N, 9.16%

2.3.2. Polymer PI-DEP

10 ml of 10% aqueous sodium hydroxide and 30 ml of



Scheme 1.

distilled water were added to a solution containing 2.0 g (2.6 mmol) of PI-PRO and 20 ml of THF. The mixture was acidified drop-wise with concentrated hydrochloric acid to bright red end point. The solution was precipitated in cold water, collected and washed several times with water. After drying, a bright red polymer was obtained. Yield: 1.6 g (85%) yield. ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.73–3.93 (br, 8H, NCH_2CH_2N), 6.82–6.96 (br, 2H, Ar-CH), 7.55–8.08 (br, 12H, Ar-CH), 10.04 (s, 1H, CHO). FT–IR (KBr pellet, cm^{-1}): 3300–3200 (Ar-CH), 1785 and 1730 (C=O), 1720 (CHO), 1600 (C=C), 1400–1200 (C–F), 1375–1300 (C–N), 1200–1100 (C–O). UV–Vis (THF): $\lambda_{max} = 442$ nm.

Anal. calcd for $C_{36}H_{23}N_5O_5F_6$ (719.59): C, 60.10%; H, 3.19%; N, 9.72%. Found: C, 59.89%; H, 3.05%; N, 9.91%.

2.3.3. Polymer PI-SOT

A mixture of 2.0 g (2.7 mmol) of PI-DEP, 0.5 g (4.2 mmol) of methansulfonylacetonitrile, and 0.3 g (4.2 mmol) of ammonium acetate was added to a 250 ml three-neck round-bottom flask connected to a condenser. This mixture was purged with nitrogen for 30 min to remove atmospheric moisture. 50 ml of distilled ethanol was added, and the reaction mixture was refluxed at 80°C for 20 h. The deep red precipitate was separated by filtration and stirred in hot methanol to remove impurities. Yield: 1.2 g (55%). ^{1}H NMR ($CDCl_3$): δ(ppm) = 3.21 (s, 3H, SO_2CH_3), 3.69–3.95 (br, 8H, NCH_2CH_2N), 6.84–6.93 (br, 2H, Ar-CH), 7.58–8.04 (br, 12H, Ar-CH and 1H, CH=C), 9.91 (s, 1H, CHO). FT–IR (KBr pellet, cm^{-1}): 3300–3200 (Ar-CH), 2250 (C≡N), 1785 and 1730 (C=O), 1720 (CHO), 1600 (C=C), 1400–1200 (C–F), 1375–1300 (C–N), 1200–1100 (C–O). UV–Vis (THF): $\lambda_{max} = 421$ nm; UV–Vis (film): $\lambda_{max} = 415$ nm.

Anal. calcd for $C_{39}H_{26}N_6O_6F_6S_1$ (820.74): C, 57.02%; H, 3.16%; N, 10.20%; S, 3.90%. Found: C, 57.36%; H, 3.42%; N, 9.96%, S, 3.17%.

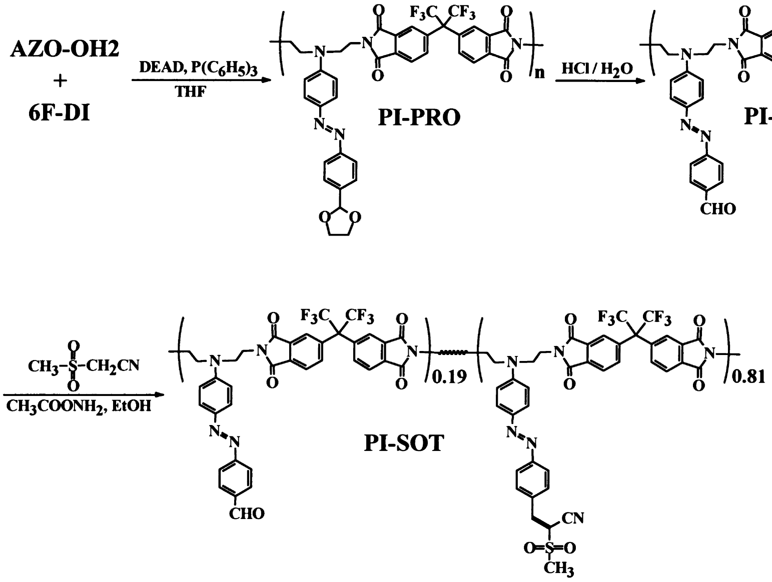
2.4. Polymer films preparation and poling

Thin polymer films were prepared by spin coating a 15 wt.% polymer solution dissolved in cyclohexanone. The solution was filtered through a 0.45μm Teflon membrane filter to remove insoluble particles. It was then coated at 1000–1100 rpm for 30–50 s, depending on the desired thickness, onto an ITO glass plate and dried in a vacuum oven at 30°C for 24 h.

Poling experiments were performed using the positive polarity of a 25 μm thick tungsten corona wire. The distance between the discharging wire and the substrate was 1.0 cm. The temperature was gradually increased at a rate of 10°C min^{-1} from room temperature to near-glass transition temperature. The sample was poled under 5 kV poling voltage at near glass transition temperature for 10 min. It was then cooled to room temperature in the presence of the electric field and the poling field removed.

2.5. Measurements

The ^{1}H NMR spectral data were obtained on a Brucker AM 300 (300 MHz) spectrometer. The FT–IR spectra were recorded on a Bio-Rad FTS-20/80 spectrometer and UV–Vis absorption spectra were measured using a Shimadzu UV-240 spectrophotometer. The average molecular weights of polymer PI-SOT were estimated by gel permeation chromatography (GPC) (column: styragel HT6E6E3, solvent: THF). DSC and TGA were performed under nitrogen atmosphere at a heating rate of 10°C min^{-1} on a Dupont 2100 analyzer. The melting points of the monomers were measured by Fisher–Johns melting apparatus. The



Scheme 2.

refractive index and thickness of the PI-SOT were determined by a prism coupler (Metricon PC-2000).

AFM measurements were made under ambient conditions using an optical lever microscope in noncontact mode (Nanoscope IIIA, Digital Instruments, Santa Barbara, CA, USA). Micromachined silicon cantilevers (Nanosensors, Germany) were used with 30–55 N m^{-1} nominal force constant and 300–360 kHz resonance frequency. In noncontact imaging, the cantilever is excited at a frequency just off resonance and the displacement amplitude of the cantilever is controlled at an operator-determined set-point. The nature of the tip–surface interaction in the noncontact mode is determined by the physical chemical properties of the surface and the microscope's set-points. It has been widely observed that noncontact images produce high-resolution images of soft materials and minimize the influence of probe–surface interactions on the sample.

For the second harmonic generation (SHG) evaluation, the Maker Fringe method was used [32]. The SHG experiments were performed with the p-polarized beam at the fundamental frequency of a mode-locked Q-switched Nd:YAG laser (1064 nm) operating at 500 Hz with forty 135 ps sub-pulses in each pulse train. Y-cut quartz of 4.65 mm thickness was used as the reference ($d_{11} = 0.5$ pm V^{-1}) for calculating the $\chi^{(2)}$ coefficient of the polymer sample. The electro-optic coefficient (r_{33}) of the poled film was measured at the 633 nm wavelength by using a simple reflection measurement technique [33]. The input beam was set at 45° to the plane of incidence so that the parallel (p-wave) and perpendicular (s-wave) components of the optical field were equal in amplitude. The reflected beam propagated through a Solei–Babinet compensator into an analyzer and a detector. The modulation in the beam was measured using a lock-in amplifier.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 shows the synthetic routes for the preparation of AZO-OH2 and 6F-DI as monomers. AZO-OH2 was synthesized by the azo-coupling reaction of 4-aminobenzaldehyde with *N*-phenyldiethanolamine in the presence of anhydrous benzene followed by the protecting reaction with ethylene glycol. The diimide monomer 6F-DI was obtained from the imidization reaction of 4,4$'$-(hexafluoroisopropylidene)diphthalic anhydride and urea without a solvent. All intermediates and monomers were characterized by common spectroscopic techniques. Their results are in good agreement with the structures presented in the synthetic scheme (see Section 2).

The Mitsunobu reaction occurs effectively at room temperature and usually gives a high yield to the alkylation of imides [34]. Thus, this method is used to obtain polymerization products, without the imidization process, at high temperature by a single step reaction. By using the Mitsunobu reaction, we have described the synthesis of NLO-active poly(ether imide) (PEI) derivatives in the polyimide family that have reasonable yield and molecular weight [35]. In the case of PEI as the NLO polymer, however, the T_g is not very high because the ether linkage gives flexibility to the chain. Thus we have prepared the polyimide structure from the diol AZO-OH2 and diimide 6F-DI by the Mitsunobu reaction, as shown in Scheme 2. Treating the AZO-OH2 and 6F-DI compounds with DEAD/triphenylphosphine in anhydrous THF solvent provides polyimide PI-PRO in ca. 60% yield. By deprotecting PI-PRO with concentrated hydrochloric acid, PI-DEP was obtained in ca. 85% yield. The Knoevenagel reaction of PI-DEP and methanesulfonylacetonitrile produced the final NLO-active

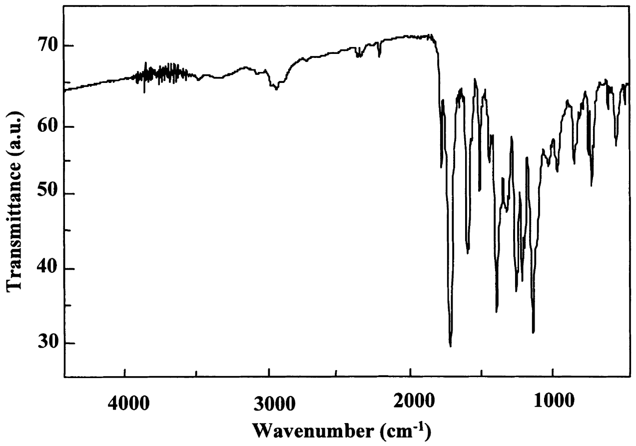


Fig. 1. FT–IR spectrum of PI-SOT with KBr pellet.

copolymer, PI-SOT, which contains 81% cyanosulfonyl-functionalized polymer units from the elemental analysis.

The structures of polymers were characterized by FT–IR, ^{1}H NMR and UV–Vis absorption spectroscopy. Fig. 1 shows the FT–IR spectrum of the final product PI-SOT. The strong peaks at 1785 and 1730 cm^{-1} are attributed to the carbonyl stretching vibration of the imide group. The weak peak at 2250 cm^{-1} is ascribed to the stretching vibration of the cyano group. As shown in Fig. 2, the ^{1}H NMR spectra of polymers show a signal broadening resulting from polymerization, but the chemical shifts are consistent with the proposed polymer structures. In PI-PRO spectrum, the peak at 5.82 ppm corresponds to the methine proton in the oxolane ring. In addition, the ^{1}H NMR spectra of PI-DEP and PI-SOT show peaks at 10.04 and 3.21 ppm, due to the aldehyde proton and methyl proton, respectively.

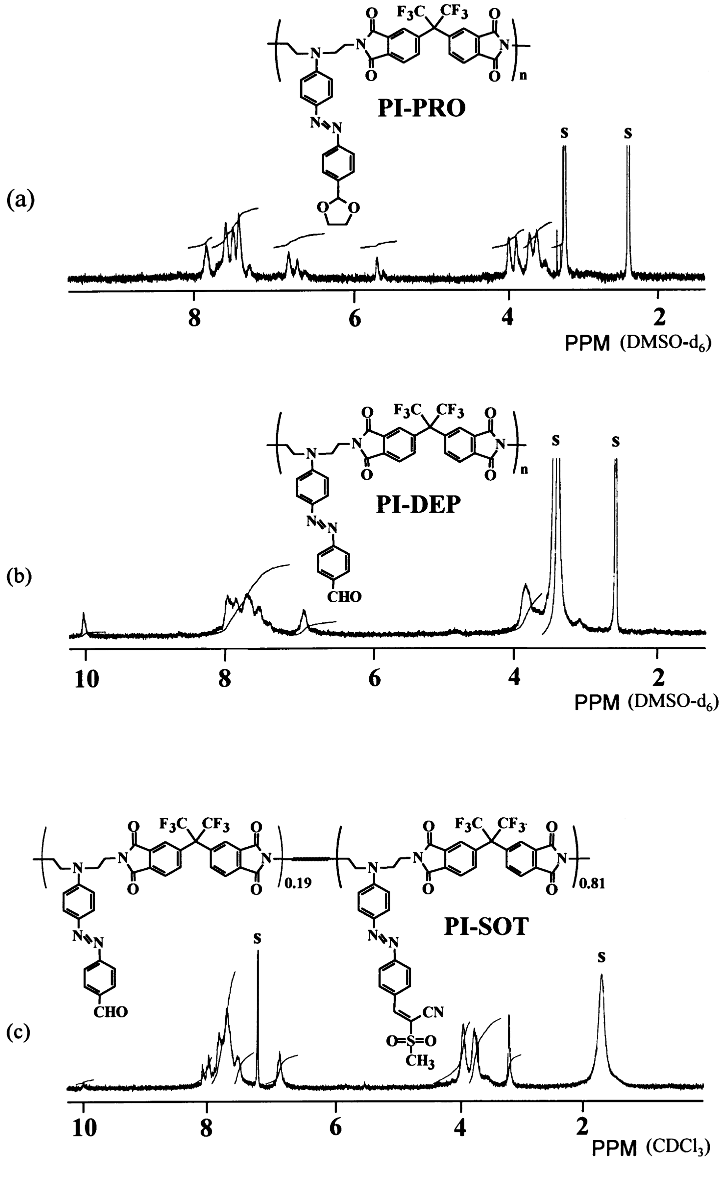


Fig. 2. ^{1}H NMR spectra of: (a) PI-PRO; (b) PI-DEP; and (c) PI-SOT in DMSO or $CDCl_3$ solvents (s: solvent signal).

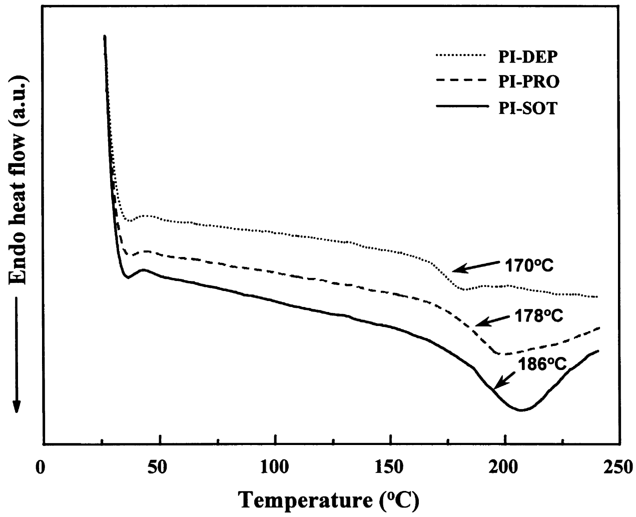


Fig. 3. DSC thermograms of PI-PRO, PI-DEP and PI-SOT with a heating rate of 10°C min^{-1}.

The final polymer is readily soluble in polar aprotic solvents, such as DMF, DMSO, THF and cyclohexanone. When cyclohexanone, in particular, is used, good optical quality films are obtained from spin coating. The molecular weight of PI-SOT was determined by GPC to be $M_n = 5650$ ($M_w/M_n = 1.4$).

3.2. Thermal properties

As shown in Fig. 3, the T_g for a series of polymers is in the 170–186°C range, depending on the structure of the NLO chromophore and the extent of functionalization. No crystalline melting transitions were detected for all of the polymers indicating that the polymers are all amorphous. Initial decomposition temperatures (T_{id}) of the polymers were determined using TGA (temperature range 25–800°C, heating rate 10° min^{-1}, flow 50 cc min^{-1} of N_2 gas). It shows initial decomposition within 190–200° due to thermal breaking of the azo group (Fig. 4). All of the polymers show residual weights of more than 40% at 800°C in nitrogen atmosphere due to the presence of high aromatic rings in the polymer structures.

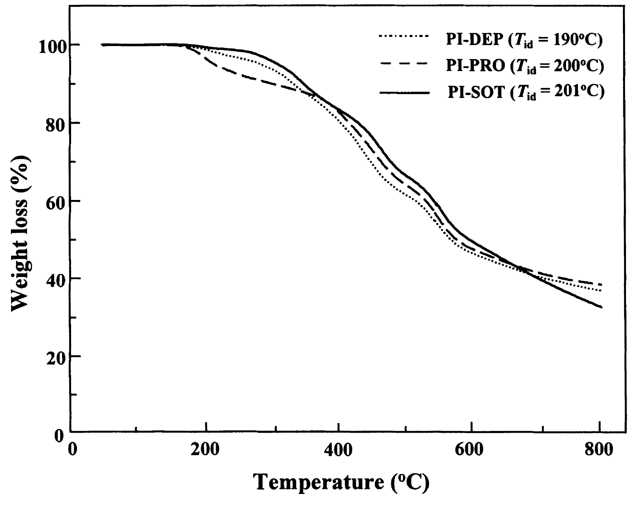


Fig. 4. TGA thermograms of PI-PRO, PI-DEP and PI-SOT with a heating rate of 10°C min^{-1}.

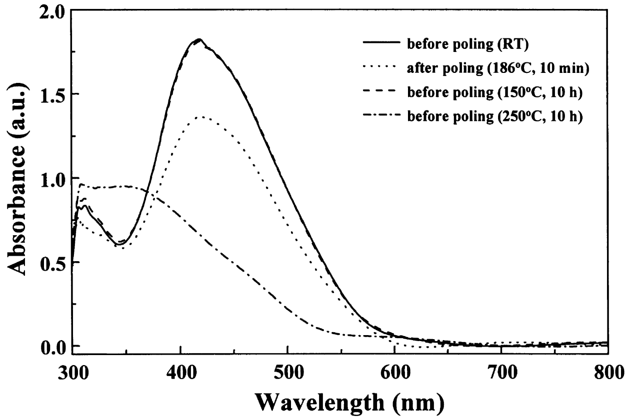


Fig. 5. UV–Vis spectra of the PI-SOT film before corona poling, after corona poling and after storage for 10 h at 150°C and 10 h at 250°C without poling.

3.3. Linear and nonlinear optical properties

The PI-SOT film was prepared by spin coating on ITO glasses from 15 wt.% cyclohexanone solution. The refractive indices of the PI-SOT film were measured by the m-line method at various wavelengths. The values for PI-SOT were 1.703 at 514 nm, 1.671 at 543 nm, and 1.618 at 633 nm, respectively. A single oscillator Sellmeier equation fit to the experimental data gave refractive indices of PI-SOT at 532 nm (1.682) and 1064 nm (1.559).

The absorption spectra of the PI-SOT film were measured with a Shimadzu UV-240 spectrophotometer (Fig. 5). They exhibited a typical absorption due to the azo-chromophore, with a maximum at 415 nm. The order parameters ($\phi = 1 - A_1/A_0$, A_0 and A_1 are absorbances of the PI-SOT film before and after corona poling) are used to characterize the poling efficiency. Under the conditions of a 5 kV poling voltage applied to the corona needle at 186°C for 10 min, the order parameter value for PI-SOT was estimated to be 0.22. The corresponding polymer film was thermally treated without poling at 150°C for 10 h and showed no change in the absorption spectrum. The reason for the disappearance of the maximum absorption peak at 415 nm, during annealing at 250°C for 10 h, is probably due to thermal breaking of the azo group in chromophore. The surface morphology of the PI-SOT films was studied using AFM before poling, after annealing and after poling. Each surface was studied in 15×15 μm areas at several points and found to be highly uniform. Fig. 6 shows high-resolution images of the surface before (Fig. 6a and b) and after (Fig. 6c and d) poling. Two observations can be made from these images. First, the root-mean-squared roughness of these surfaces is 0.2–0.3 nm.

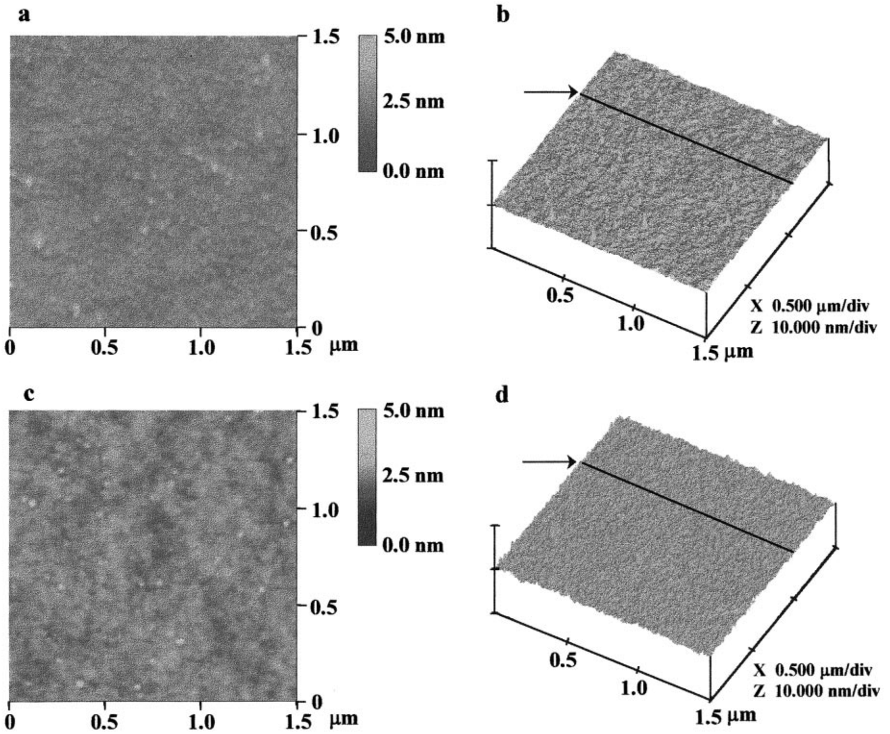


Fig. 6. AFM images of PI-SOT films: (a), (b) before; and (c), (d) after corona poling at 186°C for 10 min using a needle electrode (image size: 1.5 × 1.5 μm^2).

These surfaces are approximately one order of magnitude rougher than the smoothest silicon wafers but are typical of spin-coated polymer films. Second, Fig. 7 indicates that the before and after poling films appear to be morphologically identical. These results differ from previous studies in our laboratory that show the effect of corona-poled on BPTP films and suggest that PI-SOT films may be more stable under poling [19].

The SHG measurements were performed on poled films with 1.16 μm using a Q-switched Nd:YAG laser beam (1064 nm). The SHG intensity of the film of PI-SOT was measured using a standard Maker fringe technique. Fig. 8 shows the relationship between the SHG intensity and the incident angle. The SHG coefficient (d_{33}) of PI-SOT can be calculated from the angular dependence of the SHG intensity compared to a Y-cut quartz as a reference ($d_{11} = 0.5$ pm V^{-1}) signal [32]. From the calculation, we obtained a d_{31} value of 50 pm V^{-1} (involved resonant effect due to some absorption in SHG range) for PI-SOT. Since the relationship $d_{33} \cong 3d_{31}$ holds in polymer systems, the d_{33} value is supposed to be about 150 pm V^{-1}. From our calculation using the approximate two-level model, the nonresonant value ($d_{33}(\infty)$) of this copolymer was found to be about 47 pm V^{-1}.

We also measured the electro-optic coefficient (r_{33}) by a simple reflection technique proposed by Teng and Mann [33]. In the measurement, the sine wave modulating voltage, r_{33}, can be calculated by the equation [36],

$$r_{33} = \frac{3\lambda I_{\mathrm{m}}}{4\pi V_{\mathrm{m}} I_c n^2} \frac{(n^2 - \sin^2\theta)^{1/2}}{\sin^2\theta}$$

where λ is the optical wavelength, I_{m} is the amplitude of the

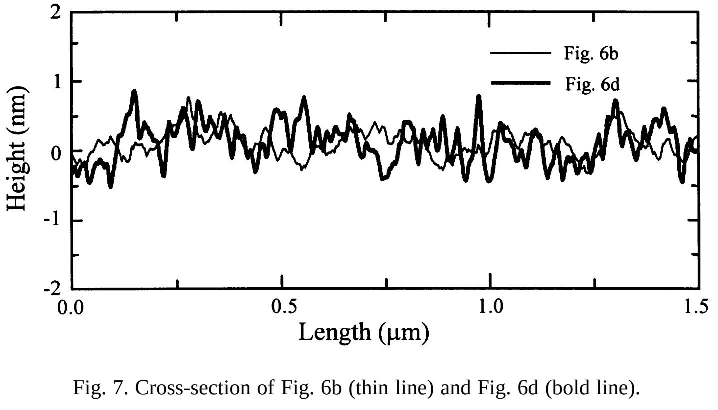


Fig. 7. Cross-section of Fig. 6b (thin line) and Fig. 6d (bold line).

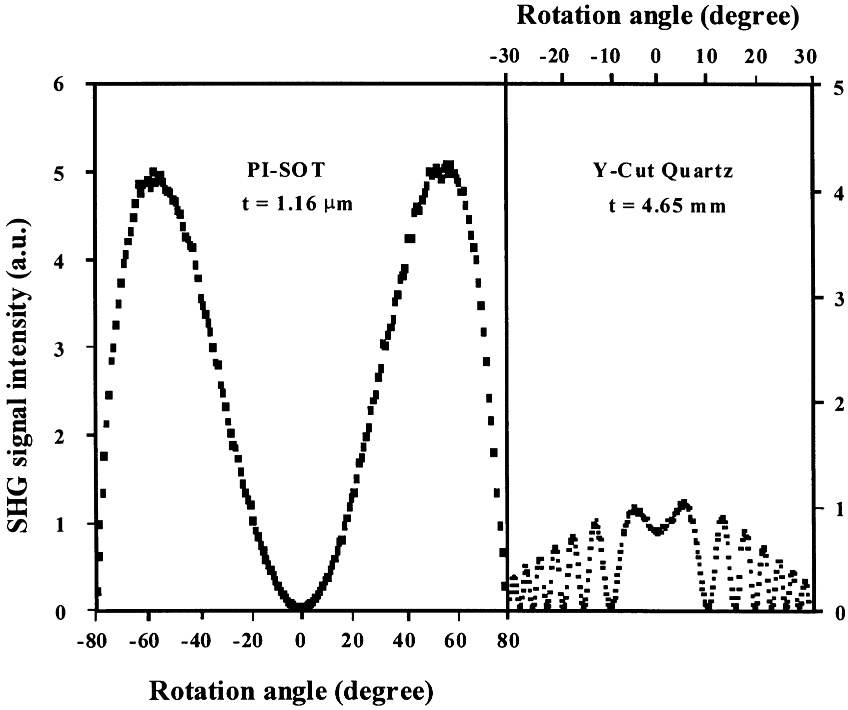


Fig. 8. Comparison of angular SHG dependence between poled PI-SOT film and Y-cut quartz plate as reference (t: thickness).

modulation, I_c is the half-intensity point, V_m is the modulating voltage, and n is the refractive index. The r_{33} value thus obtained for the PI-SOT film was 28 pm V^{-1} for the incident laser wavelength (633 nm).

Temperature-dependent SHG measurements yield information of the SHG stability as a function of temperature. Fig. 9 shows such a result for PI-SOT, where the heating rate is 5°C min^{-1}; the samples were exposed to air during the entire measurement. The SHG signal is quite stable until the temperature reaches 150°C. The SHG signal rapidly decayed when the temperature neared the polymer's T_g (186°C). The signal completely disappeared when the temperature was above the T_g. Fig. 10 shows the temporal stability of the electro-optic coefficient, r_{33}, for the PI-SOT film at room temperature in air. Under this condition, the r_{33} value of the film remained about 95% of its initial value, even after 67 days. At 100°C in air (Fig. 11), an initial decay of about 10% was observed within 1 h, but no further decay in the electro-optic coefficient was indicated within the prong time of 30 days.

In summary, we have successfully synthesized a high NLO-active polyimide by the Mitsunobu reaction of a diol type chromophore and a diimide, which does not need imidization processing at high temperature. The resulting polymer is soluble in common polar organic solvents and provides optical-quality films by spin coating. The glass

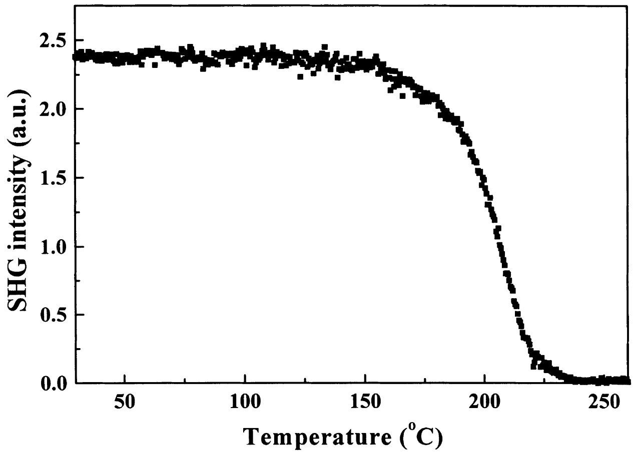


Fig. 9. Thermal stability of the SHG activity of a poled PI-SOT film heated up to 250°C.

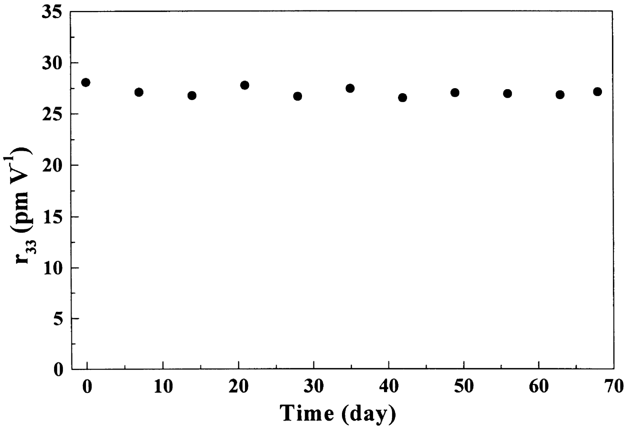


Fig. 10. Temporal stability of the electro-optic coefficient r_{33} for the PI-SOT at room temperature.

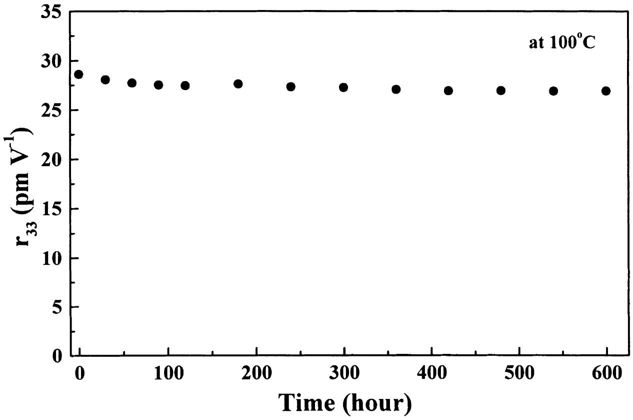


Fig. 11. Temporal stability of the electro-optic coefficient r_{33} for the PI-SOT at 100°C.

transition temperature of the final NLO polyimide was found to be 186°C. The poled polymer film exhibits a high second-order activity described by a d_{31} value of 50 pm V^{-1} and an electro-optic coefficient r_{33} of 28 pm V^{-1} at 633 nm. We also observed good temporal and thermal endurance of dipolar alignment up to about 150°C in this polyimide system.

Acknowledgements

This work was supported by the Korean Ministry of Education Research Fund for Advanced Materials in 1997 and the LG Yonam Foundation. We thank Dr Y.H. Min and Mr Y.H. Jeong for their help in measuring the SHG activity and refractive index, respectively.

References

[1] Prasad PN, Williams DJ. Introduction to nonlinear optical effects in molecules and polymers, New York: Wiley, 1991.

[2] Lee K-S, Samoc M, Prasad PN. Polymers for photonics applications. In: Aggarawal S, Russo LS, editors. Comprehensive polymer science, Oxford: Pergamon Press, 1992. pp. 407–47 Supplement.

[3] Burland DM, Miller RD, Walsh CA. Chem Rev 1994;94:31.

[4] Jeneke SA, Wynne KJ, editors. Photonic and optoelectronic polymers ACS symposium series, 672. Washington, DC: American Chemical Society, 1995.

[5] Lee K-S. Macromol Symp 1997;118:519.

[6] Mittler-Neher S. Macromol Chem Phys 1998;199:513.

[7] Lindsay GA, Singer KD, editors. Polymers for second-order nonlinear optics ACS symposium series, 601. Washinton, DC: American Chemical Society, 1995.

[8] Moehlmann GR, editor. Nonlinear optical properties of organic materials IX SPIE proceedings, 2852, 1996.

[9] Ahumada O, Weder C, Suter UW. Macromolecules 1997;30:3256.

[10] Lacroix PG, Lin W, Wong GK. Chem Mater 1995;7:293.

[11] Tsutsumi N, Fujii I, Ueda Y, Kiyotsukuri T. Macromolecules 1995;28:950.

[12] Cross EM, White KM, Moshrefzadeh RS, Francis CV. Macromolecules 1995;28:2526.

[13] Kim Y-W, Lee K-S, Jin J-I, Choi K-Y. Bull Korean Chem Soc 1996;17:607.

[14] Chebremechael F, Kuzyk MG, Lackritz HS. Prog Polym Sci 1997;22:1147.

[15] Eich M, Reck B, Yoon DY, Willson G, Bjorklund GC. J Appl Phys 1989;66:3241.

[16] Mandel BK, Kumar J, Huang JC, Tripathy SK. Makromol Chem. Rapid Commun 1991;12:63.

[17] Ranon RM, Shi Y, Steier WH, Xu C, Wu B, Dalton LR. Appl Phys Lett 1993;62:2605.

[18] Lee K-S, Choi S-W, Woo HY, Moon K-J, Shim H-K, Jeong M-Y, Lim T-K. J Opt Soc Am B 1998;15:393.

[19] Min YH, Lee K-S, Yoon CS, Do LM. J Mater Chem 1998;8:1225.

[20] Verbiest T, Burland DM, Jurich MC, Lee VY, Miller RD, Volkson W. Macromolecules 1995;28:3005.

[21] Moon KJ, Shim H-K, Lee K-S, Zieba J, Prasad PN. Macromolecules 1996;29:861.

[22] Kim HK, Moon IK, Jin MY, Choi K-Y. Korea Polym J 1997;5:57.

[23] Jen AK-Y, Drost KJ, Cai Y, Rao VP, Dalton LR. J Chem Soc. Chem Commun 1994:965.

[24] Yang S, Peng Z, Yu L. Macromolecules 1994;27:5858.

[25] Peng Z, Yu L. Macromolecules 1994;27:2638.

[26] Sotoyama W, Tatsuura S, Yoshimura T. Appl Phys Lett 1994;64:2197.

[27] Yu D, Gharavi A, Yu L. J Am Chem Soc 1995;117:11680.

[28] Yu D, Gharavi A, Yu L. Macromolecules 1996;29:6139.

[29] Saadeh H, Gharavi A, Yu L. Macromolecules 1997;30:5403.

[30] Kim HK, Moon K, Lee HJ, Han SG, Won YH. Polymer 1998;39:1719.

[31] Woo HY, Shim HK, Lee K-S. Macromol Chem Phys 1998;199:1427.

[32] Herman WN, Hayden LM. J Opt Soc Am B 1995;12:416.

[33] Teng CC, Mann HT. Appl Phys Lett 1990;56:1734.

[34] Mitsunobu O. Synthesis 1981:1.

[35] Lee K-S, Moon KJ, Woo HY, Shim HK. Adv Mater 1997;9:978.

[36] Shuto Y, Amano M. J Appl Phys 1995;77:4632.