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Synthesis of nonlinear optical polyimides containing benzothiazole moiety and their electro-optical and thermal properties

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Abstract

A series of thermally stable second-order nonlinear optical (NLO) polyimides has been synthesized. The polyimides were prepared by the ring-opening polyaddition of 4,4′-(hexafluoroisopropylidene) diphthalic anhydride and pyromellitic dianhydride with two aromatic diamines containing benzothiazole moiety as the NLO chromophore. The resulting polyimides had high number and weight-average molecular weights (M_n, M_w) up to 28 500 and 78 600, respectively, and a large glass transition temperature of 260°C. Using in situ poling and temperature ramping technique, the optimal temperatures (T_{opt}) for corona poling were obtained to get the largest second-order NLO response. The electro-optical coefficient (γ_{33}) of a polyimide at the wavelength of 830 nm was up to 22 pm/V after corona poling under its T_{opt}, and the value remained well at elevated temperatures (retained >87% at 240°C for more than 120 h). The thermal stability of NLO polyimides was studied by the UV spectrometry after poling of the films. © 2001 Published by Elsevier Science Ltd.

Keywords: Side-chain polyimide; Nonlinear optics; Electro-optical coefficient

1. Introduction

Interest in nonlinear optical (NLO) materials, both inorganic and organic, has grown tremendously over the past decades, primarily because of their potential application in the fields of optical information processing, optical sensing, and telecommunications [1–3]. Of these NLO polymers are considered to be the most promising materials because of their ease of processability, excellent thermal stability, environmental resistance, good mechanical strength and flexibility in molecular designs [4–7].

For the practical application of second-order NLO polymeric materials, both high NLO activity and thermal stability are required. Electric poling, a common technique for achieving noncentrosymmetric chromophore-ordering in NLO polymers, is thermodynamically unstable, especially at higher temperatures [8,9]. Various approaches, including incorporation of the chromophore into the polymer backbone (a main-chain or embedded side-chain system), a interpenetration polymer network method, and a cross-linking method, have been used to prevent the relaxation of chromophores caused by the thermal motion of polymer chains [10–17]. Because the latter methods tend to relatively lower glass transition temperature, the use of embedded side-chain polymers has been considered to be one of the best NLO matrix methods for stabilizing poled chromophores as well as retaining thermal stability of the polyimide backbone. While significant advances have been made recently in the first class, most of the incorporated NLO chromophores have contained dialkylamino donor substituents and all have been attached via flexible alkyl or alkoxyalkyl tether groups, either incorporated into the main chain or contained in the side chain. Miller and co-workers [18,19] had demonstrated previously that dialkylamino donor substitution is a serious source of chromophore instability at high temperatures. Furthermore, while flexible alkyl and hydroxyalkyl ether groups facilitate electric field poling, they tend to lower the T_g of the polymer, adversely affecting orientational stability. In addition, they can be a source of thermal instability at high temperatures.

Previously Naoto Tsutsumi and co-workers [20] have reported on the use of nitro-azobenzene *m*-phenylenediamine for the synthesis of NLO polymers. Enhanced orientational stability of the aligned NLO chromophore was ascribed to the rigid structure of the polyimide backbone. With a Kohlrausch–Williams–Watts stretched exponential function, [21] they estimated that a relaxation time of 3.8 years could be obtained at a temperature of 150°C. But the thermal stability and processibility of the polymer they synthesized make it unsuitable yet for a practical device.

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In this connection, nitro-benzothiazole azo (or diazo) *m*-phenylenediamine chromophores were used in this paper because of their high chemical stability, sizable molecular hyperpolarizabilities (β) and the easy reactivity with dianhydride. Moreover, we report the synthesis of four NLO polyimides with no flexible tether groups by standard condensation polymerization techniques. The resulting polymers are soluble, rigid, functionalized donor-embedded side chain polyimides with very high T_g (up to 260°C), exceptional thermal stability, and polar order stability, which are truly remarkable for a thermoplastic material.

2. Experimental section

N,*N*-dimethylfomamide (DMF) was stirred over powdered calcium hydride overnight and then distilled under reduced pressure and stored over 4 Å molecular sieves. Tetrahydrofuran (THF) was purified by distillation over sodium chips, and other reagents and solvents were obtained commercially and were used as received. The monomer, 4,4′-(hexafluoroisopropylidene) diphthalicanhydride (6FDA) used in the polyimide synthesis was obtained from TCI and used without further purification.

2.1. Monomer synthesis

*2.1.1. [(6-nitrobenzothiazol-2-yl) diazenyl] phenyl-1,3-diamine (**1**)*

2-Amino-6-nitrobenzothiazole was prepared as followed. *p*-Nitroaniline (0.1 mol, 13.8 g) and sodium thiocyanate (0.2 mol, 19.4 g) were dissolved in acetic acid (150 ml), and the reaction mixture was cooled in an ice bath and then added dropwise bromine (0.1 mol, 12 g) in acetic acid (25 ml) with stirring. After an hour, the resulting solid was filtered and dissolved in heating water, and the solution was neutralized with ammonia water. The precipitate was separated by filtering and was crystallized from ethyl acetate as an orange microcrystalline powder, m.p. 245–247°C. To 5.5 mmol *m*-phenylenediamine were added 1 ml concentrated hydrochloric acid and 10 ml water to make its salt solution. 5.5 mmol 2-amino-6-nitrobenzothiazole, 10 ml H_2O, and 5.5 mmol $NaNO_2$, were mixed to form a paste, which was poured into a mixture of crushed ice and 1.5 ml concentrated hydrochloric acid. The reaction was carried out for 0.5 h in an ice bath. The diazonium salt solution was added slowly into the solution of *m*-phenylenediamine salt during stirring and the mixture reacted for 1 h. After neutralizing with ammonia water for 0.5 h, the product was filtered and washed with water until neutral. The compound was purified on a silica gel column with the eluate acetone to afford 1.54 g (89% yield) of 4-[(6-nitrobenzothiazol-2-yl)diazenyl] phenyl-1,3-diamine (**1**). M.p. is 225–226°C. ^1H NMR (300 MHz, CD_3COCD_3, ppm): 8.06 (s, ArH, 1H), 8.00 (s, ArH, 1H), 7.84 (s, ArH, 1H), 7.12 (s, ArH, 1H), 6.58 (s, ArH, 1H), 6.15 (s, ArH, 1H), 3.35 (s, $ArNH_2$, 4H). Ancl. Calcd for $C_{13}H_{10}N_6O_2S$: C, 49.67%; H, 3.18%; N, 26.75%. Found: C, 49.71%; H, 3.16%; N, 26.78%.

*2.1.2. ,4-diamino-4′-[(6-nitrobenzothiazol-2-yl)diazenyl] azobenzen (**2**)*

First, 4-[(6-nitrobenzothiazol-2-yl)diazenyl]aniline was synthesized similar to (**1**), and then its diazonium salt solution was added dropwised into the solution *m*-phenylenediamine salt during stirring and the mixture reacted for 1 h. After neutralizing with ammonia water for 0.5 h, the resulting solid was filtered and washed with water until neutral. After drying, it was purified on a silica gel column with the eluate acetone. M.p. is 231–233°C. ^1H NMR (300 MHz, CD_3COCD_3, ppm): 8.11 (s, ArH, 1H), 8.06 (s, ArH, 1H), 7.96 (s, ArH, 1H), 7.45 (d, ArH, 2H, $J = 8.7$ Hz), 7.36 (d, ArH, 2H, $J = 8.7$ Hz), 6.68 (s, ArH, 1H), 6.51 (s, ArH, 1H), 6.09 (s, ArH, 1H), 3.37 (s, $ArNH_2$, 4H). Ancl. Calcd for $C_{19}H_{14}N_8O_2S$: C, 54.55%; H, 3.35%; N, 26.79%. Found: C, 54.63%; H, 3.36%; N, 26.81%.

*2.2. Preparation of polyimide (**3**–**6**)*

4-[(6-nitrobenzothiazol-2-yl)diazenyl]phenyl-1,3-diamine **1** (0.5 mmol) was dissolved in 5 ml of anhydrous DMF at room temperature, followed by the addition of pyromellitic dianhydride (PMDA) (0.5 mmol) at once. The solution was stirred at room temperature for 12 h. The mixture of acetic anhydride and pyridine (8 ml/4 ml, 2:1) was added to the solution at room temperature and this mixture was stirred for 12 h, and then heated to 90°C under nitrogen atmosphere for another 3 h. The polymer was precipitated into methanol and collected by filtration. The solid was further purified by dissolving in THF and reprecipitated into methanol. The resulting polyimide **3** was collected and washed with methanol in a Soxhlet extractor for 24 h and the dried under vacuum at 60°C for 24 h. ^1H NMR (300 MHz, CD_3COCD_3, ppm): 8.17 (d, ArH, 2H, $J = 8.7$ Hz), 8.06 (s, ArH, 1H), 7.99 (s, ArH, 1H), 7.93 (s, ArH, 1H), 7.38 (s, ArH, 1H), 7.25 (s, ArH, 1H), 7.08 (s, ArH, 1H). Ancl. Calcd for $C_{23}H_8N_6O_6S$: C, 55.65%; H, 1.61%; N, 16.94%. Found: C, 55.71%; H, 1.63%; N, 16.92%.

The above polymerization procedure exemplifies the synthesis of polyimides **4**–**6** where stoichiometric amount of 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), and 2,4-diamino-4′-[(6-nitrobenzothiazol-2-yl)-diazenyl] azobenzen were added, respectively.

Polyimide (**4**) ^1H NMR (300 MHz, CD_3COCD_3, ppm): 8.26 (d, ArH, 2H, $J = 8.7$ Hz), 8.12 (m, ArH, 1H), 8.09 (s, ArH, 1H), 8.03 (s, ArH, 1H), 7.96 (d, ArH, 2H, $J = 8.7$ Hz), 7.78 (s, ArH, 2H, $J = 8.7$ Hz), 7.58 (s, ArH, 1H), 7.36 (s, ArH, 1H), 7.20 (s, ArH, 1H). Ancl. Calcd for $C_{32}H_{12}F_6N_6O_6S$: C, 53.19%; H, 1.66%; N, 11.63%. Found: C, 53.26%; H, 1.68%; N, 11.67%.

Polyimide (**5**) ^1H NMR (300 MHz, CD_3COCD_3, ppm): 8.21 (d, ArH, 2H, $J = 8.7$ Hz), 8.10 (s, ArH, 1H), 8.05 (s, ArH, 1H), 7.99 (s, ArH, 1H), 7.84 (d, ArH, 2H, $J = 8.7$ Hz), 7.80 (d, ArH, 2H, $J = 8.7$ Hz), 7.43 (s, ArH, 1H), 7.33 (s, ArH, 1H), 7.16 (s, ArH, 1H). Ancl. Calcd for $C_{29}H_{12}N_8O_6S$: C, 58.00%; H, 2.01%; N, 18.67%. Found: C, 58.05%; H, 2.03%; N, 18.65%.

Polyimide (**6**) ^1H NMR (300 MHz, CD_3COCD_3, ppm): 8.26 (d, ArH, 2H, $J = 8.7$ Hz), 8.21 (s, ArH, 1H), 8.19 (s, ArH, 1H), 8.07 (s, ArH, 1H), 8.02 (d, ArH, 2H, $J = 8.7$ Hz), 7.91 (d, ArH, 2H, $J = 8.7$ Hz), 7.89 (d, ArH, 2H, $J = 8.7$ Hz), 7.78 (d, ArH, 2H, $J = 8.7$ Hz), 7.46 (s, ArH, 1H), 7.26 (s, ArH, 1H), 7.08 (s, ArH, 1H). Ancl. Calcd for $C_{38}H_{16}F_6N_8O_6S$: C, 55.21%; H, 1.94%; N, 13.56%. Found: C, 55.25%; H, 1.95%; N, 13.60%.

2.3. Characterization

The FTIR spectra were recorded as KBr pellets on a Nicolet Magna-IR 750 spectrometer. The ^1H NMR spectra were collected on a DXT-300 MHz Bruker NMR spectrometer. The elemental analyses were obtained on a Perkin–Elmer Lambda 6. A Varian Cary 50 Probe UV–Vis spectrophotometer was used to record the UV–Vis spectral date. Thermal analyses were performed by using the SETARAM DSC-131 and TGA-DTA system from TA instruments under nitrogen atmosphere. Molecular weights were determined by gel permeation chromatography (GPC) with a polystyrene standard using a WATERS SEC-244 system at 25.5°C in THF.

2.4. Optical measurement

We performed the Jiang et al. improved attenuated-total-reflection (ATR) technique for the electro-optical coefficient measurements [22]. For these measurements, the silver film was first thermally evaporated onto the hypotenuse face of a high-index prism as the bottom electrode, the thickness of the film was about 55 nm. The second, a polyimide film was spin coated onto the silver substrate to a thickness of 1–2 μm. The third, a polymer buffer layer was then coated onto the polyimide film to a thickness of 4 μm or so. Corona discharge poling was performed by alignment of the chromopphore dipoles in a high static electric field while the polyimide was heated to high mobility close to its optimal temperature. The last, another silver film was deposited onto the buffer layer as the second electrode.

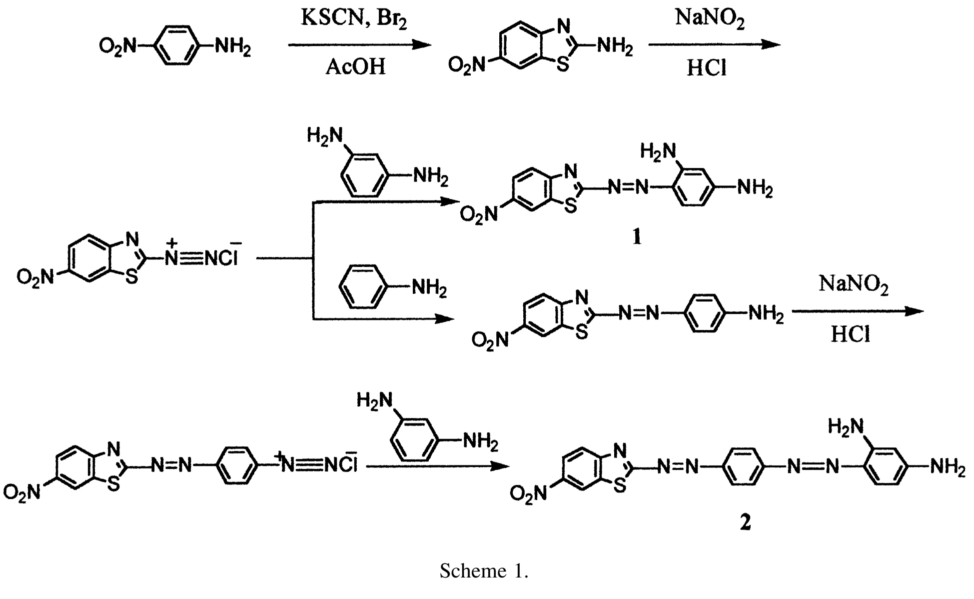
The second harmonic generation (SGH) of the poled polymeric films was measured buy using a model-locked Nd:YAG laser with pulse width of < 10 ns and 10 Hz repetition rate as a fundamental source.

3. Results and discussion

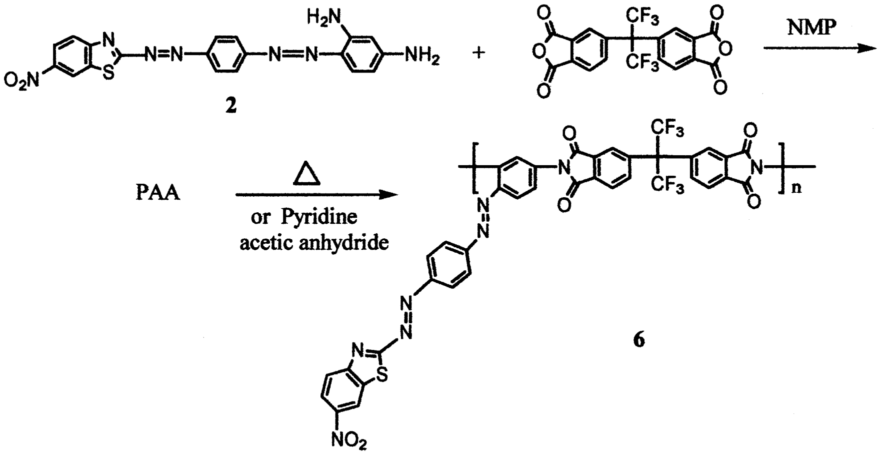
3.1. Synthesis

Previously, in order to achieve NLO side-chain polyimides, it was necessary to prepare the hydroxyl polyimides, or prepare the NLO flexible ether-containing diamino monomers. Both of the resulting NLO polyimides contained an ether chain, which lead to thermal instability at high temperatures. Our strategy for the design of NLO side-chain polyimide was to directly synthesize a kind of NLO diazo or azo *m*-phenylenediamine containing benzothiazole unit as shown in Scheme 1 (synthesis of chromophores), then reacted with dianhydride using thermal or chemical imidization as shown in Scheme 2 (synthesis of polyimide **6**).

The diamino monomers **1** and **2** were obtained simply by the azo-coupling reaction of 2-amino-6-nitrobenzothiazole or 4-[(6-nitrobenzothiazol-2-yl)diazenyl] aniline with *m*-phenylenediamine, and they can be purified greatly by using column chromatography technology. The monomers were incorporated into a variety of polyimides via condensation polymerization as shown in Scheme 2. The particular example in this scheme, employing as a starting materials, is



Scheme 1.



Scheme 2.

chosen for illustration, since the fully imidized material **6** is soluble in a many common organic casting solvents, such as cyclopentanone, cyclohexanone and THF etc. The elemental analysis values of the all compounds were generally in good agreement with the calculated values for the proposed structures. Due to the good solubility of the polyimides in THF, the molecular weight can be measured by using GPC (see Table 1.). For example, a weight-averaged molecular weight (M_w) of 78 000 with a polydispersity of 3.0 of the polyimide **5** was obtained (polystyrenes as standards).

3.2. Thermal properties of polyimides

Thermal properties of these polyimides were examined by differential scanning calorimetry (DSC) and thermogravimetry analysis (TGA) (see Figs. 1 and 2). No thermal transitions have been detected between 60 and 240°C in the DSC trace. The very high glass transition temperature ($T_g \sim 260°C$) of **5** was determined, reflecting the stable NLO diazo *m*-phenylenediamine structure.

The differental branching structure analysis (TGA) on the obtained polyimides **3**–**6** was carried out as shown in Fig. 2. It is obvious that the polyimide **5** and polyimide **6** show fairly good thermal stability. The polyimide **3** and polyimide **4**, however, are less thermally stable than the corresponding polyimides with the same polyimide backbones. This is related to the differences in chromophore groups. It is therefore anticipated that the thermal stability of the NLO chromophore improves the stability of the final NLO polymer. At the same time, the polyimide **3** and the polyimide **5** are more thermally stable than the corresponding polyimides with the same chromophore groups due to the relatively flexible dianhydride 6FAD. Nevertheless, the polyimide **4** still had the temperature of 10 wt% loss over 400°C in N_2.

3.3. Polymer characterization

All the polyimides were characterized by ^{1}H NMR spectroscopy as shown in Fig. 3. The FTIR spectra of polyimides clearly showed the characteristic imide absorption at ca. 1788, 1724, 1378, and 728 cm^{-1} as well as the characteristic absorption at ca. 1350 and 1518 cm^{-1} due to the nitro group.

3.4. Poling and relaxation dynamics study

In our experiments the in situ poling and temperature ramping technique was used to select the optimal temperature (T_{opt}) in order to get the largest second-order NLO response. At the set poling temperature increased step by step, the SHG signal was detected in different temperature after the temperature was held for 10–15 min. In this manner, the T_{opt}s of these polymers were obtained (see Fig. 4). For all materials, the SHG signals rose steadily before the T_{opt}s were reached, and then the SHG signals decreased fleetly due to the damage of the films. From the T_{opt}'s data (Table 1.) of the NLO polymers, we can see all optimal temperatures approach their glass transition temperatures.

The UV–Vis spectra of the thin films of these NLO benzothiazole derivative functionalized polyimides were

Table 1
Properties of polyimides

Polyimide	M_n	M_w	Polydispersity	T_g (°C)	T_d (°C)	λ_m (nm)	γ_{33} (pm/V)
3	27 000	69 500	2.57	253	387	477	17
4	25 500	72 000	2.82	247	363	475	15
5	26 000	78 000	3.00	260	432	492	20
6	28 500	78 600	2.76	248	418	492	22

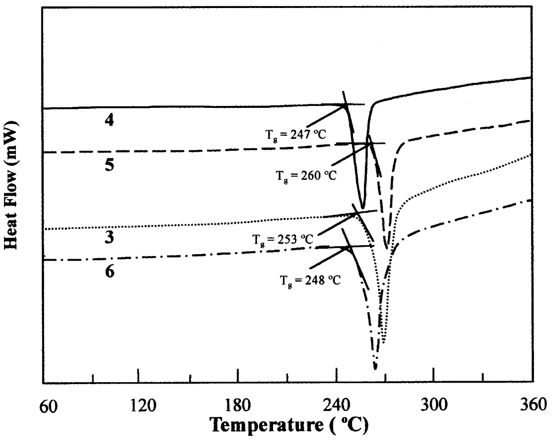


Fig. 1. DSC diagrams of polyimides with the heating rate of 10°C/min under nitrogen atmosphere.

measured and were compared to the spectra of their poled films. The data of the maximum absorption wavelegths were listed in Table 1. The absorptions can be attributed directly to the spectra of the nitro-benzothiazole azo (or diazo) *m*-phenylenediamine chromophores. After electric poling, an absorbance decrease was observed for all the films. This decrease is caused by the alignment of the chromophore dipoles [23] instead of the chromophore structure damage because this spectrum change is reversible upon thermal annealing. For example, the changes of the UV–Vis absorption spectra of polyimide **4** are shown upon unpole and poled film as well as the variation under 240°C in Fig. 5. In a similar manner, the changes can explain that this series of materials possess large alignment stability.

3.5. Electro-optic coefficient and thermal stability

The electro-optic (EO) coefficient measurements of our polyimides were performed at a wavelength of 830 nm with an experimental setup similar to that described by Jiang et al. The test sample, which is shown in cross section in Fig. 6, consists of (1) a high-index prism (ZF6, $n = 1.750$);

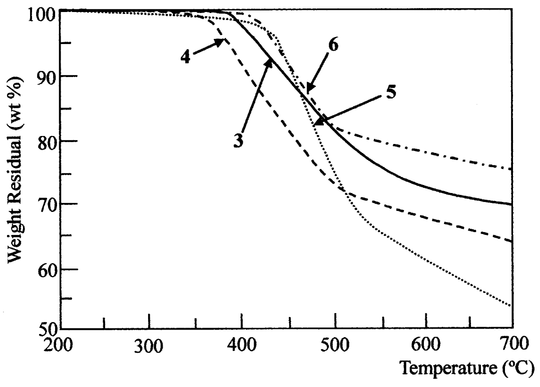


Fig. 2. TGA traces of the NLO polyimides (20°C/min).

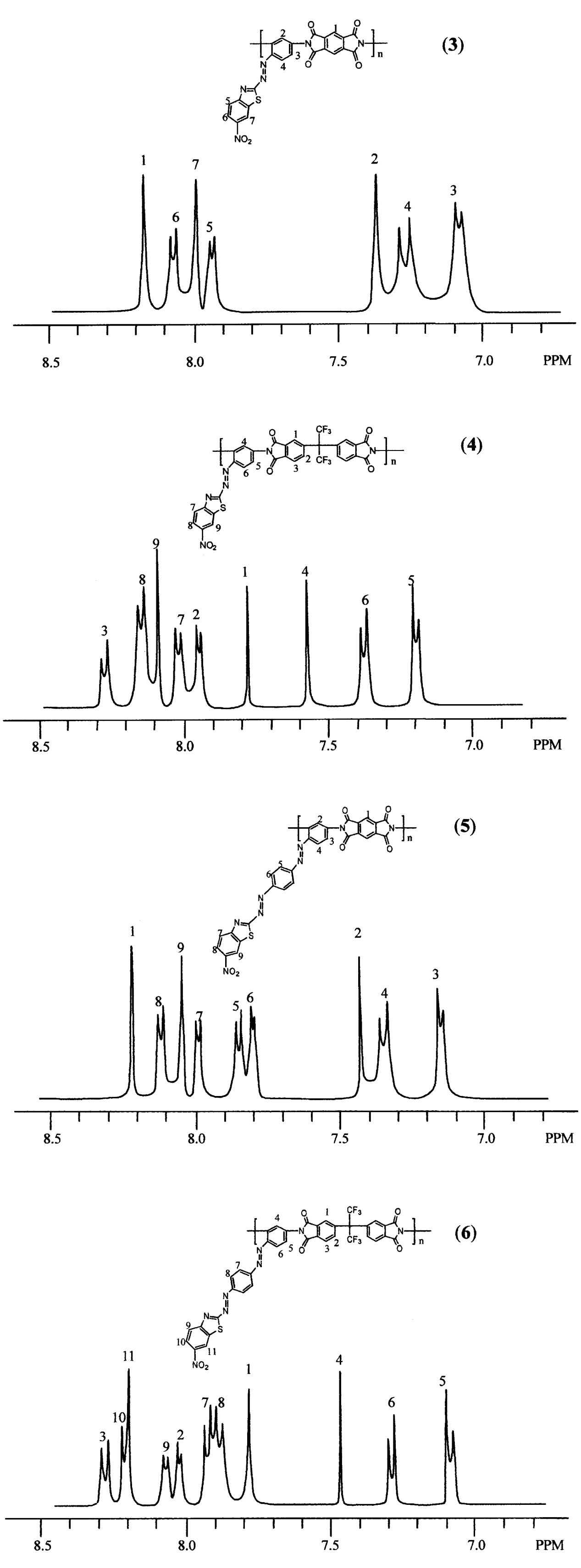


Fig. 3. ^{1}H NMR spectra of the NLO polyimides.

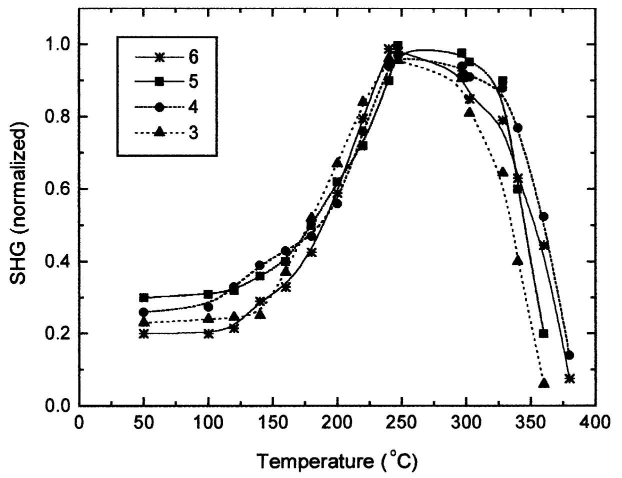


Fig. 4. The SHD signals (which select polymeric T_{opt}s are shown as a function of temperature (1.5 kV, 5°C/min).

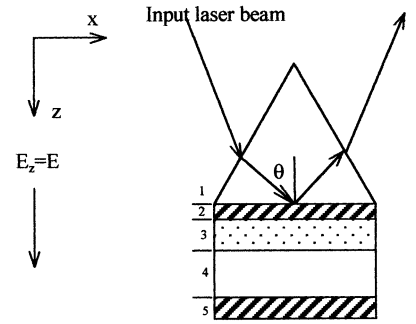


Fig. 6. Sample geometry and optical configuration of the reflection.

(2) a thin silver film; (3) a poled polymer layer; (4) a buffer layer (Akzo Nobel PC, $n = 1.550$); and (5) a base silver film. Each film above was also fabricated on a glass substrate under the same conditions and the film thickness was measured with a Soloan Technology DEKTAK profiler using the film on the glass. The highest γ_{33} value (22 pm/V) was observed with polyimide **6**, and the polyimide **5** exhibits higher γ_{33} value and polyimides **3** and **4** have much smaller γ_{33} values (see Table 1).

The thermal alignment stability of these polyimides was investigated by in situ EO coefficients measured using the heater mounted sample holder. Fig. 7 shows the long-term stability of the EO coefficients of the polyimide **6** at 240°C, and the value retained >87% for move than 120 h. The initial values of polyimides **3**, **4** and **5** retained >95, >92 and 90%, respectively at 240°C after 120 h. These thermal characteristics are an indication that the structures of these polymers may affect their electro-optical stability.

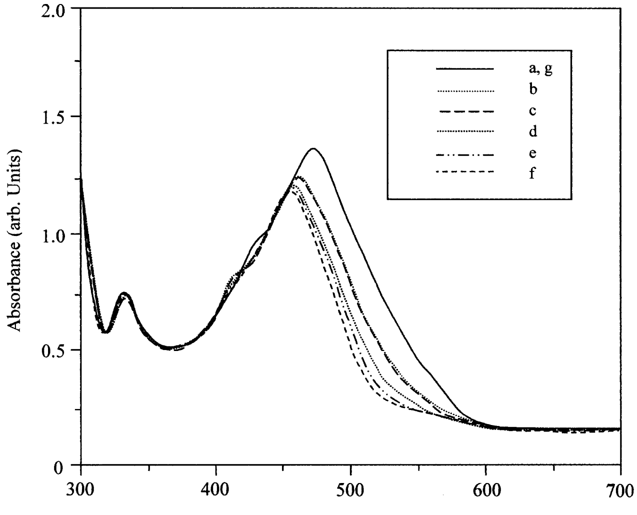


Fig. 5. UV–Vis absorption spectra of a spin-coated film of **4** for both poled (b–f) and unpoled (a, g) samples: (a) before poling ($\lambda_{\max} = 472$ nm); (b) right after poling at room temperature ($\lambda_{\max} = 457$ nm); (c) after 1 h at 240°C ($\lambda_{\max} = 459$ nm); (d) after 5 h at 240°C ($\lambda_{\max} = 461$ nm); (e) after a day at 240°C ($\lambda_{\max} = 264$ nm); (f) after a week at 240°C ($\lambda_{\max} = 465$ nm); (g) right sample at 240°C ($\lambda_{\max} = 472$ nm).

4. Conclusion

In summary, two chromophores were synthesized with nitro-benzothiazole azo (or diazo) *m*-phenylenediamine structure. With these two chromophores, a series of second-order nonlinear optical polyimides were prepared from 6FDA and BMDA by standard condensation polymerization method. Using in situ poling and temperature ramping technique, the optimal temperatures for corona poling were obtained. These materials exhibited relatively large γ_{33} values (22 pm/V at 830 nm fundamental wavelength). It was found that as the stability of the NLO chromophore increased, the glass transition temperatures (up to 260°C) of the polyimides increased accordingly. The solubility and film-formability of the fluorine-containing

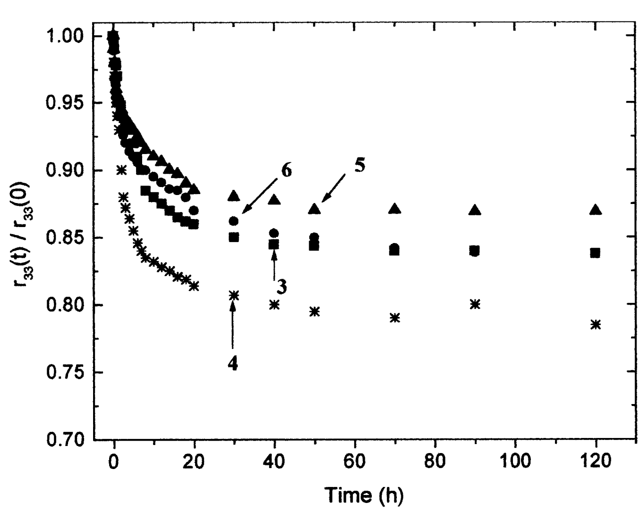


Fig. 7. Temporal stability of EO properties of polyimide **3**–**6** at 240°C in the air.

polyimides were improved compared with the NLO polyimides previously synthesized by us. The versatility of the reaction scheme and the ease of processing assure this type of NLO materials of further utilization.

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