Synthesis and Characterization of Nonlinear Optical Side-Chain Polyimides Containing the Benzothiazole Chromophores

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ABSTRACT: A series of polyimide-based second-order nonlinear optical (NLO) materials were synthesized from poly(hydroxy−imide)s, followed by the Mitsunobu reaction with NLO chromophores. These chromophores, based on a nitro group connected with benzothiazole as the acceptor end of a donor−π-bridge−acceptor chromophore and a hydroxy-functional amino group as the donor end, have specific chemical stability. The resulting polymers were highly soluble in aprotic polar solvents such as DMF, DMAc, NMP, etc. Molecular structural characterization for these polymers was achieved by ^{1}H NMR, FT-IR, and UV−visible spectroscopes. The glass transition temperature for the resulting NLO polyimides was in the range 197−247 °C, and most of them showed high thermal stability. The polymer solutions could be spin coated on the indium−tin−oxide (ITO) glass or other substrates to form optical quality thin films. The electrooptic coefficients (γ_{33}) at the wavelength of 830 nm for polymer thin films poled around the optimal temperature (T_{opt}) were in the range of 9−32 pm/V, and the value remained well at elevated temperatures for move than 120 h in the air. The NLO stability of these polyimides was also studied by studying the UV−visible spectra of their poled films.

Introduction

In recent years, polymeric second-order nonlinear optical (NLO) materials have continuously drawn interest because they have several advantages for photonic applications, such as high-speed photonic switching devices and electrooptic modulators.[1−3] For practical applications, these NLO polymeric materials must retain the high optical quality thin films, high optical damage thresholds, sufficiently large and stable NLO susceptibilities, low optical propagation loss, and feasibility of device fabrication.[1,2] Although it is extremely difficult to synthesize materials, which will solve all of these problems, they are being ameliorated by a tremendous research effort by different research groups. Numerous approaches have been developed to tackle these issues and the performances of polymers thus developed have been greatly enhanced. For example, various cross-linkable or high glass transition temperature polymers were developed to enhance the stability of dipole orientation at elevated temperatures. New chromophores with improved optical nonlinearity and thermal stability have been developed.[1,2,4−10] The origin of optical loss in some of the NLO polymers has been studied, which will help to design strategies to minimize it.[11] Among them, NLO functionalized aromatic polyimides[4,7,8,10] have shown promising potential in device applications because of their higher temperature alignment stability, better mechanical properties, and processability than other polymeric systems such as a cross-linking system and a guest−host NLO chromophore-polyimide system.

Covalent incorporation of NLO chromophores into an aromatic polyimide backbone enhances the chromophore's thermostability and material homogeneity, but it also introduces a decrease in the material's thermal stability compared to original polymeric backbone due to low chemical stable chromophore, and difficulty in polymer synthesis. Most of the functionalized NLO polyimides were prepared from the corresponding poly(amic acid)s via thermal treatments. It was reported[4,12] that polyimides derived from poly(amic acid)s exhibited the poor reproducibility of the optical quality including the optical propagation loss and side NLO chromophores also decomposed during the harsh imidization process at a high curing temperature.

Recently, we have synthesized several series of polyimides containing NLO chromophores by the easy ring-opening polyaddition of dianhydrides and nitrobenzothiazole azo (or diazo) *m*-phenylenediamine, and by the covalent binding of a chromophore onto the backbone of the fluorinated polyimide via a post-Mitsunobu reaction.[13] The resulting conclusions are that a high thermal stable NLO chromophore plays a critical role in defining the glass transition temperature of the final material and also that the harsh imidization process of the poly(amic acid) is avoided by introduction of the very mild Mitsunobu condensation, and the synthesis of the chromophore-containing diamine monomers is also not necessary. The resulting NLO polyimides were highly soluble in aprotic polar solvents, so the polymer solutions could be spin coated on the ITO glass or other substrates to form the optical quality thin films.

In this paper, we have synthesized three classes of novel NLO chromophores containing benzothiazole units (see Scheme 1) and then a series of polyimide-based second-order NLO materials were synthesized successfully from two kinds of fluorinated poly(hydroxy−imide)s, through the Mitsunobu reaction with NLO chromophores. Then we report detailed studies on the characterization of the polymers, as well as the thermal properties, the electrooptic properties, and other physical properties of the synthesized polymeric materials.

Results and Discussion

Very recently, we have synthesized a high thermal stable donor−π-bridge−acceptor chromophore, bearing

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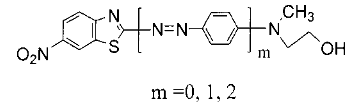
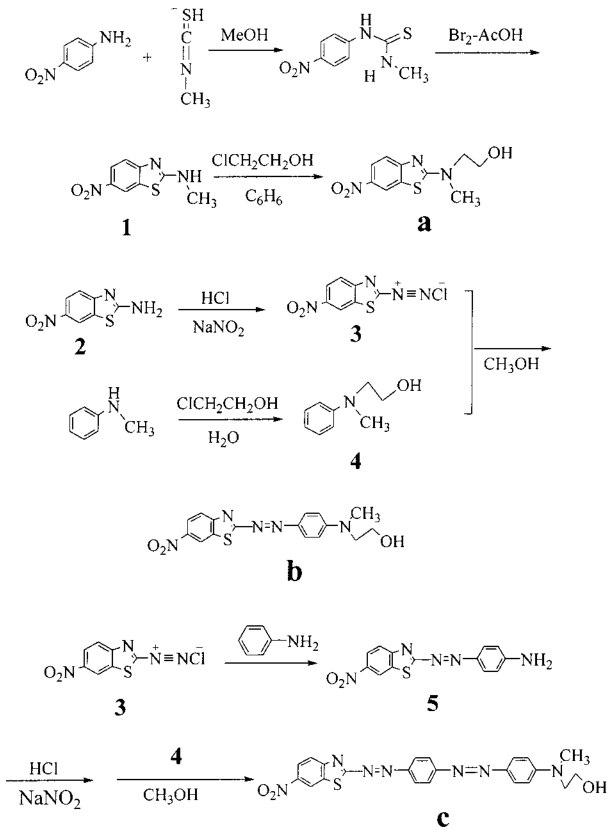
Scheme 1. Structures of Chromophores

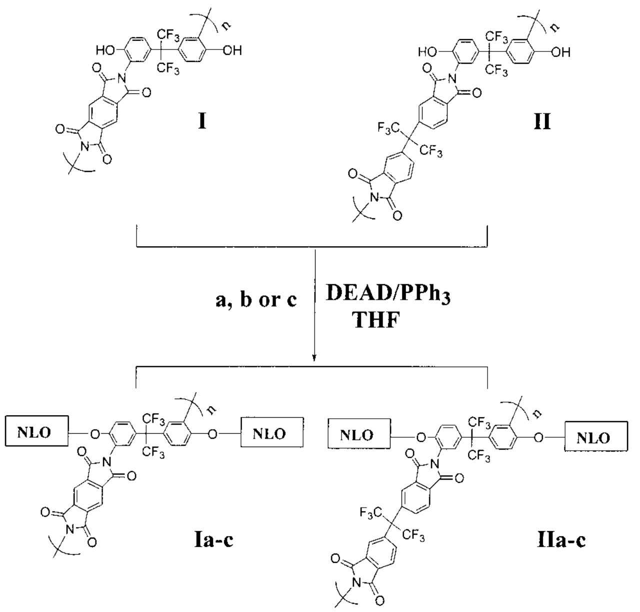


Scheme 2. Synthesis of Chromophores



a functional group, which was covalent linkaged to a polyimide backbone. Exceptional results were obtained wherein the chemical stability and optical nonlinearity of the chromophore will dramatically influence the corresponding properties of the terminal product. In this connection, the materials that we focus on in this paper utilize substituted benzothiazole as the π-bridge of donor−π-bridge−acceptor chromophores to improve thermal stability. 2-Substituted amino-6-nitrobenzothiazoles are most commonly synthesized via a two-step route.[14,15] This method, which we have used extensively in our laboratories involves the condensation of *p*-nitroaniline with thiocyanate in methanol and the bromine radical cyclization using bromine in acetic acid. In the case of the radical cyclization of the 2-methylamino- or 2-amino-6-nitrobenzothiazole, **1** or **2**, only one product was obtained, which is easily purified over column chromatography using neutral alumina (see Scheme 2). Chromophore **a** was prepared in good overall yield (89%) starting from the commercially chloroethanol under nitrogen atmosphere (Scheme 2), and the product, *N*-methyl-*N*-[4-(6-nitrobenzothizol-2-yl)]-2-aminoethanol including the hydroxy function, was recrystallized from mixture organic solvent. Preparations of chromophore **b** and **5** are outlined in Scheme 2. The syntheses start by utilizing the coupling reaction between the azonium salt of **3** with a solution of compound **4** or aniline in methanol, and the products were recrystallized from ethanol/water (1:1). The purified **5** was further coupled with **4** by a procedure similar to that for **b**, and diazo chromophore **c** with 68% yield was obtained.

Scheme 3. Synthesis of the NLO Polyimides



The polycondensation of hydroxypolyimide backbone **I** with **II** was carried in two steps: (1) polymerization of the hydroxydiamino monomer 2,2′-bis(3-amino-4-hydroxyphenyl)hexafluoropropane and the dianhydride 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6FAD) or the pyromellitic dianhydride (PMAD) to give hydroxy-containing poly(amic acid); (2) thermal imidization of the resulting poly(amic acid) solution. The monomers, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, and *N,N*-[5,5′-(hexafluoroisopropylidene)bis(2-hydroxyphenyl)]diphthalimide, were used in polymerization in order to enhance the solubility of the corresponding polymers in common organic solvents. Through the route as Scheme 3, the covalent bonding of the chromophore to the backbone of the polyimide can be easily carried out via the Mitsunobu reaction between the pendant hydroxy group on the chromophore and the phenol group on the polyimides. The elemental analysis values of the all compounds were generally in good agreement with the calculated values for the proposed structures.

All of the polymides we synthesized have good solubility in many common organic solvents, such as THF, DMF, DMAc, NMP, and even acetone, due to flexible $-CF_3$ groups in these polymers. It indicates that the incorporation of a fluorinated group into the polyimide backbone enhances its solubility. This illustrates that fluorinated polyimides can increase the solubility. Because of the good solubility of the polyimides in THF, the molecular weight can be measured by using gel permeation chromatography (GPC) (see Table 1.). Polymer **Ic**, for example, has a weight-average molecular weight (relative to polystyrene standards) M_n of 31 500 with a polydispersity index of 2.37.

Thermal properties of these polyimides were examined by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC) (see Figures 1 and 2). A differential branching structure analysis (TGA) on the obtained polyimides **Ia**−**c** and **IIa**−**c** was carried out as shown in Figure 1. It is obvious that the polyimides **Ib** and **Ic** and polyimide **IIc** show fairly good thermal stability. The polyimides **IIa**−**c**, however, are

Table 1. Physical Properties of Polyimides

polyimide	M_n	M_w	polydispersity	λ_m (nm)	T_g (°C)	T_d (°C)	T_{opt} (°C)	γ_{33} (pm/V)	loss percent (%)
Ia	32 000	69 500	2.17	420	204	388	204	9	18.9[a]
Ib	29 000	58 000	2.00	437	239	406	231	26	10.2[a]
Ic	31 500	74 500	2.37	468	247	423	248	29	13.1[b]
IIa	18 000	46 000	2.56	419	197	377	195	11	16.8[c]
IIb	22 000	44 500	2.02	437	210	395	213	24	10.9[a]
IIc	21 500	53 000	2.47	466	233	405	230	32	11.7[b]

[a] At 200 °C in the air for 120 h. [b] At 220 °C in the air for 120 h. [c] At 180 °C in the air for 120 h.

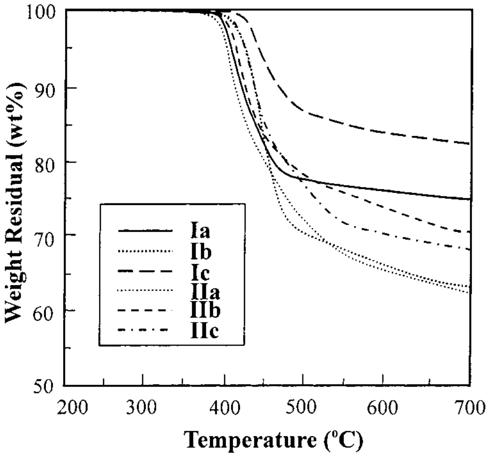


Figure 1. TGA traces of the NLO polyimides (20 °C/min).

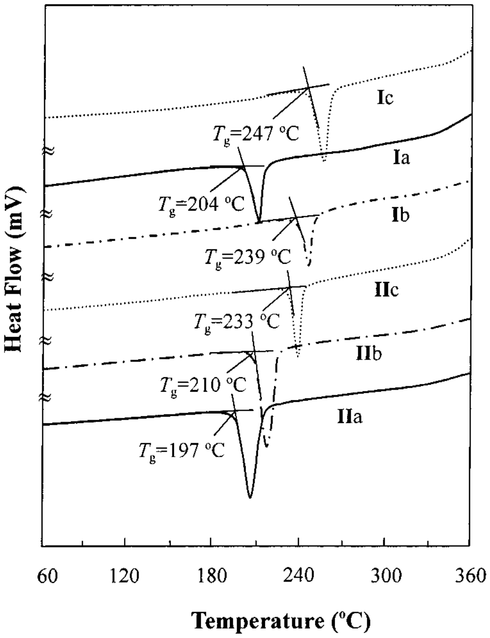


Figure 2. DSC diagrams of polymides with the heating rate of 10 °C/min under nitrogen atmosphere.

less thermally stable than the corresponding polyimides **Ia**−**c** with the same chromophore due to the flexible polyimide backbone. Furthermore, different results also lie in the same polyimide backbone with different chromophores. It is therefore anticipated that the thermal stability of the NLO chromophore improves the stability of the final NLO polymer. Nevertheless, polyimide **IIa** still had a temperature for the 5 wt % loss of over 400 °C in N_2. No thermal transitions have been detected between 60 and 190 °C in the DSC trace. The very high glass transition temperature (T_g∼247 °C) of **Ic** was determined, reflecting the stable NLO diazobenzothiazole structure and rigid polyimide backbone.

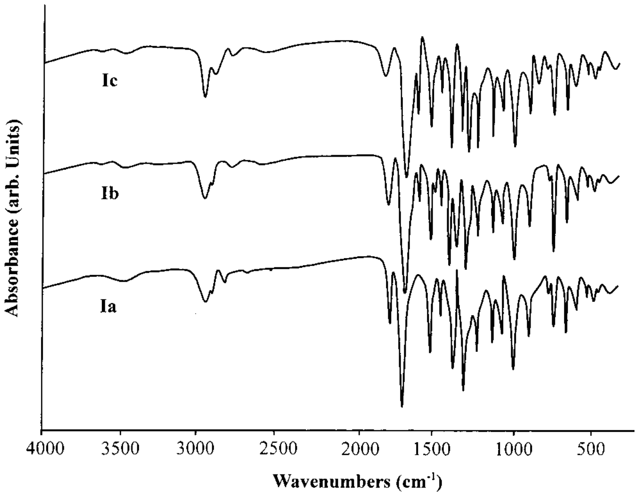


Figure 3. FTIR spectra of polyimides **Ia**−**c**

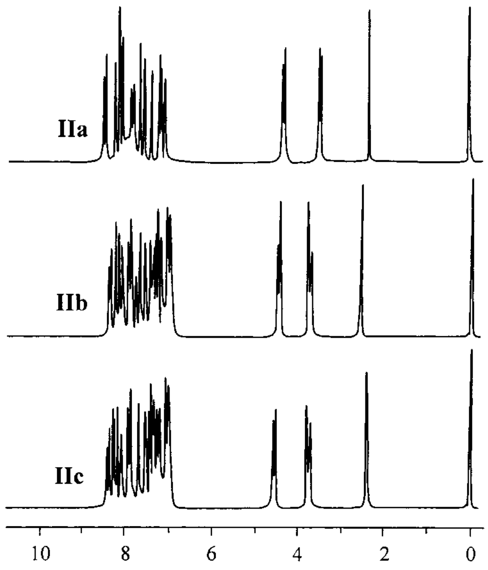


Figure 4. ^{1}H NMR spectra of the polyimides **IIa**−**c**

The structures of the polymers were confirmed by FTIR and ^{1}H NMR spectroscopy. For example, Figure 3 shows FTIR spectra of **Ia**−**c**. From the spectra, it is noted that the peaks of the characteristic imide absorption were at 1788, 1724, 1378, and 728 cm^{-1} and the absorption at 3400 cm^{-1} due to the hydroxy groups disappeared, together with obvious bands at 1350 and 1518 cm^{-1} due to the nitro group and the 1146 cm^{-1} band due to C=S function in the chromophore, which means a successful Mitsunobu condensation reaction. In Figure 4, ^{1}H NMR spectra of **IIa-c** are shown. The chemical shifts except for the −OH group due to NLO chromophore **b**, for instance, do not exhibit much change on going from chromophore **b** to terminal polymer **IIb**. However, changes in proton chemical shifts of the benzene ring bearing the NLO chromophore in polyim-

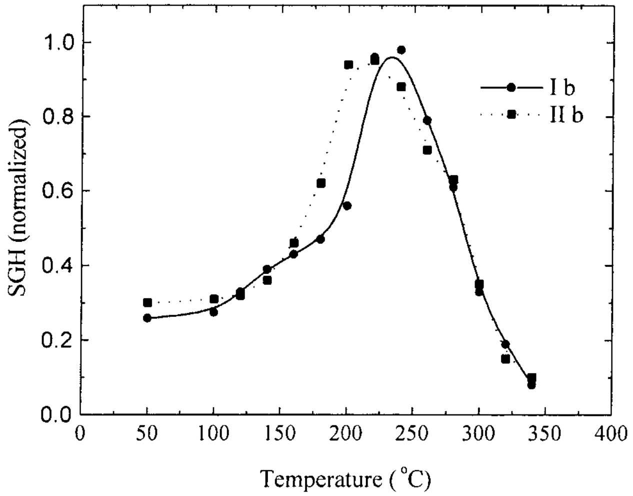


Figure 5. Second harmonic generation (SHD) signals of **Ib** and **IIb** (which select polymeric T_{opt}s) shown as a function of temperature.

ide backbone **II** are significant. In addition, hydroxy proton chemical shifts of both the hydroxypolyimide backbone and the chromophore all disppeared, where the spectral assignments clearly support the proposed structures.

High-quality films could be easily prepared from the polymer solutions in cyclopentanone by spin coating on ITO glass or other substrates. The UV−visible absorption maximum peaks of these polymeric films mainly result from $\pi-\pi^*$ electronic transitions of the NLO chromophores. A similar UV behavior suggests for the same chromophore that the absorption maximum wavelength of NLO polyimides might be affected a little by the stiffness of the backbone. Therefore, these analytical results clearly show the formation of polyimide-based NLO polymers by the incorporation of NLO chromophore into the polymer backbone with quantitative conversions after the Mitsunobu reaction.

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. As the set poling temperature increased step by step, the second harmonic generation (SHG) signal was detected at a different temperature after the temperature was held for 10−15 min. In this manner, the T_{opt}s of these polymers, for example, were obtained (see Figure 5.). For all materials, the SHG signals rose steadily before the T_{opt}s were reached, and then the SHG signals decreased rapidly 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 measured and were compared to the spectra of their poled films. The data of the maximum absorption wavelengths are listed in Table 1. The absorptions can be attributed directly to the spectra of the NLO chromophores. After electric poling, an absorbance decrease was observed for all of the films. This decrease is caused by the alignment of the chromophore dipoles[16] 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 **Ic** are shown upon unpole and poled films as well as the variation under 220 °C in Figure 6. In a like manner, the changes can explain that this series of materials possess a large alignment stability.

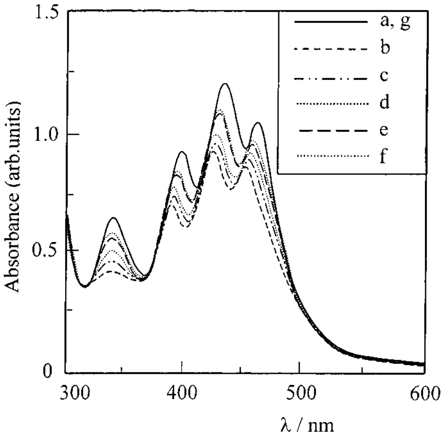


Figure 6. UV−vis absorption spectra of a spin-coated film of **Ic** for both poled (b−f) and unpoled (a, g) samples: (a) sample before poling (λ_{max} = 468 nm); (b) sample right after poling at room temperature (λ_{max} = 452 nm); (c) sample after 1 h at 240 °C (λ_{max} = 454 nm); (d) sample after 5 h at 240 °C (λ_{max} = 457 nm); (e) sample after a day at 240 °C (λ_{max} = 457.5 nm); (f) sample after a week at 240 °C (λ_{max} = 458 nm); (g) right sample at 240 °C (λ_{max} = 468 nm)

The electrooptic (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.[17] The test sample consists of a high-index prism, a thin silver film, a poled polymer layer, a buffer layer, and a base silver film. The silver film was thermally evaporated onto the hypotenuse face of a high-index prism as the first electrode. The thickness of the film was about 55 nm. A polyimide film was spin coated onto the silver substrate to a thickness of 1−2 μm, which can support four or five surface-plasmon modes with TE or TM polarization. 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 chromophore dopoles in a high static electric field while the polyimide was heated to high mobility close to its glass transition temperature. The poling voltage was 1500 V. Finally, another silver film was deposited onto the buffer layer as the second electrode. The highest γ_{33} values (32 pm/V) were observed with polyimide **IIc**, and the values retained >88.3% at 220 °C for more than 120 h (see Figure 7). Polyimides **Ic** exhibits higher γ_{33} values, and polyimides **Ia** and **IIa** have much smaller γ_{33} values (see Table 1).

In summary, we report the independent synthesis of three new high stable chromophores with high chemical stability and sizable molecular hyperpolarizabilities (β). With these three chromophores, a series of second-order nonlinear optical polyimides were successfully prepared from poly(hydroxy−imide)s, through the Mitsunobu reaction with NLO chromophores. Using in situ poling and temperature ramping technique, the optimal temperatures for corona poling were obtained. These materials exhibit relative large γ_{33} values (32 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 247 °C) of the polyimides increased accordingly. The solubility and the film-formability of the fluorine-contained polyimides were enhanced compared with those of polyimides previously

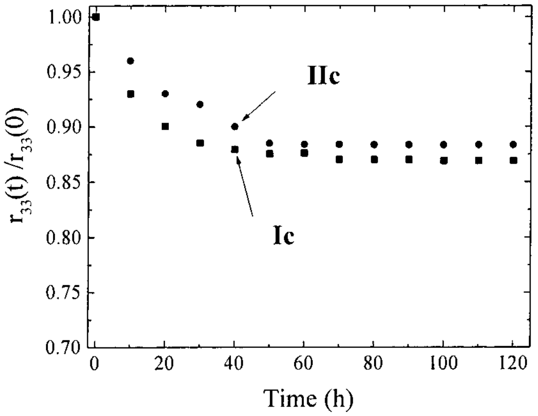


Figure 7. Temporal stability of EO properties of polyimide **Ic** and **IIc** at 220 °C in the air.

synthesized by us. The versatility of the reaction scheme and the ease of processing ensure this series of materials of further utilization.

Experimental Section

THF was purified by distillation over sodium chips and benzophenone. *N*-Methylpyridine (NMP) and dimethylformamide (DMF) were purified by distillation over phosphorus pentoxide. Pyromellitic dianhydride, 4,4′-(hexafluoroisopropylidene)diphthalic anhydride, and *N*,*N*-[5,5′-(hexafluoroisopropylidene)bis(2-hydroxyphenyl)]diphthalimide were purchased from TCI and used without further purification. All of the other chemicals were obtained commercially and were used as received unless otherwise stated.

The FTIR spectra were recorded as KBr pellets on a Nicolet Magna-IR 750 spectrometer. The ^{1}H 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−visble spectrophotometer was used to record the UV−visible spectral date. Thermal analyses were performed by using the SETARAM DSC-131 and TGA-DTA system from TA insteuments 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. m-Lines spectroscopy has been used to investigate TM and TE modes spectra of the optical films, and the experimental setup has been described elsewhere.[18,19] The electrooptic (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.[17]

Preparation of *N*-Methyl-*N*-[4-(6-nitrobenzothiazol-2-yl)]-2-aminoethanol (a). To a solution of a methyl isothiocyanate (0.01 mol) in dry MeOH (10 mL) was added an equimolar quantity of aromatic primary amine (0.01 mol) with stirring. The reaction mixture was heated on a steam bath for about 1 h, and then the solvent was distilled off. The solid residue that separated was treated with water, filtered, washed with the same, and dried. The resulting compounds were purified over neutral alumina using C_6H_6:EtOAc (9:1) to yield pure *N*-methyl-*N*′-(4-nitrobenzelene-1- yl)thiourea. *N*-methyl-*N*′-(4-nitrobenzelene-1-yl)thiourea (0.01 mol) was dissolued in acetic acid (15 mL), and the reaction mixture was cooled in an ice bath and then had bromine (1 mL) in acetic acid (10 mL) added dropwise. After about an hour, the mixture solution was poured on to crushed ice. The solid that separated was filtered, dried in each case and then purified over column chromatography using neutral alumina. It was eluted with C_6H_6:EtOAc (7:3) and the eluents on evaporation and crystallization yielded pure 2-*N*-(methylamino)-6-nitrobenzothiazole. Reaction of 2-*N*-(methylamino)-6-nitrobenzothiazole (5 mmol) with chloroethanol (6 mmol) was performed in 20 mL of ethanol. The mixture was refluxed for 4 h under nitrogen atmosphere and then was neutralized with 10% $NaCO_3$; the solid was filtered and dried. The resulting product was recrystallized, and purified *N*-methyl-*N*-[4-(6-nitrobenzothiazol-2-yl)]-2-aminoethanol (**a**) was obtained (Scheme 1). Reaction of *p*-nitroaniline with methyl isothiocuanate by refluxing in dry methanol for about 30 min, yielded an amorphous powder. It was chromatographed over neutral alumina using benzene:EtOAc (9:1) as an eluent resulting in a pure compound, *N*-methyl-*N*′-(4-nitrobenzelene-1-yl)thiourea, mp 105 °C. The FTIR spectrum (KBr) displayed absorption at 3150, 3110, and 1145 cm^{-1} which are assigned to NH, N′H, and C═S functions, respectively. The *N*-methyl-*N*′-(4-nitrobenzelene-1-yl)thiourea on reaction with bromine in acetic acid at room temperature and after the usual work up followed by column chromatography furnished a crystalline compound, mp 208 °C. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.52 (s, $-CH_3$, 3H), 3.69 (s, $-CH_2CH_2O-$, 2H), 4.26 (s, $-CH_2CH_2O-$, 2H), 7.22 (s, ArH, 1H), 7.73 (s, ArH, 1H), 8.01 (s, ArH, 1H), 9.88 (s, OH, 1H). Anal. Calcd for $C_{10}H_{11}N_3O_3S$: C, 47.43; H, 4.35; N, 16.60. Found: C, 47.58; H, 4.39; N, 16.71.

Preparation of *N*-Methyl-*N*-[4-[(6-nitrobenzothiazol-2-yl)diazenyl]phenyl]-2-aminoethanol (b). To a stirred solution of 2-amino-6-nitrobenzothiazole (5 mmol) in HCl/H_2O (1 N, 20 mL) was added sodium nitrite (5 mmol) at 0 °C. The mixture was stirred at this temperature for 1 h and then was added dropwise to *N*-methyl-2-anilinoethanol (5 mmol). The mixture was stirred at this temperature for 2 h, followed by stirring at 50 °C under N_2 atmosphere for 1 h. The resulting solid was collected by filtration and recrystallized from ethanol/water (1:1) to give a red crystal. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.48 (s, $-CH_3$, 3H), 3.71 (s, $-CH_2CH_2O-$, 2H), 4.24 (s, $-CH_2CH_2O-$, 2H), 7.12 (s, ArH, 1H), 7.31−7.40 (s, ArH, 4H), 7.84 (s, ArH, 1H), 8.00 (s, ArH, 1H), 9.86 (s, OH, 1H). Anal. Calcd for $C_{16}H_{15}N_5O_3S$: C, 53.78; H, 4.20; N, 19.61. Found: C, 53.82; H, 4.15; N, 19.54.

Preparation of 4-(*N*-2-Hydroxyethyl-*N*-methylamino)-4′-[(6-nitrobenzothiazol-2-yl)diazenyl]azobenzene (c). To 10 mL of a HCl (1 N) solution containing freshly prepared aniline (5 mmol) was added slowly an equal molar amount of 2-amino-6-nitrobenzothiazole diazonium salt in an ice bath with vigorous stirring for 1 h, followed by followed by stirring at 50 °C under N_2 atmosphere for 1 h, and then, the mixture was neutralized with ammonia water. After being stirred for 0.5 h, the precipitate was filtered and dried. The crude product was recrystallized from acetone and purified product 4-amino-4′-(6-nitrobenzothiazol-2-yl) azobenzene was obtained. 4-(*N*-2-Hydroxyethyl-*N*-methylamino)-4′-[(6-nitrobenzothiazol-2-yl)-diazenyl] azobenzene was synthesized as (**b**). ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.47 (s, $-CH_3$, 3H), 3.70 (s, $-CH_2$-CH_2O-, 2H), 4.21 (s, $-CH_2CH_2O-$, 2H), 7.16 (s, ArH, 1H), 7.28−7.45 (s, ArH, 8H), 7.85 (s, ArH, 1H), 8.03 (s, ArH, 1H), 9.88 (s, OH, 1H). The resulting solid was recrystallized from ethanol to give a red crystal. Anal. Calcd for $C_{22}H_{19}N_7O_3S$: C, 57.27; H, 5.32; N, 27.45. Found: C, 57.33; H, 5.36; N, 27.49.

Synthesis of Hydroxy-Containing Polyimide (I) Based on 5,5′-(Hexafluoroisopropylidene)bis(2-aminophenol) and Promellitic Dianhydride. The polymerization was conducted in a dry nitrogen-flushed flask at room temperature with a concentration of 15% solids by weight in DMF. A stoichiometric amount of pyromellitic dianhydride was added to a solution of *N*,*N*-[5,5′-(hexafluoroisopropylidide)bis(2-hydroxyphenyl)diphthalimide in DMF at 0 °C. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly(amic acid) solution. The viscosity of the solution increased during this period greatly. Dry xylene was added to the flask, and the poly(amic acid) was thermally cyclized at 160 °C for 3 h. Water that was eliminated by the ring-closure reaction was separated as a xylene azeotrope at the same time. The resulting solution was added dropwise into an agitated solution of methanol and 2 N HCl to obtain the brown hydroxy polyimide. The polymer was redissolved in THF and further purified by reprecipitating into a solution of methanol and 2 N HCl from its THF solution. The polymer was then filtered and dried at 60 °C under vacuum for 24 h to afford the hydroxy polyimide **I**. ^{1}H NMR (DMSO-d_6, ppm): 7.10 (d, ArH, 2H, J = 8.7 Hz), 7.33 (d, ArH, 2H, $J = 8.7$ Hz), 7.61 (s, ArH, 2H), 8.32 (s, ArH, 2H),10.63 (s, OH, 2H). Anal. Calcd for $C_{25}H_{10}N_2F_6O_6$: C, 54.74; H, 1.82; N, 5.11. Found: C, 54.83; H, 1.76; N, 5.14.

Synthesis of a Hydroxy-Containing Polyimide (II) Based on 5,5′-(Hexafluoroisopropylidene)bis(2-aminophenol) and 4,4′-(Hexafluoroisopropylidene)diphthalic Anhydride. A stoichiometric amount of 4,4′-(hexafluoroisopropylidene)diphthalic anhydride was added to a solution of *N*,*N*-[5,5′-(hexafluoroisopropylidede)bis(2-hydroxyphenyl)-diphthalimide in NMP at 0 °C. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly(amic acid) solution. The viscosity of the solution increased during this period greatly. Dry xylene was added to the flask, and the poly(amic acid) was thermally cyclized at 160 °C for 3 h. Water that was eliminated by the ring-closure reaction was separated as a xylene azeotrope at the same time. The resulting solution was added dropwise into an agitated solution of methanol and 2 N HCl to obtain the brown hydroxy polyimide. The polymer was redissolved in THF and further purified by reprecipitating into a solution of methanol and 2 N HCl from its THF solution. The polymer was then filtered and dried at 60 °C under vacuum for 24 h to afford hydroxy polyimided **II**.^{1}H NMR (300 MHz, DMSO-d_6, ppm): 7.10 (d, $J = 8.7$ Hz, ArH, 2H), 7.32 (d, $J = 8.7$ Hz, ArH,-2H), 7.60 (s, ArH, 2H), 8.33 (s, ArH, 2H), 8.36 (d, $J = 8.1$ Hz, ArH, 2H), 8.42 (d, $J = 8.1$ Hz, ArH, 2H), 10.66 (s, OH, 2H). Anal. Calcd for $C_{34}H_{14}F_{12}N_2O_6$: C, 52.68; H, 1.81; N, 3.62. Found: C, 52.83; H, 1.76; N, 3.64.

Synthesis of Polyimides Ia−c. A general procedure for the synthesis of side-chain polyimides **Ia**−**c** is as follows. Hydroxypolyimide **I** (1.50 mmol), PPh_3 (1.50 mmol), and 4-(*N*-2-hydroxyethyl-*N*-methylamino)-4′-nitroazobenzene (1.10 mmol) were dissolved in dry THF (15 mL) successively. Diethyl azodicarboxylate (DEAD) (1.50 mmol) was added dropwise into the solution under nitrogen atmosphere. The reaction mixture was stirred for 2 days at room temperature and then refluxed for 0.5 h. The resulting reaction solution was added dropwise into an agitated solution of methanol/water (300 mL, 1:1) and 2 N HCl (5 mL) in a high-speed blender. The collected solid further precipitated in THF (10 mL) and reprecipitated into the solution of methanol/water. The product **Ia** was filtered out and washed with methanol/water for several times, and dried at 60 °C under vacuum for 24 h. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.47 (s, $-CH_3$, 6H), 3.67 (s, $-CH_2CH_2O-$, 4H), 4.55 (s, $-CH_2CH_2O-$, 4H), 7.10 (s, ArH, 2H), 7.13 (d, $J = 8.1$ Hz, ArH, 2H), 7.42 (s, ArH, 2H), 7.48 (s, ArH, 2H), 7.56 (s, ArH, 2H), 8.14 (d, $J = 8.1$ Hz, ArH, 2H), 8.28 (s, ArH, 2H). Anal. Calcd for $C_{45}H_{28}F_6N_8O_{10}S_2$: C, 53.05; H, 2.75; N, 11.00. Found: C, 53.12; H, 2.80; N, 10.97.

Polyimide **Ib** was synthesized by a procedure similar to that for polyimide **Ia** by using azo chromophore **b** instead of **a**. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.51 (s, $-CH_3$, 6H), 3.76 (s, $-CH_2CH_2O-$, 4H), 4.51 (s, $-CH_2CH_2O-$, 4H), 7.11 (d, $J = 8.1$ Hz, ArH, 2H), 7.30−7.42 (s, ArH, 8H), 7.49 (s, ArH, 2H), 7.52 (s, ArH, 2H), 7.64 (s, ArH, 2H), 7.79 (m, ArH, 2H), 8.19 (d, $J = 8.1$ Hz, ArH, 2H), 8.38 (s, ArH, 2H). Anal. Calcd for $C_{57}H_{36}F_6N_{12}O_{10}S_2$: C, 55.79; H, 2.94; N, 13.70. Found: C, 55.83; H, 2.99; N, 13.67.

Polyimide **Ic** was synthesized by a procedure similar to that for polyimide **Ia** by using azo chromophore **c** instead of **a**. ^{1}H NMR (300 MHz, DMSO-d_6, ppm): 2.44 (s, $-CH_3$, 6H), 3.78 (s, $-CH_2CH_2O-$, 4H), 4.49 (s, $-CH_2CH_2O-$, 4H), 7.14 (d, $J = 8.1$ Hz, ArH, 2H), 7.23−7.47 (s, ArH, 16H), 7.55 (s, ArH, 2H), 7.58 (s, ArH, 2H), 7.75 (s, ArH, 2H), 7.96 (s, ArH, 2H), 8.15 (s, ArH, 2H), 8.29 (d, $J = 8.1$ Hz, ArH, 2H). Anal. Calcd for $C_{69}H_{44}F_6N_{16}O_{10}S_2$: C, 57.74; H, 3.07; N, 11.16. Found: C, 57.79; H, 3.11; N, 11.14.

Synthesis of Polyimides IIa−c. A general procedure for the synthesis of side-chain polyimide **IIa**−**c** is as follows. Hydroxypolyimide **II** (1.50 mmol), PPh_3 (1.50 mmol), and 4-(*N*-2-hydroxyethyl-*N*-methylamino)-4′-nitroazobenzene (1.10 mmol) were dissolved in dry THF (15 mL) successively. Diethyl azodicarboxylate (DEAD) (1.50 mmol) was added dropwise into the solution under nitrogen atmosphere. The reaction mixture was stirred for 2 days at room temperature and then refluxed for 0.5 h. The resulting reaction solution was added dropwise into an agitated solution of methanol/water (300 mL, 1:1) and 2 N HCl (5 mL) in a high-speed blender. The collected solid further precipitated in THF (10 mL) and reprecipitated into the solution of methanol/water. The product **IIa** was filtered out and washed with methanol/water for several times and dried at 60 °C under vacuum for 24 h. Anal. Calcd for $C_{54}H_{32}F_{12}N_8O_{10}S_2$: C, 52.09; H, 2.57; N, 9.00. Found: C, 52.12; H, 2.60; N, 8.96.

Polyimide **IIb** was synthesized by a procedure similar to that for polyimide **IIa** by using azo chromophore **b** instead of **a**. Anal. Calcd for $C_{66}H_{40}F_{12}N_{12}O_{10}S_2$: C, 54.55; H, 2.75; N, 11.57. Found: C, 54.62; H, 2.77; N, 11.59.

Polyimide **IIc** was synthesized by a procedure similar to that for polyimide **IIa** by using azo chromophore **c** instead of **a**. Anal. Calcd for $C_{78}H_{48}F_{12}N_{16}O_{10}S_2$: C, 56.39; H, 2.89; N, 13.49. Found: C, 56.44; H, 2.85; N, 13.51.

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References and Notes

(1) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31.
(2) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155.
(3) Dagani, R. *Chem. Eng. News* **1996**, March 4, 22.
(4) Yu, L. P.; Chan, W. K.; Bao, Z. N. *Macromolecules* **1992**, *25*, 5609.
(5) Peng, Z. H.; Yu, L. P. *Macromolecules* **1994**, *27*, 2638.
(6) Yang, S. Y.; Peng, Z. H.; Yu, L. P. *Macromolecules* **1994**, *27*, 5858.
(7) Yu, D.; Yu, L. P. *Macromolecules* **1994**, *27*, 6718.
(8) Yu, D.; Gharavi, A.; Yu, L. P. *Macromolecules* **1995**, *28*, 784.
(9) Xu, C.; Wu, B.; Todorova, O.; Dalton, L. R.; Shi, Y. Q.; Ranon, P. M.; Steier, W. H. *Macromolecules* **1995**, *26*, 5303.
(10) Verbrest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volkwen, W. *Macromolecules* **1995**, *28*, 3005.
(11) Teng, C. C.; Mortazavi, M. A.; Boudoughian, G. K. *Appl. Phys. Lett.* **1995**, *66*, 667.
(12) Marder, S. R.; Perry, J. W. *Science* **1994**, *263*, 1706.
(13) Mitsunobu, O. *Synthesis* **1981**, January, 1.
(14) Hunter, R. F.; Jones, J. W. T. *J. Chem. Soc.* **1930**, 2190.
(15) Ambati, N. B.; Anand, V.; Hanumanthu, P. *Synth. Commun.* **1997**, *27*, 1487.
(16) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dianes, A. *J. Opt. Soc. Am. B* **1989**, *6*, 733.
(17) Jiang, Y.; Cao, Z. Q.; Shen, Q. S.; Dou, X. M.; Chem, Y. L. *J. Opt. Soc. Am. B* **2000**, *17*, 508.
(18) Boudiombo, J.; Baehr, O.; Boudrioua, A.; Thevenin, P.; Loulergue, J. C.; Bath, A. *Mater. Sci. Eng.* **1997**, *B46*, 96.
(19) Tien, P. K.; Ulrich, R. *J. Opt. Sci. Am.* **1970**, *60*, 1325.

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