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Synthesis of nonlinear optical side-chain soluble polyimides for electro-optic applications

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Abstract

Some thermal stable fluorine-containing polyimides with side-chain second-order nonlinear optical (NLO) chromophores have been developed, which were prepared by one preimidized, hydroxyl polyimide, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via the Mitsunobu condensation, and the chromophore loading level in the polyimide was controlled efficiently by weight percent. Detailed physical properties showed that the resulting polyimides have good solubility in common organic solvents, relative high glass transition temperatures. Polymer waveguide devices can be easily spin-coated, ensuring a long-term alignment stability at elevated temperatures. These devices exhibit large electro-optic coefficients, 25 pm V^{-1} at 0.83 μm, which retained >95% at 120°C for more than 100 h. © 2001 Published by Elsevier Science Ltd.

Keywords: Fluorine-containing polyimide; Nonlinear optics; Electro-optic coefficient

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1. Introduction

Over the past several years, some research groups have synthesized numerous polyimides functionalized with nonlinear optical (NLO) chromophores, due to their large electro-optic (EO) coefficients, low dielectric constants desirable for high-speed devices, and flexibility in fabrication [1–4]. Recently, Jen and co-workers [5,6] reported a facile, generally applicable, two-step approach for the synthesis of NLO side-chain polyimides. This is a one-pot preparation of a preimided hydroxy-containing polyimide, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via the Mitsunobu reaction [7]. By the introduction of the chromophore at the last stage through very mild Mitsunobu condensation, the chromophore-containing diamine synthesis and the harsh imidization process of the poly(amic acid) are avoided.

In order to create a polymer waveguide material, excellent solubility, high stability, large EO coefficient, and good processability, i.e. film-formability, are particularly required. Aromatic polyimide is one of the most important classes of high-performance polymers. However, previous aromatic polyimides are restricted because of their poor solubility in organic solvents and high soften temperature. Therefore, preparation of soluble or thermoplastic polyimides has been a major research interest. When fluorine atoms (or groups containing these atoms) are incorporated into the polyimide structure, some additional properties are improved, e.g. solubility, the dielectric constant and optical losses are all reduced. In addition, the color of the polyimide becomes lower so that partially fluorinated polyimides can be used to decrease optic losses in the usage wavelength region (0.8–1.6 μm).

In this paper, we synthesized a novel chromophore and a hydroxyl polyimides based on the fluorine-containing monomers 4,4′-(hexafluoroisopropylidene) diphthalic anhydride (6FDA) and 2,2′-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via the Mitsunobu reaction. Then, we report detailed studies on the characterization of the polymers, as well as the thermal properties, the EO and other physical properties of the synthesized polymeric materials.

2. Experimental

N,*N*-dimethylacetamide (DMAc) were 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

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monomers, 6FDA and 2,2′-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane used in the polyimide synthesis were obtained from TCI and used without further purification.

*2.1. Synthesis of an NLO chromophore **3***

To a stirred solution of *p*-nitroaniline (13.81 g, 0.10 mol) in methanol/HCl (1:1, 60 ml) was added sodium nitrite (7.59 g, 0.11 mol) in ice-water (15%, m/m) at 0°C. The mixture was stirred at this temperature for 1 h, and then the mixture was added dropwise into a solution of *N*-2-hydroxyethyl-*N*-methylaniline (15.10 g, 0.10 mol) with abundance HAc–NaAc. The mixture was stirred at this temperature for 0.5 h, followed by stirring at 40–50°C for 20 min. The mixture solution was cooled down and placed for 2 h, and the solid was collected by filtration and further recrystallized from toluene/methanol (4:1) to give a bright green crystal **3** with 86% yield. ^{1}H NMR (300 MHz, acetone-d_6, ppm): 2.48 (s, –CH_3, 3H), 3.71 (s, –CH_2CH_2O–, 2H), 4.20 (s, –CH_2CH_2O–, 2H), 7.23–7.95 (m, ArH, 8H), 9.54 (s, 1H, OH). Anal. calcd for $C_{15}H_{16}N_4O_3$: C, 59.80%; H, 5.32%; N, 18.40%. Found: C, 59.93%; H, 5.26%; N, 18.45%.

2.2. Hydroxyl polyimide synthesis

The polymerization was conducted in a dry nitrogen-flushed three-neck flask with a magnetic stirrer, reverse Dean–Stark trap, and reflux condenser filled dry xylene. A stoichiometric amount of 6FDA (3.332 g, 7.50 mmol) was added to a solution of 2,2′-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane (2.747 g, 7.50 mmol) in 30 ml DMAc at 0°C. The solution was then warmed to room temperature and magnetically stirred overnight under nitrogen to form the poly(amic acid) solution. Dry xylene (30 ml) was added to the flask, and the poly(amic acid) was thermally cyclized in an oil bath at 160°C for 5 h under nitrogen atmosphere. The resulting solution was added dropwise into a solution of methanol/water (1:1, 500 ml) and 2N HCl (10 ml) in a high-speed blender to obtain the light-yellow hydroxyl polyimide **4**. The polymer was redissolved in THF, and further reprecipitated into a solution of methanol/water (1:1). The product was collected by filtration, washed by above solution for three times, and dried at 60°C under vacuum for 24 h. ^{1}H NMR (300 MHz, acetone-d_6, ppm): 7.10 (d, ArH, 2H), 7.32 (d, ArH, 2H), 7.60 (s, ArH, 2H), 8.33 (s, ArH, 2H), 8.36 (d, ArH, 2H), 8.42 (d, ArH, 2H), 8.46 (s, ArH, 2H), 10.66 (s, OH, 2H). Anal. calcd for $C_{34}H_{14}F_6N_2O_6$: C, 52.68%; H, 1.81%; N, 3.62%. Found: C, 52.83%; H, 1.76%; N, 3.64%.

2.3. Synthesis of side-chain polyimide based on 6FDA

A general procedure for the synthesis of side-chain polyimide **4a–c** is as follows. Hydroxyl polyimide **4** (0.387 g, 0.50 mmol), PPh_3 (0.393 g, 1.50 mmol) and 4-(*N*-2-hydroxyethyl-*N*-methylanino)-4′-nitroazobenzene (0.301 g, 1.00 mmol) were dissolved in dry THF (15 ml) successively. Diethyl azodicarboxylate (DEAD) (0.260 g, 1.50 mmol) was added dropwise into the solution under nitrogen atmosphere. The reaction mixture was stirred for 2 days at room temperature, then the resulting reaction solution was added dropwise into an agitated solution of methanol/water (300 ml, 1:1) and 2N 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 **4a** 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, acetone-d_6, ppm): 1.06 (s, –CH_3, 6H), 3.61 (s, –CH_2CH_2O–, 4H), 4.19 (s, –CH_2CH_2O–, 4H), 7.12 (d, ArH, 2H), 7.40 (d, ArH, 2H), 7.64 (s, ArH, 2H), 7.90 (m, ArH, 16H), 8.38 (d, ArH, 2H), 8.40 (d, ArH, 2H), 8.42 (s, ArH, 2H). Anal. calcd for $C_{64}H_{42}N_{10}F_{12}O_{10}$: C, 57.28%; H, 3.13%; N, 10.44%. Found: C, 57.42%; H, 3.15%; N, 10.38%.

Side-chain polyimide **4b** and **c** were synthesized by a procedure similar to the polymer **4a**. For **4b**, 1.20 mmol DEAD was added in 15 ml dry THF with 0.50 mmol **4**, 1.20 mmol PPh_3 and 0.75 mmol 4-(*N*-2-hydroxyethyl-*N*-methylanino)-4′-nitroazobenzene. For **4c**, 0.80 mmol DEAD was added in 15 ml dry THF with 0.50 mmol **4**, 0.80 mmol PPh_3 and 0.50 mmol 4-(*N*-2-hydroxyethyl-*N*-methylanino)-4′-nitroazobenzene.

4b ^{1}H NMR (300 MHz, acetone-d_6, ppm): 1.06 (s, –CH_3), 3.64 (s, –CH_2CH_2O–,), 4.21 (s, –CH_2CH_2O–), 7.09 (d, ArH), 7.43 (d, ArH), 7.67 (s, ArH), 7.88 (s, ArH), 8.38 (d, ArH), 8.40 (d, ArH), 8.43 (s, ArH), 10.48 (m, OH). Anal. calcd for $C_{56.5}H_{35}F_{12}N_8O_9$: C, 56.54%; H, 2.92%; N, 9.34%. Found: C, 56.62%; H, 2.87%; N, 9.45%.

4c ^{1}H NMR (300 MHz, acetone-d_6, ppm): 1.05 (s, –CH_3, 3H), 3.65 (s, –CH_2CH_2O–, 2H), 4.18 (s, –CH_2CH_2O–, 2H), 7.12 (d, ArH, 2H), 7.40 (d, ArH, 2H), 7.64 (s, ArH, 2H), 7.92 (s, ArH, 8H), 8.38 (d, ArH, 2H), 8.40 (d, ArH, 2H), 8.42 (s, ArH, 2H), 10.53 (s, 1H, OH). Anal. calcd for $C_{49}H_{28}F_{12}N_6O_8$: C, 55.60%; H, 2.65%; N, 7.94%. Found: C, 55.71%; H, 2.62%; N, 7.88%.

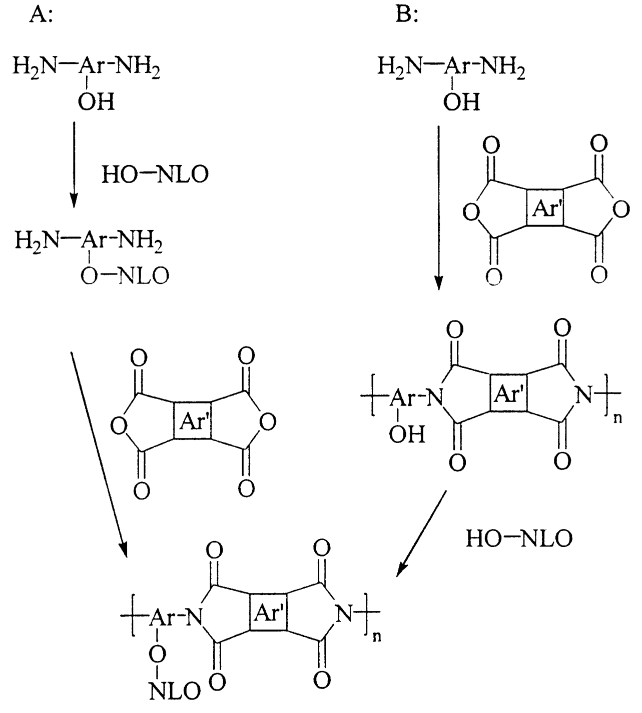
2.4. Measurement

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–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. *m*-Lines spectroscopy has been used to investigate transverse magnetic (TM) and transverse electric (TE) modes spectra of the optical films, and the experimental set-up has been described elsewhere [8,9]. The EO coefficient measurements of our polyimides were performed at a wavelength of 0.83 μm with an experimental set-up similar to that described by Jiang et al. [10].

3. Results and discussion

3.1. Synthesis

In the past decade, several synthetic routes for the side-chain NLO polyimides have been developed through chromophore-containing diamine synthesis by Yu et al. [11–14] and Miller and co-workers [15] and through Mitsunobu reaction with preimidized hydroxy-containing polyimides by Jen and co-workers [5,6]. Their routes are shown in Scheme 1 (two kinds of synthetic route of polyimides). For route A, it is necessary to prepare the chromophore-containing diamine monomers by multistep synthesis and to carry the chromophore all the way through the processes of polymerization and imidization of the poly(amic acid)s. The conditions of both the monomer synthesis and the polymerization may destroy the chromophore, which strongly limits the application of the techniques. But route B is a one-pot preparation of a preimidized, hydroxy-containing polyimide, followed by the covalent bonding of a chromophore onto the backbone of the polyimide via a mild Mitsunobu condensation, by which the troublesome synthesis of diamine monomer and the harsh imidization processes are avoided. Thus, a similar approach to route B employed to prepare the side-chain NLO polyimides.



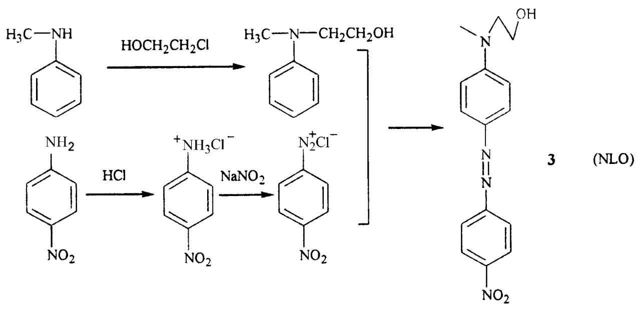
Scheme 1.

The synthetic route for an NLO chromophore, 4-(*N*-2-hydroxyethyl-*N*-methylanino)-4′-nitroazobenzene, which was prepared by the azo coupling of *p*-nitroaniline with *N*-2-hydroxyethyl-*N*-methylaniline, is outlined in Scheme 2 (synthesis of chromophore). The polycondensation of hydroxyl polyimide backbone was carried in two steps: (1) polymerization of hydroxyl diamino monomer 2,2′-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane and dianhydride 6FDA to give hydroxy-containing polyamic acid; (2) thermal imidization of the resulting poly(amic acid) solution. The monomers, **1** and **2**, were used in polymerization in order to enhance the solubility of the corresponding polymers in common organic solvents, such as THF and acetone. It indicates that the incorporation of fluorinated group into polyimide backbone enhances its solubility. Due to the resulting polymer's excellent solubility, the precipitation must be in the mixture solution of methanol and water.

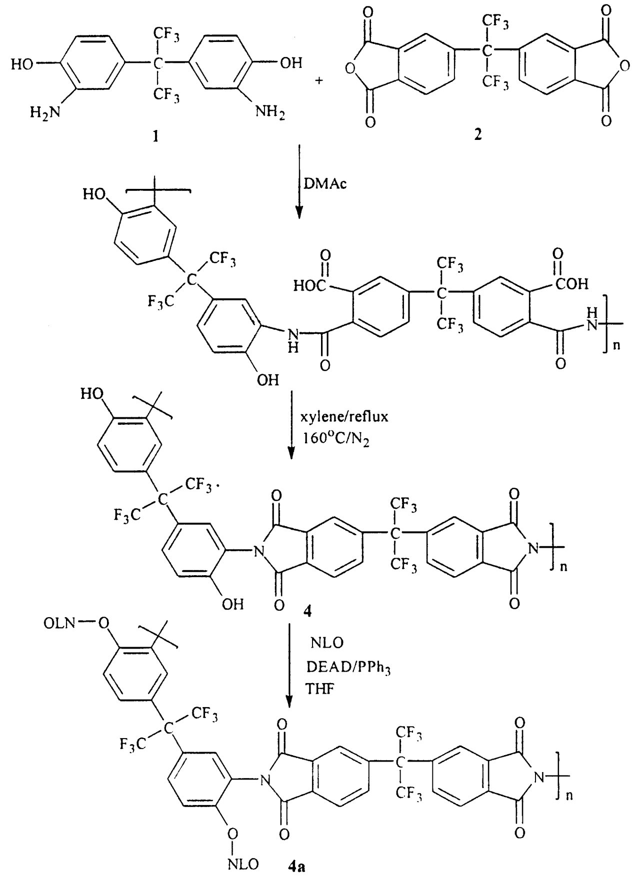
Through the route B (Scheme 3: synthesis of side-chain polyimide **4a**), the covalent bonding of the chromophore to the backbone of the polyimide can be easily via the Mitsunobu reaction between the pendant hydroxy group on the chromophore and the phenol group on the polyimides. The very mild conditions of the reaction provide us great flexibility in the alteration of the chromophore weight percent (Scheme 4: control of the chromophore loading level and the density of the intact OH group). In Table 1, the results of chromophore-containing polyimides synthesis are listed. Polyimide **4** was reacted with 1.0 equiv. (relative to the equivalent hydroxy group of the repeat units of the polymer) of terminal hydroxy group on the chromophores in THF solvent to produce side-chain polyimide **4a** with quantitative yield at room temperature. **4b** and **c** were obtained by the similar process, only polyimide **4** was reacted with 0.75 and 0.5 equiv. of terminal hydroxy group on the chromophores, respectively.

3.2. Thermal properties of functionalized polyimides

Thermal properties of these polyimides were examined by DSC and TGA measurements. DSC studies indicated that as the loading level of NLO chromophore decreased, the glass transition temperature (T_g) of the polyimide increased from 180 to 191°C (Table 1). But the glass transition



Scheme 2.



Scheme 3.

temperature of hydroxy-containing polyimide **4** was above 260°C. TGA trace (Fig. 1) showed that these polyimides have decomposition temperature (T_d) in the range of 250–280°C, which represents the decomposition of the NLO chromophore from the polymer backbone. These results support the following argument: as the NLO chromophore loading levels increase, the weight loss increases accordingly [16].

3.3. Polymer characterization

All of the NLO side-chain polyimides were soluble in organic solvents such as THF, DMF, acetone, γ-butyrolactone, and cyclopentanone. High-quality films could be easily prepared from the polymer solutions in cyclopentanone by spin-coating on substrates. The molecular weights of the polymers can thus be estimated by GPC. Polymer **4a**, for example, has a weight average molecular weight (relative to polystyrene standards) M_n of 20,800 with a polydispersity index of 2.0. The hydroxy-containing polyimide **4** has a M_n of 12,000, an M_w of 37,000 and a polydispersity of 3.1.

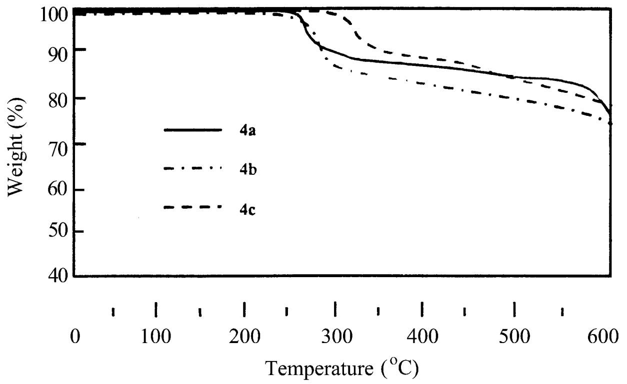


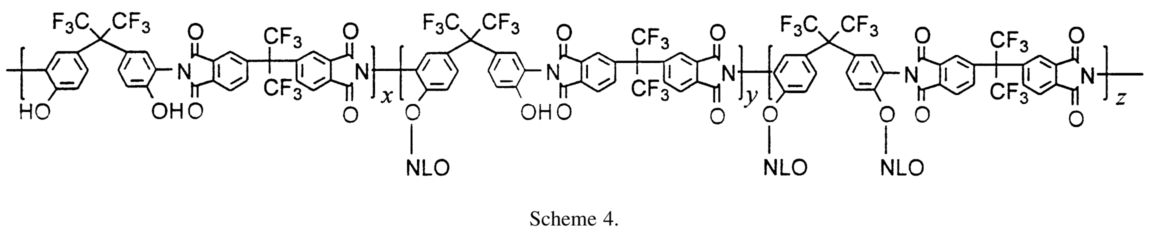
Fig. 1. TGA curves of polyimides **4a**–**c**.

The FTIR spectrum of polyimide **4** clearly showed the characteristic imide absorption at 1788, 1724, 1378 and 728 cm^{-1} as well as a broad absorption at 3400 cm^{-1} due to the phenolic hydroxy groups. After the Mitsunobu condensation for covalent bonding of the chromophores onto the polymer backbone, the new bands at 1350 and 1518 cm^{-1} due to the nitro group in the chromophore appeared. Meanwhile, the strength of the OH absorption was significantly reduced after approximately 50% of the OH groups in polymer **4** reacted with the chromophore **3** (polyimide **4c**, Fig. 2). The OH absorption almost disappeared and the NO$_2$ bands became much more intense in the spectrum of polyimide **4a** (Fig. 2), which corresponded to a more complete condensation between the OH groups in **4** and the hydroxyl chromophores.

The results of the UV–Vis study of these polyimides showed an absorption maximum at 479 nm due to the π–π* transition in the NLO chromophore (Table 1). Fig. 3 shows the ^{1}H NMR spectra of polyimide **4c** and OH chemical shift of all the polyimides where the spectral assignments clearly support the proposed structures.

3.4. Electro-optical properties

The test sample, which is shown in cross-section in Fig. 4, consists of 1, a high-index prism; 2, a thin silver film; 3, a poled polymer layer; 4, a buffer layer; 5, a base silver film. The silver film was thermally evaporated onto the hypotenuse



Scheme 4.

Table 1
Physical properties of polyimides

Polyimide	M_n	M_w	Polydispersity	λ_m (nm)	T_g (°C)	T_d (°C)	γ_{33} (pm V^{-1})
4a	20,800	41,500	2.0	479	180	250	25
4b	18,600	39,000	2.1	478	185	260	21
4c	16,300	35,800	2.2	479	191	280	13
4	12,000	37,000	3.1		260	350	

face of a high-index prism (ZF6) as the first electrode. The thickness of the film was about 55 nm. A active 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. The polyimide film was also fabricated on a glass substrate under the same conditions and the film thickness was measured with a Sloan Technology DEKTAK profiler using the film on the glass. Each film thickness in the subsequent was determined by the same method. A polymer buffer layer (Akzo Nobel PC, provided by Akzo Nobel) was then coated onto the polyimide film to a thickness of 4 μm or so. Corona discharge poling was performed by the alignment of the chromophore dipoles 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 EO coefficients of our polymeric samples were obtained at a wavelength of 0.83 μm with a similar measurement described in Ref. [10]. The highest γ_{33} value (25 pm V^{-1}) was observed with polyimide **4a**. Polyimide **4b** exhibits higher γ_{33} value and polyimide **4c** has much smaller γ_{33} value (see Table 1). This correlation between γ_{33} and the NLO chromophore density can be explained: the bulk nonlinearity is linearly proportional to the concentration of the NLO chromophore if the chromophore order parameter is similar in different samples.

The thermal alignment stability of these polyimides was investigated by in situ EO coefficients measured using the heater mounted sample holder. Fig. 5 shows the long-term stability of the EO coefficients of the polyimide **4a** at 120°C, and the value retained >95% for more than 100 h. The initial values of polyimides **4b** and **4c** decayed by ca. 10 and 12%, respectively, at 120°C after 100 h. These thermal characteristics are an indication that these polymers may be useful in photonic device applications.

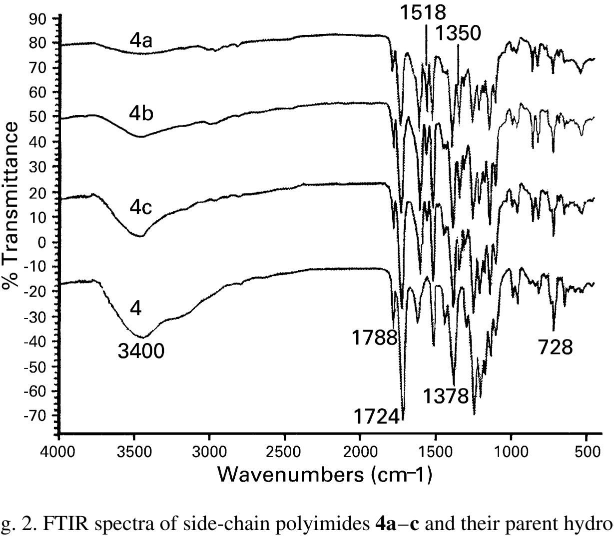


Fig. 2. FTIR spectra of side-chain polyimides **4a–c** and their parent hydroxylpolyimide **4**.

4. Conclusion

We have prepared the new fluorine-containing hydroxyl polyimide which owns excellent solubility in common organic solvents, and then, a novel NLO chromophore by the covalent bonding was introduced onto the hydroxyl polyimide via a mild Mitsunobu reaction. Moreover, a series of polyimides were obtained by controlling the chromophore loading level without degradation of chromophore. The resulting NLO polyimides exhibited a relatively high T_g (>180°C) and thermal stability up to 280°C. Films of high optical quality were prepared and their EO properties were characterized in detail. Large EO coefficient values (up to 25 pm V^{-1} at 0.83 μm) were achieved, and high thermal stability of the poled films at 120°C was observed.

In this system the solubility of the fluorine-containing was increased, but the stability also decreased due to the flexibility backbone. Recently, a kind of stable diamine monomer, NLO *m*-phenylenediamine, was used to replace 2,2′-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane, the resulting NLO polyimides showed that they owns higher

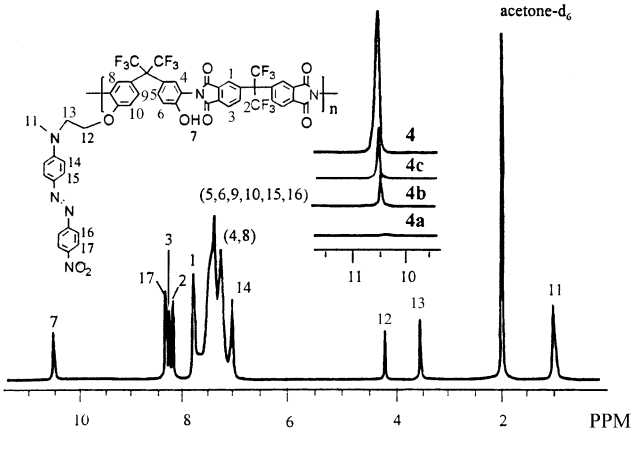


Fig. 3. ^{1}H NMR spectra of the polyimides **4c**.

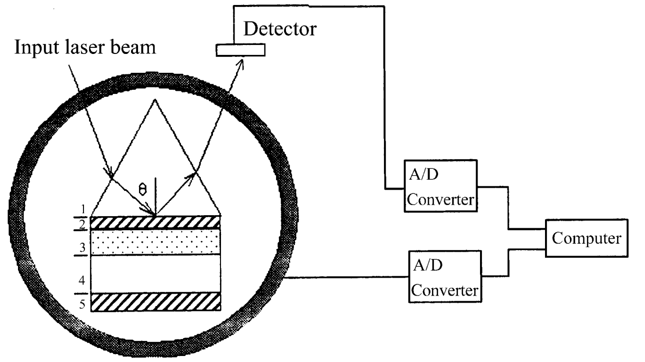


Fig. 4. Sample geometry and optical configuration of the reflection measurement technique.

stability as well as excellent film-formability. Our research activities directed will be presented in due time.

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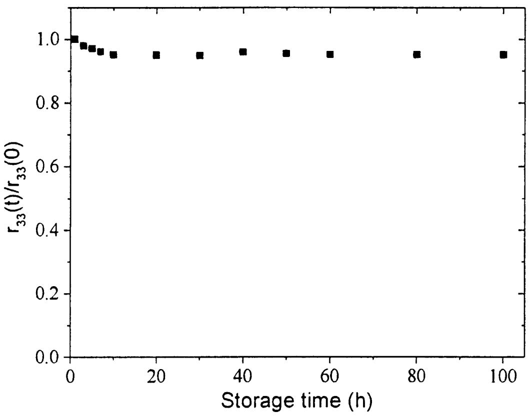

Fig. 5. Temporal stability of EO properties of polyimide **4a** at 120°C in the air.

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