



Synthesis and nonlinear optical properties of soluble fluorinated polyimides containing hetarylazo chromophores with large hyperpolarizability

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ABSTRACT

The novel fluorinated polyimides with side-chain nonlinear optical (NLO) chromophores were synthesized from hydroxyl polyimides, followed by the Mitsunobu reaction with NLO chromophores. Molecular structural characterization for the resulting polymers was achieved by ¹H NMR, FT-IR, UV-Vis spectra, elemental analysis and gel permeation chromatography (GPC). The polymers exhibit excellent solubility in common organic solvents, good film-forming properties, high glass transition temperature (T_g) in the range from 193 to 200 °C and thermal stability up to 290 °C. The polyimides **P1** and **P2** containing hetarylazo chromophores with large hyperpolarizability possess a high electro-optic (EO) coefficient (r_{33}), which is larger than that of the polyimide **P3** attached **DR1**. Excellent temporal stability and low optical losses in the range of 1.9–2.1 dB/cm at 1.55 μm were observed for these polymers. Such new NLO fluorinated polyimides are distinguished by an excellent combination of NLO activity, temporal stability, and optical loss.

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1. Introduction

Organic polymeric second-order NLO materials have been extensively studied for use in photonic devices such as EO modulators and switches, due to their large EO coefficients, ultrafast response times and easy processability [1,2]. Although the study on second-order NLO polymers has achieved some significant progresses, for the practical application, the harmony and balance of comprehensive properties (i.e., large optical nonlinearity, thermal stability, excellent temporal stability of dipole orientation and low optical loss) continue to challenge material scientists and engineers. Among the polymer systems developed, aromatic polyimides are promising for the investigation of second-order NLO materials because their high glass transition temperatures can be utilized to restrain the relaxation of the noncentrosymmetric chromophore-alignment induced by an electric field [3–6]. Various side-chain polyimide-based NLO materials exhibiting high-temperature alignment stability, high T_g and thermal stability have been developed [7–28]. In the past years a series of side-chain fluorinated polyimides second-order NLO materials [29–33] with the azo chromophores have also been synthesized by our group. In comparison with the side-chain polyimides, described in the

literature one of the most important properties of the side-chain polyimides prepared in this work is low optical losses at 1.55 μm telecommunication wavelength. Attempts to gain high temporal stability with polyimides systems often result in unsatisfactory processability, such as poor film-forming properties, because of their poor solubility in traditional spin casting solvents. There are several successful approaches to increase solubility and processability of polyimides [34–38]. In this study, a flexibilizing ether group and a fluorinated moiety are introduced into the polyimide backbone in order to increase solubility and processability of NLO polyimides with retention of high T_g and thermal stability. Due to the improved solubility of these polymers in organic solvents, the spincoated films are of good optical quality, thus reducing optical losses. And fluorinated polyimides are also known to reduce propagation loss because of their high optical transparency at telecommunication wavelengths.

It is known that larger NLO responses are indispensable for the realization of EO devices. The combination of the polyimide backbone with a chromophore of high molecular nonlinearity is expected to result in a high-performance polymeric system. In recent papers we have reported on some hetarylazo chromophores distinguished by large hyperpolarizability for nonlinear optical application [39,40]. In the paper as a consecutive work we incorporated the hetarylazo chromophores into the fluorinated polyimide matrixes with good film-forming ability, high thermal stability and glass transition temperature to obtain novel NLO side-

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chain fluorinated polyimides. The side-chain polyimides with hetarylazo chromophores show a large second-order optical nonlinearity. Thus the new side-chain NLO fluorinated polyimides exhibit good film-formability, high glass transition temperature, large and thermally stable EO activity, and low optical loss. The excellent combination of these properties in the resulting polymers has also provided a great promise in the development of EO devices and the fabrication of EO modulators and switches with them is in progress.

2. Experimental

2.1. Materials and instrumentation

The monomer, 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA), 2,2'-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane (6FHP) and 4,4'-(4,4'-isopropylidenediphenoxy)-bis(phthalic anhydride) (BPADPA) used in the polyimide synthesis were obtained from TCI and used without further purification. Disperse Red 1 (**DR1**, purity >95%) was obtained from Aldrich Chemical Co. 2-[4'-(*N*-ethyl-*N*-2-hydroxyethyl)-amino-phenylazo]-6-nitrobenzothiazole (EHNBT) and 2-[4'-(*N*-ethyl-*N*-2-hydroxyethyl)-amino-phenylazo]-5-nitrothiazole (EHNT) were prepared according to the literatures [39,41]. *N,N*-Dimethylformamide (DMF) was stirred over powered calcium hydride overnight and then distilled under reduced pressure. Cyclopentanone and tetrahydrofuran (THF) were purified by distillation and other reagents and solvents were analytically pure and used without further purification.

UV-Vis absorption spectra were measured on a Shimadzu UV 2201 spectrometer. Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet 750 series in the region of 4000–400 cm⁻¹ using KBr pellets. ¹H NMR data were obtained with a Bruker 300 MHz spectrometer using dimethyl sulphoxide (DMSO) as solvent and tetramethyl silane (TMS) as internal standard. Elemental analysis was obtained using a Perkin-Elmer Lambda 6 elemental analyzer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on NETZSCH STA449C at a heating rate of 10 °C/min under nitrogen atmosphere. Molecular weights were determined by GPC with a polystyrene standard using a WATERS SEC-244 system at 25.5 °C in THF. Atomic force microscopy (AFM) images were recorded with a Digital Instrument Dimension 3100, operated in a tapping mode that measures topography.

2.2. Synthesis of hydroxy-containing polyimide

The polymerization was conducted in a dry nitrogen-flushed three-necked flask with a magnetic stirrer. BPADPA (1.56 g, 3 mmol) and 6FDA (1.33 g, 3 mmol) were completely dissolved in 16 mL DMF, then an equal mole of 6FHP (2.20 g, 6 mmol) in 8 mL DMF was added to the mixed DMF solution 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 (16 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, V/V, 50 mL) and 2 N HCl (10 mL) in a high-speed blender to obtain the yellow hydroxy-containing polyimide. 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.

2.3. Synthesis of side-chain NLO polyimides **P1–P3**

A general procedure for the synthesis of side-chain NLO polyimides **P1–P3** is as follows. The hydroxy-containing polyimide (0.66 g, 0.41 mmol), EHNT (0.52 g, 1.62 mmol) and PPh₃ (0.64 g, 2.43 mmol) were dissolved in dry THF (15 mL) successively. Diethyl azodicarboxylate (DEAD) (0.42 g, 2.43 mmol) was added dropwise into the solution under nitrogen atmosphere. The reaction mixture was stirred for two days at room temperature, and then the resulting reaction solution was added dropwise into an agitated solution of methanol/water (1:1, 200 mL) and 2 N HCl (1 mL) in a high-speed blender. The collected solid was dissolved in THF and then precipitated into the solution of methanol/water. The product **P1** was filtered out and washed with methanol/water for several times, and dried at 60 °C under vacuum for 24 h. IR (KBr, cm⁻¹): 1780 (m, C=O), 1730 (vs. C=O), 1380 (m, CN), 1340 (s, N=O), 721 (s, imide ring). ¹H NMR (DMSO-*d*₆, ppm): δ = 1.21 (t, -CH₂CH₃, 12H), 1.67 (s, -CH₃, 6H), 3.62 (t, -CH₂-, 24H), 6.94 (d, Ar-H, 4H), 7.01 (d, Ar-H, 8H), 7.11 (d, Ar-H, 4H), 7.36 (s, Ar-H, 4H), 7.46–7.7 (m, Ar-H, 12H), 7.82 (d, Ar-H, 8H), 7.88–8.0 (m, Ar-H, 8H), 8.81 (s, Ar-H, 4H). Anal. calcd. for C₆₆H₄₇F₉N₁₂O₁₁S₂ (1419.29): C, 55.85%; H, 3.34%; N, 11.84%; S, 4.52%. Found: C, 55.60%; H, 3.20%; N, 11.61%; S, 4.50%.

Side-chain NLO polyimide **P2** was synthesized by a procedure similar to that for polyimide **P1** by using chromophore EHNBT instead of EHNT. **P2** IR (KBr, cm⁻¹): 1780 (m, C=O), 1730 (vs. C=O), 1380 (m, CN), 1335 (s, N=O), 719 (s, imide ring). ¹H NMR (DMSO-*d*₆, ppm): δ = 1.20 (m, -CH₂CH₃, 12H), 1.67 (s, -CH₃, 6H), 3.65 (t, -CH₂-, 24H), 6.94 (d, Ar-H, 4H), 7.01 (d, Ar-H, 8H), 7.12 (d, Ar-H, 4H), 7.37 (s, Ar-H, 4H), 7.44–7.7 (m, Ar-H, 12H), 7.88 (d, Ar-H, 16H), 7.91–8.0 (m, Ar-H, 4H), 8.11 (d, Ar-H, 4H), 8.15 (d, Ar-H, 2H), 8.29 (q, Ar-H, 4H), 9.02 (d, Ar-H, 4H). Anal. calcd. for C₇₄H₅₁F₉N₁₂O₁₁S₂ (1519.41): C, 58.50%; H, 3.38%; N, 11.06%; S, 4.22%. Found: C, 58.30%; H, 3.20%; N, 11.15%; S, 4.30%.

Side-chain NLO polyimide **P3** was synthesized by a procedure similar to that for polyimide **P1** by using chromophore **DR1** instead of EHNT. **P3** IR (KBr, cm⁻¹): 1780 (m, C=O), 1730 (vs. C=O), 1380 (m, CN), 1340 (s, N=O), 721 (s, imide ring). ¹H NMR (DMSO-*d*₆, ppm): δ = 1.13 (t, -CH₂CH₃, 12H), 1.67 (s, -CH₃, 6H), 3.54 (m, -N-CH₂-CH₃, 8H), 3.65 (t, -N-CH₂-CH₂-, 8H), 4.15 (t, -CH₂-CH₂-O-, 8H), 6.90–6.92 (m, Ar-H, 12H), 7.11 (d, Ar-H, 4H), 7.36 (s, Ar-H, 4H), 7.45–7.7 (m, Ar-H, 12H), 7.83–8.0 (m, Ar-H, 24H), 8.36 (d, Ar-H, 8H). Anal. calcd. for C₇₂H₅₃F₉N₁₀O₁₁ (1405.26): C, 61.54%; H, 3.80%; N, 9.97%. Found: C, 61.30%; H, 3.60%; N, 9.82%.

2.4. Thin film preparation

The polymers were dissolved in cyclopentanone and filtered through a 0.5 μm syringe filter. Thin films were prepared by spin coating the filtered polymer solution onto indium–tin oxide (ITO) glass substrates, which were carefully pre-cleaned by alcohol, acetone and distilled water sequentially in an ultrasonic bath. Prior to poling process, these thin films were dried in vacuum at 60 °C for 24 h to remove residual solvent.

2.5. Poling process, EO coefficient and optical loss measurements

The poling process for the second-order NLO polymer films was carried out using a corona poling technique. The poling voltage was maintained for 8.5 kV and the temperature was kept at approximately 10 °C lower than the *T*_g of the sample for 1 h. The sample was then cooled down to room temperature in the presence of a poling field. The thickness, indices of refraction, and optical loss were measured by a Model SPA-4000 Prism Coupler at 1.55 μm. EO coefficients of the poled samples were measured at 1.55 μm using the simple reflection technique.

3. Results and discussion

3.1. Synthesis and characterization of side-chain NLO polyimides

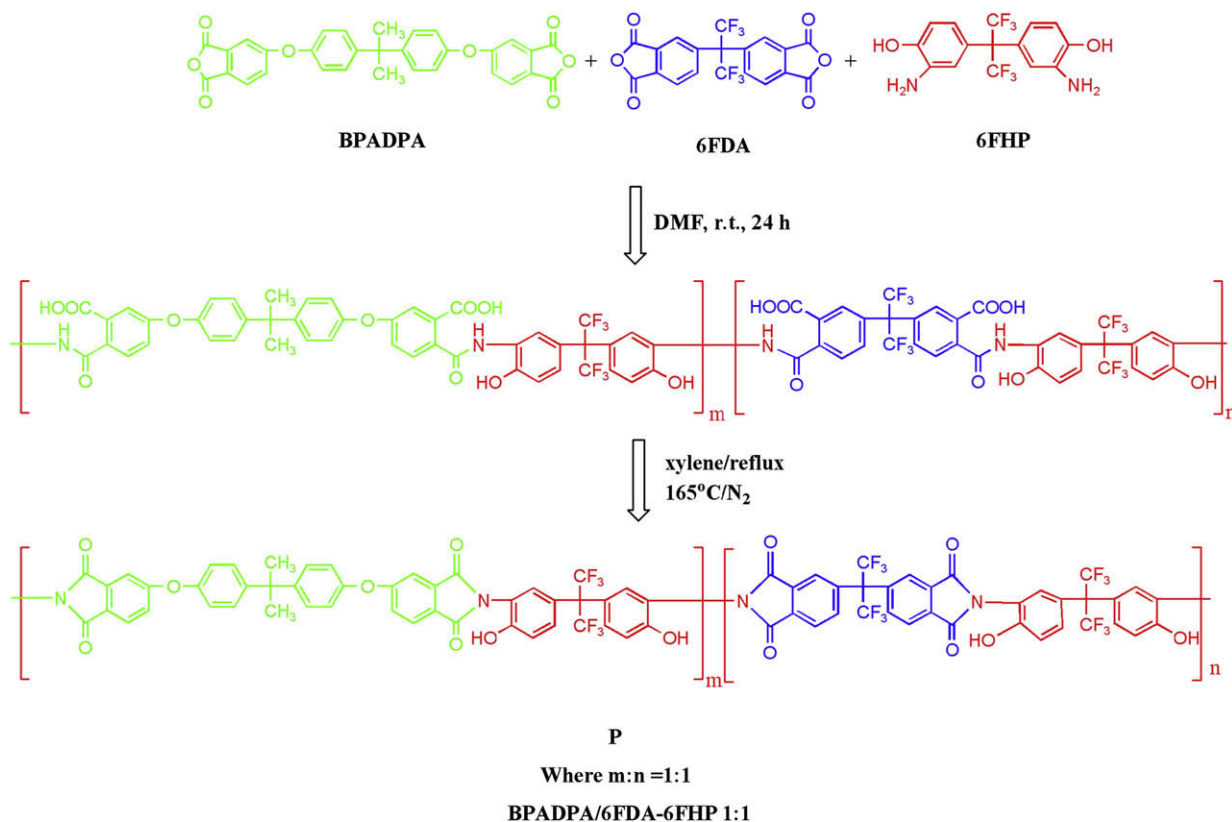
The synthesis was a two-step process. The first step was for the synthesis of hydroxyl polyimides (Scheme 1) and the second for the incorporation of the chromophores to the polymer backbone (Scheme 2). The synthesis of hydroxyl polyimides was quite straightforward via the direct polymerization of hydroxyl diamine and dianhydride monomers. Moreover, the fact that most of the dianhydride and hydroxyl diamine monomers are commercially available made the synthesis even more facile. The molar ratio (m/n) of the hydroxyl polyimide component was readily controlled through the monomer feed ratio of BPADPA to 6FDA. The molar ratio (m/n) refers to the molar ratio of BPADPA:6FDA in the initial monomer feed. The covalent bonding of the chromophore to the backbone of the polyimide can be easily carried out via the Mitsunobu condensation between the pendant hydroxyl group on the chromophores and the phenol group on the polyimides. The very mild conditions of the condensation provide us great flexibility in the choice of the chromophores (see Fig. 1 for examples).

Many chromophores with a pendant hydroxy group can be incorporated directly onto the polyimide backbone to create different NLO side-chain aromatic polyimides. The structures of polymers were characterized by FT-IR and ^1H NMR spectroscopy, respectively. The polymers show typical absorptions for a polyimide ring at 721 and 1380 cm^{-1} and the asymmetric and symmetric aromatic imide carbonyl stretch absorptions at 1780 and 1730 cm^{-1} . The strong absorption bands due to the nitrogroup in the NLO chromophore appear near 1340 cm^{-1} . These results are consistent with the proposed structures, indicating the introduction of the chromophores into the side-chains of the polyimides successfully.

^1H NMR spectra show that the chemical shifts due to NLO chromophores protons do not exhibit much change on going from chromophores to terminal polymers. Hydroxy proton chemical shifts of both the polymer backbone and the chromophore all disappeared in ^1H NMR after the reaction, where the spectral assignments clearly support the proposed structures. The elemental analysis values of all polymers are generally in good agreement with the calculated values for the proposed structures. Gel permeation chromatography indicates that the absolute weight-average molecular weights (\overline{M}_w) of **P1**, **P2** and **P3** were 41,750, 40,700 and 39,900, respectively, with the polydispersities ($\overline{M}_w/\overline{M}_n$) of 2.0, 2.1 and 2.2, respectively.

The synthetic side-chain NLO polyimides have good solubility in many common organic solvents, such as cyclopentanone, THF, DMF, DMSO, NMP, and even acetone. These polymers reveal an enhanced solubility as compared with conventional aromatic polyimides. The improved organosolubility of the polyimides can be explained by the presence of both the flexible ether linkages and the bulky NLO chromophore side groups, which determine a less efficient intermolecular packing and thus facilitate the diffusion of solvent molecules among the polymer chains. Also, it is known that the incorporation of a hexafluoroisopropylidene (6F) groups into the polymer backbones enhances the polyimide solubility without sacrificing thermal stability. The increased solubility of the polyimides leads to better quality films with enhanced nonlinearity and makes them potential candidates for practical applications in spin coating and casting processes.

Fig. 2 shows the UV-Vis spectra of polyimides **P** and **P1–P3** in the NMP solution. Correspondingly, the values of the absorption maxima (λ_{max}) are listed in Table 1. All the polymers exhibit strong absorption in the visible range. The color of the polyimides in solution is different and the polyimides **P**, **P1**, **P2** and **P3** in solution



Scheme 1. Preparation of poly(hydroxy-imide)s.

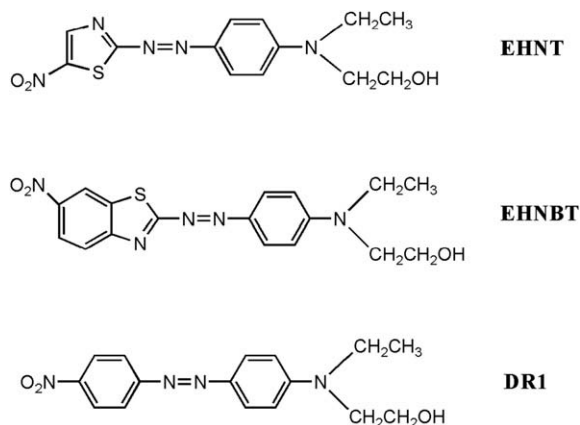


Fig. 1. Chemical structure of the NLO chromophores.

thermal stability against the chromophores EHNT and DR1. Thus P2 containing a side-chain EHNBT chromophore is the most stable among all of the synthesized NLO polyimides. The parent hydroxy-containing polyimide has a high decomposition temperature (485 °C). However P2 starts its weight loss at about 290 °C, resulted from the decomposition of the chromophore EHNBT from the polymer backbone. TGA traces show that these polyimides have decomposition temperatures in the range of 246–290 °C which are compared and even better than the previous results [31]. T_g values of P1–P3 measured by DSC is in the range of 193–200 °C. The relatively high T_g of P1–P3 would make them exhibit good thermal stability of the dipole reorientation in the polymers after poling. In addition the TGA studies show that the decomposition temperature of these polyimides is higher than the corresponding glass transition temperatures. It is indicated that high-temperature poling for a short term is feasible without damaging the NLO chromophores.

3.3. Linear optical properties

The synthesized NLO side-chain polyimides offer good processability that optical quality thin films can be easily prepared by spin coating from cyclopentanone solution. The polyimides give smooth and physically stable films with thicknesses ranging from 0.2 to 4 μm, depending on the spinning speed and the concentration of the cyclopentanone solution. The refractive indices of the NLO polymers are between 1.5630 and 1.5937 (Table 2). Fig. 4

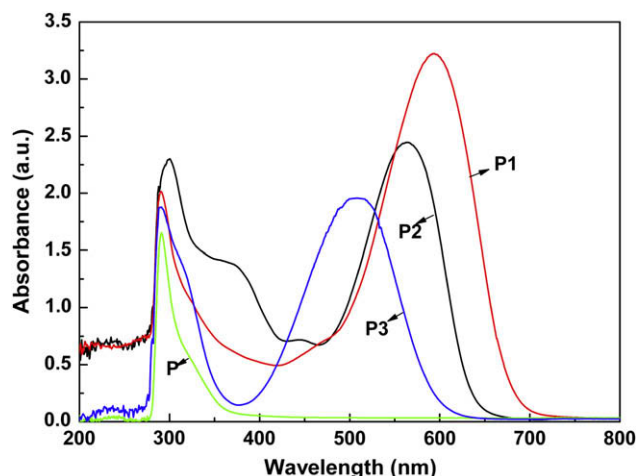


Fig. 2. UV-Vis absorption spectra of NMP solutions of polyimides P and P1–P3.

Table 1
Physical property of side-chain NLO polyimides P1–P3.

	Content (%) ^a	λ_{\max} (nm)	T_g (°C)	T_d (°C)
P1	43	594	200	246
P2	46	564	196	290
P3	44	508	193	242

^a Chromophore-side-chain content (wt/wt) in polymer.

shows the variation of refractive index of side-chain NLO polyimides P1–P3 at transverse electric (TE) mode versus temperature. The refractive index of the NLO polyimides decreases linearly when the temperature of temperature controller of prism coupler increased. The thermo-optic coefficients (dn/dT) of P1, P2, and P3 are $-1.698 \times 10^{-4}/^\circ\text{C}$, $-1.460 \times 10^{-4}/^\circ\text{C}$ and $-1.331 \times 10^{-4}/^\circ\text{C}$, respectively, for TE polarization measured at 1.55 μm. The temperature increasing causes the expanding of the film hence, reducing the optical density and varying the refractive index of the material.

One of the critical requirements for device-quality second-order NLO materials is low optical loss at the operating wavelength. As shown in Table 2, the side-chain NLO polyimides P1–P3 samples exhibit low optical losses which are in the range of 1.9–2.1 dB/cm at 1.55 μm. Optical loss may be caused by either intrinsic absorption at the operating wavelength, or the scattering of light from physical scattering centers generated during processing. The optical loss associated with C–H vibrational absorptions is a great problem at 1.55 μm operating wavelength and requires partial fluorination of polymer and chromophore to achieve acceptably low optical loss [44]. Thus fluorine atoms were incorporated into the polyimide matrixes to decrease the absorption loss of the resulting materials for application in EO devices. In addition the λ_{\max} values of the azo chromophores are below 600 nm and sufficiently far removed from the measurement wavelength that the intrinsic absorption loss of the chromophores does not likely contribute to measured loss. Therefore, in this work, we focus on manipulation of processing conditions to reduce the optical losses generated during material processing. For example, solvent choice is very important. Although the fluorinated polyimides are readily soluble in many common organic solvents, using the cyclopentanone solvent, they can be processed into excellent optical quality film by spin casting. The films of the fluorinated polyimides were flat and smooth, exhibiting good homogeneity. The homogeneity in the film decreases the scattering of incident light, thus reducing the optical loss. Up to now the rationale in film-forming abilities of polymers in different

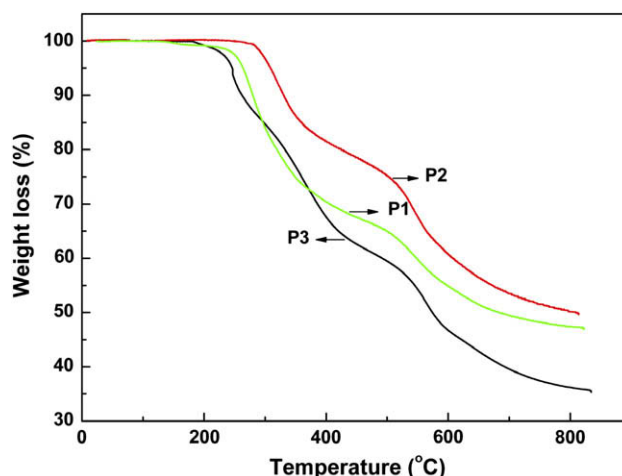


Fig. 3. TGA of side-chain NLO polyimides P1–P3.

Table 2
Optical properties of side-chain NLO polyimides **P1–P3**.

	n^a	dn/dT ($10^{-4}/^\circ\text{C}$) ^b	r_{33} ($\mu\text{m}/\text{V}$) ^c	Optical loss (dB/cm) ^d
P1	1.5937	1.698	18	2.1
P2	1.5790	1.460	14	2.0
P3	1.5630	1.331	5	1.9

^a Refractive indices at transverse electric mode measured at 1.55 μm .

^b All values for dn/dT obtained at 1.55 μm .

^c Electro-optic coefficients measured at 1.55 μm .

^d Optical loss measured at 1.55 μm .

solvents has not been found in literature. The related mechanism on this aspect is very complicated and study on the mechanism is in progress.

3.4. Nonlinear optical properties

To evaluate the NLO activities of the side-chain NLO polyimides **P1–P3**, we corona-poled the spin coated polymer films to induce noncentrosymmetric polar order. Fig. 5 shows the UV–Vis absorption spectra of the film of **P1** before and after corona poling. In the spectrum of the film after poling, a decrease in the absorbance can be observed. The same results have been obtained for **P2** and **P3**. It can be ascribed to two different factors: (1) a partial alignment of the chromophore's dipole moment along the direction of the poling field, (2) a possible partial degradation of the chromophores during the poling process. However, for the NLO polyimides, the decomposition temperatures of the chromophores are well above the poling one. Thus the decrease in absorbance after poling is an indicator of the dipole alignment and irrelevant to chromophore degradation. The order parameters ($\phi = 1 - A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after corona poling) are used to characterize the poling efficiency. According to the absorbance change, the order parameter values for **P1**, **P2**, and **P3** were estimated to be 0.26, 0.27 and 0.26, respectively, showing good poling efficiency. Surface topography of the polymers **P1** before and after poling was further observed by AFM in Fig. 6. It is found that the surface of a thin unpoled film is extremely flat. And its root mean squared roughness value is only 0.084 nm. However, this excellent quality film was drastically changed after poling, resulting in numerous hills and valleys in the surface structure. This is the result of the alignment of NLO chromophores along the poling field direction [45–47]. The roughness of the surface topography of the polymers after poling is 0.375 nm, which is still in the acceptable

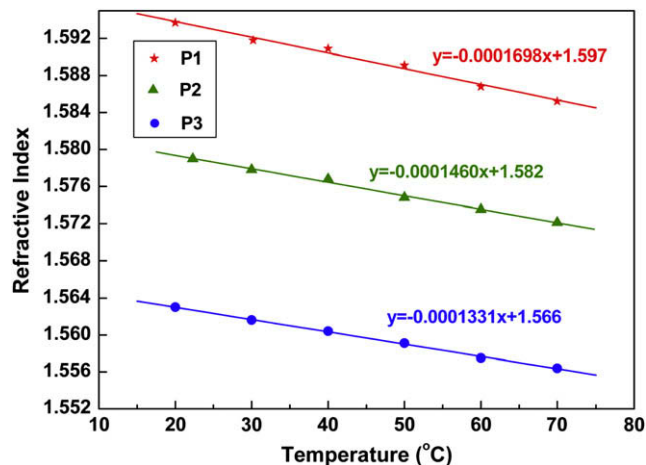


Fig. 4. Refractive index variation of side-chain NLO polyimides **P1–P3** with temperature.

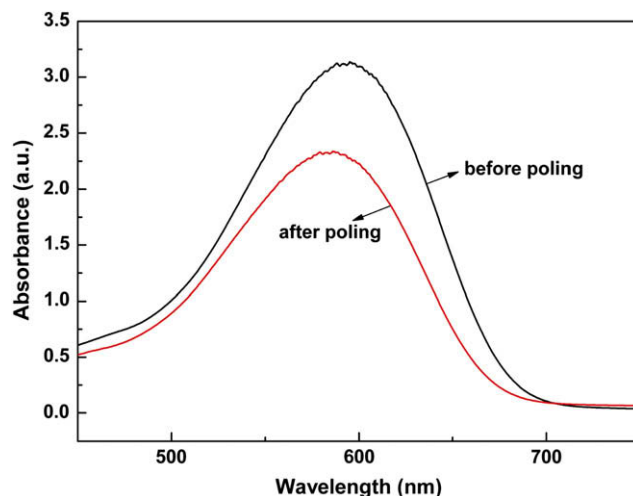


Fig. 5. UV–Vis absorption spectra of a film of polyimide **P1** before and after poling.

range. No distinct decomposition, sublimation, or obvious surface distortion existed in the film.

The electrooptic coefficients of the side-chain NLO polyimides **P1–P3** were measured by the simple reflection technique at 1.55 μm and the results are listed in Table 2. **P1**, **P2** and **P3** give 18, 14 and 5 $\mu\text{m}/\text{V}$ of r_{33} at 1.55 μm , respectively. Although **P1**, **P2**, and **P3** have

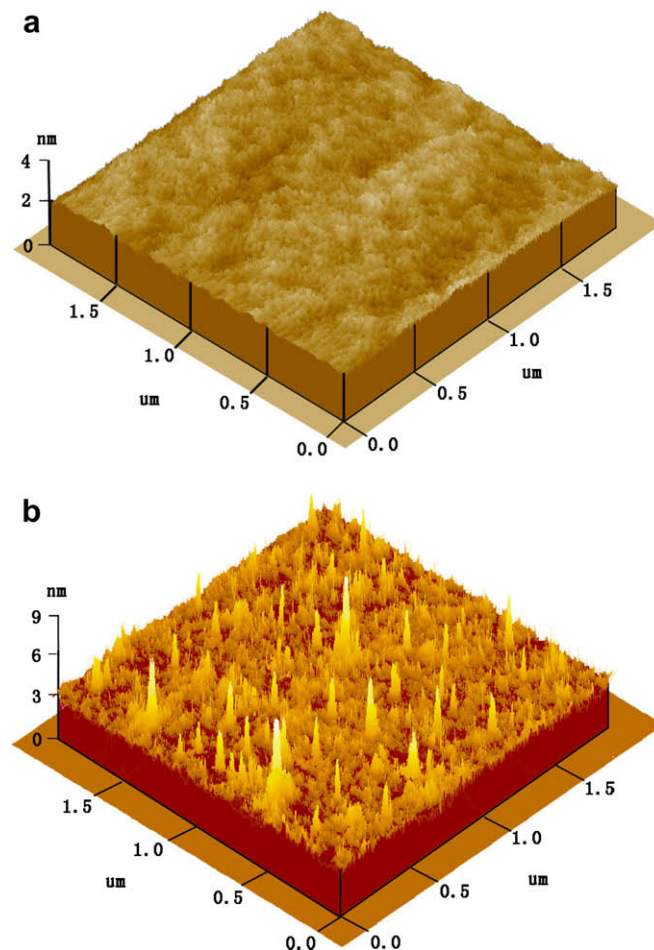


Fig. 6. AFMz images of a spin coated film of polyimide **P1**: (a) before corona poling; (b) after corona poling.

similar poling efficiency and chromophore content in polymer, **P1** and **P2** containing hetarylazo chromophores show better nonlinearity than **P3** attached **DR1**. Relatively high r_{33} values for **P1** and **P2** can be explained by the large molecular hyperpolarizabilities of hetarylazo chromophores EHNBT and EHNT with the values of 440×10^{-30} esu and 560×10^{-30} esu, respectively. However the molecular hyperpolarizability of **DR1** is 90×10^{-30} esu [48]. Because benzothiazole and thiazole have lower delocalization energy than benzene, they can offer better conjugation than benzene in donor-acceptor compounds, thus increasing the β values. However, this description is oversimplified. The electron-poor benzothiazole and thiazole, which are substituted by an electron-withdrawing NO_2 group, strongly withdraw electron density from acceptor substituent, increasing the acceptor ability of the nitro group and acting as auxiliary acceptors [49,50]. This increased acceptor ability leads to a substantial increase in NLO response. Thus the substitution of the heteroaromatic rings in donor-acceptor compounds should be expected to result in enhanced charge-transfer properties and molecular hyperpolarizabilities than in benzenoid rings. And the large molecular hyperpolarizabilities of hetarylazo chromophores contribute to high nonlinear responses for **P1** and **P2**. It can be concluded that the polyimides **P1** and **P2** with hetarylazo chromophores show improved nonlinear responses compared with the side-chain polyimides prepared before (13–25 pm/V at 0.83 μm), containing an azobenzene-type chromophore [31]. Studies on NLO response properties have also shown that the polymers bearing side-chain heteroaromatic azo chromophores possess a larger second-order NLO coefficient than their benzenoid analogues [51].

The long-term stability of the nonlinear property at elevated temperatures is very important for the practical use of NLO polymers. To investigate the long-term NLO stability of the poled polyimides, dipole reorientation of the poled polymeric film was observed by measuring the EO coefficient ($r_{33}(t)/r_{33}(t_0)$) as a function of time at 80 °C and 120 °C, respectively. Fig. 7 shows the temporal stability of EO coefficient for the poled polyimide **P1** at 80 °C and 120 °C, respectively. The r_{33} of **P1** maintains constant at 80 °C after 10% relaxation at initial stage. At 120 °C, the poled **P1** retains about 84% of its original r_{33} value after 200 h. The fast decay of the EO coefficient at the beginning of thermal treatment may result from recovery of bond angle and bond length of the oriented chromophores [52,53]. The results show high stabilities of NLO responses at elevated temperatures and are comparable to those of the side-chain polyimides prepared before [31]. At room temperature, the temporal stability of the EO coefficient of **P1** remained about 95% of its initial

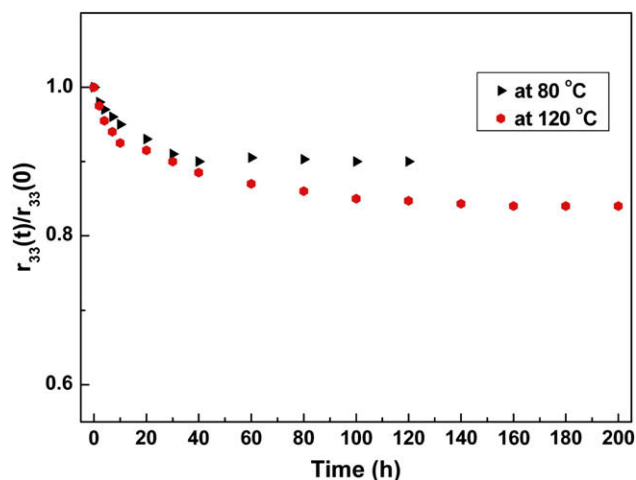


Fig. 7. Temporal stability of the EO coefficient for the poled polyimide **P1** at 80 °C and 120 °C, respectively.

value, even after 30 days. Good temporal stability originates from the chromophores being linked to the main chains of the polyimides and a stronger interaction between heteroaromatic chromophores, thus restricting the local motions of the chromophores and reducing orientation relaxation [51,54]. Based on above reasons it is reasonable to assume that polyimide **P2** have a good nonlinear stability at elevated temperatures.

4. Conclusion

We have successfully synthesized novel fluorinated polyimides containing NLO chromophores in the side-chain by the Mitsunobu reaction. The polymers exhibit high solubility that excellent optical quality thin films can be easily obtained by spin coating. The polyimides **P1** and **P2** containing hetarylazo chromophores with large hyperpolarizability achieve a high electrooptic coefficient (as high as 18 pm/V at 1.55 μm), which is larger than that of the polyimide **P3** attached **DR1**. The polymers possess high glass transition temperature (193–200 °C) with thermal stability up to 290 °C and can therefore be excellent polymeric materials with high temporal stability of the NLO effect. Low optical losses (1.8–2.1 dB/cm at 1.55 μm) were obtained for these polymers. The novel fluorinated polyimides second-order NLO materials can be regarded as a set of promising materials for EO device fabrication and the fabrication of EO modulators with them as the EO materials is in progress.

Acknowledgments

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