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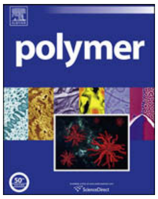

Synthesis and nonlinear optical properties of soluble fluorinated polyimides containing hetarylazo chromophores with large hyperpolarizability

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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 ^{1}H 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.

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) diphthalicanhydride (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 regents 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. ^{1}H 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 $\mathrm{PPh_3}$ (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). ^{1}H NMR (DMSO-d_6, ppm): $\delta = 1.21$ (t, $-\mathrm{CH_2}\mathbf{CH_3}$, 12H), 1.67 (s, $-\mathbf{CH_3}$, 6H), 3.62 (t, $-\mathbf{CH_2}-$, 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 $\mathrm{C_{66}H_{47}F_9N_{12}O_{11}S_2}$ (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 polymide **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). ^{1}H NMR (DMSO-d_6, ppm): $\delta = 1.20$ (m, $-\mathrm{CH_2}\mathbf{CH_3}$, 12H), 1.67 (s, $-\mathbf{CH_3}$, 6H), 3.65 (t, $-\mathbf{CH_2}-$, 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 $\mathrm{C_{74}H_{51}F_9N_{12}O_{11}S_2}$ (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 polymide **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). ^{1}H NMR (DMSO-d_6, ppm): $\delta = 1.13$ (t, $-\mathrm{CH_2}\mathbf{CH_3}$, 12H), 1.67 (s, $-\mathbf{CH_3}$, 6H), 3.54 (m, $-\mathrm{N}-\mathbf{CH_2}-\mathrm{CH_3}$, 8H), 3.65 (t, $-\mathrm{N}-\mathbf{CH_2}-\mathrm{CH_2}-$, 8H), 4.15 (t, $-\mathrm{CH_2}-\mathbf{CH_2}-\mathrm{O}-$, 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 $\mathrm{C_{72}H_{53}F_9N_{10}O_{11}}$(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.