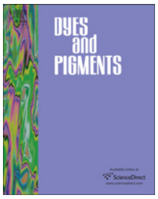
Dyes and Pigments 86 (2010) 107–114

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig



The synthesis and optical properties of novel fluorinated polyimides incorporated with highly electro-optic active thiazole and benzothiazole based chromophores

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ARTICLE INFO

Article history:
Received 12 July 2009
Received in revised form
28 November 2009
Accepted 30 November 2009
Available online 16 December 2009

Keywords:
Polyimides
Hetarylazo chromophores
NLO
Side-chain
Optical loss
Stability

ABSTRACT

Novel, non-linear optical fluorinated polyimides were prepared by the Mitsunobu reaction of hydroxyl-containing hetarylazo chromophores with hydroxyl polyimides. Their structures were verified by FT-IR, ^{1}H NMR, UV–Vis spectra, elemental analysis and gel permeation chromatography. The resulting amorphous polyimides exhibited good solubility and can be easily spin-coated into thin films with good optical quality. The high electro-optic coefficients (r_{33}) obtained for the films of poled polyimides were attributed to the introduction of hetarylazo chromophores with large hyperpolarizability within the polyimides. The polyimides possess high glass transition temperature (201–210 °C) and therefore showed excellent temporal stability, retaining 88% of their initial non-linear optical response at 110 °C for >200 h. Low optical losses in the range of 1.9–2.3 dB cm^{-1} at 1550 nm were observed for the polyimides and the values of thermooptic coefficients ranged from -1.680×10^{-4} to -2.008×10^{-4}/°C.

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1. Introduction

Polymeric materials with second-order NLO properties have attracted much interest in recent years as promising candidates for application in electro-optic and photonic devices. For practical applications, such NLO polymeric materials must display good film-forming properties, sufficiently large and stable NLO susceptibility, low optical propagation loss, high thermal stability and satisfactory processability. Although it is extremely difficult to synthesize materials which possess all of these properties, large and thermally stable EO activity and low optical loss are particularly required for device application.

Aromatic polyimides have been shown to offer a means of preventing relaxation of poled order in poled polymers owing to their high glass transition temperature. Various polyimide-based NLO materials exhibiting high-temperature alignment stability, high T_g and thermal stability have been developed [1–22]. The present authors have prepared a series of side-chain polyimides second-order NLO materials comprising azo chromophores in the past years [23]; however optical losses at 1.55 μm telecommunication wavelength were not measured. An important property of the side-chain polyimides prepared in this work was low optical loss at the 1.55 μm telecommunication wavelength. In addition, as the rigid backbone of aromatic polyimides can result in poor solubility and undesirable film formation quality, a fluorinated moiety was introduced into the polyimide backbone to increase solubility and processability. Moreover, C–F overtones have extremely low absorption in the telecommunications window, owing to their higher harmonic order and fluorinated polyimides are known to reduce propagation loss because of their high optical transparency at these particular wavelengths.

It is known that large NLO responses are indispensable for the realization of EO devices. As chromophores could play the role of NLO elements in polymeric systems, the design and synthesis of chromophores with large hyperpolarizability is very important in the development of NLO devices. Theoretical NLO studies have revealed that heteroaromatic rings play a subtle role in influence the second-order NLO properties of push–pull chromophores [24–30]. Replacing the benzene ring of a chromophore bridge with heteroaromatic rings, such as thiazole and benzothiazole, can results in an increased molecular hyperpolarizability. Thus, in recent papers some hetarylazo chromophores distinguished by large hyperpolarizability for non-linear optical application have been synthesized by our group [31,32]. The use of highly electro-optic active hetarylazo chromophores in the fluorinated polyimides is expected to result in a high-performance polymeric system. In addition, up to now we note that azo chromophores with hetero-aromatic rings have been mainly employed in guest–host systems,

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doi:10.1016/j.dyepig.2009.11.008

while very few examples of side-chain polyimides have been reported. This paper reports our efforts to extend our previous work in order to incorporate the hetarylazo chromophores to the fluorinated polyimide matrixes to obtain novel NLO side-chain fluorinated polyimides. The side-chain polyimides with hetarylazo chromophores show a large second-order optical nonlinearity. Therefore the new fluorinated polyimides with NLO hetarylazo chromophores are distinguished by an excellent combination of high glass transition temperature, processibility, large NLO activity, long-term stability and low optical loss. And these desirable properties provide great promise in the development of EO devices.

2. Experimental

2.1. Materials

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. The monomers 4,4′-(hexafluoroisopropylidene) diphthalicanhydride (6FDA) and 2,2′-bis(3-amino-4-hydroxy-phenyl) hexafluoropropane (6FHP) were obtained from Tokyo Chemical Industry (TCI) and were used without further purification. 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 literature [24,31].

2.2. Instrumentation

^{1}H NMR spectra were recorded with the use of a Bruker 300 MHz spectrometer using dimethyl sulphoxide (DMSO) as solvent and tetramethyl silane (TMS) as internal standard. FT-IR spectra were measured as KBr pellets on a Nicolet 750 series in the region of 4000–400 cm^{-1}. UV–Vis absorption spectra were measured on a Shimadzu UV 2201 spectrometer. 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 under a nitrogen atmosphere at the heating rate of 10 °C/min. Molecular weights were determined by GPC with a polystyrene standard using a WATERS SEC-244 system at 25.5 °C in THF.

2.3. Synthesis of side-chain NLO polyimides

Synthesis of side-chain NLO polyimides was carried out by the Mitsunobu reaction of hydroxy-containing polyimides with NLO chromophores, as shown in Fig. 1.

2.3.1. Synthesis of hydroxy-containing polyimide FPI based on 6FHP and 6FDA

Polymerization was conducted in a dry nitrogen-flushed, three-neck flask equipped with a magnetic stirrer. 6FDA (1.33 g, 3 mmol) was completely dissolved in 8 mL DMF, and 6FHP (1.10 g, 3 mmol) in 6 mL DMF was added at 0 °C. The solution was warmed to room temperature and magnetically stirred overnight under nitrogen to realise the poly(amic acid) solution. The viscosity of the solution increased during this period greatly. Dry xylene (8 mL) was added and the ensuing poly(amic acid) was thermally cyclized in an oil bath at 160 °C for 5 h under nitrogen. The resulting solution was added dropwise to a solution of 1:1 methanol:water solution (50 mL) and 2 M aq HCl solution (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.

2.3.2. Synthesis of hydroxy-containing polyimide PFPI based on 6FHP, pyromellitic dianhydride (PMDA) and 6FDA

PMDA (0.65 g, 3 mmol) and 6FDA (1.33 g, 3 mmol) were completely dissolved in 9 mL DMF and 6FHP (2.20 g, 6 mmol) in 8 mL DMF was added to the mixed DMF solution at 0 °C. The solution was 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 1:1 methanol/water solution (50 mL) and 2 M aq HCl solution (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.

2.3.3. Synthesis of side-chain polyimides FPI-EHNT, FPI-EHNBT, PFPI-EHNT and PFPI-EHNBT

A general procedure for the synthesis of side-chain polyimides FPI-EHNT, FPI-EHNBT, PFPI-EHNT and PFPI-EHNBT is as follows. 0.61 g of the hydroxy-containing polyimide FPI, EHNT (0.50 g, 1.57 mmol) and triphenylphosphorus (PPh$_3$: caution - incompatible with oxidizing agents, acids; 0.62 g, 2.35 mmol) were dissolved in dry THF (15 mL) successively. Diethyl azodicarboxylate (DEAD) (0.41 g, 2.35 mmol) was added dropwise to 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 FPI-EHNT 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}): 1790 (m, C = O), 1730 (vs, C = O), 1380 (m, CN), 1340 (s, N = O), 723 (s, imide ring). ^{1}H NMR (DMSO-d$_6$, ppm): δ = 1.21 (t, $-CH_2C\mathbf{H_3}$, 6H), 3.65 (t, $-C\mathbf{H_2}-$, 12H), 7.04 (d, Ar-**H**, 4H), 7.17 (d, Ar-**H**, 2H), 7.36 (d, Ar-**H**, 2H), 7.49 (s, Ar-**H**, 2H), 7.70 (s, Ar-**H**, 2H), 7.82 (d, Ar-**H**, 4H), 8.06–8.13 (m, Ar-**H**, 4H), 8.79 (s, Ar-**H**, 2H). Anal. calcd for $C_{47}H_{26}F_{12}N_7O_8S$ (1076.60): C, 52.44%; H, 2.42%; N, 9.11%; S, 2.98%. Found: C, 52.30%; H, 2.25%; N, 9.31%; S, 3.05%.

The side-chain polyimide FPI-EHNBT was synthesized by a procedure similar to that for polymide FPI-EHNT by using chromophore EHNBT instead of EHNT. FPI-EHNBT IR (KBr, cm^{-1}): 1790 (m, C = O), 1730 (vs, C = O), 1380 (m, CN), 1340 (s, N = O), 723 (s, imide ring). ^{1}H NMR (DMSO-d$_6$, ppm): δ = 1.20 (m, $-CH_2C\mathbf{H_3}$, 6H), 3.65 (t, $-C\mathbf{H_2}-$, 12H), 6.99 (d, Ar-**H**, 4H), 7.17 (d, Ar-**H**, 2H), 7.36 (d, Ar-**H**, 2H), 7.49 (s, Ar-**H**, 2H), 7.70 (s, Ar-**H**, 2H), 7.85 (d, Ar-**H**, 4H), 8.06–8.13 (m, Ar-**H**, 6H), 8.29 (q, Ar-**H**, 2H), 8.99 (d, Ar-**H**, 2H). Anal. calcd for $C_{51}H_{28}F_{12}N_7O_8S$ (1126.64): C, 54.37%; H, 2.49%; N, 8.70%; S, 2.85%. Found: C, 54.21%; H, 2.28%; N, 8.90%; S, 2.70%.

Side-chain polyimide PFPI-EHNT was synthesized by a procedure similar to that for polymide FPI-EHNT by using hydroxy-containing polyimide PFPI instead of FPI. PFPI-EHNT IR (KBr, cm^{-1}): 1780 (m, C = O), 1730 (vs, C = O), 1380 (m, CN), 1340 (s, N = O), 723 (s, imide ring). ^{1}H NMR (DMSO-d$_6$, ppm): δ = 1.20 (t, $-CH_2C\mathbf{H_3}$, 12H), 3.65 (t, $-C\mathbf{H_2}-$, 24H), 7.04 (d, Ar-**H**, 8H), 7.17 (d, Ar-**H**, 4H), 7.36 (d, Ar-**H**, 4H), 7.49 (s, Ar-**H**, 4H), 7.70 (s, Ar-**H**, 2H), 7.82 (d, Ar-**H**, 8H), 8.06–8.13 (m, Ar-**H**, 4H), 8.79 (s, Ar-**H**, 4H), 9.00 (s, Ar-**H**, 2H).

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