Available online at www.sciencedirect.com
ScienceDirect
Chinese Chemical Letters 22 (2011) 1367–1370
CHINESE CHEMICAL LETTERS
www.elsevier.com/locate/cclet

Synthesis and nonlinear optical properties of copolymers of fluoro-containing bisphenol A and chromophores

Jie Ping Shi, Hui Yang, Li Wei, Hong Wen Hu, Guo Yuan Lu *

Department of Chemistry, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China

Received 21 February 2011
Available online 28 July 2011

Abstract

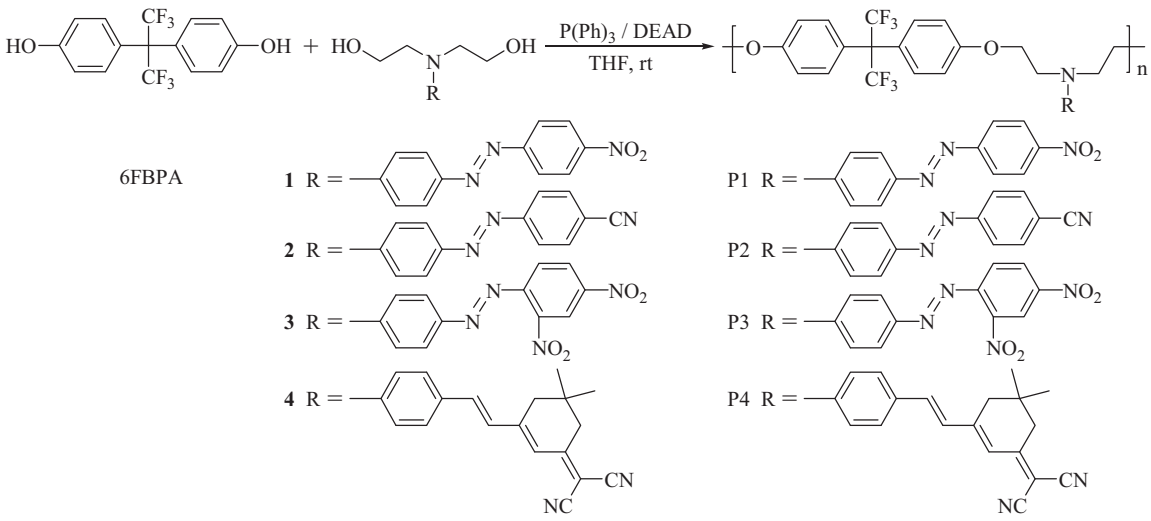
A series of new fluoro-containing copolymers have been synthesized by a Mitsunobu reaction with 4,4′-(hexafluoroisopropylidene)bisphenol A (6FBPA) and the corresponding *N*, *N*-dihydroxyethylaminoaryl azo or ring-locked triene compounds, which have high thermal stability and good solubility in organic solvents. The nonlinear optical (NLO) measurements made by Marker fringe method at 1064 nm indicate that the copolymers embedded with the ring-locked triene and azo chromophores exhibit higher macroscopic nonlinear optical coefficient (70.2 pm/V and 26.5–34.6 pm/V, respectively). Thermal analysis and UV–visible absorption spectra show that the copolymers have good thermal stability (T_d = 264–319 °C) and optical transparency ($\lambda_{max} < 500$ nm).

Keywords: NLO materials; NLO chromophores; Ring-locked triene; Mitsunobu reaction

Organic and polymeric nonlinear optical (NLO) materials have continuously drawn great interest due to their several advantages superior to conventional inorganics, such as large nonlinear optical coefficient, ultrafast response, wide response wave band, high optical damage threshold, and easy combination and modification [1]. However, there are still some major challenging topics in designing organic/polymeric second-order nonlinear optical materials. For practical applications, poled polymeric second-order nonlinear optical materials should simultaneously have large macroscopic optical nonlinearity, high thermal stability and good optical transparency, therefore several parameters should be comprehensively considered to solve the nonlinearity-transparency-thermal stability tradeoff [1,2]. Many strategies and approaches have been reported for the development of high quality polymeric NLO materials [3,4]. Usually, the effective chromophores are employed to incorporate into main-chain [3–5] or side-chain [6] polymers by covalent linkages. Moreover, main-chain polymers usually show slower relaxation of orientation order than the same kind of side-chain polymers [3,5,7]. In addition, the fluorine atoms or fluoro-containing groups are incorporated in the polymer structure, the optical losses could be reduced and the solubility in organic solvent also could be improved [8]. Therefore, in this letter, we also synthesize some fluoro-containing aromatic copolymers (P1, P2, P3 and P4) embedded with the aryl azo or ring-locked triene chromophores and report the studies on the thermal properties, optical transparency as well as macroscopic optical nonlinear properties.

* Corresponding author.
E-mail address: lugyuan@nju.edu.cn (G.Y. Lu).

1001-8417/$ – see front matter
doi:10.1016/j.cclet.2011.05.006



Scheme 1. Synthesis of the fluoro-containing copolymers.

The synthetic pathway of copolymers is shown in Scheme 1. The compounds **1**, **2**, **3** and **4** were prepared according to reported procedures [9]. The fluoro-containing copolymers were synthesized by a Mitsunobu reaction with 4,4′-(hexafluoroisopropylidene)bisphenol A (6FBPA) and the corresponding *N*, *N*-dihydroxyethylaminoaryl azo or ring-locked triene compounds **1**, **2**, **3** and **4**, respectively. General procedure is as follows: 6FBPA (0.31 g, 0.90 mmol), compound **1** (or **2**, **3**, **4**) (0.90 mmol) and triphenylphosphine (0.70 g, 2.70 mmol) were dissolved in 30 mL anhydrous THF. Diethylazodicarboxylate (DEAD) (0.38 g, 2.70 mmol) in 5 mL THF was added dropwise with stirring under N_2 atmosphere at about 5 °C. The resulting solution was stirred for 3 days at room temperature and then poured into 100 mL methanol. The polymer of red solid was collected by filtration and washed with 50 mL methanol, dried under vacuum. The yields are 65–84%. The spectra data of ^{1}H NMR, IR and elemental analyses of copolymers are in accord with the assigned structures [10].

Thermal properties of the copolymers were examined by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). The glass transition temperature Tg and decomposition temperature Td of P1, P2, P3 and P4 are 118–146 °C and about 260–320 °C (Table 1), respectively, which indicate that they have higher thermal stability. The molecular weights (Table 1) of the polymers were estimated by gel permeation. The polymers are soluble in some organic solvents such as DMF, DMSO, $CHCl_3$, THF, because the flexible CF_3 groups are incorporated in the structures. UV–visible spectra of the copolymers in dilute (10^{-5} mol/L) DMF solutions were measured on Perkin-Elmer Lambda 25 UV-vis spectrometer (Fig. 1) and the absorption bands (λ_{max}) are summarized in Table 1. The λ_{max} of P1, P2, P3 and P4 are shorter than 500 nm, which indicate that they have good optical transparency.

The macroscopic second harmonic coefficients (d_{33}) of the copolymers were determined by Marker fringe method at 1064 nm. The experimental setup was similar to that in the literature [11]. The polymers were dissolved in THF to acquire a mass percent 8% solution. Then the polymers were coated on a clear glass by a spinning coater to give

Table 1
Physical and macroscopic optical nonlinear properties of copolymers.

Polymers	$\overline{M}_w$ [a] (10^4 g/mol)	$\overline{M}_n$ [b] (10^4 g/mol)	T_g (°C)	T_d (°C)	λ_{max} (nm)	d_{33} (pm/V)
P1	3.60	1.61	118	319	466.5	34.6
P2	1.98	0.94	120	264	441.5	32.0
P3	1.72	0.86	146	314	472.5	26.5
P4	1.84	0.81	120	302	429.5	70.2

[a] Weight-average molecular weight.
[b] Number-average molecular weight.