Dyes and Pigments 84 (2010) 229–236

Contents lists available at ScienceDirect

Dyes and Pigments

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

New second-order nonlinear optical polyphosphazenes: Convenient postfunctionalization synthetic approach and application of the concept of suitable isolation group

Qi Zeng [a], Guofu Qiu [b], Cheng Ye [c], Jingui Qin [a], Zhen Li [a,*]

[a] Department of Chemistry, Hubei Key Lab on Organic and Polymeric Opto-Electronic Materials, Wuhan University, Wuhan 430072, China
[b] College of Pharmacy, Wuhan University, Wuhan 430072, China
[c] Organic Solids Laboratories, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100080, China

ARTICLE INFO

Article history:
Received 24 June 2009
Received in revised form
11 September 2009
Accepted 14 September 2009
Available online 1 October 2009

Keywords:
Polyphosphazene
Nonlinear optics
Postfunctionalization
Azo coupling
Suitable isolation groups
Structural modification

ABSTRACT

The concept of *suitable isolation group* was applied to the synthesis of nonlinear optical polyphosphazenes that contained different isolation groups attached to the side chains of polyphosphazenes using a post-functional strategy. The loading density of NLO chromophore moieties in the polymers was relatively high (0.60 per unit) and all polymers displayed good processability and relatively good NLO effects, as exemplified by an SHG coefficient (d_{33}) of 67.3 pm V^{-1} recorded for the polyphosphazene that contained the largest isolation group.

1. Introduction

Polyphosphazenes possess a unique inorganic backbone based on a repeating unit of alternating phosphorus and nitrogen atoms, bearing two substituent units on each phosphorous. Since Allcock et al. [1] synthesised the first soluble and stable polyphosphazene in 1965, literally, hundreds of divers examples of such compounds have been reported and their manifold applications as functional polymeric materials, such as fire-resistant polymers, biomedical materials, responsive membranes, battery electrolytes, fuel cell membranes, superhydrophobic surfaces, as well as nonlinear optical (NLO) polymers, reported [2–12].

Second-order nonlinear optical materials have attracted much attention owing to their potential application in photonics because of their characteristic large NLO coefficients, ultrafast response time and ease of integration [13–24]. In 1991, a second-order nonlinear optical (NLO) chromophore, Dispersed red-1 (DR-1), was attached to the backbone of polyphosphazene by Allcock et al. [25]. Improvement in the properties of NLO polyphosphazene, including NLO coefficient, loading density of NLO chromophore moieties and glass transition temperature (T_g), have been reported [26–32]. As a promising candidate for NLO polymeric materials, polyphosphazenes offer many advantages, such as high thermo-oxidative and photochemical stability and transparency of the backbone over the range, 200 nm to near-IR; additionally, the two reactive sites on each repeat unit enable good synthesis flexibility. However, the improvement in NLO properties achieved thus far has not been significant enough to satisfy all required NLO applications because of two reasons namely, the difficulty of preparing soluble NLO polyphosphazenes of high loading density of NLO chromophore moieties and synthesis difficulties caused by strong dipole–dipole interactions between the highly polar chromophoric moieties in the polymeric system. Recent research has demonstrated that according to the site isolation principle, the NLO effect of polymeric materials can be improved dramatically by the introduction of isolation spacers to the azo chromophores, which weaken the intermolecular dipole–dipole interactions between the chromophoric moieties [33–36]. The current authors have prepared different kinds of NLO polymers, in which the size of the isolation groups ranged from small to larger [37–49]. It was found that the macroscopic nonlinearity of polymers could be boosted greatly by introducing "suitable isolation group". Interestingly, our recent research has

---

* Corresponding author. Tel.: +86 27 62254108; fax: +86 27 68756757.
E-mail address: lizhen@whu.edu.cn (Z. Li).

0143-7208/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.dyepig.2009.09.008

revealed that the both the solubility and processibility of the polymers can be improved after isolation groups have been introduced [47,48].

It was therefore considered that the introduction of isolation groups within the side chain of polyphosphazenes may solve the two problems mentioned above, namely, enhance macroscopic nonlinearity and improve solubility. This paper concerns the synthesis of a series of NLO polyphosphazenes (**P2–4**), that bear NLO chromophoric side chains with different isolation spacers, using a postfunctionalization strategy. The loading density of the chromophore moieties in the polymers was as high as 0.60 per unit, a level of substitution that could not easily be realised using the conventional direct approach for the preparation of functional polyphosphazenes. All polymers were soluble in polar organic solvents and demonstrated good processability. Second harmonic generation (SHG) experiments confirmed that after the introduction of isolation groups, the SHG coefficients (d_{33}) of **P2**–**P4** increased from 33.2 to 67.3 pm V^{-1}, in accordance with an increase in the size of the bound isolation group.

2. Experimental

2.1. Instrumentation

^{1}H and ^{13}C NMR spectra were measured on a Varian Mercury300 spectrometer using tetramethylsilane (TMS; $\delta = 0$ ppm) as internal standard. The Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer-2 spectrometer in the region of 3000–400 cm^{-1} on NaCl pellets. UV–visible spectra were obtained using a Schimadzu UV-2550 spectrometer. GPC analysis was performed on an Agilent 1100 series HPLC system and a G1362A refractive index detector. Polystyrene standards were used as calibration standards for GPC. THF was used as an eluent and the flow rate was 1.0 mL/min. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer. Elemental analyses were performed by a CARLOERBA-1106 micro-elemental analyzer. Thermal analysis was performed on NETZSCH STA449C thermal analyzer at a heating rate of 10 °C/min in nitrogen at a flow rate of 50 cm^3/min for thermogravimetric analysis (TGA). The thermal transitions of the polymers were investigated using a METTLER differential scanning calorimeter DSC822e under nitrogen at a scanning rate of 10 °C/min. The thermometer for measurement of the melting point was uncorrected. The thickness of the films was measured with an Ambios Technology XP-2 profilometer.

2.2. Materials

Tetrahydrofuran (THF) was dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N*-Methylpyrrolidone (NMP; caution: decomposes upon exposure to light; combustible; incompatible with strong oxidizing agents, strong acids, reducing agents, bases) was dried over and distilled from CaH_2 under an atmosphere of dry nitrogen. Compounds **9** were obtained as reported in our previous work [49]. All other reagents were used as received.

2.3. Synthesis of *P0*

N-Ethyl-*N*-hydroxyethylaniline (1.91 g, 11.6 mmol) reacted with sodium hydride (caution: corrosive; reacts violently with water, liberating hydrogen; incompatible with water, acids, alcohols, strong oxidizing agents) (0.46 g, 60% in paraffine, 11.6 mmol) in THF (20 mL) at 60 °C overnight, then the resultant solution of the sodium salt of compound **1** was added to a solution of poly(dichlorophosphazene) (caution: toxic; flammable; reacts violently with water; contact with water liberates flammable gases; explosive when mixed with oxidizing substances; may form explosive peroxides) (0.64 g, 5.5 mmol) in 80 mL of THF, and the mixture was stirred at 60 °C for 2 days. Then $NaOCH_2CH_3$ (0.79g, 11.6 mmol) was added, and the resultant mixture stirred at 60 °C for another 2 days. The mixture was poured into water (400 mL), and the white solid was filtered, washed with water, and air-dried. The solid was dissolved in THF, and the insoluble residue was filtered out. The filtrate was evaporated to remove the bulk of THF. Then the solid was isolated and further purified by several precipitations from THF into methanol. The solid was vacuum-dried at 40 °C to yield the product (1. 20 g, 74.0%). $M_w = 1\,460\,000$, $M_w/M_n = 2.73$ (GPC, polystyrene calibration). ^{1}H NMR ($CDCl_3$): δ (ppm): 0.3–1.1 ($-CH_3$), 2.5–3.5 ($-OCH_2-$ and $-NCH_2-$), 3.5–4.2 ($-OCH_2-$), 6.0–6.6 (ArH), 6.6–7.2 (ArH).

2.4. Synthesis of *P1*

P0 (0.70 g) was dissolved in *N*-methylpyrrolindone (NMP, 3.4 mL), and then 2-(2-hydroxyethoxy)-4-nitrobenzenediazonium fluoroborate (caution: author needs to add cautionary advice here) (0.71 mg, 2.4 mmol) was added under cooling with an ice bath. The color of the solution changed to red immediately. After stirring for 8 h at 0 °C, excess anhydrous potassium carbonate was added, and the mixture was stirred for additional 1 h and then filtered. The residue was washed with DMF, the filtrates were collected, and DMF was removed under reduced pressure. Some methanol was added dropwise to precipitate the polymer. The solid was further purified by several precipitations from DMF into methanol. The solid was dried in a vacuum at 40 °C to yield a red product **P1** (0.92 g, 89%). ^{1}H NMR (DMSO-d_6): δ (ppm): 0.4–1.1 ($-CH_3$), 3.4–3.8 ($-CH_2O$), 3.8–4.2 ($-CH_2O$, $-NCH_2-$), 6.2–6.8 (ArH), 6.8–7.0 (ArH), 7.0–7.3 (ArH), 7.3–7.6 (ArH), 7.6–7.9 (ArH). IR (thin film), υ (cm^{-1}): 1339 ($-NO_2$). UV–vis (DMF, 0.02 mg/mL): λ_{max} (nm): 480 (nm). IR (thin film), υ (cm^{-1}): 1339 ($-NO_2$).

2.5. General procedure for the synthesis of *P2–P4*

P1 (220 mg, 1.00 equiv) was dissolved in DMF (2 mL), then a solution (2 mL) of compound **2** or **3** or **4** (10.0 equiv), 4-(*N*,*N*-dimethyl)aminopyridine (DMAP) (caution: toxic; incompatible with acids and oxidants) (10.0 equiv) and dicyclohexylcarbodiimide (DCC) (caution: moisture sensitive; combustible; incompatible with strong oxidizing agents; avoid exposure to air or moisture) (10.0 equiv) was added. The resultant mixture was stirred at room temperature for 72 h under an atmosphere of dry nitrogen and then filtered to remove the insoluble solid. The filtrate was added dropwise to methanol to precipitate the polymer, which was further purified by several precipitations from THF into methanol, and dried in a vacuum to a constant weight.

P2: red powder (196 mg, 78.2%). $M_w = 8\,570\,000$, $M_w/M_n = 2.08$ (GPC, polystyrene calibration). ^{1}H NMR (DMSO-d6): δ (ppm): 0.4–1.1 ($-CH_3$), 3.4–4.2 ($-NCH_2-$), 4.2–4.7 ($-OCH_2CH_2-$), 6.2–6.8 (ArH), 6.8–7.0 (ArH), 7.0–7.3 (ArH), 7.3–7.6 (ArH), 7.6–7.9 (ArH). IR (thin film), υ (cm^{-1}): 1340 ($-NO_2$). UV–vis (DMF, 0.02 mg/mL): λ_{max} (nm): 480 (nm).

P3: red powder (201 mg, 75.8%). $M_w = 5\,260\,000$, $M_w/M_n = 1.11$ (GPC, polystyrene calibration). ^{1}H NMR (DMSO-d_6): δ (ppm): 0.4–1.1 ($-CH_3$), 3.4–4.2 ($-NCH_2-$), 4.2–4.8 ($-OCH_2CH_2-$), 6.0–6.6 (ArH), 6.8–7.4 (ArH), 7.4–8.2 (ArH), 8.4–8.7 (ArH). IR (thin film), υ(cm^{-1}): 1338 ($-NO_2$). UV–vis (DMF, 0.02 mg/mL): λ_{max} (nm): 480 (nm).

P4: red powder (245 mg, 87.2%). $M_w = 6\,300\,000$, $M_w/M_n = 3.42$ (GPC, polystyrene calibration). ^{1}H NMR (DMSO-d6): δ (ppm): 0.4–1.1 ($-CH_3$), 3.4–4.2 ($-NCH_2-$), 4.2–4.8 ($-OCH_2CH_2-$), 4.8–5.2 ($-CH_2N<$), 6.0–6.6 (ArH), 6.8–7.3 (ArH), 7.3–7.7 (ArH), 7.7–8.0 (ArH). IR (thin film),