Optics & Laser Technology 49 (2013) 56–63

Contents lists available at SciVerse ScienceDirect

Optics & Laser Technology

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

Preparation and thermo-optic switch properties based on chiral azobenzene-containing polyurethane

Feiyan Ye [a], Fengxian Qiu [a,b,*], Dongya Yang [a], Guorong Cao [c], Yijun Guan [c], Lin Zhuang [c]

[a] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China
[b] Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaian 223300, China
[c] Department of Physics, Jiangsu University, Zhenjiang 212013, China

ARTICLE INFO

Article history:
Received 25 October 2012
Received in revised form
3 December 2012
Accepted 10 December 2012
Available online 12 January 2013

Keywords:
Chiral azo polymer
Optical property
Thermo-optic switch

ABSTRACT

A chiral azo chromophore compound 4-(4′-nitro-phenyl-diazenyl)-phenyl-1,2-propanediol ether (NPDPPE) was prepared with *p*-nitroaniline, phenol and R(−)-3-chloro-1,2-propanediol by the diazo-coupling reaction. Then, the chromophore molecule NPDPPE was polymerized with isophorone diisocyanate (IPDI) to obtain novel chiral azobenzene-containing polyurethane (CACPU). The chemical structures of chromophore molecule and CACPU were characterized by the FT-IR and UV–visible spectroscopy. The physical properties (thermal conductivity, thermal diffusion coefficient, and specific heat capacity) and mechanical properties (tensile strength, elongation at break and hardness) of CACPU thin films were measured. The refractive index and thermo-optic (TO) coefficient (dn/dT) of CACPU thin film was investigated for TE (transversal electric) polarizations by using an attenuated total reflection (ATR) configuration at the wavelengths of 532, 650 and 850 nm. The transmission loss of film was measured using the charge coupled device (CCD) digital imaging devices. A Y-branch switch and Mach–Zehnder interferometer (MZI) thermo-optic switches based on thermo-optic effect were proposed and the performances of switches were simulated. The results showed that the power consumption of the Y-branch thermo-optic switch was only 3.28 mW. The rising and falling times of Y-branch and MZI switches were 12.0 ms and 2.0 ms, respectively. The conclusion has potential significance to improve and develop new Y-branch digital optical switch (DOS), MZI thermo-optic switch, directional coupler (DC) switch and optical modulators.

1. Introduction

Recently, organic optical materials have continuously drawn interests because of their potential applications in the field of optical devices [1–3]. Among the organic materials, the polymeric optical materials containing azobenzene chromophores are considered candidate materials, mainly because some photo-induced responses have been demonstrated, that make them appealing materials for applications in optics and photonics as in non-linear optics [4,5], optical data storage [6,7], holographic data recording systems [8,9] and optical switch [10,11].

Polyurethane (PU) polymers combine rigid hard segment and flexible soft segment, which offer a wide range of variability in structure and properties. The polyurethane matrix forms extensive hydrogen bonding between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. Many optical polymer materials require either non-centrosymmetric or polar packing (space group) of the active material. However, controlling the organization/packing of polymer molecule is a very difficult task to accomplish, an easier way is to make the polymer candidate containing chiral unit and use its inherent chirality to prevent centrosymmetric packing. Optical switches based on chiral polymeric materials are superior to traditional optoelectronic ones based on inorganic materials because of their higher sensitivities and easier fabrication process [12]. In this work, a novel chiral azobenzene-containing polyurethane (CACPU) was prepared. The thermo-optic property, dispersion property and transmission loss of materials were investigated. 1 × 2 Y-branch and 2 × 2 Mach–Zehnder polymeric thermo-optic switch were simulated and analyzed based on the chiral azobenzene-containing polyurethane.

2. Experimental

2.1. Materials

p-nitroaniline, ethanol, N, N′-dimethylformamide (DMF), toluene, sodium nitrite ($NaNO_2$), dibutylbis(lauroyloxy)tin (T-12), methyl

---

* Corresponding author at: School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China. Tel./fax: +86 511 88791800.
E-mail address: fxqiuchem@163.com (F. Qiu).

0030-3992/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.optlastec.2012.12.009

methacrylate (MMA), *n*-butylacrylate (BA) were obtained from Sinopharm Chemical Reagent Co., Ltd. in Shanghai, China. Isophorone diisocyanate (IPDI) was supplied by Rongrong Chemical Co., Ltd. in Shanghai, China. R(−)-3-Chloro-1,2-propanediol was produced by Adamas Reagent Co., Ltd. in Shanghai, China. Phenol, azobisisobutyronitrile (AIBN) and concentrated hydrochloric acid were obtained from Hubao Chemical Co., Ltd. in Yangzhou, China.

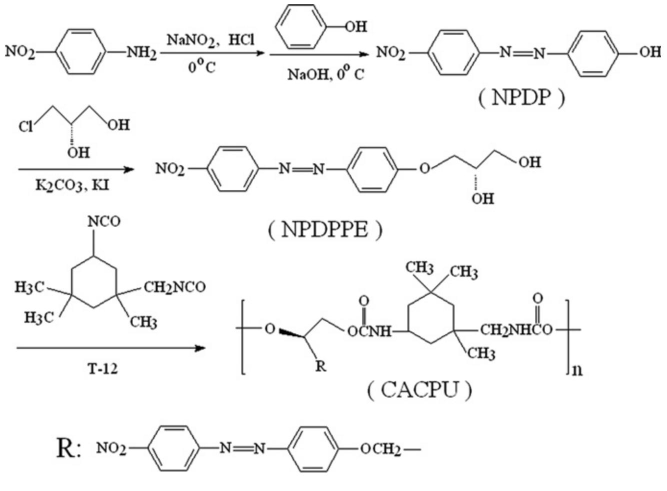
2.2. Characterization

Ultraviolet–visible (UV–vis) spectra of samples were recorded with a Shimadzu (Japan) UV-2450 spectrometer at 25 °C. Fourier transform infrared (FTIR) spectra of samples were obtained on a KBr pellet with a Nicolet (USA) AVATAR 360 FT-IR spectrometer. A minimum of 32 scans was signal-averaged with a resolution of 2 cm^{-1} in the 4000–400 cm^{-1} range. Gel permeation chromatography (GPC) was performed in THF to determine molecular weights and molecular weight distributions, M_w/M_n, of polymer samples with respect to polystyrene standards using a WATERS SEC-244 system at 25 °C in THF. The tensile strength and elongation at break testing for polymer film were carried out on a tensile tester (KY-8000A, Jiangdu Kaiyuan Test Machine, Jiangdu, China) at room temperature at a speed of 50 mm/min. All measurements had an average of three runs. The dumbbell-type specimen was 30 mm length at two ends, 0.2 mm thick and 4 mm wide at the neck. The hardness was measured with a sclerometer (KYLX-A, Jiangdu Kaiyuan Test Machine) (Jiangdu, China); measurements were done three times for the polymer sample, and the average value was calculated. The specific rotation was performed with an automatic polarimeter (Shanghai Precision Scientific Instrument, China). The melting point was measured by an X-5 microsurgery melting point detector (temperature control type) (Beijing Tech Instrument, China). The thermal conductivity, thermal diffusion coefficient, and specific heat capacity of polymer film were obtained from a thermal conductivity detector (TC3010, Xi′an Xiaxi Electronic Technology Co., Ltd, Xi′an, China) at room temperature.

2.3. Preparation of chiral azobenzene-containing polyurethane (CACPU)

A solution of $NaNO_2$ (1.035 g) in deionized water was slowly added to the solution of *p*-nitroaniline (2.07 g) in hydrochloric acid (2.5 mol/L, 10 mL). The solution was kept at 0 °C for 1 h with vigorous mechanical agitation. Then, the solution was washed with ammonia water and deionized water until the pH of the filtrate reached 7. Then, the diazonium salt solution was added to the solution of phenol (1.41 g) and sodium hydroxide (0.6 g) in deionized water (50 mL) at 0 °C and kept there for 2 h under stirring. The solid precipitate was washed with ammonia water and deionized water until the pH of the filtrate reached 7. The resultant precipitate was filtered and the crude product was recrystallized twice with ethanol. The orange-red compound 4-(4′-nitro-phenyl-diazenyl)-phenol (NPDP) was obtained.

A mixture of NPDP (1.215 g), chiral reagent R(−)-3-chloro-1,2-propanediol (0.6 g), K_2CO_3 (0.7 g) and KI (0.1 g) dissolved in DMF (40 mL) was added into a four-necked flask equipped with a mechanical stirrer, thermometer and reflux condenser, the reaction mixture was heated to 110 °C and refluxed for 4 h. After the reaction was completed, the solution containing hydroxyl groups and azobenzene chromophore group was obtained, and was acidified with hydrochloric acid and deionized water until the pH of the filtrate reached 7. The resultant precipitate was filtered and the crude product was recrystallized twice with toluene. The yellow-brown azo chromophore compound 4-(4′-nitro-phenyl-diazenyl)-phenyl-1,2-propanediol ether (NPDPPE) was obtained.



Scheme 1. Synthetic route of chiral azobenzene-containing polyurethane.

A solution of NPDPPE (1.15 g) dissolved in DMF (40 mL) was added into a four-necked flask equipped with a mechanical stirrer, thermometer and reflux condenser, and was stirred at 80 °C. Then, IPDI (1.33 g) and T-12 (0.2 mL) as catalyst were added to the flask and the reaction mixture was stirred for 3 h. Then, DMF was evaporated under reduced pressure. The product was washed with methanol for three times and then dried in a vacuum oven at 50 °C to a constant weight. The chiral azobenzene-containing polyurethane (CACPU) was obtained. The weight-averaged molecular weight (M_w) and molecular weight distributions (M_w/M_n) are 25300 and 1.28, respectively. The synthetic route of chiral azobenzene-containing polyurethane (CACPU) was shown in Scheme 1.

2.4. Preparation of film-forming agent

Methyl methacrylate (MMA, 30.7 g) and *n*-butylacrylate (BA, 39.30 g) were dissolved in DMF (50 mL). And then, the solution was added into a 250 mL three-neck flask equipped with a mechanical stirrer and a nitrogen gas blowing device. The mixture was heated to 70 °C and stirred under nitrogen atmosphere for 4 h. Meanwhile, azobisisobutyronitrile (AIBN, 0.14 g) was dissolved in DMF (20 mL) and slowly added into the three-neck flask through a dropping funnel over 1 h. Four hours later, the film-forming agent was prepared.

2.5. Preparation of film

In the experiment, the chiral azobenzene-containing polyurethane (CACPU) dissolved in DMF and the film-forming agent were mixed uniformity with mass ratio of 1:3 using ultrasonic vibration for 2 h. Then, the mixture was filtered through a syringe with a 0.45 μm Teflon filter and spin-coated onto the hypotenuse face of a prism. The film was dried in a vacuum oven at 35 °C for 12 h.

3. Results and discussion

3.1. Structure characterization

The UV–vis spectra of the NPDP, NPDPPE and CACPU were shown in Fig. 1. From Fig. 1, the maximum absorption peaks of the NPDP, NPDPPE and CACPU were observed at 383.5, 380.8 and 385.5 nm, respectively. This was mainly due to the π–π* transition absorption peak of the –N=N–groups. Compared with NPDP, the maximum absorption peak of NPDPPE appeared a blue