Synthesis of thermally stable new polyurethanes containing nitro-substituted 1,3,4-oxadiazole chromophores for second order nonlinear optical applications

R.G. Tasaganva [a], R.V. Doddamani [a], S.R. Inamdar [b], M.Y. Kariduraganavar [a],*

[a] Department of Chemistry, Karnatak University, Dharwad 580 003, India
[b] Department of Physics, Karnatak University, Dharwad 580 003, India

A B S T R A C T

Push–pull type nonlinear optical chromophores containing nitro-substituted oxadiazoles were newly synthesized and successfully condensed with tolylene-2,4-diisocyanate, 4,4′-methylenedi(phenyl isocyanate) and 3,3′-dimethoxy-4,4′-biphenylenediisocynate to yield a series of polyurethanes. The resulting chromophores and their corresponding polyurethanes were systematically characterized by FTIR, ^{1}H NMR, UV–vis and elemental analyzer. Thermal behaviors of these polyurethanes were investigated using differential scanning calorimetry and thermogravimetric analysis. After poling, the change in the molecular alignment in the polymer films was confirmed by atomic force microscopy. The inherent viscosity (η inh) of polyurethanes measured by Ubbelohde viscometer was in the range of 0.25–0.29 g/dl. High thermal endurance of poled dipoles was observed for all the polyurethanes. The second harmonic generation (SHG) coefficients (d_{33}) of the poled polyurethanes determined by the Maker fringe technique were in the range of 58.66 to 89.77 pm/V at 532 nm, signifying the acceptability for nonlinear optical devices.

© 2015 Elsevier GmbH. All rights reserved.

1. Introduction

The second-order nonlinear optical (NLO) materials are of current interest to a large number of research groups owing to their potential applications in photonics including telecommunication, digital signal processing, electro optic (EO) modulator, frequency doubling and optical inter-connects, etc. [1–3]. Both inorganic and organic materials have been the research focus for NLO applications, but inorganic materials limit their application potential due to their disadvantages such as slow response time, high absorption and degradative photorefractive effects [4,5]. Organic materials, on the other hand, offer advantages of large susceptibility, high laser damage threshold, faster response time, versatility of molecular structural modifications. Therefore, recently growing research efforts have been directed to organic materials, among which polymeric materials have attracted great interest considering their practical utility in fabrication of optical quality thin films for device applications [4–8].

Recently, several researchers pointed out that the strength of the electron-donor and electron-acceptor must be optimized for the specific π-conjugated system, and the loss of aromaticity between the neutral form and the charge separated zwitter-ionic form of the chromophore is believed to be responsible for the reduced or saturated β values [9–14]. Therefore, to achieve better hyperpolarizability so as to enhance the second-order NLO properties, attempts have been made to design the chromophores with less aromatic characteristics in the ground state by replacing the benzene ring in stilbene and azo-conjugated derivatives with easily delocalizable five-membered heteroaromatic rings [9,15–25]. Further, it is also pointed out that the hyperpolarizability could be enhanced with increasing the length of the bridge [18,26].

Besides hyperpolarizability, the stabilization of electrically induced dipole alignment is also an important point to be considered while designing the new NLO polymers. To achieve this, two approaches have been proposed: one is to use crosslinking method [27,28] and the other one is to utilize high glass transition temperature (T_g) polymers such as polyimides [29–31]. However, crosslinked polyurethanes having NLO responsive chromophores demonstrated an excellent thermal stability [31–33]. This is because; polyurethane matrix forms extensive hydrogen bonds between urethane linkages, and thereby increases

* Corresponding author. Tel.: +91 836 2215286x23; fax: +91 836 2771275.
E-mail address: mahadevappak@yahoo.com (M.Y. Kariduraganavar).

the rigidity preventing the relaxation of induced dipoles [34,35]. Polyurethanes with NLO-chromophores whose dipole moment is aligned transverse to the main-chain backbone, exhibiting large second-order nonlinearity with good thermal stability [34,36–38]. Furthermore, physically crosslinked systems through hydrogen bonds have the advantages such as homogeneity and good processability relative to the chemically crosslinked systems, which suffer from significant optical loss and poor processability. Literature explicitly indicated that 1,3,4-oxadiazole rings have been explored in electroluminescent and light emitting devices because of their good electron withdrawing effect [39–41].

Keeping these in view, we have made an attempt to design NLO responsive chromophores by incorporating 1,3,4-oxadiazole moiety. Further to enhance the NLO property, the length of the chromophore was suitably increased. To arrest the relaxation of induced dipoles, the resulting chromophores were successfully condensed with tolylene-2,4-diisocyanate, 4,4′-methylenedi(phenyl isocyanate) and 3,3′-dimethoxy-4,4′-biphenylenediisocynate to yield a series of polyurethanes. The physico-chemical properties of both chromophores and polyurethanes were studied using different spectroscopic and analytical techniques. In order to check the molecular alignment after poling the polymer films were subjected to atomic force microscopy. The details of their optical second-order activity in terms of electric field poling, and temporal stability along with thermal stability were studied.

2. Experimental

2.1. Materials

Tolylene-2,4-diisocyanate (TDI), 4,4′-methylenedi(phenyl isocyanate) (MDI) and N-phenyldiethanolamine were purchased from Sigma-Aldrich and used as received. Pyridine, piperidine, thionyl chloride, phosphorous oxychloride, sodium nitrite, sodium sulfide and hydrazine hydrate were procured from Loba Chemie, Mumbai, India. Phosphorous oxychloride was purified by distillation over phosphorous pentoxide under reduced pressure and thionyl chloride was freshly distilled before using. All other solvents and reagents were of analytical grade quality, purchased from S. D. Fine Chem. Ltd., Mumbai, India and used without further purification.

2.2. Instrumentation

The Fourier transform infrared (FTIR) spectra were recorded using Nicolet-5700 spectrometer. The ^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Ultraviolet–visible (UV–vis) spectra were measured using Hitachi U-2800 spectrophotometer with an accuracy of ±0.3 nm. The elemental analyses were performed with a Perkin-Elmer PE 2400 CHN elemental analyzer. Melting points of the chromophores were determined with open capillary tubes on a Mel-Temp apparatus and are uncorrected. Differential scanning calorimetry (DSC) and thermogravimetric analyses (TGAs) were, respectively, performed on a Mettler-Toledo DSC 822e and Perkin-Elmer Diamond TGA/DTA thermogravimetric analyzer at a heating rate of 10 °C/min in a nitrogen atmosphere. The inherent viscosity of polyurethanes was performed at 25 °C by employing Ubbelohde viscometer in DMF. Thin polyurethane films were obtained onto an indium–tin oxide (ITO) glass substrate using a spin casting technique at a rate of about 1500–2000 rpm from 5 wt% solution of the polyurethane in DMF. Prior to film casting, the polyurethane solution was filtered through a 0.20 μm Teflon membrane filter. All films were dried for 5 h in a vacuum oven at 80 °C to remove the residual solvents. The surface morphology of the thin films before and after poling was investigated with a Veeco diInnova SPM atomic force microscope (AFM). The thickness and refractive indices of the polyurethanes were measured with an accuracy of ±0.001 μm and ±0.0005 unit, respectively, using a SE 850 Ellipsometer.

2.3. Second harmonic generation (SHG) measurements

The dried film was heated up to a glass transition temperature and corona poled with an intense dc electric field as described in our earlier paper [4]. After being poled for 1 h, the polyurethane film was cooled to measuring temperature (25 and 100 °C) in the presence of electric field. The poling conditions were as follows: high voltage, 4 kV at the needle point; gap distance, ca. 0.8 cm; poling current, <0.25 mA.

The polyurethane sample was held at 45° angle to the incident laser beam to get maximum SHG output. The second harmonic measurements were performed utilizing the setup described in our previous paper [4]. A Mode-Locked Nd:YAG laser (Continuum Minilite-I, 6 ns pulse duration, 28 mJ maximum energy at 1064 nm, 10 Hz repetition rate) was used as a fundamental light source. The second harmonic signals generated by the p-polarized fundamental wavelength (1064 nm) were detected by fast photodiode (FDS010, rise time 0.9 ns, Thorlabs) and an oscilloscope (Tektronix TDS 724D, Digital Phosphor Oscilloscope) with a frequency of 500 MHz. A standard potassium dideuterium phosphate (KDP) crystal was used as a reference sample. The substrate (conducting ITO glass) contribution to the second harmonic signal, ~3 orders less than that of polyurethane films, was negligible.

2.4. Synthesis of chromophores

2.4.1. Synthesis of 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole (1) [42]

A mixture of 4-nitrobenzohydrazide (16.2 g, 90.0 mmol) and 4-nitrobenzoic acid (15.0 g, 90.0 mmol) was dissolved in 150 ml of phosphorous oxychloride (POCl$_3$) and refluxed for 16 h at 80 °C in an oil bath. After confirming the completion of reaction by TLC, the excess of POCl$_3$ was distilled off and the residue thus collected was slowly poured into cold water. The yellow solid was obtained and it was recrystallized in DMF and afforded 16.5 g (58.76%) of 1, mp: 132–34 °C; FTIR (KBr, cm^{-1}): 1618 (C=N), 1525, 1336 (N=O). ^{1}H NMR (DMSO-d_6, δ): 8.3 (d, 4H), 8.4 (d, 4H). Anal. Calcd. for C$_{14}$H$_8$N$_4$O$_5$: C, 53.84%; H 2.56%; N 17.94%. Found: C, 53.71%; H, 2.59%; N, 18.01%.

2.4.2. Synthesis of 4-(5-(4-nitrophenyl)-1,3,4-oxadiazole-2-yl) benzenamine (2)

To a boiling solution of 10 g of 2,5-bis(4-nitrophenyl)-1,3,4-oxadiazole 1 in 500 ml of 1,4-dioxane and 125 ml of water, an aqueous solution of sodium sulfide (41 ml, 1.25 M) was gradually added. During the addition, the solution was first turned to green and it was turned to red the addition was completed. After 5–6 h, the solution was filtered and poured into 500 ml of water. The orange precipitate thus obtained was recrystallized from water/acetone mixture and afforded 5.2 g (60.6%) of 2, mp: 242 °C; FTIR (KBr, cm^{-1}): 3310–3275 (N–H), 1610 (C=N), 1510, 1312 (N=O). ^{1}H NMR (DMSO-d_6, δ): 4.7 (s, 2H), 7.8–7.9 (q, 4H), 8.2–8.2 (m, 4H). Anal. Calcd. for C$_{14}$H$_{10}$N$_4$O$_3$: C, 59.57%; H, 3.54%; N, 19.85%. Found: C, 59.69%; H, 3.46%; N, 19.74%.

2.4.3. Synthesis of chromophore (a)

A solution of 0.358 g of sodium nitrite in 2.1 ml of water was added in 15 min to a stirred solution of 4-(5-(4-nitrophenyl)-1,3,4-oxadiazole-2-yl)benzenamine 2, (1.41 g, 5.0 mmol) in 7 ml of concentrated hydrochloric acid (37%) at 0–4 °C. After the completion of the addition, the reaction mixture was stirred for about