



Electro-optic polymeric films of phenylethynyl dyes with transparency in the blue region of the visible spectrum

Geoffrey A. Lindsay^{a,*}, Matthew C. Davis^a, Andrew P. Chafin^a, Stephen Fallis^a, Robert C. Hoffman^b, Timothy M. Pritchett^b, Jan Andzelm^c, Adam M. Rawlett^c, Dong Park^d, Warren N. Herman^d

^a US Navy, NAWCWD Research Department, China Lake, CA 93555, USA

^b US Army Research Laboratory, AMSRD-ARL-SE-EM, Adelphi, MD 20783, USA

^c US Army Research Laboratory, AMSRD-ARL-WM-MA, Aberdeen, MD 21005, USA

^d Laboratory for Physical Sciences, University of Maryland, College Park, MD 20740, USA

ARTICLE INFO

Article history:

Received 18 June 2009

Received in revised form 13 August 2009

Accepted 14 August 2009

Available online 17 September 2009

PACS:

42.65.An

78.20.Jq

Keywords:

Electro-optic

Polymers

Transparent

First hyperpolarizability

Dyes

Nonlinear optic

ABSTRACT

Easily processed electro-optic films are reported with potential for >100 GHz switching speeds. Dyes of the general chemical structure 1-(4-[N-ethyl-N-(2-hydroxyethyl)-amino]-phenylethynyl)-4-(4-cyano-phenylethynyl)-2,5-disubstituted benzene were attached as side groups to a polyimide backbone. Substituents on the central ring of the three-ring dye prevented aggregation at high concentrations of dye. These amorphous films exhibited absorption maxima in the range of 375–395 nm. A film containing 25% dye attached to polyimide was poled to give an electro-optic coefficient (r_{33}) of 12 ± 2 pm/V at 532 nm. Its properties were compared with the measured linear and nonlinear optical properties of several previously published dyes that have transparency in the blue-green part of the visible spectrum.

Published by Elsevier B.V.

1. Introduction

Nonlinear optical organic materials have captured our attention for over two decades [1], and are still of great interest because they can be easily processed into rugged flexible films. Optical modulation devices made from these materials can be switched and modulated at speeds greater than 100 GHz [2]. Other potential applications are in electric-field sensing [3], second-harmonic generation (SHG) [4], and parametric amplification [5]. The present study focuses on electro-optic (EO) organic films that have high transparency in the blue region (450–500 nm) of the visible spectrum. Dyes that have electronic absorption peaks beyond 400 nm usually have unacceptable optical absorption loss in the blue region at the high dye loadings necessary for EO applications (>25%). Some nonlinear optical (NLO) dyes that have an electronic absorption peak in the near infrared (NIR) also have a window at visible wavelengths in films 1 or 2 μm thick [6]; however, when

the thickness is increased to 10 μm at high loadings, NIR dyes (known to the authors) become completely opaque in the visible.

Information on dyes for second-order nonlinear optics that have some transparency in the visible spectrum can be found in excellent reviews from the pioneering era of organic NLO materials [7–9]. The work reported here is on EO polymer films that can be easily mass produced, however single crystals of dyes were also surveyed because crystals with quite large EO coefficients have been reported [10] that also have transparency at visible wavelengths [11]. In most reports, NLO single crystals are characterized by second-harmonic generation (SHG), which gives the d_{ij} coefficients [1,8]. There have been far fewer reports of measured EO coefficients, r_{ij} , of single crystals [9]. A few reports of transparent crystals are briefly reviewed here.

Single crystals of various small amino-nitrobenzene and related dyes have been reported [12,13], but most were too absorbing at 450–500 nm. A crystal of 2-methyl-4-nitroaniline (MNA) was reported to have $r_{33} = 67$ pm/V, dropping to 30 pm/V when operating at 94 GHz modulation [12]. A crystal of 4,4'-dimethylamino-cyanobiphenyl (DMACB) is more transparent than MNA in the blue region of the visible spectrum, and was reported by Zyss and

* Corresponding author. Address: NAWCWD, C/4L4200D, MS 6303, 1900 N. Knox Road, China Lake, CA 93555, USA. Tel.: +1 760 939 1630; fax: +1 760 939 1617.

E-mail address: geoffrey.lindsay@navy.mil (G.A. Lindsay).

Ledoux and coworkers [14] to have the following attractive properties: the λ_{\max} was 348 nm in chloroform and the β_{1064} was 62×10^{-30} esu by electric-field-induced SHG (EFISH). The measured EO coefficient of this crystal has not yet been reported. Ren et al. [15] reported dissolving this dye in an aromatic polyether and preparing a film that exhibited an r_{33} of 83 pm/V at 633 nm (the dye concentration was not reported). A larger dye that received much attention was 4'-nitro-benzylidene-3-acetamido-4-methoxyaniline (MNBA). An optical waveguide of MNBA on a cladding layer of MNBA-Et (the propionamide analogue) was reported to have an $r_{11} = 160$ pm/V at 633 nm [16]. A mm-thick single crystal of MNBA has an optical density of about 0.2 at 535 nm, but it has exponentially increasing absorption below 500 nm [17].

Lipscomb et al. published a comprehensive tabulation of measured EO coefficients of rather small dyes in polymer films, many of which are fairly transparent at visible wavelengths [18]. At relatively high dye concentrations, chemically attaching small dyes to a polymeric matrix is generally helpful in preventing dye aggregation. In amorphous poled films one must deal with the issue of temporal stability of dye alignment. Smaller dyes generally have poor stability of polar alignment because they have faster rotational diffusion rates. A strategy to retard the rotational diffusion rate of small dyes would be to rigidly link two smaller dyes head-to-tail [19]. The thermal-temporal stability of dye orientation is also greatly improved if the glass transition temperature (T_g) of the matrix is high enough [20]. Small *p*-nitroaniline dyes, even when attached to polymer, have poor temporal alignment stability [21]. Greater stability was obtained when these materials were crosslinked during poling; the resulting film exhibited $d_{33} = 14$ pm/V (measured by SHG at 1064 nm) [22]. In theory, rotational diffusion of the dye should be retarded in a liquid crystal phase. The rather large dye, 4-alkoxybiphenyl-4-nitrotolane ($\lambda_{\max} = 357$ nm), was attached as a side-chain to polymethylmethacrylate (PMMA) to form a liquid crystalline phase with $d_{33} = 23$ pm/V [23]; but the d_{33} decayed 20% at room temperature in 2 h due to the low glass transition temperature ($T_g \sim 50$ °C). A coumarin dye ($\lambda_{\max} = 410$ nm with sharp cut off at 450 nm) was attached as a side-chain to PMMA through an amide link; the hydrogen bonding added alignment stability [24] (the r_{33} coefficient was strongly dispersed: 12 pm/V @ 477 nm to 5 pm/V @ 514 nm). Cyanocinnamide dyes were polymerized in syndioregic main-chain configuration [25], which afforded a higher concentration of dye (80%), a higher thermal stability ($T_g \sim 200$ °C), $\lambda_{\max} = 403$ nm, and films with $r_{33} = 8.5$ pm/V at 1320 nm [26]. An azeotropic main-chain configuration of stilbene dyes also gave good results [27].

In this study, we present the synthesis and optical properties of EO films of two-ring and three-ring phenylethynyl dyes attached as side-chains to polyimide. Density Functional Theory predictions of the relative hyperpolarizability and λ_{\max} for various substitutions on the dye π -scaffolds were used as a guide for prioritizing the research. Finally, the results from the present study are compared with optical properties of selected dyes from the literature that have transparency in the blue-green region of the visible spectrum and that may have competitive EO coefficients.

2. Experimental

2.1. Methodology

Unless otherwise stated, all reagents were purchased from Sigma-Aldrich (Milwaukee, WI) and were used as-received. 2-Methyl-3-butyn-2-ol (methylol) was purchased from Farhan Laboratories (Gainesville, FL). 1-Bromo-4-nitrobenzene was obtained from Eastman Organic Chemicals (Rochester, NY). Palladium, 5% on carbon was purchased from Lancaster Synthesis,

Ltd. (Windham, NH). Sodium periodate (NaIO_4) was obtained from JT Baker (Phillipsburg, NJ). Bromobenzene (reagent grade) was obtained from Spectrum Chem. Mfg. Corp. (Gardena, CA). Palladium(II) acetate 98% was obtained from Strem Chemicals (Newburyport, MA). 6FDA (2,2-bis-(3,4-dicarboxyphenyl) hexafluoropropane dianhydride) was purchased from ChrisKev (Leawood, KS 66211) and used as-received. All NMR data were collected on a Bruker Avance II 300-MHz spectrometer (^1H at 300 MHz, ^{13}C at 75 MHz); data were processed using NUTS software from Acorn NMR (Livermore, CA); spectra are referenced to tetramethylsilane. Elemental analyses were made by Atlantic Microlab, Inc. (Norcross, GA), and are not corrected. The UV-Vis absorption spectra were recorded on a Cary 5 spectrometer at room temperature. Differential scanning calorimetry (DSC) was performed on a TA Instruments, Inc. Model Q100. The DSC T_g was taken as the midpoint of the step transition observed on the 2nd or 3rd heating scan at 10 °C/min. The gel permeation chromatography (GPC) equipment used to measure molecular weight of the polyimides was a Viscotek, Inc., model 302-050; the columns were calibrated relative to polystyrene standards; the solvent was tetrahydrofuran (THF); and the ultraviolet-visible (UV-Vis) detector was set at 280 nm.

2.2. Synthesis

The chemical structures of materials prepared for this study are shown in Scheme 1.

Unless otherwise stated below, the synthetic procedures for making the phenylethynyl dyes (**D1–D3**) are given in Ref. [28], and the generic polyimide attachment procedure, in Ref. [29].

4'-Amino-4-nitrotolane (**ANT**) final preparation step was as follows. A 500 mL round-bottomed flask equipped with magnetic stirbar was charged with 13.18 g 4-nitrophenylacetylene (0.896 mol), 21.6 g recrystallized 4-iodoaniline (0.98 mol, 1.1 equiv.), 0.95 g PPh_3 (4 mol%), 23 g piperidine (0.27 mol, 3 equiv.) and 200 mL anhydrous THF. The mixture was stirred and degassed by bubbling N_2 through the solution for 30 min. In one portion, 202 mg $\text{Pd}(\text{OAc})_2$ (1 mol%) and 340 mg CuI (2 mol%) was added to the mixture. The mixture was gently refluxed under N_2 for 4 h after which time the reaction was complete by TLC. The mixture was cooled to room temperature and the piperidine/HI salt was filtered (13.9 g, 73%). The filtrate was rotary evaporated leaving a dark red solid. The crude material was slurried with 200 mL MeCN and the product filtered. The red-orange solid was recrystallized from MeCN to give the title compound as copper-red needles (6.5 g, 31%). Mp 207–210 °C. δ_{H} (DMSO): 8.21 (d, $J = 9.3$ Hz, 2H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 6.58 (d, $J = 8.3$ Hz, 2H), 5.77 (s, NH_2); δ_{C} (DMSO): 150.48, 145.89, 133.22, 131.63, 130.62, 123.87, 113.64, 106.80, 97.59, 85.86.

Polyimide (27 mol% side-chain sites) was prepared as follows. 3,5-Bis(4-aminophenoxy)-1-hydroxymethylbenzene monomer [29], called BHB-OH (5.90 g, 17.15 mmol) and cadaverine (1.49 g, 14.61 mmol) were dissolved in 105 mL NMP. 2,2'-Bis-(3,4-dicarboxyphenyl)-hexafluoroisopropane dianhydride, called 6FDA (13.83 g, 31.13 mmol) and phthalic anhydride (0.188 g, 1.27 mmol (2 mol%)) were added in one portion. The viscous yellow solution was stirred at RT overnight under nitrogen. The solution was stirred at 180 °C for 6 h to complete imidization; the solution was precipitated into 2.0 L methanol. The off-white powder was collected on a frit, washed with methanol (1.0 L), diethyl ether (0.5 L), then air dried ~ 1 h followed by drying under high vacuum for 24 h. Yield was 18.2 g (90%); the DSC T_g was 219 °C; the GPC weight-average molecular weight (M_w) was 22,300 Da, and number-average (M_n) was 8100 Da.

Polyimide-attached aminonitrotolane (**P-ANT**) was prepared as follows. Polyimide (1.01 g) was dissolved in 10 mL anhydrous THF.

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