



Synthesis and electro-optic activities of novel polycarbonates bearing tricyanopyrroline-based nonlinear optical chromophores with excellent thermal stability of dipole alignment



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ABSTRACT

Two series of novel electro-optic (EO) polycarbonates incorporating two kinds of tricyanopyrroline-based nonlinear optical (NLO) chromophores were designed and synthesized. These new polycarbonates were prepared through the facile copolymerization of diol NLO chromophores and bisphenol A bis(chloroformate), and the successful preparations were demonstrated by ¹H NMR and Fourier transform infrared (FT-IR) spectra. These polycarbonates possessed good thermal stabilities and also showed higher glass transition temperatures (T_g) in the range of 156–165 °C. After corona poling, the EO coefficients (r_{33}) of two poled polycarbonates films were up to 52 pm/V (PC-DTCPC-Ph-2) and 46 pm/V (PC-DTCPC-FPh-2) at the wavelength of 1310 nm. The higher T_g s endow the polycarbonates' poled films with good temporal stability of poling-induced dipole alignment, and the resulting poled films of PC-DTCPC-Ph-2 and PC-DTCPC-FPh-2 could retain 95% and 93% of the initial EO activities at 85 °C for more than 500 h respectively.

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1. Introduction

During the recent decades, the organic electro-optic (EO) materials are being intensively investigated due to their potential application in high-speed EO devices with very broad bandwidth and low driving voltage, etc, and these materials have been seemed as the promising materials to replace the currently used inorganic materials (LiNbO₃) in high-speed EO modulators [1–7]. To fulfill the device's requirements, the organic EO materials should possess large EO activity, low optical loss, good processability, mechanical strength and temporal stability of the dipole orientation [8–13]. To make organic EO materials suitable for applications, much effort has been expended in developing chromophores and EO polymers [1,3,14]. Although the microscopy nonlinear optical (NLO) properties ($\mu\beta$) of chromophores have been greatly enhanced [1,3,6], a strong need remains for improving the EO activity and thermal stability of the processed materials to fulfill requirements for device fabrication processes and long-term operation. [8,15–18].

Polycarbonate has been used extensively as the host materials in the guest-host organic EO materials due to its low crystallization tendency, good solubility in halogenated solvents, good optical properties and fairly high glass transition temperature (T_g) [19,20]. Good poling efficiency is also guaranteed owing to its high dielectric constant and compatibility with large $\mu\beta$ chromophores [21]. However, the dipolar interactions between chromophores, aggregation formation and thermal relaxation of the poling-induced order usually hinder the guest-host system's practical application [14]. One of the effective approaches to solve above problems is covalent attachment of NLO chromophores onto polymer backbones, which offers many advantages over the simple guest-host materials [22,23]. However, so far there are only few researches that provide approaches to tether chromophores to the polycarbonate backbone and most of them are based on the post-functionalization. [20,24].

Our previous work reported that stable covalently attached EO polycarbonates can be prepared through directly copolymerization of the bisphenol A, diol-functionalized NLO chromophores and bisphenol A bis (chloroformate) [25]. The proposed preparation strategy offered very mild polymerization condition that the fragile chromophores could tolerate. What's more, through controlling the

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feed ratio, such a copolymerization strategy could well quantify the content of chromophores and guarantee the reproducibility of properties compared to the post-functionalization. The electron-withdrawing ability of the tricyanopyrroline (TCP) acceptor has been demonstrated stronger than the tricyanofurane (TCF) moiety used in the previously work [26–31], which offered new strategies to prepare novel EO polymers with better performances. However, to the best of our knowledge, the EO polycarbonates incorporating TCP-based chromophores have never been reported. Also, covalently attached polymers based on TCP-based chromophores rarely utilize the copolymerization strategy due to their fragile properties. Herein, we reported the details of synthesis of two series of novel polycarbonates containing the TCP-based chromophores through copolymerization of diol-functionalized TCP-based chromophores and bisphenol A bis(chloroformate). The bisphenol A was added as another monomer to adjust the concentrations of chromophores. The successful synthesis of the polycarbonates has been demonstrated by the ^1H NMR and FT-IR. The synthesized polycarbonates exhibited good film forming property and thermal stability. After corona poling, the poled polycarbonates films exhibited desired EO activities at the wavelength of 1310 nm, and the maximum r_{33} values reached to 52 pm/V and 46 pm/V for PC-DTCPC-Phs and PC-DTCPC-FPhs respectively. Owing to the Y shape structure characterization, the resultant polycarbonates possess many advantages of some other such Y type EO polymers [32–34], especially the good temporal stability of EO activities. The obtained poled films of PC-DTCPC-Ph-2 and PC-DTCPC-FPh-2 kept over 92% of the initial r_{33} values at 85 °C for over 500 h. The excellent temporal stability of EO activities endowed the new polycarbonates with potential application in EO device fabrication.

2. Experimental

2.1. Materials and instruments

All the reagents and solvents were purchased from commercial sources and used without further purification. Bisphenol A bis(chloroformate) was purchased from Tokyo Chemical Industry Co., Ltd. 1,2-dichloroethane (DCE) was freshly distilled prior to use. The protected electron donor *p*-bis(2-tert-butylidimethylsiloxyethyl)amino benzaldehyde and electron acceptor TCP were prepared according to previous literature [26,35]. ^1H NMR and ^{13}C NMR spectra were determined by Advance Bruker (400 MHz) NMR spectrometer (tetramethylsilane as internal reference). The FT-IR spectra were recorded on a Varian 3100 FT-IR spectrometer at a resolution of 2 cm^{-1} with a minimum of 64 scans. UV–Vis spectra were obtained using a Hitachi U2001 spectrophotometer. The number-average molecular weight (M_n) and weight-average molecular weight (M_w) values of the obtained polycarbonates were estimated by gel permeation chromatography (GPC), and tetrahydrofuran (THF) was used as the eluent and polystyrene (PS) standards were used for the molecular weight calibration. Thermogravimetric analysis (TGA) was determined by TA5000-2950TGA (TA co) with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under the protection of nitrogen. Differential scanning calorimetry (DSC) measurements were performed on a TA5000, 2910MDSC with a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under the protection of nitrogen. The thickness of the films were measured with an Ambios Technology XP-1 profilometer. The index of the films were measured with a Model 2010 prism coupler (Metricon) instrument.

2.2. Synthesis of compound TCP chromophores 1

Chromophore TCPC was prepared according to the literature [26]. To a solution of TCP acceptor (1.84 g, 10 mmol) in 30 mL

ethanol, *p*-bis(2-tert-butylidimethylsiloxyethyl)amimobenzaldehyde (3.8 g, 8.8 mmol) was added, and the mixture was refluxed for 1 h with stirring and then cooled to room temperature. The pure chromophore TCPC was filtered and washed with cool ethanol. Yield: 60%. ^1H NMR (400 MHz, CD_3COCD_3), δ (ppm): 8.53 (d, $J = 15.2\text{ Hz}$, 1H), 7.73 (d, $J = 8.8\text{ Hz}$, 2H), 6.93 (d, $J = 15.2\text{ Hz}$, 1H), 6.87 (d, $J = 8.8\text{ Hz}$, 2H), 3.81 (t, $J = 6.0\text{ Hz}$, 4H), 3.71 (t, $J = 5.6\text{ Hz}$, 4H), 0.88 (s, 18H), 0.03 (s, 12H); MS (MALDI-TOF): m/z calcd for $\text{C}_{32}\text{H}_{45}\text{N}_5\text{O}_3\text{Si}_2$: 603.9, found: 603.0.

2.3. Synthesis of compound 2a

TCPC (500 mg, 0.83 mmol) and potassium carbonate (286 mg, 2.1 mmol) was added to 50 mL of dry acetonitrile. The mixture was heated to reflux for 5 min under the protection of N_2 . And then, benzyl bromide (220 mg, 1.29 mmol) was added. The reaction mixture was refluxed for another 30 min. The inorganic salts were filtered. After removal of the solvent, the residue was purified by column chromatography using hexane/acetone (5:1) as eluent to give the product as green solid, yield: 52%. ^1H NMR (400 MHz, CDCl_3), δ (ppm): 8.56 (d, $J = 15.2\text{ Hz}$, 1H), 7.60 (d, $J = 8.5\text{ Hz}$, 2H), 7.42–7.28 (m, 3H), 7.20 (d, $J = 7.2\text{ Hz}$, 2H), 7.08 (d, $J = 15.2\text{ Hz}$, 1H), 6.80 (d, $J = 8.7\text{ Hz}$, 2H), 5.33 (s, 2H), 3.83 (t, $J = 5.2\text{ Hz}$, 4H), 3.71 (t, $J = 5.2\text{ Hz}$, 4H), 0.87 (s, 18H), 0.02 (s, 12H). ^{13}C NMR (100 MHz, CDCl_3), δ (ppm): 167.62, 155.81, 154.32, 151.12, 144.53, 135.25, 134.35, 129.88, 129.07, 127.56, 125.32, 113.85, 112.89, 112.59, 112.36, 97.79, 61.27, 54.57, 45.12, 26.65, 19.03, –4.59. MS (MALDI-TOF): m/z calcd for $\text{C}_{39}\text{H}_{51}\text{N}_5\text{O}_3\text{Si}_2$: 694.0, found: 693.6.

2.4. Synthesis of DTCPC-Ph

To a solution of compound 2a (300 mg, 0.43 mmol) in 30 mL acetone, 2 mL 1N HCl was added, and the mixture was stirred at room temperature for 6 h. After the solvent was removed, the crude product was purified by column chromatography using hexane/acetone (2:1) as eluent to give the product as green solid yield: 90%. ^1H NMR (400 MHz, Acetone/ DMSO-d_6 (5:1)), δ (ppm): 8.57 (s, 1H), 7.78 (s, 2H), 7.37 (t, $J = 7.3\text{ Hz}$, 2H), 7.29 (dd, $J = 13.4, 7.2\text{ Hz}$, 3H), 7.11 (s, 1H), 7.01 (d, $J = 8.8\text{ Hz}$, 2H), 5.30 (s, 2H), 4.79 (s, 2H), 3.74 (s, 8H). ^{13}C NMR (100 MHz, Acetone/ DMSO-d_6 (5:1)), δ (ppm): 167.69, 156.98, 155.14, 150.41, 144.60, 136.52, 134.57, 129.66, 128.50, 127.11, 125.16, 114.55, 114.40, 113.24, 113.13, 112.12, 96.53, 59.62, 54.89, 45.13. MS (MALDI-TOF): m/z calcd for $\text{C}_{27}\text{H}_{23}\text{N}_5\text{O}_3$: 465.5, found: 465.7.

2.5. Synthesis of compound 2b

TCPC (500 mg, 0.83 mmol) and potassium carbonate (286 mg, 2.1 mmol) was added to 50 mL of dry acetonitrile. The mixture was heated to reflux for 5 min under the protection of N_2 . And then, 3,5-bis(trifluoromethyl) benzyl bromide (396 mg, 1.29 mmol) was added. The reaction mixture was refluxed for another 30 min. The inorganic salts were filtered. After removal of the solvent, the residue was purified by column chromatography using hexane/acetone (5:1) as eluent to give the product as green solid, yield: 52%. ^1H NMR (400 MHz, CD_3COCD_3), δ (ppm): 8.53 (d, $J = 15.2\text{ Hz}$, 1H), 8.05 (s, 2H), 7.99 (s, 1H), 7.78 (d, $J = 8.0\text{ Hz}$, 2H), 7.08 (d, $J = 15.2\text{ Hz}$, 1H), 7.03 (d, $J = 9.2\text{ Hz}$, 2H), 5.54 (s, 2H), 3.94 (t, $J = 5.6\text{ Hz}$, 4H), 3.84 (t, $J = 5.2\text{ Hz}$, 4H), 0.87 (s, 18H), 0.03 (s, 12H); ^{13}C NMR (100 MHz, CD_3COCD_3), δ (ppm): 168.03, 157.28, 154.90, 150.61, 144.95, 140.52, 134.31, 132.3 (q, $^2J_{\text{C-F}} = 26\text{ Hz}$), 128.41, 125.72, 123.0 (p, $^1J_{\text{C-F}} = 273.7\text{ Hz}$), 114.37, 112.60, 112.11, 98.09, 61.52, 54.47, 45.02, 30.62, 26.26, 18.83, –5.31; MS (MALDI-TOF): m/z calcd for $\text{C}_{41}\text{H}_{49}\text{F}_6\text{N}_5\text{O}_3\text{Si}_2$: 830.0, found: 830.5.

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