

Cross-Linkable Zwitterionic Polyimides with High Electrooptic Coefficients at Telecommunication Wavelengths

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A series of nonlinear optical (NLO) polyimides were prepared by grafting 4–16 wt % zwitterionic pyridinium tricyanoquinonedimethane chromophore with a large negative hyperpolarizability ($\beta_0 = -590 \times 10^{-30}$ esu) onto the host polyimides through an ester bond formation. To enhance the temporal stability of the poled NLO polymers, a new thermally reactive group, i.e., 5-aminobenzocyclobuteneone, was introduced into the NLO polymer systems to effect the cross-linking during the thermal poling process. The resulting NLO polyimides showed good solubility in polar aprotic solvents such as *N,N*-dimethylformamide and could form uniform films by casting or spin coating without any noticeable chromophore aggregation or phase separation as examined under an optical microscope. These NLO polyimides had glass transition temperatures in the range of 170–213 °C and were thermally stable up to 270 °C. The electrical resistivity of NLO polyimides was found to be on the order of 10^{15} Ω·cm at 80 °C and dependent on the applied voltages. As the temperature increased, the resistivity dropped monotonically to 2.4×10^{11} Ω·cm at 200 °C. With a 10 wt % chromophore loading (or a number density of 15×10^{19} cm⁻³) in the polymer, the electrooptic (EO) coefficient (r_{33} at 1550 nm) reached 45 pm/V. No substantial decrease in EO coefficients was observed after the test cell was kept in the dark at 85 °C under nitrogen after 1200 h nor when the test cell was irradiated with 1550 nm light (50 μW/4 mm²) for 10 h at ambient temperature in air.

1. Introduction

Second-order nonlinear optical (NLO) polymers are promising candidates for high-speed electrooptic (EO) devices in information processing and telecommunications.^{1–7} Recently, NLO polymers with very high EO coefficients (e.g., >60 pm/V),^{2–4} were reported and prototype polymer-based Mach–Zehnder modulators^{5–7} with bandwidths over 100 GHz and drive voltages lower

than 1 V were demonstrated. Despite these significant progresses, challenges remain in the development of organic NLO materials suitable for practical EO device applications. Research on NLO polymers that possess high EO coefficients and good material stability (e.g., temporal, thermal, mechanical, and chemical stabilities) is active and typically involves the development of NLO chromophores and suitable host polymers.^{1b,c}

In the search for chromophores with large optical nonlinearities, which are characterized by their large scalar products of off-resonance hyperpolarizability (β_0) and dipole moment (μ), much effort has focused on “push–pull” molecules that have large positive β values (i.e., neutral ground states) and moderate dipole moments. Molecules that have predominantly charge-separated ground states received relatively less attention, although both theoretical and experimental studies showed that these molecules were capable of yielding very large optical nonlinearities (i.e., high negative β value and large dipole moment).^{8–10}

A few zwitterionic chromophore systems with high $\mu\beta$ values have been reported in recent years.^{9,10} Pyri-

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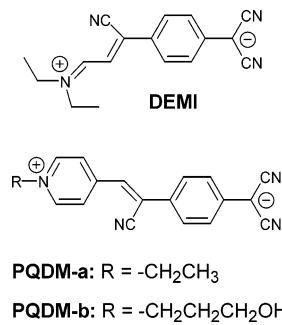


Figure 1. Chemical structures of zwitterionic chromophores.

dinium tricyanoquinonedimethanes (e.g., PQDM-a, Figure 1)¹¹ and the structural analogue DEMI (Figure 1) are a known class of zwitterionic chromophores. DEMI has a large β_0 value of -350×10^{-30} esu or a $\mu\beta_0$ value of -9450×10^{-48} esu in chloroform,⁹ while a newly synthesized hydroxyl-containing PQDM-b (Figure 1)¹² has an even larger β_0 value of -590×10^{-30} esu ($\beta = 1930 \times 10^{-30}$ esu at 1.07 μ m in DMF) from hyper-Rayleigh scattering measurements.¹³ By taking into account the very large dipole moment expected for this type of chromophore in polar media (e.g., ~ 50 D),¹⁴ the PQDM chromophores offer an unusually high value of $\mu\beta_0$ for EO applications. Considering the fact that high EO coefficients have not been realized with zwitterionic polymers, it is necessary to demonstrate the potential of extremely high EO activity of zwitterionic polymers derived from PQDM chromophores. Accordingly, our approach involves incorporation of PQDM-b into the acid-containing polyimides having a range of glass transition temperatures and use of a new thermally cross-linking agent, 5-aminobenzocyclobuteneone (BC-BO),¹⁵ to achieve network formation and prevent chromophore relaxation.

2. Results and Discussion

Host Polymers. From the material's aspect, the development of NLO polymers suitable for EO device applications depends on both the chromophores and the host polymers. In general, the host polymer should be structurally compatible to form a covalent bonding with the chromophore, physically able to provide a desired (polar or nonpolar) medium, and chemically reactive to form a network to stabilize the oriented chromophores. Thus, a thermally cross-linkable polymer with high glass transition temperature (T_g) is often selected as a host. To find a suitable type of host polymers for the

zwitterionic PQDM chromophores, high- T_g polycarbonate, poly(ether sulfone)s, and polyimides were screened in a doping test. Among them, polyimides were found to be able to accommodate more PQDM (~ 5 wt %) than the other two types of polymers (< 2 wt %). Thus, the polyimide was chosen as a host and designed to have the carboxylic acid group for linking the PQDM chromophore (e.g., PQDM-b) through an ester bond formation.

Given the good thermal stability of PQDM chromophores (up to 270 °C), host polyimides with a T_g higher than 250 °C were first synthesized from 3,5-diaminobenzoic acid and various dianhydride monomers.¹⁶ However, only small EO coefficients (< 4 pm/V) were achieved for the resulting NLO polyimides, and the prolonged heating at a temperature higher than 245 °C led to the color fading in the NLO polymers during the poling process. To allow for an efficient poling at a lower temperature, a relatively flexible diamine, 3,5-bis(4-aminophenoxy)benzoic acid (DAPBA), was synthesized and polymerized with 4,4'-(4,4'-isopropylidene-diphenoxyl)bis(phthalic anhydride) (BPADPA). The host polyimide **1a** had a T_g of 232 °C and inherent viscosity of 0.42 dL/g in *N,N*-dimethylacetamide (DMAc) (Scheme 1). In the presence of phthalic anhydride (4 mol % relative to BAPBA) as an end-capping agent, polymerization of BAPBA and BPADPA afforded the host polyimide **1b** with a lower T_g (222 °C) and a lower viscosity (0.33 dL/g in DMAc). End-capped **1b** is expected to be able to yield NLO polymers with a higher chain mobility than **1a**, due to its shorter chain length. Both **1a** and **1b** were prepared by the conventional two-step method, i.e., the formation of poly(amic acid)s and subsequent chemical imidization with acetic anhydride and pyridine. To free all the acid groups in the polymers, it was necessary to add an excess amount of acetic acid before workup. The ¹H NMR and IR spectra of **1a** and **1b** were consistent with the polymer structures and showed no trace of pyridine being present. TGA analysis indicated an onset temperature of 425 °C for 5% weight loss in nitrogen. Polymers **1a** and **1b** were readily soluble in tetrahydrofuran (THF), DMAc, and *N,N*-dimethylformamide (DMF), and could be cast into flexible tough films.

NLO Polymers. Grafting of chromophore PQDM-b onto host polymers **1a** and **1b** was carried out using 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide (EDC) as a coupling reagent (Scheme 1). A new thermally reactive compound, BCBO, was introduced in a concentration of 20 mol % relative to the acid groups in the host polymers during the grafting reaction. It has been demonstrated that the BCBO group by itself or in a variety of polymers can undergo a ring-opening reaction at temperatures above 200 °C to form a reactive vinylketene intermediate.¹⁵ The subsequent dimerization and polymerization of the vinylketene groups lead to the polymer cross-linking or curing. The residual carboxylic acid groups in host polymers were blocked by using either 3,5-di-*tert*-butylphenol (DBP) or 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-1-octanol (PDFO) during the grafting reaction, which also served as a means to

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Scheme 1. Synthesis of Host and NLO Polyimides

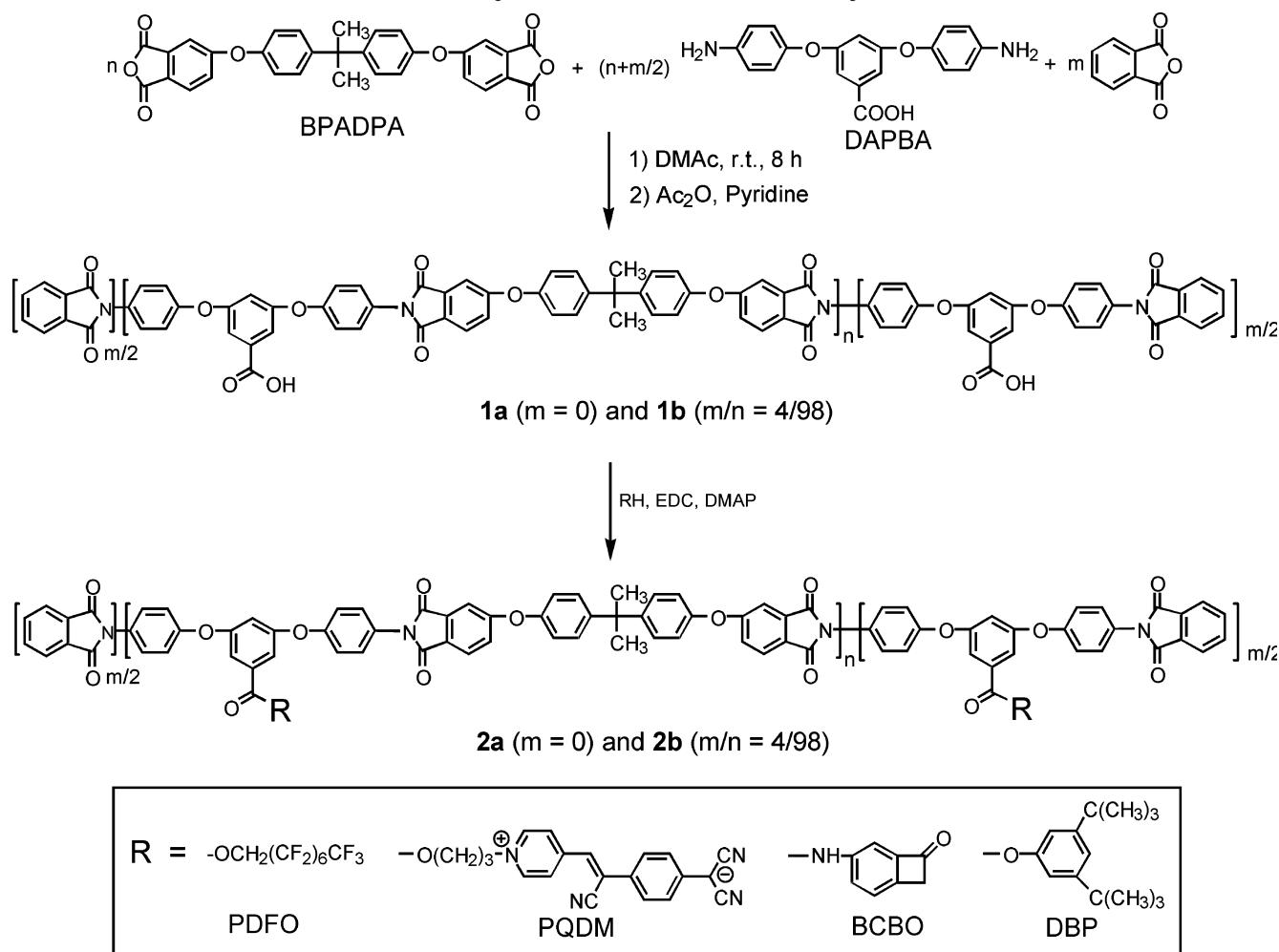


Table 1. Characterization of NLO Polymers 2a and 2b

NLO polymer	[PQDM] (wt %) (ND, cm^{-3}) ^a	T_g^b (°C)	n ^c	r_{33}^{d} (pm/V)
2a	9 (13×10^{19})	213	1.644	18
2b _{4%}	4 (6×10^{19})	170	1.632	38
2b _{10%}	10 (15×10^{19})	189	1.655	45
2b _{16%}	16 (23×10^{19})	209	1.662	24

^a The weight percentage (wt %) of PQDM-b in NLO polymer, calculated from a calibration equation of $A = 114.66C + 0.0696$, where A is absorption and C is concentration (mg/mL), which is established from the PQDM absorption at 664 nm in DMF solution. The number density (ND) was calculated using a density of 0.81 g/mL for each NLO polymer as estimated by the density-matching method (i.e., adjusting the ratio of water and methanol to 8:1 in volume so that the polymer film was suspended in the solution to a half-height). ^b Measured by TMDSC in nitrogen. ^c Refractive index at 1555 nm. ^d Electrooptic coefficient at 1550 nm.

adjust the polymer properties such as the T_g and refractive index. Accordingly, the NLO polymers **2a** and **2b** were derived from **1a** and **1b**, respectively, with different amounts of PQDM-b in the feed. The three analogous polymers **2b** contain 4, 10, and 16 wt % PQDM and are denoted as **2b**_{4%}, **2b**_{10%}, and **2b**_{16%} accordingly (Table 1).

All the NLO polymers appeared to be deep blue in color and have a maximum absorption at 664 nm in DMF (spectrum a, Figure 2). IR spectra showed the characteristic bands of the cyano groups at 2170 and 2130 cm^{-1} and of the imides at 1780 and 1720 cm^{-1} .

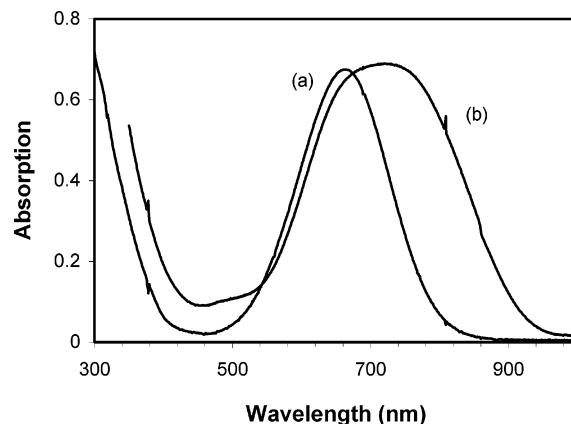


Figure 2. UV-vis absorption spectra of **2a** (a) in DMF solution (6.0×10^{-5} g/mL) and (b) in a thin film (1.06 μ m in thickness).

The ^1H NMR spectra of polymers **2a** and **2b** displayed the expected peaks corresponding to the moieties of the host polyimides PQDM-b, BCBO, and DBP (or PDFO) and those due to the formation of *N*-acylurea side products.¹⁷ The *N*-acylurea groups were formed in a concentration of about 13–17 mol % relative to the acid groups in the host polymers and did not adversely affect

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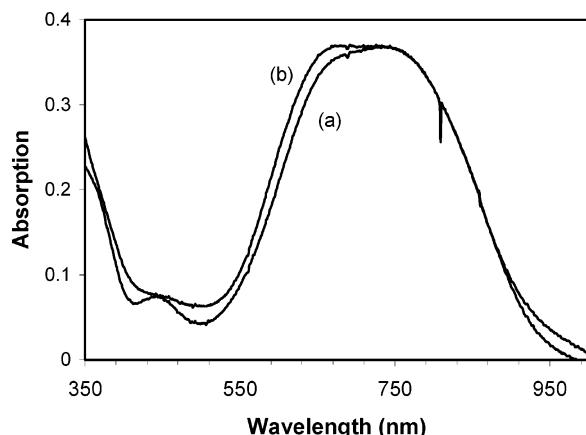


Figure 3. UV-vis absorption spectra of a thin film of **2b**_{4%} with a thickness of 0.94 μm (a) before and (b) after heating at 200 $^{\circ}\text{C}$ in nitrogen for 1 h.

the thermal and optical properties of the corresponding NLO polymers. The T_g values of the NLO polymers were found to be in the range between 170 and 213 $^{\circ}\text{C}$ by temperature-modulated DSC (TMDSC) and increased with an increase of PQDM in the polymer (Table 1). A nonreversible exothermic transition with an onset temperature at 215 $^{\circ}\text{C}$ and a maximum temperature at 240 $^{\circ}\text{C}$ existed for all the NLO polymers, which is attributed to the ring-opening reaction of BCBO. The onset decomposition temperatures of NLO polyimides in nitrogen were around 270 $^{\circ}\text{C}$, which is similar to that of PQDM-b. Isothermal heating of **2b**_{10%} at 210 $^{\circ}\text{C}$ in nitrogen for 40 min gave a total weight loss of less than 0.5%. The results from these thermal studies are useful in determining the poling parameters such as the temperature range and poling time.

NLO polyimides **2a** and **2b** were readily soluble in polar aprotic solvents such as DMF, DMAc, and 1-methyl-2-pyrrolidinone (NMP) but not in THF. Uniform films with a thickness of 1–3 μm could be prepared on glass, a silicon wafer, or an ITO electrode by either solution casting or spin coating from their DMF/cyclopentanone solutions. A broadening and a red shift of the charge-transfer absorption band were observed for the polymer films in comparison with the polymer solution, regardless of the PQDM content in the polymers. This implies the existence of π – π stacking interactions between PQDM and the polymer backbone (spectrum b, Figure 2). No phase separation in the polymer films was observable under an optical microscope, and no new absorption band due to chromophore aggregations was found in the UV-vis spectra. Heating a film of polymer **2b**_{4%} at 200 $^{\circ}\text{C}$ in nitrogen for 1 h did not change the chromophore absorption (Figure 3), further confirming the adequate stability of these NLO polymers as required for poling. The polymer films retained their blue color for a period of more than one year when they were stored in the dark. Since the electrical property of NLO polymers is another of the important factors that need to be taken into account for the development of EO waveguide devices, the temperature dependence of the electrical resistivity of NLO polymer films was studied under different field strengths. As shown in Figure 4, the resistivity of **2b**_{10%} was on the order of 10¹⁵ $\Omega\cdot\text{cm}$ at 80 $^{\circ}\text{C}$ and related to the applied voltages. As the temperature increased, the electrical resistivity dropped

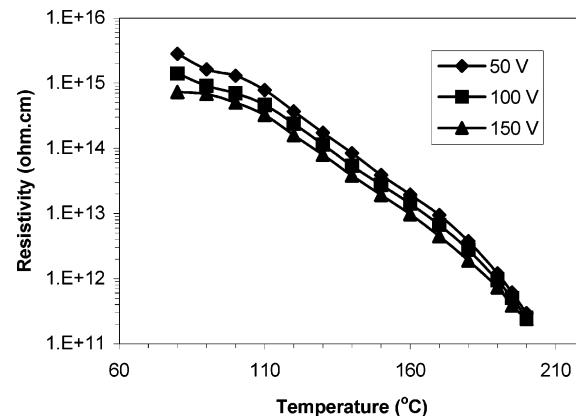


Figure 4. Temperature dependence of the electrical resistivity of a thin film (4.8 μm in thickness) of **2b**_{10%}.

monotonically to 2.4 \times 10¹¹ $\Omega\cdot\text{cm}$ at 200 $^{\circ}\text{C}$ and the field effect diminished. Accordingly, the cladding materials used in the EO waveguide device should have an electrical resistivity lower than that of NLO polymers (e.g., **2b**) within the range of the poling temperatures, to achieve the effective poling voltage across the core layer of the NLO polymer. Thus, these zwitterionic polyimides have thermal and electrical properties that can meet some basic requirements for EO device applications (e.g., fabrication, poling, and modulation).

EO Properties. For EO measurements, thin films of polymers **2a** and **2b** on ITO were prepared and dried at 160–180 $^{\circ}\text{C}$ under vacuum (1 mmHg) for 2 h before a thin layer (\sim 150 nm) of gold was sputtered as a top electrode onto the polymer films. In contact poling, the electric field was turned on at 180 $^{\circ}\text{C}$ and the voltages applied across the films were maintained in a range of 0.6–0.8 MV/cm while the current across the films was kept below 10 μA . The heating profile follows 180 $^{\circ}\text{C}$ (5 min), 200 $^{\circ}\text{C}$ (5 min), 215 $^{\circ}\text{C}$ (20 min), and 230 $^{\circ}\text{C}$ (10 min). After poling, all the polymer films became insoluble in common organic solvents, indicating the formation of the cross-linked polymer networks.

The EO coefficients (r_{33} , pm/V) of poled **2a** and **2b** were measured with the Teng–Man setup¹⁸ at 1550 nm and seemed to correlate with the T_g values and the chromophore content. Polymers **2a** and **2b**_{10%}, which have similar amounts of chromophore but different T_g values, had the lowest (18 pm/V) and the highest EO coefficients (45 pm/V), respectively (Table 1). The higher T_g (213 $^{\circ}\text{C}$) for polymer **2a** indicates its lower chain mobility than that of polymer **2b**_{10%}, which is believed to hamper the orientation of chromophores in the resulting polymer networks during the poling stage at 180–230 $^{\circ}\text{C}$. Furthermore, the three analogous polymers **2b**, regardless of the PQDM content (4–16 wt %), had lower T_g values (170–209 $^{\circ}\text{C}$) than **2a** (213 $^{\circ}\text{C}$) and displayed higher EO coefficients (24–45 pm/V) than **2a** (18 pm/V) (Table 1).

Among the three NLO polymers **2b**, polymer **2b**_{4%}, which contains only 4 wt % or a number density of \sim 6 \times 10¹⁹ cm^{-3} of PQDM chromophore had the lowest T_g (170 $^{\circ}\text{C}$) and showed an r_{33} value of 38 pm/V. This r_{33} value is larger than that (31 pm/V) of the LiNbO₃ crystal

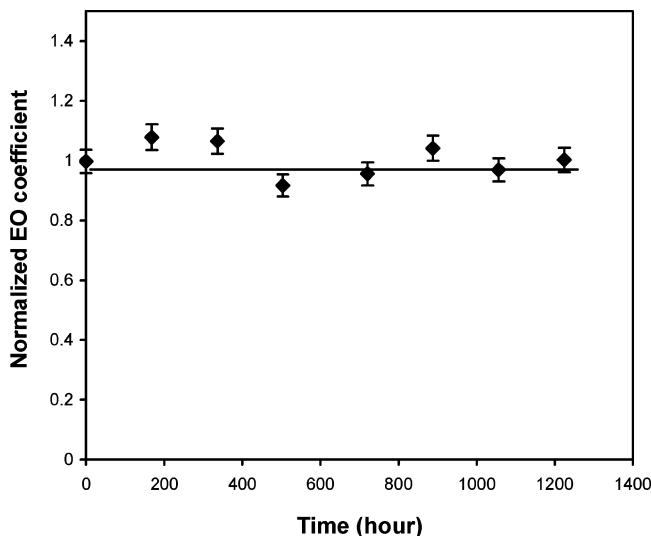


Figure 5. Temporal stability of the poled polymer **2b**_{4%} at 85 °C in nitrogen. Normalized EO coefficient as a function of the baking time.

currently used in the commercial EO Mach-Zehnder modulators and comparable to that of the NLO polymer containing one of the best push-pull chromophores at the same level of the number density¹⁴ and represents the first example of an efficient NLO zwitterionic polymer. An increase of the PQDM content in **2b** to 10 wt % led to a further increase of the r_{33} value to 45 pm/V for **2b**_{10%}, but a drop to 24 pm/V was observed for **2b**_{16%} with 16 wt % PQDM. Although there was no visible chromophore aggregation in the polymer films, chromophore-chromophore interactions are believed to increase significantly above a critical loading density due to the high dipole moments, resulting in an inefficient chromophore orientation during the poling and thus a decrease in macroscopic NLO response. The temporal stability of the EO activity for the poled samples based on polymers **2b**_{4%} and **2b**_{10%} was probed by measuring the test cells that were kept in the dark at 85 °C in nitrogen. No substantial decrease of EO coefficients was observed after heating for 1200 h (Figure 5), which can be attributed to the polymer networks formed via the BCBO cross-linking groups. In addition, the EO signal remained constant when the test cell was irradiated with the 1550 nm light (50 μ W/~4 mm²) continuously for 10 h at ambient temperature in air.

3. Conclusion

The first reported NLO polyimides containing a low loading (4–10 wt %) of zwitterionic PQDM chromophore show high EO coefficients (38–45 pm/V), desirable thermal and electrical properties, and good temporal stability at 85 °C and under irradiation with 1550 nm light, which has demonstrated a high potential of zwitterionic NLO polymers for EO device applications. Further structural modifications on both PQDM chromophores and host polymers are needed to reduce the chromophore-chromophore or dipole-dipole interactions and thus to achieve even higher EO coefficients.

4. Experimental Section

Materials. BPADPA was obtained from Aldrich and purified by recrystallization from acetic anhydride. All other chemicals were purchased from Aldrich-Sigma Canada and used as received. The syntheses of PQDM-b¹² and 5-aminobenzocyclobutene¹⁵ were reported previously. DMAc was dried over calcium hydride and distilled under vacuum.

Measurements. ¹H NMR spectra (400 MHz) were recorded on a Bruker-400 spectrometer. The chemical shifts relative to tetramethylsilane as internal reference are reported on the parts per million scale. Infrared spectra were recorded on a Bomen Michelson 120 FTIR spectrophotometer. Glass transition temperatures (T_g) of host polymers and NLO polymers were determined by standard differential scanning calorimetry (DSC) and temperature-modulated DSC (TMDSC), respectively, in nitrogen on a TA DSC Q100 instrument. A typical TMDSC experiment was run with a heating rate of 3 °C/min, a modulation amplitude of 1 °C, and a modulation period of 60 s. The decomposition temperatures were determined using a TA TGA 2950 instrument at a heating rate of 10 °C/min in nitrogen. The inherent viscosities of the polymers were measured with an Ubbelohde capillary viscometer at 30.0 ± 0.1 °C with a concentration of 0.5 g/dL in DMAc. UV-vis spectra were obtained on a Perkin-Elmer Lambda 900 UV-vis/near-IR spectrophotometer. The refractive indices were measured with a Metricon 2010 prism coupler. The thicknesses of the films were measured using an α -step 200 surface profiler. The temperature dependence of the electrical resistivity of a thin film (4.8 μ m in thickness) of **2b**_{10%} was obtained by measuring the electric current across the polymer film sandwiched between ITO-coated glass and a gold layer sputtered on top of the film at voltages of 50, 100, and 150 V with a Keithley digital electrometer that has a measuring range of 10⁻¹–10⁻¹¹ A. At each given temperature and voltage, the sample was allowed to equilibrate for 600 s before reading. Electrooptic coefficients at 1550 nm were measured at room temperature using a reflective Teng-Man setup.

DAPBA. A solution of 3,5-dihydroxybenzoic acid (7.7 g, 0.05 mol), 1-chloro-4-nitrobenzene (17.3 g, 0.11 mol), potassium carbonate (24.2 g, 0.17 mol), and toluene (20 mL) in DMAc (40 mL) was stirred at 90 °C for 30 min before the temperature was raised to 150 °C. The water formed during the reaction was removed through a Dean-Stark trap. When no more water formed, toluene was removed completely from the reaction flask. After being stirred at 150 °C for 48 h, the reaction solution was cooled to room temperature and poured into 600 mL of aqueous HCl solution (2 M). The precipitated solid was collected by filtration, washed with methanol (20 mL) and boiling diethyl ether three times, and dried in air. The yellow solids or 3,5-di(4-nitrophenoxy)benzoic acid, were obtained in 16.0 g (81%) yield and then hydrogenated in the presence of palladium on carbon (10%). The resulting diamine DAPBA was purified by column chromatography (R_f = 0.6, acetone/EtOAc, 1:1, v/v) and obtained as a light yellow solid in 90% yield: ¹H NMR (400 MHz, DMSO-*d*₆) δ 6.927 (2H, d, *J* = 2.4 Hz), 6.806 (4H, d, *J* = 8.8 Hz), 6.620 (1H, t, *J* = 2.4 Hz, 2.4 Hz), 6.605 (4H, d, *J* = 8.8 Hz); MS (EI, *m/e*) 336 (M⁺, 100).

Host Polymer 1a. To a solution of DAPBA (0.3294 g, 0.9793 mmol) in anhydrous DMAc (5 mL) was added BPADPA (0.5097 g, 0.9793 mmol). After the solution was stirred at room temperature for 8 h, acetic anhydride (1 mL) and pyridine (0.5 mL) were added. The reaction solution was stirred at room temperature overnight and then at 80 °C for 1 h. Acetic acid (1 mL) was added dropwise to the solution before the polymer solution was poured slowly into methanol (300 mL). The white polymer precipitate was collected by filtration, washed thoroughly with hot methanol, and dried in a vacuum oven (1 mmHg) at 120 °C overnight: yield 0.76 g (91%); $[\eta]_{inh}$ = 0.42 dL/g (DMAc, *c* = 0.5 g/dL); ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.12 (br s), 7.95 (d, *J* = 6.4 Hz), 7.28–7.46 (m), 7.10 (d, *J* = 6.4 Hz), 1.73 (s); IR (KBr, cm⁻¹) 1781, 1721 ($\nu_{C=O}$ of imide and carboxylic acid); T_g = 232 °C (DSC); T_d (onset) = 425 °C (TGA, nitrogen).

Host Polymer 1b. To a solution of DAPBA (5.2577 g, 15.631 mmol) in anhydrous DMAc (65 mL) were added BPADPA (7.9735 g, 15.319 mmol) and phthalic anhydride (0.0926 g, 0.6252 mmol). The resulting solution was stirred at room temperature for 8 h, followed by addition of acetic anhydride (8 mL) and pyridine (4 mL). The resulting viscous solution was stirred at room temperature for another 12 h and at 80 °C for 1 h. Acetic acid (6 mL) was then added slowly to the reaction flask. After being cooled to room temperature, the polymer solution was poured slowly into a mixture of methanol (600 mL) and acetic acid (20 mL). The white polymer precipitate was collected by filtration, washed thoroughly with hot methanol, and dried in a vacuum oven (1 mmHg) at 120 °C overnight: yield 12.4 g (97.2%); $[\eta]_{inh} = 0.33$ dL/g (DMAc, $c = 0.5$ g/dL); ^1H NMR (400 MHz, DMSO- d_6) δ 13.41 (br s), 7.98 (d, $J = 6.4$ Hz), 7.52 (d, $J = 7.2$ Hz), 7.29–7.42 (m), 7.16 (d, $J = 6.4$ Hz), 7.11 (br s), 1.75 (s); IR (KBr, cm^{-1}) 1778, 1719 ($\nu_{\text{C}=\text{O}}$ of imide and carboxylic acid); $T_g = 222$ °C (DSC); $T_d(\text{onset}) = 418$ °C (TGA, nitrogen).

NLO Polymers 2a. To an ice-cooled, magnetically stirred solution of **1a** (0.131 g, 0.159 mmol), PQDM-b (0.021 g, 0.064 mmol), BCBO (0.004 g, 0.032 mmol), DBP (0.013 g, 0.064 mmol), and 4-(dimethylamino)pyridine (0.021 g, 0.175 mmol) in anhydrous DMAc (3 mL) was added EDC (0.036 g, 0.191 mmol). The solution was allowed to warm to room temperature and stirred for 24 h. Additional amounts of DBP (0.008 g, 0.039 mmol) and EDC (0.010 g, 0.052 mmol) were then added. After another 24 h, the reaction solution was added dropwise into methanol (200 mL) to precipitate the polymer product. The crude product was filtered and washed in a Soxhlet extractor with methanol overnight. The polymer was then redissolved in DMAc (3 mL) and precipitated into methanol (200 mL). Polymer **2a** was collected by filtration and dried at 100 °C under vacuum: yield 0.15 g (88%); ^1H NMR (400 MHz, DMSO- d_6) δ 10.46 (br s), 8.96 (br s), 8.24 (br s), 7.91 (br s), 7.80 (br s), 6.85–7.45 (br m), 4.62 (br s), 4.36 (br s), 3.72 (br s), 2.21 (br s), 1.70 (s), 1.25 (s); IR (KBr, cm^{-1}) 2176 and 2131 ($\nu_{\text{C}=\text{N}}$ of cyano groups), 1785 and 1729 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 213$ °C (TMDSC); $T_d(\text{onset}) = 276$ °C (TGA, nitrogen).

NLO Polymers 2b. As a typical procedure for **2b**_{4%}, to an ice-cooled, magnetically stirred solution of **1b** (0.408 g, 0.500

mmol), PQDM-b (0.041 g, 0.125 mmol), BCBO (0.013 g, 0.100 mmol), PDFO (0.110 g, 0.275 mmol), and 4-(dimethylamino)pyridine (0.067 g, 0.55 mmol) in anhydrous DMAc (6 mL) was added EDC (0.115 g, 0.60 mmol). After the solution was stirred at room temperature for 24 h, more PDFO (0.100 g, 0.250 mmol) and EDC (0.023 g, 0.120 mmol) were added. After another 24 h, the reaction solution was added slowly to methanol (250 mL), and the resulting crude polymer product was filtered and washed with methanol in a Soxhlet extractor overnight. The blue polymer was dissolved in DMAc (5 mL) and then precipitated into methanol (300 mL). The polymer **2b**_{4%} was collected by filtration and dried at 100 °C under vacuum: yield 0.45 g (80%); ^1H NMR (400 MHz, DMSO- d_6) δ 10.45 (br s), 8.96 (br s), 8.25 (br s), 6.88–7.98 (br m), 5.07 (br s), 4.62 (br s), 4.37 (br s), 3.72 (br s), 2.28 (br s), 1.70 (br s); IR (KBr, cm^{-1}) 2178 and 2144 ($\nu_{\text{C}=\text{N}}$ of cyano groups), 1777 and 1723 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 170$ °C (TMDSC); $T_d(\text{onset}) = 278$ °C (TGA, nitrogen).

Data for 2b_{10%}:

yield 85%; ^1H NMR (400 MHz, DMSO- d_6) δ 10.46 (br s), 8.96 (br s), 8.25 (br s), 6.87–7.92 (br m), 5.08 (br s), 4.63 (br s), 4.37 (br s), 3.72 (br s), 2.17 (br s), 1.70 (br s); IR (KBr, cm^{-1}) 2177 and 2138 ($\nu_{\text{C}=\text{N}}$ of cyano groups), 1777 and 1721 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 189$ °C (TMDSC); $T_d(\text{onset}) = 272$ °C (TGA, nitrogen).

Data for 2b_{16%}:

yield 82%; ^1H NMR (400 MHz, DMSO- d_6) δ 10.47 (br s), 8.96 (br s), 8.24 (br s), 6.84–7.92 (br m), 5.08 (br s), 4.62 (br s), 4.37 (br s), 3.72 (br s), 2.15 (br s), 1.70 (br s); IR (KBr, cm^{-1}) 2176 and 2137 ($\nu_{\text{C}=\text{N}}$ of cyano groups), 1777 and 1720 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 209$ °C (TMDSC); $T_d(\text{onset}) = 267$ °C (TGA, nitrogen).

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