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Development of Zwitterionic Nonlinear Optical Polyimides for Electro-Optic Applications

By
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A thesis submitted to
the Faculty of Graduate Studies and Research
In partial fulfillment of the requirements for the degree of
Doctor of Philosophy

The Department of Chemistry
Carleton University
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ABSTRACT

Aiming at the understanding of the structure-property relationships and the development of second-order nonlinear optical (NLO) polymers for electro-optic (EO) device applications, this thesis research explores the potential of a new class of zwitterionic chromophores, *Z*- β -[1-substituted-4-pyridinium]- α -cyano-4-styryldicyanomethanide (trivial name: Pyridinium quinonedimethane, PQDM), as an active component in NLO polymers. Design and modification of NLO polymers were focused on enabling a high loading of chromophores in polymers and high poling efficiency. For the first time, the NLO polymers containing zwitterionic chromophores were demonstrated to show large EO coefficients (15 – 45 pm/V) at the telecommunication wavelength of 1550 nm. These NLO polymers also have good film-forming ability, good temporal stability of EO activity at elevated temperatures (e.g., 85 °C), and adequate electrical resistivity (e.g., 10^{-15} Ω -cm), making them attractive for EO applications. Some important findings from this thesis work are highlighted below.

- (1) A hydroxyl-containing PQDM was readily prepared in gram quantity. From the Hyper-Rayleigh scattering experiment, a large $\mu\beta$ value of $27,000 \times 10^{-48}$ esu at zero frequency was determined for PQDM. The chromophores exhibit a large negative solvatochromism, high thermal stability in nitrogen ($T_{d, \text{onset}} = 270$ °C), and good solubility in DMF, NMP and other amide-type solvents.
- (2) A polyimide was chosen as a host, owing to its good compatibility with the highly polar PQDM chromophores. A series of polyimides containing the carboxylic acid groups were designed to be different in chain flexibility, chain length, and topologies

(linear and branched). The host polyimides have the glass transition temperatures (T_g) ranging from 208 °C to 348 °C.

- (3) A series of NLO polyimides were readily prepared by grafting the acid-containing polyimides with PQDM in the presence of a coupling agent. A new crosslinker [5-aminobenzocyclobutenone (BCBO)] and a site-blocking agent 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) were introduced as well into NLO polyimides. The resulting NLO polyimides contained the chromophores in the range of 4 - 29 wt.% (or number density, $6 - 52 \times 10^{19} \text{ cm}^{-3}$). The NLO polyimides with T_g in the range of 165 – 220 °C are deemed to be suitable for further poling and EO studies, as thermal crosslinking of the BCBO moiety takes place at around 215 °C.
- (4) The poling conditions were optimized through investigations into various factors such as voltage, poling temperature and poling time. High EO coefficients up to 45 pm/V were achieved, which is larger than that (31 pm/V) of lithium niobate being used in commercial EO modulators. The NLO polyimides retained the poling-induced EO activity at 85 °C over 1000 h in air. The correlation between the polymer structure and EO activity was studied.

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LIST OF SYMBOLS AND ABBREVIATIONS

ε	Dielectric constant
ρ	Electrical resistivity, $\Omega \cdot \text{cm}$
$\chi^{(2)}$	Seond-order susceptibility, cm^2/esu ($4.19 \times 10^{-4} \text{ m/V}$)
λ_{max}	Maximum absorption wavelength
$[\eta]_{\text{inh}}$	Inherent viscosity
$\langle \cos^3 \theta \rangle$ and Φ	Order parameter
6FDA	4,4'-(Hexafluoroisopropylidene)diphthalic anhydride
APDAPB	4-aminophenyl 3,5-di(4-aminophenyloxy)benzoate
API	Acid-containing polyimide
BCBO	5-Aminobenzocyclobutenone
BLA	Bond-length-alternation
BPADA	2,2'-bis(4-(4-aminophenoxy)phenyl)propane
BPADPA	4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride)
BPI	Branched polyimide
CT	Charge transfer
DABA	3,5-Diaminobenzoic acid
DAPBA	3,5-Di(aminophenyloxy)benzoic acid
DB	Degree of branching
DBP	3,5-Di- <i>tert</i> -butylphenol
DBU	1,8-diazabicyclo[5,4,0]undec-7-ene
DEMI	4-[1-Cyano-3-diethylamino-2-propenylidene]-2,5-cyclohexadiene-

	1-ylidenepropanedinitrile
DMAc	N, N-dimethylacetamide
DMAP	4-Dimethylaminopyridine
DMF	N, N-dimethylformamide
DMSO	Dimethyl sulfoxide
DSC	Differential scanning calorimetry
EDC	1-(3-(Dimethylamino)propyl)-3-ethylcarbodiimide
EFISH	Electric field-induced second harmonic generation
EGTM	Ethylene glycol bis(anhydro-trimellitate)
EO	Electro-optic
esu	Electrostatic units
f	Local field factor
FDA	9,9-Bis(4-aminophenyl)fluorene
HMDA	Hexamethylenediamine
HQDPA	1,4-bis(4-aminophenoxy)benzene
HRS	Hyper-Rayleigh scattering
I	Electrical current, A
IR	Infrared
ITO	Indium-tin oxide
n	Refractive index
N	Number density
NLO	Nonlinear optical
NMR	Nuclear magnetic resonance

NPI	Nonlinear optical polyimide
ODPA	4,4'-oxydiphthalic anhydride
PDFO	2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-Pentadecafluoro-1-octanol
PQDM	β -[1-Substituted-4-pyridinium]- α -cyano-4-styryldicyanomethanide (trivial name: pyridinium tricyanoquinonodimethane)
r_{33}	Electro-optic coefficient in the poling field direction, pm/V
SHG	Second harmonic generation
T	Temperature, °C
TCNQ	7,7,8,8-tetracyanoquinodimethane
T_d	Decomposition temperature, °C
T_g	Glass transition temperature, °C
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMDSC	Temperature-modulated differentail scanning calorimetry
UV-Vis	Ultraviolet-visible
V	Voltage, volt
V_π	full wave modulation voltage, volt
β	Molecular first hyperpolarizability, cm ⁵ /esu or esu (4.19×10^{-10} m ⁴ /V)
β_0	Zero-frequency molecular first hyperpolarizability
μ	Dipole moment, Debye (10^{-18} esu/cm or 3.336×10^{-30} C/m)

Chapter I Background and Objectives

I.1 Introduction

Second-order nonlinear optical (NLO) polymers have been developed for high-speed (broadband), low-drive-voltage, electro-optic (EO) modulators for fiber optical communications.¹⁻¹⁰ The interest stems from their achievable large EO coefficients, low refractive index dispersion from microwave to optical frequencies, excellent processability, and their potential for low cost. Recent advances are highlighted by the demonstration of a prototype Mach-Zehnder interferometer based on NLO polymers with an operational bandwidth of greater than 100 GHz and at sub-1 V drive voltage (full wave modulation voltage, V_π).¹¹⁻¹³ These milestone studies have not only stimulated more scientific interest in NLO polymers, but also pushed these highly efficient EO materials closer to practical applications. High-speed modulators (e.g., 40 GHz) based on NLO polymers have recently been fabricated and offered to purchase¹⁴ and various prototype EO devices are being actively pursued by a number of companies and US government laboratories, such as Pacific Wave Industries, IPITEK Corporation, and US Navy NAWCWPNS at China Lake.^{14,15}

In response to this rapidly growing field of research and in light of the great potential of NLO polymers in practical applications in fiber-optic communications, Nortel Networks, TRILabs, Carleton University and the University of Durham jointly initiated a program on NLO polymers and EO modulators in 2000, which triggered this thesis research. The ultimate goal of the research is to obtain highly efficient NLO

polymers suitable for use in high-speed EO modulators. The strategy for material research aims to unlock the potential of a new class of zwitterionic chromophores and to incorporate these chromophores into suitable host polymer. In this chapter, the background and the rationale for the development of zwitterionic NLO polymers are described.

I.2 Basics to Electro-Optic Materials

EO coefficient

Electro-optic or Pockels effect is a linear dependence of the refractive index of a bulk material or system on the electric field. π -Conjugated organic materials have ultra-fast response (tens to hundreds of femtoseconds) of the refractive index to the electric field and can be used to modulate the phase of propagating light at very high frequencies. The relationship between the applied electric field (E) and the refractive index (n) can be expressed as

$$rE \approx 2 \Delta n/n^3 \approx 2(d/L)(1/n^3) \quad (1)$$

where r is the EO coefficient and d is the difference in the travelling distances between the light with and without the electric field for a finite length of L . For many EO applications, a critical requirement is the drive voltage (V_π) for shifting the phase of the light by one-half of the wavelength ($\lambda/2$). According to eq 1, the drive voltage is defined:

$$V_\pi = \lambda h/n^3 r L \quad (2)$$

with h being the sample thickness. Clearly, the minimization of V_π relies on the maximization of r .

The magnitude of r of a polymer depends on the magnitude of electric field-induced nonlinear response in polarization, which in turn depends on the polarizability of individual chromophore molecules and the noncentrosymmetric assembly of these molecules in bulk. In general, the nonlinear responses are orders of magnitude smaller than the linear response and thus the electric polarization of a NLO polymer can be written as:

$$P_i(\omega) = \chi^{(1)}_{ij}(\omega)E_j(\omega) + \chi^{(2)}_{ijk}(-\omega; \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2) + \chi^{(3)}_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3)E_j(\omega_1)E_k(\omega_2)E_l(\omega_3) + \dots \quad (3)$$

where $\chi^{(1)}_{ij}(\omega)$ is the linear polarizability, $\chi^{(2)}_{ijk}(-\omega; \omega_1, \omega_2)$ and $\chi^{(3)}_{ijkl}(-\omega; \omega_1, \omega_2, \omega_3)$ are the frequency-dependent second-order and third-order susceptibilities, respectively. Second-order NLO effects, including the EO effect, second harmonic generation (SHG) and frequency up/down-conversions, arise from the second-order electric polarization (the second term in eq 3). In relating the macroscopic $\chi^{(2)}$ with the molecular first hyperpolarizability (β), eq 4 applies,

$$\chi_{ijk}(-\omega; \omega_1, \omega_2) = Nf(\omega)f(\omega_1)f(\omega_2) \langle \beta_{ijk}(-\omega; \omega_1, \omega_2) \rangle_{ijk} \quad (4)$$

where N is the number density of NLO chromophores, f is the local field factor taking into account the attenuation of applied electric field by the dielectric properties of host, and $\langle \beta \rangle$ is the weighted sum of β values over all orientations. Note that the second-order polarization of NLO polymers exist only in noncentrosymmetric structures. With the presence of an inversion center,

$$\begin{aligned} P^{(2)}_i(\omega) &= \chi^{(2)}_{ijk}(-\omega; \omega_1, \omega_2)E_j(\omega_1)E_k(\omega_2) \\ &= \chi^{(2)}_{ijk}(-\omega; \omega_2, \omega_1)[-E_j(\omega_1)][-E_k(\omega_2)] = -P^{(2)}_i(\omega) = 0. \end{aligned} \quad (5)$$

The EO coefficient r_{33} of a noncentrosymmetric or poled polymer can be related to the second-order susceptibility $\chi^{(2)}$ and the molecular β by

$$r_{33} = 2\langle\chi_{zzz}^{(2)}\rangle/n^4 = 2Nf\langle\beta(-\omega;\omega,0)\rangle/n^4 = 2Nf\beta\langle\cos^3\theta\rangle/n^4 \quad (6)$$

where the subscript 3 indicates the poling field direction, z is the direction along with the molecular permanent dipole moment and θ is the angle between the field direction and the z -direction. Thus, to maximize the EO coefficient of NLO polymers, the following four factors are to be optimized: number density (N), local field factors (f), molecular first hyperpolarizability (β), and order parameter ($\langle\cos^3\theta\rangle$).

Number density

NLO chromophores are incorporated into polymers mainly for processing purpose. The more chromophores are incorporated and noncentrosymmetrically oriented by the poling field, the larger the EO coefficient will be. To increase the number density, either chromophores or host polymers should be developed to have a good compatibility with each other. Covalent coupling of chromophores with host polymers is highly desirable for increasing the number density as well as for improving the stability of the induced dipole orientation. However, a high chromophore loading may lead to attenuation of the poling efficiency caused by strong electrostatic interactions between highly polar chromophores.⁵ The maximum number density for the known NLO polymers is on the order of $30 \times 10^{19} \text{ cm}^{-3}$, for a maximum of EO coefficient.⁵

Local field factor

In dielectric NLO polymers, the actual electric field felt by an individual chromophore differs from the applied electric field because of the surrounding dipole fields from other polarizable molecules. To correct this dielectric effect, a local field factor (f) is introduced and can be expressed in its general form:¹⁶

$$f(\omega) = \varepsilon(\omega)(L\varepsilon_{\infty} + 1 - L) / [\varepsilon(\omega)(1 - L) + L\varepsilon_{\infty}] \quad (7)$$

where $\varepsilon(\omega)$ is the dielectric constant at frequency ω , $\varepsilon_{\infty} = n^2$ is the dielectric constant at optical frequencies and L is a tensor used to take into account the shape of the cavity into which the chromophore can be accommodated.

For a spherical cavity ($L = 1/3$), one has

$$f(\omega)^S = \varepsilon(\omega)(\varepsilon_{\infty} + 2) / [2\varepsilon(\omega) + \varepsilon_{\infty}] \quad (8)$$

Values of L and f for different cavity shapes are shown in Table I-1.¹ For given values of ε at low and optical frequencies, the largest f_0 and f_{∞} are obtained for spherically shaped chromophores.

Table I-1. Local field factors using various models (using values of $\varepsilon = 3.6$ and $\varepsilon_{\infty} = 2.9$)

b/a	L_I	f_0^E	f_{∞}^E	f_0^S	f_{∞}^S
1.0	0.333	1.75	1.63	1.75	1.63
0.8	0.276	1.61	1.52		
0.6	0.210	1.46	1.40		
0.4	0.135	1.29	1.26		
0.2	0.056	1.12	1.11		

Note: b and a refer to two principle axes of the NLO chromophore. The superscript E and S indicate that the factors are appropriate for prolate ellipsoidal and spherical chromophores, respectively.

Molecular first hyperpolarizability

To develop NLO polymers for EO device applications, chromophores with large molecular β must be used. According to the two-state model by Oudar and Chemla,¹⁷ the molecular β is related to the transition dipole moment (μ_{ge}), the difference between excited and ground state dipole moments ($\mu_{ee}-\mu_{gg}$), and the HOMO-LUMO transition energy (E_{ge}):

$$\beta \propto \mu_{ge}^2(\mu_{ee}-\mu_{gg})/E_{ge}^2 \quad (9)$$

The validity of this relationship was verified from extensive studies on the structure-property relationships of NLO chromophores, in particular from the systematic studies carried out by Cheng et al. at Du Pont.^{18,19} By examining the optical nonlinearities of chromophores with the different donor and acceptor groups and with the different π -conjugated bridging units, Cheng found that the use of the strongest donor and acceptor groups did not necessarily lead to the largest β for a given π -system. An optimal combination of donor and acceptor strengths has to be pursued for maximization of the $\mu\beta$ value. In addition, for a given set of donors and acceptors, the β could be increased significantly by extending the polyene bridging unit and the use of polyphenylene as the π -conjugated connector resulted in no improvement in the $\mu\beta$ value. Based on these observations, Gorman and Marder²⁰ proposed a simple model that correlates β with the degree of charge separation in the ground state, which is characterized by a physical quantity of bond-length alternation (BLA). The BLA is defined as the average of the difference in length between adjacent carbon-carbon bonds in a polymethine chain. For dipolar molecules, BLA can vary from positive to zero and to negative, depending on the

relative contributions of neutral resonance form and charge-separated resonance form to the ground state, which in turn depend on the donor and acceptor strengths. For the given donor and acceptor groups, the magnitude of BLA depends on the transition energy, which in turn depends on the nature and the length of the π -conjugated bridge.²¹ The different dielectric surroundings also contribute to the magnitude and the sign of BLA due to the induced ground-state polarization. Figure I-1 shows the correlation between β and BLA. On going from the positive maximum of BLA to the negative maximum, β first increases, peaks at an intermediate BLA, decreases, passes through zero at the null point of BLA, and repeats the pattern inversely for negative BLA. Note that both neutral and zwitterionic molecules are capable of yielding large β . The negative sign of β for zwitterionic molecules indicates that the direction of intramolecular charge transfer in these molecules is opposite to that in neutral molecules.

Figure I-1. Sinusoidal relationship between β and bond-length alternation

Order parameter

Electric field poling is a process of paramount importance, which transforms molecular second-order optical nonlinearity into the material's NLO properties. The poling efficiency or order parameter is related to the strength of dipole-field interactions and the mobility of chromophores. When the inter-chromophore electrostatic interaction within a NLO polymer is insignificant and can be neglected, the order parameter is approximated:²²

$$\langle \cos^3 \theta \rangle = \mu f_p E / 5kT \quad (10)$$

where μ is the dipole moment, E is the electric poling field, k is Boltzmann constant and T is the poling temperature. Combining eq 6 and eq 10, one has the EO coefficient of a NLO polymer:

$$r_{33} = (2N_f f_p E) (\mu \beta) / (5kT n^4) \quad (11)$$

For a given NLO polymer system, the EO coefficient is proportional to the number density and the strength of poling field. However, when the inter-chromophore electrostatic interaction takes into effect, a tradeoff between the number density and the order parameter $\langle \cos^3 \theta \rangle$ exists.^{5,23}

I.3 Material Requirements for Electro-Optic Applications

NLO polymers with large EO coefficients are being developed for a wide range of applications such as fiber and satellite telecommunications, photonic detection of electromagnetic radiation, backplane interconnects between the processors of supercomputers, ultrafast analog-to-digital converters, and optical gyroscopes.¹⁻¹⁰ In comparison with the inorganic lithium niobate that is being used in commercial EO

modulators,²⁴ NLO polymers have significant advantages in terms of matching propagating speed between electrical and optical signals (broader bandwidths), achievable much higher EO coefficients (lower V_π), good processability and the possibility of integration with semiconductor circuits. However, to compete with the established technologies of lithium niobate²⁴ and to be used in practical EO devices, NLO polymers have to demonstrate their cost-effectiveness and meet the stringent material requirements.

First of all, the NLO polymer must exhibit a large EO coefficient. According to eq 1, the drive voltage of a Mach-Zehnder EO device is proportional to the inverse of EO coefficient. To achieve low-loss transduction between the electrical and optical signals (the gain is inversely proportional to V_π^2 and the noise figure is proportional to V_π^2 in the low-gain limit), a low drive voltage is required.²⁵ It was estimated that to realize a digital-level drive voltage [e.g., the drive voltage (~ 5 V) of lithium niobate], the r_{33} value on the order of 30 pm/V is needed; to achieve a sub-1 V drive voltage, the r_{33} value on the order of 100 pm/V is required.⁵

The chromophore and the host polymer must have a good thermal stability (e.g. > 250 °C) to survive the high-temperature poling and device processing conditions. The poling induced acentric structure has to be stable at the device processing temperatures such as ~ 200 °C for a short period of time and in operation at ambient temperatures (up to 80 °C) for years.

To be processed into waveguide devices, NLO polymers must have good solubility in common organic solvents and can form high-quality thin films (e.g., 1-5 μm) by the conventional methods such as spin-coating and solution casting. A good chemical

resistance is also a must for NLO polymers, since the multilayer-structured devices are typically prepared by alternate deposition of cladding, core, and cladding materials by spin-coating.

Optical transparency of NLO polymers at the operating wavelengths is important and should be as high as possible. Unlike the SHG applications that require optical clarity at both fundamental and double frequencies, EO applications need optical transparency in the infrared region. In general, the charge-transfer absorptions of NLO chromophores are in the range of 500 – 700 nm and contribute little to the linear absorption at the telecommunication wavelengths such as 1.3 μm and 1.5 μm . The overtone absorption from C-H, O-H and N-H bonds is known as the major source for optical loss and should be considered during the material design. The overall optical loss due to the intrinsic absorptions of NLO polymers should be ideally controlled on the order of 1 dB/cm or less at 1.3 – 1.6 μm .

For fiber-optic communication applications, the intensity of transmission light is typically of the order of tens of milli-watts. The NLO polymer must not undergo any photochemical decomposition under the irradiation at the telecommunication wavelengths. It has been found that the photochemical stability of most NLO polymers depends on the amount of oxygen present, lattice hardness (oxygen diffusion rates) and chromophore structures (sites sensitive to singlet oxygen attack). Device packaging (such as shielding the NLO materials from visible light and removing oxygen by hermetic sealing) or/and use of singlet oxygen or radical quencher²⁶ often can improve the photochemical stability.

A good mechanical strength of the polymer waveguide is required. The glass

transition temperature (T_g) of NLO polymers should be high enough so that no deformation of the waveguide structure should occur during high-temperature device processing and packaging.

A low conductivity of the NLO polymer is also needed so that dielectric loss at modulation frequencies can be diminished and further matches with the cladding materials with a higher electrical conductivity in a waveguide device.²⁷

I.4 Development of Nonlinear Optical chromophores

Since the discovery of large SHG signals from donor/acceptor functionalized benzenes in 1970,²⁸ numerous dipolar chromophores in the form of

have been developed and examined for SHG and EO applications. However, until late 1990s, the chromophores suitable for EO device applications were developed.²⁹ Such a long period for the chromophore development is mainly attributed to the difficulties in optimization of molecular $\mu\beta$ and other critical properties such as thermal stability ($> 250^\circ\text{C}$), photochemical stability, optical transparency, and processability in a given chromophore.

I.4.1 Chromophore design and synthesis

Optimization of molecular $\mu\beta$

To achieve large $\mu\beta$ values, predominant efforts have focused on increasing the β value of NLO chromophores. According to the two-state¹⁷ and the BLA²⁰ models, an

increase of molecular β comes from the decrease of HOMO-LUMO transition energy or BLA and the use of suitable electron donor and acceptor groups. In addressing the low transition energy, extensively π -conjugated connective segments of various types were developed, including polyenes, aromatic rings, the combined ethylene and aromatic units, and azobenzenes. The development of NLO chromophores in 1980s typically involved using stilbene and azobenzene bridging moieties.² However, only moderate $\mu\beta$ and thermal stability were achieved (e.g., **2**, Table I-2). The incorporation of these chromophores into polymer systems did not lead to highly electrooptically active materials.¹ Polyene bridges are known to be capable of yielding NLO chromophores with a very large molecular $\mu\beta$ (e.g., **8**, Table I-2),³⁰⁻³² but dipolar compounds with unsubstituted polyene moieties are chemically unstable and therefore not suitable for practical EO applications.³⁰⁻³² Recent designs for chromophores with large $\mu\beta$ values and good stability to heat and light involve the use of a steric group to protect the polyene bridges and a combination of the ethylene unit and aromatic rings (e.g., benzene and heteroaromatics).^{6,21,33} Table I-2 shows the structures and $\mu\beta$ values of some representative NLO chromophores.

In general, those with the aromatic bridging moieties tend to be more bond-length alternated in the ground states than a simple polyene bridge of a comparable length. To lower the transition energy or BLA of such molecules, Marder and co-workers^{20,34,35} proposed two designs to decrease the difference in the energy potentials between the two limiting resonance structures, i.e., the neutral and the charge-separated structures. One is

to make up for the loss of aromaticity in one part of the π -bridge upon polarization by using structures (e.g., acceptors in the studies) that can gain aromaticity upon polarization

Table I-2. Representative NLO chromophores with $\mu\beta (\times 10^{-48} \text{ esu})$ values at $1.9 \mu\text{m}$

Nature of π -conjugated connective segment					
1		580	3		1040
2		800 (1.58 μm)	4		2190 (1.58 μm)
Length of π -conjugated connective segment					
5		6700	7		9800
6		13000	8		1457 (n = 1) 3945 (n = 2) 9831 (n = 3)
Donor and Acceptor pairing					
9		1300	11		15000
10		6100	12		18000

in the other part of the π -bridge. Typical acceptors of this type include thiobarbituric acid³⁶ (**8**, Table I-2), 3-phenyl-5-isoxazolone,³⁶ and 3-methyl-1-phenylpyrazol-5-one.³⁷ The other one is to replace benzene rings in the π -bridge with heteroaromatics such as thiophene³⁸ (**3**, Table I-2) and thiazole³⁹ (**4**, Table I-2). Such heterocyclic rings have lower aromatization energy, allowing for more contributions from the charge-separated resonance forms to the ground state and thus a smaller BLA. As shown in Table I-2 (compounds **1** – **4** and **8**), both designs proved efficient in increasing the $\mu\beta$ values.

The effect of a conjugation length on the $\mu\beta$ value can be seen from some chromophores in Table I-2. Upon addition of one ethylene unit in the π -bridge, $\mu\beta$ value increases from 6700×10^{-48} esu for **5**⁴⁰ to 9800×10^{-48} esu for **7**⁴⁰. The further insertion of an isophorone-locked ethylene unit into **7** led to an even larger $\mu\beta$ value of 13000×10^{-48} esu for **6**³¹. A doubling of $\mu\beta$ value for **8** (Table I-2) was observed upon insertion of each additional ethylene unit into the π -bridge.⁴¹ As noted above that increasing the polyene length does not represent a practical approach to optimization of the molecular $\mu\beta$ due to the increased chemical instability. However, the combination of heteroaromatic rings and ethylene units in the π -system as shown by compounds **5** – **7** usually leads to good thermal and photochemical stability. Recently, sterically protected (ring-locked) polyenes were successfully exploited in the π -bridging structures to increase the conjugation length and to produce high- $\mu\beta$ chromophores with good thermal stability.^{31,42,43} A typical example is the CLD chromophore,⁴³ in which the cyclic olefinic moiety is incorporated in the center of the chromophore to prevent reactive species from coming close to attacking the π -bridge, to enforce a trans conformation of the polyene to increase an effective

conjugation and to change the shape of the chromophore so that intermolecular interaction can be diminished.

In addressing the effect of donor and acceptor groups on the molecular $\mu\beta$, significant enhancement has been demonstrated through optimization of the donor/acceptor pairing.^{18,19} For electron donors, the state-of-the-art chromophores involve the use of dialkylamines or diarylamines. Although the two do not differ greatly, studies have indicated that a larger $\mu\beta$ value could result by using diarylamine than by using dialkylamine.⁴⁴ A different BLA due to the different electronic effects was believed to account for such observation. Most studies on donor/acceptor groups concentrated on the acceptor part. A wide variety of electron-withdrawing groups are available and structure modifications can be readily carried out (Appendix I). Table I-2 shows some examples (5 and 9 – 12) that have primarily the same donor and π -bridging structures but different acceptor groups. More than 10 times of magnitude increases of $\mu\beta$ are observed upon changing the dicyanovinyl electron-accepting group for 9^{6,45} to more efficient electron-accepting groups for 11 and 12.^{6,46} Theoretical studies have predicted large increase of $\mu\beta$ for even small modifications on the acceptor group (Figure I-2).⁴⁷

Figure I-2. Calculated optical nonlinearities of chromophores with modified acceptors

There is a large number of structure designs in the framework of the two-state and BLA models and to yielding large $\mu\beta$ values available from the intensive chromophore developments in the past 20 years. The appendix summarizes some representative examples that are categorized according to the different π -bridge units. The most successful designs are represented by the FTC (12, Table I-2) and CLD-type chromophores having the $\mu\beta$ values greater than 15000×10^{-48} esu at $1.9 \mu\text{m}$. It was stated that $\mu\beta$ values as large as 60000×10^{-48} esu or greater could be achieved by relatively simple modifications on the FTC and CLD structures.³³ To date, NLO polymers based on FTC and CLD-type chromophores have demonstrated EO coefficients around 100 pm/V .³³

Optimization of auxiliary properties

In addition to the large $\mu\beta$ value, NLO chromophores must show good auxiliary properties such as good solubility in common organic solvents, ease to be assembled into a noncentrosymmetric structure, good thermal/photochemical stability and transparency at telecommunication wavelengths. Large, planar conjugated segments such as fused aromatic rings should be generally avoided in the structure design since poor solubility often results.⁴⁸ Spheroidal topology was proposed and shown by Dalton et al. to decrease

the intermolecular electrostatic interactions.⁴⁹ Dendritic structures have recently drawn great attention in yielding chromophore with good solubility and processability.^{3,4}

The molecular size and rigidity of chromophores affect the poling efficiency and relaxation of dipole orientations.¹ Large rigid chromophores are likely to be less easy to be oriented than smaller and more flexible chromophores under the same poling conditions. But very small molecules (such as *p*-nitroaniline) do not possess large $\mu\beta$ values and the dipole order tends to relax too quickly.⁵⁰ To improve the temporal stability of EO response in poled NLO polymers, chromophores with the multi reactive functionalities were developed for the formation of the crosslinked networks.⁵¹ To facilitate the formation of noncentrosymmetric structures, chromophores with different structural features such as λ -shape and chiral structures were also developed.^{52,53}

Twieg et al.⁴⁴ found that chromophores containing the diarylamine donors were more stable than those containing the dialkylamine donors. They also revealed a strong correlation between a poor thermal stability with a low oxidation potential.^{54,55} Due to the presence of the electron-rich donors and π -bridges, NLO chromophores are usually labile to oxygen, in particular under the exposure to light. Singlet oxygen scavengers have lately been incorporated into NLO polymer systems to improve the photochemical stability.²⁶

Finally, the synthetic efficiency and chromophore purity are the important factors to the EO applications as well. Since the most NLO chromophores with high $\mu\beta$ values have extensively conjugated structures and commonly require modifications on the π -bridges for an improved thermal stability and solubility, the current synthetic routes are typically multi-steps and are not suitable for large-scale (e.g., hundreds of kilograms)

industrial productions. However, the continued efforts on new synthetic methods and processes (for example, the microwave-assisted synthesis of 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran as an acceptor⁵⁶) should permit the production of NLO chromophores in kilogram quantities at an acceptable cost in the future.

I.4.2 Zwitterionic nonlinear optical chromophores

According to the BLA model,²⁰ chromophores with neutral ground states have positive β and chromophores with zwitterionic ground states have negative β . Although for both cases large β values are accessible, predominant effort focuses on the exploration of neutral chromophores and little attention has been paid to zwitterionic chromophores. This situation is being subjected to change lately with the demonstrations of several zwitterionic chromophores having extremely large $\mu\beta$ values (e.g., -27000×10^{-48} esu at $1.9 \mu\text{m}$).^{37,57-61} Table I-3 shows some representative zwitterionic chromophores. According to structure, chromophores in Table I-3 can be classified into three: (1) (phenyl)polyenes end-capped with donor and acceptor groups (**14** – **16**), (2) molecules containing heteroaromatics (e.g., thiophene) in the π -bridge (**17**), and (3) $\text{D}^+-\pi-\text{A}^-$ tertiary amine/TCNQ adducts (**18** – **20**). The charge-separated ground states of these chromophores are inferable from their strong negative solvatochromism and were demonstrated by the X-ray crystallography and theoretical modeling as well.^{62,63} In comparison with neutral chromophores of comparable sizes (e.g. **5**: $\mu\beta_{1.9\mu\text{m}} = 6200 \times 10^{-48}$ esu or **9**: $\mu\beta_{1.9\mu\text{m}} = 1300 \times 10^{-48}$ esu), zwitterionic chromophores exhibited much larger $\mu\beta$ values (e.g., **17**: $\mu\beta_{1.9\mu\text{m}} = -27000 \times 10^{-48}$ esu),⁶⁴ due primarily to the increased dipole

Table I-3. Typical examples of zwitterionic chromophores and their properties

Structures	Properties
13 ³⁷	$\lambda_{\text{NaOH aq}} = 500 \text{ nm}$ $\mu\beta_0 = -6914 \times 10^{-48} \text{ esu}^a$
14 ³⁷	$\lambda_{\text{MeOH}} = 501 \text{ nm}$ $\mu\beta_0 = -3300 \times 10^{-48} \text{ esu}$
15 ⁵⁷ <p>a: R = CH₃; R₁ = H; n = 1 b: R = CH₃; R₁ = H; n = 2 c: R = CH₃; R₁ = H; n = 3</p>	a: $\lambda_{\text{DMF}} = 570 \text{ nm}$; $\mu\beta_0 = -2213 \times 10^{-48} \text{ esu}$ b: $\lambda_{\text{DMF}} = 600 \text{ nm}$; $\mu\beta_0 = -6444 \times 10^{-48} \text{ esu}$ c: $\lambda_{\text{DMF}} = 615 \text{ nm}$; $\mu\beta_0 = -8900 \times 10^{-48} \text{ esu}$
16 ⁵⁷ <p>a: R = CH₃; n = 1 b: R = CH₃; n = 2 c: R = CH₃; n = 3</p>	a: $\lambda_{\text{DMF}} = 605 \text{ nm}$; $\mu\beta_0 = -2496 \times 10^{-48} \text{ esu}$ b: $\lambda_{\text{DMF}} = 705 \text{ nm}$; $\mu\beta_0 = -3354 \times 10^{-48} \text{ esu}$ c: $\lambda_{\text{DMF}} = 810 \text{ nm}$; $\mu\beta_0 = \text{N/A}$
17 ⁵⁸	$\lambda_{\text{MeOH}} = 609 \text{ nm}$ $\mu\beta_{1.9\mu\text{m}} = -27000 \times 10^{-48} \text{ esu}$
18 ⁵⁹	$\lambda_{\text{DMF}} = 693 \text{ nm}$ $\mu\beta_0 = -9450 \times 10^{-48} \text{ esu}$
19 ⁶⁰	$\lambda_{\text{DMF}} = 694 \text{ nm}$ $\beta_{1.06\mu\text{m}} = -1270 \times 10^{-30} \text{ esu}^b$
20 ⁶¹	$\lambda_{\text{MeCN}} = 712 \text{ nm}$ $\lambda_{\text{LB film}} = 565 \text{ nm}$ $\chi^{(2)}_{\text{zzz}} = 180 \text{ pm/V}$

^a β_0 is the zero-frequency molecular first hyperpolarizability and can be obtained using the formula: $\beta = \beta_0 \times (1/\lambda_{\text{max}})^4 / \{[(1/\lambda_{\text{max}}^2) - (4/\lambda^2)] \times [(1/\lambda_{\text{max}}^2) - (1/\lambda^2)]\}$; ^b Calculated by Pariser-Parr-Pople method.

moment (e.g., **17**: $\mu = 33$ D; **5**: $\mu = 6$ D). Chromophore **18**, also denoted as DEMI, is about half the size of FTC (**12**, Table I-2), but showed larger $\mu\beta$ value at zero frequency (DEMI: $\mu\beta_0 = -9450 \times 10^{-48}$ esu; FTC: $\mu\beta_0 = 8825 \times 10^{-48}$ esu).^{6,59}

Due to the low requirement for extensive conjugations in yielding large $\mu\beta$ values, zwitterionic chromophores are typically easier to be prepared than neutral chromophores. Scheme I-1 shows the one-step, high-yield synthesis of DEMI.⁵⁹ However, despite the large $\mu\beta$ values and ease in preparation, zwitterionic chromophores face serious challenges in areas of stability to heat and light and a strong tendency to aggregate. To be usable in practical EO applications, zwitterionic chromophores must be optimized to have the required properties and a suitable polymer host needs to be developed.

Scheme I-1. Synthesis of zwitterionic chromophore DEMI

Considering the DEMI analogues **19** and **20**, although no $\mu\beta$ value were reported, comparative studies by Cross and co-workers⁶⁵ indicated a larger β_0 for these molecules than that ($\beta_0 = 350 \times 10^{-30}$ esu) for DMEI (Figure I-3). By taking the calculated μ of 45 D and assuming the number density of 10×10^{20} cm⁻³ and the local field factor of 2.3, Cross et al.⁶⁵ predicted an EO coefficient of 210 pm/V for NLO polymers derived from **20**.

Figure I-3. The calculated molecular β_0 of DEMI and its analogue **20** as a function of local field. Symbols overlaid on the plot for DEMI indicate the proposed local field values and thus the corresponding static β_0 in the following media: (∇) PMMA, (O) chloroform, ($\diamond$) dichloromethane.

I.5 Development of Nonlinear Optical Polymers

Having a NLO chromophore with a large $\mu\beta$ value and good auxiliary properties at hand, incorporation of the chromophore into a suitable polymer system needs to be carried out in order to enable a good processability and an efficient noncentrosymmetric alignment of the chromophore under an external electric field. As described in section I.3, the resulting NLO polymers must meet the stringent material requirements. In general, development of NLO polymers for EO applications involves three steps: (i) modification of NLO chromophores for incorporation into polymers, (ii) design and synthesis of NLO polymers, and (iii) demonstration of large EO activity and good temporal stability of the EO response in poled NLO polymers. To date, various NLO polymer systems have been

explored and can be divided into guest-host systems, main-chain NLO polymers, side-chain NLO polymers, crosslinked NLO polymers, and NLO dendrimers and dendronized polymers.

Guest-host NLO polymers

The earliest polymer systems investigated for NLO applications are guest-host systems,⁶⁶ which are obtained by dissolving the NLO chromophore guest into a polymer host.⁶⁷ Such systems are advantageous in terms of ease in preparation, but suffer from low chromophore loading, fast order relaxation in poled NLO polymers, and poor solvent-resistance during multilayer device fabrication. Twieg and coworkers⁶⁸ investigated the temperature dependence of the relaxation time (τ) in various guest-host systems and found that the following relationship holds:

$$\tau(T) = A \exp[-B/(T_g + 50 - T)] \quad (12)$$

where A and B are positive constant independent of polymer host and the guest molecule, and T is the temperature of interest. To achieve a good temporal stability of the poling-induced EO response, such as for a 10-year term, the T_g of a guest-host NLO polymer should be at least 100 °C higher than the ultimate operating temperature. Recently, a few thermally stable guest-host NLO polymers were formulated by incorporating NLO chromophores into high- T_g polymers, e.g., polyimides and polyquinolines.^{69,70}

Main- and side-chain NLO polymers

In order to increase the number density and temporal stability of EO response, NLO chromophores are incorporated into polymers through covalent bonding, either in the main-chain or side-chain. In comparison with side-chain NLO polymers, main-chain

NLO polymers are expected to have a better temporal EO stability since large segmental motions of the polymer backbone are required for order relaxation, which diminishes the effect from sub- T_g relaxation. The early development of main-chain NLO polymers focused on “head-to-tail” polymers with the hope that the dipole moments of constitutive chromophore units would add up to yield a large dipole moment of the polymer chain.⁷¹ However, such an adding-up phenomenon was not observed in polymer films due probably to chain entanglements.⁷² To facilitate the formation of noncentrosymmetric structures, Lindsay and co-workers⁷³ designed and synthesized “head-to-head” main-chain NLO polymers, in which NLO chromophores were connected with U-shaped bridging groups to allow a parallel chromophore alignment. Hogan-Esch and co-workers⁷⁴ proposed ABCD tetrablock NLO polymers, in which the block C and the NLO block B are incompatible. The interaction between blocks A and D through hydrogen bonding was expected to lead to a noncentrosymmetric self-assembly. Up to date, large EO activity of main-chain NLO polymers has yet to be demonstrated.

Covalent coupling of NLO chromophores as a side chain to polymer backbone represents an efficient approach to prepare NLO polymers for practical EO applications.¹ There is a significant flexibility in optimization of properties for side-chain NLO polymers through modification of backbone structures, adding side groups, and introduction of crosslinking functionalities. Unlike main-chain NLO polymers, whose preparation depends on chromophore-containing monomers with high purity, side-chain NLO polymers can be achieved either by polymerizing chromophore-containing monomers or through a post-functionalization. In order to obtain a good thermal stability of poling-induced dipole order, side-chain NLO polymers typically explore the use of

high- T_g polymers such as polyurethane,⁷⁵⁻⁷⁸ polyquinoline,^{79,80} and polyimide.⁸¹⁻⁸⁵ A brief description of these three polymer systems is given.

NLO polyurethanes can be readily prepared by interacting a diol-containing chromophore with an aromatic diisocyanate such as 2,4-toluene diisocyanate or 4,4'-diisocyanato-3,3'-dimethoxyphenyl.⁷⁵⁻⁷⁸ These polymers commonly have good solubility in common organic solvents and good film-forming ability. Crosslinking networks can be easily enabled by addition of a tri-functional monomer such as triol or triisocyanate, therefore, the chromophore-containing monomer does not have to be extremely pure to afford a high-molecular-weight (high-Mw) linear polymer for a good film-forming ability. Dalton and co-workers carried out extensive studies on electric poling and thermal curing of various NLO polyurethanes.^{51,78} Large EO coefficients, up to 41 pm/V, were achieved and good temporal stability of EO response at elevated temperatures was demonstrated. Disadvantages of polyurethane systems include the sensitivity of EO coefficient to the poling conditions and a high optical loss (e.g., 3 dB/cm⁷⁸) caused by the overtone absorption of polar N-H and O-H bonds.

Jen and co-workers^{79,80} recently exploited high-temperature polyquinolines as a new optical polymer system for EO applications. Through copolymerization or post functionalization, Jen et al. obtained a few series of side-chain NLO polyquinolines with T_g above 200 °C. Large EO coefficients on the order of 20 pm/V were obtained and long-term stability of the EO response at 85 °C for more than 1000 h was demonstrated.

Polyimides are among the most promising systems for producing practically usable EO materials. In addition to their high T_g , good mechanical strength, and low optical loss, polyimides have good compatibility with polar NLO chromophores and can

be readily modified by using different polymerizing monomers. In general, to obtain polyimides with good solubility, flexible ether linkage is incorporated into the backbone, which also serves as a means to adjust the T_g of polymers. The preparation of NLO polyimides typically involves various post-functionalizations⁸³ or mild polymerization methods such as Mitsunobu condensation⁸² and addition polymerization.⁸¹ The traditional synthetic approach through diamine and dianhydride for polyimides is not used to prepare NLO polyimides due to the poor accessibility to high- $\mu\beta$ chromophore-containing monomers. Polymer **21**⁸⁶ is a side-chain NLO polyimide that was prepared by polymer functionalization. The hydroxyl-functionalized polyimide (**21**, R = H) was first prepared and subsequently grafted with the acid-containing, branched CLD chromophore (R_1OH) using 1,3-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) as the condensation reagents.⁸⁶ A high chromophore loading (taking into account only the core part) (25 wt.%) was achieved and a high EO coefficient (71 pm/V) at 1.3 μm was found after poling. The poled **21** retained more than 90% of its original r_{33} value after 600 h at 85 °C.

Crosslinked NLO polymers

To achieve long-term temporal stability of EO response, NLO polymers that can undergo crosslinking reactions during or after the poling process have been extensively explored. In addition to the above mentioned crosslinkable NLO polyurethanes,^{51,78} epoxy resins,⁸⁷⁻⁸⁹ polymers containing ethylene or acetylene units,⁹⁰ and polymers containing trifluorovinyl (TFV) groups^{91,92} were studied. Most recently, Luo et al.⁹³ reported an interesting crosslinkable system based on the thermally reversible Diels-Alder reaction. In contrast to the conventional concept that thermal crosslinking of NLO polymers should take place above the poling temperatures, Luo et al. demonstrated the polymer crosslinking while cooling from the poling process. A good temporal stability (~80% of the original r_{33} value) of the crosslinked NLO polymer was found at 70 °C over 250 h.

Dendritic NLO polymers

NLO polymers with dendritic topologies have demonstrated the current highest EO coefficients (e.g., 60 – 111 pm/V) for covalent-bonded chromophore-polymer systems.^{3,4,94} The concept of fabricating such type of NLO polymers can be regarded as an alternative to the preparation of chromophores with a spherical shape, which is believed to be beneficial to decreasing the intermolecular interaction and to improving the poling efficiency. Chromophores in dendritic polymers are structurally shielded from neighboring chromophores by the attached bulky branches. Since the dipole movement is related to only the motions of branches and slightly affected by other chromophore dipoles, dendritic NLO polymers commonly have high poling efficiency and good

temporal stability of EO response upon immobilization of branches by crosslinking. Polymer **21**⁸⁶ represents a dendronized NLO polymer that was found to have an extremely high poling efficiency of 81% by comparing the EO coefficient obtained by the parallel electrode poling and the calculated theoretical value.

I.6 Poling and EO Measurement

Poling techniques

To realize the noncentrosymmetric structure required for a macroscopic EO activity, NLO polymers are commonly poled by parallel electrode poling or corona poling techniques. In the parallel electrode poling, the NLO polymer film sandwiched between two electrodes (Figure I-4) is heated up to the T_g and the poling voltage is applied through electrodes. The drawback of this technique is the limited voltage that can be applied due to dielectric in the polymer film. Careful attention has to be given to material purity, thin-film processing, and electrode design. Advantages of this method are the ease in control of poling conditions (such as voltage) and no damage to the surface of polymer films.

Figure I-4. Schematic diagram of the parallel electrode poling setup.

In the corona poling (Figure I-5), a sharp needle or wire is charged to several kilovolts to ionize the surrounding atmosphere and deposit charges onto the surface of

polymer films. High poling fields on the order of the polymer dielectric strength can be achieved in this way. Owing to the low surface conductivity of polymer films, charge leakage will be localized at the defect sites but does not cause a macroscopic short circuit. Depending on the polarity of the corona wire, either positive or negative charges can be deposited on top of polymer films. Hampsch et al.⁹⁵ have investigated the effect of corona polarity on the poling efficiency and found that a larger and more stable SHG signal could be obtained by using the positive corona poling method.

Figure I-5. Schematic diagram of the corona poling setup.

Determination of order parameter

In the poling process, an efficient alignment of chromophores along the poling field or a large order parameter is always desired. Experimentally, the order parameter denoted as Φ can be determined through measuring the refractive index parallel ($n_{||}$) and perpendicular ($n_{\perp}$) to the direction of poling field and using the equation of $\Phi = (n_{||} - n_{\perp}) / (n_{||} + 2n_{\perp} - 3n_0)$, where n_0 is the refractive index before poling.⁹⁶ Electronic absorption spectrum can also be used to evaluate the poling efficiency: $\Phi = 1 - (A_{\perp}/A_0)$,

where $A_{\perp}$ and A_0 is the absorbance of an poled (light is polarized perpendicular to the poling direction) and unpoled polymer sample, respectively.⁹⁷ Typically, the order parameters of electrically poled amorphous NLO polymers are on the order of 0.2 – 0.3.

In the early text, we have addressed a few factors that affect the order parameter, such as poling voltage, polymer chain mobility (or T_g), and intermolecular electrostatic interactions. Notably, the order parameter of a poled NLO polymer is also a function of poling time. The studies of Kajzar and co-workers⁹⁸ have indicated that, at a finite poling temperature, the build up of the order parameter Φ with poling time (t) may be described by a monoexponential function:

$$\Phi = \Phi_{\infty} [1 - e^{-(t/\tau)}] \quad (13)$$

where τ is the time constant and Φ_{∞} is the plateau (saturation) value, both depending on the poling temperature.

Measurement of EO coefficient

An ellipsometric technique has been used by Teng and Man for the determination of EO coefficient (Figure I-6).⁹⁹ For this method, a laser beam polarized 45° with respect to the plane of incidence is introduced into the sample cell on the back and the reflected beam at the gold layer is allowed to go through a Soleil-Babinet compensator, an analyzer, and into a detector. The output intensity is given by

$$I_o = 2I_c \sin^2(\psi_{sp}/2) \quad (14)$$

where I_c is half the maximum intensity, and ψ_{sp} is the phase difference between the parallel (p) and perpendicular (s) wave components of the beam as they pass through the polymer film. When a modulating voltage $V = V_m \sin \omega_m t$ is applied, the output intensity

is modulated as a result of the modulation of ψ_{sp} due to the change of refractive index. For small modulation voltages and when the intensity is biased at the half intensity I_c , the modulated signal I_m is proportional to this phase difference. With the approximation $n_s \approx n_p \approx n$ and the assumption $r_{33} = 3 \times r_{13}$, a relationship between r_{33} and I_m can be established

$$r_{33} = (3\lambda I_m / 4\pi V_m I_c n^2) \times [(n^2 - \sin^2 \theta)^{3/2} / (n^2 - 2\sin^2 \theta)] \times [1/\sin^2 \theta] \quad (15)$$

where θ is the incident angle and λ is the optical wavelength. Experimentally, I_m and I_c are to be measured. The r_{33} value is calculated from eq. 15.

Figure I-6. Schematic diagram of the reflective Teng-Man setup.

I.7 Rationale and Objectives

In the search for useful and efficient NLO materials for EO applications, research efforts have been focused on the development of NLO chromophores with $\mu\beta$ values and good auxiliary properties and appropriate polymer matrices to host these chromophores. With regard to NLO chromophore, some structure-property relationships have been

established and successfully used to direct new chromophore designs.^{5,6,33} As a result, a wide range of NLO chromophores with very large $\mu\beta$ values has recently been prepared. The incorporation of these chromophores into polymers demonstrated large EO coefficients after poling.¹⁻¹⁰ However, the practical application of these high- $\mu\beta$ chromophores is still limited due to the difficulties in realizing NLO polymers with good processability, large EO coefficients (or high number density and poling efficiency) and long-term temporal stability of poling-induced EO response. To overcome these difficulties, an understanding of structure-property relationship of NLO polymers and systematic optimization of host polymers appear to be extremely important.

For the thesis research on NLO materials, we are interested in zwitterionic chromophores due to their large $\mu\beta$ values and ease in preparation. Their relatively small sizes and large dipole moments (section I.4.2) are also of great importance for the efficient poling. Among the known zwitterionic chromophores, a class of PQDM chromophores (e.g., **19**⁶⁰, Table I-3) was chosen as a core material in our study. Structurally similar to DEMI⁵⁹ (**18**, Table I-3) that has one ($\mu\beta_0 = -9450 \times 10^{-48}$ esu) of the highest reported $\mu\beta$ values, PQDM was theoretically predicted to have a large β of 1270×10^{-30} esu at $1.06 \mu\text{m}$.⁶⁰ Comparative EFISH studies¹⁰⁰ showed a much larger SHG signal (0.528) for PQDM doped in poly(methyl methacrylate) (PMMA) than that (0.306) for DEMI in PMMA. Theoretical studies⁶⁵ indicated a great potential of PQDM in yielding NLO polymers with very large EO coefficients (e.g., 210 pm/V). As an additional merit, PQDM chromophores are quite soluble in some common organic solvents and can be easily modified. Figure I-7 shows the potential modifications of

PQDM chromophores. Conceivably, the reactive functionalities (e.g., hydroxyl group) can be readily introduced to PQDM through the R group; the molecular shape (e.g., to a spherical shape) can be modified by using bulky R' and R'' groups; and the molecular conformation (or the conjugation) can be manipulated by the size of the R''' group. All of the above features make PQDM very promising for NLO applications.

Figure I-7. Potential structural modifications of PQDM chromophores.

However, the development of highly active NLO polymers containing zwitterionic chromophores remains challenging to date. The main obstacles to progress arise from a tradeoff between poling efficiency and chromophore loading, particularly due to strong electrostatic interactions between zwitterionic chromophores. So far, only a few NLO polymers containing zwitterionic chromophores have been prepared,^{37,101-103} and the large EO coefficients of these polymers have yet to be demonstrated. The use of inappropriate host polymers can be accounted for the failure in achieving a large EO activity. It has been observed in our group and in others that the inter-chromophore aggregation can be effectively diminished by using polar, heterocyclic polymers (e.g., polyimides and polyquinoline). These polar polymers usually have a high T_g and thus may be considered as a potential host for the zwitterionic chromophores. Considering a great potential of zwitterionic NLO polymers for EO applications, it is necessary to

unlock the potential of zwitterionic PQDM chromophores and establish the basics and know-how to underpin the research on NLO polymers and EO devices.

According to the above rationale and justification for this research, the overall objective of this thesis is to systematically study the structure-property relationship and to obtain NLO polymers with a large and stable EO activity. Specifically, this thesis intends to obtain a functionalized zwitterionic PQDM, to synthesize a series of NLO polymers, to correlate the EO properties with the structures and to demonstrate a large EO coefficient (e.g., greater than 31 pm/V for lithium niobate) and a long-term temporal stability of EO response.

I.8 References

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Chapter II Design, Synthesis and Characterization of Zwitterionic Nonlinear Optical Chromophores

II.1 Introduction

β -[1-Substituted-4-pyridinium]- α -cyano-4-styryldicyanomethanide (trivial name: pyridinium quinonedimethane, PQDM, Figure II-1) was first prepared by Metzger and Ashwell in 1984.¹ The zwitterionic structure of this chromophore was confirmed by the X-ray crystallography.¹ In the following years, a few analogous compounds (α -PQDM, QQDM, and α -QQDM, Chart II-1) were prepared by the authors and were investigated for their photochromism, electrical rectification effect, and NLO effect as well.²⁻⁵ By assembling QQDM ($R = C_{16}H_{33}$) into a single molecular layer of Langmuir-Blodgett (LB) films, Aswhell⁵ obtained an exceptionally large second-order NLO coefficient $\chi^{(2)}_{zzz} = 180 \text{ pm/V}$. The ground-state dipole moments of PQDM and QQDM were determined to be $43 \pm 8 \text{ D}$.²

Due to the structural similarity to 4-[1-cyano-3-diethylamino-2-propenylidene]-2,5-cyclohexadiene-1-ylidenepropanedinitrile⁶ (acronym: DEMI, Figure II-1) that has a $\mu\beta$ value ($\mu\beta_0 = -9450 \times 10^{-48} \text{ esu}$) greater than that ($\mu\beta_0 = 8825 \times 10^{-48} \text{ esu}$) of FTC chromophore⁷ (Figure II-1), PQDM and QQDM were subjected to a comparative study with DEMI by Cross and co-workers.⁸ In the EFISH experiments, PQDM in poly(methyl methacrylate) (PMMA) (SHG = 0.528) yielded a more intense SHG signal than DEMI in PMMA (SHG = 0.306);⁹ and in the theoretical studies much larger β maximum was

shown for QQDM than for DEMI.⁸ Given the good solubility in common organic solvents and good thermal stability (e.g. > 250 °C), PQDM appears quite promising for NLO applications.

Figure II-1. Structures of PQDM, its analogues (α -PQDM, QQDM, and α -QQDM) and FTC

A viable approach to NLO polymers with high number densities is through the covalent bonding of NLO chromophores to the host polymers. This seems to be necessary for zwitterionic PQDM chromophores since the amount of PQDM that can be doped in a polymer is quite limited due to the chromophore aggregation. The picolinium moiety in PQDM, functionalized with a hydroxyl-containing substituent, was chosen as the site of modification. Various hydroxyl-containing picolinium halides can be readily prepared from the reactions of 4-picoline with different bromo alcohols and are used to make

hydroxyl-containing PQDM. In selecting the bromo alcohols, the rigidity and length of the spacer between the hydroxyl group and the core structure of PQDM are considered. It is believed that a flexible spacer (e.g., 3 to 6-carbon aliphatic chain) will be appropriate. In this chapter, we describe the synthesis and characterization of hydroxyl-substituted PQDM chromophores.

II.2 Synthesis and Characterizations

Synthesis

The synthesis of PQDM involves the condensation reaction between picolinium halide and lithium TCNQ adduct or TCNQ. Several reaction conditions were investigated by Aswell and Metzger et al.,^{1-3, 10} but all of them resulted in low reaction yields (e.g., 6 – 60%). Our initial effort in preparation of hydroxyl-containing PQDM with the reported methods failed to produce the product with over 10% yield. In order to improve the synthetic efficiency and be able to prepare hydroxyl-containing PQDM in gram quantity, the reaction condition was optimized by a former graduate (Cara Weir) and two current group members (Andrew Beaudin and Tayebah Hadizad) through investigating carefully the effect of different solvents, different organic bases and different feed ratios.¹¹ It was found that the highest reaction yield [97% for PQDM (R = -C₈H₁₇), Figure II-1] could be obtained by reacting two equivalents of lithium TCNQ adduct with one equivalent of picolinium halide in refluxing acetonitrile with the presence of two equivalent of a strong organic base {1,8-diazabicyclo[5.4.0] undec-7-ene, DBU}.¹¹ By subjecting the hydroxyl-containing picolinium halides to the same reaction condition, PQDM chromophores

(PQDM-a, PQDM-b, and PQDM-c) were obtained in yields of 45 – 68% (Scheme II-1).

Scheme II-1. Synthesis of hydroxy-containing PQDM

The three hydroxyl-containing PQDM synthesized in this work contain either one hydroxyl or two hydroxyl groups. PQDM-a and PQDM-b were prepared to contain hydroxypropyl and hydroxyhexyl substituents, respectively. The 3- or 6-carbon distance from the hydroxyl group to the PQDM core structure is expected to allow for a good mobility for the chromophores covalently bonded to the polymer side chains. The diol-containing chromophore (PQDM-c) is a potential monomer for making linear and hyperbranched polyesters and polyurethanes.

Characterization

The ^1H and ^{13}C NMR spectra and IR spectra of the synthesized hydroxyl-containing PQDM are all consistent with the desired structures. Although small impurity peaks are observable in the ^1H NMR spectra and cannot be removed by recrystallization of these chromophores from acetonitrile, they are not expected to affect the purity of NLO polymers. From the NMR data, the impurity content was estimated to be around 2%. Figure II-2 shows the ^1H NMR spectrum of PQDM-a and the peaks are assigned to

the structure. In comparison with the chemical shifts (8.98 and 8.00 ppm) of protons on the *N*-alkylated picolinium bromide (1-hydroxypropyl-4-picoline, Scheme II-1), the chemical shifts of the corresponding protons (H_d and H_e) remain basically unchanged, indicating a pyridinium moiety in the structure of PQDM-a. The zwitterionic structure of PQDM and its analogues have been analyzed by both X-ray crystallography and mechanical quantum calculations.^{1,12,13} All the studies showed the positively charged pyridinium ring structure but revealed a quinonoid nature for the central six-membered ring. In our study, the chemical shifts of protons H_g and H_e are different from what predicted (e.g., 6.44 ppm for both H_g and H_e , by Chemdraw Ultra 7.0) for a tricyanoquinodimethane structure. Figure II-3 displays the IR spectrum of PQDM-a. Two peaks are observed at 2174 and 2132 cm^{-1} , indicating the two different locations of cyano groups.

Figure II-2. ^1H NMR spectrum (400 MHz) of PQDM-a in $\text{DMSO}-d_6$

Figure II-3. IR spectrum of PQDM-a (KBr pellet)

Solubility

All the hydroxyl-containing PQDM (PQDM-a, PQDM-b, and PQDM-c) are readily soluble in polar aprotic solvents such as DMF, DMSO and NMP, but moderately soluble in non-amide polar solvents such as acetonitrile, methanol and acetone. PQDM is essentially insoluble in less polar solvents such as chloroform, THF and benzene.

UV-Vis absorption and solvatochromism

Due to the same 'push-pull' backbone, the hydroxyl-containing PQDMs showed the similar charge-transfer (CT) absorption band at 654 nm in DMF (Figure II-4) and give a bright blue color ($\epsilon = 37600$ for PQDM-a). Upon addition of water, the absorption of PQDM in DMF shifted to shorter wavelengths and turned into purple ($\lambda_{\text{max}} = 550$ nm) at a volume ratio of 5:1 (H₂O/DMF). Subsequent addition of DMF to the solution moved the absorption back to around 650 nm. To investigate this solvatochromism, the

maximum absorption wavelengths of PQDM-a in various solvents were measured (Figure II-4). As shown in Table II-1, the absorption band shifts hypsochromically with increasing the solvent polarity. From the less polar THF to the polar methanol, a blue shift as large as 125 nm was found. Since a CT absorption band is closely related to the electronic state in the chromophore structure, such a large solvatochromic shift indicates a large polarizability of PQDM. In addition, this negative solvatochromism of PQDM chromophores confirms the zwitterionic structure at the local fields of solutions.

Figure II-4. UV-Vis absorption spectrum of PQDM-a ($c = 1.19 \times 10^{-5}$ M): (a) methanol, (b) acetonitrile, (c) DMF, (d) acetone and (e) THF [due to the poor solubility of PQDM in THF, the solution was prepared by adding 20 μ L of PQDM in DMF (0.8 g/L) into 4 mL of THF].

Table II-1. Solvatochromic data for PQDM-a in selected solvents

Solvent	$\lambda_{\max}$ (nm)	Extinction coefficient [Log(ϵ)]	Polarity index ^a	Dielectric constant ^b
Methanol	621	4.48	6.6	32.7
Acetonitrile	653	4.57	6.2	37.5
DMF	654	4.54	6.4	36.7
Acetone	681	4.62	5.4	20.7
THF	746	4.75	4.2	7.6

^a Snyder polarity index (<http://home.planet.nl/~skok/techniques/hplc>). ^b Dielectric constants from "Handbook of Chemistry and Physics" 76th Edition, 1995-1996.

Stability

The thermal stability of hydroxy-containing PQDM was assessed by thermogravimetric analysis (TGA) under nitrogen. A high onset temperature for 5% weight loss was found at 287 °C and the starting decomposition temperature was around 270 °C, as seen for PQDM-a (Figure II-5). Such a thermal stability is comparable to that ($T_d = 275$ °C) of CLD¹⁴ and meets the requirements for most material processing and device fabrications.

Figure II-5. TGA trace of PQDM-a in nitrogen with a heating rate of 10 °C/min.

Since the hydroxy-containing PQDM is to be grafted onto acid-containing polymers, the chemical stability of PQDM-a to acids and bases should be evaluated. PQDM-a was found to be not stable to a strong acid. The blue color of PQDM-a in DMF disappeared immediately upon addition of hydrochloric acid. The addition of triethylamine to neutralize the solution did not bring back the original color. PQDM-a was also found to be labile to acetic acid, although the color bleaching was slower and took hours. In a DMF solution containing benzoic acid, PQDM-a retained its blue color for days. PQDM-a is found to be stable to organic bases such as pyridine, piperazine and DBU, but not to strong alkali such as aqueous sodium hydroxide solution. PQDM-a appeared to be stable to acyl chloride and the hydrochloride generated during reactions with the presence of an excess amount of pyridine.

Although Ashwell³ stated that the PQDM chromophores could undergo reversible photochromism in solutions, this was not observed in our study. PQDM-a in DMF lost its blue color in two days under indoor light and the blue color did not come back after the bleached solution was placed in darkness. When a solution of PQDM-a in DMF was stored in darkness, the bright blue color remained for months. A detailed study on the decomposition of PQDM chromophores was done by a former student in our group.¹¹ The results showed a good photo-stability of PQDM-a in DMF if in the absence of oxygen. The crystals showed a much better stability to the indoor light, as no discernible change in color occurred over weeks.

NLO Properties

In 1990, Ashwell³ calculated the molecular β value to be 1270×10^{-30} esu at $1.06 \mu\text{m}$ for PQDM ($R = -\text{CH}_3$, Figure II-1). In the following years, although there were studies on exploring the NLO application of PQDM chromophores,^{5,8} the β (or $\mu\beta$) values of PQDM chromophores were not determined experimentally. Lately, the Wang group at Carleton University and a physics group at Universiteit Antwerpen jointly determined the β value of PQDM-a and other zwitterionic chromophores. In DMF solution and at $1.07\text{-}\mu\text{m}$ wavelength, PQDM-a was found to have a β_{zzz} as large as 1930×10^{-30} esu by the Hyper-Rayleigh scattering experiment. Based on this measurement, a zero-frequency β_0 of -590×10^{-30} esu was estimated. By taking the dipole moment of the analogue QQDM ($\mu = 45$ D), an extraordinary large $\mu\beta_0$ value of -26550×10^{-48} esu was obtained, which is about two fold larger than that of FTC.

II.3 Conclusions

Hydroxyl-containing PQDM chromophores have been synthesized in moderate yields (45 – 68%) for the covalent coupling with polymers. These chromophores showed a good solubility in common organic solvents, large negative solvatochromism, and good thermal stability. The Hyper-Rayleigh scattering experiments found a very large molecular β (-590×10^{-30}) for one of the PQDM chromophores, demonstrating the great potential of this type of chromophores for NLO applications.

II.4 Experimental Section

Lithium TCNQ salt was prepared according to the literature procedure.¹⁵ All other reagents and solvents were purchased from Aldrich and used as received.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AMX 400 MHz or a Gemini 200 MHz spectrometer. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR spectrometer. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 900 UV-Vis-NIR spectrophotometer. Thermogravimetric analysis was done on a Seiko TG/DTA 220 in nitrogen at a heat rate of 10 °C/min.

Synthesis of Picolinium Halides

A general synthetic approach is illustrated with 1-(1-hydroxypropyl)-4-picoline as follows: To a solution of 4-picoline (9.6 g, 0.1 mol) in ethanol (100 mL) was added 3-bromo-1-propanol (15.3 g, 0.11 mol). The mixture solution was stirred at reflux for 2 h and then the solvent was removed under vacuum. The resulting light yellow viscous liquid was washed thoroughly with diethyl ether (3 × 100 mL) and then dried under vacuum at 60 °C: 21.6 g (92% yield); ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.98 (2H, d, J = 6.8 Hz), 8.00 (2H, d, J = 6.8 Hz), 4.64 (2H, t, J = 7.0 Hz, 7.0 Hz), 3.44 (2H, t, J = 6.0 Hz, 6.0 Hz), 2.62 (3H, s), 2.06 (2H, p, J = 6.8 Hz, 6.0 Hz, 6.0 Hz, 6.8 Hz); IR (neat, cm⁻¹): 3332 (ν_{O-H} of hydroxy group), 1642 (ν_{C=N} of picolinium unit), 1518 (ν_{C=C} of aromatic ring).

1-(1-Hydroxyhexyl)-4-picoline: 90% yield; ¹H NMR (400 MHz, DMSO-*d*₆): δ 9.01

(2H, d, $J = 6.4$ Hz), 8.02 (2H, d, $J = 6.4$ Hz), 4.57 (2H, t, $J = 7.2$ Hz, 7.2 Hz), 4.01 (1H, br), 3.37 (2H, t, $J = 6.4$ Hz, 6.4 Hz), 2.26 (3H, s), 1.89 (2H, m), 1.21-1.49 (6H, m).

1-(1,2-Dihydroxypropyl)-4-picoline: 97% yield; Purified by crystallization from ethanol (m.p. 157-158 °C); ^1H NMR (200 MHz, DMSO- d_6): δ 8.88 (2H, d, $J = 6.4$ Hz), 7.97 (2H, d, $J = 6.4$ Hz), 5.66 (1H, br s), 5.20 (1H, br s), 4.77 (1H, dd, $J = 13.0$ Hz, 3.2 Hz), 4.47 (1H, dd, $J = 13.0$ Hz, 8.0 Hz), 3.89 (1H, m), 3.47–3.53 (1H, m), 3.27–3.33 (1H, m), 2.60 (3H, s).

Synthesis of PQDM chromophores

A general synthetic approach is illustrated with PQDM-a as follows: To a solution of acetonitrile (100 mL) in a round-bottomed flask were added a salt of lithium TCNQ (1.00 g, 4.70 mmol) and 1-(1-hydroxypropyl)-4-picoline (0.55 g, 2.35 mmol). While at reflux, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 1.0 mL) was added dropwise and the resulting green solution was stirred at reflux with monitoring by using an UV–Vis spectrophotometer. After 30 h, the heating was stopped and the reaction vessel was allowed to cool to room temperature. The dark blue precipitate was collected by filtration and recrystallized from acetonitrile to give a blue powder: 0.52 g, 68% yield; ^1H NMR (400 MHz, DMSO- d_6): δ 8.94 (2H, d, $J = 6.4$ Hz), 8.26 (2H, d, $J = 6.4$ Hz), 7.79 (1H, s), 7.54 (2H, d, $J = 8.4$ Hz), 6.82 (2H, d, $J = 8.4$ Hz), 4.75 (1H, t, $J = 4.8$ Hz, 4.8 Hz), 4.57 (2H, t, $J = 4.8$ Hz, 4.8 Hz), 3.45 (2H, q, $J = 5.2$ Hz, 4.8 Hz, 5.2 Hz), 2.07 (2H, quint, $J = 6.4$ Hz, 6.4 Hz, 6.4 Hz, 6.4 Hz); IR (KBr, cm^{-1}): 3403 ($\nu_{\text{O-H}}$ of hydroxyl group),

2174 and 2132 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1633 ($\nu_{\text{C}\equiv\text{N}}$ of picolinium moiety), 1565, 1547 ($\nu_{\text{C}=\text{C}}$ aromatic ring); MS (SI, m/e): 329 ($\text{M}+\text{H}^+$).

PQDM-b: 45% yield; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.97 (2H, d, $J = 6.4$ Hz) 8.30 (2H, d, $J = 6.4$ Hz), 7.83 (1H, s) 7.60 (2H, d, $J = 7.8$ Hz), 6.85 (2H, d, $J = 7.8$ Hz) 4.50 (2H, t, $J = 4.8$ Hz, 4.8 Hz), 3.40 (2H, m), 1.92 (2H, m), 1.32-1.42 (6H, m).

PQDM-c: 43% yield; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.88 (2H, d) 8.30 (2H, d) 7.88 (1H, s) 7.60 (2H, d) 6.87 (2H, d) 5.50 (1H, s) 4.70 (2H, d) 4.38 (2H, t); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): 149.5, 146.9, 144.9, 128.2, 125.6, 124.6, 123.7, 120.9, 119.4, 118.3, 116.7, 70.3, 70.2, 62.9.

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Chapter III Design, Synthesis, and Characterization of Polyimides as a Host for Zwitterionic Nonlinear Optical Chromophores

As discussed in Chapter I, the successful use of an NLO polymer in EO devices depends on the development of NLO chromophores with large $\mu\beta$ values and host polymers that can impart efficiently the large molecular $\mu\beta$ to a large and stable macroscopic EO activity. Many criteria for NLO polymers, such as processability, optical transparency at telecommunication wavelengths, temporal stability of EO response, and dielectric constant (related to the bandwidth), are related to and dictated by the host polymers. In this chapter, the design, synthesis and characterization of a series of polyimides as a potential host for the hydroxyl-functionalized, zwitterionic PQDM chromophore (PQDM-a, Chapter II) are described.

III.1 Design

To develop suitable host polymers for the zwitterionic chromophores, some challenges in terms of, for example, the incorporation method and the number density, must be met. Zwitterionic chromophores are commonly highly labile to some (e.g., acidic) reaction conditions. Thus, mild reaction conditions should be used for the chemical incorporation. On the other hand, the extremely large dipole moment of zwitterionic chromophores can cause strong electrostatic interactions between chromophores. In order to achieve high chromophore loading and poling efficiency, host polymers must be developed to diminish the intermolecular electrostatic interactions and

to allow for good chromophore mobility under the poling conditions. Thus, we took the following into consideration when designing the host polymers.

- (1) Good compatibility. Host polymers should contain some polar units in the structure and have moderate dielectric constants (e.g., 3-4). The relatively polar environment provided by the host polymers may diminish the inter-chromophore electrostatic interactions and enhance the poling efficiency.
- (2) Reactive functionality. To increase the number density, PQDM has to be incorporated into the polymers *via* covalent bonding. The functional group in host polymers should allow an efficient coupling reaction under mild reaction conditions. Since PQDM is functionalized with a hydroxyl group, a carboxylic acid group can be used for coupling and thus should be introduced into the polymer backbone.
- (3) Glass transition temperature (T_g). To achieve a good temporal stability of poling-induced EO response, the minimum chain mobility is desirable. However, to align the chromophores under a poling field, the host should have good chain mobility. The T_g of (NLO) polymers are also governed by the poling and lattice hardening temperatures.
- (4) Processability. The host polymers should be readily soluble in common organic solvents for subsequent grafting reactions and should form tough, flexible and transparent thin films. The polymer films should adhere well to the substrates such as silicon, ITO glass and other polymer films.

- (5) Optical transparency. The host polymers should have a low content of C-H, N-H and O-H bonds. These bonds are known to have overtone absorptions near the telecommunication wavelengths, which causes the optical loss.

In the search for a suitable host polymer for PQDM, polycarbonate, poly(ether sulfone)s and polyimides were selected and tested for compatibility with PQDM. All the polymers are amorphous and have good film-forming ability. The mixtures of PQDM/polymers were dissolved in *N,N*-dimethylformamide (DMF) and cast into thin films on glass. Among these polymers, polyimides appeared to be the most promising. A relatively high amount of PQDM (~ 5 wt.%, $N \approx 8 \times 10^{19} \text{ cm}^{-3}$) could be blended into Ultem polyimide and polyimide derived from 6FDA and 4,4'-phenylphenone diamine without showing phase separation in thin films under microscope. A good adhesion of the PQDM/polyimide thin films to the ITO glass and silicon wafer was also observed. Thus, polyimide was chosen in our study as a host for PQDM. To enable the covalent bonding of hydroxyl-containing PQDM to the host polyimide, carboxylic acid groups are introduced to the polyimide backbone. Using 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide (EDC) as a coupling agent, a series of NLO polyimides can be prepared. In addition, a thermally reactive group benzocyclobutenone (BCBO)¹ can be introduced into the polymer as a crosslinker. BCBO undergoes the thermal ring-opening reaction and dimerization around 200 °C (Scheme III-1).

Scheme III-1. Ring-opening and dimerization of BCBO

III.2 Linear polyimides

A series of acid-containing polyimides **API1** – **API9** were first designed and synthesized (Scheme III-2, Table III-1). These polymers have a wide range of T_g (or chain mobility) due to the use of different monomers (e.g., wholly aromatic, ether-linked, semi-aromatic and aliphatic, Scheme III-2). It was expected that, by investigating the poling and EO activity of NLO polymers derived from these host polymers, a suitable host polymer required for an efficient poling could be identified.

The first acid-containing polyimide prepared in the series is **API1** and it has a rigid-rod backbone structure. The polycondensation reaction of 6FDA and 3,5-diaminobenzoic acid (DABA) in *m*-cresol at 200 °C yielded the white fibrous **API1** in high molecular weight (inherent viscosity of 0.76 dL/g) and with a high T_g of 348 °C and good thermal stability (402 °C for 5 % weight loss) in nitrogen. Although the T_g of **API1** is higher than the thermal degradation temperature of PQDM (270 °C), grafting of PQDM chromophores onto the polyimide backbone was expected to bring the T_g down to a temperature suitable for the electric poling.

API1 has a good solubility in common organic solvents such as DMF, DMSO, and NMP. Due to the presence of carboxylic acid groups, **API1** was also soluble in less polar solvents such as tetrahydrofuran (THF) and acetone. Tough, flexible and transparent films on different substrates (e.g., silica, silicon, and ITO coated glass) can be readily prepared by solution casting or spin-coating. However, poling of NLO polyimides derived from **API1** (Chapter IV) failed to detect an EO signal, indicating a poor polymer chain mobility under the poling conditions (1.5 MV/cm, 245 °C).

Scheme III-2. Synthesis of acid-containing polyimides as a potential host for PQDM

Table III-1. Synthesis and characterization of acid-containing polyimides API1 – API9

Polymers	Monomer		T_g^a (°C)	$[\eta]_{inh}^b$ (dL/g)
	Dianhydride(s)	Diamine(s)		
API1	6FDA	DABA	348	0.72
API2	6FDA	DABA (75%) + FDA (25%)	381	0.55
API3	6FDA	DABA (75%) + HQDPA (25%)	347	0.62
API4	6FDA	DABA (75%) + HMDA (25%)	315	0.48
API5	6FDA (50%) + EGTM (50%)	DABA	310	0.36
API6	ODPA	DABA (50%) + BPADA (50%)	270	0.58
API7	BPADPA	DABA	289	0.40
API8	BPADPA (50%) + EGTM (50%)	DABA	258	0.34
API9	EGTM	DABA	249	0.23

^a Measured by DSC in nitrogen with a heating rate of 10 °C/min; ^b Measured at 30 °C with a concentration of 0.5 g/dL in DMAc.

The polyimides **API2** – **API9** have the structural features such as a kink, flexible ether linkage, or aliphatic segments in their backbones (Scheme III-2, Table III-1). DABA was used as a monomer for all the polymers to provide the carboxylic acid functionality. The polyimides **API5** and **API7** – **API9** were prepared by the traditional two-step method, i.e., the formation of poly(amic acid) followed by the chemical imidization using acetic anhydride and pyridine. In comparison, low molecular weight polymers were obtained from the one-step method, i.e., in *m*-cresol at 200 °C. However, due to the strong acid-base interaction between pyridine and the acid groups in the polymer,² a large amount of pyridine may be trapped in the product. In order to free all the acid groups, an excess of acetic acid was added before work-up in two-step polymerization. The IR spectra of these polymers showed no absorption corresponding to free pyridine or the protonated pyridine. The ¹H NMR spectrum of **API7** also did not show any resonance peak attributable to the pyridine unit. All the resulting polymers can form tough and flexible free-standing films, except for **API9** whose films cannot be peeled off the substrate, due to its low molecular weight.

The introduction of a kink into the polyimide backbone, through the copolymerization of FDA (25 mol.%) and DABA (75 mol.%) with 6FDA, led to an increase in *T_g*, as seen for **API2** (381 °C) relative to **API1**. The copolymerization of hexamethylenediamine (25 mol.%) and DABA (75 mol.%) with 6FDA afforded **API4** with a lower *T_g* of 315 °C. The polymerization of more flexible BPADPA with DABA gave **API7** with a *T_g* of 289 °C, and copolymerization of BPADPA (50 mol.%) and EGTM (50 mol.%) with DABA yielded **API8** with an even lower *T_g* of 258 °C. The NLO

polymers derived from these acid-containing polyimides were prepared and only the one derived from **API8** showed a T_g around 245 °C, (Chapter IV).

To improve the chain mobility of host polyimides, more flexible linkages such as ether and ester need to be introduced into the polymer backbone (as shown in Figure III-1). Thus, an acid-containing diamine (**DAPBA**) with two flexible ether linkages was synthesized (Scheme III-3). The nucleophilic substitution reaction between 1-chloro-4-nitrobenzene and 3,5-dihydroxybenzoic acid in DMAc in the presence of potassium carbonate afforded the dinitro compound (**DNPBA**) in 81% yield, which was subsequently hydrogenated to give **DAPBA** in a high yield (90%). The NMR and mass spectroscopy data is consistent with the chemical structure of **DAPBA**.

Figure III-1. An example of rigid chain segments in the host polyimides

Scheme III-3. Synthesis of diamine **DAPBA**

The polycondensation of DAPBA with BPADPA *via* the typical two-step process gave the white fibrous polyimide **API10** (Scheme III-4, Table III-2). The imide structure of **API10** was confirmed by the ^1H NMR and IR spectra. **API10** had a moderate inherent viscosity of 0.42 dL/g in DMAc and a good film-forming ability. DSC and TGA indicated the T_g at 232 °C and the onset temperature at 425 °C for 5% weight loss in nitrogen. NLO polyimides prepared from **API10** had a T_g in the range of 213 – 218 °C (Chapter IV) and exhibited the EO coefficients of around 20 pm/V after poling.

In order to further increase the chain mobility of **API10**, DAPBA and BPADPA were polymerized in the presence of phthalic anhydride (1 – 20 mol.% relative to DAPBA) as an end-capping agent (Scheme III-4, Table III-2). A series of host polyimides **API11a** – **API11d** with the different inherent viscosities (0.22 – 0.37 dL/g in DMAc) and T_g (208 – 227 °C) were obtained by use of a different amount of phthalic anhydride (PA). Polyimides with shorter chains and lower T_g are expected to have a better chain mobility, which may lead to a better poling efficiency and thus a higher EO coefficient. Among the four end-capped polyimides, **API11a** – **API11c** can form flexible films by casting from their DMAc solutions; **API11d** formed a brittle film due to its low molecular weight.

Scheme III-4. Poly(ether imide)s derived from DAPBA

Table III-2. Synthesis and characterization of DAPBA-based poly(ether imide)s

Polymers	Feed Ratio (mol %) ^a		T _g ^b (°C)	[η] _{inh} ^c (dL/g)	T _d ^d (°C)
	BPADPA	PA			
API10	1.00	0.00	232	0.42	483
API11a	0.99	0.02	227	0.37	490
API11b	0.98	0.04	222	0.33	489
API11c	0.95	0.10	222	0.30	493
API11d	0.90	0.20	208	0.22	491

^a Molar ratio relative to DAPBA; ^b Measured in nitrogen with a heating rate of 10 °C/min; ^c Measured at 30.0 °C in DMAc with a concentration of 0.5 g/dL; ^d Onset temperature for 5% weight loss in nitrogen with a heating rate of 10 °C/min.

III.3 Branched polyimides

NLO polymers with dendritic or hyperbranched structures were recently demonstrated to have extremely high EO coefficients (e.g., 60 - 100 pm/V).^{3,4} In these polymer systems, NLO chromophores were covalently bonded to the host and were believed to be well separated from each other so that strong inter-chromophore electrostatic interactions were effectively depressed.⁵ The good chain mobility of dendritic or hyperbranched polymers also contributed to the high poling efficiency and high EO coefficients. Encouraged by these studies, highly branched acid-containing polyimides **BPIs** (Scheme III-6) were designed and synthesized as a host for PQDM. Due to the existence of a significant amount of branches with different lengths, **BPIs** resemble the linear polymers with a high polydispersity and should have a good chain mobility. The NLO polymers based on **BPIs**, depicted in Figure III-2, are expected to be poled efficiently and show a large EO coefficient.

Figure III-2. A representation of branched NLO polyimides

To construct the highly branched structure of the acid-containing polyimides, a novel aromatic triamine, 4-aminophenyl 3,5-di(4-aminophenyloxy)benzoate (APDAPB) (Scheme III-5), was designed and synthesized. The intermediate trinitro compound (NPDNPB) was prepared from DNPBA in two steps. NPDNPB was readily isolated from the reaction mixture in a high yield of 84% and pure enough for the next reaction after filtration and washing with hot ethanol. The hydrogenation of NPDNPB was carried out in a mixture of ethanol and THF and in the presence of palladium on carbon (10%) under a hydrogen pressure of 40 lbs/in². The pure triamine (APDAPB) was obtained in 70% yield after running the crude product through a silica-gel packed column with ethyl acetate as the eluent. The structure and purity of APDAPB were confirmed by the MS and NMR spectroscopies and thin layer chromatography.

Scheme III-5. Synthesis of triamine APDAPB

Two acid-containing polyimides (**BPI1** and **BPI2**) with different branching degrees were prepared by copolymerization of triamine APDAPB, diamine DAPBA, and dianhydride BPADPA *via* the two-step process (Scheme III-6, Table III-3). Due to the high reactivity of anhydride and amine groups, the polycondensation reaction was carried out in a dilute DMAc solution (~3%, wt/v) and by adding the dianhydride very slowly into the diamine/triamine mixture to avoid the gel formation.^{6,7} Phthalic anhydride was used as the end-capping agent. Since a high content of the acid groups in host polymers is needed for a high chromophore loading, the molar ratio of triamine to diamine in feed was kept low at 0.1 for **BPI1** and 0.25 for **BPI2**. According to equation (1), defined by Hawker and Fréchet⁸ for calculation of the degree of branching (DB):

$$DB = (D + T)/(D + T + L) \quad (1)$$

where D, T, and L refer to the numbers of dendritic, terminal, and linear units in the polymer, **BPI1** and **BPI2** have a calculated DB of 17% and 33%, respectively (Table III-3).

Table III-3. Synthesis and characterization of branched acid-containing polyimides

Polymers	Feed Ratio (mol.%) ^a			T _g ^b (°C)	DB ^c (%)	[η] _{inh} ^d (dL/g)	T _d ^e (°C)
	DAPBA	APDAPB	PA				
BPI1	0.90	0.10	0.10	217	17	0.46	467
BPI2	0.75	0.25	0.25	227	33	0.53	465

^a Molar ratio of amines and phthalic anhydride relative to BPADPA; ^b By DSC in nitrogen with a heating rate of 10 °C/min; ^c Calculated degree of branching based on the feed ratio; ^d Inherent viscosity measured at 30.0 °C in DMAc with a concentration of 0.5 g/dL; ^e Onset temperatures for 5% weight loss measured in nitrogen with a heating rate of 10 °C/min.

Scheme III-6. Synthesis of branched acid-containing polyimides

BPI1 and **BPI2** were obtained as off-white solids with inherent viscosities of 0.46 and 0.53 dL/g, respectively. Both polymers are readily soluble in polar aprotic solvents such as DMAc and NMP, indicating the absence of crosslinking in the polymer. Unlike the linear acid-containing polyimides that showed good solubility in THF, **BPI1** and

BPI2 are only partially soluble in THF. The DSC analysis showed a lower T_g of 217 °C for **BPI1** and of 227 °C for **BPI2**, both are lower than that (232 °C) of the linear polymer **API10**. TGA gave basically the same thermal degradation traces in nitrogen with the onset temperatures for 5% weight loss being around 465 °C. Transparent thin films of **BPI1** and **BPI2** were cast on glass slides from their DMAc solutions and could be peeled off as tough, flexible and free-standing films.

III.4 Conclusions

Based on the comparative studies on chromophore doping, poly(ether imide)s were chosen as a host for the highly polar PQDM chromophore. A wide range of acid-containing linear and branched polyimides having different T_g (208 – 348 °C) and molecular weights ($[\eta]_{inh} = 0.22 - 0.45$ dL/g) were prepared. The acid groups in host polyimides allow for chemical grafting of the hydroxyl-containing PQDM.

III.5 Experimental Section

Materials. 4,4'-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA), 4,4'-oxydiphthalic anhydride (ODPA), 1,4-bis(4-aminophenoxy)benzene (HQDPA), and 2,2'-bis(4-(4-aminophenoxy)phenyl)propane (BPADA) were purchased from Chriskev Inc. and used as received. Ethylene glycol bis(anhydro-trimellitate) (EGTM) (Chriskev Inc.) and 4,4'-(4,4'-isopropylidenediphenoxy)bis(phthalic anhydride) (BPADPA) (Aldrich) were purified by recrystallization from acetic anhydride. 3,5-diaminobenzoic acid (DABA) was purchased from Aldrich and recrystallized from water under argon twice. 9,9-Bis(4-aminophenyl)fluorene (FDA) was purchased from Ken Seika Corp. and used

without further purification. Hexamethylenediamine (HMDA) (Aldrich) was purified by recrystallization from hexane. DMAc was dried over calcium hydride and vacuum distilled. Other chemical reagents were purchased from Aldrich and used as received.

Characterization. Melting points were obtained with a Fisher-Johns apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian Gemini-200 or Bruker-400 spectrometer. The chemical shifts relative to tetramethylsilane as internal reference are reported in the ppm scale. Infrared measurements were performed on a Bomem Michelson 120 FTIR spectrophotometer. Solubility tests were carried out by dissolving about 10 mg of polymer in 1 mL of a given solvent. Differential scanning calorimetric (DSC) analysis was carried out in nitrogen on a TA DSC Q100 with a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The onset temperature for 5% weight loss was determined using a Seiko 120 TG/DTA analyzer at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ in nitrogen. Inherent viscosities of polymers were measured in DMAc with an Ubbelohde capillary viscometer at 30.0 ± 0.1 $^{\circ}\text{C}$ with a concentration of 0.5 g/dL.

3,5-Di(4-nitrophenoxy)benzoic acid (DNPBA)

A mixture of 3,5-dihydroxybenzoic acid (7.7 g, 0.05 mol), 1-chloro-4-nitrobenzene (17.3 g, 0.11 mol), and potassium carbonate (24.2 g, 0.17 mol) in toluene (20 mL) and DMAc (40 mL) was stirred at 90 $^{\circ}\text{C}$ for 30 min. Then, the reaction temperature was raised to 150 $^{\circ}\text{C}$. Water formed during the reaction was removed through a Dean-Stark trap. When no more water formed, toluene was removed. After stirring at 150 $^{\circ}\text{C}$ for 48 h, the reaction solution was cooled to room temperature and poured into 600 mL of hydrochloric acid solution (2 M). The precipitates were collected

by filtration, washed with methanol (20 mL) once and with boiling diethyl ether three times: 16.0 g (81% yield); mp. 233-234 °C; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 13.51 (1H, s), 8.27 (4H, dd, $J = 9.2$ Hz, 2.4 Hz), 7.47 (2H, d, $J = 2.0$ Hz), 7.37 (1H, d, $J = 2.0$ Hz), 7.28 (4H, dd, $J = 9.2$ Hz, 2.4 Hz); MS (EI, m/s): 396 (M^+ , 100%).

3,5-Di(aminophenyloxy)benzoic acid (DAPBA)

A suspension of 3,5-bis(4-nitrophenoxy)benzoic acid (15.0 g, 44.6 mmol), palladium on carbon (10%, 0.4 g) and two drops of acetic acid in ethanol (50 mL) was shaken under a hydrogen pressure of 40 lbs/sq. inch for three days. The solution was filtered through celite that was then washed three times with THF (20 mL). The filtrate and washings were combined and roto-evaporated. The residue was run through a silica-gel column (acetone/EtOAc, 1/1, $R_f = 0.6$) to give light yellow solid product: 11.5 g (90% yield); mp. 230 °C (decompose); ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 6.93 (2H, d, $J = 2.4$ Hz), 6.81 (4H, d, $J = 8.8$ Hz), 6.62 (1H, t, $J = 2.4$ Hz, 2.4 Hz), 6.61 (4H, d, $J = 8.8$ Hz); MS (EI, m/s): 336 (M^+ , 100%).

p-Nitrophenyl 3,5-di(4-nitrophenyloxy)benzoate (NPDNPB)

A mixture of 3,5-bis(4-nitrophenoxy)benzoic acid (8.0 g, 0.02 mol) and thionyl chloride (4.4 mL, 0.06 mol) in chloroform (100 mL) was stirred at 65 °C for 3 h. The solvent was removed by roto-evaporation at 60 °C under the reduced pressure to give a yellow solid, which was then dissolved in THF (100 mL). To the THF solution, pyridine (6 mL) was added and followed by the addition of *p*-nitrophenol (3.34 g, 0.024 mol). The solution was stirred at room temperature for 4 h. The yellow precipitate was collected by

filtration, washed with hot ethanol and dried at 60 °C in a vacuum oven (1 mmHg) overnight to give yellow powdered product: 8.5 g (84 % yield); mp. 184-188 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.28 – 8.36 (6 H, m), 7.76 (2 H, d, *J* = 2.0 Hz), 7.41 (2 H, dt, *J* = 9.2 Hz, 3.0 Hz, 2.2 Hz), 7.15 – 7.18 (5 H, m); MS (EI, m/s): 517 (M⁺, 3%).

***p*-Aminophenyl 3,5-di(4-aminophenoxy)benzoate (APDAPB)**

A mixture of 4-nitrophenyl 3,5-bis(4-nitrophenoxy)benzoate (5.0 g, 9.7 mmol), palladium on carbon (10 %, 0.2 g) and two drops of acetic acid in ethanol/THF (1/1, 25 mL) was shaken in a sealed glassware under a hydrogen pressure of 40 lbs/sq. inch for 18 h. The suspension solution was filtered through celite to remove palladium on carbon and the solvent was removed by roto-evaporation. Column chromatography (EtOAc, R_f = 0.45) yielded the pure yellow triamine product: 2.9 g (70 % yield); mp. 185-186 °C; ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.06 (2 H, d, *J* = 2.4 Hz), 6.79 – 6.85 (6 H, m), 6.73 (1 H, t, *J* = 2.4 Hz, 2.4 Hz), 6.61 (4 H, dt, *J* = 8.8 Hz, 3.0 Hz, 2.2 Hz), 6.55 (2 H, dt, *J* = 8.8 Hz, 3.2 Hz, 2.2 Hz), 5.10 (2 H, br); ¹³C NMR (100 MHz, DMSO-*d*₆): δ 164.86, 161.10, 147.19, 146.55, 144.95, 140.91, 132.06, 122.32, 121.79, 115.43, 114.51, 110.36, 110.14; MS (EI, m/s): 427 (M⁺, 46%).

A typical one-step synthesis of acid-polyimide APII

To a solution of 3,5-diaminobenzoic acid (0.3043 g, 2.000 mmol) in *m*-cresol (15 mL) was added 6FDA (0.8885 g, 2.000 mmol). The mixture was stirred at 60 °C for 1 h, and then at 200 °C overnight. The water produced during reaction was removed through a Dean-Stark trap. After cooling to room temperature, the viscous solution was poured

slowly into methanol (500 mL). The polymer as white powders was collected by filtration, washed thoroughly with hot methanol, and dried at 120 °C under vacuum (1 mmHg): 1.09 g (97% yield); $[\eta]_{\text{inh}} = 0.76$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 348$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 402$ °C (TGA, nitrogen); $^1\text{H NMR}$ (200 MHz, DMSO- d_6): δ 9.41-9.49 (4H, m), 9.23 (2H, d, $J = 6.8$ Hz), 9.11 (1H, s), 9.05 (2H, s); IR (KBr, cm^{-1}): 1780, 1724 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API2: 96% yield; $[\eta]_{\text{inh}} = 0.55$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 381$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 453$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1785, 1728 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API3: 97% yield; $[\eta]_{\text{inh}} = 0.62$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 347$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 412$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1788, 1728 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API4: 86% yield; $[\eta]_{\text{inh}} = 0.48$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 315$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 398$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1790, 1714 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API6: 92% yield; $[\eta]_{\text{inh}} = 0.58$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 270$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 446$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1784, 1729 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

A typical two-step synthesis of acid-polyimide API10

To a solution of DAPBA (0.3294 g, 0.9793 mmol) in anhydrous DMAc (5 mL) was added added 4,4'-(4,4'-isopropylidene diphenoxy)bis(phthalic anhydride) (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 at 80 °C for 1 h. Acetic acid (1 mL) was added to the solution. After the polymer solution was cooled to room temperature, it 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 (1 mmHg) oven at 120 °C overnight: 0.76 g (91% yield); $[\eta]_{\text{inh}} = 0.42$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 232$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 483$ °C (TGA, nitrogen); $^1\text{H NMR}$ (200 MHz, DMSO- d_6): δ 13.12 (s), 7.95 (d, $J = 2.4$ Hz), 7.08-7.53 (m), 1.71 (s); IR (KBr, cm^{-1}): 1781, 1721 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API5: 90% yield; $[\eta]_{\text{inh}} = 0.36$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 310$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 386$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1784, 1725 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API7: 94% yield; $[\eta]_{\text{inh}} = 0.40$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 289$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 493$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1783, 1719 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API8: 97% yield; $[\eta]_{\text{inh}} = 0.34$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 258$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 430$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1780, 1718 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

API9: 95% yield; $[\eta]_{\text{inh}} = 0.23$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 249$ °C (DSC); $T_{d, 5 \text{ wt.}\%} = 380$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1776, 1726 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

A typical synthesis of end-capped polyimide APII1b

To a solution of DAPBA (5.2577 g, 15.631 mmol) in anhydrous DMAc (65 mL) was added 4,4'-(4,4'-isopropylidene diphenoxy)bis(phthalic anhydride) (7.9735 g, 15.319 mmol) and phthalic anhydride (0.0926 g, 0.6252 mmol). The resulting solution was stirred at room temperature for 6 h and then acetic anhydride (8 mL) and triethyl amine (4 mL) were added. The reaction solution was stirred at room temperature for another 10 h and at 80 °C for 1 h. To the viscous solution was added slowly acetic acid (10 mL). After the resulting precipitate was dissolved at 60 °C with stirring, the polymer solution was poured slowly into methanol (1 L). The precipitated white polymer product was collected by filtration, washed thoroughly with hot methanol, and dried in a vacuum (1 mmHg) oven at 120 °C overnight: 12.4 g (97% yield); $[\eta]_{inh} = 0.33$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 222$ °C (DSC); $T_d, 5 \text{ wt.}\% = 489$ °C (TGA, nitrogen); $^1\text{H NMR}$ (400 MHz, DMSO- d_6): δ 13.42 (s), 7.98 (d, $J = 2.4$ Hz), 7.52 (d, $J = 7.2$ Hz), 7.29-7.42 (m), 7.11-7.21 (m), 1.75 (s); IR (KBr, cm^{-1}): 1778, 1719 ($\nu_{C=O}$ of imide and carboxylic acid).

APII1a: 96% yield; $[\eta]_{inh} = 0.37$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 227$ °C (DSC); $T_d, 5 \text{ wt.}\% = 490$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1773, 1720 ($\nu_{C=O}$ of imide and carboxylic acid).

APII1c: 98% yield; $[\eta]_{inh} = 0.30$ dL/g (DMAc, $c = 0.5$ g/dL); $T_g = 222$ °C (DSC); $T_d, 5 \text{ wt.}\% = 493$ °C (TGA, nitrogen); IR (KBr, cm^{-1}): 1776, 1719 ($\nu_{C=O}$ of imide and carboxylic acid).

API11d: 95% yield; $[\eta]_{\text{inh}} = 0.22 \text{ dL/g}$ (DMAc, $c = 0.5 \text{ g/dL}$); $T_g = 208 \text{ }^\circ\text{C}$ (DSC); $T_{d, 5 \text{ wt.}\%} = 491 \text{ }^\circ\text{C}$ (TGA, nitrogen); IR (KBr, cm^{-1}): 1776, 1717 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

A typical synthesis of branched acid-polyimides

To a solution of DAPBA (0.2326 g, 0.6916 mmol) and APDAPB (0.0328 g, 0.0768 mmol) in DMAc (10 mL), was added a solution of BPADPA (0.4000 g, 0.7685 mmol) in DMAc (10 mL) over a period of 1.5 h. After the solution was stirred at room temperature for 10 min, phthalic anhydride (0.0114 g, 0.0768 mmol) in DMAc (2 mL) was added. The solution was stirred at room temperature for another 5 h and became viscous. Acetic anhydride (3 mL) and pyridine (1.5 mL) were then added. After stirring at room temperature overnight and at $80 \text{ }^\circ\text{C}$ for 1 h, acetic acid (4 mL) was added. The polymer solution was poured into methanol (300 mL) to give white solid polymer **BPI1** as white powders, which then was washed thoroughly with hot methanol and dried in a vacuum (1 mmHg) oven at $120 \text{ }^\circ\text{C}$ overnight: 0.58 g (90% yield); $[\eta]_{\text{inh}} = 0.46 \text{ dL/g}$ (DMAc, $c = 0.5 \text{ g/dL}$); $T_g = 217 \text{ }^\circ\text{C}$ (DSC); $T_{d, 5 \text{ wt.}\%} = 467 \text{ }^\circ\text{C}$ (TGA, nitrogen); IR (KBr, cm^{-1}): 1775, 1717 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

BPI2: 88% yield; $[\eta]_{\text{inh}} = 0.53 \text{ dL/g}$ (DMAc, $c = 0.5 \text{ g/dL}$); $T_g = 227 \text{ }^\circ\text{C}$ (DSC); $T_{d, 5 \text{ wt.}\%} = 465 \text{ }^\circ\text{C}$ (TGA, nitrogen); IR (KBr, cm^{-1}): 1773, 1719 ($\nu_{\text{C=O}}$ of imide and carboxylic acid).

III.6 References

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Chapter IV Synthesis and Characterization of Nonlinear Optical Polyimides

A wide range of linear and branched polyimides containing carboxylic acid groups have been designed and prepared as potential hosts for the zwitterionic PQDM to obtain NLO polymers with large EO activity and good auxiliary properties (Chapter III). Crosslinkable NLO polyimides can be obtained through grafting the hydroxyl-containing PQDM and thermally reactive 5-aminobenzocyclobutenone (BCBO) onto the host polyimide backbones. In this chapter, NLO polyimides are prepared, characterized, and studied for their thermal relaxation and stability at the anticipated poling temperatures.

IV.1 Synthesis and Characterization

Synthesis

Grafting of PQDM onto acid-containing polyimides was effected by using 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide (EDC) and 4-dimethylaminopyridine (DMAP).^{1,2} The grafting reaction was also investigated using other coupling agents such as trimethylchlorosilane/pyridine, *p*-toluenesulfonyl chloride/pyridine, diethyl azodicarboxylate (DEAD)/triphenyl phosphite (TPP), and 1,3-dicyclohexylcarbodiimide (DCC). These conditions gave low yields and tend to be unreliable as far as reproducibility. In contrast, the grafting reactions using EDC gave relatively high yields (70 – 75 mol.% of grafting in terms of the acid groups in the host polyimides). The good solubility of EDC and the urea by-product allows ease in purification of the NLO polyimides. Although PQDM is labile to acetic acid (Chapter II), it appeared to be stable

to acid-containing polyimides, particularly in the presence of an organic base such as pyridine or DMAP.

Scheme IV-1. Preparation of NLO polyimides

Scheme IV-1 shows the general synthesis of NLO polyimides (NPI1 – NPI7, Table IV-1) using EDC/DMAP. The reactions were carried out at room temperature in *N,N*-dimethylacetamide (DMAc) by adding EDC to a mixture of acid-containing polyimides, PQDM, and BCBO. 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.³⁻⁵ The subsequent dimerization and polymerization of the vinylketene groups lead to the polymer crosslinking or curing. To

Table IV-1. Structures of NLO polyimides

NPI1	
NPI2	
NPI3	
NPI4	
NPI5	
NPI6a - NPI6c	
	$m/n = 1/99.5; 4/98; 10/95$
NPI-7	
R =	

block the residual acid groups in PQDM-grafted polymers, 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) was added to the grafting reaction. The short, bulky DBP and the long, flexible PDFO are expected to affect differently the T_g and the refractive index of NLO polyimides.

The NLO polyimides (NPI1 – NPI7) were obtained in 80 – 92% yields and were deep blue in color. The chemical structures of grafted NLO polyimides were consistent with their IR spectra, showing the characteristic peaks of the cyano groups at 2170 and 2130 cm^{-1} and of the imides at 1780 and 1720 cm^{-1} , and ^1H NMR spectra, displaying the expected resonance associated with protons on the structures of host polyimides, PQDM, BCBO and DBP (or PDFO). The total content of PQDM, BCBO, and DBP (or PDFO) in the resulting NLO polyimides, with each related to the feed ratio, were estimated from the ^1H NMR spectra to be in the range of 70 – 75 mol.% relative to the acid groups in the host polymers. Side reactions of EDC with the acid groups in the polymers to form the *N*-acylurea side-chains^{1,6} still existed during the grafting reactions, as evidenced by the presence of the peaks attributable to the *N*-acylurea of EDC in the ^1H NMR spectra (Figure IV-1). The content of *N*-acylurea in the polymers was estimated from the NMR data to be 13 – 17 mol.% relative to the acid groups in the host polyimides. Due to the covalent-bonding of *N*-acylurea to the backbone, no adverse effect on the thermal and EO properties of the resulting NLO polyimides is expected.

Figure IV-1. ^1H NMR spectrum of **NPI6b3** (Table IV-5) in $\text{DMSO-}d_6$. The structures inside show the possible acylurea by-products.

Tables IV-2 to IV-6 summarize the synthesis and characterization of NLO polyimides **NPI1** – **NPI7**. In addition to the difference in the backbone structures (Table IV-1), these NLO polymers also differ in the PQDM content (e.g., **NPI1a** – **NPI1c**; **NPI4a** – **NPI4c**; **NPI5a** and **NPI5b**; **NPI6b1**, **NPI6b3**, and **NPI6b5**), the molecular weight of host polymer (e.g., **NPI5c**, **NPI6a**, **NPI6b1**, and **NPI6c**), the degree of branching (i.e., **NPI7a** and **NPI7b**), that if the polymer contain the thermally reactive BCBO unit (e.g., **NPI6b2** and **NPI6b3**), and which compound, DBP or PDFO, was used to block the residual carboxylic acid groups (e.g., **NPI6b4** and **NPI6b3**). Dependence of poling efficiency (or EO coefficient) of NLO polymers on these structural factors are investigated.

Table IV-2. Characterization of NLO polyimides **NPI1 – NPI3**

NLO Polyimides ^a	PQDM ^b (wt.%)	BCBO ^c (mol.%)	$\lambda_{\max}$ (DMF, nm)	n (1.5 μm)	T_g ^d (°C)	T_d ^e (°C)
NPI1a	13	10	658	1.598	ND	290
NPI1b	22	0	658	1.616	ND	275
NPI1c	29	0	659	1.642	ND	278
NPI2	19	10	663	1.645	ND	268
NPI3	15	10	664	1.669	ND	287

^a The residual acid groups were blocked with DBP. ^b Actual PQDM content in weight percentage. ^c Molar ratio relative to the acid groups in the polymers. ^d Measured by TMDSC in nitrogen (10 °C/min). ND: not detectable. ^e Onset temperature for 5% weight loss measured by TGA in nitrogen with a heating rate of 10 °C/min.

Table IV-3. Characterization of NLO polyimides **NPI4**

NLO Polyimides ^a	PQDM ^b (wt.%)	BCBO ^c (mol.%)	$\lambda_{\max}$ (DMF, nm)	n (1.5 μm)	T_g ^d (°C)	T_d ^e (°C)
NPI4a	9	20	664	1.636	243	280
NPI4b	12	20	664	1.657	244	281
NPI4c	16	10	663	1.673	246	273

^a The residual acid groups were blocked with DBP. ^b PQDM content in weight percentage. ^c Molar ratio relative to the acid groups in the polymers. ^d Measured by TMDSC in nitrogen (10 °C/min). ^e Onset temperature for 5% weight loss measured by TGA in nitrogen.

Table IV-4. Characterization of NLO polyimides **NPI5**

NLO Polymers ^a	PQDM ^b (wt.%)	BCBO ^c (mol.%)	$\lambda_{\max}$ (DMF, nm)	n (1.5 μm)	T_g ^d (°C)	T_d ^e (°C)
NPI5a	9	20	662	1.641	214	285
NPI5b	13	10	663	1.659	219	274

^a The residual acid groups were blocked with DBP. ^b PQDM content in weight percentage. ^c Molar ratio relative to the acid groups in the polymers. ^d Measured by TMDSC in nitrogen (10 °C/min). ^e Onset temperature for 5% weight loss measured by TGA in nitrogen.

Table IV-5. Characterization of NLO polyimides

NLO Polyimides ^a	PQDM ^b (wt.%)	BCBO ^c (mol.%)	$\lambda_{\max}$ (DMF, nm)	n (1.5 μm)	T_g ^d (°C)	T_d ^e (°C)
NPI5c	4	20	663	1.632	169	317
NPI-6a	4	20	664	1.640	169	316
NPI6b1	4	20	663	1.632	170	329
NPI6b2	10	0	663	1.646	178	280
NPI6b3	11	20	663	1.654	190	285
NPI6b4	11	20	663	1.653	213	292
NPI6b5	16	20	663	1.662	209	288
NPI6c	5	20	663	1.634	165	317

^a The residual acid residues were blocked with PDFO, except for **NPI6b4** in which the residual acid groups were blocked with DBP. ^b PQDM content in weight percentage. ^c Molar ratio relative to the acid groups in the polymers. ^d Measured by TMDSC in nitrogen (10 °C/min). ^e Onset temperature for 5% weight loss measured by TGA in nitrogen.

Table IV-6 Characterization of branched NLO polyimides **NPI7**

NLO Polyimides ^a	PQDM ^b (wt.%)	BCBO ^c (mol.%)	$\lambda_{\max}$ (DMF, nm)	n (1.5 μm)	T_g ^d (°C)	T_d ^e (°C)
NPI7a	10	0	663	1.665	218	285
NPI7b	11	0	663	1.669	221	287

^a The residual acid groups were blocked with DBP. ^b PQDM content in weight percentage. ^c Molar ratio relative to the acid groups in the polymers. ^d Measured by TMDSC in nitrogen (10 °C/min). ^e Onset temperature for 5% weight loss measured by TGA in nitrogen.

Determination of PQDM Content

For the determination of actual PQDM content in NLO polyimides, a concentration calibration equation of PQDM in DMF solution was established at the maximum absorption of 654 nm:

$$A = 114.66 \times C + 0.0696 \quad (1)$$

where A is the absorption and C is the concentration of PQDM in g/L. Although there is a slight difference in the maximum absorption between PQDM and NLO polyimides (~10 nm), the error should be negligible when A is taken at the maximum absorption of NLO polyimides.

Solubility and Film Forming Ability

Due to absence of carboxylic acid groups, all the NLO polyimides became insoluble in less polar, hydrogen-bond-forming solvents like THF and acetone, but remained soluble in polar aprotic solvents such as DMF, DMAc, and NMP (Table IV-7). Introduction of flexible ether linkage into the backbone, use of the fluorinated aliphatic

PDFO to replace the bulky DBP, or chain branching does not have significant effect on the solubility of NLO polymers.

Table IV-7. Solubility of some typical NLO polyimides

Polymers	Acetone	THF	CHCl ₃	Cyclopentanone	DMSO	DMF	NMP	<i>m</i> -Cresol
NPI1a	–	–	–	–	+	+	+	+
NPI4a	–	–	–	–	+	+	+	+
NPI5a	–	–	–	–	+	+	+	+
NPI6a	–	–	–	–	+	+	+	+
NPI7a	–	–	–	–	+	+	+	+

Note: “–” insoluble; “+” soluble at room temperature. The solubility is tested by dissolving about 10 mg of the sample in 1 mL of the solvent.

Films of **NPI1** – **NPI7** in thickness of 1 – 3 μm can be readily prepared by either casting or spin-coating of their solutions in DMF. Cyclopentanone, although being a nonsolvent for these NLO polyimides, was found to be a good additive (1/9 – 1/1, v/v, relative to DMF) for spin-coating to yield thin films with well controlled thickness and uniformity. All the films were dark blue in color and adhered well to a variety of substrates such as glass, ITO coated glass, and silicon. Tough, flexible, and transparent films can be peeled off the substrates by immersing the films on substrates in distilled water (Figure IV-2). Under optical microscope no sign of phase separation in any of the NLO polyimide films was observed, even for **NPI1c** that has a very high PQDM content (29 wt.%, or $N = 5.2 \times 10^{20} \text{ cm}^{-3}$ when assuming the polymer density is 1 g/cm^3). The

good stability or dispersion of PQDM in NLO polyimide films indicates a success in design of the host polymer in terms of achieving a high number density.

Figure IV-2. Films of **NPI1b** (ca. 2 μm thick): (a) on ITO substrate, (b) free standing.

IV.2 Properties

Optical Absorption

A slight shift (4 – 10 nm) of the charge transfer (CT) band to longer wavelengths was observed for the NLO polyimides in DMF solution in comparison with that (654 nm) of PQDM. For example, **NPI1a** – **NPI1c** in DMF solutions showed a red-shift about 4 nm in the CT absorption and **NPI2** – **NPI7** showed a larger shift of 10 nm (Figure IV-3, Table IV 2-6). Since the intramolecular CT absorption of organic molecules is related to the electronic environment, this bathochromic shift in absorption may be attributed to an interaction between the polyimide backbones and PQDM. Indeed, an hypsochromic shift in the λ_{max} (from 504 nm to 492 nm, in DMF) was observed for disperse red 1 (DR1) in one of the host polyimides (**API4**). This different shift of λ_{max} in direction can be

attributed to the negative and positive solvatochromism of PQDM (Chapter II) and DR1, respectively.

Figure IV-3. UV-Vis absorption spectra in DMF: (a) PQDM, (b) NPI1a, and (c) NPI5a.

In comparison with the absorption of NLO polyimides in DMF solution, the CT absorption of NLO polyimide films showed a distinct peak broadening (~ 100 nm) and an bathochromic shift (~ 50 nm) (Figure IV-4). Since the PQDM loading (e.g., 13 – 29 wt.% for NPI1a – NPI1c and 4 – 16 wt.% for NPI6b1 – NPI6b5) and film preparation method (i.e., casting and spin-coating) did not change the λ_{max} , inter-chromophore interactions in the solid state cannot be accounted for these absorptional changes. Given that a bathochromic shift and broadening of absorption are often observed in aromatic polyimides due to the formation of intermolecular CT complexes,⁷ the peak broadening may be attributed to a CT complex formation between PQDM and polyimide backbones.

In addition, the less polar environment of polyimides (e.g., $\epsilon = 3.8$ for **NPI6b4**, measured by DEA on films at 40 °C) relative to that ($\epsilon = 36.7$) of DMF may also cause the red shift of the CT absorption due to the negative solvatochromism of PQDM. In parallel, a CLD-type chromophore (neutral chromophore with positive solvatochromism) shows very different λ_{max} values in various polymer matrices: 657 nm in poly(methyl methacrylate), 667 nm in amorphous polycarbonate, and 698 nm in polyquinoline (PQ-100).^{8,9}

Figure IV-4. UV-Vis absorption spectra of **NPI1b** (spectra a and b) and **NPI5a** (spectra c and d) in DMF solution (spectra a and c) and as thin films on glass slides (spectra b and d).

The refractive indices of **NPI1** – **NPI7** thin films were measured by the prism coupling method and are listed in the Tables IV-2 to IV-6. The major factors affecting the refractive index are the backbone structure and PQDM content. With the increase of PQDM in the polymer, the refractive index increased. A large increase by 0.044 was

found when the PQDM content was increased from 13 wt.% for **NPI1a** to 29 wt.% for **NPI1c**. The replacement of the pendant group of DBP with the fluorinated PDFO in NLO polyimides did not lead to a substantial change in the refractive index (e.g., **NPI6b3** and **NPI6b4**, Table IV-5).

Figure IV-5. Representative standard DSC heating scans in nitrogen with a heating rate of 10 °C/min: (a) **NLP1b**, (b) **NPI4c**, and (c) **NPI5a**.

Thermal Relaxation

The T_g of **NPI1a** – **NPI1c** were first investigated by standard DSC, which showed a broad, endotherm-like transition centred around 210 °C (e.g., trace a, Figure IV-5). Although similar DSC traces were observed in other NLO polymer systems and the transitions were regarded as the T_g ,^{10,11} parallel electrode poling of **NPI1a** – **NPI1c** thin films at 215 – 245 °C yielded no EO signal. Since the standard DSC revealed the similar broad transitions at 210 °C for all the polyimides **NPI2** – **NPI7** with different backbones

(e.g., traces b and c, Figure IV-5), this endotherm-like transition could not be from the glass transitions but rather from some other thermal processes such as melting or evaporation of the volatiles trapped in the polymers.

In order to acquire clear glass transitions for **NPI1** – **NPI7**, temperature-modulated DSC (TMDSC) was done in nitrogen by heating the NLO polyimide samples at a rate of 3 °C/min, with a modulation amplitude of 1 °C and a modulation period of 1 min. Figure IV-6 displays the typical reversing, nonreversing, and total TMDSC traces for **NPI6b4**. A distinct glass transition was observed at 213 °C in the reversing trace (b, Figure IV-6), but not in the total trace (c, Figure IV-6) that resembles the standard DSC heating traces (a-c, Figure IV-5). The broad thermal transition observed by standard DSC at 210 °C appeared clearly as an endotherm in the nonreversing trace (a, Figure IV-4), but was shifted to a lower temperature at 185 °C in TMDSC. Since the wide-angle X-ray crystallography of **NPI6b4** did not reveal any crystal diffraction patterns and the enthalpy of this endothermic transition showed no dependence on the PQDM content (Table IV-8), melting of crystals cannot be accounted for this transition. A clear nonreversible exothermic transition starting from 218 °C and peaked at 250 °C was observable for **NPI6b4** (a, Figure IV-6) and all the other NLO polyimides containing BCBO unit, which is attributable to the ring-opening reaction of BCBO and subsequent crosslinking reactions. Tables IV-2 to IV-6 list the T_g of **NPI1** – **NPI7** measured by TMDSC. **NPI1** – **NPI3** derived from very rigid host polymers showed no T_g before the degradation temperature of PQDM (270 °C), while **NPI4** – **NPI7** derived from more flexible host polymers were found to have T_g in the range of 165 – 246 °C. In comparison with the

corresponding host polyimides, the NLO polyimides prepared by grafting of PQDM, BCBO, and DBP or PDFO showed lower T_g by 10 – 60 °C, depending on the use of DBP or PDFO. Polymers containing the long aliphatic PDFO unit exhibited much lower T_g than those containing DBP unit, such as **NPI6b3** ($T_g = 190$ °C) and **NPI6b4** ($T_g = 213$ °C) (Table IV-5). For NLO polymers containing thermally reactive BCBO units, no glass transition could be detected once the polymer sample had been heated to 260 °C, indicating the formation of crosslinking networks.

Figure IV-6. TMDSC traces of **NPI6b4**: (a) total, (b) reversing and (c) nonreversing traces, as measured at a heating rate of 3 °C/min, a modulation period of 1 min, and a modulation amplitude of 1 °C in nitrogen.

Table IV-8. Weight loss (TGA) and enthalpy (ΔH , TMDSC) of NLO polyimides with different PQDM content

NLO polymers	PQDM (wt.%)	Weight Loss (%) ^a	ΔH (J/g) ^b
NPI6b1	4	2.5	15.8
NPI6b3	11	2.6	17.7
NPI6b5	16	2.5	8.7

^a Weight loss of NLO polyimides at 240 °C in nitrogen. ^b Enthalpy of the endotherm on the total trace of TMDSC.

The thermal relaxation behavior of NLO polyimides containing no crosslinking BCBO units was also investigated by dielectric analysis at elevated temperatures. Figure IV-7 shows the semi-logarithmic plot of the dielectric constant (ϵ' , plot a of Figure IV-7) and the dielectric loss tangent ($\tan \delta$, plot b of Figure IV-7) of a thin film of **NPI6b4** (11.5 μm thick) versus temperature and frequencies ranging from 10^0 to 10^4 Hz. To remove the possible effect of volatile, the polymer film was first heated to 200 °C in nitrogen at a rate of 10 °C/min and subsequently quenched to room temperature. From the dielectric constant spectrum (plot a, Figure IV-7), two relaxation modes are observable around 185 °C and 220 °C at low frequencies ($f = 1$ and 2.15), corresponding to the movement of polar PQDM side chains (β transitions) and main chain (α transition) of **NPI6b4**, respectively. As the frequency is raised, the two relaxation processes coalesced and moved to higher temperatures.

Figure IV-7. Dielectric spectra of NPI6b4 film (11.5 mm thick, preheated to 200 °C and quenched to room temperature): (a) temperature and frequency dependence (from top to bottom: 1 Hz, 2.15 Hz, 4.64 Hz, 10 Hz, 21.5 Hz, 46.4 Hz, 100 Hz, 215 Hz, 464 Hz, 1000 Hz, 2150 Hz, 4640 Hz, 10000 Hz) of the relative permittivity; (b) temperature and frequency dependence (in the same order as above) of the tan δ .

Similarly, the dielectric loss tangent spectrum (plot b, Figure IV-7) shows two transitions around 185 °C and 218 °C when $f = 1$, attributable to β and α transitions, respectively. The large magnitude of the β transition in the dielectric loss tangent spectrum indicates the good PQDM mobility in the NLO polymer. At higher frequencies, e.g., greater than 4.64 Hz, the α and β processes become undistinguishable and only one transition due to the $\alpha\beta$ relaxation remains, which shifts to higher temperatures as the frequency increases. In comparison with the TMDSC analysis of **NPI6b4**, which showed comparable T_g (α transition) at 213 °C, dielectric analysis appears to be a more powerful method to studying the thermal relaxation behavior of NLO polymers and detected the β transition around 185 °C. Since β transition, related to the movement of side chains, is detrimental to the temporal stability of the noncentrosymmetric structure in poled polymers, it is desirable to depress this secondary relaxation process by the polymer crosslinking.

Thermal Stability

In order to find application in EO devices, NLO polymers must be thermally stable to the material processing temperature, poling temperature, and device processing and packaging temperatures. Two simple methodologies for characterizing thermal stability of NLO polymers are the thermogravimetric analysis (TGA) and the UV-Vis spectroscopy. The former tells the temperature at which the decomposition of NLO polymers begins to occur; the latter shows whether the electronic state of NLO chromophores is subjected to a change upon heating.

The thermal stability of **NPI1** – **NPI7** in nitrogen was first assessed by TGA. All

the polymers showed the onset temperatures for 5% weight loss above 270 °C, which are comparable to that (287 °C) of PQDM. Figure IV-8 compares the TGA traces between PQDM and a NLO polymer **NPI6b4**. Although a small weight loss (~ 2.5 wt.%, e.g., trace b, Figure IV-6) was observed for all the NLO polymers at around 200 °C, it can be removed by first heating the polymers to 200 °C (trace c, Figure IV-8). No correlation between this weight loss and the PQDM content (Table IV-8) is found, excluding the possibility of PQDM decomposition. Provided that the weight loss temperature coincide with endothermic transition in the standard DSC traces, evaporation of trapped volatile such as DMAc can be concluded.

Figure IV-8. TGA traces of (a) PQDM, (b) **NPI6b4** that was dried at 100 °C under vacuum, and (c) **NPI6b4** preheated to 200 °C (10 °C/min) and subsequently cooled rapidly to room temperature in nitrogen.

The good thermal stability of **NPI1** – **NPI7** was also demonstrated by heating the polymers at a high temperature for a long period of time. For example, when **NPI6b3** was isothermally heated at 210 °C in nitrogen for 120 min, a weight loss of less than 1.5

wt.% was found (Figure IV-9). The decomposition rate is very low, about 0.012 wt.% per minute.

Figure IV-9. Isothermal TGA curve of **NPI6b3** at 210 °C in nitrogen. The sample was heated to 210 °C (10 °C/min) in nitrogen and was held at 210 °C for 60 seconds before collecting data.

The thermal stability of the **NPI1** – **NPI7** thin films in nitrogen and in air was evaluated by measuring the UV-Vis and IR spectroscopy (Figure IV-10 and Figure IV-11). As shown in Figure IV-10, when an **NPI1a** thin film was heated at 200 °C for 1 h in nitrogen, the CT absorption remained basically unchanged (plot a, Figure IV-10). In contrast, when the film was heated in air, a rapid decrease in the CT absorption was observed (plot b, Figure IV-10). Clearly, oxygen plays some role in the color bleaching. The decomposition behavior of PQDM in solution and in the solid state (guest-host in polyether sulfone) has been investigated by a former graduate student*. The study results showed that PQDM chromophores are labile to the presence of oxygen, especially upon

* Cara Weir "Synthesis and Stability Studies of Z- β -(1-Substituted-4-Pyridinium)- α -Cyano-4-Styryldicyano methanide Nonlinear Optical Chromophores" *M.Sc. Thesis*, Carleton University 2003.

exposure to visible light and heating. An oxygen-involved oxidation of PQDM was proposed. The same may also explain the color fading for the **NPI1a** film in air at high temperatures. Evidently, the IR spectra of **NPI1a** film showed the disappearance of characteristic peaks of PQDM, i.e., the stretching of the cyano groups at 2130 and 2170 cm^{-1} , when the film was heated in air (Figure IV-11). In contrast, no substantial change in the IR spectrum was found when the polymer film was heated in nitrogen (Figure IV-11).

Figure IV-10. UV-Vis absorption spectra of thin film of **NPI1a** when being heated at 200 °C in (a) nitrogen and (b) air over time.

Figure IV-11. IR spectra of **NPI1a** thin film at 200 °C in nitrogen (top) and in air (bottom) at the different heating time, in reference to PQDM in KBr pellet.

Photo Stability

The stability of NLO polyimides **NPI1** – **NPI7** under exposure to the indoor light and in dark was investigated in the presence or absence of air. The NLO polyimides in DMAc, when being open to air and under the indoor light, were bleached rapidly (e.g., in

two days), whereas those being bubbled with nitrogen and then sealed in a vial retained the color for weeks. When being stored in dark, the polymer solutions remained the original blue color for nearly two years. The polymer films that were dried at high temperatures (e.g., 160 – 200 °C) showed a better stability to the indoor light than the films dried at lower temperatures (e.g. < 120 °C). In darkness, no color change was noticed for the films that were dried at 160 – 200 °C.

The photochemical stability of DEMI-type chromophores in PMMA was studied by Ren et al.¹² By irradiating the polymer waveguide with visible and infrared light, Ren et al. revealed a strong correlation between the photodegradation and the presence of oxygen. It was suggested that a photooxidation of olefinic bonds in the DEMI chromophore led to a permanent bond scission and the loss of color in the samples. They also observed the disappearance of characteristic cyano peaks around 2187 cm⁻¹ and the appearance of a new peak near 1715 cm⁻¹, indicating the formation of the carbonyl groups as a result of air oxidation. For our NLO polyimides, the disappearance of the cyano absorptions around 2175 and 2135 cm⁻¹ was observed for the bleached films, but the new carbonyl peak was not discernible due to overlapping with the imide peaks. Because of the structural similarity between DEMI and PQDM, the following reaction (Scheme IV-2) could be proposed to account for the photo-degradation of PQDM-containing polyimides. Upon exposure to the indoor visible light, singlet oxygen generated by the inter-band absorption of PQDM chromophores attacks the reactive olefinic bond, followed by the elimination of the CN group. Therefore, to achieve a good environmental stability, the NLO polyimides should be shielded from visible wavelength

light and stored oxygen free. Alternatively, steric protective groups can be introduced to the olefinic moiety to stop various reactive species from coming close.

Scheme IV-2. Proposed photooxidation reaction of PQDM

IV.3 Conclusions

A series of NLO polyimides were prepared in 80-92 % yields through grafting the zwitterionic PQDM onto acid-containing polyimides. The reactive BCBO group was introduced to the side chains to enable the polymer crosslinking. Typical features of these NLO polyimides are: (1) a wide range of polymers with the PQDM content from 4 wt.% to 29 wt.%; (2) thermal crosslinking at temperatures around 215 °C, which is higher or comparable to the T_g of most NLO polyimides; (3) different T_g due to different backbone structures, different pendant groups (PDFO or DBP), and different PQDM loading; (4) linear or branched polymer structures and (5) good film-forming ability and high thermal stability ($T_d > 270$ °C).

IV.4 Experimental Section

Materials. See Chapter III for the synthesis of host polyimides. 3,5-Di-tert-butylphenol (DBP), 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide (EDC) and *N,N*-dimethylaminopyridine (DMAP) were purchased from Aldrich and used as received.

N,N-Dimethylacetamide (DMAc) was dried over calcium hydride, vacuum distilled, and stored over molecular sieves (3 Å).

Characterization. ^1H NMR spectra were recorded on a Varian Gemini-200 or Bruker-400 spectrometer. The chemical shifts relative to tetramethylsilane as internal reference are reported in the ppm scale. Infrared measurements were performed on a Bomen Michelson 120 FTIR spectrophotometer. Solubility tests were carried out by dissolving about 10 mg of polymer in 1 mL of studied solvent. Standard differential scanning calorimetric (DSC) analysis and temperature modulated DSC (TMDSC) were carried out in nitrogen on a TA DSC Q100. A typical TMDSC experiment was run with a heating rate of 3 °C/min, modulation amplitude of 1 °C, and modulation period of 60 second. The onset temperature for 5% weight loss was determined using a Seiko 120 TG/DTA analyzer at a heating rate of 10 °C/min in nitrogen. Dielectric measurements were performed on a DEA 2970 dielectric analyzer. On both sides of the polymer films, a gold layer (~ 50 nm) was sputtered as the electrodes. The films were sandwiched between two gold-coated ceramic masks that are connected to the ac supply. The field frequency was varied in the range of 1 –10⁴ Hz. UV-Vis spectra were obtained on a Perkin Elmer Lambda 900 UV/Vis/NIR spectrophotometer. Refractive indices were measured by a Metricon 2010 prism coupler. Thickness of films were measured using an alpha-step 200 surface profiler.

Concentration calibration for PQDM

For the accurate determination of PQDM content in NLO polyimides, a concentration calibration equation was established by measuring the absorption (*A*) of

PQDM in DMF at five concentrations (C , $\times 10^{-2}$ g/L): 0, 1.2, 1.9, 2.2, 2.7 and 2.9. The absorption of these samples at 654 nm was recorded (in the order of concentration): 0, 1.5342, 2.1574, 2.5626, 2.9430 and 3.6364. By plotting the absorption against the concentration and by fitting the data with a straight line, the linear relationship between absorption and PQDM concentration is defined:

$$A = 114.66 \times C + 0.0696$$

To determine the PQDM content in NLO polyimides, a polymer sample with known weight is dissolved in a certain volume of DMF and the intensity of CT absorption is recorded, from which the weight of PQDM is calculated and used to give the weight percentage of PQDM in NLO polyimides.

A typical procedure for the synthesis of NPIIc containing PQDM and DBP

To an ice-cooled, magnetically stirred solution of APII (Chapter III) (0.341 g, 0.609 mmol), PQDM (0.150 g, 0.457 mmol), DBP (0.031 g, 0.152 mmol) and DMAP (0.074 g, 0.609 mmol) in anhydrous DMAc (4 mL), was added EDC (0.122 g, 0.639 mmol). The solution was allowed to warm up to room temperature and stirred for 36 h. Then, 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 re-dissolved into DMAc (4 mL) and precipitated into methanol (200 mL). Polymer NPIIc was collected by filtration and dried at 100 °C under vacuum: 0.46 g (88% yield); PQDM: 28.8 wt.% in the polymer; IR (KBr, cm^{-1}):

2177 and 2131 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1783 and 1726 ($\nu_{\text{C}=\text{O}}$ of imide); T_g = not detected (TMDSC); $T_{d, 5 \text{ wt.}\%} = 278^\circ\text{C}$ (TGA, nitrogen).

NPI1b: 83% yield; PQDM: 21.8 wt.% in the polymer; IR (KBr, cm^{-1}): 2177 and 2135 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1784 and 1726 ($\nu_{\text{C}=\text{O}}$ of imide); T_g = not detected (TMDSC); $T_{d, 5 \text{ wt.}\%} = 275^\circ\text{C}$ (TGA, nitrogen).

A typical procedure for the synthesis of NPI5a containing PQDM, BCBO and DBP

To an ice-cooled, magnetically stirred solution of **API10** (Chapter III) (0.131 g, 0.159 mmol), PQDM (0.021 g, 0.064 mmol), BCBO (0.004 g, 0.032 mmol), DBP (0.013 g, 0.064 mmol) and DMAP (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 up 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 re-dissolved into DMAc (3 mL) and precipitated into methanol (200 mL). Polymer **NPI5a** was collected by filtration and dried at 100°C under vacuum: 0.15 g (88% yield); PQDM: 8.8 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 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 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1785 and 1729 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 214^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 285^\circ\text{C}$ (TGA, nitrogen).

NPI1a: 86% yield; PQDM: 13.4 wt.% in the polymer; IR (KBr, cm^{-1}): 2177 and 2138 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1788 and 1724 ($\nu_{\text{C}=\text{O}}$ of imide); T_g = not detected (TMDSC); $T_{d, 5 \text{ wt.}\%} = 296^\circ\text{C}$ (TGA, nitrogen).

NPI2: 78% yield; PQDM: 18.7 wt.% in the polymer; IR (KBr, cm^{-1}): 2176 and 2138 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1784 and 1719 ($\nu_{\text{C}=\text{O}}$ of imide); T_g = not detected (TMDSC); $T_{d, 5 \text{ wt.}\%} = 278^\circ\text{C}$ (TGA, nitrogen).

NPI3: 84% yield; PQDM: 14.7 wt.% in the polymer; IR (KBr, cm^{-1}): 2178 and 2142 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1780 and 1717 ($\nu_{\text{C}=\text{O}}$ of imide); T_g = not detected (TMDSC); $T_{d, 5 \text{ wt.}\%} = 287^\circ\text{C}$ (TGA, nitrogen).

NPI4a: 80% yield; PQDM: 9.0 wt.% in the polymer; IR (KBr, cm^{-1}): 2176 and 2138 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1779 and 1733 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 243^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 280^\circ\text{C}$ (TGA, nitrogen).

NPI4b: 81% yield; PQDM: 11.6 wt.% in the polymer; IR (KBr, cm^{-1}): 2178 and 2138 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1777 and 1734 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 244^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 281^\circ\text{C}$ (TGA, nitrogen).

NPI4c: 92% yield; PQDM: 16.4 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.80 (br m), 8.97 (br s), 7.51 - 8.80 (br m), 7.35 (br s), 7.09 (br s), 6.74 (br s), 4.74 (br s), 4.66 (br s), 4.44 (br s), 3.72 (br s), 2.44 (br s), 1.68 (br s); 1.27 (br s); IR (KBr, cm^{-1}): 2177 and 2136 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1777 and 1729 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 246^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 273^\circ\text{C}$ (TGA, nitrogen).

NPI5b: 83% yield; PQDM: 13.4 wt.% in the polymer; IR (KBr, cm^{-1}): 2174 and 2138 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1773 and 1717 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 218\text{ }^\circ\text{C}$ (TMDSC); $T_{d, 5\text{ wt.}\%} = 274\text{ }^\circ\text{C}$ (TGA, nitrogen).

NPI6b4: 78% yield; PQDM: 11.0 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 10.50 (br s), 8.96 (br s), 8.80 (br s), 8.24 (br s), 7.92 (br s), 7.62 (br s), 7.10 – 7.45 (br m), 6.88 (br s), 4.62 (br s), 4.37 (br s), 3.72 (br s), 2.07 (br s), 1.70 (br s); 1.24 (br s); IR (KBr, cm^{-1}): 2176 and 2142 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1774 and 1719 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 213\text{ }^\circ\text{C}$ (TMDSC); $T_{d, 5\text{ wt.}\%} = 292\text{ }^\circ\text{C}$ (TGA, nitrogen).

A typical procedure for the synthesis of NPI6b1 containing PQDM, BCBO and PDFO

To an ice-cooled, magnetically stirred solution of **API11b** (Chapter III) (0.408 g, 0.500 mmol), PQDM (0.041 g, 0.125 mmol), BCBO (0.013 g, 0.100 mmol), PDFO (0.110 g, 0.275 mmol), and DMAP (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, additional PDFO (0.100 g, 0.250 mmol) and EDC (0.023 g, 0.120 mmol) were added. After stirring at room temperature for another 24 h, the reaction solution was added slowly into 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 into DMAc (5 mL) and then precipitated into methanol (300 mL). The polymer **NPI6b1** was collected by filtration and dried at $100\text{ }^\circ\text{C}$ under vacuum: 0.45 g (80% yield); PQDM: 3.9 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 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 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1777 and 1723 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 170^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 329^\circ\text{C}$ (TGA, nitrogen).

NPI5c: 80% yield; PQDM: 3.9 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.50 (br s), 8.96 (br s), 8.70 (br s), 8.24 (br s), 7.93 (br s), 7.11 – 7.46 (br m), 6.87 (br s), 5.07 (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}): 2177 and 2142 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1776 and 1722 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 169^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 317^\circ\text{C}$ (TGA, nitrogen).

NPI6a: 85% yield; PQDM: 4.1 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.49 (br s), 8.94 (br s), 8.74 (br s), 8.25 (br s), 7.93 (br s), 7.11 – 7.46 (br m), 6.87 (br s), 5.08 (br s), 4.62 (br s), 4.37 (br s), 3.72 (br s), 2.13 (br s), 1.70 (br s); IR (KBr, cm^{-1}): 2178 and 2142 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1773 and 1733 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 169^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 316^\circ\text{C}$ (TGA, nitrogen).

NPI6b3: 85% yield; PQDM: 10.5 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): 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 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1777 and 1721 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 189^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 285^\circ\text{C}$ (TGA, nitrogen).

NPI6b5: 82% yield; PQDM: 16.1 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): 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 ($\nu_{\text{C}\equiv\text{N}}$ of

cyano groups), 1777 and 1720 ($\nu_{\text{C=O}}$ of imide); $T_g = 209\text{ }^\circ\text{C}$ (TMDSC); $T_{d, 5\text{ wt.}\%} = 288\text{ }^\circ\text{C}$ (TGA, nitrogen).

NPI6c: 85% yield; PQDM: 4.6 wt.% in the polymer; ^1H NMR (400 MHz, DMSO- d_6): δ 10.51 (br s), 8.97 (br s), 8.77 (br s), 8.25 (br s), 7.94 (br s), 6.84 – 7.47 (br m), 5.08 (br s), 4.63 (br s), 4.38 (br s), 3.72 (br s), 2.10 (br s), 1.71 (br s); IR (KBr, cm^{-1}): 2176 and 2140 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1776 and 1733 ($\nu_{\text{C=O}}$ of imide); $T_g = 165\text{ }^\circ\text{C}$ (TMDSC); $T_{d, 5\text{ wt.}\%} = 317\text{ }^\circ\text{C}$ (TGA, nitrogen).

Synthesis of NPI6b2 containing PQDM and PDFO

To an ice-cooled, magnetically stirred solution of **API11b** (Chapter III) (1.630 g, 2.000 mmol), PQDM (0.328 g, 1.000 mmol), PDFO (0.400 g, 1.000 mmol), and DMAP (0.244 g, 2.000 mmol) in anhydrous DMAc (20 mL) was added EDC (0.459 g, 2.400 mmol). After the solution was stirred at room temperature for 24 h, additional PDFO (0.200 g, 0.500 mmol) and EDC (0.069 g, 0.360 mmol) were added. After stirring at room temperature for another 24 h, the reaction solution was added slowly into methanol (350 mL) and the resulting crude polymer product was filtered and washed with methanol in a Soxhlet extractor overnight. The blue polymer was dissolved into DMAc (15 mL) and then precipitated into methanol (300 mL). The polymer **NPI6b2** was collected by filtration and dried at $100\text{ }^\circ\text{C}$ under vacuum: 1.9 g (82% yield); PQDM: 9.6 wt.% in the polymer; ^1H NMR (400 MHz, DMSO- d_6): δ 10.45 (br s), 8.97 (br s), 8.25 (br s), 6.86 – 7.97 (br m), 5.05 (br s), 4.62 (br s), 4.36 (br s), 3.72 (br s), 2.27 (br s), 1.70 (br s); IR

(KBr, cm^{-1}): 2178 and 2136 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1777 and 1729 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 178\text{ }^\circ\text{C}$ (TMDSC); $T_{d, 5\text{ wt.}\%} = 280\text{ }^\circ\text{C}$ (TGA, nitrogen).

A typical procedure for the synthesis of branched NPI7a containing PQDM and DBP

To an ice-cooled, magnetically stirred solution of **BPI1** (Chapter III) (0.400 g, 0.454 mmol), PQDM (0.104 g, 0.318 mmol), DBP (0.028 g, 0.136 mmol), and 4-dimethylaminopyridine (0.055 g, 0.454 mmol) in anhydrous DMAc (3 mL) was added EDC (0.104 g, 0.545 mmol). After the solution was stirred at room temperature for 24 h, additional DBP (0.028 g, 0.136 mmol) and EDC (0.046 g, 0.240 mmol) were added. After stirring at room temperature for another 24 h, the reaction solution was added slowly into methanol (200 mL) and the resulting crude polymer product was filtered and washed with methanol in a Soxhlet extractor overnight. The blue polymer was dissolved into DMAc (3 mL) and then precipitated into methanol (200 mL). The polymer **NPI7a** was collected by filtration and dried at $100\text{ }^\circ\text{C}$ under vacuum: 0.46 g (86% yield); PQDM: 9.8 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.45 (br s), 8.95 (br s), 8.24 (br s), 7.92 (br s), 7.74 (br s), 7.10 – 7.51 (br m), 6.85 (br s), 4.63 (br s), 4.37 (br s), 2.10 (br s), 1.70 (br s), 1.25 (s); IR (KBr, cm^{-1}): 2174 and 2138 ($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1776 and 1719 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 218\text{ }^\circ\text{C}$ (TMDSC); $T_{d, 5\text{ wt.}\%} = 285\text{ }^\circ\text{C}$ (TGA, nitrogen).

NPI7b: 84% yield; PQDM: 11.3 wt.% in the polymer; ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ 10.44 (br s), 8.94 (br s), 8.23 (br s), 7.90 (br s), 7.72 (br s), 7.10 – 7.50 (br m), 6.84 (br s), 4.62 (br s), 4.36 (br s), 2.10 (br s), 1.68 (br s), 1.25 (s); IR (KBr, cm^{-1}): 2174 and 2137

($\nu_{\text{C}\equiv\text{N}}$ of cyano groups), 1775 and 1717 ($\nu_{\text{C}=\text{O}}$ of imide); $T_g = 221^\circ\text{C}$ (TMDSC); $T_{d, 5 \text{ wt.}\%} = 287^\circ\text{C}$ (TGA, nitrogen).

IV.5 References

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Chapter V Electro-Optic Properties of Nonlinear Optical Polyimides

V.1 Introduction

There are two major parameters in the context of EO modulation in a waveguide device: the bandwidth and the drive voltage. While a large modulation bandwidth that relies mainly on the speed matching between electrical and optical signals is inherently enabled for organic materials due to their low refractive-index dispersion from microwave to infrared optical frequencies, achievement of a low drive voltage requires a combination of the material development, device design, and processing. With regard to the core material of an EO waveguide modulator, large macroscopic optical nonlinearity in terms of EO coefficient (r_{33}) has to be achieved through aligning the dipoles of NLO chromophores effectively in a host under an external poling field.

Thus, poling efficiency of NLO polymers is of importance and usually characterized as an order parameter of $\langle \cos^3 \theta \rangle$. It depends on a number of factors, from both the material and technical aspects. Increasing the poling voltage as a way to achieve a high order parameter has limitations due to the dielectric breakdown. Currently, electrode-poling voltages of around 100 V/ μm are achievable for highly efficient NLO polymers.^{1,2} Dalton and co-workers³ systematically investigated the factors affecting the order parameter of poled polymers, showing that intermolecular electrostatic interactions associated with dipole moment, shape, and concentration of chromophores play an important role in lowering the maximum number density and poling efficiency. For NLO polymers based on zwitterionic PQDM, strong inter-chromophore electrostatic

interactions can be expected due to the very large dipole moment of PQDM. However, the use of compatible polyimide hosts with relatively high dielectric constants (e.g. 3.8 for **NPI6b4**) may attenuate the fields associated with intermolecular electrostatic interactions and alleviate the problem in achieving a high poling efficiency. In this chapter, we describe the poling conditions and EO properties of NLO polyimides **NPI1** – **NPI7** (Chapter IV). The electrical properties of NLO polyimide films are also studied. The correlation studies of EO coefficients with the poling conditions, polymer structures, and chromophore loading are discussed.

V.2 Studies on the Poling Conditions

For the poling studies, NLO polyimide films with thickness of 1-3 μm on ITO coated glass substrate (2.25 sq. cm) were prepared by either solution casting or spin coating. The films were dried at 160 – 180 $^{\circ}\text{C}$ under vacuum (1 mmHg) for 2 h before corona poling or before sputtering a thin layer (~ 150 nm) of gold as a top electrode onto the polymer films for parallel electrode poling to ensure the removal of volatile. Both parallel electrode and corona poling were carried out in an inert atmosphere such as nitrogen and argon.

V.2.1 Conducting properties of NLO polyimides

Understanding the electrical conduction of organic polymers is important in the development of high-performance electrical insulators and intrinsically conducting polymers.⁴ For NLO polymers, the study of conductivity as a function of factors such as voltage, temperature, and time is critical for the modulator design and optimization of the

poling process.⁵⁻⁸ In addition, the conductivity of NLO polymers dictates the cladding materials with the complementary conductivity.^{9,10} In this work, two NLO polyimides, **NPI6b3** and **NPI6b2** with and without the BCBO groups, respectively, were used as a representative for the conductivity studies. These two polymers have a similar PQDM content (10 wt.% for **NPI6b2** and 11 wt.% for **NPI6b3**) and comparable T_g (178 °C for **NPI6b2** and 190 °C for **NPI6b3**).

Electrical Resistivity

Figure V-1 shows a resistivity-temperature curve of **NPI6b2** as a thin film under an applied field of 33 V/ μm . The data [electrical current, I (A)] was collected with a 600-second waiting time after each temperature step, and was translated into the electrical resistivity by the equation

$$\rho = (V \times S) / (L \times I) \quad (1)$$

where ρ is the electrical resistivity ($\Omega\cdot\text{cm}$), V is the applied voltage (volt), S is the area of electrode ($S = 0.122 \text{ cm}^2$) and L is the film thickness (cm). At low temperatures (e.g., < 80 °C), the polymer was found to have a high electrical resistivity on the order of $10^{15} \Omega\cdot\text{cm}$. With the increase of temperature, the resistivity decreased, which became more distinct in the temperature range of 120 – 160 °C. The decrease of resistivity slowed down after the temperature reached 170 °C and experienced a small rebound around 200 °C (which might be due to a noise or instrument error). The presence of a ‘knee’ at around 170 °C and the small change in the electrical resistivity of **NPI6b2** at temperatures above 180 °C indicate the rubber state of **NPI6b2**.⁴ The polymer has an

electrical resistivity of $2.9 \times 10^{10} \Omega\cdot\text{cm}$ at 217°C , which is about 5 orders of magnitude smaller than the resistivity ($3.4 \times 10^{15} \Omega\cdot\text{cm}$) at 65°C .

Figure V-1. Temperature dependence of electrical resistivity for **NPI6b2** thin film ($1.5 \mu\text{m}$). The applied voltage is 50 V and the relaxation time after each temperature step is 600 seconds. The dashed lines indicate the trend of change in the resistivity.

The temperature dependence of the resistivity of **NPI6b3** thin film at different voltages 50 V, 100 V and 150 V ($10 \text{ V}/\mu\text{m}$, $21 \text{ V}/\mu\text{m}$ and $31 \text{ V}/\mu\text{m}$) is shown in Figure V-2. Similar to that of **NPI6b2**, the resistivity of **NPI6b3** decreased with an increase in temperature. However, no sharp decrease of resistivity in the temperature range of $120 - 160^\circ\text{C}$ was observed. The low-temperature resistivity ($2.8 \times 10^{15} \Omega\cdot\text{cm}$ at 80°C) for **NPI6b3** was comparable to that of **NPI6b2** ($1.9 \times 10^{15} \Omega\cdot\text{cm}$ at 80°C) of **NPI6b2**, but the high-temperature resistivity of **NPI6b3** ($2.4 \times 10^{11} \Omega\cdot\text{cm}$ at 200°C) of **NPI6b3** is one order of magnitude larger than that ($2.0 \times 10^{10} \Omega\cdot\text{cm}$ at 200°C) of **NPI6b2**. Since

electron transportation in amorphous polymers is related to the chain mobility and the rearrangement of free volumes,⁴ this larger resistivity of **NPI6b3** relative to **NPI6b2** may be attributed to a partial polymer crosslinking of **NPI6b3** occurred during the measurement. Evidently, no turning point in resistivity of **NPI6b3** was observed around the T_g .

A field-dependence of electrical resistivity was observed for **NPI6b3** at low temperatures. For example, upon increasing the applied voltage from 50 V to 150 V at 80 °C, the electrical resistivity of **NPI6b3** decreased by 75% from $2.8 \times 10^{15} \Omega\cdot\text{cm}$ to $0.7 \times 10^{15} \Omega\cdot\text{cm}$. With the increase of temperature, such a field-dependence diminished. At 200 °C, the three different voltages led to basically the same resistivity.

Figure V-2. Dependence of electrical resistivity of **NPI6b3** thin film (4.8 μm) on temperature and voltage. The relaxation time is 900 seconds for each voltage change and is 300 seconds for each temperature change.

Current-voltage (I - V) property

Figure V-3 displays the current-voltage (I - V) curve for **NPI6b2** at 200 °C. The data represents current, in the unit of μA , measured 60 seconds after each voltage step. A linear increase of current with voltage was observed and the electrical breakdown occurred at 51 $\text{V}/\mu\text{m}$ in this case. In order to achieve a higher field (e.g., > 65 $\text{V}/\mu\text{m}$) for parallel electrode poling, the voltage has to be increased very carefully. Further purification of this polymer after several precipitations and reverse precipitation did not lead to a better stability to the high electric field.

Figure V-3. Current-voltage curve for **NPI6b2** (1.46 μm) at 200 °C.

The I - V curve of **NPI6b3** at 200 °C is shown in Figure V-4. The applied voltage was increased gradually in steps of 10 V (about 2 $\text{V}/\mu\text{m}$) every 60 seconds until an avalanche electrical breakdown occurred. A linear I - V relationship was found at the fields below 48 $\text{V}/\mu\text{m}$, but an ascent was observed at high electric fields, e.g. above 55 $\text{V}/\mu\text{m}$,

which may be attributed to the increased charge injection from the electrode and/or charge tunneling within the film.⁸ In comparison with **NPI6b2**, **NPI6b3** showed a better stability to high electric fields. A field of $73 \text{ V}/\mu\text{m}$ was readily achieved for this polymer.

Figure V-4. Current-voltage curve of **NPI6b3** ($4.8 \mu\text{m}$) at 200°C .

Current relaxation

Upon application of a dc field, the chromophore dipoles within NLO polymer films will relax along the field direction. The relaxation time depends on the polymer T_g (and/or sub- T_g transitions), temperature and electric field, but a few minutes to hours may well be needed to establish steady-state conditions. In the steady state, the chromophore dipoles are oriented, motions of polymer chains due to the orientation of dipoles become insignificant and the conductivity of the polymer reaches a plateau. To determine the relaxation time (τ) to a steady (or quasi-steady) state at poling temperatures, which is important since the order parameter (Φ) at a finite poling time (t) can be related to τ and

the steady-state order parameter (Φ_r) $\{\Phi = \Phi_r [1 - e^{-(t/\tau)}]\}$,^{11,12} electrical current with time can be measured. Notably, however, the change of electrical current with time may not be governed by the dipole relaxation (and/or chain motions), other factors such as buildup of space charge and equilibration of charge injection and of thermal excitation of electrons can contribute to the change.^{5-8,13} Therefore, the time required to achieve a steady current value should be used only as a reference in determining the poling time. Figure V-5 shows the current relaxation of **NPI6b2** at different temperatures under a voltage of 50 V. A decrease in current was observed at temperatures above the T_g (180 °C), indicating the dipole and volume relaxations.

Figure V-5. Electrical current of **NPI6b2** thin film (1.50 μm) under a field of 50 V, as a function of time and temperature.

To study the current-relaxation behavior of NLO polyimides around poling temperatures, **NPI6b2** and **NPI6b3** thin films were kept at 200 °C under a field of 51

$\text{V}/\mu\text{m}$ and $71 \text{ V}/\mu\text{m}$, respectively. It was found that the steady-state current value for **NPI6b2** could be achieved around 20 min., whereas the current for **NPI6b3** with crosslinkable BCBO units in the structure did not evolve into an obvious steady-state value within 50 min. This slow current evolution of **NPI6b3** may be attributable to the reduced chain mobility due to partial polymer crosslinking.

Figure V-6. Current relaxation of **NPI6b2** (75 V, $1.46 \mu\text{m}$) at 200°C .

Figure V-7. Current relaxation of **NPI6b3** thin film (340 V, 4.8 μm) at 200 °C.

V.2.2 Poling conditions

Poling Temperature

Typically, the electric poling of NLO polymers is carried out around the T_g , as the segmental chain relaxation at such a temperature allows for good chromophore mobility. However, T_g is not the only factor governing the poling temperatures. Others like thermal stability, crosslinking, dielectric breakdown and viscoelasticity should be considered. For example, although the onset temperatures for **NPI1** – **NPI7** to decompose are above 270 °C and little weight loss was observed for isothermally heated NLO polyimides at 210 °C (Chapter IV), the blue color of NLO polyimide films faded rapidly at temperatures above 245 °C. Within a period of 20 – 40 min, the poling temperatures in the range of 220 – 230 °C are appropriate because no substantial color change of the polymer films was observed. The BCBO-containing polyimides crosslink around 215 °C. Thus, poling at

temperatures higher than 215 °C will lead to the formation of a crosslinked network, an increase in T_g and decrease in the chain mobility or a probability of chromophore orientation. In addition, the NLO polymer films may fail under a high electric field at high temperatures. Evidently, electrical breakdown of **NPI6b2** films tends to occur at low voltages (e.g., $> 50 \text{ V}/\mu\text{m}$) when the temperature is above 220 °C.

The temperature dependence of poling and EO coefficients of NLO polymers was investigated through using **NPI6b4** as a model polymer that has the β transition of 187 °C and T_g of 213 °C and contains 20 mol.% of BCBO (relative to the acid groups in the host polyimides). Four thin films with thickness in the range of 2.0 – 2.6 μm were prepared by solution casting, dried at 175 °C under vacuum for 2 h, and poled separately at different temperatures (e.g., 180 – 230 °C) under the same field strength per micron. As shown in Table V-1, **NPI6b4** displayed relatively small EO coefficients ($\sim 5 \text{ pm/V}$) when being poled at 180 °C and 210 °C, moderate EO coefficients ($\sim 12 \text{ pm/V}$) at 220 °C, and the largest EO coefficients ($\sim 20 \text{ pm/V}$) at 230 °C. Although the polymer crosslinking begins around 215 °C, it appeared necessary to pole the polymer at such a high temperature to realize a high EO coefficient. Similar observations were also made with other NLO polyimides **NPI5** – **NPI7**. In all the cases, the largest EO coefficient was obtained through poling at a higher temperature than the T_g , typically within the range of 220 – 230 °C. In order to diminish the negative effect of crosslinking on the chromophore orientation, electric (both parallel electrode and corona) poling practically involves a process that begins at low temperatures over a long time (e.g., 30 – 50 min at 180 °C, 200 °C, and 210 °C) and ends with holding at temperatures above 220 °C for around 20 min.

Table V-1. EO coefficients and poling conditions for **NPI6b4**

Entry	r_{33} (pm/V)	Poling condition $T(V, I, t)^a$ °C (V, μ A, min)	Film thickness (μ m)	n (1.5 μ m)
1	5.5, 6.3, 5.6	180 (230, 12, 42)	2.3	1.6542
2	5.4, 6.0, 4.1	180 (200, 10, 26); 210 (210, 13, 20)	2.0	1.6540
3	14.3, 12.2, 12.8	210 (250, 5, 32); 220 (250, 8, 8)	2.6	1.6550
4	20.6, 26.1, 21.0	215 (200, 4, 14); 230 (200, 5, 14)	2.2	1.6542

^a T = temperature, V = poling voltage, I = current, and t = time

Poling Voltage

For the poling of NLO polymers, an as-high-as-possible field is desired to afford a strong dipole-field interaction and a high order parameter. However, to simply pursue the high voltage is not appropriate, since dielectric breakdown may often occur, especially when parallel electrode poling technique is used. To achieve the best poling results, the electric field was varied in our study according to the temperature and the magnitude of electric current. The voltage dependence of current was also used to guide the increase of voltage in order to avoid electric failure of NLO polymer films. As discussed above that an abrupt breakdown may occur for NLO polyimides containing no BCBO unit at high fields, but an ascent should appear first for NLO polyimides containing BCBO units before the breakdown. In general, the current was kept below 10 μ A and the actual voltages applied across the films, taking into account the field loss through current, were in the range of 60 – 120 V/ μ m. Notably, even for films prepared from the same NLO

polyimide, different quality of these films may lead to different conductivity and achievable high fields (Table V-2).

Table V-2. EO coefficients **NPI5a** and **NPI5b** poled under different conditions

Polymers		r_{33} (pm/V)	Poling condition $T(V, I, t)^a$ °C (V, μ A, min)	Film thickness (μ m)	n (1.5 μ m)
NPI5a	1	21.5, 15.4, 19.5	226 (500, 10, 5)	2.82	1.6406
	2	26.8, 25.4, 23.6	226 (370, 16, 10)	3.03	1.6410
	3	18.4, 19.6, 22.1	230 (500, 14, 10)	4.11	1.6409
	4	17.2, 12.9, 11.2	226 (350, 6, 15)	3.63	1.6433
NPI5b	1	20.1, 15.4, 18.3	226 (270, 13, 20)	2.09	1.6610
	2	14.6, 14.5, 13.5	227 (350, 21, 7)	2.66	1.6594
	3	20.0, 17.7, 18.9	230 (300, 10, 23)	2.97	1.6619
	4	10.7, 14.6, 15.2	235 (400, 18, 30)	2.08	1.6575

^a T = temperature, V = poling voltage, I = current, and t = time

For corona poling, a negative voltage of 6 – 8 KV was applied to the needle electrode that was positioned 2 cm above the NLO polyimide films. The electric current across the films was controlled below 5 μ A. For both parallel electrode and corona poling, the electric field was turned on above 160 °C and kept on after the poling until the sample cooled down to below 60 °C.

Poling Time

The poling time is determined according to the current relaxation study, which shows the dipole relaxation of PQDM under a poling field at 200 °C may reach a steady state around 20 min. for polymers containing no BCBO units and longer time for those containing BCBO units. At higher temperatures, the dipole relaxation under the field is expected to be faster due to the decreased viscosity $\{\eta(T) = A \exp[-B/(T + 50 - T_g)]\}$.¹⁴ However, the polymer crosslinking in some of the NLO polyimides at around 215 °C may demand a longer poling time. Thus, to diminish the crosslinking effect on the dipole orientation, NLO polymers were poled for a long period of time (30 – 50 min) before the crosslinking temperature to enable the maximum orientation at low temperatures (180 – 210 °C) and subsequently poled at high temperatures (e.g., 220 – 230 °C) for about 20 min to allow dipole orientation and to densify the poled NLO polymers. No clear dependence of EO coefficients on the high-temperature poling time was observed in our study though (Table V-2). For a better determination of poling time, it would be highly desirable to monitor *in-situ* the NLO response with field and temperature by methods such as EFISH.¹¹

V.3 Correlation Study of EO Coefficient and Polymer Structures

In order to achieve a good temporal stability as well as a good poling efficiency, NPI1 – NPI7 were designed and prepared to have relatively high T_g but different backbone rigidity. To improve the chain mobility, NLO polyimides having different chain lengths (or different molecular weights of host polyimides) and different degrees of branching were prepared. A long aliphatic group, or PDFO, was also introduced as side

chains into NLO polyimides. Thermally reactive BCBO unit was added to the side chains to enable the formation of crosslinking network. The reactive temperature of BCBO in these polyimides was found around 215 °C. High PQDM loading (e.g. 16 – 29 wt.%, $N = 2.4 - 5.2 \times 10^{20} \text{ cm}^{-3}$) could be achieved with these polyimides without phase separation in cast films. All of these structural variables are expected to affect the poling efficiency and EO properties of NLO polyimides.

Figure V-8. Correlation of EO coefficients and the backbone rigidity (T_g of host polyimides) of homologous series of NLO polyimides.

Effect of polymer backbone structure

Figure V-8 illustrates the dependence of EO coefficients of poled polymers on the backbone flexibility, as characterized by the T_g of host polyimides. The poling

temperature was controlled below 250 °C due to the color bleaching of NLO polyimides at high temperatures. **NPI1** – **NPI3** having rigid backbones exhibited no EO signal after poling at temperatures above 240 °C at 100 – 150 V/μm. Blending 5 wt.% of a low- T_g polyimide derived from 6FDA and 1,4-bis(3-aminopropyl)piperazine ($T_g = 163$ °C) with **NPI1b** afforded a small EO coefficient of 2 pm/V. For semi-rigid copolymer **NPI4c** ($T_g = 246$ °C), small EO coefficients about 4 pm/V were obtained. Further increase of the chain flexibility by adding more ether linkages into the polymer backbone led to a sharp increase in the EO coefficient (20 pm/V), as evident in case of **NPI5a**.

Effect of polymer side chain

An alternative approach to increase chain mobility can be done through adding flexible side chains. In our study, two compounds were used to block the residual carboxylic acid during the synthesis of NLO polyimides: 3,5-di-*tert*-butylphenol (DBP) and 2,2,3,3,4,4,5,5,6,6,7,7,8,8-pentadecafluoro-1-octanol (PDFO). In comparison, the PDFO-containing polyimide **NPI6b3** exhibited a T_g of 190 °C, which is 23 °C lower than that of the DBP-containing polyimide **NPI6b4** (Table V-3). Accordingly, the parallel electrode poling of **NPI6b3** yielded a higher EO coefficient (38 – 46 pm/V) than that (20 – 26 pm/V) of **NPI6b4**, due to the higher chain mobility.

Effect of polymer chain length (or molecular weight)

In order to improve the polymer chain mobility, NLO polyimides derived from host polymers with different molecular weights were prepared. Although a decrease in T_g by 5-24 °C was observed for host polyimides having lower molecular weights, no substantial difference in the T_g among **NPI5c**, **NPI6a**, **NPI6b1**, and **NPI6c** was found

(Table V-3). The high content of PDFO in these NLO polyimides (55 mol.% feed ratio relative to the acid groups in the host polyimides) is likely to contribute more than the molecular weight to the change in T_g . The poling of these polymers yielded comparable EO coefficients in the range of 26 – 29 pm/V (Table V-3).

Table V-3. EO coefficients of NLO polymers with different chain mobility under different poling conditions

Polymer	PQDM (wt.%)	T_g (°C)	r_{33} (pm/V)	Poling condition $T(V, I, t)^a$ °C, (V, μ A, min)	Film Thickness (μ m)
NPI6b3	11	190	46.4, 44.5, 38.2,	225 (240, 5, 30)	2.3
NPI6b4	11	213	20.6, 26.1, 21.0	230 (200, 5, 14)	2.2
NPI5c^b	4	169	25.9, 26.7, 33.3	240 (6000, 1, 33)	1.9
NPI6a	4	169	34.9, 30.3, 27.6	226 (200, 11, 26)	1.6
NPI6b1	4	170	39.0, 38.3, 34.8	220 (150, 4, 20)	1.5
NPI6c	5	165	15.5, 31.4, 18.4	220 (180, 10, 30)	2.1
NPI7a^b	10	218	23.1, 24.6, 17.7	220 (8000, 4, 20)	2.4
NPI7b	11	221	14.2, 10.8, 12.7,	230 (300, 3, 21)	1.9

^a T = temperature, V = poling voltage, I = current, and t = time. ^b Corona poling results are given because the electrode poling gave only small EO coefficients.

Effect of polymer chain branching

A branched NLO polyimide was expected to have a better chain mobility than the linear ones, due to the large free volume and branches of different lengths. However, the branched **NPI7a** and **NPI7b** exhibited comparable T_g as well as EO coefficients (e.g., 12

– 23 pm/V) with those (e.g., 15 – 20 pm/V) of linear NLO polyimides such as **NPI5** (Table V-2 and Table V-3), indicating similar chain mobility between the linear and the branched polymers.

Effect of PQDM content

To impart a large microscopic optical nonlinearity in NLO chromophores to a large macroscopic EO coefficient in NLO polymers, high number density of chromophore in bulk polymers is highly desired. However, the high number density cannot be simply achieved by adding a large amount of chromophores in the host polymer, as phase separation will eventually occur. It has been found recently that the poling efficiency could be significantly attenuated at above a certain concentration of chromophores in polymers,³ due to the increased intermolecular electrostatic interactions. For the FTC and CLD-type chromophores developed by Dalton et al.,³ the limit concentrations were around $N = 30 \times 10^{19} \text{ cm}^{-3}$. The use of more spherical chromophores and polar host media were proposed to increase this critical concentration of chromophores.

NLO polyimides containing a different amount of PQDM were prepared in our study. The maximum chromophore loading was achieved around 29 wt.% ($N = 52 \times 10^{19} \text{ cm}^{-3}$) without showing any phase separation in solution-cast films, indicating the good compatibility of PQDM with the polyimides. Three NLO polyimides, i.e., **NPI6b1**, **NPI6b3**, and **NPI6b5**, were prepared by grafting 4 wt.%, 11 wt.%, and 16 wt.% of PQDM, respectively. Accordingly, the number density is $6 \times 10^{19} \text{ cm}^{-3}$, $16 \times 10^{19} \text{ cm}^{-3}$, and $24 \times 10^{19} \text{ cm}^{-3}$. Table V-4 shows the poling and EO coefficients of these three

polymers. **NPI6b1** (4 wt.% of PQDM) had the lowest T_g of 170 °C and showed the r_{33} value of 38 pm/V. This r_{33} value is greater than that of LiNbO₃ (31 pm/V), which is currently used in the commercial EO modulators, and comparable to those of FTC/CLD-based NLO polymers with similar number densities. With the increase of PQDM content to 11 wt.%, **NPI6b3** exhibited a lower T_g (190 °C) and an even larger r_{33} value of 45 pm/V. The EO coefficient of **NPI6b3** did not increase in proportion to the increase of number density, indicating the attenuation of poling efficiency due to the increased intermolecular interactions. Evidently, when the PQDM content was increased to 16 wt.%, a drop of EO coefficient to 24 pm/V was observed for **NPI6b5** (T_g = 209 °C).

Table V-4. EO coefficients of NLO polyimides with different PQDM content

	PQDM	T_g	r_{33}	Poling $T(V, I, t)^a$	Film thickness	n_{1555}
Polymer	(wt.%)	(°C)	(pm/V)	°C, (V, μ A, min)	(μ m)	
NPI-6b-1	4	170	39.0, 38.3, 34.8	220 (150, 4, 20)	1.45	1.640
NPI-6b-3	11	190	46.4, 44.5, 38.2,	225 (240, 5, 30)	2.34	1.658
NPI-6b-5	16	209	26.7, 24.9, 21.4	226 (260, 7, 28)	2.5	1.667

^a Poling conditions: T = temperature, V = poling voltage, I = current, and t = time.

V.4 EO stability

For practical device applications, the poling-induced EO activity of NLO polymers must be stable at the device fabrication (short-term, around 200 °C) and operational temperatures (years, up to 80 °C). In order to achieve the required stability, a

covalent coupling of chromophore with a high- T_g host polymer and the lattice hardening of the resulting NLO polymer are commonly pursued, as in our studies.

The temporal stability of the EO activity for poled NLO polyimides were probed in nitrogen and in air by monitoring the changes in the EO coefficients of the poled sample cells that were kept in dark at 85 °C. Figures V-9 and V-10 show the results from the two typical sample cells. No substantial decrease of EO coefficient was observed for both **NPI5a** in nitrogen and **NPI5b** in air after 1200 h. Figure V-11 shows another example of **NPI6b1** that has a lower T_g than those of un-poled **NPI5a** and **NPI5b**. The EO coefficient remained constant after the test cell was heated at 85 °C in nitrogen and in dark over 1000 h. The photo-stability of NLO polyimides was assessed by irradiating a poled polymer sample with the infrared light (1550 nm, 50 $\mu\text{W}/\sim 4 \text{ mm}^2$) continuously for 10 h at ambient temperatures in air. And no change in the EO signal was found.

Figure V-9. Temporal stability of poled **NPI5a** at 85 °C in nitrogen

Figure V-10. Temporal stability of poled **NPI5b** at 85 °C in air

Figure V-11. Temporal stability of poled **NPI6b1** at 85 °C in nitrogen

V.5 Conclusions

This work demonstrates the first case that high- $\mu\beta$ zwitterionic chromophores can be used to yield NLO polymers with large EO coefficients.

NLO polyimides based on the zwitterionic PQDM were successfully poled to yield large EO coefficients (15 – 45 pm/V). The poling conditions were studied according to the electrical properties of NLO polymers and various factors such as temperature, electric field and poling time. A significant dependence of the EO coefficient on the polymer chain flexibility and the T_g was found, while the molecular weight and the branched structure of the NLO polymers played a less significant role in the poling efficiency. Chromophore-chromophore electrostatic interaction was found to be severe enough at a high PQDM content to diminish the EO activity, although the host polyimides proved effective to accommodating PQDM at high concentrations. Thus, further modification for PQDM to become more spherical in shape is desirable. An excellent long-term stability of the induced EO activity of the resulting zwitterionic NLO polyimides at 85 °C was demonstrated.

V.6 Experimental Section

Materials. See Chapters III and IV for the syntheses of host polyimides and NLO polyimides, respectively.

Electrical resistivity.

Electrical resistivity of thin films was obtained by measuring the electric current across the polymer films sandwiched between an ITO coated glass and a gold layer

sputtered on top of the film with a Keithley digital electrometer that has a measuring range of $10^{-1} - 10^{-11}$ ampere. For resistivity measurements at a constant voltage, current was read after an 600-second equilibration time; for resistivity measurements at varying temperature and voltage, the equilibration time is 900 seconds for each voltage change and 300 seconds for each temperature change; for the current-voltage properties at constant temperature, data was read 60 seconds after each voltage change. The electrical resistivity is calculated using the equation

$$\rho = (V \times S)/(L \times I)$$

where ρ is the electrical resistivity ($\Omega \cdot \text{cm}$), V is the applied voltage (volt), S is the area of electrode ($S = 0.122 \text{ cm}^2$), L is the film thickness (cm), and I is the current through the sample (A).

Poling station

The parallel electrode poling set-up (Figure I-4, Chapter I) is equipped with a hot plate, whose temperature is sensed by a thermal couple and controlled digitally ($\pm 1^\circ \text{C}$), and a high voltage supply (0 – 3 kV) (Bertan Associates, INC. Model 215). All the components are assembled in a sealed box, through which an inert gas such as nitrogen can flow to remove the air for a high-temperature poling. For parallel electrode poling, uniform polymer films with thickness in 1-3 μm range on a square ITO coated glass substrate (2.25 cm^2) were prepared, dried at $160 - 180^\circ \text{C}$ under vacuum (1 mmHg) for 2 h, and sputtered on a thin layer ($\sim 150 \text{ nm}$) of gold as a top electrode. In order to lower the probability of electrical breakdown due to film defects, a dumbbell configuration of the gold electrode, which has a smaller area than a round disk, was made. During poling

and EO measurements, the electrode contact is positioned at the small gold area (diameter $d = 2$ mm), while the incident light is directed at the big gold part ($d = 6$ mm). A resistor with impedance of $10^7 \Omega$ is connected in series with the polymer circuit to regulate the poling current.

For corona poling (Figure I-5, Chapter I), a negative high voltage generator (0 – 10 kV, Bertan Associates, INC. Model 210-10N) was used to ionize the nitrogen or argon atmosphere. The temperature was controlled digitally and has an uncertainty of ± 1 °C. The needle electrode was positioned 2.0 – 2.5 cm above the polymer films. The current through the films was controlled to be below 5 μ A to avoid electric failure.

Teng-Man setup

The Teng-Man setup¹⁵ (Figure I-6, Chapter I) was equipped with a 1550-nm laser (ILX Lightwave LDC 3724B), a Soleil-Babinet compensator (Thorlabs Inc. SBC-IR), a Lock-in amplifier (Stanford Research Systems SR830 DSP), a detector (Newport 1830-C), a frequency generator (AVTECH Av-151B-C), an oscilloscope (LeCory 9400A) and other optical components such as polarizer and analyzer. For the measurement, the incident angle (θ) is set to be 20°, the drive voltage (V_m) is 48.5 V and the signal frequency is 1 KHz. The intensity of modulated signal (I_m) is recorded and the EO coefficient is calculated by the equation:

$$r_{33} = (3\lambda I_m / 4\pi V_m I_c n^2) \times [(n^2 - \sin^2 \theta)^{3/2} / (n^2 - 2\sin^2 \theta)] \times [1 / \sin^2 \theta] \quad (13)$$

Where I_c is the half intensity of incident light.

V.7 Reference

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CONTRIBUTIONS TO KNOWLEDGE

1. β -[1-Hydroxypropyl-4-pyridinium]- α -cyano-4-styryldicyano methanide was prepared and grafted onto host polyimides to yield a wide range of NLO polyimides with different structural features.
2. Poling conditions for the resulting zwitterionic NLO polyimides were optimized.
3. The first zwitterionic NLO polymer with a large EO coefficient (45 pm/V) at the telecommunication wavelength was demonstrated.
4. The structural effect (including backbone structures, side chain structures, molecular weight, chain branching and chromophore loading) on the EO properties was studied.
5. Excellent long-term temporal stability (no substantial decrease was observed at 85 °C over 1000 h) of poling-induced EO response of NLO polyimides was demonstrated.

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1. Wang, Z. Y.; Song, N.; Beaudin, A. M. R.; Weir, C. A. M.; Cross, G. H.; Szablewski, M. “Zwitterionic Chromophores and Polymers Containing Such Chromophores”, US patent, application No. 10/227,846

Appendix

Table 1. Donor-bridge-acceptor (D – B – A) chromophores

Bridge	Donor	Acceptor	$\mu\beta$ ($\times 10^{-48}$ esu)
Me ₂ N-	-NO ₂	80 ^{ref1}
	Et ₂ N-		450 at 1.9 μ m; T _d : 295 °C; λ =450 nm ^{ref2}
		550 at 1.9 μ m; T _d : 390 °C; λ =472 nm ^{ref2}
		760 at 1.9 μ m; T _d : 300 °C; λ =488 nm ^{ref2}
Me ₂ N-	-NO ₂	275
Et ₂ N-		780 (n = 1) at 1.9 μ m; T _d : 260 °C; λ =480 nm ^{ref2}
		1720 (n = 1) at 1.9 μ m; T _d : 295 °C; λ =503 nm ^{ref2}
		13,500 (n = 2) at 1.90 μ m; r ₃₃ =55 pm/V at 1330 nm ^{ref3} (20 wt.-% in PC)
		$\beta = 1128 \times 10^{-30}$ esu (n=3); T _d : 212 °C, λ =590 nm (dioxane)
	Me ₂ N-		370 (n = 0) ^{ref4} 1475 (n = 1) 3945 (n = 2) 9831 (n = 3)
		312 (n = 0) ^{ref5} 1202 (n = 1) 3156 (n = 2) 8171 (n = 3)
	(HOCH ₂ CH ₂) ₂ N -		Not reported (n=1); λ =581 nm ^{ref6}

Table 2. Donor-bridge-acceptor (D – B – A) chromophores

Bridge	Donor	Acceptor	$\mu\beta$ ($\times 10^{-48}$ esu)
$n = 1-4$	Me ₂ N-	-NO ₂	482 (n = 1) ^{ref14} 813 (n = 2) 1074 (n = 3) 1700 (n = 4)
	Ph ₂ N-		788 (n = 1) (1.90 μm) ^{ref17}
	Bu ₂ N-	$R = (\text{Et})_2\text{CH}, \text{C}_{12}\text{H}_{25}, \text{C}_{18}\text{H}_{37}$ $X = \text{Br}^- \text{ or } \text{C}_{18}\text{H}_{37}\text{OSO}_3^-$	
	(HOCH ₂ CH ₂) ₂ N-		926
Ph ₂ N-		1720; T _d : 313 °C ^{ref15}
	Bu ₂ N-		2520; T _d : 268 °C ^{ref15}
	(p-MePh) ₂ N-		2570; T _d : 367 °C ^{ref15}
	TBDMOS		35,000 (R=φ) at 1.90 μm ^{ref8} 14300 (R = C ₆ H ₁₃), T _d = 254 °C, $\lambda = 650 \text{ nm}$ ^{ref9}
Me ₂ N-		$\beta(0)$ (HRS $\times 10^{-30}$ esu): 116; $\lambda = 495 \text{ nm}$ ^{ref10}
		a) R=ph, R ₁ =CH ₂ CH ₂ OH b) R=o-pyridyl, R ₁ =ph	$\beta(0)$ (HRS $\times 10^{-30}$ esu): ^{ref10} a) 133; $\lambda = 447 \text{ nm}$ b) 206; $\lambda = 454 \text{ nm}$
		a) R=H; b) R=Et; c) R=CH ₂ COOH	$\beta(0)$ (HRS $\times 10^{-30}$ esu): ^{ref10} a) 514; $\lambda = 450 \text{ nm}$ b) 477; $\lambda = 463 \text{ nm}$ c) 424; $\lambda = 460 \text{ nm}$
(HOCH ₂ CH ₂) ₂ N-		Not reported; $\lambda = 671 \text{ nm}$ ^{ref6}
Me ₂ N-	-NO ₂	800 at 1.579 nm ^{ref11}
	1100 at 1579nm by EFISH; T _d : 335 °C, $\lambda = 490 \text{ nm}$ ^{ref12}
	Et ₂ N-		4100 ^{ref1}
Me ₂ N-	-NO ₂	1040 (1.064 μm) ^{ref13}
Me ₂ N-	-NO ₂	$\mu = 9.1 \text{ D}$; $\beta = 59.4 \times 10^{-30} \text{ esu}$; $\lambda = 319 \text{ nm}$ ^{ref14}

Table 3. Heterocycle-based chromophores

Bridge	Donor	Acceptor	$\mu\beta$ ($\times 10^{-48}$ esu)
Et ₂ N-	-NO ₂	700 (n = 1)
		830 at 1.90 μm ; T _d : 340 °C (n = 1) <small>ref2</small>
		1300 (X = S; n = 1) at 1.90 μm <small>ref15</small>
		2300 at 1.90 μm ; T _d : 302 °C (X = S; n = 1) <small>ref2</small>
		2400 (n = 1) at 1.90 μm <small>ref16</small>
		3100 at 1.90 μm ; T _d : 264 °C (X = S; n = 1) <small>ref2</small>
		6700 (n = 1); T _d : 240 °C; A=640nm 10600 (n = 2); λ =662nm <small>ref17</small>
		6848 at 1.90 μm ; T _d : 250 °C; r_{33} = 36 pm/V @1.33 μm (25 wt.% in PQ-100) (n = 1); λ =604nm <small>ref17</small>
	Bu ₂ N-		15,000 (n = 1) at 1.90 μm <small>ref15</small>
	2000 (n = 1) at 1.90 μm <small>ref15</small>
	3300 (n = 1) at 1.90 μm <small>ref15</small>
		6100 (n = 1) at 1.90 μm <small>ref15</small>
	Ph ₂ N-		3510 at 1.90 μm ; T _d : 315 °C; λ =601nm
		Not reported; T _d : 340; λ =566nm <small>ref17</small>
	(H ₁₇ C ₈) ₂ N-		r_{33} =31 pm/V at 1550 nm in PC (2 mol%); T _d :210 °C; λ =867 nm <small>ref18</small>

Table 4. Heterocycle-based chromophores

Bridge	Donor	Acceptor	$\mu\beta$ ($\times 10^{-48}$ esu)
	Et ₂ N-	-NO ₂	560
	Et ₂ N-		13,000 at 1.90 μm ^{ref15}
	TBDMSO		$r_{33} \sim 68$ pm/V in APC (30 wt.%) ^{ref20}
	AcO		FTC: 18,000 ($R_1 = R_2 = n\text{-Bu}$; $n = 1$) at 1.90 μm ^{ref15}
	Bu ₂ N-		$r_{33} = 65$ pm/V@1.33 μm (20 wt.% in PMMA) ($R_1 = R_2 = \text{H}$, $n=2$) ^{ref15}
			($n=2$) at 1.90 μm ^{ref21} 1) $R_1 = \text{CH}_2\text{OTBDMS}$, $R_2 = \text{H}$, $R_3 = \text{CF}_3$ 2) $R_1 = \text{CH}_2\text{OTBDMS}$, $R_2 = \text{H}$, $R_3 = \text{CH}_3$
	Ph ₂ N-		3940 at 1.9 μm ($n=1$); T_d : 308 °C; $\lambda=611$ nm ^{ref17}
	Bu ₂ N-		10,600 at 1.9 μm ($n=1$); T_d : 249 °C; $\lambda=661$ nm ^{ref17}
	Et ₂ N-		14300 at 1.9 μm ($n=2$); T_d : 238 °C; $\lambda=655$ nm ^{ref17}
	Ph ₂ N-		4120 at 1.9 μm ($n=1$); T_d : 343 °C; $\lambda=575$ nm ^{ref17}
	Bu ₂ N-		6840 at 1.9 μm ($n=1$); T_d : 250 °C; $\lambda=623$ nm ^{ref17}
	(Hex) ₂ N-		19,400 at 1.90 μm ^{ref22}
			10,400 at 1.90 μm ^{ref22}
			7450 at 1.9 μm ; T_d : 200 °C; $\lambda=718$ nm ^{ref17}
	(Ph ₂)N-		10,200
			Decompose upon day light and air; $\lambda=712$ nm ^{ref17}

Table 5. Heterocycle-based chromophores

Bridge	Donor	Acceptor	$\mu\beta$ ($\times 10^{-48}$ esu)
	Me ₂ N-	-NO ₂	640 ^{ref13}
	(HOCH ₂ CH ₂) ₂ N-		
	Et ₂ N-	-NO ₂	2190 (R = ϕ) ^{ref23}
	Bu ₂ N-		5320 (R = Cl) ^{ref23}
			1658 (R = Cl) ^{ref23}
	PhCH ₂ (Me)N-	-NO ₂	R = HOC ₂ H ₄
	HOC ₂ H ₄ (Me)N-		R = PhCH ₂
	D1 = HOC ₂ H ₄ (Me)N- D2 = Et ₂ N-		1) 840; T _d : 369 °C; λ =467 nm ^{ref24} 2) 1300; T _d : 354 °C; λ =512 nm 3) 2500; T _d : 340 °C; λ =540 nm
	MeO-	-NO ₂	μ = 5.1 D; β = 30.7 $\times 10^{-30}$ esu; λ =358 nm

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