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# Synthesis of polyurethanes and polyimides for photorefractive applications

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## Abstract

Well-defined multifunctional polymers, bearing charge transporting (CT) and nonlinear optical (NLO) functionality covalently attached to each repeat unit, were synthesized and characterized. High glass transition temperature ($T_g$) polyurethanes, comprised of alternating CT and NLO units, were synthesized from NLO functionalized diols and *N*,*N*-bis(4-isocyanatophenyl)aniline. Polyimides, exhibiting high thermal stabilities, were obtained from a fluorinated dianhydride and a multifunctional (CT and NLO) diamine. The functionalized polyimides were obtained in two ways: by formation of a brominated polyimide derivative and subsequent Heck coupling with styrene derivatives; and direct polycondensation of a fully functionalized triarylamine diamine analog with 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA). Phosphonate ester and nitro electron-withdrawing groups were utilized in the NLO moieties.

*Keywords*: Photorefractive; Polyimide; Polyurethane

## 1. Introduction

The photorefractive (PR) effect, found in materials that are both photoconductive and have nonlinear optical (NLO) properties, is avidly being pursued for optical processing applications. The PR effect can be defined as a spatial modulation of the index of refraction due to charge redistribution (space–charge field) in an optically nonlinear material. The effect arises when charge carriers, generated photolytically by a spatially modulated light intensity, separate and become trapped to produce a nonuniform space–charge distribution. The resulting internal space–charge electric field then modulates the refractive index to create a phase grating which can diffract a light beam [1]. Photorefractivity holds great potential in holographic optical data storage, beam steering, optical computing and switching and integrated optics [2]. PR materials can, in principle, execute such integrated optoelectronic operations as switching, modulation, thresholding, and parallel processing for image processing and display [2]. Until 1990, only inorganic materials were found to be photorefractive. Since then, organic crystals and, more recently, polymers that are photorefractive have been synthesized [1].

To be photorefractive, a material must combine photosensitivity and photoconductivity, while possessing a field dependent refractive index, most commonly through the electro-optic effect. Uniform illumination results in an equilibrium charge distribution and erases the hologram (Fig. 1). Hence, PR materials are suitable for reversible and real time holography and information storage. A unique property of the PR effect is the nonlocal nature of the index grating, that is the light and refractive index pattern are out of phase. This gives rise to asymmetric energy transfer (two beam coupling), in which one of the writing beams gains energy at the expense of the other, a property that can potentially be exploited for all optical image amplification[1].

The first observation of the PR effect in an organic material involved an organic crystal of 2-(cyclooctylamino)-5-nitro pyridine doped with 7,7,8,8-tetracyanoquinodimethane [3]. The growth of high quality doped organic crystals, however, is a very difficult process, and generally impractical, because most dopants are expelled during crystal preparation or inhibit the growth of large crystals. On the other hand, polymers can be doped with a wide array of low molar mass molecules with relative ease. Further, polymers may be formed into a variety of thin films and other application-specific configurations. The second-order nonlinearity of polymers containing NLO chromophores can be produced by poling, whereas in crystals it depends on the

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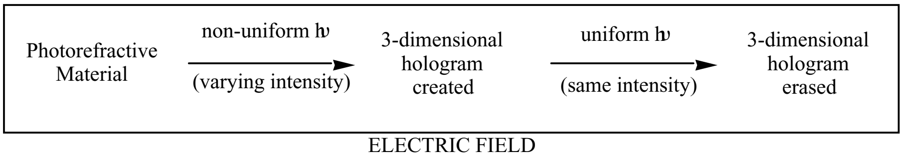


Fig. 1. Schematic illustration of hologram recording and erasure in a PR material.

rare subset of crystals with noncentrosymmetric crystal structures.

Several physical processes that are important in organic materials do not occur in inorganic materials. The quantum efficiency of charge generation and mobility of the charges in inorganic PR materials is field independent while both phenomena are field dependent in organic materials, as has been demonstrated in a number of PR polymers [4]. The mobility is also strongly dependent upon the interparticle separation between transport molecules, which means that the transport molecules must be present in high enough concentration to form a connected network for the hopping of carriers.

Polymeric PR materials promise many of the traditional advantages associated with polymers, such as good thermal stability, low dielectric constants, and ease of processing. To manifest the photorefractive effect, it is thought that these polymeric materials must contain photocharge generating (CG) and transporting (CT) functionality, charge trapping sites and NLO chromophores. Finally, the index of refraction must depend on the space–charge field. The mere physical presence of these functionalities does not guarantee that any diffraction grating produced by optical illumination arises from the PR effect. Hence, a polymeric material can potentially be made photorefractive by incorporating these properties directly into the polymer or by doping guest molecules into the polymer to produce these properties. It is usually desirable to incorporate some of the elements covalently into the polymeric host itself to minimize the amount of inert volume in the material and inhomogeneities due to phase separation and aggregation.

A key component of polymeric PR materials are the NLO moieties, which consist of a π-electron bridge connecting electron-donating and electron-withdrawing substituents. The disparity in electron distribution is necessary to induce the asymmetry required for second-order optical nonlinearity, such as the electro-optic (EO) effect. The delocalization of the π electrons along the molecular axis leads to an increased electron density at the acceptor site at the expense of electron density at the donor group, resulting in a permanent dipole moment $\mu$. Second-order nonlinearity is typically induced in a polymer by applying an electric field to align the chromophores near the polymer's glass transition temperature ($T_g$) via poling. The alignment of the molecules can be permanent or quasi-permanent, in which case the molecules remain aligned only as long as the field is applied to the material. A strategy often used is crosslinking during poling to achieve large net alignment; at the same time the $T_g$ of the polymer is increased [5].

A number of composite systems have been reported where a polymer possessing one of the requisite functionalities (Fig. 2), e.g., covalently attached NLO chromophores, is doped with the others (CG and CT dopants) or a photoconductive polymer, e.g., poly(*N*-vinylcarbazole), is doped with the sensitizer and NLO dopants [1,6]. The high small molecule dopant loading levels necessary (up to 50 wt%) result in some major disadvantages in this meta-stable system, such as phase separation (crystallization) of the dopants. In addition, plasticizers and compatibilizers are often used to lower the $T_g$ of the polymer and/or increase solubility of the dopants in the host polymer, respectively. This, in turn, dilutes the effective concentration of the CT, CG, and NLO moieties, potentially diminishing the efficiency and sensitivity of the PR polymer composite.

It naturally followed that polymers were developed in which all the necessary moieties were covalently attached (Fig. 3). Several "fully functionalized" polymeric systems have been reported although not all have unambiguously demonstrated photorefractivity [1]. A number of reports of "fully functionalized" polymeric systems have appeared, with most synthetic strategies based on the formation of random copolymers. The random nature of the copolymers, however, is accompanied by uncertainty in the distribution of groups and reproducibility in producing and processing the material. Shortcomings of the majority of single-component systems reported to date include the random orientation

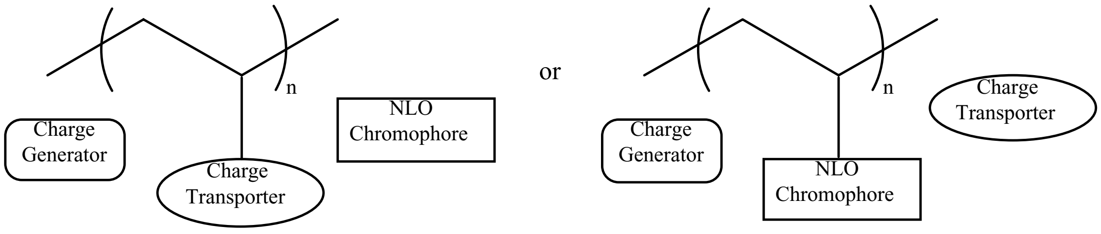


Fig. 2. Illustration of PR polymer composites.

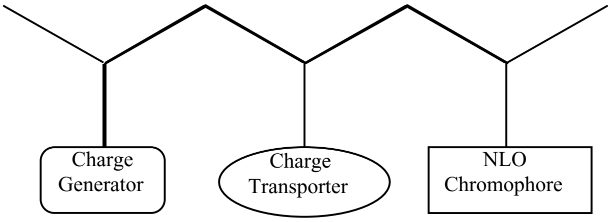


Fig. 3. Illustration of a “fully functionalized” PR polymer.

and spacing of charge transport moieties and synthetic difficulties. The major challenges in the field of organic PR materials are: to increase stability from phase separation; increase temporal stability; increase thermal stability; increase diffraction efficiency; improve charge transport efficiency; tunable wavelength sensitivity; improve electro-optic coefficients; create efficient synthetic methods, and develop reproducible processing methods.

Our research aims to address both stability and synthetic efficacy challenges in creating well-defined, single-component PR polymers. We have introduced two paradigms of such macromolecular architecture, as illustrated in Fig. 4. In the first paradigm, the NLO chromophores are incorporated into the CT moiety, while the second involves formation of a perfectly alternating arrangement of CT and NLO units. We have recently prepared siloxane polymers based on the former strategy (see, e.g. in Fig. 5). Thus, we were able to develop and implement a versatile synthetic methodology to create well-defined polymers bearing a high concentration of CT and NLO moieties [7–10]. The syntheses were quite efficient. Siloxane polymers were prepared bearing carbazole, diphenylamine, or triphenylamine CT groups and phosphonate ester or nitro-containing NLO moieties.

A phosphonate ester was selected as the electron-withdrawing functionality for our NLO component for several reasons. First, the phosphonate ester group has been shown to be nearly as effective as a nitro group for enhancing the electro-optic properties in aniline derivatives [9]. Second, the phosphonate ester is a strong hydrogen acceptor for hydrogen bonding. It has been used effectively in forming miscible polymer blends [11], and is expected to aid in the formation of hydrogen bond stabilized composites through favorable enthalpic gains effected by hydrogen bonding. Finally, it imparts excellent solubility to polymers [12]. In fact, we recently reported the first synthesis of, and electro-optic characterization of, a 4-amino-4′-phosphorylated stilbene derivative [13].

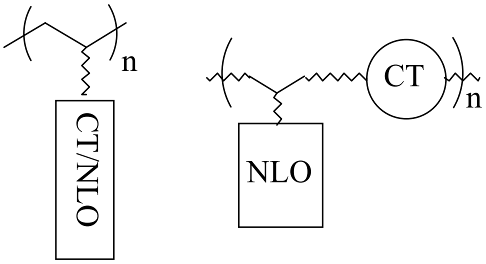


Fig. 4. Paradigms for well-defined CT and NLO-containing single component-type PR polymers.

The synthetic methodology we developed is characterized by “high fidelity” and is adaptable to allow the preparation of a “catalog” of polymers. This latter aspect is potentially important for systematic structure-property investigations in which the CT and/or NLO functionalities can quite easily be systematically varied. Herein, we report the preparation of novel, well-defined polyimides and polyurethanes based on both of our architectural paradigms. These polymers, when doped with CG dopants, are expected to exhibit PR behavior.

## 2. Experimental

### 2.1. Measurements

$^1$H NMR spectra were recorded on Bruker AM-300 or AC-200 spectrometers. FT-IR spectra were recorded on a Perkin–Elmer Spectrum 2000 spectrometer. UV–visible spectroscopic measurements were recorded using a Hewlett–Packard diode array spectrophotometer (model 8452A). GC/MS analyses were obtained with a Hewlett–Packard model 5972A MSD instrument. DSC analyses were secured with a TA Instruments model 2920 DSC using a scan rate of 20°C/min (under $N_2$). $T_g$s were obtained from the scan after which no appreciable change was observed. Thermogravimetric analyses (TGA) were performed using a TA Instruments model 2050 instrument using a scan rate of 10°C/min under $N_2$ atmosphere. Decomposition temperatures (thermal stabilities) are reported as the temperatures at which substantial decomposition begins to occur. Elemental analyses were obtained from the University of Toledo Instrumentation Center and the Wright–Patterson AFB Analysis Laboratory. Molecular weight distributions were determined by size exclusion chromatography (SEC, Waters 519 RI, 40°C, 1 ml/min) in THF or DMF using a series of Waters Styragel columns (HR 1, HR 3, and HR 4) calibrated with polystyrene standards. Number-average ($M_n$) and weight-average ($M_w$) molecular weights were calculated. High and low resolution mass spectra were obtained using JEOL model SX102A and AX505H mass spectrometers, respectively. 3-Nitrobenzyl alcohol doped with NaI was used as the matrix for fast atom bombardment (FAB) measurements. $NH_3$ was employed as reagent gas for chemical ionization (CI) measurements.

### 2.2. Synthesis of 4-bis(2-hydroxyethyl)amino-4′-(diethyl phosphono)stilbene (**3**)

A mixture of 4-bromo-*N*,*N*-diethanolaniline (1.5 g, 7.0 mmol), styrene phosphonate [13] (1.51 g, 0.31 mmol), $Pd(OAc)_2$ (0.15 g, 0.7 mmol), tri-*o*-tolyl phosphine (0.429 g, 1.4 mmol) and 1.1 ml of $Et_3N$ in 30 ml of $CH_3CN$ was heated in a screw capped tube purged with

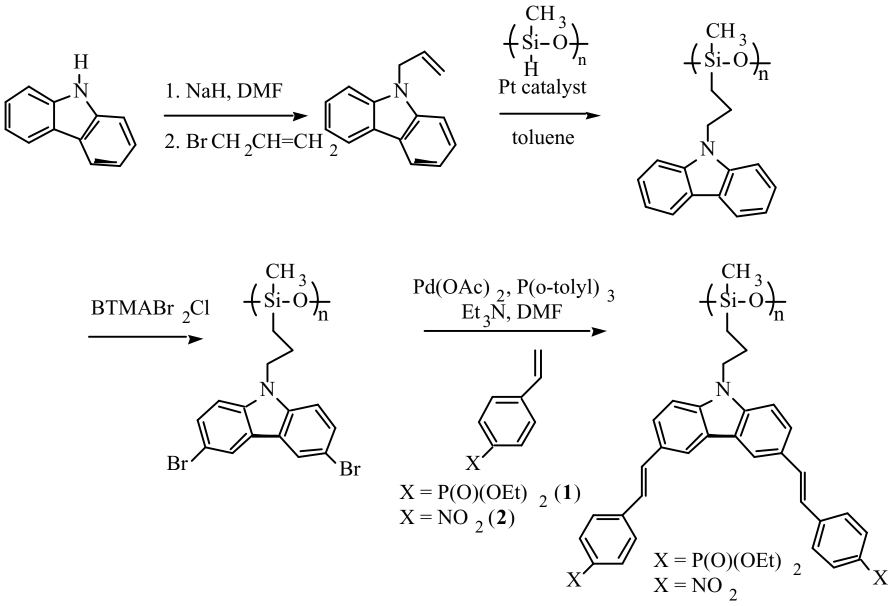


Fig. 5. Synthesis of carbazole-based PR polysiloxanes.

argon at 90°C for 48 h. The reaction mixture was cooled, filtered, poured into cold water, and extracted with EtOAc. The organic extract was dried over magnesium sulfate and the solvent was removed in vacuo. Stilbene **3** was further purified by flash chromatography through silica gel, affording 1.21 g of fluorescent yellow solid (65%). UV ($10^{-5}$ M) $\lambda_{max} = 256$ nm (240–460 nm); $^1$H NMR (CDCl$_3$): $\delta$ 1.30 (t, 6H), 3.60 (t, 4H), 3.85 (t, 4H), 4.05 (m, 4H), 4.55 (s, 2H), 6.70 (d, 2H), 6.85 (d, 1H), 7.1 (d, 1H), 7.35 (d, 2H), 7.45 (dd, 2H), 7.60 (dd, 2H). High resolution MS (FAB), [M + Na$^+$] calc: 442.1759, actual: 442.1769 amu.

### 2.3. Synthesis of 4-bis(2-hydroxyethyl)amino-4′-nitrostilbene (*4*)

A mixture of 4-bromo-*N,N*-diethanolaniline (0.872 g, 3.35 mmol), 4-nitrostyrene [7] (0.500 g, 3.35 mmol), Pd(OAc)$_2$ (0.0752 g, 0.335 mmol), tri-*o*-tolyl phosphine (0.204 g, 0.670 mmol), and Et$_3$N (0.513 ml, 3.685 mmol) in DMF was heated in a screw capped tube purged with argon at 90°C for 48 h. The reaction mixture was cooled, filtered, and poured into ice cold water. The organic layer was extracted with EtOAc. The organic extract was dried over MgSO$_4$ and solvent was removed in vacuo. Stilbene **4** was further purified by flash column chromatography through silica gel, affording a red solid (mp = 174–176°C) in 75% yield. $^1$H NMR (DMF-d$_7$): ($\delta$ 3.6–3.8 (bm, OH, OCH$_2$), 3.9 (t, NCH$_2$), 6.7 (d, ArH *ortho* to N), 6.9–7.1 (2d, =CH stilbene), 7.2–7.8 (ArH), 8.2 (d, ArH *ortho* to NO$_2$).

### 2.4. Synthesis of N,N-bis(4-isocyanatophenyl)aniline (*6*)

A solution of bis(tricholoromethyl)carbonate (0.719 g, 2.42 mmol) in dry toluene was added dropwise to a stirred solution of 4,4′-diaminotriphenylamine (**5**) (1.0 g, 3.633), prepared by reduction of the corresponding dinitro derivative, in dry toluene at room temperature under N$_2$. The reaction mixture was stirred at 100°C for 2 h. The reaction mixture was filtered and the solvent was evaporated, resulting in 1.01 g of a dark oil (80%). $^1$H NMR (benzene-d$_6$): $\delta$ 6.45 (d, 4H, ArH *ortho* to N), 6.70 (d, 4H, ArH *ortho* to NCO), 6.90 (m, 3H, ArH of Ph), 7.05 (m, 2H, ArH *ortho* to N in Ph). High resolution MS (EI, 70 eV) calc: [M$^+$]: 327.1008, actual: 327.1007 amu.

### 2.5. Synthesis of phosphorylated polyurethane (*7*)

A 40 ml heavy walled glass vial was charged with diol **3** (0.3558 g, 0.848 mmol) and 5 ml of dry DMF. Diisocyanate **6** (0.3618 g, 1.102 mmol) was added, along with another 5 ml of DMF. Two drops of Et$_3$N was added to facilitate the polymerization. The polymerization mixture was stirred at 90°C, yielding a dark viscous solution. The reaction was stopped after 36 h and then added dropwise into cold methanol. Polymer **7** precipitated out as a dark green solid. It was reprecipitated to purify it further, resulting in a yellow solid (75%). $^1$H NMR (DMF-d$_7$): $\delta$ 1.2 (t, OCH$_2$CH$_3$), 3.4–3.8 (bm OCH$_2$CH$_2$N), 4.1 (q, OCH$_2$CR$_3$), 6.9–7.1 (2d, ArH), 6.7, 7.1 (2d, =CH stilbene), 7.2 (m, ArH), 7.5–7.6 (bd, ArH), 7.6–7.8 (bm, ArH), 7.9–8.1 (bm, ArH). FT-IR neat film: 3435 cm$^{-1}$, 3247 cm$^{-1}$ ($\nu$ N–H of urethane), 2935 cm$^{-1}$($\nu_{as}$ CH$_2$), 2878 cm$^{-1}$ ($\nu_{as}$ CH$_2$), 1659 cm$^{-1}$ ($\nu_{as}$ C=O of urethane), 1439–1416 cm$^{-1}$ ($\nu$ bending CH$_2$), 1391 cm$^{-1}$ ($\nu$ CH$_3$ stretching), 1255 cm$^{-1}$ ($\nu$ P=O phosphonate ester), 1104, 1062 cm$^{-1}$ ($\nu$ P–O–C stretch). Elem. anal.: theoretical: %C = 67.55, %H = 5.80, %N = 7.50; actual: %C = 66.91, %H = 5.70, %N = 7.88.

$M_n = 24,800$, $M_w = 46,300$. Thermal analysis: $T_g = 165°C$, polymer stable up to 210°C in $N_2$.

### 2.6. Synthesis of nitrostilbene polyurethane (**8**)

A 20 ml heavy walled glass vial was charged with diol **4** (0.1889 g, 0.575 mmol) and 5 ml of dry DMF. Diisocyanate **6** (0.2449 g, 0.748 mmol) in 5 ml of DMF was added. Two drops of $Et_3N$ was added to facilitate the polymerization. The polymerization mixture was stirred at 90°C, yielding an orange-red viscous solution. The reaction was stopped after 48 h and added dropwise into cold methanol. Polymer **8** precipitated out as an orange-red solid powder (78%). It was reprecipitated and washed with methanol. UV: ($\lambda_{max} = 308$ nm (range 260–580 nm). $^1$H NMR (DMF-$d_7$): $\delta$ 3.6–3.9 (bm, $CH_2N$), 4.2–4.4 (bm, $OCH_2$), 6.7–7.8 (m, ArH and =CH stilbene), 8.1–8.3 (d, ArH *ortho* to $NO_2$). FT-IR (neat film) cm$^{-1}$: 3430 ($\nu$ N–H of urethane), 2961 ($\nu_{as}$ $CH_2$ stretch), 1681 ($\nu$ C=O of urethane, broad), 1504 ($\nu_{as}$ $NO_2$ stretching), 1310–1220 ($\nu_s$ $NO_2$ stretch), 927 ($\nu$ *trans* C=CH bend). Elem. anal.: theoretical: %C = 69.61, %H = 5.07, %N = 10.68; actual: %C = 69.02, %H = 5.38, %N = 10.89. $M_n = 17,600$, $M_w = 33,800$. Thermal analysis: $T_g = 130°C$, polymer stable up to 220°C in $N_2$.

### 2.7. Synthesis of brominated polyimide (**10**)

A 20 ml vial was charged with 4-bromo-4′,4″-diaminotriphenylamine (**9**) (0.500 g, 1.412 mmol) and 2 g of dry NMP. The mixture was stirred until complete dissolution of the diamine was achieved, and then 4,4′-(hexafluoroisopropylidene)diphthalic anhydride (6-FDA) (0.627 g, 1.412 mmol) was added and washed in with another 2 g of NMP. The polymerization mixture turned dark red. It was stirred for a period of 48 h to yield a highly viscous polyamic acid solution (**PAA-1**).

To **PAA-1** was added dry pyridine (0.451 g, 5.70 mmol) and acetic anhydride (0.582 g, 5.70 mmol). The reaction mixture was stirred for approximately 16 h at ambient temperature, and finally at 70°C for an additional 6 h. The resulting polyimide solution was then precipitated in water with vigorous stirring and washed thoroughly with methanol. The dark powder was dried for 48 h under vacuum, resulting in 0.904 g of **10** (82%). $^1$H NMR (DMF-$d_7$): $\delta$ 6.9 (d, ArH), 7.0 (d, ArH), 7.1 (bt, ArH), 7.3 (d, ArH), 7.4–7.6 (bm, ArH anhydride), 7.9 (s, ArH anhydride), 8.1–8.2 (bm, ArH *ortho* and *meta* to imide N). Elem. anal.: theoretical: %C = 58.29, %H = 2.38, %N = 5.51; actual: %C = 57.85, %H = 2.52, %N = 5.17. $M_n = 28,100$, $M_w = 45,600$. Thermal analysis: $T_g = 243°C$, polymer stable up to 300°C in $N_2$.

### 2.8. Synthesis of phosphorylated polyimide (**11**) via Heck reaction of **10**

A 20 ml heavy walled vial was charged with **10** (0.400 g, 0.525 mmol), **1** (0.151 g, 0.63 mmol), $Et_3N$ (0.011 g, 0.063 mmol), and 5 ml of freshly distilled DMF. The reaction mixture was heated to 85°C and stirred vigorously. The color of the reaction mixture turned dark red from green after 32 h. The reaction mixture was heated for a total of 64 h, yielding a dark red viscous liquid. The resulting solution was then precipitated in distilled water with vigorous stirring and washed thoroughly with methanol. The dark powder was dried under vacuum, affording 200 mg of polyimide **11**. UV–vis: ($\lambda_{max} = 294$ nm (range 258–576 nm). FT-IR (neat film) cm$^{-1}$: 2963 ($\nu$(sp$^2$ C–H stretch), 1661 ($\nu$ (C=O imide stretch), 1505 ($\nu$ phenyl C=C stretching), 1257 ($\nu$ P=O of phosphonate ester), 1102, 1063 ($\nu$ POC stretch), 967 ($\nu$ *trans* C=CH bend); Elem. anal.: theoretical: %C = 63.85, %H = 3.72, %N = 4.56; actual: %C = 62.48, %H = 3.40, %N = 4.79. $M_n = 31,200$, $M_w = 48,400$. Thermal analysis: $T_g = 212°C$, polymer stable up to 230°C in $N_2$.

### 2.9. Synthesis of N,N-bis(4-aminophenyl)-4-stilbenephosphonic acid diethyl ester (**12**)

In a screw cap vial was taken 4-bromo-4′,4″-diaminotriphenylamine (**9**) (1.0035 g, 2.85 mmol), **1** (0.6163 g, 2.565 mmol), $Pd(OAc)_2$ (0.064 g, 0.285 mmol), of tri-*o*-tolylphosphine (0.173 g, 0.570 mmol), and $Et_3N$ (0.32 g, 3.135 mmol) in 30 ml $CH_3CN$. The reaction mixture was heated while stirring at 100°C in an oil bath. After complete consumption of **1** (TLC), the reaction mixture was passed through Celite and poured into ice cold water, yielding a dark brown precipitate. The solid was filtered and dried under vacuum. The product was further purified by column chromatography ($CH_2Cl_2$/EtOAc), resulting in 1.0104 g (77%) of **12**. $^1$H NMR ($CDCl_3$): $\delta$ 1.3–1.4 (t,H, $OCR_2CH_3$), 3.6 (bs, 4H, $NH_2$), 4.1 (m, 4H, $OCH_2CR_3$), 6.6 (d, 4H, *ortho* to $NH_2$), 6.8 (d, 2H, *ortho* to 3° N), 6.9 and 7.1 (m, 2H, =CHstilbene), 7.3 (d, 2H, *meta* to 3° N), 7.5 (dd, 2H, *meta* to $P(O)(OR)_2$), 7.7 (dd, 2H, ArH *ortho* to $P(O)(OR)_2$). UV–vis: $\lambda_{max} = 406$ nm (range 270–522 nm).

### 2.10. Synthesis of phosphorylated polyimide (**13**)

A 20 ml vial was charged with diaminostilbene **12** (0.3025 g, 0.589 mmol) and 1 g of dry NMP. The mixture was stirred until complete dissolution of diamine was achieved, followed by addition of 6-FDA (0.2616 g, 0.589 mmol) and 1 g of NMP. The mixture turned dark red in color, it was stirred for 48 h, yielding a dark red viscous polyamic acid solution (**PAA-2**).

To **PAA-2** was added dry pyridine (0.188 g, 2.378 mmol) and acetic anhydride (0.243 g, 2.378 mmol). The reaction mixture was stirred for 16 h at ambient temperature and finally at 70°C for an additional 6 h. The resulting polyimide solution was then precipitated into water with vigorous stirring and washed thoroughly with methanol. The dark colored powder was dried for 48 h under vacuum, affording 0.304 g of polyimide **13**. $^1$H NMR (DMF-$d_7$): $\delta$ 1.3 (t, 6H,

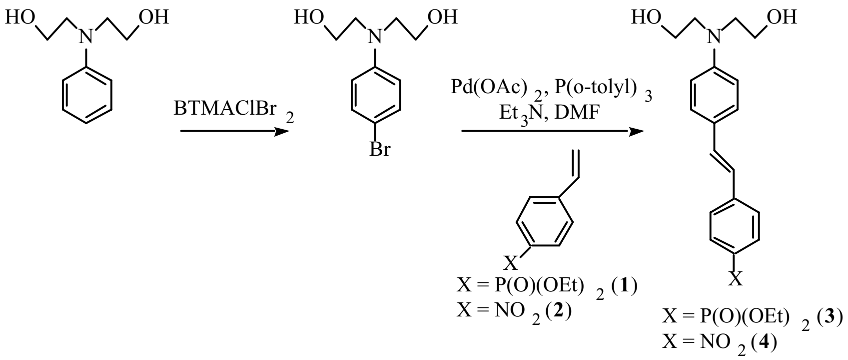


Fig. 6. Synthesis of NLO-containing diols.

$OCR_2CH_3$), 4.1 (m, 4H, $OCH_2CR_3$), 7.1–8.2 (24H, ArH). Elem. Anal.: theoretical: %C = 63.85, %H = 3.72, %N = 4.56; actual: %C = 62.25, %H = 3.69, %N = 4.42. Elem. anal.: theoretical: %C = 63.85, %H = 3.72, %N = 4.56; actual: %C = 63.29, %H = 3.87, %N = 4.21. $M_n = 26,300$, $M_w = 48,700$. UV–vis: $\lambda_{max} = 298$ nm (260 – 476 nm). Thermal analysis: $T_g = 167$°C, polymer stable up to 249°C in $N_2$.

## 3. Results and discussion

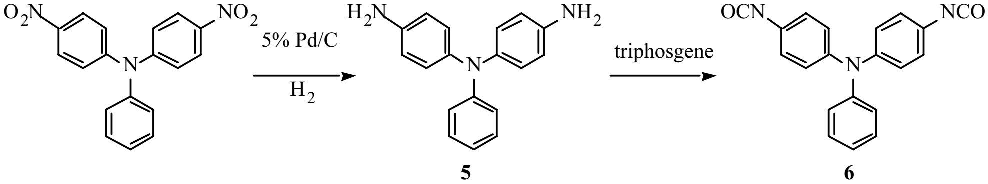
### 3.1. Alternating CT and NLO constructs: polyurethanes

Our aim was to utilize the highly efficient and atom economical Pd-catalyzed Heck reaction to prepare stilbene-based NLO chromophoric diols. The diols would then be condensed with a charge transporting diisocyanate. The synthesis of 4-bis(2-hydroxyethyl)amino-4′-(diethyl phosphono)stilbene **3** was conducted as outlined in Fig. 6. The first step involved rapid regioselective bromination of *N*,*N*-diethanolaniline using benzytrimethylammonium chlorobromate [7]. The next step involved the Heck reaction between 4-bromo-*N*,*N*-diethanolaniline and styrene phosphonate **1** [13]. This was accomplished using 10 mol% palladium (II) acetate and 20 mol% tri-*o*-tolylphosphine. To increase the efficiency of the reaction by lowering the volume of activation, the reaction was performed in a heavy walled screw cap vial at 90°C. Good yield of phosphorylated diol **3** was realized, the structure of which was confirmed by both $^1$H NMR and high resolution FAB MS. 4-Bis(2-hydroxyethyl)amino-4′-nitrostilbene **4** was synthesized in an analogous manner (Fig. 6) in good yield as a red solid [17].

It has been established previously that triarylamines possess photoconductive and hole transporting properties [14]. A charge transporting triarylamine-based diisocyanate (Fig. 7) was prepared by reduction of 4,4′dinitrotriphenylamine with 5% Pd/C and $H_2$. The resulting diamine, 4,4′-diaminotriphenylamine (**5**), was treated with triphosgene (bistrichloromethylcarbonate), affording the 4,4′-diisocyanatotriphenylamine **6** as a brown solid whose structure was confirmed by $^1$H NMR, FT-IR and high resolution MS.

A phosphorylated stilbene-containing polyurethane **7** was synthesized by triethylamine-catalyzed reaction of 4-bis(2-hydroxyethyl)amino-4’-(diethyl phosphono)stilbene **3** with the charge transporting diisocyanate **6**, as shown in Fig. 8. A yellowish polyurethane with alternating CT and NLO moieties was obtained, having $\lambda_{max} = 316$ nm and absorption extending to 438 nm. The relatively long absorbance maximum is suggestive of charge transfer interaction between the NLO chromophore and the CT unit. The TGA analysis showed that this polymer possesses high thermal stability, decomposing above 210°C. The $T_g$ of the material was found to be 165°C. These results indicate that the material should have sufficient stability of poled order.

A nitro analog to polyurethane **8** was prepared by triethylamine-catalyzed polycondensation of (*N*,*N*-diethanol)-4′-amino-4-nitrostilbene **4** and the charge transporting diisocyanate **6** (Fig. 8). The $\lambda_{max}$ for **8** was also 316 nm but its absorption extended to 548 nm. The $^1$H NMR spectrum was consistent with the polyurethane structure. The TGA analysis revealed high thermal stability of the polymer, with decomposition beginning at 220°C. The $T_g$ of polyurethane **8** was 130°C, indicating that the material should exhibit a highly stable poled order and would possess good thermal



**5** **6**

Fig. 7. Synthesis of 4,4′-diisocyanatotriphenylamine.

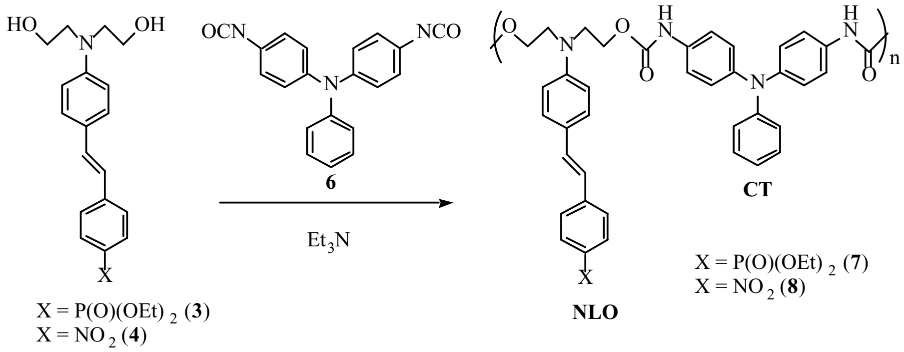


Fig. 8. Synthesis of polyurethanes with alternating CT and NLO units.

stability. Thus, it was demonstrated that this methodology is versatile, permitting preparation of well-defined polyurethanes with alternating CT and NLO moieties.

### 3.2. Multifunctional CT and NLO constructs: polyimides

To realize high $T_g$ and high thermal stability, the synthesis of well-defined, single-component polyimides was undertaken. The fluorinated dianhydride 6-FDA was selected to achieve both good solubility and high thermal stability. The aromatic polyimide moiety has also been postulated to assist in charge transport [15]. Two approaches were investigated. The first approach involved preparing a multifunctional diamine bearing CT and NLO functionality, and conducting a condensation polymerization between the diamine and 6-FDA. The second strategy called for the preparation of an arylbromide-containing polyimide, followed by Heck reaction with an appropriate styrene derivative. Both methods are described below and result in the formation of polyimides with diamine units comprised of CT triarylamine-based NLO chromophores.

Brominated polyimide **10** was prepared with a view to making multifunctional PR polyimides with different NLO chromophores. *N*-(4-bromophenyl)-*N*,*N*-bis(4-aminophenyl) amine (**9**, a charge transporting diamine) was subjected to polycondensation with 6-FDA, as shown in Fig. 9. The intermediate polyamic acid was chemically imidized. Polyimide **10** was also obtained as a green powder, soluble in THF and DMF. The absorption spectrum revealed a maxima at 318 nm and absorption ranging from 246 to 414 nm. Polyimide **10** was highly thermally stable and displayed a $T_g$ of 243°C. It was stable until a temperature of 216°C, after which only a 1.5% weight loss occurred between 216°C and 500°C. NMR and elemental analysis clearly established the structure of the product. IR was a useful diagnostic tool to identify the characteristic imide and Ar–Br bond stretching absorptions.

To demonstrate the usefulness of **10** as a building block to

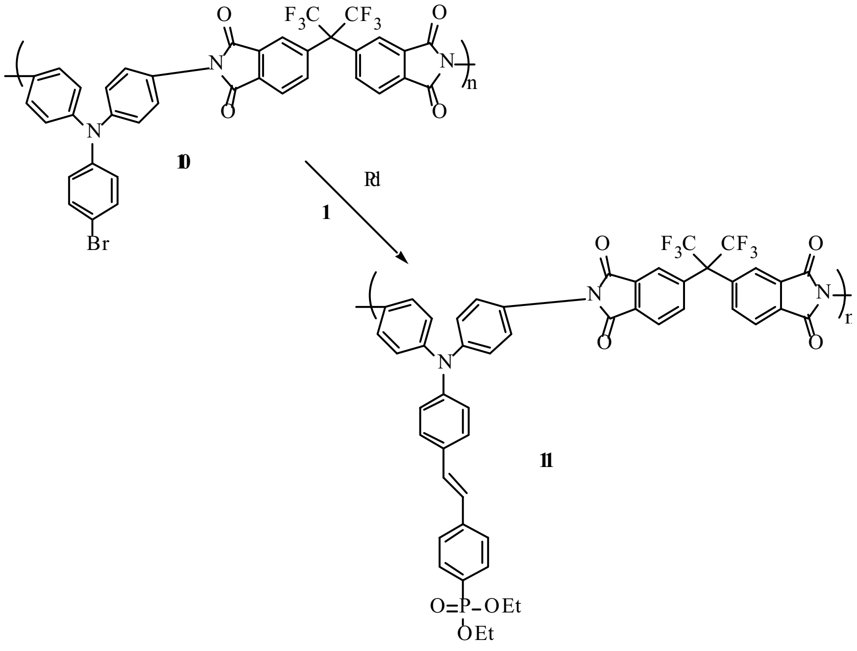


Fig. 9. Synthesis of brominated polyimide **10**.

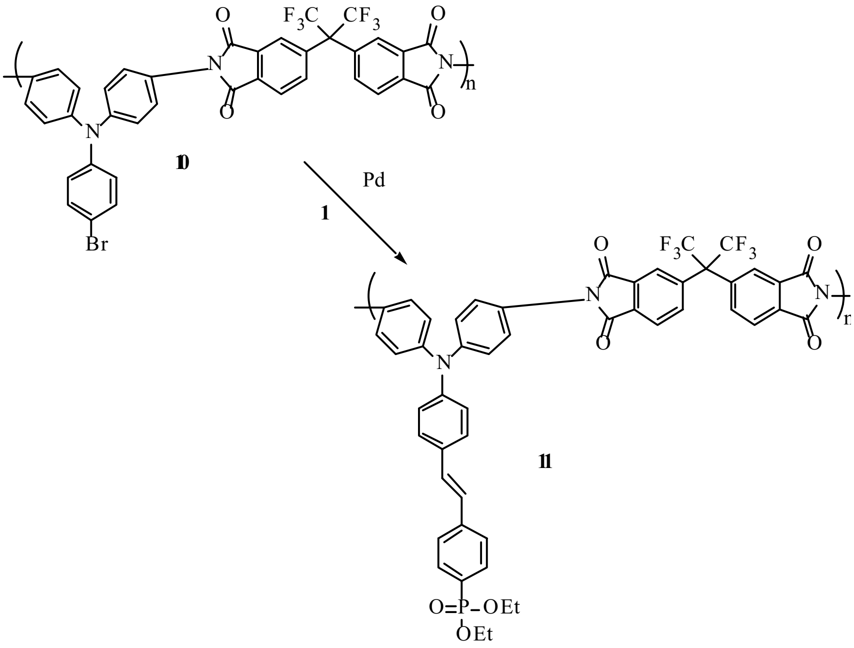


Fig. 10. Synthesis of phosphorylated polyimide **11** via Heck reaction of **10**.

create single component PR polymers, it was treated with styrene phosphonate **1** in a Pd-catalyzed Heck reaction (Fig. 10). A deep red, THF- and DMF-soluble powder was obtained having $\lambda_{max} = 294$ nm and an absorption range of 258 – 576 nm. The $T_g$ for phosphorylated polyimide **11** was relatively high at 212°C and no weight loss was detected up to 230°C. $^1H$ NMR and IR spectroscopic analyses were consistent with the structure. Elemental analysis data indicated 73% repeat unit substitution.

The second approach to create PR polyimides involved the preparation of a diamine possessing both CT and NLO moieties, such as *N*,*N*-bis(4-aminophenyl)-4-stilbenephosphonic acid diethyl ester **12**. The synthesis of this chromophore highlights the effectiveness and generality of the Heck reaction, as shown in Fig. 11. *N*,*N*-bis(4-nitrophenyl)-4-bromoaniline was generated by the reaction of 4-fluoronitrobenzene and 4-bromoaniline in the presence of CsF in DMSO [16]. The resulting dinitrotriphenylamine was

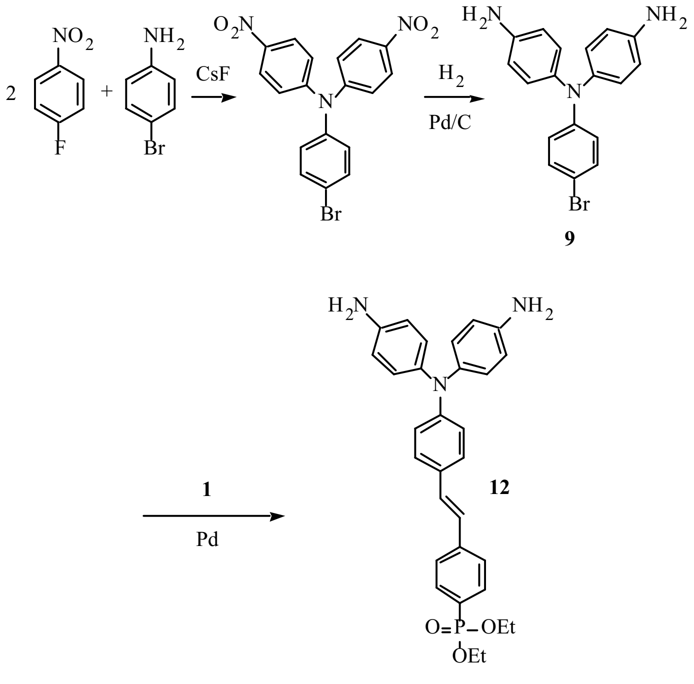


Fig. 11. Preparation of *N*,*N*-bis(4-aminophenyl)-4-stilbenephosphonic acid diethyl ester **12**.

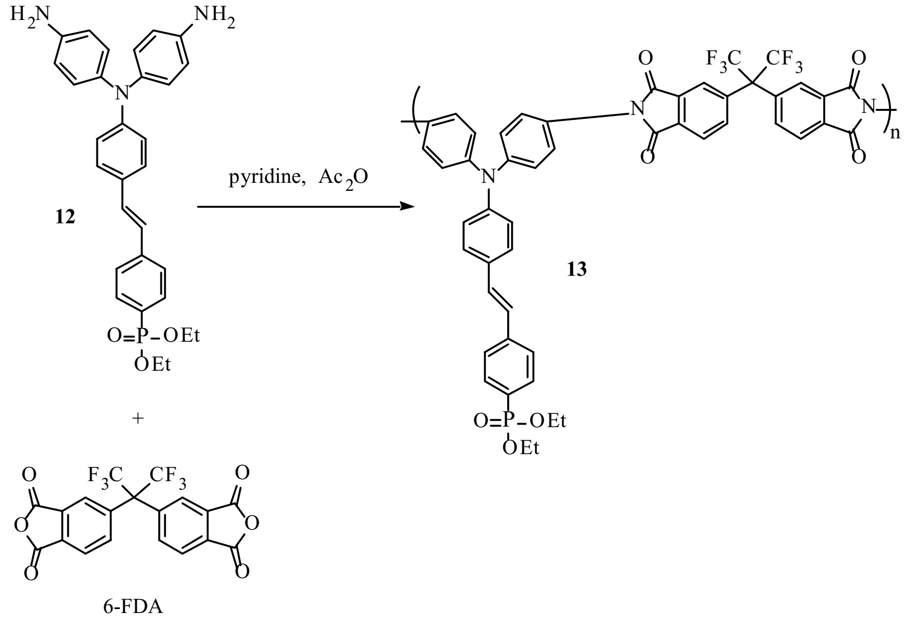


Fig. 12. Preparation of phosphorylated polyimide **13** via polycondensation of **12** and 6-FDA.

then reduced with 4 wt% of 5% Pd/C and hydrogen, affording good conversion to *N*,*N*-bis(4-aminophenyl)-4-bromoaniline(**9**). Controlling the wt% of Pd was essential in avoiding displacement of bromine. Higher weight percents led to a mixture of products resulting from reduction of nitro and bromine groups. The final step in this sequence involved the Heck reaction between the diaminobromotriphenylamine derivative and styrene phosphonate **1**. $^1$H NMR indicated the presence of the *trans* stilbene olefinic protons. FT-IR clearly indicated the presence of a *trans* stilbene double bond. Phosphorylated diamine **12** exhibited UV–visible absorbance from 270–522 nm with $\lambda_{max} = 406$ nm and IR absorbances at 1274 cm$^{-1}$ (P=O stretch), 1128 cm$^{-1}$ (P–O–C stretch), and 1070 cm$^{-1}$ (P–O–C stretch).

In the final step of this strategy, the CT/NLO diamine **12** was subjected to polycondensation with 6-FDA, resulting in formation of phosphorylated polyimide **13** (Fig. 12). The reaction was carefully monitored for color and viscosity changes, and chemical imidization (via a mixed anhydride method) was utilized to complete imide formation. Polyimide **13** was obtained as dark brown solid, soluble in THF and DMF. The polymer had a broad absorption band with the maxima at 298 nm, ranging from 260–476 nm. Polyimide **13** was stable up to 249°C, with a $T_g$ observed at 167°C, providing a clear indication of the possibility of long term stability and stable poled order. $^1$H NMR and elemental analysis unambiguously indicated formation of the desired polymer.

## 4. Conclusion

The Pd-catalyzed Heck reaction proved to be a very efficient and atom economical approach to the synthesis of stilbene diol derivatives. Stilbene diol monomers bearing either phosphonate ester or nitro electron-withdrawing groups have been synthesized. The regiospecific bromination and Heck reactions clearly show the utility and the generality of these processes to control and efficiently prepare new monomers and polymers.

Phosphorylated NLO chromophore-containing materials were generally fluorescent yellow. They had relatively sharp absorption bands that did not extend as far into the visible region as the analogous orange-red nitro compounds. A novel charge transporting triaryldiisocyanate was synthesized and fully characterized.

Two different polyurethanes with well-defined, alternating NLO and CT units were prepared through a rationally designed synthesis. The red-shifted nature of the UV–visible spectrum revealed possible charge transfer interaction between the NLO chromophore and the CT unit. The polyurethanes synthesized have high thermal stability up to about 210°C, with relatively high $T_g$ values, a clear indication that good long term stability can be expected from these materials. Both polymers synthesized were soluble, typically in THF and/or DMF. This research represents the first use of a phosphonate ester group as an electron-withdrawing group in the synthesis of stilbenoid PR polyurethane-based polymers.

CT and NLO-containing polyimides were successfully prepared by two distinct strategies. These polymers displayed high $T_g$ values along with high thermal stabilities. The resulting polymers were soluble in DMF and NMP. Through Pd-catalyzed coupling reactions, the brominated polyimide should prove useful as a substrate for creation of an array of PR polyimides possessing different NLO moieties.

The methodology developed here is versatile, and is fully expected to lead to a “catalog” of PR-type polyurethanes and polyimides in which the NLO chromophore can be controllably and systematically varied. Such a prospect will render a wide array of materials available for elucidation of critical molecular structure–PR property relationships.

## Acknowledgements

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