Syntheses of Second-Order Nonlinear Optical Polyurethanes for Electrooptic Etalons

N. Patrick Wang and Thomas M. Leslie*

Department of Chemistry, University of Alabama in Huntsville, Huntsville, Alabama 35899

Shuping Wang and Stephen T. Kowel

Department of Electrical and Computer Engineering, University of Alabama in Huntsville, Huntsville, Alabama 35899

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Four polyurethanes containing high-β NLO chromophores side-chain units have been synthesized and characterized. These polymers have a very high chromophore density and large solubility in normal organic solvents. We have been able to build transmission mode Fabry–Perot etalons using three of the NLO polyurethanes. Etalons using disperse red 19 (DR 19) polymers (polymer 1 and 2) as the optoelectronic spacer layer with a thickness of about 1 μm show a large modulation efficiency which is comparable to the highest value so far reported for a reflection etalon device with a 4 μm NLO polymer film. Polymer 3 (DCV-IPDI polyurethane) has been repeatedly poled under a dc electric field as high as 210 V/μm. Polymer 4, an ionic polymer, experiences dielectric breakdown during parallel plate poling due to the high mobility of the small counterion, BF_4^-.

Introduction

Organic polymers hold the promise to surpass traditional electrooptic crystals used in integrated optical modulators such as $LiNbO_3$. The most important advantages include large electrooptic coefficients, lower dielectric constants desirable for high-speed devices, compatibility with many types of substrates, and flexibility of fabrication methods.[1-3] Therefore, a growing research effort has been directed in recent years toward second-order nonlinear optical (NLO) polymers. In particular, side-chain NLO polymeric materials have been of interest since NLO chromophores can be covalently attached to the polymer backbone resulting in a higher chromophore density and, subsequently, larger optical nonlinearities. Many side-chain NLO polymer systems[4-21] have been synthesized, among which polyurethanes[12-14] have shown great potential in NLO applications due to ease of synthesis, the ability to form high-quality films, high glass transition temperatures, high electric resistance, and low moisture retention.

NLO polymer materials technology is rapidly maturing and is expected to appear in commercial devices within a few years.[3] To date, this class of materials have been used to fabricate high-speed Mach–Zehnder intensity modulators,[22,23] directional couplers,[24] waveguide devices,[1,2,25-28] Fabry–Perot etalons,[29-34] and

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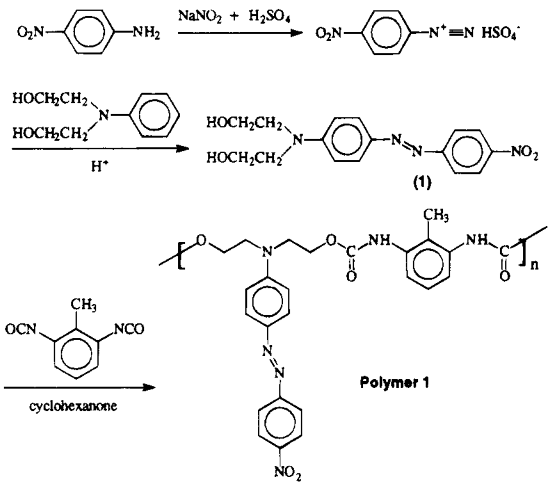
Scheme 1. Synthesis of DR19-TDI Polyurethane (Polymer 1)



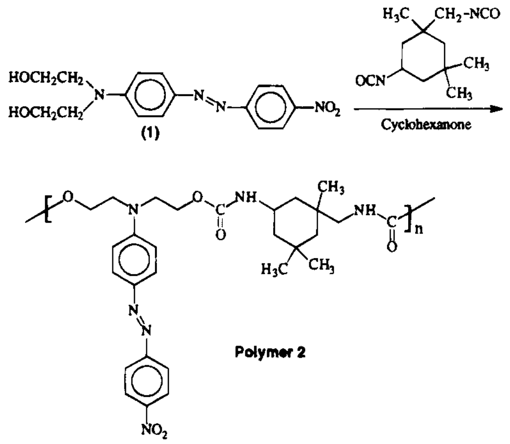
other structures. Improved materials having such properties will be crucial for developing future optically based telecommunications systems and computers. Fabry–Perot (FP) etalons have been considered as a particularly useful technique in characterizing the electrooptic properties of NLO polymers.[29–34] FP etalons also have potential applications in the areas of free-space optical interconnects, where Si-compatible modulators are required to convert electrical information to optical information which can be broadcast to one or more receiving devices.[34–36]

Recently we have synthesized four new second-order NLO polyurethanes containing a high-$\chi^{(2)}$ NLO chromophore side chains. We have reported one of the highest poling fields, 210 V/μm, for the etalons fabricated using polymer 3 (DCV-IPDI polyurethane) as the electrooptic spacer layer.[33] The etalons using disperse red 19 polyurethanes (polymer 1 and 2) show a modulation efficiency of 1.2%, one of the largest values so far reported. In addition, we synthesized and characterized a new polyurethane (polymer 4, styrylpyridinium-TDI polyurethane) containing a DAST-like ionic chromophore in the side chain. We failed to pole polymer 4 due to the mobility of free ions in the material. In this paper we present the syntheses and characterizations of the polymers, as well as the fabrication and test results of transmission mode FP etalons.

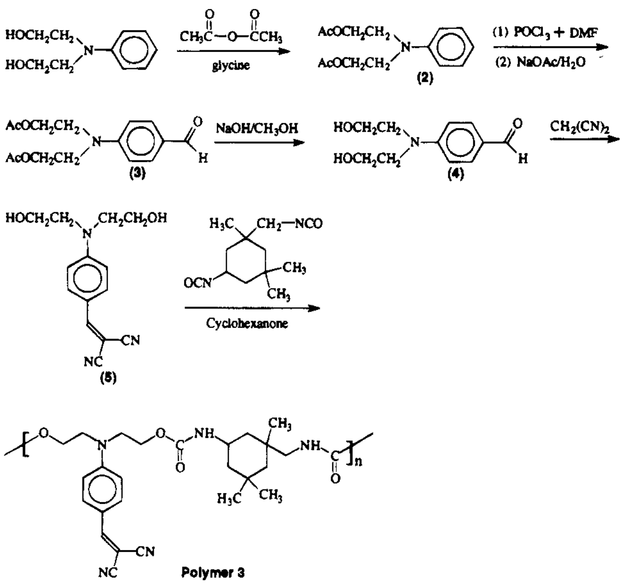
Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were taken from an IBM-Bruker 200 MHz FT NMR spectrometer. The UV–vis absorption spectra of polymers were obtained on a Hewlett-Packard 8452A diode array spectrophotometer. Melting points of the intermediates and monomers were determined using a Nikon Optiphot-2 microscope and Mettler FP82HT hot stage. The glass transition temperatures (T_g) were determined with a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of 10 °C/min. The number average molecular weights of the polymers were measured by gel permeation chromatography (GPC) in tetrahydrofuran (THF) with polystyrene as the reference. Thickness of all films were measured using a Form Talysurf Precision Ind. profilometer. A Consolidated Vacuum Corp. resistive evaporator was used for the gold deposition.

Scheme 2. Synthesis of DR19-IPDI Polyurethane (Polymer 2)



Scheme 3. Synthesis of DCV-IPDI Polyurethane (Polymer 3)



Materials. Cyclohexanone, the solvent used in polymerization, was purified by distillation over K_2CO_3. All other starting materials, reagents, and solvents purchased from Eastman, Fisher, or Aldrich were used without further purification unless otherwise noted. The syntheses of monomers and polymers were carried out according to the reaction schemes shown in Scheme 1–4.

Disperse Red 19 (1). *p*-Nitroaniline (10 g, 0.07 mol) was dissolved in a solution of 18 M sulfuric acid (10 mL) and ice water (100 mL). The mixture was cooled in an ice water bath to 5 °C or less. Sodium nitrite (5 g in 20 mL of H_2O, 0.07 mol) was added to the *p*-nitroanilinesulfate solution with stirring at a slow enough rate that the temperature of the reaction remained at 5–10 °C. The mixture was stirred for another 45 min. A solution of *N*-phenyldiethanolamine (13.4 g, 0.07 mol) dissolved in a mixture of dimethylformamide (5 mL) and 10% sodium hydroxide (5 g in 50 mL of H_2O) was added

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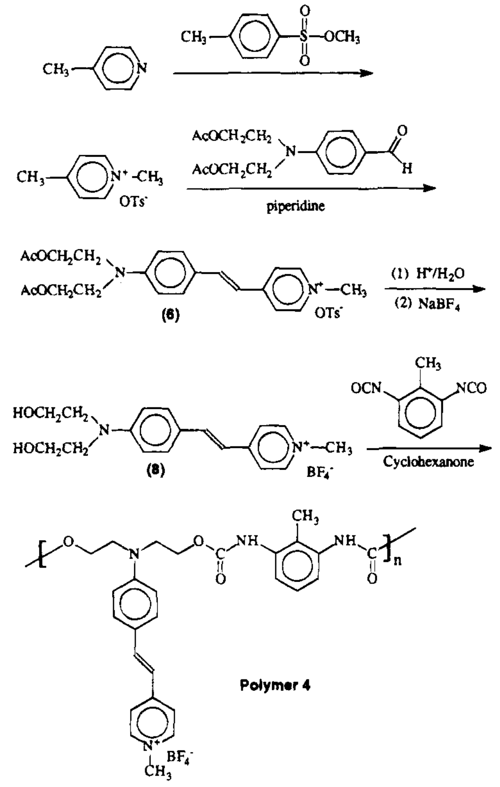
Scheme 4. Synthesis of Styrylpyridinium-TDI Polyurethane (Polymer 4)



dropwise to the *p*-nitrophenyldiazonium sulfate at 5−10 °C. The resulting mixture was then acidified with glacial acetic acid. The brown precipitate was collected and washed several times with deionized water. Recrystallization with hot filtration from 1-propyl alcohol gave shiny maroon plates of disperse red 19 (17.5 g, 76%), mp 203−206 °C, ^{1}H NMR (DMSO-d_6), δ from TMS: 3.60 [br s, 8H, $-N(C\mathit{H}_2C\mathit{H}_2OH)_2$], 4.87 [br. s, 2H, $-N(CH_2CH_2O\mathit{H})_2$], 6.90 [d, $J = 9.2$ Hz, 2H, arom CH ortho to $-N(CH_2CH_2OH)_2$], 7.82 [d, $J = 9.2$ Hz, 2H, arom CH meta to $-N(CH_2CH_2OH)_2$], 7.93 [d, $J = 9.0$ Hz, 2H, arom CH meta to $-NO_2$], 8.35 [d, $J = 9.0$ Hz, 2H, arom CH ortho to $-NO_2$].

***N,N*-Bis(2-acetyloxyethyl)aniline (2).** To a mixture of acetic anhydride (51.0 g, 0.5 mol) and *N*-phenyldiethanolamine (36.2 g, 0.2 mol), a small amount of glycine was added as catalyst. The mixture was stirred at room temperature for 2 days. TLC showed complete transformation to compound **2**. About 150 mL of ethyl ether was added to the above mixture, and then a 15% ammonia solution was used to extract the acetic acid and excess acetic anhydride out of the mixture. The organic layer was washed with water twice and dried over anhydrous magnesium sulfate. The ethyl ether was removed on the rotovap to yield 52 g (98%) of compound **2**, an oily liquid. By TLC on silica gel and ethyl ether as eluting solvent, R_f was measured to be 0.71 for the compound **2**, 0.34 for the starting material, and 0.55 for the monosubstituted intermediate. ^{1}H NMR (DMSO-d_6) δ from TMS: 1.95 [s, 6H, $-N(CH_2CH_2OCOC\mathit{H}_3)_2$]; 3.54 [t, $J = 6.1$ Hz, 4H, $-N(C\mathit{H}_2CH_2OCOCH_3)_2$]; 4.10 [t, $J = 6.3$ Hz, 4 H, $-N(CH_2C\mathit{H}_2OCOCH_3)_2$]; 6.58 [t, $J = 7.2$ Hz, 1 H, arom CH para to $-N(CH_2CH_2OCOCH_3)_2$]; 6.72 [d, $J = 8.0$ Hz, 2H, arom CH meta to $-N(CH_2CH_2OCOCH_3)_2$]; 7.12 [t, $J = 8.0$ Hz, 2H, arom CH ortho to $-N(CH_2CH_2OCOCH_3)_2$].

4-[*N,N*-Bis(2-acetyloxyethyl)amino]benzaldehyde (3). Anhydrous DMF (0.6 mol, 46.5 mL) was cooled in an ice-water bath, and then phosphorous oxychloride (0.2 mol, 18.6 mL) was added dropwise with stirring from a syringe placed through the rubber septum. A bright yellow Vilsmeier−Haack reagent was formed. Compound **2** (0.2 mol) was added quickly to the Vilsmeier−Haack reagent. After stirring for a half hour, the mixture was heated in oil bath at 90 °C for 2 h. The mixture was cooled and poured into an ice water−sodium acetate (1 mol) solution with vigorous stirring. The product was extracted from water with ethyl ether. The organic portion was washed with 100 mL of 5% K_2CO_3 aqueous solution to remove any remaining acid in the ethyl ether and then dried over anhydrous $MgSO_4$. The solvent was removed on the rotovap to yield 53 g (92%) of compound **3**, a very viscous oily liquid. By TLC on silica gel and ethyl ether as eluting solvent, R_f was 0.46. ^{1}H NMR (DMSO-d_6) δ from TMS: 1.99 [s, 6H, $-N(CH_2CH_2OCOC\mathit{H}_3)_2$]; 3.73 [t, $J = 5.9$ Hz, 4H, $-N(C\mathit{H}_2CH_2OCOCH_3)_2$]; 4.21 [t, $J = 5.8$ Hz, 4H, $-N(CH_2C\mathit{H}_2OCOCH_3)_2$]; 6.93 [d, $J = 9.1$ Hz, 2H, arom CH ortho to $-N(CH_2CH_2OCOCH_3)_2$]; 7.70 [d, $J = 9.0$ Hz, 2H, arom CH meta to $-N(CH_2CH_2OCOCH_3)_2$]; 9.69 [s, 1H, $-C\mathit{H}O$].

4-[*N,N*-Bis(2-hydroxyethyl)amino]benzaldehyde (4). Compound **3** (0.18 mol) was dissolved in about 200 mL of methanol. K_2CO_3 (5 g) was weighed out and dissolved in 10 mL of H_2O. The mixture was then added to the solution of compound **3** with stirring. The solution quickly turned to yellow. An immediate check by TLC showed three spots (compound **3**, monosubstituted intermediate, and compound **4**). The conversion was completed after stirring at room temperature for 1 h. By TLC on silica gel and ethyl ether as eluting solvent, R_f is 0.20. The remained insoluble K_2CO_3 was filtered out, and then the volatile liquid in the mixture was removed on the rotovap to yield 29.5 g (78%) of compound **4**. It was used in the next step without further purification. This is a modification of the method found in patents EP 0350112A1 and EP 0359648A1.[37] ^{1}H NMR (DMSO-d_6) δ from TMS: 3.54 [br m, 8H, $-N(C\mathit{H}_2C\mathit{H}_2OH)_2$], 5.00 [br s, 2H, $-N(CH_2CH_2O\mathit{H})_2$], 6.82 [d, $J = 8.9$ Hz, 2H, arom CH ortho to $-N(CH_2CH_2OH)_2$], 7.64 [d, $J = 8.8$ Hz, 2H, arom CH meta to $-N(CH_2CH_2OH)_2$], 9.63 [s, 1H, $-C\mathit{H}O$].

4-(2,2-Dicyanovinyl)[*N,N*-bis(2-hydroxyethyl)]-aniline (DCV, 5). Compound **4** (29.5 g, 0.14 mol) was dissolved in 200 mL of 2-propanol, and then malononitrile (10.0 g, 0.15 mol) was added to the solution. The mixture was heated to reflux in an oil bath overnight and then cooled to get red crystals. The crystals were collected and recrystallized from toluene with hot filtration. The orange crystals of compound **5** (26.0 g, 72%) were obtained, mp 127.8−129.6 °C. ^{1}H NMR (DMSO-d_6) δ from TMS: 3.60 [br d, 8H, $-N(C\mathit{H}_2C\mathit{H}_2OH)_2$], 4.85 [br t, 2H, $-N(CH_2CH_2O\mathit{H})_2$], 6.91 [d, $J = 9.3$ Hz, 2H, arom CH ortho to $-N(CH_2CH_2OH)_2$], 7.82 [d, $J = 9.0$ Hz, 2H, arom CH meta to $-N(CH_2CH_2OH)_2$], 8.02 [s, 1H, $-CH{=}C(CN)_2$].

1-Methyl-4-{4′-[*N,N*-bis(2-acetyloxyethyl)amino]styryl}-pyridinium Tosylate (6). To about 200 mL of toluene, picoline (9.8 g, 0.105 mol) and methyl tosylate (19.6 g, 0.105 mol) were added. The mixture was heated to form a salt which was insoluble in toluene. While boiling, DMF was added to the toluene salt mixture until the crystals dissolved. Then compound **3** (31.0 g, 0.105 mol) was added to the mixture. Drops of piperidine were added as catalyst until the solution just turned to red. The mixture was then refluxed for 2 days with a Dean−Stark trap to remove water. After more than an equivalent amount of water was collected, the reaction was cooled to room temperature. Orange crystals of compound **6** (54.5 g, 94%) were collected. ^{1}H NMR (DMSO-d_6) δ from TMS: 1.99 [s, 6H, $-N(CH_2CH_2OCOC\mathit{H}_3)_2$]; 2.28 [s, 3H, $C\mathit{H}_3C_6H_4SO_3^-$]; 3.70 [br m, 4H, $-N(C\mathit{H}_2CH_2OCOCH_3)_2$]; 4.19 [br m, 7H, $N^+-C\mathit{H}_3$ and $-N(CH_2C\mathit{H}_2OCOCH_3)_2$]; 6.90 [d, $J = 8.8$ Hz, 2H, arom CH ortho to $-N(CH_2CH_2OCOCH_3)_2$]; 7.11 [d, $J = 8.3$ Hz, 2H arom CH meta to $-SO_3^-$]; 7.19 [d, $J = 16.2$ Hz, 1H, $-C\mathit{H}{=}CH-$ closer to $-N(CH_2CH_2OCOCH_3)_2$]; 7.48 [d, $J = 8.0$ Hz, 2H, arom CH ortho to $-SO_3^-$; 7.59 [d, $J = 8.8$ Hz, 2H, arom CH meta to $-N(CH_2CH_2OCOCH_3)_2$]; 7.90 [d, $J = 16.2$ Hz, 1H, $-CH{=}C\mathit{H}-$ farther from $-N(CH_2CH_2OCOCH_3)_2$]; 8.05 [d, $J = 6.8$ Hz, 2H, arom CH meta to N^+-CH_3]; 8.70 [d, $J = 6.8$ Hz, 2H, arom. CH ortho to N^+-CH_3].

1-Methyl-4-{4′-[*N,N*-bis(2-hydroxyethyl)amino]styryl}-pyridinium Tosylate (7). Compound **6** (about 0.1 mol) was dissolved in 100 mL of 3 M HCl. The solution was gently heated for 1.5 h and then neutralized with K_2CO_3. The solution was cooled to room temperature and dark red crystals were obtained. The crystals were recrystallized from distilled water and then recrystallized from methanol. About 31 g

(66%) of compound **7** was obtained, mp 179−181 °C. ^{1}H NMR (DMSO-d_6), δ from TMS: 2.28 [s, 3H, $\mathrm{C}\mathit{H}_3\mathrm{C_6H_4SO_3^-}$]; 3.54 [br m, 8H, $-\mathrm{N(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{OH)_2}$]; 4.16 [s, 3H, $\mathrm{N^+{-}C}\mathit{H}_3$]; 4.88 [br s, 2H, $-\mathrm{N(CH_2CH_2O}\mathit{H}\mathrm{)_2}$]; 6.79 [d, J = 8.9 Hz, 2H, arom CH ortho to $-\mathrm{N(CH_2CH_2OH)_2}$]; 7.13 [m, 3H, $-\mathrm{C}\mathit{H}\mathrm{{=}CH}-$ closer to $-\mathrm{N(CH_2CH_2OH)_2}$ and arom CH meta to $-\mathrm{SO_3^-}$]; 7.51 [m, 4H, arom CH meta to $-\mathrm{N(CH_2CH_2OH)_2}$ and arom CH ortho to $-\mathrm{SO_3^-}$]; 7.88 [d, J = 16.1 Hz, 1H $-\mathrm{CH{=}C}\mathit{H}-$ farther from $-\mathrm{N(CH_2CH_2OH)_2}$]; 8.02 [d, J = 6.8 Hz, 2H, arom CH meta to $\mathrm{N^+{-}CH_3}$]; 8.66 [d, J = 6.8 Hz, 2H, arom CH ortho to $\mathrm{N^+{-}CH_3}$].

1-Methyl-4-{4′-[*N*,*N*-bis(2-hydroxyethyl)amino]styryl}-pyridinium Tetrafluoroborate (8). A saturated $\mathrm{NaBF_4}$ solution was added into an aqueous solution of compound **7** (31 g, 0.067 mol). An orange-reddish precipitate was formed. The mixture was heated until all of the precipitate dissolved and then cooled to room temperature. Red crystals were collected and recrystallized from distilled water and then baked overnight in an oven at 120 °C. Compound **8** (22 g, 85%) was obtained, mp 150−152 °C. ^{1}H NMR (DMSO-d_6) δ from TMS: 3.57 [br d, 8H, $-\mathrm{N(C}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{OH)_2}$]; 4.16 [s, 3H, $\mathrm{N^+{-}C}\mathit{H}_3$]; 4.83 [br t, 2H, $-\mathrm{N(CH_2CH_2O}\mathit{H}\mathrm{)_2}$]; 6.80 [d, J = 8.2 Hz, 2H, arom CH ortho to $-\mathrm{N(CH_2CH_2OH)_2}$]; 7.13 [d, J = 16.1 Hz, 1H, $-\mathrm{C}\mathit{H}\mathrm{{=}CH}-$ closer to $-\mathrm{N(CH_2CH_2OH)_2}$]; 7.54 [d, J = 8.2 Hz, 2H, arom CH meta to $-\mathrm{N(CH_2CH_2OH)_2}$]; 7.89 [d, J = 16.0 Hz, 1H $-\mathrm{CH{=}C}\mathit{H}-$ farther from $-\mathrm{N(CH_2CH_2OH)_2}$]; 8.03 [d, J = 6.0 Hz, 2H, arom CH meta to $\mathrm{N^+{-}CH_3}$]; 8.67 [d, J = 6.2 Hz, 2H, arom CH ortho to $\mathrm{N^+{-}CH_3}$].

DR19-TDI Polyurethane (Polymer 1). Disperse red 19 (**1**, 39.9 g, 0.12 mol) was dissolved in about 200 mL of freshly distilled cyclohexanone (not completely dissolved at room temperature). Then toluene diisocyanate (80% 2,4-isomer and 20% 2,6-isomer) (21.4 g, 0.12 mol) was added. The mixture was heated at about 110 °C overnight with stirring. The mixture was cooled and filtered through glass wool into methanol. The precipitate was collected and redissolved in THF. The solution was then filtered through a glass fiber filter paper into methanol. The precipitation was repeated four more times, and finally a red fine powdered polymer **1** (45 g, 74%) was obtained. The synthesis of polymer **1** has also been reported by other groups.[14]

DR19-IPDI Polyurethane (Polymer 2). Disperse red 19 (**1**, 14.00 g, 0.042 mol) was added to a 200 mL round-bottom flask with 100 mL of freshly distilled cyclohexanone. Then isophorone diisocyanate (9.0 mL, 0.042 mol) was added to the flask. The mixture was heated at about 120 °C for 2 days with stirring. The mixture was cooled and then filtered through glass wool into toluene with vigorous stirring. Polymer **2** was collected and redissolved in THF. The solution was precipitated in toluene again. Then polymer **2** was precipitated in 2-propanol three times. Finally polymer **2** (15 g, 65%) was obtained.

DCV-IPDI Polyurethane (Polymer 3). Compound **5** (26.0 g, 0.10 mol) was dissolved in 200 mL of freshly distilled cyclohexanone and then isophorone diisocyanate (21.5 mL, 0.10 mol) was added. The mixture was heated in an oil bath at 110−120 °C with stirring over a weekend. The mixture was cooled and then filtered through glass wool into $\mathrm{CH_3OH}$ to precipitate polymer out. A brown-black gummy polymer was obtained and then redissolved in THF. The solution was filtered through a glass fiber filter paper into 2-propanol to get a brown powdered polymer. The precipitation in 2-propanol was repeated three times. Finally a yellow polymer (30 g, 63%) was obtained.

Styrylpyridinium-TDI Polyurethane (Polymer 4). Compound **8** (10.27 g, 0.027 mole) and toluene diisocyanate (80% 2,4-isomer and 20% 2,6-isomer; 3.78 mL, 0.027 mol) were added to about 100 mL of freshly distilled cyclohexanone. The chromophore monomer was not dissolved completely at room temperature. The mixture was heated with stirring at about 110 °C for a week. The mixture turned to clear and then formed a lot of insoluble gellike polymer that stuck on the wall of the flask. The gellike polymer was dissolved in pyridine. The solution was filtered through glass wool and precipitated into water. The polymer was collected and redissolved in pyridine. The solution was then filtered through a glass fiber filter paper into methanol. The polymer was precipitated in methanol one more time. A bright red polymer (9.5 g, 60%) was obtained. Recently, the syntheses and properties of polymers with similar ionic chromophores have been reported.[19−21]

Table 1. Physical Properties of Polymers 1−4

	mol wt[a]	glass transition T_g (°C)	λ_{max} (nm)	chromophore density wt (%)
polymer 1	3282	137	464	65
polymer 2	5380	137	464	60
polymer 3	5006	145	430	54
polymer 4	see text	170	462	69

[a] In THF with polystyrene standards.

Fabrication of Etalons. FP etalons were fabricated by depositing partially transmitting gold on clean glass substrates followed by fabrication of the NLO polyurethane film by spin coating. The second partially transmitting gold mirror was then deposited.

To prepare the electrooptic film, the NLO polyurethane was dissolved into cyclohexanone (pyridine for polymer 4) with a weight concentration of 18−25% solids. The solution was filtered using 0.2 μm pore size filter directly onto the gold-coated glass surface. The sample was baked in air for 1 h to remove the majority of any volatiles. The residual solvent was removed by baking the samples in a vacuum oven for 24 h. The thicknesses of the mirrors were monitored by a crystal sensor. Mirror thicknesses are approximately 50 nm. The NLO polyurethane spacer layer thicknesses are in the range 1.0−2.0 μm.

Parallel Plate Poling. To exhibit an electrooptic effect, the NLO units in the polymer must be noncentrosymmetric. High electric field poling was utilized to orient the chromophores along the applied electric field and thus produce a noncentrosymmetric arrangement. Poling was achieved by placing the device in a Mettler FP82 hot stage at a temperature 5 °C above T_g and applying a high dc voltage across the NLO polyurethane film for about 1 h. The temperature was then lowered to room temperature with the electric field still applied.

Electrooptic (EO) Measurements. The device was characterized by measuring both the transmittance T, and modulation of the transmittance ΔT, as a function of incident angle using a He−Ne laser as the light source. Transmission of the incident light was monitored using a silicon PIN photodiode with the sample cell mounted on a precision rotary stage. For transmittance measurements, the incident light was modulated by a chopper wheel at 470 Hz. The synchronized output of the chopper was used as the reference for the lock-in amplifier. Electrooptic modulation measurements of the device were obtained by applying a 20 V_{pp} 1 kHz sinusoidal wave across the electrodes at room temperature. The synchronized output of the electric field was also used as the reference for the lock-in amplifier. The details of the FP etalon fabrication, parallel plate poling, and EO characterization has been discussed elsewhere.[33]

Results and Discussion

Physical Properties of Polymers. All the intermediate compounds and monomers obtained are pure enough to give satisfactory NMR spectra. The assignments of the ^{1}H peaks for all three chromophore monomers and the intermediates are listed in the Experimental Section.

Four NLO polyurethanes were synthesized by step polymerization with cyclohexanone as the solvent. The formation of the polymers can be demonstrated by NMR, GPC, and DSC. ^{1}H NMR peak for $-\mathrm{O}\mathit{H}$ (at around δ 4.85) from all three monomers vanishes completely after polymerization, while other peaks, such as aromatic ^{1}H peaks, retain but become much broader in the polymers

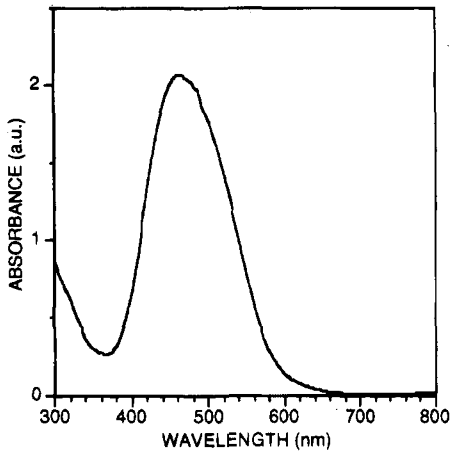


Figure 1. Absorption spectrum of a thin film of polymer 1 (DR19-TDI polyurethane). λ_{max} = 464 nm.

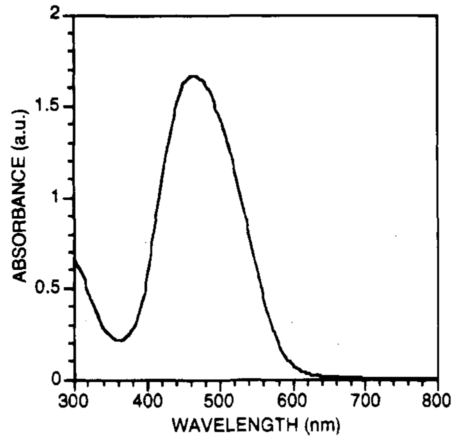


Figure 2. Absorption spectrum of a thin film of polymer 2 (DR19-IPDI polyurethane). λ_{max} = 464 nm.

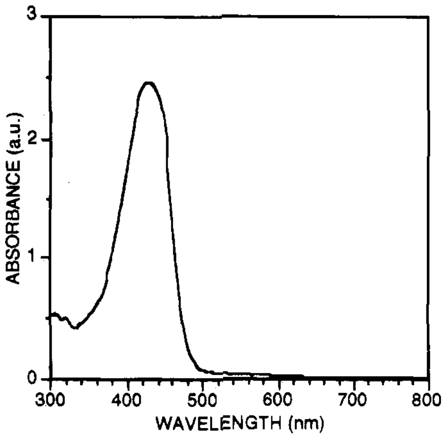


Figure 3. Absorption spectrum of a thin film of polymer 3 (DCV-IPDI polyurethane). λ_{max} = 430 nm.

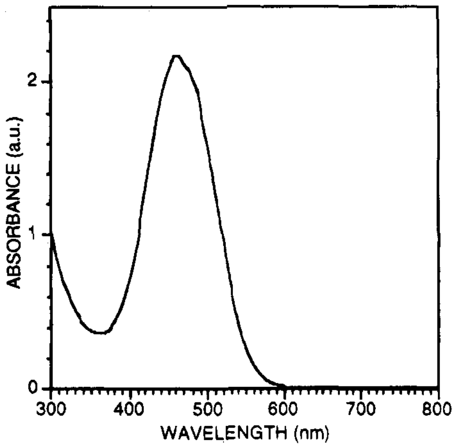


Figure 4. Absorption spectrum of a thin film of polymer 4 (styrylpyridinium-TDI polyurethane). λ_{max} = 462 nm.

(NMR data of the polymers are not shown). As shown in Table 1, the number average molecular weights of polymer 1–3 are measured to be 3000–6000. Polymer 4 does not dissolve in THF, and thus its molecular weight was not determined by GPC. The DSC thermograms of all four polymers show obvious glass transitions. Both polymer 1 and 2 have the same glass transition temperature, T_g, of 137 °C. Polymers 3 and 4, as listed in Table 1, possess higher T_g's, 145 and 170 °C, respectively.

Polymer 3 was formed over the period of 3 days in cyclohexanone at 110 °C. Air was not removed from the reaction by purging with inert gas, and some oxidation of the dicyanovinyl groups may occur with the prolonged heating cycle. On filtration through glass fiber filter paper, some dark impurity was removed, but mostly the color of the polymer changed to yellow on precipitation into 2-propanol. When redissolved into THF, the solution was brown. The polymer became bright yellow again when reprecipitated into 2-propanol. On dissolution of the polymer into freshly distilled cyclohexanone, the polymer took on a brown appearance once more due to the solvatochromic nature of the material. Once a thin film of the polymer was spin-coated and dried, it was the same bright yellow color as in dry powder form.

The UV–vis absorption spectra of polymers 1–4 in thin film form are shown in Figures 1–4, respectively. Polymers 1 and 2 have the same chromophore (DR19) side chain, so they have the same λ_{max}, at 464 nm. However, polymer 1 shows a 90% transmission at 633 nm (He–Ne laser light), while polymer 2 shows a 98% transmission at the same wavelength in thin film (about 2 μm) form. This is attributed to a slight solvatochromic shift due to the aromatic TDI comonomer and the nonaromatic aliphatic IPDI comonomer. This solvatochromic shift is consistent with what is expected for the shift if benzene and cyclohexane are used as solvents. Benzene shows a slight red shift relative hexane or cyclohexane.[38] The chromophore of polymer 3,4-(2,2-dicyanovinyl)[*N*,*N*-bis(2-hydroxyethyl)]aniline (DCV) is yellow. Therefore, polymer 3 has no absorption at 633 nm. It is chosen because its absorption band is far away from the He–Ne laser wavelength (633 nm) used for electrooptic measurements, and thus resonance effects are avoided. Polymer 4, containing a DAST-like chromophore (one of its analogue molecules has been reported to have one of highest second-order molecular hyperpolarizabilities[39]), shows a narrower absorption band than the azo-based DR 19 polymers with a blue shift of the absorption band edge relative to DR 19 polymers.

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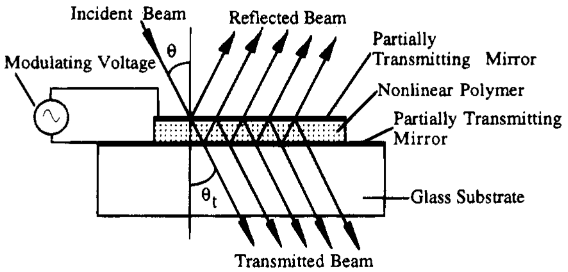

Figure 5. Schematic of transmission mode Fabry–Perot etalon.

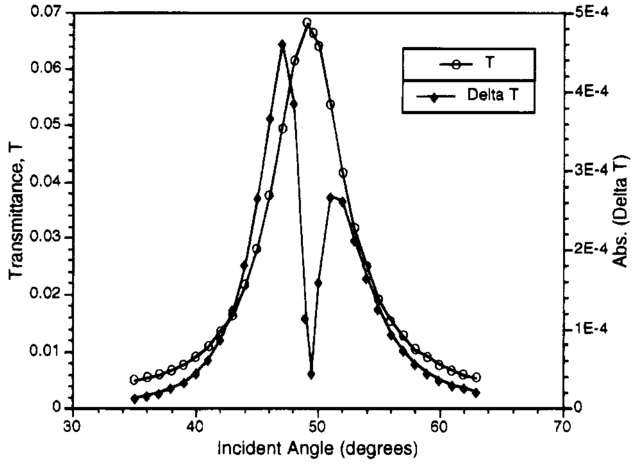

Figure 6. Experimental transmittance and modulation vs incident angle for polymer 1.

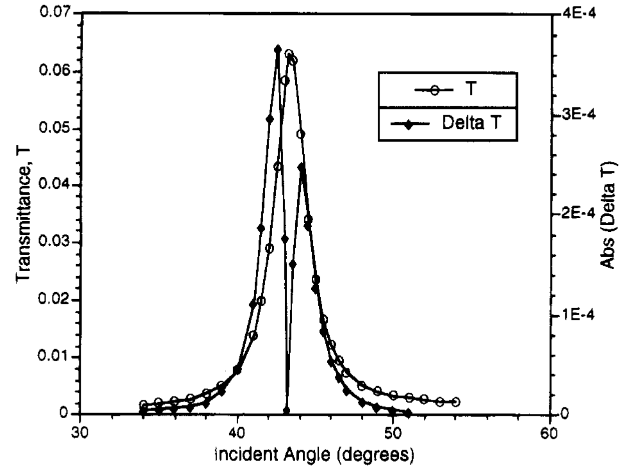

Figure 7. Experimental transmittance and modulation vs incident angle for polymer 2.

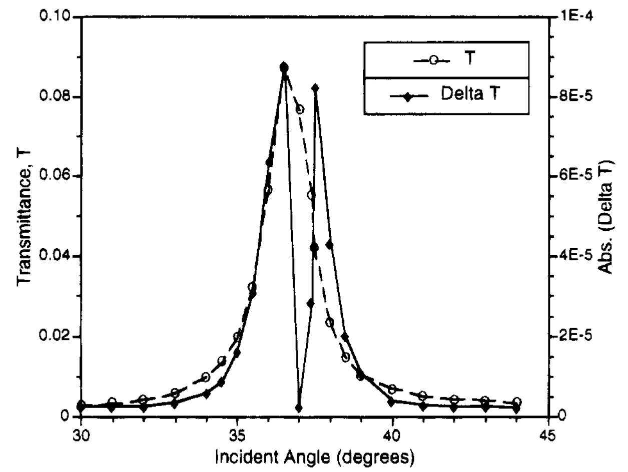

Figure 8. Experimental transmittance and modulation vs incident angle for polymer 3.

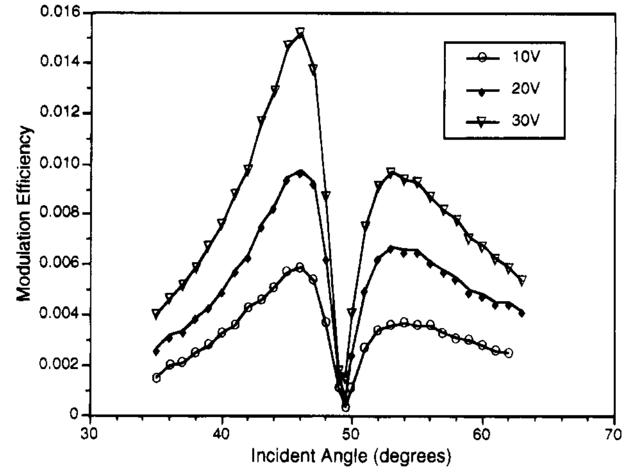

Figure 9. Dependence of modulation on V_{pp} for polymer 1.

Table 2. Electrooptic Measurements of Polymers 1–3

	poling temp (°C)	poling voltage (V/μm)	thickness of polymer film (μm)	modulation efficiency (%), $V_{pp} = 20$ V
polymer 1	145	63	0.8	1.0
polymer 2	145	80	1.5	1.2
polymer 3	150	210	1.9	0.2

EO Modulation of FP Etalons. Figure 5 shows the structure of transmitting mode FP etalons. The two gold mirrors also serve as electrodes during poling. Polymers 1–3 have been successfully poled using parallel plate poling. The experimental transmittance and the modulation for TM polarization of the laser light are shown in Figure 6–8. The modulation efficiencies, defined as $\Delta T/T$, are determined and listed in Table 2. Polymer 1 (DR 19-TDI polyurethane) shows good modulation efficiency (1.0%), but its transmittance vs angle peak is very broad (as shown in Figure 6) in part due to a partial absorption of the He–Ne light at its band edge. As shown in Figure 7, polymer 2 (DR 19-IPDI polyurethane) with a film thickness of 1.5 μm exhibits a modulation efficiency of 1.2% for a transmission etalon which is comparable to the highest value (1.5% for a reflection device with a 4 μm NLO polymer film) reported recently.[32] Polymer 3, containing DCV chromophores, shows much smaller modulation value, as indicated in Figure 8, because DCV has a smaller $\mu\beta$ value than DR 19. Note how the acceptance angle of the etalon becomes more narrow as the absorption band edge of the polymer is moved farther from the He–Ne laser line. Although polymer 3 gives a much smaller modulation value than that of DR 19 polymers, the etalons using polymer 3 as the spacer layer have been successfully poled with a dc electric field as high as 210 V/μm,[33] we believe, the highest so far reported for a working device with an etalon geometry. Man et al.[28] have reported a poling field "in excess of 200 V/μm" for a reflection measurement technique. Figure 9 shows that the modulation efficiency of an etalon made of polymer 1 increases linearly with increasing modulating voltage. This is the characteristic behavior of second-order NLO materials.

Because of the multipass nature of FP etalon, the absorption of the laser light by the NLO spacer layer severely affects the performance of the device. As discussed above, a small absorption of the laser causes a much broader transmittance vs angle peak. If the absorption becomes significant, the transmitting light is too weak to be measured, and thus the etalon becomes useless at that laser wavelength.

Polymer 1 with 90% transmission will depole if exposed to the high-intensity (50 mW) He−Ne laser for prolonged period of time. One can see a degradation of performance in the etalon until there is no EO response. The polymer, however, is not degraded because we have repoled the same etalon and obtained the same modulation value. Therefore, the loss of the modulation is due to thermal effects only and not dye degradation. No effects are observed on the performance of the etalons made with polymers 2 and 3 with repeated use. For etalons made with polymer 2, the modulation efficiency decreases to about 80% of its original value after storing at room temperature for a month. This is due to partial relaxation of the aligned dipoles in the polymer. However, the modulation value of the etalon does not decrease further after more than 3 months.

Polymer 4 is a very good insulator ($\sim 10^{10}\ \Omega$ for a 1.5 μm film) at room temperature. At its glass transition temperature (T_g), however, it experiences dielectric breakdown during parallel plate poling. We attribute the dielectric breakdown to the high mobility of small BF_4^- anions in the polymers. Choi et al.[19] have reported that the use of a bulky anion (tetraphenylborate) in an ionic polymethacrylate led to a reduced ionic mobility and then allowed the polymer to be efficiently poled above its T_g. Our future work will be to synthesize the ionic chromophore with cation and anion covalently bound in the same molecule.

Conclusions

In summary, polyurethanes containing high $\mu\beta$ NLO chromophores in the side chain have been synthesized and characterized. We have been able to build transmission mode FP etalons using three newly synthesized NLO polyurethanes. These polymers afford thin, optically clear films with promising modulation efficiencies. The etalons using the DR 19 polymers (polymer 1 and 2) as the optoelectronic spacer layer with a thickness of about 1 μm show a large modulation efficiency of 1.2% which is comparable to the highest value reported. Polymer 3 (DCV-IPDI polyurethane) has been repeatedly poled under a dc electric field as high as 210 V/μm, we believe the highest so far reported for a working device with an etalon geometry. We attribute this accomplishment to the very high quality of the polymer obtained after rigorous purification. Polymer 4, an ionic polymer, is a good insulator at room temperature but experiences dielectric breakdown during parallel plate poling at its T_g due to the high mobility of the small anions. Our future work will be to synthesize a new polymer containing the ionic chromophore with cation and anion covalently bound in the same molecule.

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