Progress toward Device-Quality Second-Order Nonlinear Optical Materials: 2. Enhancement of Electric Field Poling Efficiency and Temporal Stability by Modification of Isoxazolone-Based High μβ Chromophores

A. W. Harper,[†] S. S. H. Mao, Y. Ra, C. Zhang, J. Zhu, and L. R. Dalton*

Loker Hydrocarbon Research Institute, Departments of Chemistry and of Materials Science & Engineering, University of Southern California, Los Angeles, California 90089-1661

Sean Garner, Antao Chen, and William H. Steier

Center for Photonic Technology, Department of Electrical Engineering, University of Southern California, Los Angeles, California 90089-0483

Isoxazolone (ISX) acceptor based chromophores terminated with hydroxyl functional groups were synthesized, spin cast into optical quality 1−2 μm thick films, poled in the presence of an electric field, and thermoset into polyurethane networks to lock in the poling-induced acentric chromophore order. Alkyl groups were introduced into the chromophore backbone (π-electron bridge) to increase chromophore solubility and to inhibit electrostatic interactions between these "high μβ" chromophores. Thermosetting polyurethanes containing alkyl-substituted chromophores exhibited much (1.7−1.9 times) higher electrooptic coefficients than polymers containing unsubstituted chromophores. Chromophores with hydroxyl groups on only the donor end of the molecule were processed into hardened "themoset" materials, exhibiting a dynamic thermal stability (temperature at which the macroscopic optical nonlinearity is first observed to decrease in a thermal ramping experiment) of poling-induced dipolar order of ∼80 °C, while chromophores with hydroxyl groups on both the donor and acceptor ends display a dynamic thermal stability of poling-induced acentric order of ∼110 °C. Optical loss in these materials originates from the scattering of incident light by chromophore aggregates, rather than from intrinsic (resonant) optical absorption of the chromophores. Alkyl groups in the modified chromophores serve as "bumpers" to sterically prevent aggregation of chromophores driven by strong, spatially anisotropic, intermolecular electrostatic interactions. Steric inhibition of aggregation serves not only to enhance poling efficiency (and thus, electrooptic coefficients) but also to minimize scattering losses.

Introduction

Second-order nonlinear optical (NLO) polymers have been considered to be important electrooptic materials due to their potential for yielding devices characterized by large bandwidth (>100 GHz), low drive voltage requirement (<5 V), and facile integration with very large scale integration (VLSI) semiconductor electronics to create "opto-chips".[1,2] Device-quality materials must fulfill several requirements: (1) good processibility to optical-quality thin films; (2) large electrooptic (EO) coefficients (r_{33}); (3) high temporal stability of poling-induced dipolar chromophore order; and (4) low optical loss at operational wavelengths.[1b,2a] Optimization of any individual above-mentioned property is not difficult; however, simultaneous realization of all requirements is not a trivial task.[2a,b] To obtain materials with large EO coefficients, chromophores with high molecular hyperpolarizability (β) must be employed. For materials with high chromophore loading (employed to achieve sizable EO coefficients), chromophore−chromophore intermolecular distances become sufficiently small that

† Current address: Department of Chemistry, Texas A&M University.

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electrostatic interactions between chromophores start to interfere with poling efficiency. Under the influence of intermolecular electrostatic interactions, chromophores tend to align in an antiparallel fashion, which severely attenuates the poling-induced parallel alignment (formation of a dipolar chromophore lattice). In addition, chromophore aggregation induces the phase separation and forms small scattering centers which are the major source of optical loss.

To overcome the above-mentioned problems associated with intermolecular electrostatic interactions, to increase the chromophore solubility, and to decrease intermolecular electrostatic interaction by sterically preventing chromophore−chromophore close approach we incorporated sterically bulky groups into the chromophore backbone (π-electron bridge segment of the chromophore). Here, we report the chemical modification of isoxazolone acceptor based nonlinear optical chromophores and the incorporation of these chromophores into polyurethane networks to form device-quality materials.

A large number of high $\mu\beta$ chromophores have been synthesized recently,[2c−i] and some of these exhibit significant macroscopic nonlinearities when doped in polymer matrixes and poled in an electric field.[2c,3] Unfortunately, the bulk nonlinearity (electrooptic coefficients) of these composites decays rapidly, due to the fast relaxation of dipolar alignment (acentric chromophore order). Long-term stability of electrooptic activity is a potential problem associated with composite materials.[2a,b] To realize a stable dipolar alignment (acentric order), polymers with high glass transition temperatures (T_g) such as polyimides may be used.[4] However, the processing of polyimides involves high reaction temperatures and strong acidic conditions during the imidization reaction.[5] Many high $\mu\beta$ chromophores cannot survive at such harsh conditions. Polymer lattice hardening under mild conditions is a critical prerequisite for processing high $\mu\beta$ chromophores into device-quality materials.

Formation of urethane linkages from alcohol (phenol) and isocyanate occurs at relatively low temperatures and neutral pH conditions and, therefore, is suitable for the above purpose. Recently we have devoted considerable effort to the incorporation of high $\mu\beta$ chromophores into polyurethane networks, aiming to achieve materials with both high EO coefficients and good temporal stability. To incorporate high $\mu\beta$ chromophores into polyurethane networks, hydroxyl functionality was introduced into chromophores to react with isocyanates.

An important issue that arises in the discussion of the thermal stability of electrooptic activity is that of comparing the relative thermal stability of different materials. Thermal stability can, of course, be defined simply as the time required for a given amount (e.g., 1/e) of the poling-induced electrooptic activity to be lost with time at a fixed temperature. However, since electrooptic materials must be very robust for use in devices, such kinetic experiments require years if carried out at ambient temperatures. Even at elevated temperatures of 100−125 °C, thousands of hours are typically required for conventional kinetic experiments. We have attempted to facilitate comparison between materials by defining a thermal ramping experiment (analogous to thermal gravimetric analysis) where optical nonlinearity (electrooptic activity or equivalently second harmonic generation) is monitored as a function of time while increasing the sample temperature at a fixed rate (e.g., 5−10 °C/min).[4a] The temperature at which optical nonlinearity is first observed to decrease is used to define the thermal stability.[4a] We refer to the thermal stability measured in this way as the "dynamic thermal stability".

Results and Discussion

The synthesis of isoxazolone acceptor based chromophores is shown in Scheme 1. Reaction of aniline derivatives with acetic anhydride was effected to protect the two hydroxyl groups on the donor end of the chromophores. Subsequent reaction with POCl₃ afforded 4-aminobenzaldehyde. Reaction of this benzaldehyde with the thiophene derivative, followed by reaction with POCl₃, produced chromophore donor bridge fragments **1** and **2**. Coupling of **1** and **2** with the isoxazolone acceptor **3** via a Knovenegel condensation yielded chromophores ISXDO (**4**)[6b] and ISXDOBu (**5**).[6c] Similarly, coupling of **1** and **2** with isoxazolone acceptor **6** resulted in chromophores ISXTO (**7**)[6b] and ISXTOBu (**8**),[6c] respectively. Isoxazolone acceptor **3** is commercially available, while **6** was synthesized in three steps (Scheme 2). Piperidine was used as a catalyst in the Knovenegel condensation. Since the chromophores are unstable toward weak organic bases, the amount of catalyst is critical to obtain chromophores in pure form and high yields.

The thermal stability of these chromophores was studied by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The onset decomposition temperatures of the trifunctionalized chromophores **7** and **8** were around 180 °C, which is lower than those of the difunctionalized chromophores **4** and **5** (~210 °C).[6b] Presumably, introduction of the phenol group on the acceptor (instead of phenyl) decreased the thermal stability of the chromophore. The decomposition temperatures of these chromophores were similar in both nitrogen and oxygen environments, suggesting that oxygen is not a significant factor in the chromophore thermal decomposition mechanism. In addition, chromophores **7** and **8** decompose at higher temperatures in cross-linked polyurethanes (30% chromophore loading, 210 °C), which indicates that the polymer matrix can somehow stabilize chromophores.

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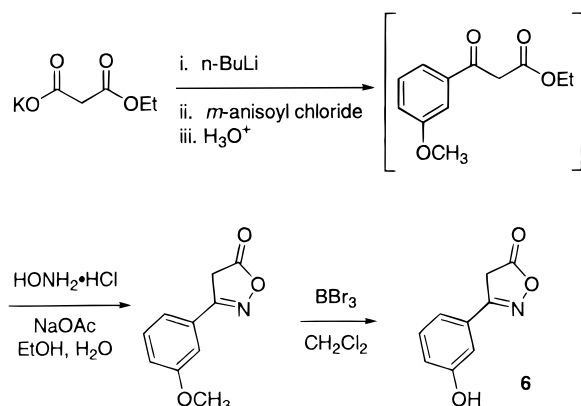
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Scheme 1
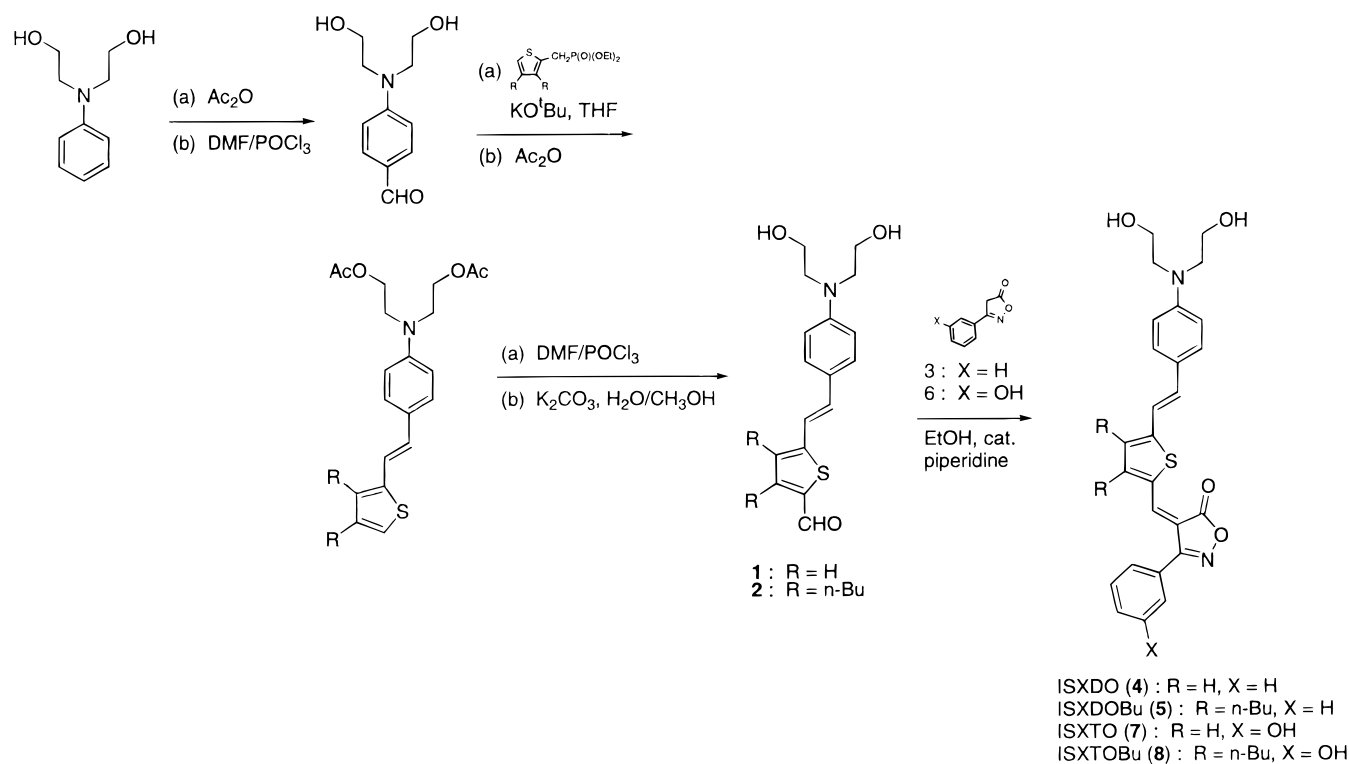
Scheme 2

The chemical stability of these chromophores has also been investigated. ISX chromophores are stable toward many organic reagents under neutral pH conditions. However, they decompose immediately under strong acidic or basic conditions. No decomposition was observed in weak acids such as acetic acid, while in weak basic condition, the decomposition takes place from a few seconds (in Et$_2$NH, aniline, piperidine, Na$_2$CO$_3$) to a few hours (in Et$_3$N). The instability of chromophores in weak base suggests avoiding the use of amines as catalysts in polyurethane reactions.

The new chromophores are soluble in most organic solvents. As expected, the chromophores with butyl substituents (**8** and **5**) are more soluble than those without butyl substituents (**7** and **4**).

The chromophores are purple in nonpolar solvents such as hexanes, and blue in polar solvents such as DMSO. A large positive solvatochromism is observed for chromophores **7** and **8**, as shown in Figure 1. Interestingly, we found that introduction of butyl groups into

chromophore **8** caused a bathochromic shift of ∼20 nm, which may be attributed to electronic structure changes of the chromophore.[7] These chromophores also exhibited different absorption maxima in the solid state. For example, chromophore **6** has a λ_{max} value of 558 nm in PMMA, and 573 nm in cross-linked polyurethane, while chromophore **7** has λ_{max} values of 575 and 590 nm in PMMA and polyurethane, respectively. The higher λ_{max} values of these chromophores in polyurethane compared to PMMA can be attributed to the higher dielectric constant of thermoset polyurethane (9.5) vs PMMA (3.9).

Reaction of these chromophores with excess tolylene diisocyanate (TDI) at 80 °C generated low molecular weight oligomers. These oligomers bear isocyanate terminal groups and thus can further reacted with a triol (triethanol amine, TEA) to give a viscous solution. High optical quality thin films can be obtained by spin-coating this solution on indium tin oxide (ITO) substrates. After addition of TEA, control of the precuring time is critical to obtaining optical quality films. Thin films from the materials precured over a 2 h duration exhibited lower poling efficiencies, which could be attributed to over-cross-linking of the polyurethane lattice. Precuring for a short period (<10 min) afforded cloudy, thus unusable films.

Corona poling was employed to induce acentric (dipolar) macroscopic chromophore order. During electric poling at elevated temperatures (80−140 °C), further cross-linking of the polyurethane oligomers proceeded simultaneously with poling. The films, before poling, were soluble in most organic solvents, which reflected the oligomeric nature of the material. Tough and insoluble films were obtained after poling. This insolu-

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(7) We have also observed a similar red shift in Disperse Red type chromophores with alkyl substituents on the phenylene backbone.
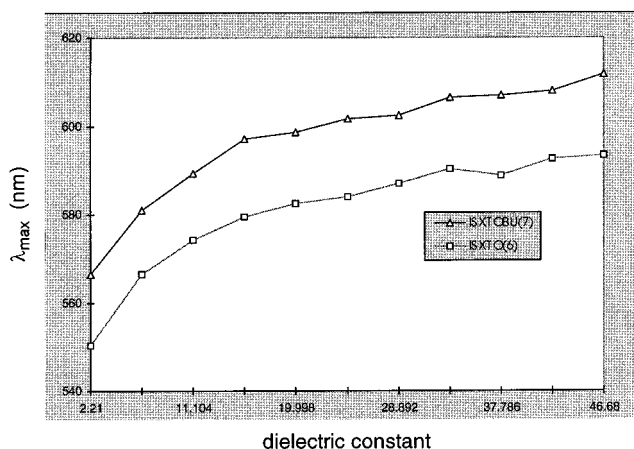
Figure 1. Solvatochromism of chromophores **6** and **7**.

bility suggested the formation of a three-dimensional cross-linked network. For the materials of this study, film thickness varied from 1.7 to 2.7 μm, depending on the precuring time and the spin rate. The refractive index of these polymer films, at the wavelength of 1.06 μm, was ~1.65.

The electrooptic coefficients (r_{33}) were measured by the ATR technique at 1.06 μm,[8a] and the value was dependent on chromophore loading density. At the same chromophore loading (35%), materials with butyl-substituted chromophores (PU-ISXTOBu and PU-ISXDOBu[6c]) gave much higher electrooptic coefficients (15−17 pm/V) than those without butyl substituents (6−9 pm/V for PU-ISXDO[6b]). The nearly doubled poling efficiency may be attributed to the suppression of the chromophore electrostatic interaction by the butyl groups on the chromophore backbone.

Chromophore **7** (ISXTO) was not soluble enough to be incorporated into polyurethane materials. After precuring and spin casting, cloudy films were obtained. The SEM picture of the film shows the crystallization of the chromophore (Figure 2).

As shown in Figure 3, the materials with trifunctionalized chromophores, e.g., **8** (PU-ISXTOBu), exhibited higher temporal stability of dipole alignment (nonlinearity) than those with difunctionalized chromophores, e.g., **5** (PU-ISXDOBu[6c]). A dynamic temporal stability of ~110 °C was achieved in the former material, in comparison with ~80 °C in the later material. This higher temporal stability may be attributed to the firm anchoring of the chromophores to the polyurethane lattice at both donor and acceptor ends in the former materials, which inhibits the mobility of the aligned chromophores.

The UV−vis−NIR spectrum of a 10% CHCl$_3$ solution of chromophore **8** is shown in Figure 4. No significant absorption was observed at 0.98, 1.06, and 1.30 μm wavelengths. The NIR spectrum of a film (1 mm thick) consisting of 30% chromophore in polyurethane is also shown in Figure 5. Although the absorption peak broadens in solid state, the absolute absorption at operational (e.g., 1.3 μm) wavelengths is still low. These spectra suggest to us that material optical loss is not dominated by intrinsic chromophore absorption.

Optical loss (e.g., see Figure 6) in these materials was measured at 0.98 μm employing the method of Teng.[8b] When chromophore **8** was doped into a polymer matrix (PMMA composite system), the resultant films exhibited moderate optical loss (1−3 dB/cm, depending on the chromophore concentration). The graph of optical loss versus chromophore concentration is given in Figure 7. From the data, we observed that the optical loss is not linearly proportional to the chromophore loading density. The highly nonlinear curve suggests that optical loss in this system is not defined by chromophore absorption, but by the formation of scattering centers induced by chromophore aggregation. As we noted previously, chromophores without butyl groups are much less soluble than the chromophores with butyl groups and experience increased chromophore−chromophore interactions. Therefore, it is much easier for the former to phase separate from the PMMA polymer matrix. The formation of chromophore aggregates caused an increase in optical loss, which became unmeasurably high in this case. The SEM picture (Figure 2) also shows this type of phase separation (crystallization). Interestingly, a sample bleached at high temperature exhibited the same optical loss value, which clearly indicates that the optical loss in these materials did not derive from the intrinsic chromophore absorption. We found that inhomogeneity of the thin films, arising during the thermosetting reaction and poling, was the major source for optical loss. This type of scattering loss can be reduced by control of processing conditions.

As noted above, there are two factors that can contribute to attenuation of electrooptic activity and increase in optical loss with increasing chromophore loading. The first is intermolecular electrostatic interactions among chromophores and the second is the free energy of mixing of the chromophore and host polymer (i.e., solute/solvent compatibility). Statistical mechanical calculations and comparison of theoretical and experimental results for a number of systems strongly suggest that the former is important.[9] The nearly quantitative agreement between theory and experiment[9] cannot be ignored and it is intuitively reasonable when it is realized that at high chromophore loading intermolecular electrostatic interactions significantly exceed thermal energies for high hyperpolarizability (polarizability/dipole moment) chromophores. The very existence of a large dipole moment ensures that intermolecular electrostatic interactions will favor centric chromophore order over acentric order.[9] The quantitative contribution of chromophore/polymer host interactions is more difficult to assess, and we make no effort to do so here. Intuitively, we believe such interactions to be somewhat important.

Experimental Section

Anhydrous dioxane, THF, tolylenediisocyanate (TDI), triethanolamine (TEA) were purchased from Aldrich. TDI was distilled and kept in a nitrogen atmosphere until used. Ethyl

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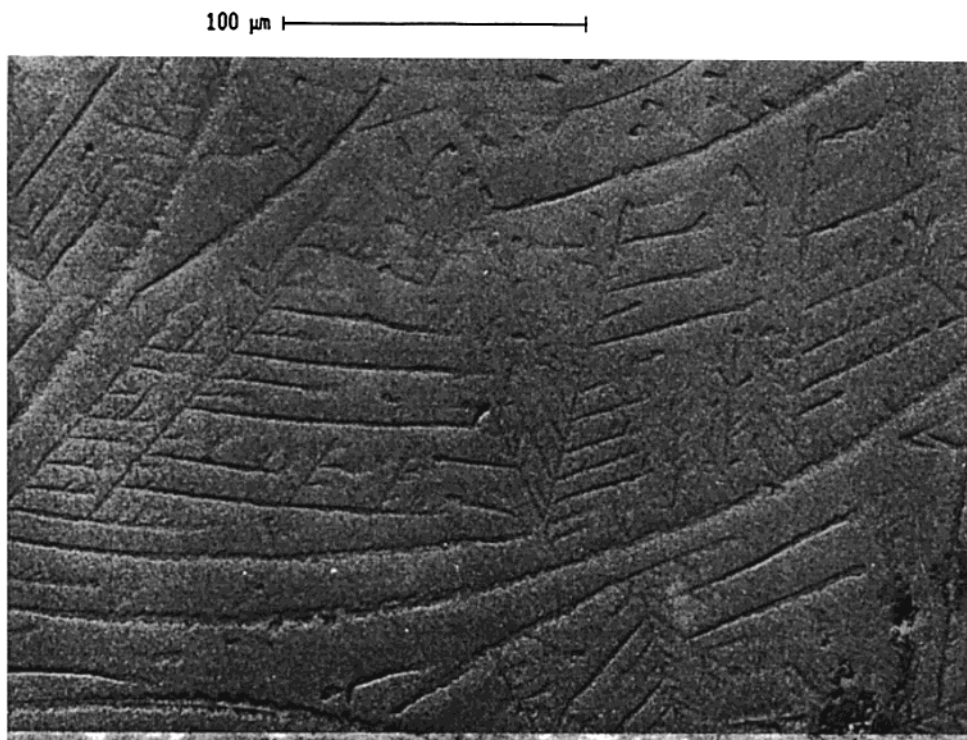
100 μm ⊢━━━━━━━━━━━━━━━━⊣

Figure 2. Phase separation in thin films containing chromophore **7**.
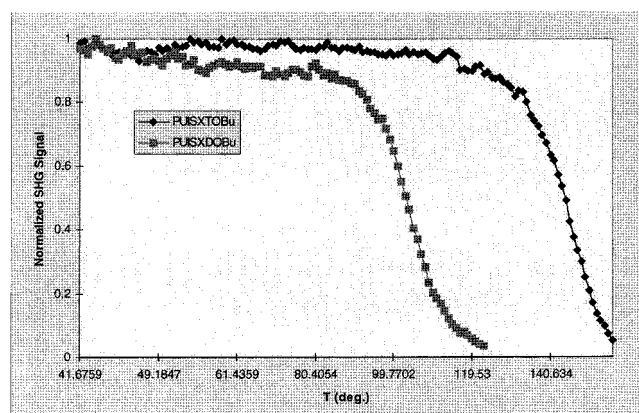

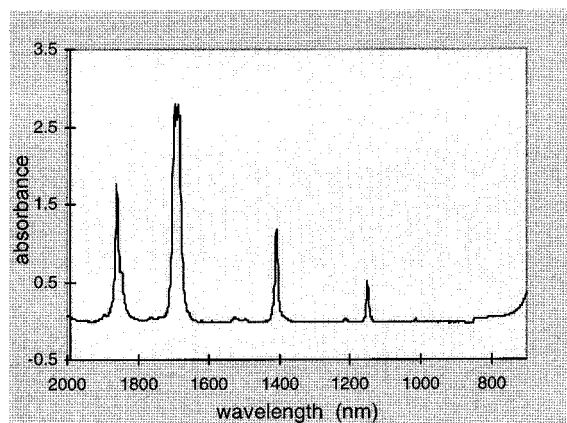**Figure 3.** Comparison of temporal stabilities of PU−ISX-TOBu and PU−ISXDOBu.

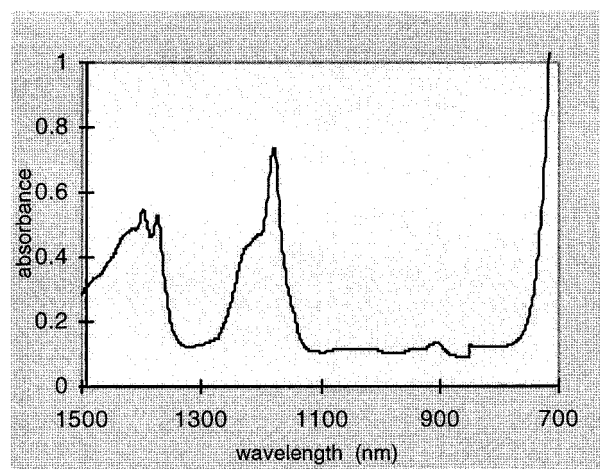**Figure 4.** Near-infrared absorption spectrum of ISXTOBu in chloroform (10 wt/vol %).

Figure 5. Near-infrared absorption spectrum of PU−ISX-TOBu (30 wt/wt %, 1 mm thick).

using a Perkin-Elmer Lambda-4C UV−vis spectrophotometer with a 1 cm^3 quartz cell. Decomposition temperatures were determined with a Shimadzu Thermogravimetric Analyzer, under nitrogen (or oxygen) atmosphere and using a heating rate of 5 °C/min. Melting points and polymerization temperatures measurements were taken by employing a Perkin-Elmer DSC-7. Near-IR absorption was measured utilizing an AVIV Spectrophotometer 14 DS UV−vis−IR. FTIR measurements (using a Perkin-Elmer 7700 IR-FT spectrometer) were made on pressed KBr pellets or polymer films spin cast on a sodium chloride crystal disk.

3-(*m*-Methoxyphenyl)-5-isoxazolone. A THF solution (1000 mL) of ethyl hydrogen malonate (77.92 g, 0.587 mol) and 2,2′-dipyridyl (indicator, 30 mg) was cooled to −70 °C, and then 750 mL of *n*-butyllithium (1.6 M in hexane, 1.2 mol) was added dropwise under argon atmosphere until the persistence of a pink color was observed. The reaction mixture was warmed to −5 °C, stirred for 30 min, and then recooled to −70 °C. A solution of *m*-anisoyl chloride (58.59 g, 0.34 mol) in 80 mL of tetrahydrofuran was added dropwise. After this addition, the mixture was stirred at −70 °C for 1 h and then warmed to
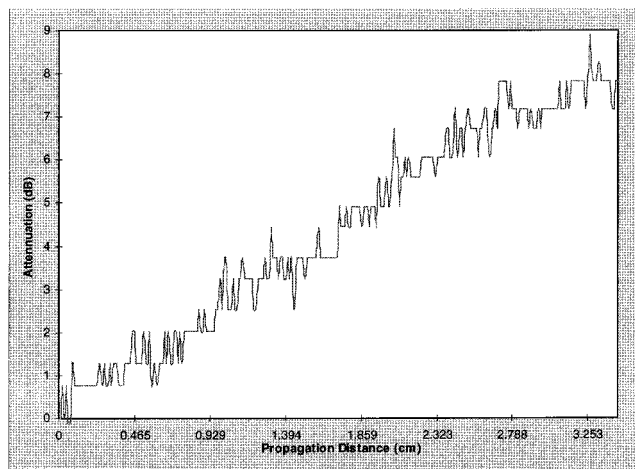
hydrogen malonate was purchased from Lancaster and used without further purification.

^{1}H and ^{13}C{^{1}H} NMR spectra were acquired on a Bruker-250-FT-NMR spectrometer. Optical spectra were obtained

Figure 6. Optical attenuation profile of chromophore **7** doped in poly(methyl methacrylate).
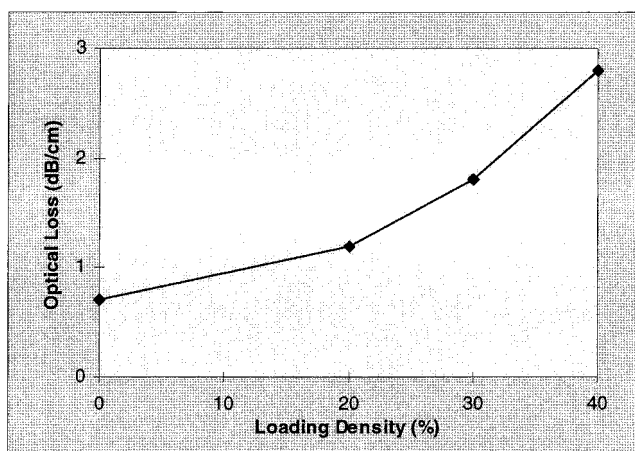

Figure 7. Optical loss versus loading density for chromophore **7** doped in poly(methyl methacrylate) at various concentrations.

−20 °C. This solution was then quenched with 120 mL of concentrated HCl in 250 mL of water. The resulting mixture was rotovapped to remove THF, diluted with 500 mL of water, and extracted with CH_2Cl_2 (2 × 100 mL). The combined CH_2Cl_2 extracts were washed with saturated $NaHCO_3$ solution, water, dried over $MgSO_4$, and evaporated to dryness (77.28 g).

The above crude product was mixed with ethanol (400 mL), hydroxyamine hydrochloride (24.45 g, 0.323 mol), sodium acetate trihydrate (47.9 g, 0.352 mol), and water (250 mL). The resulting solution was refluxed for 65 min and then cooled to 0 °C. Red crystals were obtained. Recrystallization from 1:1 (v:v) mixture of ethanol and water yielded shiny red flake crystals (29.77 g, 45.8%): mp 113−115 °C; ^{1}H NMR (DMSO-d_6) δ 3.84 (s, 3 H), 4.35 (br s, 1 H), 5.78 (br s, 1 H), 7.14 (d, 7.8 Hz, 1 H), 7.31 (s, 1 H), 7.34 (d, 8.5 Hz, 2 H), 7.46 (t, 7.8 Hz, 1 H) (^{1}H NMR shows this compound to exist in the enol form, in this solvent); ^{13}C NMR (DMSO-d_6) δ 34.84, 55.52, 80.64, 111.86, 116.92, 117.40, 118.90, 129.25, 130.45, 159.74. Anal. $C_{10}H_9NO_3$ requires C, 62.82; H, 4.74; N, 7.33. Found: C, 62.94; H, 4.80; N, 7.31.

3-(*m*-Hydroxyphenyl)-5-isoxazolone (6). A total of 3 g (0.0157 mol) of 3-(methoxyphenyl)isoxazolone was dissolved in 75 mL of CH_2Cl_2, and the solution was cooled to −78 °C. Then, 47 mL of 1.0 M hexane solution of BBr_3 (0.047 mol) was added dropwise. The mixture was stirred at −78 °C for 1 h, followed by 2 h at room temperature. Pink solids were precipitated out from the solution to yield 2.7 g of **6** (93%): ^{1}H NMR (acetone-d_6) δ 8.01 (s, 1 H), 7.43 (m, 2 H), 7.32 (d, 1 H), 7.15 (d, 1 H), 3.86 (s, 2 H). Anal. $C_9H_7NO_3$ requires C, 61.02; H, 3.98; N, 7.91. Found: C, 60.94; H, 4.00; N, 7.81.

Chromophore 8. A total of 0.3 g (0.6993 mmol) of **2** and 0.12 g (0.6993 mmol) of **6** were dissolved in 10 mL of CH_2Cl_2. Two drops of a 10% piperidine solution in CH_2Cl_2 were added. The mixture was refluxed for 5 h. Half of the solvent was evaporated and then the product was precipitated out of the solution. The product was washed with cold methanol, yield 92%: ^{1}H NMR (acetone-d_6) δ 8.82 (s, 1 H), 7.63 (s, 1 H), 7.54 (d, 2 H) 7.37 (m, 4 H isoxazolone ph), 6.81 (d, 2 H) 4.185 (t, 2 H), 3.77 (q, 4 H), 3.6 (q, 4 H), 2.75 (m, 6 H), 1.47 (m, 10 H), 0.9 (dt, 4 H); [13]NMR (acetone-d_6) 166.45, 165.4, 159.03, 155.61, 160.68, 141.52, 138.31, 135.97, 131.27, 130.8, 130.0, 129.4, 124.7, 120.6, 118.28, 116.3, 115.5, 113.1, 109.0, 60.17, 54.8, 35.37, 34.07, 28.11, 27.06, 23.66, 23.41, 14.03, 13.83. Anal. $C_{34}H_{40}N_2O_5S$ requires C, 69.36; H, 6.85; N, 4.76. Found: C, 69.50; H, 6.72; N, 4.67.

Polyurethane. A mixture of the ISX chromophores and TDI in dioxane was heated at 80 °C for 40 min, and then a dioxane solution of TEA was added. The mixture was further cured at 80 °C for 40 min. The resulting viscous solution was filtered through a 0.2-μm microfilter, and then spin-coated onto ITO-coated glass substrates and dried in vacuo.

Poling and Optical Measurements. Corona poling was employed to align the NLO chromophores, and the poling protocols were determined from IR and DSC characterization of the films. Electrooptic coefficient and thickness of the films were measured by the attenuated total reflectance (ATR) technique at 1.064 μm.[8a] Temporal stability of dipole alignment was measured by monitoring the decay of the second-harmonic signal as a function of temperature. Optical loss data were measured at 0.98 mm, using the immersion technique described by Teng.[8b]

Conclusions

Minor modification of chromophores resulted in significant changes of the properties of ISX second-order NLO materials. Introduction of alkyl groups onto isoxazolone-based chromophores likely inhibited chromophore−chromophore close approach and thus attenuated intermolecular electrostatic interactions. As predicted by modified London theory,[9] chromophore intermolecular electrostatic interactions tend to align chromophores in an antiparallel fashion competing with the poling force which acts to align chromophores parallel to each other. By attenuating chromophore intermolecular electrostatic interactions, poling efficiency was enhanced dramatically. In addition, attachment of alkyl groups to the chromophore backbone increased the chromophore solubility, which together with the aforementioned attenuation of chromophore−chromophore electrostatic interactions, suppressed crystallization, and optical loss.

By anchoring chromophores, to a three-dimensional cross-linked polymer lattice, from both donor and acceptor ends, the temporal stability of poling-induced electrooptic activity was enhanced significantly. Optical loss in our thermosetting NLO materials originated from the scattering centers formed during thermosetting reactions, rather than from intrinsic resonance absorption by chromophores.