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Progress toward Device-Quality Second-Order Nonlinear Optical Materials. 1. Influence of Composition and Processing Conditions on Nonlinearity, Temporal Stability, and Optical Loss

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We report the incorporation of a new trifunctionalized disperse red-type chromophore into a polyurethane thermosetting system. Six polymers with different chromophore loading and NCO/OH ratios were synthesized. This system exhibited very good poling efficiencies, and the optimum chromophore loading density ranged from 30 to 40%. Decreasing chromophore loading caused an attenuation of macroscopic nonlinearity, due to the lowering of chromophore concentration in the polymer; while increasing chromophore loading above 40% also attenuated the nonlinearity, presumably because of chromophore−chromophore electrostatic interactions starting to compete with the electric field−chromophore dipole interactions at high chromophore concentration. Materials with a NCO/OH ratio equal to or greater than unity have much higher temporal stability of dipole alignment than materials with a NCO/OH ratio less than 1. By anchoring the chromophores at both the donor and acceptor ends, the temporal stability of dipole alignment was enhanced significantly. For such materials, the optical loss of unpoled materials with nonstoichiometric NCO/OH ratios was observed to be high; however, this loss could be reduced to less than 1 dB/cm by adjusting the NCO/OH ratio to unity. It is generally believed that poling induced optical loss is a serious problem associated with second-order NLO materials prepared by electric field poling. In our study, we found this type of optical loss could be reduced to only 0.2 dB/cm by careful control of processing conditions.

Introduction

Organic second-order nonlinear optical (NLO) materials have attracted considerable attention due to their potential application in optical signal processing and telecommunications.[1,2] These materials are typically made from organic chromophores with high microscopic nonlinearities (β), incorporated into polymer matrixes, and poled with an electric field to achieve a noncentrosymmetric dipole alignment.[2a] Recently, many high-β chromophores have been reported.[2c−g] If their remarkably high microscopic nonlinearities could be efficiently translated into macroscopic nonlinearities, the new organic materials derived from these high-β chromophores would surpass traditional electrooptic crystals used in integrated electrooptic modulators.[3] To obtain device-quality materials, several critical issues must be addressed:[2a]. Materials must exhibit (1) good processibility, which can be achieved by incorporation of chromophores into polymer matrices; (2) high macroscopic nonlinearity, which requires an efficient dipole alignment induced by an electric field (good poling efficiency); (3) high temporal stability of dipole orientation, which can be achieved by attaching chromophores

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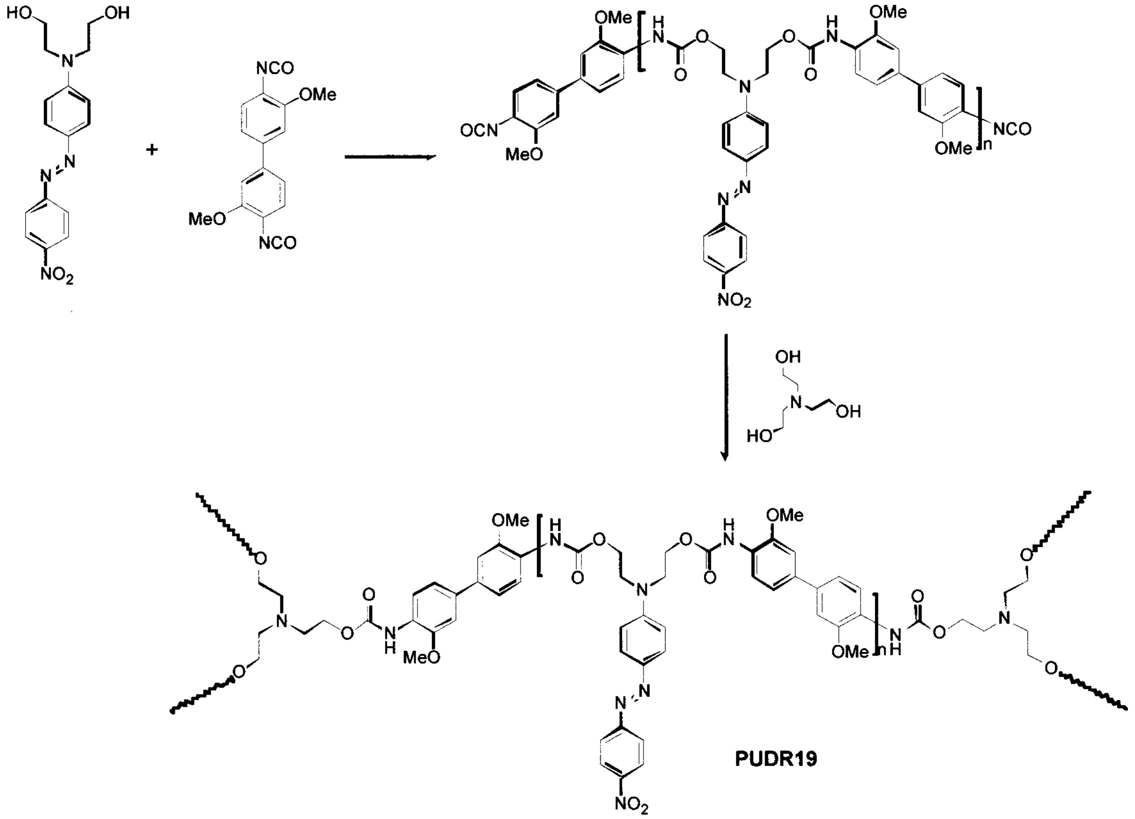
Scheme 1



to high-T_g polymers or cross-linked organic networks; (4) low optical loss at the operating wavelength.

Optimization of any individual above-mentioned property is not difficult; however, simultaneous realization of all requirements to achieve device-quality materials is not a trivial task.[2a,b] Since all these properties are interrelated, optimization of one very often causes the attenuation of others. For example, to achieve a high temporal stability of dipole alignment, researchers have employed a high-T_g polymer (polyimide), in which the dipole orientation can be stabilized at operational temperatures of electrooptic devices due to the freezing of chromophore movement when the temperature is decreased from the poling temperature.[4] However, since the processing (spin casting, poling) of a high-T_g polymer such as polyimide demands high temperatures or involves strong acidic conditions, high optical quality films are not always achieved. In addition, the decomposition of chromophores, especially those with high molecular hyperpolarizabilities, may occur.[2a,5] An attempt to gain a high temporal stability with high-T_g polymers often results in unsatisfactory processibility, low poling efficiency, and high optical loss.

To achieve a good balance of processibility, nonlinearity, temporal stability, and optical loss, new approaches were developed in this laboratory and elsewhere, in which processible oligomers were poled and thermally cured into cross-linked materials under mild conditions.[2a,b] This approach generally offered a combination of good processibility and good poling efficiency. In addition, since the resulting cross-linked materials exhibit high glass transition temperatures, the dipole orientation may be stabilized at elevated temperatures.

Cross-linked polyurethanes have shown great potential in NLO applications, due to ease of synthesis, the ability to form high-quality films, high glass transition temperatures, and good solvent resistance.[6] An example is the PUDR19 material, in which the donor end of the chromophore disperse-red 19 is covalently attached to the polyurethane network.[6a–c] The synthesis of PUDR19 is shown in Scheme 1. This material offers a relatively high E–O coefficient, good temporal stability, and low optical loss, and a good combination of these properties makes PUDR19 a useful material for the fabrication of prototype devices.[7] During the course of synthesis and processing of PUDR19, we found that good properties are not always achievable, and subtle changes in processing conditions often caused a dra-

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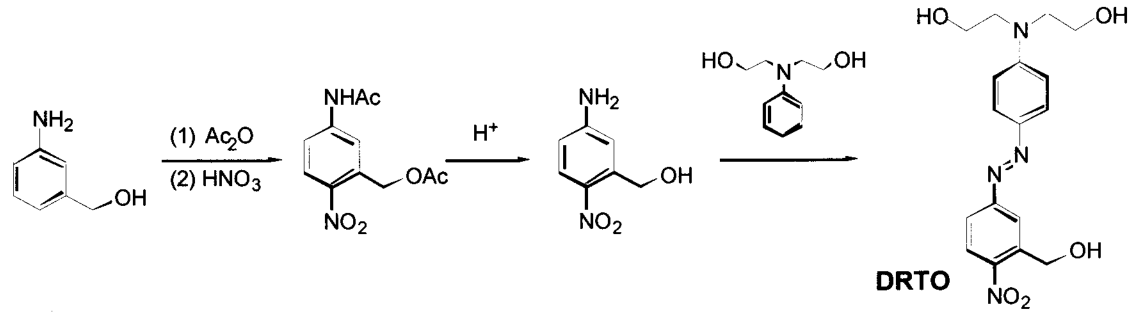
Table 1. Linear and Nonlinear Optical Properties of PUDRTO Polymers

polymers	LD (%)[a]	NCO/OH	M_w/M_n[b]	n[d]	r_{33} (pm/V)[e]	T_{stab} (°C)[f]	loss (dB/cm)
PUDRTO−1	42	1.6	800/590	1.720	10	120	N/A
PUDRTO−2	35	2.2	590/430	1.640−1.720	14.4	110−120	6.6[g]
n-PUDRTO−1	35	0.57	890/590[c]	1.640−1.660	12	90	cloudy films
n-PUDRTO−2	37	1.0	980/640[c]	1.689−1.692	14.8	110	0.86;[h] 3.6[g]
n-PUDRTO−3	32	1.0	1200/700[c]	1.675−1.676	12	115	1.0[h]
r-PUDRTO	30	1.0	N/A	1.640−1.660	15.4	90	3.4;[h] 6.6[g]

[a] Loading density of DRTO, represented by percentage of $(HOCH_2CH_2)_2C_6H_4(N{=}N)C_6H_4NO_2$. [b] Weight and number average molecular weight of prepolymers, polystyrene standards, anhydrous THF as solvent. [c] Prepolymer after addition of TEA. [d] Refractive indexes at 1.06 μm, obtained from ATR method. [e] Measured at 1.06 μm with ATR technique. [f] Temporal stability of nonlinearity, represented by the temperatures at that the SHG signals start to drop. [g] Optical loss measured at 0.98 μm before poling. [h] Optical loss measured at 1.3 μm before poling.

Scheme 2



matic attenuation on poling efficiency and temporal stability. Moreover, high optical loss materials can result from inadequate attention to processing conditions. This prompted us to pursue a systematic study of the influence of processing conditions on optical and NLO properties.

In this paper, we report synthesis and processing of polyurethane networks containing a new trifunctionalized disperse red-type chromophore. A systematic study of influence of polymer composition and processing conditions on NLO properties has been pursued. During our study, we found that good poling efficiency could be achieved by applying an electric field in the early stages of polymerization. Temporal stability could be enhanced by attaching chromophores to the polyurethane network via both donor and acceptor ends. By careful control of the processing conditions, we were able to reduce the poling-induced optical loss from ca. 9 to 0.2 dB/cm. The various sources of optical loss in organic second-order NLO materials will be discussed.[8,9]

Results and Discussions

Materials Syntheses and Characterization. The chromophore disperse red triol (DRTO) was synthesized in three steps, as shown in Scheme 2. The detailed procedure has been reported previously.[10] To remove trace amounts of ionic impurities, which may produce detrimental effects during subsequent electric field poling, the chromophore was recrystallized from methanol several times before use. DRTO is soluble in common organic solvents and exists as shiny needles after recrystallization. It is stable in acidic and basic conditions, melts at 162 °C, and decomposes at 270 °C.

It is well-known that the properties of polyurethanes are strongly affected by composition and stoichiometry of OH and NCO functionalities.[11] To systematically investigate the influence of materials' composition and stoichiometry on poling efficiency, temporal stability, and optical loss, we synthesized six different thermosetting polyurethanes from DRTO and tolylenediisocyanate (TDI, Table 1). Reaction of DRTO with excess of TDI at 80 °C afforded low molecular weight oligomers, which were characterized by gel permeation chromatography with anhydrous THF as the solvent (Table 1). Direct spin-coating of these oligomers gave high optical quality thin films, which were then subjected to electric poling to form materials PUDRTO-1 and PUDRTO-2 (Scheme 3). As shown in Table 1, PUDRTO materials contain an excess of isocyanate functionality, which may self-react during the poling at elevated temperature to form allophanate linkages (vide infra).[11] Neutralization of these excess isocyanate groups with triethanolamine (TEA), followed by spin-coating and electric field poling, gave materials n-PUDRTO-1, n-PUDRTO-2, and n-

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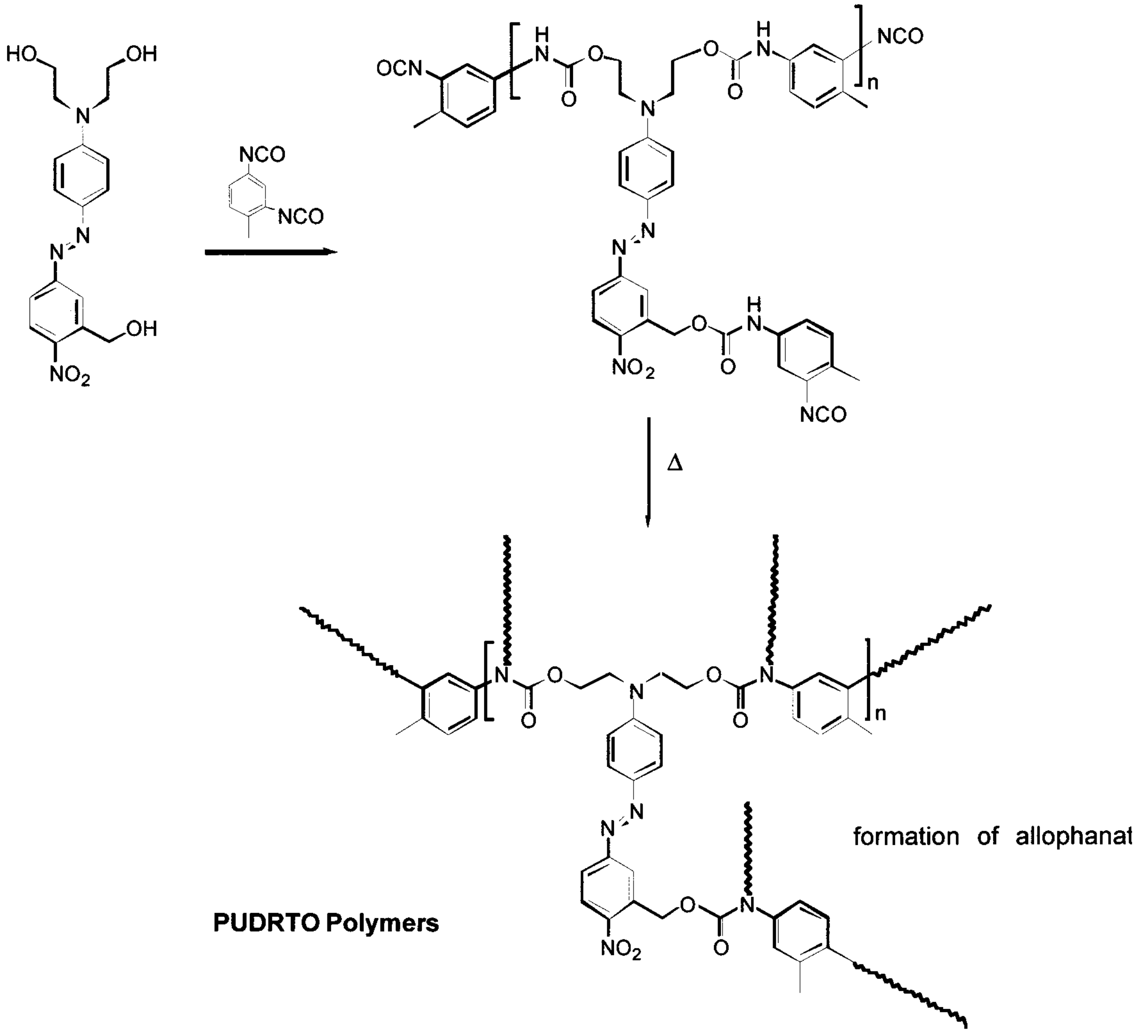
Scheme 3



PUDRTO-3 (Scheme 4). The material r-PUDRTO was obtained via reaction of TDI with 2 equiv of 2,5-dimethyl-2,5-hexanediol (to form oligomers with isocyanate terminal groups), followed by reaction with stoichiometric DRTO (Scheme 5). Use of other diisocyanates was attempted in our study; however, their use usually yielded low-quality films with extraordinary scattering loss. We also found that precuring time had a very important effect on film quality. Precuring for a short period of time gave solutions with low viscosity, therefore affording cloudy films, while precuring for a long time either gave a gel that could not be spun on substrates or formed good-quality films that could not be poled efficiently.

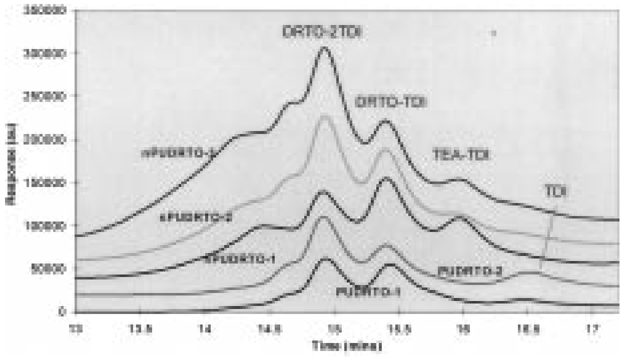
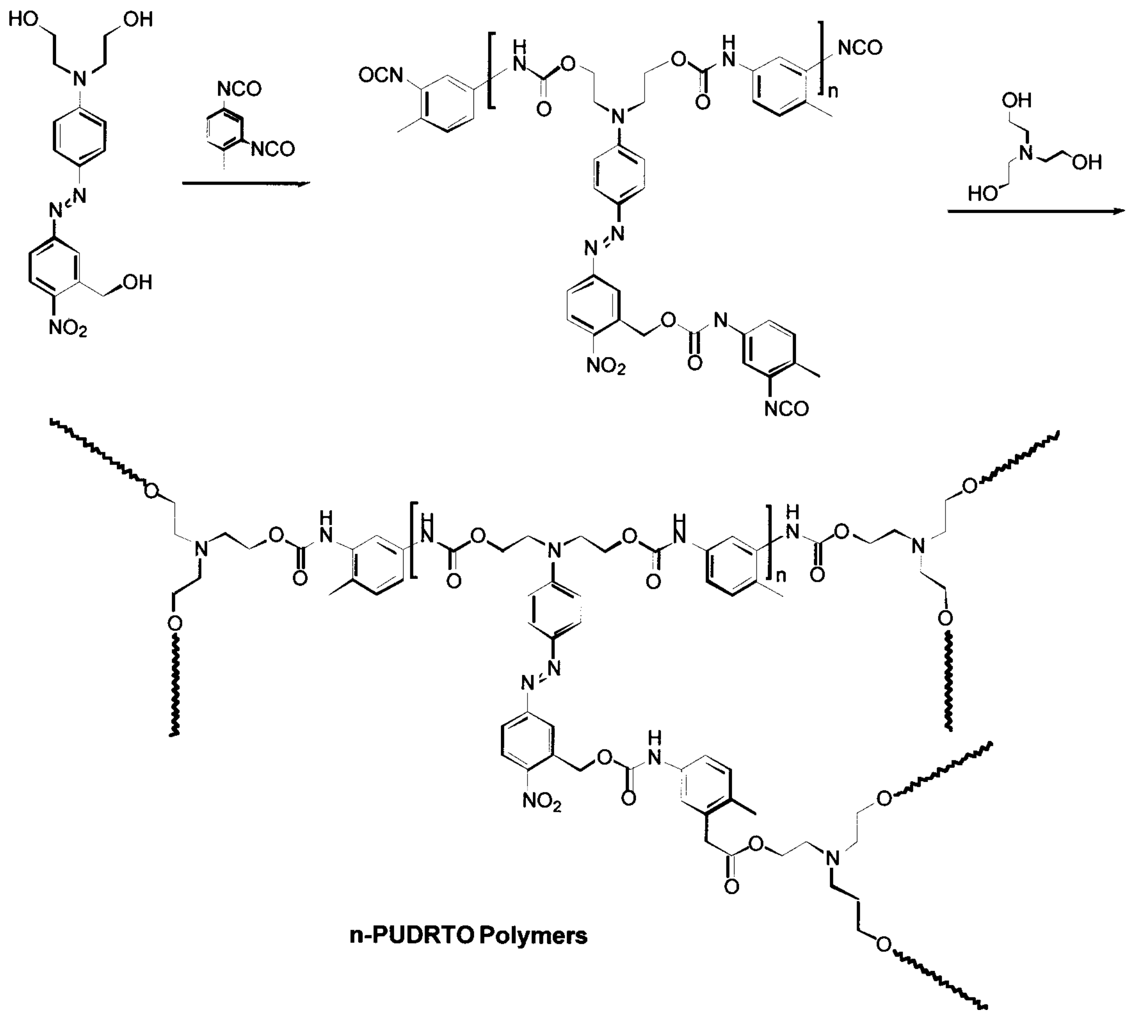


Figure 1. GPC traces of PUDRTO prepolymers before electric poling.

The films before poling were soft and could be redissolved in organic solvents. GPC traces for these prepolymers are shown in Figure 1, clearly indicating the oligomeric nature of the materials at this stage. During the electric poling, elevated temperatures (e.g., 120 °C) were employed. At these high temperatures, further reaction between isocyanate and hydroxyl groups (to form urethane linkages) or between isocyanate groups (to form allophanate linkages) occurred to form a fully cross-linked polyurethane network. After electric poling, the films were tough and solvent resistant. In addition, the isocyanate resonance peak in their FT-IR spectra disappeared. These observations indicated the formation of three-dimensional polyurethane networks during the poling process.

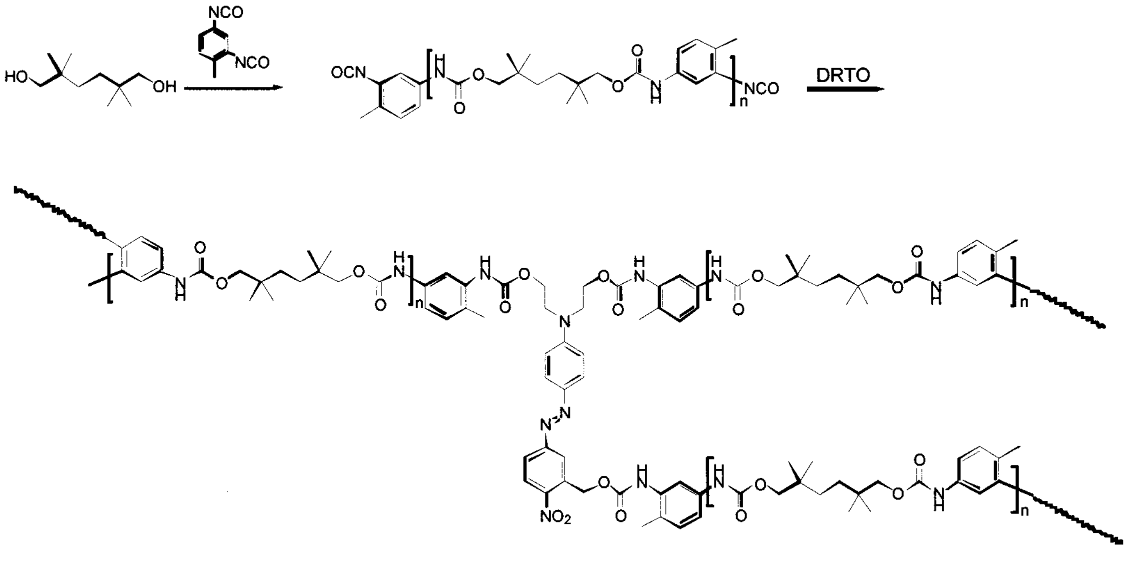
From FT-IR studies, we found that reaction of hydroxyl and isocyanate functionalities proceeded much faster in solution than in solid state. At 80 °C, the reaction of a stoichiometric amount of diisocyanate and DRTO afforded an insoluble gel within 1.5 h, and the reaction went to completion in a few hours, as indicated by the disappearance of the isocyanate resonance peak in the IR spectra. In contrast, this reaction was found much slower in solid films; it did not go to completion even after heating of the films at 80 °C for 24 h. At

Scheme 4



n-PUDRTO Polymers

Scheme 5



r-PUDRTO

120 °C, the reaction went to completion in 100 min, as evidenced by the disappearance of the isocyanate resonance at 2250 cm^{-1} in the IR spectra.

It is worth noting that during the processing, the presence of water molecules in the prepolymer sample is detrimental to film quality, as well as the poling efficiency and the temporal stability of the final materials. It was consistently observed that the films spun in a humid environment were cloudy and could not be poled efficiently. Under an optical microscope, white spots were observed inside the films, which were presumably generated from the reaction of isocyanate groups with water molecules. It is well-known that isocynate reacts with water to generate amine and carbon dioxide,[11] and this gas formation (CO_2) most likely is the source of the white spots we observed in the polymer films under humid conditions. However, we cannot rule out the possibility of phase separation, since in a polymer with excess OH functionality we also observed similar whitening phenomenon. Reaction of water with isocyanate will cause the mismatch of the OH functionality with the NCO functionality and leave an excess of OH functionality. Considering the small molecular weight of water (18, vs 361 for DRTO), it is not difficult to understand that even a very small amount of moisture may cause a serious problem with respect to the material properties. To avoid the influence of atmospheric moisture, we therefore processed all our materials in a nitrogen-filled glovebox with a moisture level less than 5 ppm.

Recently, Boogers et al.[6f] reported the synthesis of polyurethanes containing DANS chromophores. A distinct T_g of 155 °C was observed in their thermosetting materials, which was explained by the low degree of cross-linking. In their procedure, prepolymers were precured in DMF at 80 °C for 10 min and 145 °C for 30 min. The solvent they used (DMF) is generally known for high content of water and high affinity for water molecules in environment. Perhaps, the presence of water molecules in DMF solvent consumed part of the isocyanate functionality and caused the nonstoichiometry of NCO/OH ratio in the final materials. This nonstoichiometry likely resulted in incomplete cross-linking, which may account for the low temporal stability of their polymer system. Our observation that processing of materials in a humid environment causes the attenuation of temporal stability is consistent with Boogers' results.

Electric Poling. After the materials were spun on glass substrates coated with indium−tin oxide (ITO) or gold, they were dried in vacuo overnight to remove the excess solvent trapped inside. At this stage, films were still soft, and immediate application of an electric field can cause damage of films and introduce significant poling-induced optical losses. To maintain film quality during poling, an electric field was normally applied after heating films at a higher temperature (e.g., 100 °C) for a few minutes. This preheating is crucial to reduction of poling induced optical loss (vide infra).[8a]

A typical poling protocol is shown in Figure 2. After films were attached on the poling stage, the temperature was then ramped to 80 °C in 5 min. The electric field was turned on at ca. 70 °C, and a low voltage (4 kV) was applied at this time. After heating at 80 °C for 15 min, the temperature was raised to 120 °C, and a voltage of 6 kV was applied. Poling was continued at 120 °C for 30 min, and then the temperature was further increased to 140 °C. Finally, the films were cooled to room temperature while the electric field was maintained.

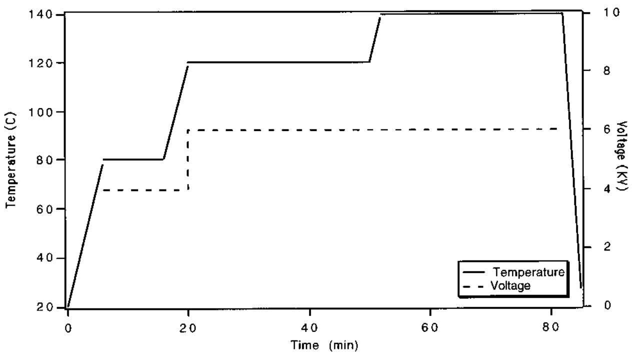


Figure 2. Typical poling profile used for thermosetting polyurethanes cross-linkable trilinker polymers.

Optical Measurements. The materials made from the above procedures gave high optical quality films. The film thickness and refractive indexes of these materials were measured from the attenuated total reflection (ATR) method.[12] The thickness varied from 0.7 to 2 μm, depending on the precuring time and the spin rate. The refractive indexes of the films varied from 1.64 to 1.72, depending on chromophore loading density (Table 1). Materials with higher loading density have higher refractive indexes, due to higher chromophore concentration.

The electrooptic coefficients (r_{33}) of PUDRTO materials were measured by the ATR technique, and the data are listed in Table 1 along with the loading density. The PUDRTO system afforded better poling efficiency than the commonly used PUDR19 system. The E−O coefficients (r_{33}) for PUDR19 are typically 6−8 pm/V, and occasionally materials with r_{33} above 10−12 pm/V can be obtained. For PUDRTO materials, the average E−O coefficient (r_{33}) is around 12−14 pm/V, and occasionally, r_{33} values as high as 15 pm/V can be achieved. We found that the optimum chromophore loading ranged from 30% to 40%. Further decrease of chromophore loading causes a significant attenuation of E−O coefficient, due to the lowering of chromophore concentration in polymer. Increase of loading density above 40% also attenuated the E−O coefficient (e.g., PUDRTO-1), presumably due to the strong chromophore−chromophore electrostatic interaction, which may defeat the poling force (the interaction between electric field and chromophore dipole). In addition, chromophore aggregation was frequently observed during processing in polymer systems with very high chromophore loading.

Prepolymers cured at elevated temperatures for a very long time usually have a high extent of cross-linking and some associated attenuation of poling efficiency. Prepolymers cured for shorter times normally gave materials that exhibit very good poling efficiency, presumably the low extent of cross-linking in these "soft" films allows the chromophores to align relatively easy. However, film damage may occur for these "soft" films, and a good balance of lattice hardness needs to be maintained.

Temporal Stability of Dipole Alignment. The temporal stability of dipole alignment of PUDRTO materials was measured by monitoring the decay of the second harmonic generation signal as a function of temperature. We define the temperature at which the SHG signal starts to drop as the temporal stability. We found generally that the PUDRTO materials exhibited higher temporal stability than the PUDR19 material

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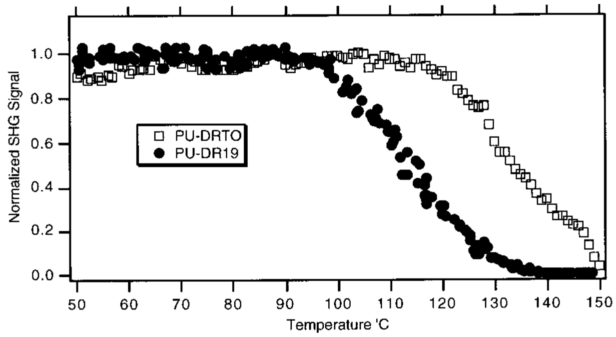


Figure 3. Temporal stability of typical PUDR19 and PUDRTO materials. The heating rate was 10 °C/min.

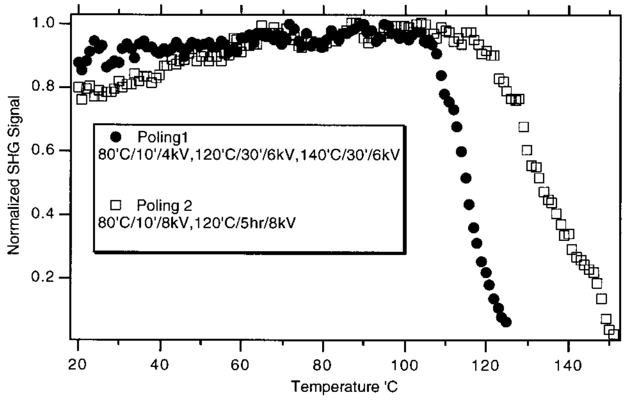
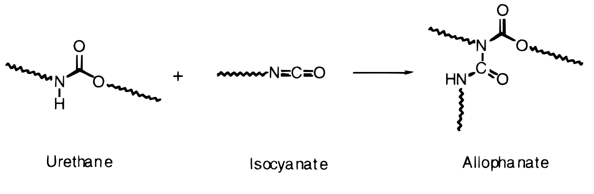


Figure 4. Temporal stability of PUDRTO-1 material, with short and long time poling at elevated temperatures. The heating rate was 10 °C/min.

(Figure 3). The temporal stability for PUDRTO materials is typically around 90−120 °C without compromise of the electrooptic coefficient (Table 1); occasionally this value can reach above 125 °C; while the typical temporal stability for PUDR19 material is ca. 80−95 °C, occasionally materials with temporal stability above 100 °C can be obtained. The higher temporal stability of PUDRTO materials can be attributed to the firm anchoring of the DRTO chromophores to the polyurethane lattice at both donor and acceptor ends, which strongly inhibits the mobility of the aligned chromophores.

Materials with an excess of isocyanate groups (NCO/OH > 1, e.g., PUDRTO-1 and PUDRTO-2) have the highest temporal stability of all the PUDRTO materials. This temporal stability can be further enhanced by poling for a longer period of time at elevated temperatures. For example, we observed an increase of temporal stability by 10 °C when the same film of PUDRTO-2 was subjected to a longer poling period at 120 °C (Figure 4). This slightly enhanced temporal stability can be attributed to the slow formation of allophanates (eq 1),[11] which was evident from our FT-IR experiments. At high temperature, the excess isocyanate groups can further react with the NH functionality in the urethane linkages to form extended cross-link sites. It is well-known in the polyurethane industry that the formation of allophanate occurs at high temperature and leads to additional cross-linking, which serves to improve the thermal properties of polyurethane networks.[11]

 (1)

Materials with stoichiometric numbers NCO and OH groups (NCO/OH = 1, n-PUDRTO-2 and n-PUDRTO-3) have comparable temporal stability to the PUDRTO-1 and -2 materials, while materials with a NCO/OH ratio below 1 exhibited reduced temporal stability (cf. 90 °C for n-PUDRTO-1). It is not difficult to understand that in materials with a NCO/OH ratio of 1, a fully cross-linked network forms at elevated temperature; therefore those materials should have the highest glass transition temperature and give the highest temporal stability. Materials with excess NCO functionality may also give a fully cross-linked lattice because the excess NCO produces allophanates at high temperature, which leads to completion of cross-linking and stabilizes the dipole orientation. The FT-IR spectrum of these materials (after poling) did not show the distinct absorption peak of NCO (ca. 2200 cm^{-1}), which suggests the further reaction of excess NCO to form allophanates. In contrast, the material with excess hydroxyl functionality cannot form a fully cross-linked network, even after high-temperature curing since the dangling hydroxyl groups do not undergo self-reaction. This explains the low temporal stability of the n-PUDRTO-1 material. When flexible chains are introduced into the polymer lattice, the temporal stability also drops significantly, presumably due to the ease of free movement of chromophores in the "flexible" network. This effect may explain the low temporal stability of the r-PUDRTO material (temporal stability of ca. 90 °C).

Optical Loss. One of the critical requirements for device-quality second-order NLO materials is low optical loss at the operating wavelength.[2a] However, sufficient attention has not been focused on this issue. In contrast to the large number of papers published on the improvement of macroscopic nonlinearity and temporal stability,[2a] very few papers on optical loss of NLO materials exist in the literature.[8,9]

Optical loss may be caused by either intrinsic absorption of NLO chromophores at the operating wavelength, or the scattering of light from physical scattering centers generated during processing.[8a] To determine the intrinsic absorption loss of the chromophore, we recorded UV−vis−NIR absorption spectra of 20% solutions (various solvents) and of 1 mm thick solid 20% chromophore/PMMA films. The optical densities at the operational wavelengths (either 980 nm or 1.3 μm) was then compared with that of the pure solvent or polymer matrix. We found generally that chromophores with λ_{max} values below 600 nm did not have significant absorption at wavelengths of 980 or 1300 nm, and the loss measured in a PMMA host via an immersion technique[13] is around 1 dB/cm. These observations suggest that the intrinsic absorption of individual chromophores with λ_{max} below 600 nm does not contribute significantly to optical loss of the final materials. In this study, the chromophore DRTO has a λ_{max} value

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[13] Teng, C. *Appl. Opt.* **1993**, *32*, 1051.

of 470 nm, which is far from the operating wavelengths of electrooptic modulators. In its near-IR spectrum region, peaks corresponding to C−H overtones were observed at ca. 1200 and 1500 nm, but other than these no significant absorption could be detected. We believe that the intrinsic absorption loss of nonaggregating DRTO chromophores will not contribute to the optical loss of the final PUDRTO materials. Therefore, in this work, we focus on manipulation of materials composition and processing conditions to reduce the optical losses generated during material processing.

In our study, the optical loss data were measured via an immersion technique.[13] To exclude the poling-induced optical loss, we first measured the optical losses of unpoled materials at both 980 nm and 1.3 μm, and the data are summarized in Table 1. Materials with nonstoichiometric NCO/OH ratio have very high loss even before poling. For example, the PUDRTO-2 material (with a NCO/OH ratio of 2.2) has the appearance of a clear film with a measured loss of 6.6 dB/cm at 1.3 μm, while the n-PUDRTO-1 (with a NCO/OH ratio of 0.57) is a cloudy film with an unmeasurably high loss. We attempted to vary the processing conditions (e.g., precuring time, drying condition, etc.) for these materials, and the loss still remained high. On the thin films we observed the slow formation of white spots in a few days, and the originally clear films turned cloudy. This phenomena could be attributed to aggregation of excess small TDI and TEA molecules (phase separation) and/or the reaction of excess of isocyanate groups with water molecules in the environment. The white spots are scattering centers large enough to be observed under an optical microscope.

To neutralize the excess diisocyanate in PUDRTO-1 and -2 materials, triethanolamine (TEA) was added to the prepolymer to form n-PUDRTO-2 and n-PUDRTO-3 (Scheme 4). While the poling efficiency was unaffected, the optical losses were reduced to 3.6 dB/cm at 980 nm and 0.86 dB/cm at 1.3 μm for n-PUDRTO-2 and 1 dB/cm at 1.3 μm for n-PUDRTO-3. The optical loss at 1.3 μm can be reduced to values around 1 dB/cm by adjusting the NCO/OH ratio to unity, however the loss at 980 nm, which is closer to the absorption maximum of the chromophore, still remained high. We found that this high loss at the shorter wavelength was related to the formation of excimers from chromophore aggregation, which caused the tail of the chromophore absorption peak to shift significantly toward longer wavelength. Details of this phenomenon will be published separately.

We have also employed a reversed condensation procedure, as shown in Scheme 5. The material thus obtained (r-PUDRTO) has an optical loss of 6.7 dB/cm at 980 nm, and 3.4 dB/cm at 1.3 μm. Presumably this high optical loss is due to the formation of chromophore excimers caused by the facile chromophore aggregation in this “flexible” polymer system, and the low temporal stability is also consistent with this assumption.

After a systematic study of the influence of composition on optical loss of these unpoled samples, we were able to obtain materials with loss below 1 dB/cm at 1.3 μm. However, we found when these films were subjected to electric field poling, the optical loss can increase dramatically. This type of loss is defined as poling induced optical loss, which is caused by poling-induced inhomogeneity of the films.[8a]

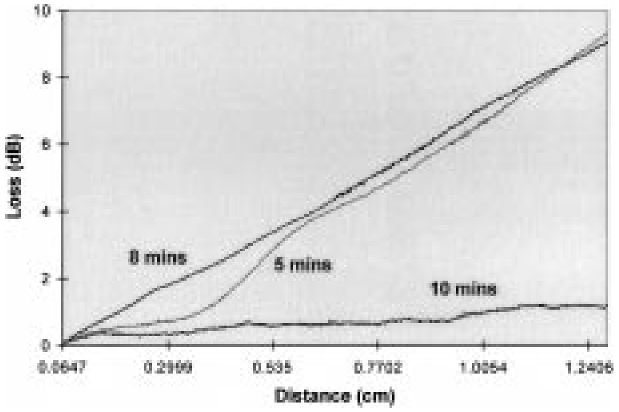

Figure 5. Optical loss profiles of n-PUDRTO materials with different preheating time.

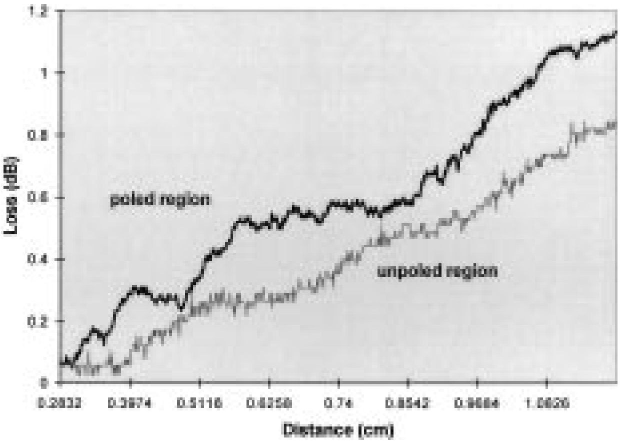

Figure 6. Optical loss profiles of n-PUDRTO material in both unpoled and poled regions.

The first few attempts to pole the n-PUDRTO-2 material caused a dramatic increase of optical loss to a value above 10 dB/cm. We found that the magnitude of the poling-induced optical loss is directly related to the extent of cross-linking of the films before applying electric field. Less extended cross-linking generally afforded a high poling efficiency but resulted in higher poling-induced optical loss. Presumably, this higher loss is caused by the bombardment of ions (used in corona poling to generate an electric field across the thin film) on the still “soft” surface. The ion bombardment on soft films is the major source of poling-induced optical loss. During the electric poling, if the film is still soft (T_g is much lower than the poling temperature), the ion bombardment frequently cause formation of indentations. A SEM picture of a damaged PUDRTO film is shown in Figure 7. The inhomogeneity in the damaged film causes the scattering of incident light, and induces the optical loss. We realized that in order to reduce poling induced optical loss, control of the extent of cross-linking was crucial.

To reduce poling-induced optical loss, we added a preheating step into the material processing. n-PUDRTO films, prepared as previously mentioned, were heated at 100 °C for various time periods before poling. As shown in Table 2, the poling induced optical loss is very sensitive to this preheating time. Figure 4 shows the influence of preheating time on poling induced

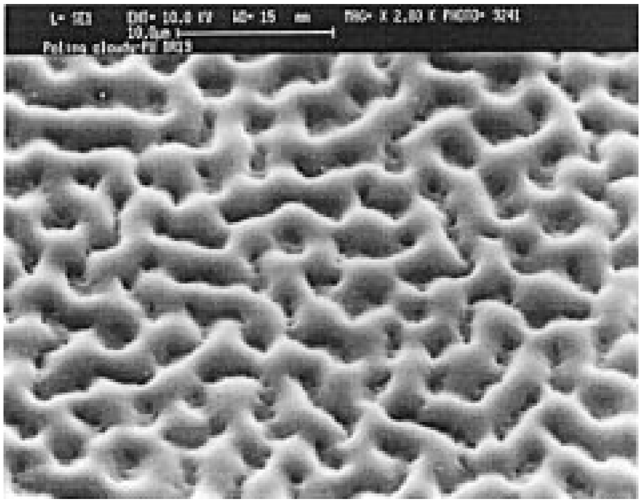

Figure 7. SEM picture of a film damaged during corona poling.

Table 2. Optical Loss Data of n-PUDRTO-2 with Different Preheating Conditions[a,b]

preheating time (min)	poling profile	optical loss (dB/cm)
5	(a)[c]	10.3
8	(a)[c]	6.7
8	(b)[d]	3−6
10	(b)[d]	1.0

[a] Measured after poling. [b] Measured at 1.3 μm. [c] Poling profile a: ramp from 20 °C to 120 °C at a rate of 10 °C/min; apply 6 kV at 20 °C, then 6 kV/120 °C for 50 min. [d] Poling profile b: ramp from 20 to 120 °C at a rate of 10 °C/min, apply 5 kV at 20 °C and increase to 6 kV at 70 °C, then 6 kV/120 °C for 50 min.

optical loss. With the poling profile (a), the film baked for 5 min had an optical loss of 10.3 dB/cm; after heating for 8 min, the loss dropped to 6.7 dB/cm. Using the poling profile (b), the film baked for 8 min yielded a loss of 3−6 dB/cm; the different values were due to irregular formation of poling-induced cloudiness (damage) on the film. For the film baked for 10 min, the optical loss dropped to ca. 1.0 dB/cm consistently over the whole film. From the 5 min loss profile in Figure 5, we can observe the regions with different slopes (optical losses), which clearly indicate the formation of inhomogeneous regions in the film. This inhomogeneity can be attributed to the formation of scattering centers caused by the electric field. Figure 5 shows the loss profile of a poled region and an unpoled region in the PUDRTO-2 thin film. The optical loss in the unpoled region is around 0.86 dB/cm, and that in the poled region is 1 dB/cm. After the films were preheated at 100 °C for 10 min, the poling-induced optical loss was reduced to only 0.2 dB/cm. From this loss profile (Figure 6), a slight inhomogeneity can be observed in the poled region as indicated by the uneven slope of the profile. We should note that this inhomogeneity is much less than that in the sample baked for 5 min (see Figure 5).

Conclusion

Lattice hardening via cross-linking reactions is an efficient way to stabilize poling-induced noncentrosymmetric order. Generally, partial cross-linking is induced by heating briefly at a certain temperature, before applying the poling field, to increase the viscosity and avoid dielectric breakdown with application of the poling field. Poling and lattice hardening are accomplished simultaneously at elevated temperatures, and the poling field is then maintained until the sample cools to room temperature. The advantage of this approach is that a material with a finite T_g and good solubility in common organic solvents can be processed into optical quality films, poled at modest temperatures, and then hardened into a high-T_g material which is solvent resistant. However, since the lattice hardening and poling occur simultaneously, the NLO properties such as nonlinearity and optical loss are very sensitive to the processing conditions. By careful control of processing conditions, materials with good poling efficiency, high temporal stability, and low optical loss can be obtained.

Experimental Section

General Procedures. Anhydrous dioxane, tolylenediisocyanate (a mixture of tolylene 2,4- and 2,6-diisocyanate, TDI), triethanolamine and 2.5-dimethyl-2,5-hexanediol were purchased from Aldrich. TDI was vacuum distilled and kept in nitrogen atmosphere before use. Others were used as received. ^{1}H and ^{13}C{^{1}H } NMR were taken on a Bruker-250-FT-NMR spectrometer. UV−vis spectra were obtained from a Perkin-Elmer Lambda-4C UV/vis spectrophotometer; and UV−vis−NIR absorption was measured on an AVIV spectrophotometer 14 DS UV−vis−IR spectrometer. Thermal analyses were performed under nitrogen on a Shimadzu thermogravimetric analyzer, with a heating rate of 5 °C/min. Melting points and other phase transition temperatures were measured on a Perkin-Elmer DSC-7 spectrometer. FT-IR spectra were taken on a Perkin-Elmer 7700 IR-FT spectrometer, by using either pressed KBr pellets or polymer films cast on a sodium chloride crystal disk.

PUDRTO-1. DRTO (0.050 g, 0.14 mmol) was dissolved in anhydrous dioxane (0.50 g) at 80 °C, and then tolylenediisocyanate (TDI, 0.60 g of a 10% dioxane solution, 0.34 mmol) was added. The mixture was heated at 80 °C for 40 min to form the prepolymer, which was spin-coated on ITO glass, and poled under electric field to form the PUDRTO-1 material. The loading density of this material is 41%, based on the percentage of DR19 fragment.

PUDRTO-2. DRTO (0.050 g, 0.14 mmol) was dissolved in anhydrous dioxane (0.50 g) at 80 °C, and then TDI (0.80 g of a 10% dioxane solution, 0.46 mmol) was added. The mixture was heated at 80 °C for 40 min to form the prepolymer, which was spin-coated on ITO glass, and poled under electric field to form the PUDRTO-2 material. The loading density of this material is 35%, based on the percentage of DR19 fragment.

n-PUDRTO-1. DRTO (0.050 g, 0.14 mmol) was dissolved in anhydrous dioxane (0.50 g) at 80 °C, and then TDI (0.50 g of a 10% dioxane solution, 0.29 mmol) was added to the solution. The mixture was heated at 80 °C for 40 min, and then triethanolamine (TEA, 0.30 g of a 10% dioxane solution, 0.20 mmol) was added. The mixture was heated at 80 °C for another 5 min to form the prepolymer, which was spin-coated on ITO glass, and poled under electric field to give the n-PUDRTO-1 material. The loading density of this material is 37%, based on the percentage of DR19 fragment.

n-PUDRTO-2. DRTO (0.050 g, 0.14 mmol) was dissolved in anhydrous dioxane (0.50 g) at 80 °C, and then TDI (0.60 g of a 10% dioxane solution, 0.34 mmol) was added to the solution. The mixture was heated at 80 °C for 40 min, and then triethanolamine (TEA, 0.13 g of a 10% dioxane solution, 0.087 mmol) was added. The mixture was heated at 80 °C for another 20 min to form the prepolymer, which was spin-coated on ITO glass, and poled under electric field to give the n-PUDRTO-2 material. The loading density of this material is 37%, based on the percentage of DR19 fragment.

n-PUDRTO-3. DRTO (0.050 g, 0.14 mmol) was dissolved in anhydrous dioxane (0.50 g) at 80 °C, and then TDI (0.73 g of a

10% dioxane solution, 0.42 mmol) was added to the solution. The mixture was heated at 80 °C for 40 min, and then triethanolamine (TEA, 0.21 g of a 10% dioxane solution, 0.14 mmol) was added. The mixture was heated at 80 °C for another 20 min to form the prepolymer, which was spin-coated on ITO glass, and poled under electric field to give the n-PUDRTO-3 material. The loading density of this material is 32%, based on the DR19 fragment.

r-PUDRTO. 2.5-Dimethyl-2,5-hexanediol (0.030 g, 0.21 mmol) and TDI (0.073 g, 0.42 mmol) were dissolved in 1.0 g of dioxane and heated at 80 °C for 2 h. DRTO (0.050 g, 0.14 mmol), dissolved in 0.50 g of dioxane, was then added to solution. The mixture was heated at 80 °C for another 40 min to form the prepolymer, which was spin-coated on ITO glass, and poled under electric field to give the r-PUDRTO material. The loading density of this material is 30%, based on the DR19 fragment.

Film Fabrication and Electric Poling. A solution of prepolymers (oligomers) was filtered through a 0.2 μm microfilter, then subsequently spin-coated onto ITO plates, and dried in vacuo at room temperature overnight before poling. Glass substrates coated with an ultrathin film of indium−tin oxide (ITO) were used for corona poling and ATR measurements. Due to the high absorption of ITO, the ITO-coated glass substrates cannot be used in optical loss measurement. We then use either polished optical glass slides with the refractive index of 1.47 or silicon wafer coated with gold as substrates for optical loss measurements.

Electric poling was achieved in a corona poling stage at elevated temperatures, using an ITO-grounded corona-discharge setup, with a tip-to-plane distance of ca. 1.5 cm. The poled films were then cooled to room temperature in the presence of the electric field. The needle voltage was adjustable, ranging from 0 to 12 kV. The temperature of the heating plate could be varied from room temperature to 250 °C. Different poling protocols were tried on the films to find optimized poling conditions. The poling process was carried out in several steps at programmed temperatures and poling voltages in order to realize both high poling efficiency and a high degree of cross-linking.

NLO Measurements. Second-order nonlinear optical properties, r_{33}, and refractive indexes were measured via an ATR (attenuated total reflection) technique.[12] The ATR measurement was performed on an ATR laser, ILX Lightwave series 120 (1.064 μm) diode pumped ring laser and lock-in amplifier Standford Research System SR 510.

Optical measurements at 0.98 μm were carried out at DEACON Research Inc., and those at 1.3 μm were measured in our laboratory by using an immersion technique or fabricating actual waveguides on silicon substrates. The “immersion technique”[13] measurement involves immersing of NLO film at an angle into a liquid with a refractive index slightly higher than that of the guided film. A beam is guided along the film as the film is dipped into the fluid by undergoing a continuous total internal reflection. The guided beam then emerges from the intersection, between the liquid surface and the film surface, becoming outcoupled by the liquid. The intensity of the emerging guided light as a function of propagation distance is plotted, and the slope is calculated to yield the optical loss value.

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