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Electric Poling and Relaxation of Thermoset Polyurethane Second-Order Nonlinear Optical Materials: Role of Cross-Linking and Monomer Rigidity

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ABSTRACT: A high $\mu\beta$ isophorone-derived phenyltetraene chromophore (denoted CLD-5) was synthesized. The chromophore was modified with a hexyl group at the middle of the π-conjugate bridge to improve solubility and processability and was dihydroxy-functionalized for covalent incorporation into various cross-linked PU polymer systems. Its electrical poling and relaxation behavior in PU polymer thin films were studied. First, the chromophore was incorporated into conventional TDI/TEA polyurethane, and an electrooptic (EO) coefficient of 57.6 pm/V at 1.06 μm was obtained, which is 28% higher than that obtained from nonhexylated chromophore (CLD-2) in the same polyurethane system. Two new polyurethane systems, poly[(phenyl isocyanate)-*co*-formaldehyde] (PPIF)/triethanolamine (TEA) and PPIF/bisphenyl-1,1′-dimethanol (BPDM), were designed to study the influence of cross-link density and monomer rigidity on electrical field poling of chromophore dipoles and relaxation behavior of poling-induced chromophore alignment. CLD-5/PPIF/TEA polymer has the highest cross-link density (3.07 mmol/g) among all the polyurethanes studied here. It gains 38 °C in thermal stability but loses 50% of EO activity as compared with the CLD-5/TDI/TEA polyurethane material, which has a cross-link density of 1.91 mmol/g. A higher EO coefficient (41 pm/V), lower optical loss of 2.56 dB/cm at 1.3 μm, and the highest dynamic stability (133 °C) were obtained for the CLD-5/PPIF/BPDM polyurethane EO material, which has the lowest cross-link density (1.27 mmol/g) and the most rigid monomers. The results indicate that excessive cross-linking deteriorates electric poling of long chromophores in a cross-linked polymer thin film. Therefore, cross-linking by itself is not necessarily a good approach to achieving high thermal stability of electrical field-induced chromophore alignment in polyurethane systems.

1. Introduction

Organic polymeric second-order nonlinear optic (NLO) materials have been of great interest for many years due to the potential for commercial electrooptic (EO) device applications.[1] Development of device quality material has been very challenging because all the critical material properties are interrelated, and optimizing one of the properties often causes attenuation of the others. For example, cross-linking can be used to increase thermal stability of chromophore alignment, but meanwhile it could lead to a sacrifice of electrooptic coefficient as a result of reduced free volume and increased chain entanglement in the polymer matrix.

Polyurethane systems have been shown to have great potential in NLO applications due to ease of synthesis and excellent compatibility with high $\mu\beta$ chromophores.[2] A polyurethane system based on toluene-2,4-diisocyanate (TDI) and triethanolamine (TEA) has been studied extensively in our group. The typical dynamic stability of dilinkable chromophore incorporated TDI/TEA polyurethane EO material is around 90 °C, which is not high enough for applications in practical devices.[2] Although a substantial amount of work has been published on polyurethane NLO materials, little attention has been paid to the systematic study of the effect of monomer characteristics on thermal stability, poling efficiency, and optical loss.[3] In this work, we investigated different approaches to increase thermal stability and studied dependence of EO activity on monomers and processing conditions in an effort to find a balanced polyurethane system for EO applications.

Elevated poling temperature may decrease achievable poling efficiency since thermal energy tends to randomize aligned dipoles, and cross-linking would very likely sacrifice electrooptic activity due to reduced free volume. To obtain high electrooptic coefficients in more rigid and cross-linked systems, chromophores with very high $\mu\beta$ values are required. We have synthesized a series of phenyltetraene bridged chromophores; among them, CLD-1 (shown in Figure 1) has given so far one of the largest electrooptical coefficients in a highly stable polycarbonate host.[4] To incorporate CLD-1 type chromophore into cross-linked polymer systems, a dihydroxyl variant of CLD-1 (denoted CLD-2, Figure 1) was synthesized. However, due to limited solubility of CLD-2, an electrooptic coefficient of only 45 pm/V was obtained from its poled TDI/TEA polyurethane film.[5] In this study, we developed a synthetic scheme to modify the CLD-2 chromophore with a hexyl group. The improved solubility of the hexylated chromophore allows a wider processing window for incorporation of CLD-5 into polyurethane and other polymer systems. In this report, we show that the thermal stability of polyure-

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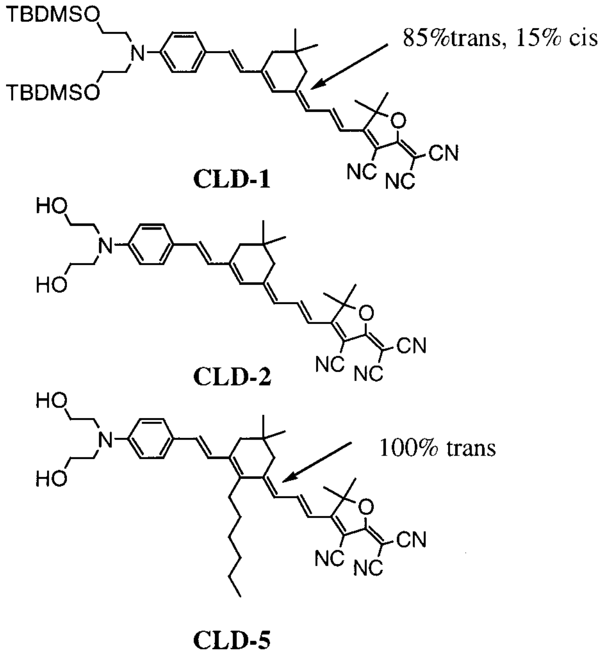

Figure 1. Chemical structures of the phenyltetraene chromophores.

thane NLO materials can be improved either by increasing cross-link density or by using more rigid cross-linkers. The second approach is superior to the first one as it produces higher dynamic stability and better poling efficiency.

2. Results and Discussion

2.1. Synthesis and Characterization of Chromophore CLD-5. The multistep synthesis of hexyl-derivatized chromophores CLD-5 is shown in Figure 2a. The synthesis of the aminobenzaldehyde (**I**) has been described previously.[2d] The *n*-hexyl-substituted isophorone (**II**) was synthesized according to a modified literature method.[6] The steric hindrance of the hexyl group decreases the reactivities and selectivities of all reactions in Figure 2a that involve the modified isophorone ring. The yields are generally lower than the yields of the corresponding reactions involving a simple isophorone structure. In the conjugate systems of CLD chromophores and their donor-bridge precusors, only the C=C double bonds that are derived from the cyclohexenone (indicated by arrows in Figure 1) could exhibit cis/trans conformations. In the nonhexylated version of CLD donor bridges and chromophores, trans isomers are dominant. For example, CLD-1 is 85% trans isomer. In the hexylated compounds (compound **IV**, CLD-4, and CLD-5), the sterical hindrance of the hexyl group makes the energetically unfavored cis conformations disappears completely. The ^{1}H NMR spectra of CLD-4 and its nonhexylated version are given in Figure 2b for exemplary comparison. The sterical hindrance of the hexyl group is also expected to retard the cis−trans isomerization at elevated temperatures.

The chromophore charge-transfer absorption peak wavelengths are 628.4 nm in dioxane and 660.8 nm in chloroform. The UV−vis absorption $\lambda_{\max}$ is essentially the same as that of CLD-2.[5] This indicates that the hexyl group does not cause notable change in charge transfer excitation of the chromophore. In other words, CLD-5 has essentially the same hyperpolarizabilities as CLD-2. The decomposition temperature of CLD-5 is 254 °C, 9 °C higher than that of CLD-2. The difference in their thermal decomposition temperatures may be attributed to the hexyl group, which eliminates the cis isomer at room temperature and retards trans−cis isomerization at high temperatures.[8]

2.2. Synthesis, Characterization, and Electrooptic Study of CLD-5 Polyurethanes. Because of the reactive nature of urethane prepolymers and the difference in monomers used, it is not meaningful to compare the performance of different polyurethanes under the same synthetic and processing conditions. In this study, synthetic and processing conditions of three polyurethanes studied are different from each other and are optimized to obtain the best physical and EO properties for each system.

2.2.1. CLD-5/TDI/TEA Polyurethane Material. A. The Effect of the Hexyl Group. First, CLD-5 was incorporated into TDI/TEA polyurethane to study the effect of the hexyl group on material processing and electrooptic (EO) coefficient. A 17 wt % loading level was adopted to give the same number density as that of CLD-2 reported in ref 5. The prepolymer solution was prepared using the conventional procedure established in our group for incorporation of chromophores into TDI/TEA polyurethane. Thus, the chromophore CLD-5 was allowed to react with the isocyanate cross-linker TDI at 80 °C for 40 min to cap the hydroxy group with TDI. The trilinker triethanolamine was then added, and the mixture was heated for another 20 min to form an viscous prepolymer solution. During the procedure, great attention was paid to the dissolution behavior of the chromophore and resulting oligomers. The chromophore was fully dissolved during the first 40 min of reaction. But when the solution was cooled for adding the trilinker, a substantial amount of precipitate formed. Thin-layer chromatography showed that the precipitate was not CLD-5 but is TDI-capped CLD-5. Fortunately, the precipitate was dissolved upon reaction with TEA. Good quality films were obtained by spin-coating the solution onto ITO-coated glass substrates. The vacuum-dried film was precured at 120 °C for 1 min and then poled at 110 °C for 60 min with a stepwise voltage profile: 5.5 kV for 5 min, 6 kV for 5 min, and 6.5 kV for 50 min. A r_{33} of 55 pm/V was measured for the poled film. This r_{33} value was substantially higher than the r_{33} obtained from the CLD-2/TDI/TEA polyurethane thin film.[5] The higher r_{33} value of CLD-5/TDI/TEA material was attributed to the improved solubility of CLD-5 and reduced interchromophore electrostatic interaction by the hexyl side group.[4d] The poled films showed a dynamic stability of 80 °C, which is normal for TDI/TEA-based polyurethane EO materials.

B. Modified CLD-5/Polyurethane Synthesis. The precipitation of TDI-capped CLD-5 during the prepolymer reaction can introduce some uncertainty to the processing because precipitate formation may vary from one run of reaction to another. To eliminate this potential problem, a new prepolymer preparation procedure was studied. In the new procedure, three reactants were mixed together at one time to make a 10 wt % solution in dioxane. The mixture was then heated at 80 °C for 25 min. No precipitate was observed during the reaction, and after the solution was cooled to room temperature. The different behavior of the chromophore in two prepolymer synthetic procedures can be explained by the different composition of the mixture during the reaction. In the new procedure, after the

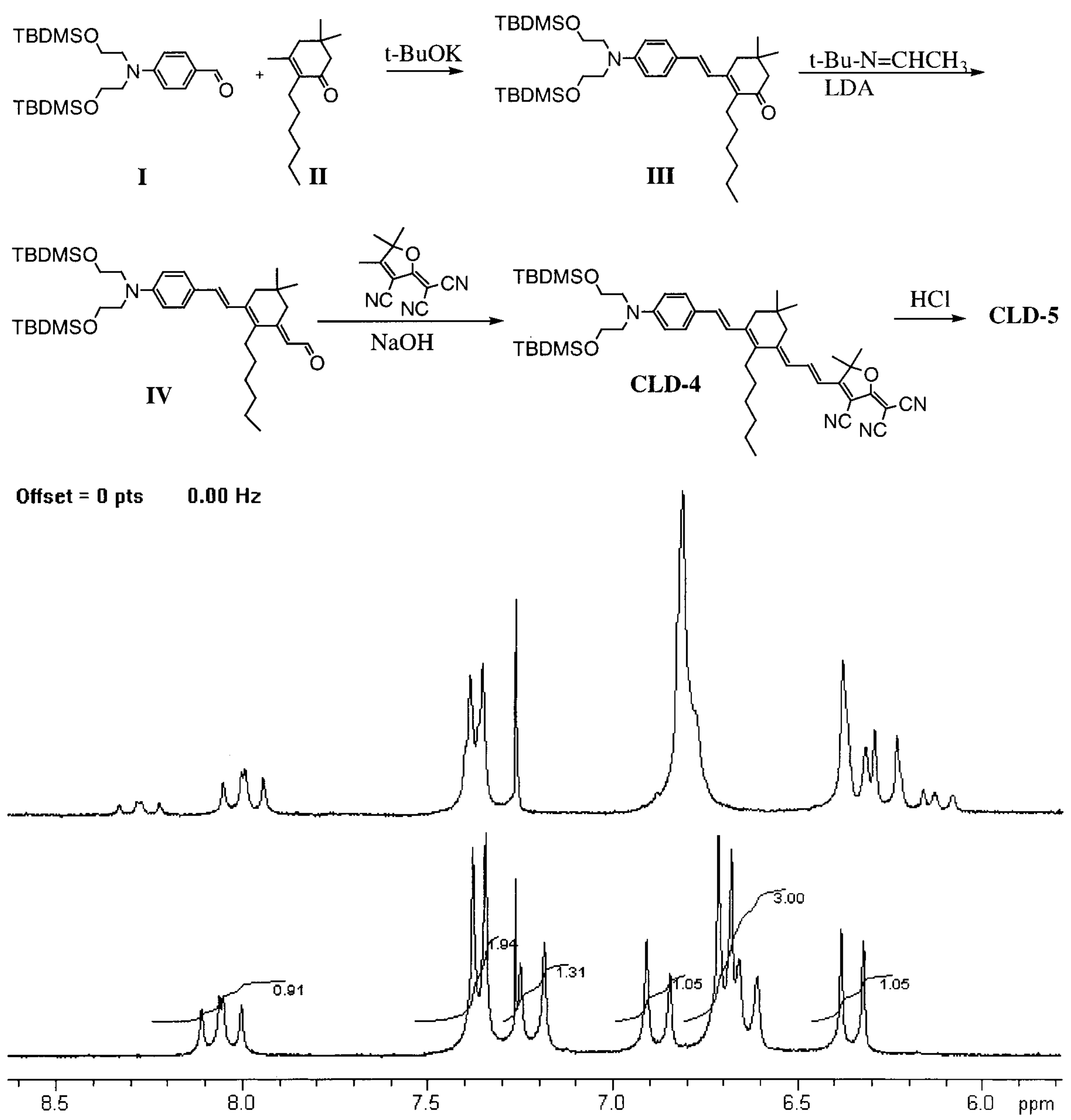

Figure 2. (a) Synthetic scheme of chromophore CLD-5. (b) ^{1}H NMR spectra (in $CDCl_3$) of CLD-4 (bottom) and its nonhexylated version (top). Only the aromatic region is shown for better comparison. The quartets between 7.8 and 8.6 ppm belong to the middle one of the three protons located between the cyclohexene ring and the five-membered acceptor ring. Only one quartet shows up in the spectrum of CLD-4, indicating that only one isomer exists.

reaction had started for some time (about 10 min), there were not any chemical species dominant in the solution as indicated by thin-layer chromatography, the solution was a complex mixture of oligomers of different molecular formula. The possibility for any one of the oligomers to crystallize out was simply zero. It should also be noted that in the new procedure most CLD-5 molecules were only partially reacted to TDI due to the short reaction time (25 min compared to 40 + 20 min in the conventional procedure), thus having higher mobility in film compared to the chromophore in film fabricated from the conventional solution. Furthermore, the new procedure is advantageous in that it no longer requires a second addition of reactant, thus avoiding the exposure of the solution to the moisture in air which is harmful to the polyurethane reaction.[2c] The same procedure for film preparation and electrical poling was followed, and a slightly higher r_{33} of 57.6 pm/V was obtained. As expected, the new prepolymer synthesis procedure did not have a notable effect on the thermal stability of the final EO material, since it is the final curing condition, not the prepolymer synthesis condition, that determines the rigidity of final material.

2.2.2. CLD-5/PPIF/TEA Polyurethane Material. To improve thermal stability, new polyurethane materials were synthesized from poly[(phenyl isocyanate)-*co*-formaldehyde] (PPIF) and TEA as shown in Figure 3. PPIF, an oligomer with average 3.2 −NCO, can be considered as a trilinker. Therefore, both cross-linkers in this polyurethane are trilinkers, making the new polymer a highly cross-linked system. The new prepolymer synthesis procedure was followed except that reaction temperature was reduced to 70 °C to elongate the optimal reaction time from about 15 to 25 min. Longer time helped reduce the error in reaction time control which is critical to obtaining consistent results.

The greatest difficulty involved in studying a new cross-linked polyurethane EO materials arises from the

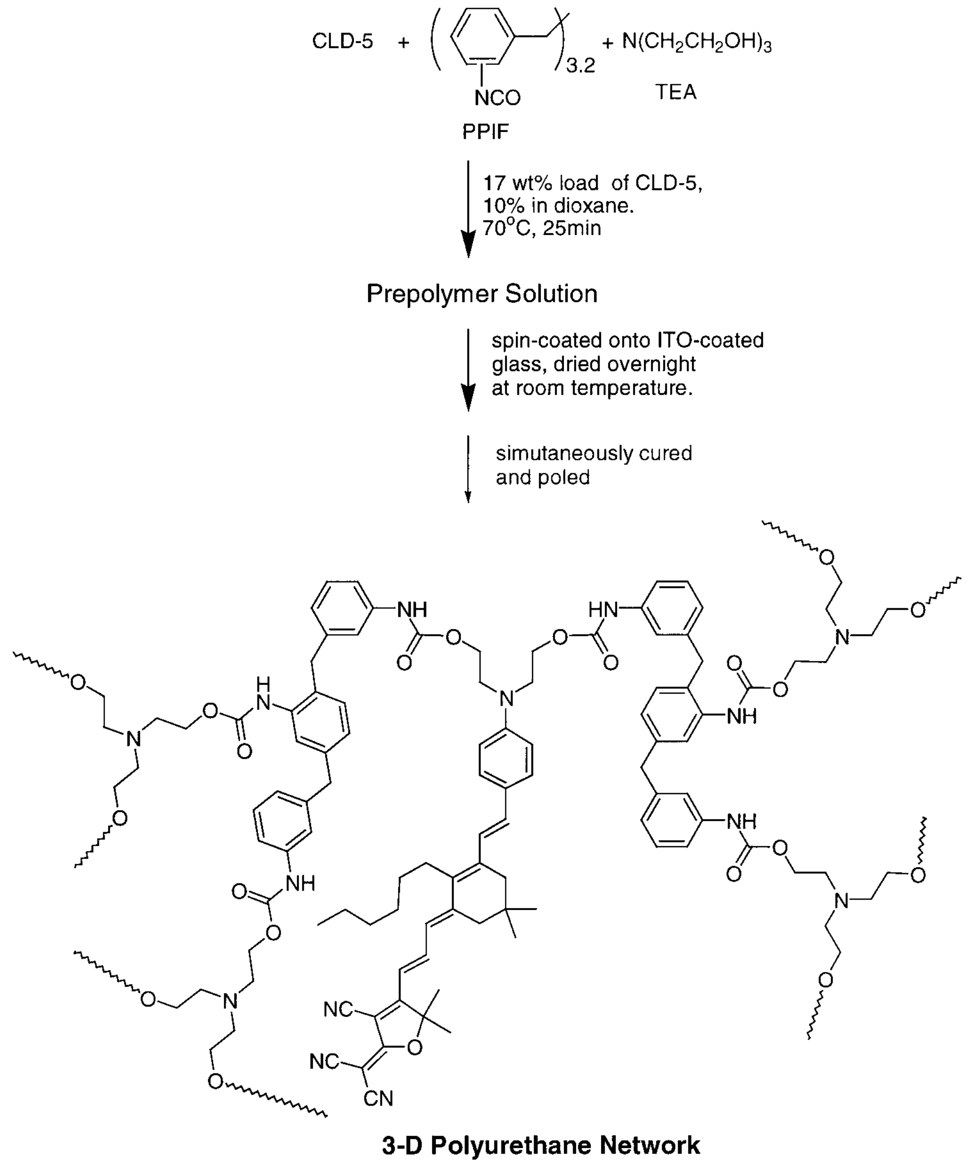

Figure 3. Synthesis and processing of CLD-5/PPIF/TEA polyurethane.

fact that one cannot obtain useful information from thermal analysis to help determine their optimal poling temperatures. The glass transition temperature is commonly used as a reference to determine poling temperature of guest–host EO polymers and covalently attached linear polymers. However, the glass transition is no longer meaningful for a reactive polyurethane system with high cross-link density. To determine the optimal processing condition of thin films of a new polyurethane material, usually several different poling temperature profiles are designed on the basis of the knowledge obtained from well-studied polyurethane systems and the difference between new monomers and previously used monomers. The designed profiles are then tested to find the optimal poling profile.

After being dried in vacuo overnight (~8–10 h) the films are very tough and not soluble to any organic solvent. A poling profile (Figure 4a) similar to that used for CLD-5/TDI/TEA was used first. Much higher temperatures were used since the new system was much more rigid than the TDI/TEA system. The resulting film only gave 4.7 pm/V at 1.3 μm. The low r_{33} value means a low chromophore poling efficiency and was an indication of low mobility of chromophore in the polyurethane matrix. We believed that the low efficiency was due to over cross-linking of the film before applying the poling voltage. To our surprise, the effect of cross-linking on poling efficiency has not been addressed specifically in the literature. One possible reason is that in most studies on cross-linked EO polymers small-sized chromophores like nitroaniline, DANS, and DR-19 were frequently used.[2c,6] The lengths of these molecules are only 30–60% of the length of CLD-5 studied here, and their volumes are only 20–30% of the volume of CLD-5. These small chromophores need much smaller free volume to reorient in polymer matrix. Therefore, cross-linking did not appear to cause serious problems to electrical poling in the earlier studies of cross-linked EO polymers. It is well understood now that polymers containing short chromophores as active components cannot provide enough bulk nonlinearity for practical applications. Chromophores with longer conjugate bridge are becoming dominant in the EO material research, and practical devices have been fabricated from them.[4e]

To minimize the detrimental effect of cross-linking on chromophore alignment, electrical poling needs to be performed before the polymer film becomes fully cross-linked. Every step of material preparation, from pre-

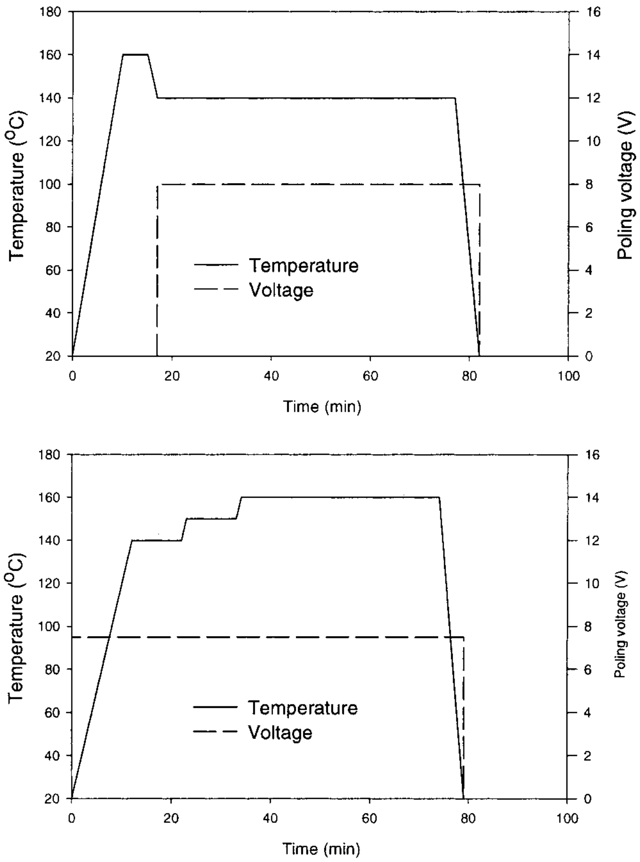

Figure 4. Poling temperature and voltage profile for CLD-5/PPIF/TEA polyurethane films: (a) an unoptimized poling/curing profile leading to low EO coefficient; (b) the optimized poling/curing profile.

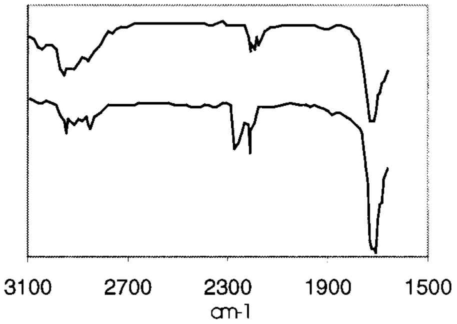

Figure 5. FT-IR spectra of CLD-5/PPIF/TEA films: top, film heated using the temperature profile in Figure 4b; bottom, unheated film.

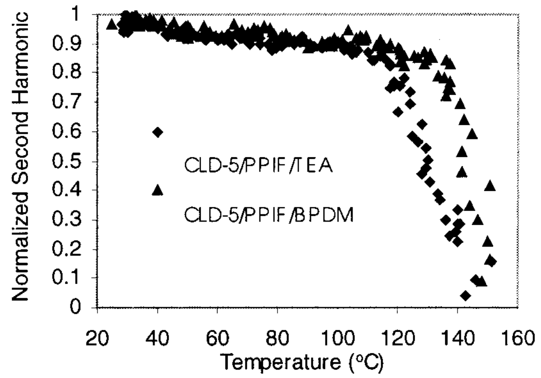

Figure 6. Dynamic stability of CLD-5/PPIF/TEA and CLD-5/PPIF/BPDM films both poled and cured at 160 °C (temperature ramping rate 10 °C/min).

polymer synthesis, vacuum-drying, film storage, to film poling and curing, has to be carefully designed. As already shown, a very low r_{33} can result from the use of a nonoptimized poling/curing scheme. We also found that the urethane reaction happened during the room temperature (23−25 °C) vacuum-drying process as the films became insoluble after overnight drying. In this study care was taken to make sure all the films were only vacuumed for 12 h and then characterized/processed within 6 h. With all the precautions taken, we then focused on the last and the most critical step, the electrical poling and thermal curing. From the preliminary poling test described above, we learned that the films were already very tough after overnight drying, and the precuring process might not be necessary to avoid film damaging. In newly designed and tested poling/curing schemes, pooling voltage was turned on at the very beginning of the process, though stepwise temperature profile was used to avoid possible film damaging and chromophore bleaching. The profile shown in Figure 4b represents the optimal poling condition found for CLD-5/PPIF/TEA films. EO coefficients in the range 27−34 pm/V were obtained at 1.06 μm. A film coated on KBr substrate was heated using the temperature profile in Figure 4b, and its FT-IR spectrum was taken to see whether the final curing temperature and duration were enough for complete cross-linking. The result is given in Figure 5 together with the spectrum of the unheated fresh film. It shows that the PPIF isocyanate peak at 2283 cm^{-1} disappeared completely. The thermal stability of the above poled CLD-5/PPIF/TEA film was 118 °C as shown in Figure 6. Although the thermal stability is higher than that of CLD-5/TDI/TEA film, the EO coefficient obtained is only 50−60% of the r_{33} obtained from CLD-5/TDI/TEA film.

2.2.3. CLD-5/PPIF/BPDM Polyurethane Material. Through the comparative study of the highly cross-linked TDI/TEA and PPIF/TEA systems, we learned that excessive cross-linking should be avoided in order to obtain reasonably high EO coefficient. To gain balanced performances of both thermal stability and material nonlinearity, a new CLD-5/polyurethane based on PPIF and bisphenyl-1,1′-dimethanol (BPDM) dilinker was designed. Both the cross-linkers are highly aromatic, and the dilinker BPDM is more rigid than trilinker triethanolamine in CLD-5/PPIF/TEA. The new polymer would be more rigid but less densely cross-linked than PPIF/TEA, and should afford a better poling efficiency. The prepolymer solution preparation and film fabrication are summarized in Figure 7. The prepolymer reaction was monitored by GPC. The molecular weights of prepolymer at different reaction times are listed in Table 1. Molecular weight increased from 910 to 980 when reaction time was increased from 25 to 40 min. The low molecular weight suggests that the major components in the prepolymer were monomers and oligomers between 25 and 40 min of reaction time. Nevertheless, it was found longer reaction times (above 40 min) generally lead to reduced poling efficiency. A reaction time of 30 min was found optimal to balance the film quality and the poling efficiency. After being dried in a vacuum for 12 h, films were poled within 6 h. Although the films were softer than CLD-5/PPIF/TEA films, precuring was found to be unnecessary. Instead, stepwise poling voltage profiles with lower initial

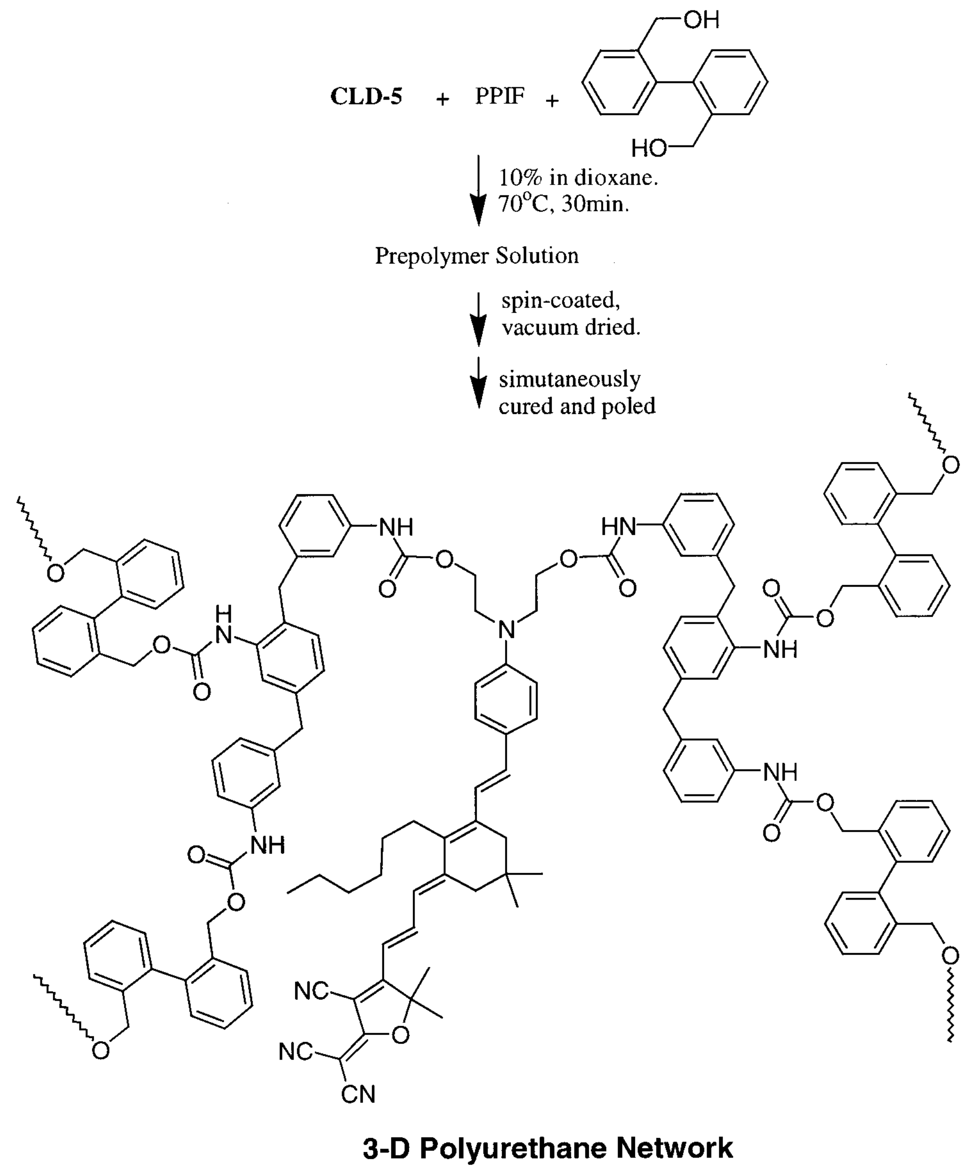

Figure 7. Synthetic and processing scheme of CLD-5/PPIF/BPDM polyurethane.

Table 1. Molecular Weight of CLD-5/PPIF/BPDM vs Reaction Time

reaction time (min)	M_w	M_n	M_p[a]
25	910	690	990
30	940	710	960
35	970	720	1010
40	980	750	1030

[a] M_p = peak molecular weight.

temperature and poling voltage were used to avoid film damage and chromophore bleaching. An electrooptic coefficient 41 pm/V at 1.06 μm was obtained using the poling profile in Figure 8. The films coated on KBr substrates were used for IR study to monitor the curing process. IR spectra were recorded for three films: an uncured fresh film, a film being cured according to the temperature scheme except using only 20 min at 150 °C, and a film being fully cured according to the scheme. The results, given in Figure 9, show that, after being cured at 150 °C for 20 min, the PPIF −NCO peak at 2271.5 cm^{-1} almost disappeared. The thermal stability of the poled film was dependent on final poling temperature and time. Higher temperature and longer curing gave better thermal stability although the cross-linking reaction was complete at an early time of the high-temperature curing precess. When the curing/poling time at 150 °C was increased from 20 min to 1 h, the stability increased from 104 to 118 °C. The dynamic stability reached 133 °C (shown in Figure 6) when the film was poled at 160 °C for 1 h.

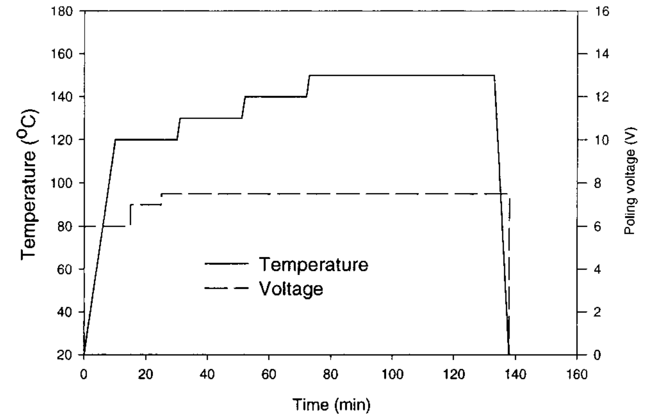

Figure 8. Optimal poling profile of CLD-5/PPIF/BPDM.

Table 2. Cross-Link Densities and Properties of Three Polyurethane Systems

	CLD-2/TDI/TEA	CLD-5/TDI/TEA	CLD-5/PPIF/TEA	CLD-5/PPIF/BPDM
cross-link density (mmol/g)	1.96	1.91	3.07	1.27
dynamic thermal stability (°C)	<80	80	118	133
EO coefficient (pm/V)	45	55	30	41
optical loss at 1.3 μm (dB/cm)		2.7	2.8	2.4−2.56

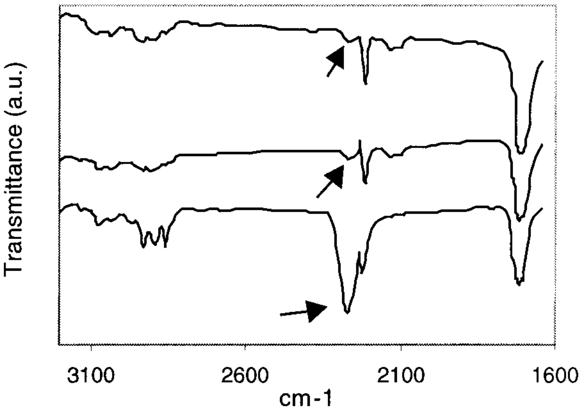

Figure 9. FT-IR spectra of CLD-5/PPIF/BPDM films: top, film heated using the temperature profile in Figure 8; middle, film heated using the temperature profile in Figure 8, except only 20 min was used at the last stage; bottom, unheated film.

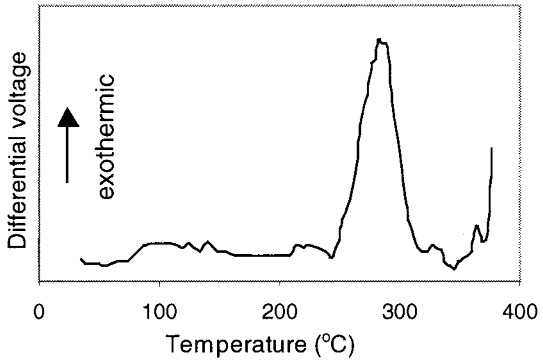

Figure 10. DTA curve of CLD-5/PPIF/TEA.

2.2.4. Chemical Stability of Chromophore in Polyurethane Environment. In polyurethane, the N−H in the urethane structure (−O−NH−C=O) is a potential nucleophilic attacker of electron acceptor in CLD-5. It is of interest to see whether it would cause decomposition of the chromophore at a temperature lower than the decomposition temperature (T_d) of the pure chromophore. Cured CLD-5/PPIF/TEA polyurethane film was scratched off the substrate and was used as the sample for differential thermal analysis (DTA). The DTA curve (given in Figure 10, noisy due to the limited amount of sample) shows a decomposition temperature of 248.6 °C, which is only 5 °C lower than that of the pure chromophore. It indicates that the polyurethane environment is not detrimental to the chromophore stability.

2.2.5. Optical Loss Study of New Polyurethanes. Low optical loss is an important requirement for electrooptic materials. The optical losses of the polyurethane thin films were measured by the immersion method.[9] The films were made by spin-coating prepolymer solution onto SiO_2-coated silica wafers and were dried in a vacuum at room temperature overnight. The optical loss for CLD-5/PPIF/BPDM film was 2.4 dB/cm before curing and 2.56 dB/cm at 1.3 μm after 40 min curing at 150 °C. This result shows that thermal curing does not increase optical loss of the polyurethane material significantly.

To find whether the optical loss was mainly caused by the chromophore absorption, we measured the loss of blank PPIF/BPDM polymer film synthesized and fabricated using the same conditions. Surprisingly, the optical loss was even higher than that of CLD-5-loaded films. The lowest optical loss measured for the uncured film was 2.9 dB/cm. The results suggest that the polymer itself, not the chromophore, was the major source of the optical loss.

The optical losses of unheated CLD5/TDI/TEA and CLD-5/PPIF/TEA film were 2.7 and 2.8 dB/cm, respectively. The higher optical loss in CLD-5/PPIF/TEA is presumably due to the high content of N−H bond in this polymer, since vibrational overtone absorption of C−H and especially polar N−H and O−H bonds is the source of optical loss in 1.3 μm region.[10]

3. Conclusion

In Table 2, we list the cross-link densities and the properties of three polyurethane materials studied togather with the previously reported result[5] of nonhexylated chromophore CLD-2 in TDI/TEA polyurethane. The cross-link density is defined as the number of branching points (in millimoles) per gram of material. Among the five monomers used in this work, only TEA and PPIF provide branching point. The cross-link density of CLD-5/PPIF/TEA is 1.61 times that of the conventional TDI/TEA system and is 2.41 times that of CLD-5/TDI/TEA. It is clear that excessive cross-linking is harmful to electrical poling of polyurethane material and that cross-linking by itself is not enough to provide very high thermal stability of electrical field-induced chromophore alignment. The use of rigid monomer is the key to obtain both good thermal stability and high poling efficiency. We also demonstrated the importance of side group derivatization of high $\mu\beta$ chromophores. The appropriate side group not only increases the processability of the material but also enhances electric poling efficiency of chromophore dipole.

4. Experimental Section

4.1. General Methods of Material Characterization. All chemicals were purchased from Aldrich and were used as received. All reactions were carried out under argon unless otherwise specified. ^{1}H NMR and ^{13}C NMR were taken on a Bruker-250 FT NMR spectrometer; tetramethylsilane was added to all NMR solvents as internal standard unless otherwise stated. UV−vis spectra were obtained from a Perkin-Elmer Lambda-4C UV/vis spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc. Mass spectroscopy analyses were done at the UC Riverside Mass Spectrometer Center. Thermal analyses were performed on a Shimadzu differential thermoanalyzer under nitrogen atmosphere at a heating rate of 10 °C/min. Melting points were determined in capillary tubes on a Mel-Temp II melting point apparatus unless otherwise indicated. Melting points were not corrected. Polymer molecular weights were determined by Waters GPC setup: differential refractrometer R401, differential refractrometer electronics unit, pump model 510, and Styragel HR2

7.8 × 300 mm column. IR measurements were performed on a Perkin-Elmer FT-IR spectrometer, Spectrum 2000.

4.2. Synthesis of Chromophore CLD-5. The synthesis of the starting material, compound **I**, has been reported elsewhere. 2-Hexylisophorone was obtained from isophorone in 92% yield according to a literature method.[7] ^{1}H NMR ($CDCl_3$): δ 2.29 (t, 6.32 Hz, 2H), 2.23 (s, 2H), 2.21 (s, 2H),1.92 (s, 3H), 1.30 (m, 8H), 1.00 (s, 6H), 0.88 (t, 6.42 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 198.55, 151.93, 134.53, 51.16, 46.75, 32.43, 31.56, 29.25, 28.90, 27.99, 24.80, 22.41, 21.04, 13.88. Anal. Calcd for $C_{15}H_{26}O_1$: C, 81.02; H, 11.79. Found: C, 81.18; H, 11.87.

3-[*p-N,N*-Bis(2-*tert*-butyldimethylsiloxyethyl)aminostyryl]-5,5-dimethyl-2-hexyl-cyclohex-2-enone (III). Potassium *tert*-butoxide (30.32 g, 97%, 0.262 mol) was added to a solution of *p-N,N*-bis(2-*tert*-butyldimethylsiloxyethyl)aminobenzaldehyde (**I**, 53.4 g, 0.122 mol) and 2-hexylisophorone (**II**, 26.6 g, 0.118 mol) in diglyme (200 mL, dried over KOH) over 3 min. The ice bath was used to keep the temperature below 50 °C. The reaction mixture was stirred at room temperature for 25 min and then was poured into dilute acetic acid (0.28 mol of HOAc in 200 mL of water). The extra acid was neutralized saturated aqueous sodium bicarbonate. The organic layer was separated, washed with water, dried with magnesium sulfate, and condensed by rotary evaporation to dryness. The residue was purified by a silica gel column using ethyl acetate/hexane (1/20, v/v) as eluent to afford 8.33 g of thick red oil. ^{1}H NMR ($CDCl_3$): δ 7.36 (d, 8.81 Hz, 2H), 7.14 (d, 16.06 Hz, 1H), 6.88 (d, 16.09 Hz, 1H), 6.69 (d, 8.91 Hz, 2H), 3.78 (t, 6.06 Hz, 4H), 3.56 (t, 5.89 Hz, 4H), 2.53 (br, 2H), 2.48 (s, 2H), 2.29 (s, 2H), 1.33 (m, 8H), 1.05 (s, 6H), 0.90 (s, 18H), 0.89 (3H, a triplet hidden in the 18H peak at 0.90 ppm), 0.04 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$): δ 198.87, 148.41, 147.67, 134.47, 134.19, 128.52, 124.38, 121.71, 111.54, 60.21, 53.42, 51.37, 39.82, 32.27, 31.65, 29.90, 29.37, 28.39, 25.79, 24.30, 22.54, 18.13, 14.07, −5.46 ppm. Anal. Calcd for $C_{38}H_{67}NO_3Si_2$: C, 71.08; H, 10.52; N, 2.18. Found: C, 71.34; H, 10.47; N, 2.17.

Compound IV. A solution of lithium diisopropylamine (4.7 mL, 1.5 M in THF, 7.05 mmol) in THF (12 mL) was cooled to −20 °C. *N-tert*-Butylacetimine (0.666 g, 6.7 mmol) was added, and the mixture was allowed to warm to 0 °C and was kept at the temperature for 15 min. It was recooled to −20 °C and 3-[*p-N,N*-bis(2-*tert*-butyldimethylsiloxyethyl)aminostyryl]-5,5-dimethyl-2-hexylcyclohex-2-enone (**III**, 4.31 g, 6.71 mmol, in 15 mL of THF) was added over 3 min. It was stirred for 5 more min and was stopped by adding 1 N acetic acid solution. The product was extracted with hexane and the extract was washed with sodium bicarbonate solution, dried with magnesium sulfate, and condensed to dryness. The residue was purified by a silica gel column using ethyl acetate/hexane (1/20, v/v) to afford 0.55 g of red oil product and recovered 3.45 g of starting material **III**. ^{1}H NMR ($CDCl_3$): δ 10.13 (d, 8.22 Hz, 1H), 7.33 (d, 8.80 Hz, 2H), 7.15 (d, 15.54 Hz, 1H), 6.77 (d, 16.38 Hz, 1H), 6.68 (d, 9.13 Hz, 2H), 6.20 (d, 7.94 Hz, 1H), 3.78 (t, 5.84 Hz, 4H), 3.55 (t, 5.74 Hz, 4H), 2.68 (s, 2H), 2.52 (br, t, 2H), 2.38 (s, 2H), 1.34 (m, 8H), 1.01 (s, 6H), 0.89 (s, 18H), 0.89 (3H, a triplet hidden in the 18H peak at 0.89 ppm), 0.04 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$): δ 191.53, 157.46, 148.14, 140.57, 133.16, 132.65, 128.23, 124.87, 123.47, 122.31, 111.59, 60.23, 53.43, 40.40, 39.38, 31.59, 30.15, 29.78, 29.52, 28.22, 27.26, 25.79, 22.57, 18.15, 14.03, −5.47 ppm. Exact mass calcd for $C_{40}H_{69}N_1O_3Si_2$: 668.493. Found: 668.489.

CLD-4. Compound **IV** (0.55 g, 0.823 mmol) and 2-dicyanomethylene-3-cyano-4,5,5-trimethyl-2,5-dihydrofuran (0.198 g, 0.988 mmol) were dissolved in 5 mL of ethanol that contained 7 mg of sodium hydroxide. The solution was refluxed for 3.5 h, and then 10 mL of water was added dropwise to precipitate out the product. The crude product was collected by filtration, washed with water, dried in vacuo, and purified by a silica gel column using ethyl acetate/hexane (1/7 to 1/5, v/v) to give 245 mg of pure product: yield 35%. ^{1}H NMR ($CDCl_3$): δ 8.06 (q, $J_1 = 12.02$ Hz, $J_2 = 14.74$ Hz, 1H), 7.36 (d, 8.89 Hz, 2H), 7.22 (d, 16.29 Hz, 1H), 6.88 (d, 15.79 Hz, 1H), 6.70 (8.78 Hz, 2H), 6.63 (d, 12.09 Hz, 1H), 6.35 (d, 14.96 Hz, 1H), 3.78 (t, 5.77 Hz, 4H), 3.57 (t, 5.83 Hz, 4H), 2.61 (br, t, 2H), 2.44 (s, 4H, an overlap of two 2H singlet peaks), 1.71 (s, 6H), 1.43 (br, m, 8H), 1.01 (s, 6H), 0.89 (s, 18H), 0.89 (3H, a triplet hidden in the 0.89 ppm 18H peak), 0.03 (s, 12H) ppm. ^{13}C NMR ($CDCl_3$): δ 176.35, 173.46, 155.48, 148.88, 145.13, 144.08, 135.16, 134.78, 128.94, 124.92, 124.27, 122.39, 115.82, 112.80, 112.06, 111.90, 111.77, 96.78, 93.93, 60.40, 55.68, 53.57, 40.87, 40.71, 31.78, 30.64, 30.18, 29.72, 28.43, 27.25, 26.70, 25.97, 22.76, 18.35, 14.24, −5.28 ppm. Exact mass calcd for $C_{51}H_{76}N_4O_3Si_2$: 848.543. Found: 848.546.

CLD-5. Hydrochloric acid (1 N, 1 mL) was added to a solution of chromophore CLD-4 (0.18 g, 0.212 mmol) in acetone (12 mL). The mixture was stirred at room temperature for 1 h, and then $NaHCO_3$ (0.2 g) was added to neutralize the acid. The crude product was precipitated out by slow addition of water (10 mL), collected by filtration, and washed with water. It was then redissolved in hot acetone (50 mL), and water (40 mL) was added to the hot solution slowly. The solution was cooled to room temperature, and the product was filtered. Recrystallization from dioxane and hexane gave 122 mg of shinny green crystalline: yield 93%. ^{1}H NMR ($CDCl_3$): δ 8.05 (q, $J_1 = 11.84$ Hz, $J_2 = 14.40$ Hz, 1H), 7.39 (d, 9.14 Hz, 2H), 7.23 (d, 16.57 Hz, 1H), 6.87 (d, 15.60 Hz, 1H), 6.73 (d, 8.31 Hz, 2H), 6.63 (d, 12.21 Hz, 1H), 6.36 (d, 15.02 Hz, 1H), 3.92 (t, 4.82 Hz, 4H), 3.67 (t, 4.34 Hz, 4H), 3.02 (br, 2H), 2.6 (t, br, 2H), 2.44 (s, 4H, overlap of two 2H), 1.71 (s, 6H), 1.42 (br, m, 8H), 1.02 (s, 6H), 0.93 (t, 6.57 Hz, 3H) ppm. Anal. Calcd for $C_{39}H_{48}N_4O_3$: C, 75.45; H, 7.79; N, 9.02. Found: C, 75.50; H, 7.84; N, 9.18.

4.3. Polymer Syntheses and Film Fabrication. Synthesis of Prepolymer Solution of CLD-5/TDI/TEA. The weight loading density was 17%. In a drybox, chromophore CLD-5 (12.1 mg, 0.039 mmol of −OH), TDI (39.1 mg, 0.449 mmol of −NCO), 460.8 mg of dioxane, and a stirring bar were placed in a 2 mL vial. The mixture was stirred at 80 °C for 40 min. Then a solution of TEA (20.4 mg, 0.410 mmol of −OH) in 184 mg dioxane solution was added, and the mixture was heated for 20 min.

Synthesis of Prepolymer Solution of CLD-5/PPIF/TEA. In a drybox, chromophore CLD-5 (10.0 mg, 0.0322 mmol of −OH), anhydrous dioxane (90 mg), poly[(phenyl isocyanate)-*co*-formaldehyde] (PPIF, 349 mg of 10 wt % dioxane solution, 0.278 mmol of −NCO), triethanolamine (TEA, 123 mg of 10 wt % dioxane solution, 0.247 mmol of −OH), and a tiny stirring magnet were placed in a 2 mL vial. The vial was tightly capped and was heated at 70 °C for 25 min.

Synthesis of Prepolymer Solution of CLD-5/PPIF/BPDM. In a drybox, chromophore CLD-5 (10.0 mg, 0.0322 mmol of −OH), anhydrous dioxane (90 mg), poly[(phenyl isocyanate)-*co*-formaldehyde] (272 mg of 10 wt % dioxane solution, 0.218 mmol of −NCO), bisphenyl-1,1′-dimethanol (BPDM, 199 mg of 10 wt % dioxane solution, 0.186 mmol of −OH), and a tiny stirring magnet were placed in a 2 mL vial. The vial was tightly capped and was heated at 70 °C for 30 min.

Film Fabrication. The prepolymer solutions were filtered through 0.2 μm Teflon syringes filters and were spin-coated onto ITO-coated glass substrates. A film thickness of 2 ± 0.5 μm was obtained by using spin rate of 330−380 rpm. Films were dried at room temperature under vacuum for 6−12 h. Dried films were stored in a desiccator and were poled within 12 h.

Electric Poling, Electrooptic Coefficient, Thermal Stability, and Optical Loss Measurement. Chromophore dipole alignment was induced by corona-discharge-generated electric field poling with a setup described earlier.[2c] Poling voltage ranged from 5 to 8 kV. The electrooptic coefficients of the poled films were measured at 1.06 μm by the attenuated total reflection[11] (ATR) method 5−10 min after the poling voltage was turned off. Thermal stability of poled polymer film was measured by a second-harmonic-generation setup. Sample films were heated at a ramping rate of 10 °C/min while the second-harmonic-generation (SHG) signal was monitored. A Spectro-Physics DCR-11 mode-locked, Q-switched Nd:YAG laser (1.064 μm) with pulse width of <10 ns and repetition rate of 10 Hz was used as the fundamental source for SHG. The sample film was at a 45° angle to the incident beam. The optical loss was measured at 1.3 μm by the immersion technique,[8] which involves immersing of NLO film at an angle into a liquid with a refractive index slightly higher than that of polymer film. A laser beam is coupled into the film and is guided along the film by continuous total internal reflection. When the guided beam reaches the film−liquid interface, it is outcoupled by the liquid. The intensity of the emerging guided beam as a function of propagation distance is plotted, and the slope is calculated to yield the optical loss value. The films for optical loss measurement were obtained by spin-coating prepolymer solution onto a SiO_2-coated silica wafer and were dried in a vacuum at room temperature overnight.

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References and Notes

(1) (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; John Wiley & Sons: New York, 1991. (b) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, K.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060−1080.

(2) (a) Chen, M.; Yu, L.; Dalton, L. R.; Shi, Y.; Steier, W. H. *Macromolecules* **1991**, *24*, 5421−5428. (b) Chen, M.; Dalton, L. R.; Yu, L. P.; Shi, Y. Q.; Steier, W. H. *Macromolecules* **1992**, *25*, 4032−4035. (c) Mao, S. S. H.; Ra, Y.; Guo, L.; Zhang, C.; Dalton, L. R. *Chem. Mater.* **1998**, *10*, 146−155. (d) Harper, A. W.; Mao, S. S. H.; Ra, Y.; Zhang, C.; Zhu, J.; Dalton, L. R. *Chem. Mater.* **1999**, *11*, 2886−2891.

(3) (a) Park, C.-K.; Zieba, J.; Zhao, C.-F.; Swedekk, B.; Wijekoon, W. M. K. P.; Prasad, P. N. *Macromolecules* **1995**, *28*, 3713−3717. (b) Boogers, J. A. F.; Klaase, P. Th. A.; de Vlieger, J. J.; Tinnemans, A. H. A. *Macromolecules* **1994**, *27*, 205−209. (c) Chen, J.; Zhu, J.; Dalton, L. R.; Lee, S.-S.; Zhang, H.; Chen, A.; Steier, W. H. *Polym. Prepr.* **1998**, *39* (2), 1059−1060.

(4) (a) Shi, Y.; Zhang, C.; Zhang, H.; Bechtel, J. H.; Steier, W. H.; Robinson, B. H.; *Science* **2000**, *288*, 119−122. (b) Zhang, C.; Robinson, B. H.; Dalton, L. R.; Oh, M. C.; Zhang, H.; Steier, W. H.; Shi, Y.; Van Eck, T.; Leung, D.; Moss, A.; Ermer, S.; Liakatas, I.; Cai, C.; Bosshard, Ch.; Gunter, P.; Harper, A. W.; Lee, C. *J. Am. Chem. Soc.*, in press. (c) Zhang, C.; Ren, A. S.; Wang, F.; Zhu, J.; Dalton, L. R. *Chem. Mater.* **1999**, *11*, 1966−1968. (d) Liakatas, I.; Cai, C.; Bösch, M.; Jäger, M.; Bosshard, Ch.; Günter, P.; Zhang, C.; Dalton, L. R. *Appl. Phys. Lett.* **2000,** *76*, 1368−1370. (e) Oh, M. C.; Zhang, H.; Szep, A.; Chuyanov, V.; Steier, W. H.; Zhang, C.; Dalton, L. R. *Appl. Phys. Lett.* **2000**, *76*, 3525−3527.

(5) (a) Zhang, C.; Ren, A. S.; Wang, F.; Dalton, L. R.; Lee, S.-S.; Garner, S. M.; Steier, W. H. *Polym. Prepr.* **1999**, *40* (1), 49−50. (b) Zhang, C. Dissertation, University of Southern California, 1999.

(6) (a) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, *94*, 31−75. (b) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 155−173.

(7) Stork, G.; Benaim, J. *J. Am. Chem. Soc.* **1971**, *93*, 5938−5939.

(8) (a) Jen, A. K.-Y.; Rao, V. P.; Drost, K. J.; Wong, K. Y.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2057−2058. (b) Rao, V. P.; Wong, K. Y.; Jen, A. K.-Y.; Drost, K. *J. Chem. Mater.* **1994**, *6*, 2210−2212.

(9) Teng, C. *Appl. Opt.* **1993**, *32*, 1051−1054.

(10) (a) Hida, Y.; Onose, H.; Imamura, S. *IEEE Photonics Technol. Lett.* **1993**, *5*, 782−784. (b) Hida, Y.; Onose, H.; Imamura, S. *Jpn. J. Appl. Phys.* **1995**, *34*, 6416−6422. (c) Eldada, L.; Xu, C.; Stengel, K. M. T.; Shacklette, L. W.; Yardley, J. T. *J. Lightwave Technol.* **1996**, *14*, 1704−1713. (d) Usui, M.; Hikita, M.; Watanabe, T.; Amano, M.; Sugawara, S.; Hayashida, S.; Imamaura, S. *J. Lightwave Technol.* **1996**, *14*, 2338−2343. (e) Eldada, L.; Shacklette, L. W.; Norwood, R. A.; Yardley, J. T. *Org. Thin Films Photonics Applications* **1997**, *14*, 5−7.

(11) Dentan, V.; Lévy, Y.; Dumont, M.; Robin, P.; Chastaing, E. *Opt. Commun.* **1989**, *69*, 379−383.

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