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Synthesis and properties of novel polyurethanes containing 2,4-dioxybenzylidenecyanoacetate group as a NLO-chromophore for electro-optic applications

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Summary

Methyl 2,4-bis-(2’-hydroxyethoxy)benzylidenecyanoacetate (**3**) was prepared by hydrolysis of methyl 2,4-bis-(2’-vinyloxyethoxy)benzylidenecyanoacetate (**2**). Diol **3** was condensed with 2,4-toluenediisocyanate, 3,3’-dimethoxy-4,4’-biphenylene-diisocyanate, and 1,6-hexamethylenediisocyanate to yield polyurethanes **4-6** containing the NLO-chromophore 2,4-dioxybenzylidenecyanoacetate. The resulting polyurethanes **4-6** were soluble in common organic solvents such as acetone and DMF. Polymers **4-6** showed a thermal stability up to 280ºC in TGA thermograms with T_g values obtained from DSC thermograms in the range of 66-114ºC. The SHG coefficients (d_{33}) of poled polymer films were around 7.8×10^{-9} esu.

Introduction

Nonlinear optical (NLO) materials based on organic compounds have been extensively studied over the past decade because of their potential applications in the field of telecommunications, optical signal processing, optical switching, etc (1-3). Among the organic materials the NLO polymers are considered candidate materials, mainly because they offer many advantages such as mechanical endurance, light weight, chemical resistance, and good processability to form optical devices (4-7). One of the current challenges is to design novel NLO polymers having optimized properties. In the developments of NLO polymers for electrooptic device applications, stabilization of electrically induced dipole alighment is important considerations. Two approaches to minimize the randomization have been proposed. One is to use crosslinked systems (8-11) and the other is to utilize a high T_g polymers such as polyamides (12-13). Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. Crosslinked polyurethanes bearing azobenzene dyes showed enhanced thermal stability (14-15). Polyurethanes functionalized with hemicyanine (16) and thiophene chromophore (17) in side chain showed high thermal stability of aligned dipoles up to 150ºC. Physically crosslinked systems via hydrogen bonds have the advantages such as homogenity and good processibility relative to the chemically crosslinked systems, which suffer from significant optical loss and poor processibility. Recently we prepared polyurethanes having 3,4-dioxy-4’-nitrostilbene as a NLO-chromophore. These polymers are soluble in common organic solvents and showed a thermal stability up to 300ºC with a T_g of 109-114ºC. The electro-optic coefficient (r_{33}) of poled polymer films was in the range of 20-25 pm/V at 633 nm, which is acceptable for NLO device applications (18). This work is now extended to the synthesis of another polyurethanes containing NLO chromophore. In this work we prepared three novel polyurethanes containing 2,4-dioxybenzylidenecyanoacetate unit, which is presumably effective NLO-chromophore in the main chain. We selected 2,4-dioxybenzylidenecyanoacetate group as NLO-chromophore because it will have a large dipole moment and is easy to synthesize. After confirming the structure of the resulting polymers we investigated the properties such as T_g, thermal stability, and second harmonic generation (SHG) activity (d_{33}).

Experimental

Materials

The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2-Chloroethyl vinyl ether and 2,4-dihydroxybenzaldehyde were used as received. 2,4-Toluenediisocyanate (TDI) was purified by distillation under reduced pressure. 3,3’-Dimethoxy-4,4’-biphenylenediisocyanate was recrystallized from ethyl acetate. Piperidine was dried with calcium hydride and fractionally distilled. *N,N*-Dimethylformamide (DMF) was purified by drying with anhydrous calcium sulfate, followed by distillation under reduced pressure. 2-Iodoethyl vinyl ether was prepared from 2-chloroethyl vinyl ether by the halogen exchange reaction.

Measurements

IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian 300MHz NMR spectrometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures (T_g) were measured on a DuPont 910 differential scanning calorimeter in a nitrogen atmosphere. DuPont 951 thermogravimetric analyzer with a heating rate of 10ºC/min up to 700ºC was used for the thermal degradation study of polymers under nitrogen. The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. As the temperature was raised to 110ºC, 6kV of corona voltage was applied and kept 110ºC for 30 min. The number average molecular weight (M_n) and weight average molecular weight (M_w) of the polymers were estimated by gel permeation chromatography (GPC) (columns styragel HR5E4E; solvent THF). The refractive index of the sample was measured by the optical transmission technique (19). The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. As the temperature was raised to 110ºC, 6kV of corona voltage was applied and kept 110ºC

for 30 min. Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode which measures topography. Second harmonic generation (SHG) measurement, which was carried out immediately after poling, Q-switched Nd:YAG laser (λ=1064 nm) with pulse width of 10 ns and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes (20-23). Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

*2,4-Bis-(2'-vinyloxyethoxy)benzaldehyde (**1**)*

2,4-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (82.9 g, 0.60 mol), and 2-iodoethyl vinyl ether (49.5 g, 0.25 mol) were dissolved in 400 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80ºC for 15 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 300 mL of water, and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielded 25.0 g (90% yield) of pure product **1**. Mp=68-69ºC. ^{1}H NMR ($CDCl_3$) δ 4.03-4.35 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.50-6.62 (m, 4H, 2 =CH-O-, aromatic), 7.82-7.86 (d, 1H, aromatic), 10.35 (s, 1H, -CHO). IR (KBr) 3100, 3082 (w, =C-H), 2954, 2875 (m, C-H), 1674 (vs, C=O), 1615 (vs, C=C), 1575 (s, C=C) cm^{-1}.

*Methyl 2,4-bis-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2**)*

Piperidine (0.13 g, 1.5 mmol) was added to a solution of compound **1** (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 200 mL of 1-butanol with stirring at 0ºC under nitrogen. After stirring for 3 h at 0ºC, the reaction mixture was cooled to -10ºC for crystallization. The product was filtered and washed successively with cold 1-butanol (80 mL), water (30 mL), and cold 1-butanol (20 mL). The obtained pale yellow product was recrystallized from 1-butanol to give 9.49g (88% yield) of **2**. Mp=96-97ºC. ^{1}H NMR ($CDCl_3$) δ 3.89 (s, 3H, -CO_2CH_3), 4.02-4.34 (m, 12H, 2 CH_2=, 2 -O-CH_2-CH_2-O-), 6.46-6.65 (m, 4H, 2 =CH-O-, aromatic), 8.36-8.428(d, 1H, aromatic), 8.70 (s, 1H, aromatic). IR (KBr) 3044 (w, =C-H), 2954, 2943 (m, C-H), 2222 (s, CN), 1705 (vs, C=O), 1622, 1611, 1594, 1583 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.82; N, 3.83.

*Methyl 2,4-bis-(2'-hydroxyethoxy)benzylidenecyanoacetate (**3**)*

Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl 2,4-bis-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2**) (9.34 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0ºC. The mixture was stirred at 80ºC for 8 h under nitrogen. The resulting solution was extracted with diethyl ether (80 mL) three times. The organic layer was washed successively with saturated sodium chloride, sodium hydrogen carbonate, and water, followed by drying with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product. The obtained pale yellow product was recrystallized from ethyl acetate to give 6.87 g (86% yield) of **3**. Mp: 168-170ºC. ^{1}H NMR ($CDCl_3$) δ 2.78-2.85 (m, 2H, -OH), 3.84-3.89

(s, 3H, CO_2CH_3), 3.90-3.98 (m, 2H, -CH_2-OH), 4.16-4.28 (m, 2H, -O-CH_2-), 6.72-6.76 (m, 2H, aromatic), 8.32-8.36 (d, 1H, aromatic), 8.70-8.72 (d, 1H, -Ph-CH=). IR (KBr) 3514, 3435 (s, O-H), 3044 (w, =C-H), 2955 (m, C-H), 2216 (m, CN), 1709 (vs, C=O), 1612, 1578 (vs, C=C) cm^{-1}. Anal. Calcd for $C_{15}H_{17}NO_6$: C, 58.63; H, 5.57; N, 4.56. Found: C, 58.76 H, 5.63; N, 4.65.

Synthesis of polyurethanes ***4-6***

A representative polycondensation reaction procedure (the case of **4**) was as follows: 2,4-Toluenediisocyanate (1.74 g, 0.01 mol) was added slowly to a solution of 3.07 g of diol **3** (0.01 mol) in 50 mL of anhydrous DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80ºC. After heating 6 h with stirring the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of cold water. The precipitated polymer was collected and reprecipitated from DMSO into methanol. The final product was dried under vacum to give 3.85 g (80% yield) of polymer **4**: η_{inh}=0.23 dL/g (c, 0.5 g/dL in DMSO at 25ºC). ^1H NMR (DMSO-d_6) δ 1.94-2.21 (m, 3H, -CH_3), 3.95-4.02 (m, 3H, -$COOCH_3$), 4.06-4.85 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.88-7.32 (m, 6H, aromatic), 8.48-8.63 (m, 1H, Ph-CH=), 8.75-8.92 (m, 2H, N-H). IR (KBr) 3398 (s, N-H), 2926 (m, C-H), 2220 (m, CN), 1710 (vs, C=O), 1593 (s, C=C) cm^{-1}. UV/Vis (DMSO) λ_{max}=390, ε=13200. Anal. Calcd for $(C_{24}H_{23}N_3O_8)_n$: C, 59.87; H, 4.81; N, 8.73. Found: C, 59.96; H, 4.95; N, 8.66. Polymer **5**: ^1H NMR (DMSO-d_6) δ 3.71-4.02 (m, 9H, -OCH_3), 4.08-4.96 (m, 8H, 2 -O-CH_2-CH_2-O-), 6.66-7.31 (m, 6H, aromatic), 7.62-7.68 (m, 1H, aromatic), 8.06-8.26 (m, 2H, aromatic), 8.54-8.64 (m, 1H, Ph-CH=), 8.90-9.02 (m, 2H, N-H). IR (KBr) 3373 (m, N-H), 2951, 2843 (m, C-H), 2220 (w, CN), 1719 (m, C=O), 1587 (s, C=C) cm^{-1}. UV/Vis (DMSO) λ_{max}=392, ε=12500. Anal. Calcd for $(C_{31}H_{29}N_3O_{10})_n$: C, 61.69; H, 4.84; N, 6.96. Found: C, 61.78; H, 4.75; N, 6.88. Polymer **6**: η_{inh}=0.28 dL/g (c, 0.5 g/dL in DMSO at 25ºC). ^1H NMR (DMSO-d_6) δ 1.15-1.44 (m, 8H, -$(CH_2)_4$)-, 2.83-2.99 (m, 4H, 2-NH-CH_2-), 3.69-4.37 (m, 11H, -OCH_3, 2 -O-CH_2-CH_2-O-), 5.66-5.75 (m, 2H, 2-NH-), 7.16-7.78 (m, 3H, aromatic). IR (KBr) 3355 (s, N-H), 2932, 2858 (m, C-H), 2220 (w, CN), 1728 (m, C=O), 1651 (s, C=C) cm^{-1}. UV/Vis (DMSO) λ_{max}=390, ε=11600. Anal. Calcd for $(C_{23}H_{29}N_3O_8)_n$: C, 59.87; H, 4.81; N, 8.73. Found: C, 58.10; H, 6.15; N, 5.84.

Results and Discussion

Synthesis and characterization of polymers ***4-6***

2,4-Bis-(2'-vinyloxyethoxy)benzaldehyde (**1**) was prepared by the reaction of 2-iodoethyl vinyl ether with 2,4-dihydroxybenaldehyde. Methyl 2,4-bis-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2**) was prepared by the condensation reaction of **1** with mthyl cyanoacetate (24). Compound **2** was hydrolyzed to yield acetaldehyde and diol **3**. The chemical structure of the compounds was identified by ^1H NMR, IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Diol **3** was condensed with 2,4-toluenediisocyanate, 3,3'-dimethoxy-4,4'-biphenylenedi isocyanate, and 1,6-hexamethylenediisocyanate in a dry DMF solvent

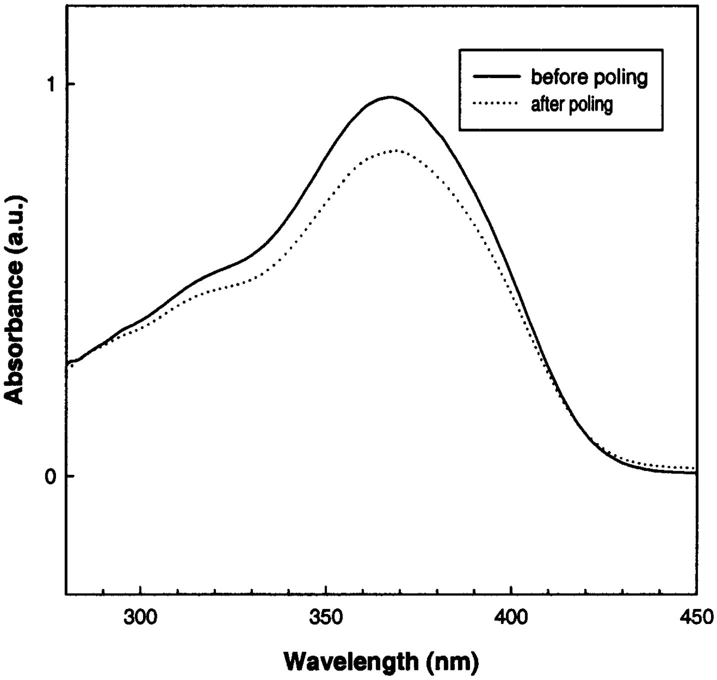

Figure 1. UV-Vis absorption spectra of a polymer film (4) before and after poling.

to yield polyurethanes **4-6** containing the NLO-chromophore dioxybenzylidenecyanoacetate. Polymerization results are summarized in Table 1. The polymerization yield was 75-88%. The chemical structures of the resulting polymers were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. ^{1}H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signal at 8.90-9.02 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1710-1720 cm^{-1} indicating the presence of urethane bond. The number average molecular weight (M_n) of the polymers were determined to be 12500 (M_w/M_n=2.10) for polymer **4**. We now have well defined polyurethanes (**4-6**) and investigate their properties.

Properties of polymers

The polymers **4-6** were soluble in common solvents such as acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. Polymers **4-6** isolated from methanol were yellow colored amorphous materials. The inherent viscosities were in the range of 0.20-0.25 dL/g. Polymers **4-6** showed strong absorption near 390 nm by the NLO-chromophore dioxybenzylidenecyanoacetate group. The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. Polymers

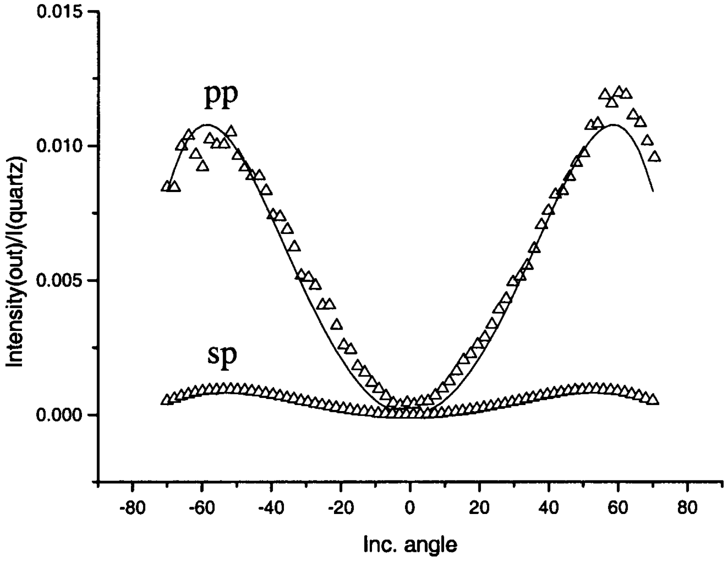

Figure 2. Angular dependence of SHG signal in a poled polymer (**4**) film.

4-6 showed a thermal stability up to 280°C from their TGA thermograms as shown in Table 2. Glass transition temperature (T_g) values of the polymers **4-6** measured by DSC were around 66-114°C. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. As the temperature was raised to 110°C, 6kV of corona voltage was applied and kept 110°C for 30 min. The UV-Vis absorption spectra of the polymer sample **4** before and after the poling are presented in Figure 1. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer **4** exhibited a decrease in absorption due to birefringence.

From the absorbance change, the order parameter of the poled film could be estimated, which is related to the poling efficiency. The estimated order parameter value Φ was deduced to be 0.14 ($\Phi=1-A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after poling). Domain structures of NLO-chromophores for the poled thin-film samples were obtained using atomic force microscopy (AFM). AFM images showed that the surface of the film sample is extremely flat and clean. However, this good quality film was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which were aligned the poling direction. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser (20-23). Nonlinear optical properties of polymer **4-6** are summarized in Table 3. The refractive index of the sample was measured by the optical transmission technique (19). The transmittance of thin film includes the information of the thickness, refractive index and extinction coefficient of that. So by analyzing the transmittance, we can determine those parameters. In order to determine the microscopic second-order susceptibility of the polymer, the angular

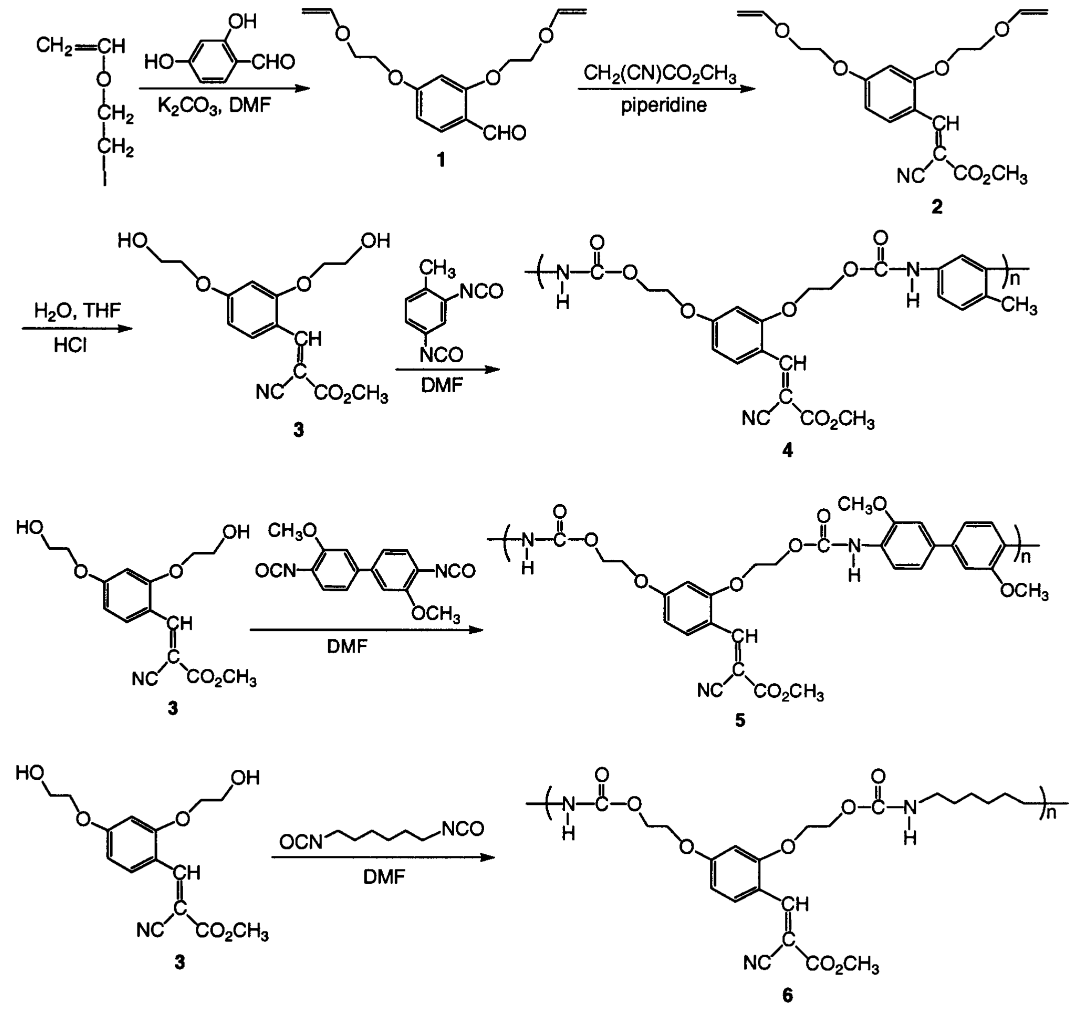

Table 1. Polymerization of **3**[a] with TDI[b], DMBPI[c], and HDI[d] in DMF

Monomer	Monomer/ Sovent (mol/L)	Diol **3** to Diisocyanate (mol%)	Time (h)	Yield (%)	η_{inh}[e] (dL/g)	M_n[f]	M_w[f]
3, TDI	0.40	1.0	6	88	0.23	11800	24600
3, TDI	0.80	1.0	8	90	0.26	12500	26300
3, DMBPI	0.40	1.0	8	82	0.24	11200	23800
3, DMBPI	0.80	1.0	10	85	0.23	12600	27900
3, HDI	0.40	1.0	8	83	0.21	10500	21600
3, HDI	0.80	1.0	10	84	0.23	11400	22700

[a] 3= Methyl 2,4-bis-(2'-hydroxyethoxy)benzylidenecyanoacetate.
[b] TDI=2,4-Toluendiisocyanate.
[c] DMBPI=3,3'-Dimethoxy-4,4'-biphenylenediisocyanate.
[d] HDI=1,6-hexamethylenediisocyanate.
[e] Inherent viscosity of polymer: Concentration of 0.5 g/dL in DMSO at 25 °C.
[f] Measured by GPC in THF using polystyrene standard.

Table 2. Thermal Properties of Polymers **4-6**

Polymer	T_g[a], °C	Degradation temp, °C[b]			Residue[b] at 700 °C, %
		5%-loss	20%-loss	40%-loss	
4	114	295	330	383	4.3
5	101	292	321	376	11.2
6	66	272	294	340	1.7

[a] Determined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of 10°C/min under nitrogen atmosphere.

[b] Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

SHG dependence was recorded. Figure 2 shows the angular dependence of SHG signal in a poled polymer **4**. The SHG coefficient d_{33} was calculated through the method developed by Herman et al (23). The SHG measurements revealed a d_{33} value of 7.8 x 10^{-9} esu for polymer **4**. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polyurethane, there was not resonant contribution to this d_{33} value. There is no negligible decay of the d_{33} signal over two hundreds hours in temporal stability measurements of the polymer **4** at 90°C.

Table 3. Nonlinear Optical Properties of Polymers **4-6**

Polymer	λ_{max}[a] (nm)	d_{33}[b] (esu)	Φ[c]	d_{31}[b] (esu)	d_{33}/d_{31}
4	369	$7.83x10^{-9}$	0.14	$2.92x10^{-9}$	2.68
5	386	$9.65x10^{-9}$	0.81	$3.36x10^{-9}$	2.87
6	382	$8.43x10^{-9}$	0.56	$3.02x10^{-9}$	2.79

[a] Polymer film after corona poling.

[b] SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes (20).

[c] Order parameter $\Phi=1-A_1/A_0$, A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively.

Conclusion

We prepared polyurethanes **4-6** having 2,4-dioxybenzylidenecyanoacetate as a NLO-chromophore in the main chain. Polymers **4-6** were soluble in common organic solvents. The resulting polymers **4-6** showed a thermal stability up to 280°C with a T_g of 66-114°C. SHG coefficients (d_{33}) of corona poled polymer films were 7.8 x 10^{-9} esu and exhibited good temporal NLO stability at elevated temperatures for hundreds of hours, which are acceptable for NLO device applications. We are now in the process of extending the polymerization system to the synthesis of other type of NLO polymers and the results will be reported elsewhere.

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