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SYNTHESIS OF POLYURETHANES CONTAINING DIOXYBENZYLIDENECYANOACETATE AS AN NLO-CHROMOPHORE FOR ELECTRO-OPTIC APPLICATIONS

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NOTE

SYNTHESIS OF POLYURETHANES CONTAINING DIOXYBENZYLIDENECYANOACETATE AS AN NLO-CHROMOPHORE FOR ELECTRO-OPTIC APPLICATIONS

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ABSTRACT

Methyl 2,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (**3**) was prepared by hydrolysis of methyl 2,4-di-(2'-vinylloxyethoxy)benzylidenecyanoacetate (**2**). Diol **3** was condensed with 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate to yield polyurethanes **4** and **5** containing the NLO-chromophore 2,4-dioxybenzylidenecyanoacetate. The resulting polyurethanes were soluble in common organic solvents such as acetone and DMF. T_g values of the polymers obtained from DSC thermograms were in the range of 101–114°C and electro-optic coefficient (r_{33}) of the poled polymer films was in the range of 12–15 pm/V at 633 nm. Polymers **4** and **5** showed a thermal stability up to 300°C in TGA thermograms, which is acceptable for NLO device applications.

Key Words: Methyl 2,4-di-(2'-hydroxyethoxy)benzylidenecyanoacetate; 2,4-Toluenediisocyanate; 3,3'-Dimethoxy-4,4'-biphenylenediisocyanate; Polyurethanes; Electro-optic coefficient.

INTRODUCTION

Nonlinear optical (NLO) materials based on organic compounds have been extensively studied over the past decade because of their potential applications in

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the field of telecommunications, optical signal processing, optical switching, etc. [1-3]. Among the organic materials the NLO polymers are considered good candidates for making the optical devices, 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 development of NLO polymers for electro-optic (EO) device applications, stabilization of electrically induced dipole alignment is an important consideration. Two approaches to minimize the randomization have been proposed. One is to use crosslinked systems [8-10] and the other is to utilize a high T_g polymers such as polyamides [11-12]. 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 [13-15]. Polyurethanes functionalized with hemicyanine [16] and thiophene chromophore [17] in side chain showed high thermal stability of aligned dipoles up to 150°C. Physically crosslinked systems via hydrogen bonds have advantages such as homogeneity and good processability relative to the chemically crosslinked systems, which suffer from significant optical loss and poor processability. 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 300°C with a T_g of 109-114°C. The EO 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 two new polyurethanes containing a oxybenzylidenecyanoacetate unit, which is presumably an effective NLO-chromophore in the main chain. After analyzing the structure of the resulting polymers, we investigated the properties such as T_g , thermal stability, and EO coefficient. We now report the results of the initial phase of the work.

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. ^1H 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. A DuPont 951 thermogravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ up to 700°C was used for the thermal degradation study of polymers under nitrogen. The alignment of the NLO-chromophore of the polymers was carried out by the corona poling method. As the temperature was raised to 110°C , 6kV of corona voltage was applied and kept at 110°C for 30 minutes. The EO coefficient (r_{33}) of the corona poled polymer film was measured by a simple reflection technique [19]. Melting points were measured in a Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

2,4-Di-(2'-Vinylloxyethoxy)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 80°C for 15 hours 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 a crude product, which was recrystallized from *n*-butanol yielded 25.0 g (90% yield) of pure product **1**. Mp = $68\text{--}69^\circ\text{C}$. ^1H NMR (CDCl_3) δ 4.03-4.35 (m, 12H, 2 $\text{CH}_2=$, 2 -O- $\text{CH}_2\text{-CH}_2\text{-O-}$), 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-Di-(2'-Vinylloxyethoxy)benzylidenecyanoacetate (2)

Piperidine (0.13 g, 1.5 mmol) was added to a solution of 2,4-di-(2'-vinylloxyethoxy)benz aldehyde **1** (8.35 g, 30 mmol) and methyl cyanoacetate (3.27 g, 33 mmol) in 200 mL of *n*-butanol with stirring at 0°C under nitrogen. After stirring for 3 hours at 0°C , the reaction mixture was cooled to -10°C for crystallization. The product was filtered and washed successively with cold *n*-butanol (80 mL), water (30 mL), and cold *n*-butanol (20 mL). The obtained pale yellow product was recrystallized from *n*-butanol to give 9.49 g (88% yield) of **2**. Mp= $96\text{--}97^\circ\text{C}$. ^1H NMR (CDCl_3) δ 3.89 (s, 3H, $-\text{CO}_2\text{CH}_3$), 4.02-4.34 (m, 12H, 2 $\text{CH}_2=$, 2 -O- $\text{CH}_2\text{-CH}_2\text{-O-}$), 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 $\text{C}_{19}\text{H}_{21}\text{NO}_6$: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.62; H, 5.82; N, 3.83.

Methyl 2,4-Di-(2'-Hydroxyethoxy)benzylidenecyanoacetate (3)

Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl 2,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (**2**) (9.34 g, 0.026 mol) in 60 mL of dry THF with stirring under nitrogen at 0°C. The mixture was stirred at 80°C for 8 hours 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 a crude product. The obtained pale yellow product was recrystallized from ethyl acetate to give 6.87 g (86% yield) of **3**. Mp: 168-170°C. ^1H 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, $-\text{CH}_2-\text{OH}$), 4.16-4.28 (m, 2H, $-\text{O}-\text{CH}_2-$), 6.72-6.76 (m, 2H, aromatic), 8.32-8.36 (d, 1H, aromatic), 8.70-8.72 (d, 1H, $-\text{Ph}-\text{CH}=\text{C}$). 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 $\text{C}_{15}\text{H}_{17}\text{NO}_6$: C, 58.63; H, 5.57; N, 4.56. Found: C, 58.76 H, 5.63; N, 4.65.

Synthesis of Polyurethanes 4 and 5

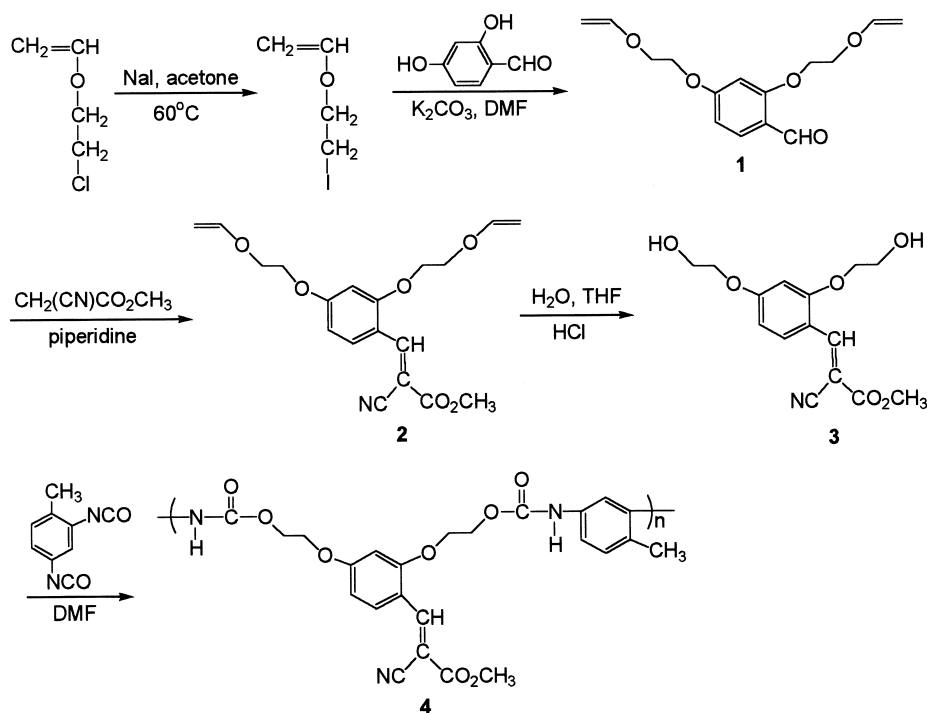
A representative polycondensation reaction procedure (the case of **4**) was as follows: 2,4-Toluenediisocyanate (1.74 g, 0.01 mol) was added slowly to a solution of 3.45 g of diol **3** (0.01 mol) in 50 mL of anhydrous DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80°C. After heating for 6 hours 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 vacuum to give 4.15 g (80% yield) of polymer **4**: $\eta_{\text{inh}}=0.23$ dL/g (c, 0.5 g/dL in DMSO at 25°C). ^1H NMR ($\text{DMSO}-d_6$) δ 1.94-2.21 (m, 3H, $-\text{CH}_3$), 3.95-4.02 (m, 3H, $-\text{COOCH}_3$), 4.06-4.85 (m, 8H, 2 - $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 6.88-7.32 (m, 6H, aromatic), 8.48-8.63 (m, 1H, $\text{Ph}-\text{CH}=\text{C}$), 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) $I_{\text{max}}=390$, $\epsilon=13200$. Anal. Calcd. for $(\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_8)_n$: C, 59.87; H, 4.81; N, 8.73. Found: C, 59.96; H, 4.95; N, 8.66. Polymer **5**: ^1H NMR ($\text{DMSO}-d_6$) δ 3.71-4.02 (m, 9H, $-\text{OCH}_3$), 4.08-4.96 (m, 8H, 2 - $\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 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, $\text{Ph}-\text{CH}=\text{C}$), 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) $\lambda_{\text{max}} = 392$, $\epsilon = 12500$. Anal. Calcd. for $(\text{C}_{31}\text{H}_{29}\text{N}_3\text{O}_{10})_n$: C, 61.69; H, 4.84; N, 6.96. Found: C, 61.78; H, 4.75; N, 6.88.

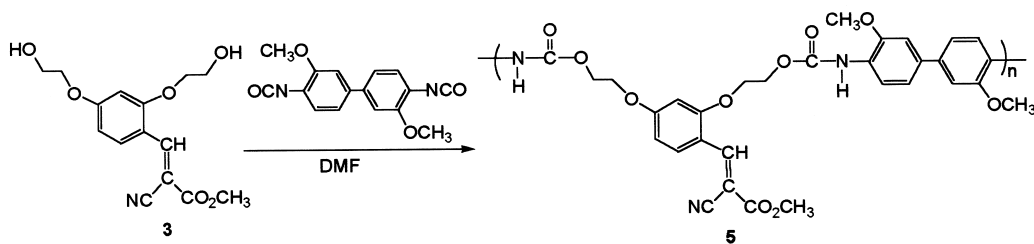
RESULTS AND DISCUSSION

Synthesis and Characterization of NLO Polyurethanes

2,4-Di-(2'-vinylxyethoxy)benzaldehyde (**1**) was prepared by a reaction of 2-iodoethyl vinyl ether with 2,4-dihydroxybenzaldehyde. Trifunctional compounds methyl 2,4-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (**2**) was prepared by the condensation reaction of **1** with methylcyanoacetate [20]. 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. Polymers **4** and **5** were prepared by the polyaddition reaction between a diol **3** and 2,4-toluenediisocyanate (TDI) and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate in a dry DMF solvent. The polymerization yield was 75-85%. The chemical structure of the compounds



Scheme 1.



Scheme 2.

was identified by ^1H NMR, IR spectra, and elemental analysis. ^1H 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 8.75–9.02 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 1719 cm^{-1} indicating the presence of urethane bond. We now have well defined polyurethanes (4–5) and investigate their properties.

Properties of Polyurethanes

The polymers **4** and **5** were soluble in common solvents such as acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. Polymers **4** and **5** isolated from methanol were yellow colored amorphous materials. The inherent viscosities were in the range of 0.25–0.30 dL/g. Polymers **4** and **5** showed strong absorption near 390 nm by the NLO-chromophore oxybenzylidenecyanoacetate in the main chain. 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 1. Polymers **4** and **5** showed good thermal stability and did not decompose below 300°C as shown in Table 1. The polymers

Table 1. Thermal Properties of Polymers **4** and **5**

Polymer	T_g , ($^\circ\text{C}$) ^a	Degradation temp. ($^\circ\text{C}$) ^b			Residue ^b at 700 $^\circ\text{C}$ (%)	r_{33} ^c (pm/V) ^c
		5%-loss	20%-loss	40%-loss		
4	114	295	330	383	5.3	12
5	101	292	321	376	11.2	15

^aDetermined from DSC curves measured on a DuPont 910 differential scanning calorimeter with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

^bDetermined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere.

^cEO coefficients were measured by simple reflection technique [20].

show a double phase degradation pattern in their TGA thermograms. T_g values of the polymers **4** and **5** measured by DSC were around 101-114°C, which is acceptable for EO device applications. The EO coefficient (r_{33}) of corona poled polymer films measured by simple reflection technique (20) was in the range of 12-15 pm/V at 633 nm.

CONCLUSION

We prepared two polyurethanes **4** and **5** having 2,4-dioxybenzylidenecyanoacetate as a NLO-chromophore in the main chain. Polymers **4** and **5** were soluble in common organic solvents. The resulting polymers **4** and **5** showed a thermal stability up to 300°C with a T_g of 101-114°C. The EO coefficient (r_{33}) of corona poled polymer films were in the range of 12-15 pm/V at 633 nm, which is acceptable for NLO device applications.

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