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Synthesis of polyurethanes containing dioxynitrostilbene as a NLO-chromophore and their properties

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Summary

3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**2**) were prepared by the reaction of 2-iodoethanol with 3,4-dihydroxy-4'-nitrostilbene (**1**). Diol **2** was condensed with 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocynate to yield polyurethanes **3** and **4** containing the NLO-chromophore 3,4-dioxy-4'-nitrostilbene. Polymers **3** and **4** were soluble in common organic solvents such as acetone and DMSO. T_g value of the resulting polymers was in the range of 109-114°C. Electrooptic coefficient (r_{33}) of the poled polymer films were in the range of 20-25 pm/V at 633 nm. Polymers **3** and **4** showed a thermal stability up to 300°C in TGA thermograms, which is acceptable for NLO device applications.

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 crosslinking method (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 (14-16). Polyurethanes functionalized with hemicyanine (17) and thiophene chromophore (18) in side chain showed high thermal stability of aligned dipoles up to 150°C. 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. In this work we prepared two new polyurethanes containing oxynitrostilbene unit, which is presumably effective NLO-chromophore in the main chain. After analyzing the structure of the resulting polymers

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we investigated the properties such as T_g, thermal stability, and electrooptic (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. 4-Nitrophenylacetic acid, 3,4-dihydroxybenzaldehyde, and 2-iodoethanol were used as received. 2,4-Toluenediisocynate (TDI) was purified by distillation under reduced pressure. 3,3'-Dimentoxy-4,4'-biphenylenediisocynate 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.

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 10°C/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 corona poling method. As the temperature was raised to 100°C, 6kV of corona voltage was applied and kept 100°C for 30 min. The electrooptic coefficient (r_{33}) of the corona poled polymer film was mesured by simple reflection technique (19). Melting points were measured in Buchi 530 melting point apparatus and are corrected. Viscosity values were obtained by using a Cannon-Fenske viscometer.

3,4-Dihydroxy-4'-nitrostilbene (**1**)

Compound **1** was prepared by a known method (20) from 3,4-dihydroxybenzaldehyde and 4-nitrophenylacetic acid, and recrystallized from 80% aqueous ethanol. Mp=196-197°C. ^{1}H NMR ($CDCl_3$) δ 6.89-6.92 (d, 2H, aromatic), 7.06-7.24 (m, 3H, aromatic), 7.40-7.46 (d, 1H, aromatic), 7.83-7.86 (d, 2H, aromatic), 8.24-8.27 (d, 2H, aromatic). IR (KBr) 3439 (s, O-H), 3031 (w, =C-H), 2875 (w, C-H), 16703, 1589(vs, C=C) cm^{-1}.

3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**2**)

3,4-Dihydroxy-4'-nitrostilbene (7.71 g, 0.03 mol), anhydrous potassium carbonate (24.9 g, 0.18 mol), and 2-iodoethanol (23.8 g, 0.12 mol) were dissolved in 100 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 80°C for 12 h under nitrogen. The resulting solution was cooled to room temperature, diluted with 200 mL of water, stirrd, filtered, and the obtained product was washed with 100 mL of water. Thus obtained product was recrystallized from ethanol to give 9.22g (89% yield) of **2**. Mp=150-154°C. ^{1}H NMR ($CDCl_3$) δ 3.72-3.80 (m, 4H, $-O-CH_2-CH_2-O-$), 3.96-4.11 (m, 4H, $-O-CH_2-CH_2-O-$), 6.93-7.47 (m, 5H, aromatic), 7.78-7.83(m, 2H, aromatic), 8.17-8.23 (m, 2H, aromatic). IR (KBr) 3501 (s, O-H), 2926 (m, C-H), 1589 (s, C=C) cm^{-1}. UV/Vis (DMSO) λ_{max}=392, ε=21140. Anal. Calcd for $C_{18}H_{19}NO_6$: C, 62.60; H, 5.54; N, 4.06. Found: C, 62.52; H, 5.48; N, 4.11.

Synthesis of polyurethanes **3** *and* **4**

A representative polyaddition procedure (the case of **3**) was as follows: 2,4-Toluenediisocynate (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 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. Thus obtained polymer was dried under vacum to give 4.15 g (80% yield) of polymer **3**: η_{inh}=0.21 dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 1.90-2.25 (m, 3H, $-CH_3$), 3.64-4.83 (m, 4H, 2 $-O-CH_2-CH_2-O-$), 6.77-8.32 (m, 12H, aromatic), 8.48-8.95 (m, 2H, N-H). IR (KBr) 3377 (s, N-H), 2927, 2885 (m, C-H), 1709 (s, C=O), 1591 (vs, C=C) cm^{-1}. UV/Vis (DMSO) λ_{max}=391, ε=14360. Anal. Calcd for $(C_{27}H_{25}N_3O_8)_n$: C, 62.42; H, 4.85; N, 8.09. Found: C, 62.55; H, 4.98; N, 8.17. Polymer **4**: η_{inh}=0.23 dL/g (c, 0.5 g/dL in DMSO at 25°C). ^{1}H NMR (DMSO-d_6) δ 3.26-3.35 (m, 6H, $-OCH_3$), 3.74-4.85 (m, 4H, 2 $-O-CH_2-CH_2-O-$), 6.98-8.21 (m, 15H, aromatic), 8.55-9.14 (m, 2H, N-H). IR (KBr) 3398 (m, N-H), 2939, 2837 (m, C-H), 1728 (s, C=O), 1589 (s, C=C) cm^{-1}. UV/Vis (DMSO) λ_{max}=393, ε=12660. Anal. Calcd for $(C_{34}H_{31}N_3O_{10})_n$: C, 63.64; H, 4.87; N, 6.55. Found: C, 63.78; H, 4.95; N, 6.46.

Results and Discussion

Synthesis and characterization of polymers **3** *and* **4**

3,4-Dihydroxy-4'-nitrostilbene (**1**) wase prepared by the condensation of 4-nitrophenyl-acetic acid with 3,4-dihydroxybenzaldehyde according to a literature procedure (20). 3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**2**) was prepared by the reaction of 2-iodo-ethanol with **1**. The chemical structure of the compounds was identified by proton-NMR, IR spectra, and elemental analysis. All the analytical data confirmed the expected chemical structure. Compound **2** showed strong uv absorption bands around 392 nm measured in chloroform. Polymers **3** and **4** were prepared by polyaddition between a diol **2** and 2,4-toluenediisocynate (TDI) and 3,3'-dimetoxy-4,4'-biphenylenediisocynate in a dry DMF solvent. The polymerization yield was 75-85%. The chemical structure of the compounds was identified by proton-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 8.5-9.0 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 1728 cm^{-1} indicating the presence of urethane bond. We now have well defined polyurethanes (**3-4**) and investigate their properties.

Properties of polymers **3** *and* **4**

The polymers **3** and **4** were soluble in common solvents such as acetone, DMF, and DMSO, but were not soluble in methanol and diethyl ether. Polymers **3** and **4** isolated from methanol were white colored amorphous materials. The inherent viscosities were in the range of 0.20-0.25 dL/g. Polymers **3** and **4** showed strong absorption near 390 nm by the NLO-chromophore oxynitrostilbene 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 **3** and **4** showed a good thermal stability and did not decompose below 300°C as shown in Table 1. The polymers show a double phase degradation pattern in their TGA thermograms. T_g values of the polymers **3** and **4** measured by DSC were around 109-114°C, which is acceptable for electrooptic device applications. The electrooptic coefficient (r_{33})of corona poled polymer films measured by simple reflection technique (16) was in the range of 20-25 pm/V at 633 nm.

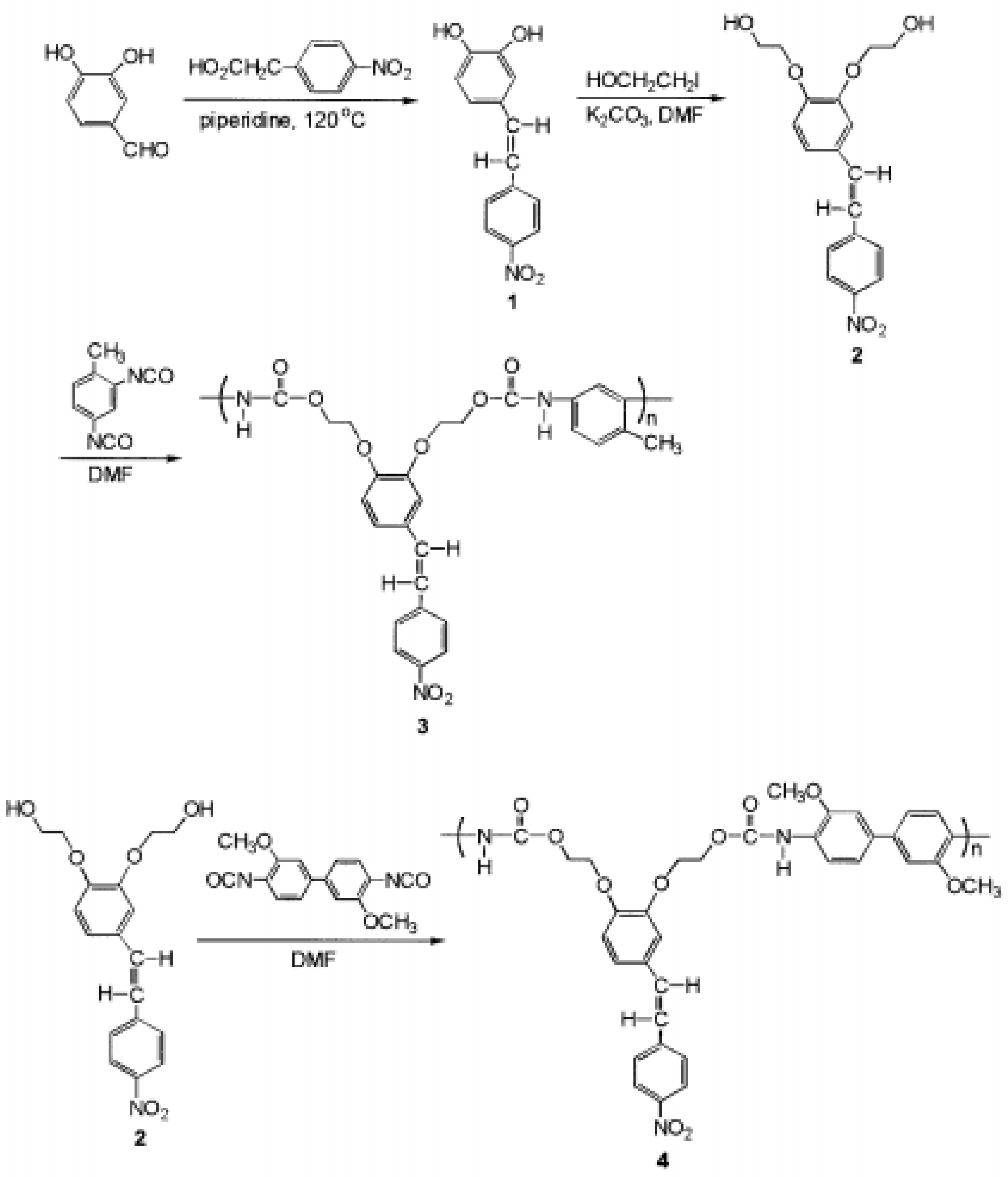

Table 1. Thermal properties of polymers **3** and **4**

Polymer	T_g[a], °C	Degradation temp, °C[b]			Residue[b] at 700 °C, %	r_{33}[c] (pm/V)
		5%-loss	20%-loss	40%-loss		
3	109	298	330	385	2.7	20
4	114	297	329	411	3.3	25

[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.
[c]EO coefficients were measured by simple reflection technique (19).

Conclusion

We prepared two polyurethanes **3** and **4** having 3,4-dioxy-4'-nitrostilbene as a NLO-chromophore in the main chain. Polymers **3** and **4** were soluble in common organic solvents. The resulting polymers **3** and **4** showed a thermal stability up to 300°C with a T_g of 109-114°C. The electrooptic coefficient (r_{33}) of corona poled polymer films was in the range of 20-25 pm/V at 633 nm, which is 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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References

1. Chelma DS, Zyss J (ed) Nonlinear Optical Properties of Organic Molecules and Crystals vol 12 Academic Press New York 1987
2. Prasad PN, Williams DJ (ed) Introduction to Nonlinear Optical Effects in Molecules and Polymers John Wiley & Sons New York 1991
3. Zyss J (ed) Molecular Nonlinear Optics Materials Physics and Devices Academic Press Orlando FL 1994
4. Burland DM, Miller RD, Walsh C Chem Rev (1994) 94: 31
5. Dalton LR, Harper AW, Ghosn R, Steiner WH, Ziari M. Fetterman H, Shi Y, Mustacich RV, Jen AKY, Shea KJ Chem Mater (1995) 7: 1060
6. Dalton LR, Harper AW, Ghosn R, Laquindanum J, Liang Z, Hubble A, Xu C, Adv Mater (1995) 7: 519
7. Marks TJ, Ratner MA (1995) Angew Chem Int Ed Engl 34: 155
8. Williams DJ (ed) Nonlinear Optical Properties of Organic and Polymeric Materials ACS Sym Ser 233 1983
9. Ranon PM, Shi Y, Steiner WH, Xu CH, Dalton LR Organic Thin Films for Photonics Applications, OSA 1993 Technical Didest Series 17: 10
10. Han KS, Park SK, Shim SY, Jahng WS, Kim NJ (1998) Bull Korean Chem Soc 19: 1165
11. Han KS, Park SK, Shim SY, Lee YS, Jahng WS, Kim NJ (1998) Bull Korean Chem Soc 19: 1165
12. Becker MW, Sapochak LS, Ghosn R, Dalton LR (1994) Chem Mater 76: 104
13. Stahelin M, Walsh C, Burland DM, Miller RD, Twieg R, Volksen WJ (1994) J Appl Phys 94: 31
14. Boogers JAF, Klaase PTA, Vlieger JJD, Tinnemans AHA (1994) Macromolecules 27: 205
15. Park CK, Zieba CF, Zhao CF, Swedek B, Wijekoon WMKP, Prasad PN (1995) Macromolecules 28: 3713
16. Tsutumi N, Yoshizaki S, Sakai W, Kiyotsukuri T (1995) Macromolecules 28: 6437
17. Moon KJ, Shim HK, Lee KS, Zieba J, Prasad PN (1996) Macromolecules 29: 861
18. Woo HY, Lee KS, Shim HK (1998) Polym Preprints 39: 1097
19. Teng CC, Mann HT (1990) Appl Phys Lett 56: 30
20. Cullinane NM (1923) J Chem Soc 123: 2053