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Synthesis and Characterization of Polyurethanes Containing Dioxynitrostilbenyl Group as a NLO-Chromophore

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3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**2**) was prepared and condensed with 2,4-toluenediisocyanate and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate to yield polyurethanes **3** and **4** containing the NLO-chromophore dioxynitrostilbenyl group. Polymers **3-4** were soluble in common organic solvents. Polymers **3-4** showed a thermal stability up to 300°C in TGA thermograms with T_g values in the range of 109-114°C in DSC thermograms. The SHG coefficients (d_{33}) of poled polymer films were around 3.2 x 10^{-9} esu.

Keywords 3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene; 2,4-Toluene diisocyanate; Glass transition temperature; SHG coefficient (d_{33})

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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 switching, etc. Among the organic materials the NLO polymers are considered candidate materials, mainly because they offer many advantages such as light weight and good processability to form optical devices [1]. One of the current challenges is to design novel NLO polymers having optimized properties. In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles. In this work we prepared novel polyurethanes containing dioxynitrostilbenyl unit, which is presumably effective NLO-chromophore. After confirming the structure of the resulting polymers we investigated the properties such as T_g, thermal stability, and second order NLO activity.

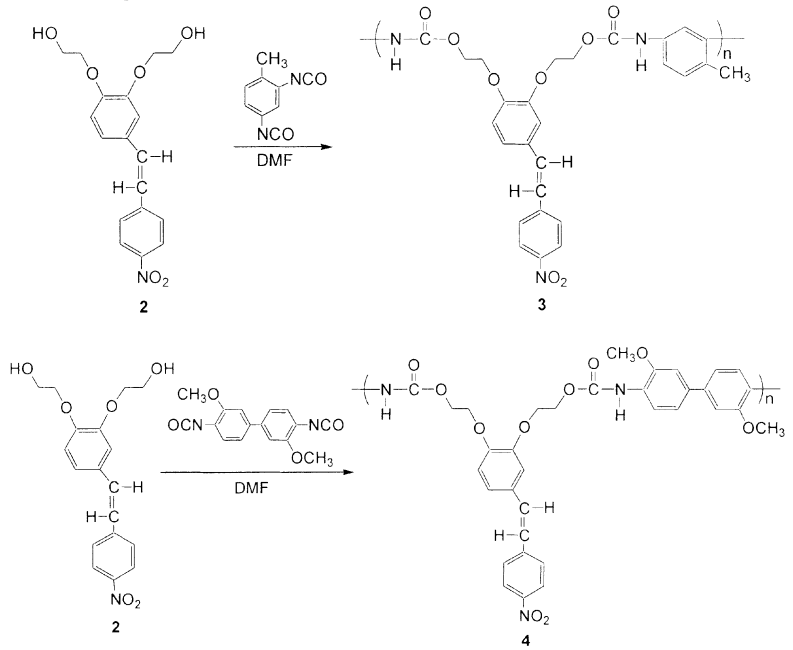
EXPERIMENTAL

Polyurethanes **3** and **4** were prepared according to a literature procedure [2]. The alignment of the NLO-chromophore of the polymers was carried out by corona poling method (6.5kV, 122°C, 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) measurements were made using a Maker fringe technique [4].

RESULTS AND DISCUSSION

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

3,4-Di-(2'-hydroxyethoxy)-4'-nitrostilbene (**2**) was prepared by the reaction of 2-iodoethanol with 3,4-dihydroxy-4'-nitrostilbene (**1**). Polymers **3-4** were prepared by polyaddition between a diol **2** and 2,4-toluenediisocyanate (TDI) and 3,3'-dimethoxy-4,4'-biphenylenediisocy anate in a dry DMF solvent (Scheme 1). The chemical structures of the compounds were confirmed by ^{1}H NMR, IR spectra, and elemental analysis. The signal at 8.5-9.1 ppm of the ^{1}H NMR spectra assigned to the amine proton indicates the formation of urethane linkage.



SCHEME 1. Synthetic method of polymers **3** and **4**.

Properties of polymers **3-4**

The polymers **3-4** were soluble in common solvents such as acetone and DMF. Polymers **3-4** showed a thermal stability up to 300°C with T_g values around 109-114°C in DSC thermograms. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled at 122°C and 6.5kV of corona voltage. The UV-Vis absorption spectra of the polymer samples before and after the poling were recorded. After the poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectra of polymers **3-4** exhibited a decrease in absorption due to birefringence. AFM images show 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. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser [3]. The SHG coefficient d_{33} was calculated through the method developed by Herman et al [4]. The SHG measurements revealed a d_{33} value of 3.2×10^{-9} esu for polymer **3**.

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