Synthesis and Second-Order Nonlinear Optical Properties of Cross-Linked Polyurethanes with Hemicyanine-Type Chromophores

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ABSTRACT: The crosslinked polyurethanes with three different bonding sites were prepared by the reaction of poly[(phenylisocyanate)-co-formaldehyde], which has one cross linking site located at every phenylene moiety, and hydroxy-functionalized chromophores. To obtain the high nonlinear optical activity of polymers, hemicyanine-type chromophore with high molecular hyperpolarizability (β) was introduced into the polyurethane structure. The $\chi^{(2)}$ values of the resulting poled and cured polymers ranged between 16.8 pm/V~37.4 pm/V at 1.064 μm wavelength. According to thermal stability studies of second harmonic generation activity on PU-VP, it was found that the decay of $\chi^{(2)}$ value was minimized due to the lattice hardening of polyurethane matrix with three bonding sites.

Introduction

One of the critical problems in the development of second-order non-linear optical (NLO) polymers is to stabilize the dipole alignments induced by an electric field, especially at elevated temperatures. Attachment of chromophores as pendants to flexible polymer backbone or the incorporation of chromophores as components of the polymer backbone leads to improvement in the stability of poling-induced order relative to dye doped systems. However, additional lattice hardening is required for device applications. Recently, several works focused on this issue was published, in which crosslinking reactions were utilized to stabilize the dipole orientation after electric poling. After Eich et al. described thermosetting epoxy polymer first, many researchers developed new types of crosslinked second-order NLO polymers using functional groups such as cinnamic groups, maleimide group or ethynyl group. In all these systems, some degrees of stabilization of aligned dipoles was noticed. More recently, functionalized NLO monomers and polymers which can be reacted with isocyanate group have been proven to be useful approach for preparing the second-order NLO polymers with good long-term stability.

In this paper, we report the synthesis of new crosslinked polyurethanes obtained by the novel crosslinking reaction and their physicochemical and optical properties. In addition, we also discuss the details of their optical second-order activity in terms of electrical poling and thermal stability. In particular, the stability of the poling-induced dipole of polyurethane derived from the three different cross-linkable monomers are compared.

Experimental

Materials. All the reagent grade chemicals were obtained from various commercial sources. Poly (phenylisocyanate-co-formaldehyde) (PPCF) was purchased from Aldrich. Dimethylformamide (DMF) (Junsei) was purified by distilling under reduced pressure over anhydrous magnesium sulfate and further dried over a molecular sieve. 2,4-Toluene disiocyanate (Aldrich) was purified by the distilling under reduced pressure.

Measurements. $^1$H-NMR spectra of all intermediates and monomers were recorded on a Bruker FT-NMR AC200 (200 MHz) spectrometer. IR spectra of polymers were obtained with a Boemen Mi-
chelson series FT-IR spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a DuPont 9900 analyzer. The SHG experiments were performed with the polarization beam at the fundamental frequency of amode-locked Q-switched Nd : YAG laser operating at 500 Hz with 135 ps subpulses in each pulse train. The NLO activity of the polymer films was produced by electric poling induced by corona discharge.

4-[N-(2-Acetoxyethyl)-N-methylamino]benzaldehyde (1a). A flask was filled with 80 mL of anhydrous DMF while being cooled in ice bath. Then, 16.75 g (109 mmol) of phosphorus oxychloride was added dropwise with stirring. After 30 min, 17.9 g (92.8 mmol) of N-acetoxyethyl-N-methylenamine was added to the above solution. This mixture was heated at 60 °C for 2 h. Thereafter, the mixture was then cooled and poured over crushed ice in a beaker and neutralized to pH 6~8 by dropwise addition of saturated sodium acetate solution. The mixture was extracted with ethyl acetate and the extracts were washed with water, dried with magnesium sulfate, and then concentrated. The resulting raw material was purified by column chromatography to yield 14.5 g (70.6%) of the yellowish liquid product.

1H-NMR (CDCl3) δ 9.72 (s, 1H), 7.71 (d, 2H), 6.73 (d, 2H), 4.25 (t, 2H), 3.67 (t, 2H), 0.66 (s, 3H), 1.97 (s, 3H).

N-Hydroxypropyl-γ-picolinium chloride (2). A mixture of 9.57 g (102 mmol) of 4-picoline and 9.71 g (102 mmol) of 3-chloropropanol was heated at 90 °C for 2.5 days. The hygroscopic solid produced was purified by washing several times with acetone. The product yield was 73%.

1H-NMR (D2O) δ 8.70 (d, 2H), 7.90 (d, 2H), 4.67 (t, 2H), 3.87 (t, 2H), 2.67 (s, 2H), 2.25 (m, 2H).

E-N'-Hydroxypropyl-4-[2-(4-bis(2-hydroxyethyl)aminophenyl)ethenyl]pyridinium tetraphenylborate (4a). To a solution of 6.48 g (29.3 mmol) of 1a and 5.5 g (29.3 mmol) of picoline salt 2 in 100 mL of methanol a catalytic amount of 0.5 mL of piperidine was added and the mixture was then refluxed. After 2 days, methanol was evaporated and the residue was washed several times with acetone. The resulting viscous red liquid 3a was dissolved in water. To this solution was added the solution of sodium tetraphenylborate (10.0 g, 29.3 mmol) in water. The red solid that precipitated was filtered and then washed with water several times. The yield was 7.6 g (41%).

1H-NMR (DMSO-d6) δ 8.65 (d, 2H), 7.97 (d, 2H), 7.88 (d, 1H), 6.57 (d, 2H), 7.18-6.75 (m, 23H), 4.77 (br, t, 2H), 4.45 (br, t, 2H), 3.59-3.40 (m, 6H), 3.03 (s, 3H), 2.01 (m, 2H).

E-N'-Hydroxypropyl-4-[2-(4-bis(2-hydroxyethyl)aminophenyl)ethenyl]pyridinium chloride (3b). To a solution of 13.2 g (70 mmol) of compound 2 and 20.0 g (70 mmol) of the compound 1b in 150 mL of methanol a catalytic amount of 0.5 mL of piperidine was added and the mixture was then refluxed. After 2.5 days, methanol was evaporated and a large amount of acetone was added and stored in the refrigerator for 1 day. The precipitated solid was washed several times with acetone by decanting. The yield was 84%.

1H-NMR (DMSO-d6) δ 8.7 (d, 2H), 8.02 (d, 2H), 7.90 (d, 1H), 7.54 (d, 2H), 7.13 (d, 1H), 6.80 (d, 2H), 4.49 (t, 2H), 3.52-3.35 (m, 10H), 2.03 (m, 2H).

E-N'-Hydroxypropyl-4-[2-(4-bis(2-hydroxyethyl)aminophenyl)ethenyl]pyridinium tetraphenylborate (4b). To a solution of 7.50 g (19.8 mmol) of 3b in 200 mL of water, a solution of 6.77 g (19.8 mmol) of sodium tetraphenylborate in 200 mL of water was added dropwise. Red precipitate formed immediately. The precipitate was collected by filtration and then dried. The product yield was 12.4 g (95%).

1H-NMR (DMSO-d6) δ 8.65 (d, 2H), 7.97 (d, 2H), 7.87 (d, 1H), 7.55 (d, 2H), 7.19-6.75 (m, 23H), 4.82-4.75 (m, 3H), 4.44 (t, 2H), 3.60-3.40 (m, 8H).

Synthesis of Cross-linked Polyurethanes (PUV, PU-P, and PU-VP). To a solution of diol monomer 4a (240 mg) in 250 mg of anhydrous dimethylacetamide and 1,000 mg of cyclopentanone 47.6 wt% solution (320 µL, d=1.06) of PPICF in DMF was added. Similarly, the diol monomers 5 and 4b were reacted with 220 µL and 221 µL of PPICF in DMF, respectively.

Results and Discussion

Synthesis and Characterization of Monomers and Polymers. Novel cross-linkable stilazolium
Scheme I. Synthetic routes for monomers.

salt monomers 5 having tetraphenylborate as the counter anion was synthesized using the similar pathway reported in the literature. The monomer 4a and 4b were obtained by the synthetic approach, as shown in Scheme I.

The picoline salt 2 having terminal hydroxy group was reacted with the aldehyde compounds 1a or 1b to give stilbazolium salts having chloride as the counter anion. These stilbazolium salts 3a and 3b are hygroscopic and well dissolved in water and methanol. Thus, the purification of the compounds in the fine powder form was very difficult. At first, stilbazolium salts was dissolved in methanol and then large amount of acetone was poured into this solution. The mixture was cooled in refrigerator and the upper layer solution was discarded. Scratching the residue by a spatula produced reddish powder. Ion exchange reactions from the chloride to the tetraphenylborate anion were performed using sodium tetraphenylborate, either in water or methanol. The water was better solvent for the isolation because the use of methanol resulted in the formation of solid that was unfilterable.

The synthetic routes for the three cross-linked polyurethane systems (PU-V, PU-P and PU-VP) were shown in Scheme II. All dried monomers were reacted with liquid polymer PPICF. The isocyanate/hydroxy (NCO/OH) ratios of both react- tants were equivalent. PPICF was a highly viscous liquid and was diluted to about 50 wt.% for microsyringe handling. The monomers were dis- solved in the solvent (DMF : cyclopentanone=1 : 4 by weight) and the diluted PPICF was added and mixed thoroughly for 5 min. There resulting mixtures were directly spin-coated at 400–900 rpm after filtration using 0.45 μm pore-size syringe filter. After 1.2 h, the solutions did not exhibit flow characteristics to gel formation. The quality of the spin-coated film was improved by using the co- solvent system compared to DMF only. The coated films were directly poled and their SHG signal was measured at the in-situ poling set-up.

The FT-IR spectra of the three cross-linked polymer systems were shown in Figure 1. No significant difference in vibration frequency was observed among the samples. All polymers exhibited a sharp absorption peak at 1716 cm⁻¹ from the carbonyl stretching vibration. The absorption peak at 2276 cm⁻¹ from the isocyanate group of PPICF was not observed.

The results from TGA and DSC of cross-linked polyurethane PU-VP are given in Figure 2. The characteristic glass transition is not observed. The
Scheme II. Polymerization steps for PU-V, PU-P and PU-VP.

5 \( R_1 = CH_2CH_2OH, R_2 = CH_2CH_2CH_2CH_3 \)
4a \( R_1 = CH_3, R_2 = CH_2CH_2CH_2OH \)
4b \( R_1 = CH_2CH_2OH, R_2 = CH_2CH_2CH_2OH \)

1) Spin coating
2) Poling / \( \Delta \)

In order to check the stability of three cross-linked films which were cured under the same condition (100°C for 4 h), solubility test was performed by dipping films into DMF at an ambient temperature for 2 h. Figure 3 shows normalized UV-visible absorption changes for the same films dipped in DMF solvent for 1 and 2 h. For PU-P and PU-V films, dipping for 1 h produced a large reduction of UV absorbance. This is probably due to the solvation of oligomer and low crosslink density portion of the material in the DMF solvent. No further change in UV absorbance was observed with the increased dipping time (2 h). On the other hand, for PU-VP, almost no change in UV absorbance was observed with the dipping time. This indicates that the crosslink density for this system was higher than PU-P and PU-V systems.

Second-Order NLO Properties of Cross-Linked Polyurethanes. In general, the polymeric NLO materials for the measurement of second harmonic generation (SHG) was spin-coated on indium tin oxide (ITO) glass. We also used ITO glass but polymeric films became turbid during the poling. The surface charge of the film during the poling was measured and the surface charge was found to be very small under the ITO glass substrate. This im-

Cross-Linked NLO Polyurethanes

Figure 1. FT-IR spectra of various cross-linked polyurethanes (PU-V, PU-P and PU-VP).

Figure 2. TGA and DSC thermograms of PU-VP (heating rate 10°C/min).

Figure 3. Changes of normalized UV-visible absorbances of the polyurethane films under same cured condition (100°C, 4 h) according to the dipping time into DMF solvent.

Figure 4. In situ scan profiles obtained from cross-linked polyurethanes coated on normal corning glass.

plies that a large amount of electrical current passed through the polymeric film and resulted in some deformation of the polymer film. When we changed the substrate to normal corning glass, turbidity did not occur and the transparent film was obtained after poling.

In Figure 4, typical profiles of our in-situ poling experiments on the cross-linked polymers using normal corning glass are shown. A rapid build-up of SHG signals is observed directly by raising temperature after the poling field was imposed across the polymeric films. When the temperature approached 120°C, a sharp increase in the SHG signal started. It should be noted that in the temperature range between 75°C and 120°C, no decrease was detected in the corona discharge produced electric potential on the film surface. The temperature was cooled down after the stabilization of SHG at 120°C. The signal was rapidly increased as soon as the cooling started. This phenomenon reveals that an instant decrease of thermal conductivity affect poling efficiency. After the sample reached room temperature the electric field was removed. The electric surface potential of the sample discharged rapidly to zero and at the same time a fast drop in the SHG signal intensity occurred in two samples made from monomer 4a and 4b. In contrast, a fast increase in the SHG signal was observed in the sample prepared from monomer 5. Similar trend was also obtained with linear polyurethane (PU1-C4B) using the same monomer.18 After 15 minutes, the signals stabilized to the saturation level. In most polymers, as the corona voltage is turned off, a similar fast decay shown in PU-5 and PU-VP is observed. This phenomenon is attributed to the release of charge.
Table I. Chromophore Contents and Thermal Stability Data of $\chi(2)$ Values for Crosslinked Polyurethanes

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Bonding Direction</th>
<th>Chromophore Content (wt.%)</th>
<th>$\chi(2)$ Value (pm/V)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>25 °C</td>
<td>75 °C</td>
</tr>
<tr>
<td>PU-V</td>
<td>vertical</td>
<td>69.2</td>
<td>37.4</td>
</tr>
<tr>
<td>PU-P</td>
<td>parallel</td>
<td>68.4</td>
<td>16.8</td>
</tr>
<tr>
<td>PU-VP</td>
<td>vertical &amp; parallel</td>
<td>69.7</td>
<td>30.2</td>
</tr>
</tbody>
</table>

*Bonding directions indicate approximate angle between dipole of chromophore and two bonding sites.
*Retained percent age of initial NLO activity to the corresponding temperature.

Figure 5. Comparison on the SHG signal intensity of poled PU-V, PU-P and PU-VP films. Y-cut quartz plate was used as a standard ($d_{11}$ value $0.8 \times 10^{-10}$ esu).

Figure 6. Thermal stability of SHG response for PU-VP (measured every 30 min interval).

Carriers rapped in the film. Thus, the SHG signal increases after removal of the poling field in PU-V is highly unusual. No reference related to this phenomenon has been found in the literatures. For our system, one can expect that after the electric field was removed the chromophore molecules tilt slightly from their initial orientation induced by the field. Suppose that in their new orientation a set of higher $d_{xx}$ parameters was generated by the beam, then it should produce an increase in the observed SHG signal intensity. However, the fact that in the other two cross-linked systems which the dipole tilt was restricted by the terminal hydroxy group showed very different behaviors confirms this hypothesis.

In order to determine the macroscopic second-order susceptibility ($\chi^{(2)}$) after poling was completed, the sample was removed from the poling stage and its angular SHG dependence was recorded, and then compared with the value ($d_{11} = 0.8 \times 10^{-10}$ esu) obtained from a 1 mm thick Y-cut quartz plate. Figure 5 shows SHG profile of three different polymers with quartz as a standard. The poled and cured polymer films showed a relatively high second-order optical activity. The measured $\chi^{(2)}$ values of PU-V, PU-P and PU-VP were $8.9 \times 10^{-14}$ (37.4 pm/V), $4.0 \times 10^{-14}$ (16.8 pm/V) and $7.2 \times 10^{-14}$ esu (30.2 pm/V), respectively, as listed in Table I. Considering the similar chromophore density, the reason for the lower $\chi^{(2)}$ value of PU-P reflects that the cross-linking effect is decreased significantly in parallel to the locking structure.

The thermal endurance of SHG activity for all samples from room temperature to 225 °C (Figure 6) was also monitored. The SHG signal was checked at about every thirty minutes during stepwise temperature increase. The magnitude of $\chi^{(2)}$ decreased only to 85–94% of the initial value for temperatures below 100 °C. It was found that in PU-VP the decay of thermal stability was minimized due to lattice hardening of polyurethane with three bonding sites. For this sample SHG signal was still detectable even at 200 °C, but the NLO activity in PU-V and PU-P disappeared at 175 °C. The depoling processes were irreversible and the SHG signal did not recover when the materials.
were brought back to room temperature.

In conclusion, three types of second-order NLO cross-linked polyurethanes derived from PPICF and hemicyanine-type derivatives having bulky tetraphenylborate anion were prepared under in-situ conditions, then simultaneously poled and thermally cross-linked. The three resulting materials exhibited high second-order activities described by $\chi^{(2)}$ values between 16.8–37.4 pm/V. The poled and thermally cured polymeric films demonstrated improved temporal stabilities of their non-linear optical properties according to increased number of cross-linking site and parallel locking.

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References