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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF NLO DYE-CONTAINING POLYURETHANE

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Abstract Polyurethane attached hemicyanine dye with tetraphenylborate anion was synthesized. This polymer was soluble in dimethylformamide and could be processed into thin film by spin coating. The poled polymer film showed a large second-order nonlinear optical coefficient ($\chi^{(2)} = 4.0 \times 10^{-7}$ esu) and good temporal stability.

Keywords: Polyurethane, Second Harmonic Generation(SHG), Hemicyanine, Nonlinear Optics(NLO)

INTRODUCTION

Developments of optical telecommunication and optical information processing have led to a tremendous growth in research on nonlinear optical (NLO) materials. Recently polymeric materials have been of particular interest due to their promising potential applications in these areas. This interest has arisen from the ease of processibility, large optical nonlinearity, high laser damage threshold and fast response time possible with polymers.[1-3]

In polymeric nonlinear optical materials, the NLO active molecules, ie, dyes, are incorporated either by doping (guest/host system) or by attaching covalently into amorphous polymers. The noncentrosymmetric alignment of the dyes in both approaches can be achieved by the application of a strong electric field near the glass transition temperature.

As NLO active dyes, many organic compounds have been studied. Recently, particular attention has been paid to the hemicyanine dye, since it has large second-order NLO susceptibility. Also it was reported that the second harmonic intensity of the dye is strongly anion-dependent, usually increases with the increasing anion size.[4] However, many studies for second-order nonlinear activity using hemicyanine moieties were focused on organics or polymeric Langmuir-Blodgett materials.[5-9] Thus, we are interested in the incorporation of hemicyanine moiety with tetraphenylborate anion onto polyurethane backbone. In this system,

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hydrogen bonding between urethanes may improve the temporal stability of the NLO response and the use of bulky counter ion may reduce the relaxation of dyes in the polymer matrix.

EXPERIMENTAL

Synthesis of Monomer: N,N-Bis(hydroxyethyl)aminobenzene(1). A mixture of 2-chloroethanol (177 g, 2.2 mol), aniline (93 g, 1.0 mol) and sodium hydroxide(96%, 91.6 g, 2.2 mol) was stirred at 100°C for 3 days. The mixture was cooled to room temperature, extracted with methylene chloride and washed with water. The organic layer was dried with anhydrous magnesium sulfate, concentrated and purified by recrystallization with diethyl ether/ petroleum ether. The product yield was 87%. ^{1}H-NMR ($CDCl_3$): δ= 7.2(m, 2H), 6.7(m, 3H), 4.5(s, 2H), 3.7(t, 4H), 3.5(t, 4H).

N,N-Bis(2-acetyloxyethyl)aminobenzene(2). Compound **1** (25.96 g, 0.14 mol) was dissolved in 200ml of methylene chloride . To this solution, acetic anhydride(43.9 g) and pyridine(32 g) was added, and then the resulting mixture was refluxed. After 1 day, the reaction mixture was cooled and washed with water. The organic layer was dried with anhydrous magnesium sulfate, and then concentrated. The product was purified by vacuum distillation. Yellow viscous oil was obtained(83%). ^{1}H-NMR($CDCl_3$): δ=7.2(m, 2H), 6.8(m, 3H), 4.3(t, 4H), 3.6(t, 4H), 2.1(s, 6H).

4-(N,N-Bis(2-acetyloxyethyl)amino)benzaldehyde(3). To a flask was placed 40 ml of anhydrous dimethylformamide while the flask was cooled in ice bath. Then phosphorus oxychloride(25.4 g, 0.17 mol) was added dropwise with stirring. After 30 min, compound **2** (40 g, 0.15 mol) was added to the flask. The solution was heated at 90°C for 2 hours. The reaction mixture was then cooled and poured over crushed ice in beaker, and neutralized to pH 6-8 by dropwise addition of saturated sodium acetate solution. The mixture was extracted with ethyl acetate. The extracts were washed with water, dried with magnesium sulfate, and then concentrated. The residue was purified by column chromatography. Yellowish oil was obtained(96%). ^{1}H-NMR($CDCl_3$): δ= 9.7(s, 1H), 7.7(d, 2H), 6.8(d, 2H), 4.2(t, 4H), 3.7(t, 4H), 2.0(s, 6H).

N-butyl-γ-picolinium bromide(4). A mixture of 4-picoline(18 g, 0.19 mol), n-butylbromide (26.5 g, 0.19 mol) and acetonitrile(120 ml) was heated at 80°C for 1 day. The removal of solvent gave hygroscopic solid(90%). ^{1}H-NMR(D_2O): δ= 9.26(d, 2H), 7.7(d, 2H), 4.7(t, 2H), 2.5(s, 3H), 1.8(m, 2H), 1.2(m, 2H), 0.8(t, 3H).

E-N-Butyl-4-(2-(4-bis(2-hydroxyethyl)aminophenyl)ethenyl)pyridinium bromide(5). To a solution of compound **4** (6.15 g) and compound **3** (8.24 g, 0.028 mol) in methanol (100 ml) was

added catalytic amount of piperidine(0.5 ml), and then the mixture was refluxed. After 2 days, methanol was evaporated and small portion of acetone was added. Scratching of the residue by a spatula gave red solid. This solid was washed with acetone several times. The yield was 59%. ^{1}H-NMR(D_2O): δ= 8.1(d, 2H), 7.6(d, 2H), 7.3(m, 3H), 6.6(m, 3H), 4.0(t, 2H), 3.7(t, 4H), 3.5(t, 4H), 1.7(m, 2H), 1.2(m, 2H), 0.8(t, 3H).

E- N- Butyl- 4- (2-(4-bis(2-hydroxyethyl)aminophenyl)ethenyl)pyridinium tetraphenylborate (6). Compound **5** (10 g, 0.025 mol) was dissolved in methanol(200 ml). To the solution was added sodium tetraphenylborate(8.1 g, 0.025 mol) in methanol(200 ml). Red precipitate was formed immediately. The precipitate was collected by filtration and then dried. The product yield was 78%. UV: λ_{max}= 496 nm. ^{1}H-NMR(DMSO-d_6): δ= 8.7(d, 2H), 7.9(d, 2H), 7.8(d, 1H), 7.5(d, 2H), 7.2-6.7(m, 23H), 4.8(t, 2H), 4.4(t, 2H), 3.5(m, 8H), 1.8(m, 2H), 1.3(m, 2H), 0.9(t, 3H).

Polymer Synthesis: To a solution of compound **6** (1.5 g) in 20 ml of anhydrous dimethylacetamide was added 2,4-toluene diisocyanate gradually. The mixture was heated at 80°C for 5 hours with stirring. The reaction mixture was allowed to cool to room temperature, and poured into cold water. Red precipitate was formed, filtered, washed with water, and dried by vacuum. The polymer yield was 85%. UV:λ_{max}= 484 nm. IR: ν= 1720 cm^{-1}(C=O stretching). ^{1}H-NMR(DMSO-d_6): δ= 9.6(br s, 0.5H), 8.9(br s, 0.5H), 8.7(m, 2H), 7.9(m, 3H), 7.5(m, 3H), 7.2-6.7(m, 25H), 4.3(m, 6H), 3.7(br.s, 4H), 2.1(br s,3H), 1.8(m, 2H), 1.2(m, 2H), 0.9(t, 3H).

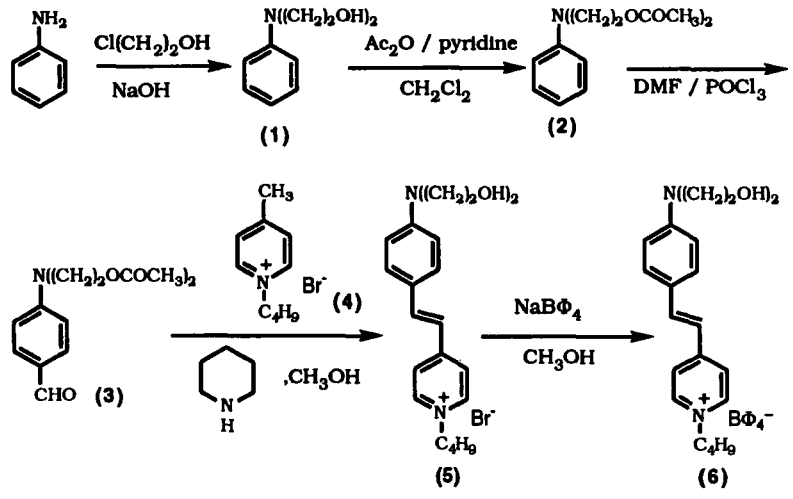
Characterization: ^{1}H-NMR spectra of synthesized compounds were recorded on a Brucker AM spectrometer. FT-IR spectra of the monomer and polymer were obtained with Bomem Michelson series FT-IR spectrophotometer. UV-visible spectra were measured by Shimadzu UV-3100S. Differential scanning calorimetry(DSC) and thermogravimetry(TGA) were performed under nitrogen gas atmosphere with duPont 9900 analyzer.

Film Preparation: Polymer films were spin coated at 400-600 rpm onto indium-tin oxide (ITO) conductive glass substrate using filtered solution in dimethylformamide. All the films were dried in oven at 80°C to remove the solvent. Thickness was measured using Tencor-Instruments Alpha-step 100.

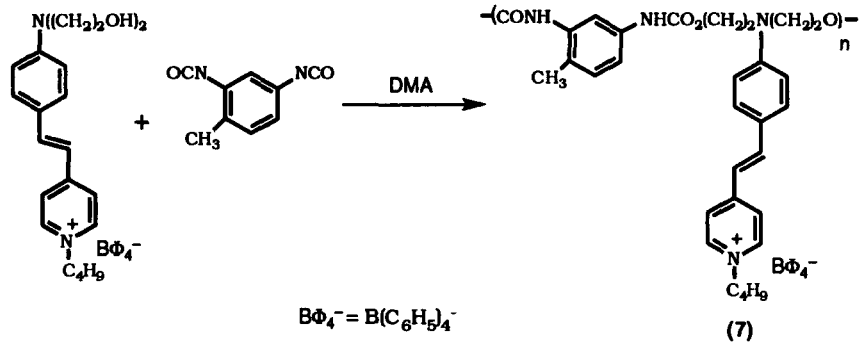
RESULTS AND DISCUSSION

Synthesis and Characterization: As the overall pathway of monomer synthesis outlined in Scheme I, in the first step, aniline was allowed to react with chloroethanol in strong basic condition at 100°C for 3 days to yield the diethanolamine derivative **1**. The hydroxyl group of product **1** was then protected using acetic anhydride in pyridine medium. The aldehyde

(Scheme I)



(Scheme II)



compound 3 was obtained in 96% yield by Vilsmeier formylation of 2. A subsequent reaction of 3 with N-butyl-γ-picolium bromide afforded stilbene compound 5 in 59 % yield. Finally, the monomer 6 was synthesized by ion-exchange reaction of 5 and sodium tetraphenylborate. The resulting monomer contains a diol functional group that provides its incorporation into a polymer chain through a polycondensation step. All intermediates including monomer were characterized by conventional spectroscopic techniques. The results were well convinced of each products.

The polymerization of monomer 6 with 2,4-toluene diisocyanate is described in Scheme II. Polyurethane having hemicyanine dye of salt type 7 was prepared by the step growth process in anhydrous dimethylacetamide. The polymer yield was 78%. By the addtion of

dibutyltin dilaurate as a catalyst in the reaction mixture, the polymerization was not accelerated, and so high molecular weight polymer could not be achieved. The molecular weight of polyurethane was detected with $\overline{M}n$=12,000, $\overline{M}w$=20,000 from the GPC using polystyrene as standard. The polymer was soluble in dimethylformamide and could be processed into a film of good quality by spin coating.

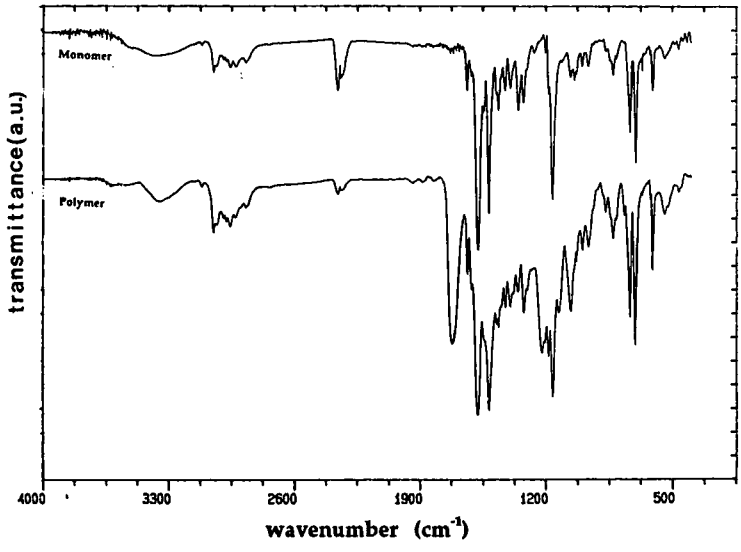


FIGURE 1 FT-IR spectra of diol monomer **6** and polyurethane polymer **7**

The polymer structure was characterized by IR, NMR and UV spectroscopy. As shown in Figure 1, the stretching vibrations for the isocyanate group were nearly absent in the FT-IR spectrum of polymer **7**. The carbonyl absorption peak due to urethane linkage was observed around 1720 cm^{-1} after polymerization. The ^{1}H-NMR spectral data of the polyurethane showed the signal broadening due to the polymerization, but chemical shifts were consistent with the polymer structure(see, Exp. Section). The UV-VIS spectra of monomer and polymer are presented in Figure 2. The absorption maxima, λ_{max} due to a π–π^* transition of stilbene chromophore in **6** and **7** were centered at 496 nm and 484 nm, respectively. When the monomer dye was introduced in the polyurethane chain, the absorption maximum showed blue shift of 12 nm. This UV absorption pattern indicates that electronic interaction between polymer chain and stilbene dye occurred in the polymer matrix.

Thermal and Optical Properties: The thermal property of the polymer **7** was studied using differential scanning calorimetry (DSC) (25-300°C, 10°C/min, N_2) (Figure 3). The polyurethane

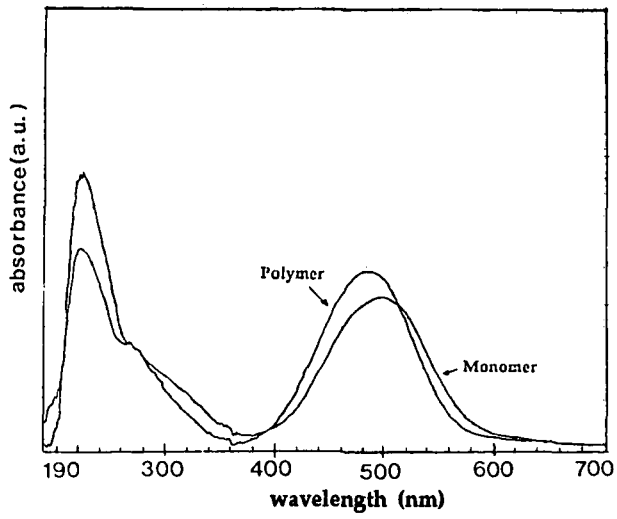


FIGURE 2 UV-VIS spectra of diol monomer **6** and polyurethane polymer **7**

derived from toluene 2,4-diisocyanate showed higher glass transition temperature(T_g) than those of common flexible polyurethanes, due to the rigidity of the polymer backbone. The T_g was detected at 121°C after annealing at 190°C for 1 hour. No evidence of melting point was observed in DSC curve, which indicates that this polymer is noncrystalline. Thermogravimetric analysis(TGA) (25-1,000°C, 20°C/min, N_2) of polymer revealed an onset of weight loss at 225°C.

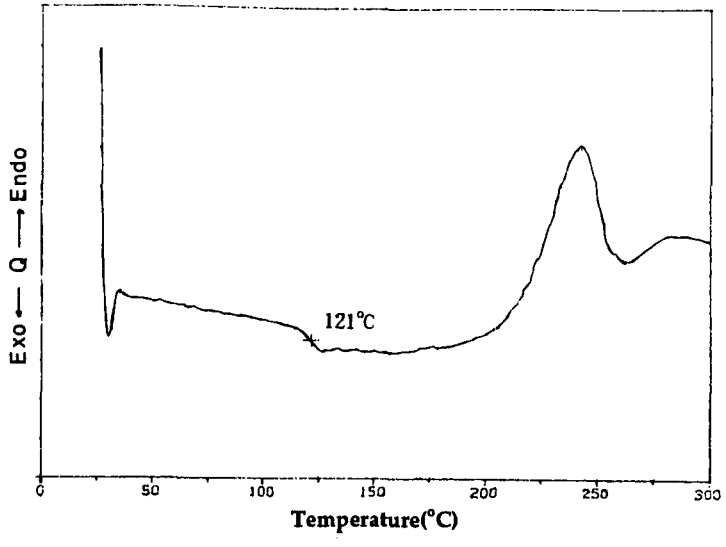


FIGURE 3 DSC thermogram of polyurethane polymer **7** (heating rate, 10°C/min, N_2)

The first weight loss corresponds to the decomposition of tetraphenylborate group. The value of theoretically calculated weight loss was exactly matched with molecular weight of tetraphenylborate part in the overall molecular weight of polymer repeating units.

The second harmonic generation(SHG) measurement has been performed with a mode locked Q-switched Nd:YAG laser operating at 500 Hz. Each pulse train at 1.064 μm contained 40 sub-pulses with a pulse width of 135 ps each. Polar alignment of the dyes in polyurethane matrix was achieved by *in-situ* corona poling at 5 KV. The second-order susceptibility of poled film at optimal conditions was measured using angular dependence method. The $\chi^{(2)}$ value was calculated by comparing the SHG intensity from the film with that from a Y-cut quartz crystal. The $\chi^{(2)}$ value of the polyurethane was about 4×10^{-7} esu(assuming the refractive indices $n_{\omega}=1.6$ and $n_{2\omega}=1.75$) which seemed to be very high value resulting from the function as powerful acceptor of boron salt chromophore. According to the studies of the temporal stability, no significant decay of the SHG intensities was observed within 10 days. This result strongly suggests that the bulky chromophore of tetraphenylborate units and hydrogen bondings between polyurethane backbones prevent the relaxation of dyes after poling. The detailed SHG investigations concerned about temporal and thermal stability are currently in progress.

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REFERENCES

1. K. -S. Lee, M. Samoc and P. N. Prasad(ed. S. L. Aggarwal), Comprehensive Polymer Science(1st Supplement), Pergamon Press, Oxford, 1992.
2. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wily, New York, 1991.
3. S. R. Marder, J. E. Sohn and G. D. Stucky, Materials for Nonlinear Optics Chemical Perspective, ACS Symp. Ser. 455 , 1990.
4. G. J. Ashwell, R. C. Hargreaves, C. E. Baldwin, G. S. Bahra and C. R. Brown, Nature, 357 , 393(1992).
5. I. R. Girling, N. A. Cade, P. V. Kolinsky, J. D. Earls, G. H. Cross and I. R. Petrson , Thin Solid Films , 132 , 101(1985).
6. L. M. Hayden, S. T. Kowel and M. P. Srinivasan, Opt. Comm. , 61(5) , 351(1987).
7. J. S. Schildkraut, T. L. Penner, C. S. Willand and A. Ulman, Opt. Lett., 13(2), 134(1988).
8. K. Kajikawa, K. Shirota, H. Takezoe and A. Fukuda, JPN. J. Appl. Phys., 29 , 913(1990).
9. P. Kodge, Ziad Ali-Adib, D. West and T. King , Macromolecules , 26 , 1789(1993).