Synthesis and Second-Order Nonlinear Optical Properties of Tricyanovinylated Polybenzoxazole

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(Received September 30, 1997)

ABSTRACT: We have developed the second-order nonlinear optically (NLO) active polybenzoxazole as a new thermally stable NLO polymeric system. This polybenzoxazole was synthesized by direct polycondensation of diacid monomer containing *N*-phenyl pendant with 2,2-bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane using phosphorus pentoxide/methanesulfonic acid as a condensing agent and solvent, followed by a post-substitution of tricyanovinyl group. The resultant polybenzoxazole had a glass transition temperature of about 180°C and an initial decomposition temperature of about 300°C. Electro-optic coefficient of this polybenzoxazole film poled at 1.5 MV cm⁻¹ was 34 pm V⁻¹ (at 633 nm), and its NLO activity was quite stable at 100°C during long period.

KEY WORDS Polybenzoxazole / Nonlinear Optics / Tricyanovinyl / Thermal Stability / Electro-Optic Coefficient /

For photonic devices such as electro-optic modulator or optical switch, polymeric second-order nonlinear optical (NLO) materials might be a promising candidate for low cost devices and their mass productions due to their excellent processability compared to general lithium niobate crystals.^{1–3} Large electro-optic coefficient (r_{33}), its long-term temporal stability, low optical loss, and good photostability of polymeric NLO materials are required for the practical photonic applications. One of the most critical problems in polymeric systems is the gradual decay of NLO activity during prolonged period. Recently, several successful polyimides systems have been reported for temporally stable photonic devices, which had high glass transition temperatures and decomposition temperatures.^{4–8} We have recently found that polybenzoxazole might also be one of the good candidates for thermally stable NLO materials comparable to polyimide.

In our previous study, we have successfully synthesized several novel NLO chromophores having a benzoxazole π -conjugated bridge, which are more thermally stable and highly NLO active than conventional stilbene type chromophores.⁹ The main-chain benzoxazole polymer was chosen for the same reason as the side-chain benzoxazole chromophore of polymethylmethacrylate copolymer (Figure 1). Fully aromatic polybenzoxazole was known to have excellent thermal and oxidative stability comparable to polyimides.¹⁰ Moreover, it is expected that polybenzoxazoles could have lower moisture absorption than polyimides because polybenzoxazoles have no carbonyl groups in their structure, providing for more reliable materials for photonic devices.

In this study, we report the synthesis, thermal and nonlinear optical properties of polybenzoxazole.

EXPERIMENTAL

Materials

4-Fluorobenzonitrile and *N*-phenyldiethanolamine were used as received from Aldrich Chemical Co. 2,2-Bis(3-amino-4-hydroxyphenyl)-1,1,1,3,3,3-hexafluoropropane (6FAP) was supplied by Central Glass Co., Japan as white powder; mp 243–245°C. Phosphorus pentoxide/methanesulfonic acid (PPMA) was obtained commercially from Tokyo Chemical Industry Co.

Characterization and Measurement

FT-IR, UV-Vis, and ¹H NMR spectra were recorded on a Mattson Alpha Centauri spectrophotometer, a Shimadzu UV-240, and a Varian Gemini 200 NMR spectrometer (200 MHz), respectively. Differential scanning calorimeter (DSC) and thermogravimetry (TG) were performed with Dupont thermal analyzer. Electro-optic coefficient was measured by the modified simple reflection method proposed by Teng *et al.*, and the film processing, poling, and electro-optic measurement procedure was reported by our recent literature in detail.¹¹

Figure 1. NLO active PMMA copolymer (PMBz) containing benzoxazole chromophores and polybenzoxazole (6FPBO-TCN).

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Figure 2. Synthesis of NLO active polybenzoxazole.

Synthesis of Diacid Monomer

In a 500 mL flask, 4-fluorobenzonitrile (24.2 g, 20 mmol) and *N*-phenyldiethanolamine (9.06 g, 50 mmol) were dissolved in 100 mL of *N,N*-dimethylformamide (DMF). Potassium carbonate (13.8 g, 0.1 mol) was added into the solution, and stirred for 24 h at 100°C, and then the mixture was poured into water. The white precipitate was collected by filtration, and recrystallized from methanol to give white crystals of dicyano compound; mp 97–98°C. The yield was 19.2 g (65%). The infrared (IR) spectrum (KBr) exhibited absorption at 2220 cm⁻¹ (CN). The ¹H nuclear magnetic resonance (NMR) spectrum [dimethyl sulfoxide (DMSO)-*d*₆] showed peaks at δ 3.83 (t, 4H, NCH₂), 4.20 (t, 4H, OCH₂), 6.61 (t, 1H, ArH), 6.80 (d, 2H, ArH), 7.08 (d, 4H, ArH), 7.14 (t, 2H, ArH), and 7.70 ppm (d, 4H, ArH).

The portion of 10.0 g (26 mmol) of dicyano compound was dissolved in a mixed solution of 25 g of sodium hydroxide, 150 mL of methanol, and 450 mL of water. The solution was heated at reflux with stirring for 3 days. The solution was cooled, and the pH value was adjusted by diluted hydrochloric acid to about 3–4. The white precipitate was collected by filtration and washed with water, and dried under vacuum; mp 233–235°C. Yield: 10.8 g (99%). IR (KBr): 1681 cm⁻¹ (C=O). ¹H NMR (DMSO-*d*₆): δ 3.83 (t, 4H, NCH₂), 4.20 (t, 4H, OCH₂), 6.61 (t, 1H, ArH), 6.80 (d, 2H, ArH), 6.96 (d, 4H, ArH), 7.14 (t, 2H, ArH), 7.82 (d, 4H, ArH), and 12.6 ppm (s, 2H, COOH). Anal. calcd for C₂₄H₂₃NO₆ (421.4): C, 68.4%; H, 5.50%; N, 3.32%. Found: C, 68.3%; H, 5.52%; N, 3.34%.

Synthesis of Polybenzoxazole (6FPBO)

In a 50 mL flask fitted with mechanical stirrer, diacid (1 g, 2.37 mmol) was dissolved in 12 mL of PPMA, and 6FAP (0.869 g, 2.37 mmol) was added to this solution at room temperature. The mixture was stirred for 5 h at 140°C under nitrogen. After cooling, the polymer so-

lution was poured into an aqueous alkaline solution, and the precipitated polymer was collected and heated at reflux in methanol for 2 h. The polymer powder was collected by filtration, and washed thoroughly with water, and dried under vacuum. Yield: 1.57 g (84%). The inherent viscosity measured in 1-methyl-2-pyrrolidinone (NMP) at a concentration of 0.5 g dL⁻¹ at 30°C, was 0.26 dL g⁻¹. IR (KBr): 1602 (C=N, C=C), 1251 (C–O–C) cm⁻¹. ¹H NMR [tetrahydrofuran (THF)-*d*₈]: δ 4.09 (4H, NCH₂), 4.43 (4H, OCH₂), and 6.79–8.30 ppm (19H, ArH).

Tricyanovinylolation of Polybenzoxazole (6FPBO-TCN)

The 1.0 g of polybenzoxazole was dissolved in 10 mL of DMF at room temperature under nitrogen. Tetracyanoethylene (0.197 g, 1.54 mmol) was added into this solution. This solution was reacted with stirring for 12 h at 80°C. Then, the solution was poured into water to precipitate, and the red polymer powder was filtered, washed with water, and dried under vacuum. Yield: 1.05 g (92%). The inherent viscosity at a concentration of 0.5 g dL⁻¹ at 30°C in NMP, was 0.27 dL g⁻¹. IR spectrum (KBr): 2217 (CN), 1603 (C=N, C=C), 1250 (C–O–C) cm⁻¹. ¹H NMR (THF-*d*₈): δ 4.14–4.53 (8H, OCH₂CH₂N), and 7.10–8.31 ppm (18H, ArH).

RESULTS AND DISCUSSION

Synthesis of Diacid Monomer and Polybenzoxazole

Synthesis of *N*-phenylated diacid monomer was shown in Figure 2. Diacid compound was easily synthesized in high yield by a condensation of *N*-phenyldiethanolamine with 4-fluorobenzonitrile, followed by alkaline hydroly-

sis. The fluorine containing bisaminophenol monomer, 6FAP was introduced to enhance the solubility of polybenzoxazole. The 6FPBO was synthesized by one-step thermal polycondensation of diacid 4 with 6FAP

Figure 3. ^1H NMR spectra of polybenzoxazole before (6FPBO) and after tricyanovinylolation (6FPBO-TCN).

using the procedure reported by Ueda *et al.*¹² Typically, PPMA was used as a dehydrating agent and polymerization medium at 140°C . Polybenzoxazole with moderate inherent viscosity of 0.27 dL g^{-1} was successfully obtained. As a NLO chromophore, *N,N*-disubstituted-4-tricyanovinylaniline was introduced by post-tricyanovinylolation of *N*-phenyl pendants of 6FPBO. The tricyanovinylolation method has been well established by ROI Technology researchers and others.^{13–15} The post tricyanovinylolation of 6FPBO was generally carried out by reacting 6FPBO with tetracyanoethylene (1.1 equiv.) in DMF at 80°C for 12 h.

The degree of substitution of tricyanovinyl group in *N*-phenyl pendant was quantitative, which was determined by ^1H NMR spectroscopy. After tricyanovinylolation, the peak of proton at *para*-position (6.8 ppm) in *N*-phenyl was completely disappeared and those at *ortho*- and *meta*-position (7.0 and 7.1 ppm) in *N*-phenyl were shifted to 7.1 and 8.2 ppm because of strong electron-affinity of tricyanovinyl group as shown in Figure 3.

General and Nonlinear Optical Properties of Polybenzoxazole

The thermal properties of polybenzoxazole were summarized in Table I. The precursor polymer, 6FPBO had a little low glass transition temperature of about 144°C due to the flexible aliphatic main chain. The glass transition temperature (T_g) of polybenzoxazole (6FPBO-TCN) after tricyanovinylolation increased up to 180°C , ascribing to the introduction of extended rigid tricyanovinyl unit. Moreover, the thermal stability determined by TG was remarkably enhanced as shown in Figure 4. The initial decomposition temperature of 6FPBO-TCN was about 300°C , meaning that polybenzoxazole might

Table I. Properties of polybenzoxazoles

	η_{inh}^a dL g^{-1}	T_g^b $^\circ\text{C}$	T_d^c $^\circ\text{C}$	λ_{max}^d nm	r_{33}^e pm V^{-1}
6FPBO	0.26	144	300	—	—
6FPBO-TCN	0.27	180	340	510	34

^a Determined at a concentration of 0.5 g dL^{-1} at 30°C in NMP.

^b Glass transition temperatures measured by DSC at a heating rate of $20^\circ\text{C min}^{-1}$. ^c Initial decomposition temperatures measured by TG at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen. ^d Maximum absorption in film. ^e At a wavelength of 633 nm.

Figure 4. TG curves of 6FPBO and 6FPBO-TCN.

be one of the promising NLO materials with excellent thermal stability. Polybenzoxazole film with tricyanovinylaniline chromophores had a UV maximum absorption (λ_{max}) of 510 nm.

The 6FPBO-TCN was soluble in organic solvents such as tetrahydrofuran, pyridine, cyclohexanone and 1,1,2,2-tetrachloroethane, therefore could be spin-casted onto an indium tin oxide (ITO) coated substrate to give an optically transparent polymer film.

For the dipole alignment of chromophores we tried contact poling by applying electric field to sandwich type sample. Gold was evaporated as a top electrode on the thin film of 6FPBO-TCN casted onto ITO substrate as a bottom electrode. The polybenzoxazole film showed high breakdown voltage, therefore could be processed even at higher poling field. At a poling field of 1.5 MV cm^{-1} , the electro-optic coefficient, r_{33} was 34 pm V^{-1} at a wavelength of 633 nm measured by simple reflection method. The temporal stability of r_{33} was measured at 100°C , which is simply evaluated by the curve of $r_{33}(t)/r_{33}(0)$ vs. time, as shown in Figure 5. The r_{33} value of 6FPBO-TCN after 1 week at 100°C was maintained to 90% of initial r_{33} value, that was similar trend to general polyimide system.¹⁴

The dipole alignment behavior in polybenzoxazole and polyimide system can be compared through the UV-Vis absorbance spectra before and after poling. For this, we synthesized a corresponding polyimide (6FPI-TCN) with tricyanovinyl chromophore (Figure 6). The detail synthesis of 6FPI-TCN will be reported elsewhere. Figure 7 shows the UV-Vis spectra of 6FPBO-TCN and 6FPI-TCN, before and after poling, respectively. The order

Figure 5. Temporal stability of electro-optic coefficient of 6FPBO-TCN.

Figure 6. The structure of polyimide (6FPI-TCN).

Figure 7. UV-Vis spectra of unpoled 6FPBO-TCN and poled 6FPBO-TCN; and unpoled 6FPI-TCN and poled 6FPI-TCN, respectively.

parameter, $(\Phi = 1 - A_p/A_0)$ was obtained by measuring the maximum absorbance of unpoled film (A_0) and poled film (A_p) by UV spectroscopy. It was found that poling efficiency of polybenzoxazole was a little different from

that of polyimide when poled at each T_g . Poled polybenzoxazole films had always lower order parameter values (0.17–0.22) than poled polyimide films (0.30–0.35) at similar poling conditions (film thickness, voltage, and time), implying more difficulty of dipole alignment in polybenzoxazole system. It was perhaps attributed to better chain packing of polybenzoxazole due to non-existence of carbonyl groups, resulting smaller free volume to move chromophores.

CONCLUSIONS

As a new type of thermally stable NLO polymeric system, polybenzoxazoles were synthesized by direct polycondensation of diacid containing *N*-phenyl pendant with bisaminophenol using PPMA, followed by post-substitution of tricyanovinyl group. This NLO polybenzoxazole had a high glass transition temperature of about 180°C and an initial decomposition temperature of about 300°C, meaning excellent thermal stability comparable to polyimide system. Electro-optic coefficient of polybenzoxazole film poled at 1.5 MV cm⁻¹ was measured to 34 pm V⁻¹ (at 633 nm) and showed its long term stability.

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