Synthesis and nonlinear optical properties of PMMA copolymers having novel benzoxazole chromophores attached with various electron-withdrawing groups

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For improvements of thermal stability and nonlinear optical (NLO) activity of chromophores, we newly synthesized a series of NLO chromophores incorporating aromatic benzoxazole unit as a π-conjugated bridge with various electron-withdrawing groups, such as nitrophenyl, nitrothiophene, nitrofuran, dicyanovinylphenyl, and nitrophenylethenyl group. Polymethylmethacrylate copolymers (PMBz) containing these benzoxazole chromophores were synthesized and their properties were investigated by thermogravimetry and ultraviolet-visible spectroscopy. The PMBz copolymers exhibited better thermal and ultraviolet stabilities than the corresponding copolymer with general stilbene chromophores (PMSt). Moreover, temporal stability of nonlinear optical coefficient (d_{33}) of PMBz copolymer increased in comparison with that of PMSt. The copolymer with benzoxazole–nitrothiophene chromophores had the largest d_{33} value of 153 pm/V (at 1.064 mm) and nonresonant d_{33} calculated by the two-level model was 21.3 pm/V. © 1998 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Polymeric nonlinear optical (NLO) materials are very promising candidates for the practical photonic applications such as light modulators and frequency doublers, due to their excellent processability and low dielectric constants[1,2]. The NLO polymers require large nonresonant second harmonic generation coefficient (d_{33}), electro-optic coefficient (r_{33}), long-term temporal stability of d_{33} and r_{33}, low optical loss, and good photostability, etc.[3,4]. Among these, much research has been focused on the enhancement of NLO activity and improvement of its temporal stability during prolonged periods. For higher NLO activity, a variety of NLO chromophores have been designed and synthesized by changing the strength of electron donors and electron acceptors, and the type of π-conjugated bridge or its length in the chemical structure of chromophore[5–12]. Most of them involve stilbene and azobenzene type chromophores which can be easily synthesized using the Wittig reaction or diazonium coupling, and have also reasonably high second-order hyperpolarizability and dipole moment. On the other hand, highly thermally stable NLO chromophores have been highlighted, since high-glass transition temperature polymers like polyimides have been used as polymer matrices for lessening the gradual decay of NLO activity, which was one of the critical problems in polymeric NLO systems. They have been also designed by displacing more thermally stable π-conjugated bridge, electron donors, or acceptors[13–15].

As a novel π-conjugated bridge with improved thermal and photochemical stabilities, we recently attempted to introduce an aromatic benzoxazole unit as a π-conjugated bridge in a chromophore structure[16,17]. It was successfully synthesized by condensation reaction of *o*-aminophenol with an aldehyde compound, followed by oxidation. In our earlier work, we demonstrated the difference in thermal and temporal stabilities of benzoxazole from that of stilbene-based NLO chromophores bearing polymethylmethacrylate (PMMA) copolymers[16].

It is well known that optical nonlinearity of chromophores could be increased by control of electron-donating and -withdrawing strength, by lowering π-conjugation energy, or by bond length alternation of π-conjugation bridge[18–20]. In this study, using commercial aldehyde compounds as an electron acceptor, a variety of benzoxazole derivatives were synthesized. We report here in detail the synthesis and characterization of new benzoxazole NLO chromophores with electron acceptors, such as nitrophenyl, nitrothiophene, and nitrofuran groups. In addition, their second harmonic generation properties of PMMA copolymers bearing several benzoxazole chromophores as a side chain are investigated.

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EXPERIMENTAL

Materials

2-Benzyloxy-4-fluoro-1-nitrobenzene (**1**) was synthesized according to the method reported elsewhere. 2-(Methylamino)ethanol (**2**), 4-nitrobenzaldehyde (**5a**), 5-nitro-2-thiophenecarboxaldehyde (**5b**), 5-nitro-2-furaldehyde (**5c**), 4-nitrophenylcinnamaldehyde (**5e**), 10% palladium on carbon, and lead acetate (95%) were from Aldrich. 4,4′-Dicyanovinylbenzene was synthesized by Knoevenagel reaction of terephthaldehyde with malononitrile.

Synthesis of starting compound (3)

N-Methyl-N-(2-hydroxyethyl)-3-benzyloxy-4-nitroaniline (**3**). To a solution of 37.04 g (0.15 mmol) of 2-(benzyloxy)-4-fluoronitrobenzene (**1**) and 22.34 g (0.30 mmol) of 2-(methylamino)ethanol (**2**) in 200 ml of N,N-dimethylformamide (DMF), 20.72 g (0.15 mol) of potassium carbonate was added all at once with stirring, and the mixture was heated at 100°C for 3 h. The mixture was poured into 1 l of water and the yellow precipitate was filtered and then dried under vacuum. The yellow powder was dissolved in tetrahydrofuran (THF) and dropped into hexane to precipitate. Yield: 43.1 g (95%). The product could be purified by recrystallization from ethyl acetate to give yellow crystals.

mp 104–106°C. ^{1}H n.m.r. (DMSO-d_6): δ 3.04 (s, 3H, NCH$_3$), 3.52 (s, 4H, CH$_2$), 4.79 (s, 1H, OH), 5.28 (s, 2H, OCH$_2$), 6.35–6.41 (m, 2H, ArH), 7.31–7.52 (m, 5H, ArH), and 7.89 ppm (d, 1H, ArH).

Anal. calc. for C$_{16}$H$_{18}$N$_2$O$_4$ (302.33): C, 63.57%; H, 6.00%; N, 9.27%. Found: C, 63.5%; H, 6.09%; N, 9.21%.

Synthesis of imine compounds (6a–6e)

Synthesis of a typical imine compound **6a** was carried out as described below.

4′-Nitrobenzylidene-2-(E)-hydroxy-4-[N-methyl-N-(2-hydroxyethyl)amino]aniline (**6a**). A portion of 9.07 g (0.03 mol) of **3** was dissolved in 200 ml of DMF and then a mixture of 1 g of 10% of palladium on carbon in 10 ml of DMF was added. The mixture was vigorously stirred under hydrogen at ordinary pressure at room temperature for 12 h. Then, 4.53 g (0.03 mmol) of 4-fluorobenzaldehyde (**5a**) was added all at once to the mixture solution and stirred for 2 h. The mixture was filtered to remove the catalyst on carbon, and the filtrate solution was poured into 1 l of water. The black crystals were filtered and washed with water, then dried under vacuum. The product was recrystallized from a mixture solvent of THF and hexane to give fine black crystals, and finally dried overnight in vacuum. The yield was 7.76 g (82%).

mp 194–196°C; UV-vis: λ$_{max}$ (CHCl$_3$) 473 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.94 (s, 3H, NCH$_3$), 3.34–3.55 (m, 4H, CH$_2$), 4.71 (t, 1H, OH), 6.20 (s, 2H, ArH), 6.26 (d, 1H, ArH), 7.36 (d, 1H, ArH), 8.24 (m, 4H, ArH–NO$_2$), 8.82 (s, 1H, =CH), and 8.94 ppm (s, 1H, ArOH).

Anal. calc. for C$_{16}$H$_{17}$N$_3$O$_4$ (315.33): C, 60.95%; H, 5.43%; N, 13.33%. Found: C, 60.9%; H, 5.49%; N, 13.4%.

The other imine compounds (**6b–6e**) were synthesized by similar procedures.

6b: Yield: 79%; mp 190–193°C; UV-vis: λ$_{max}$ (CHCl$_3$) 526 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.94 (s, 3H, NCH$_3$), 3.39 (m, 4H, CH$_2$), 4.72 (t, 1H, OH), 6.19–6.29 (m, 2H, ArH), 7.26–8.10 (m, 3H, ArH), 8.95 (s, 1H, =CH), and 9.23 ppm (s, 1H, ArOH).

6c: Yield: 77%; mp 164–167°C; UV-vis: λ$_{max}$ (CHCl$_3$) 530 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.94 (s, 3H, NCH$_3$), 3.32–3.42 (m, 2H, NCH$_2$), 3.50–3.58 (m, 2H, OCH$_2$), 4.71 (t, 1H, OH), 6.18–6.30 (m, 3H, ArH), 7.34–7.39 (m, 1H, ArH), 7.79 (d, 1H, ArH), 8.69 (s, 1H, =CH), and 9.17 ppm (s, 1H, ArOH).

6d: Yield: 81%; mp 218–220°C; UV-vis: λ$_{max}$ (CHCl$_3$) 520 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.94 (s, 3H, NCH$_3$), 3.34–3.41 (m, 2H, NCH$_2$), 3.50–3.53 (m, 2H, OCH$_2$), 4.71 (t, 1H, OH), 6.19 (s, 1H, ArH), 6.26 (d, 1H, ArH), 7.36 (d, 1H, ArH), 8.08 (d, 2H, ArH), 8.21 (d, 2H, ArH), 8.50 (s, 1H, =CH), 8.75 (s, 1H, =CH), and 8.85 ppm (s, 1H, ArOH).

6e: Yield: 76%; mp 190–192°C; UV-vis: λ$_{max}$ (CHCl$_3$) 479 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.94 (s, 3H, NCH$_3$), 3.34–3.42 (m, 2H, NCH$_2$), 3.48–3.58 (m, 2H, OCH$_2$), 4.70 (t, 1H, OH), 6.17–6.32 (m, 2H, =CH), 7.15–7.38 (m, 3H, ArH), 7.79 (d, 2H, ArH), 8.23 (d, 2H, ArH), 8.55 (s, 1H, =CH), and 8.85 ppm (s, 1H, ArOH).

Synthesis of benzoxazole compound (7a–7e)

Synthesis of a typical benzoxazole compound **7a** was carried out as described below.

6-[N-Methyl-N-(2-hydroxyethyl)]amino-2-(4-nitrophenyl)-1,3-benzoxaol (**7a**). A portion of 6.31 g (0.02 mmol) of **6a** was dissolved in 300 ml of THF and then 9.35 g of lead tetraacetate (95%) was slowly added with stirring. The mixture was vigorously stirred at room temperature for 2 h. The mixture was filtered to remove lead diacetate, and the filtrate solution was concentrated by evaporation, and then poured into hexane. The precipitated product was recrystallized from THF to give dark red crystals and dried overnight at 80°C in vacuum. The yield was 5.31 g (85%).

mp 201–203°C; UV-vis: λ$_{max}$ (CHCl$_3$) 433 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.99 (s, 3H, NCH$_3$), 3.46–3.59 (m, 4H, CH$_2$), 4.72 (t, 1H, ArH), 6.83 (s, 1H, ArH), 6.94 (d, 1H, ArH), 7.56 (d, 1H, ArH), and 8.20–8.35 ppm (m, 4H, ArH–NO$_2$).

Anal. cald. for C$_{16}$H$_{15}$N$_3$O$_4$ (313.31): C, 61.34%; H, 4.83%; N, 13.41%. Found: C, 61.2%; H, 4.85%; N, 13.3%.

7b: Yield: 82%; mp 201–203°C; UV-vis: λ$_{max}$ (CHCl$_3$) 477 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.99 (s, 3H, NCH$_3$), 3.46–3.58 (m, 4H, CH$_2$), 4.73 (t, 1H, OH), 6.82–6.93 (m, 2H, ArH), 7.73 (d, 1H, ArH), and 8.16 ppm (d, 1H, ArH).

7c: Yield: 80%; mp: 204–206°C; UV-vis: λ$_{max}$ (CHCl$_3$) 453 nm; ^{1}H n.m.r. (DMSO-d_6): δ 3.00 (s, 3H, NCH$_3$), 3.35–3.41 (m, 2H, NCH$_2$), 3.49–3.58 (m, 2H, OCH$_2$), 4.72 (t, 1H, OH), 7.48–6.95 (m, 3H, ArH), 7.53 (d, 1H, ArH), and 7.87 ppm (d, 1H, ArH).

7d: Yield: 78%; mp 184–186°C; UV-vis: λ$_{max}$ (CHCl$_3$) 479 nm; ^{1}H n.m.r. (DMSO-d_6): δ 3.00 (s, 3H, NCH$_3$), 3.34–3.49 (m, 2H, CH$_2$), 3.54–3.58 (m, 2H, OCH$_2$), 4.72 (t, 1H, OH), 6.85 (d, 1H, ArH), 6.90 (s, 1H, ArH), 7.55 (d, 1H, ArH), 8.07 (d, 1H, ArH), 8.15 (d, 1H, ArH), and 8.46 ppm (s, 1H, =CH).

7e: Yield: 80%; mp 202–204°C; UV-vis: λ$_{max}$ (CHCl$_3$) 442 nm; ^{1}H n.m.r. (DMSO-d_6): δ 2.97 (s, 3H, NCH$_3$), 3.56–3.59 (m, 2H, OCH$_2$), 4.71 (t, 1H, OH), 6.72 (d, 1H, ArH), 6.82 (s, 1H, ArH), 7.37 (d, 1H, –CH=CH–), 7.45 (d, 1H, ArH), 7.60 (d, 1H, –CH=CH–), 7.93 (d, 2H, ArH), and 8.17 ppm (d, 2H, ArH).

Synthesis of vinyl monomer (9a–9e)

Synthesis of a typical vinyl monomer **9a** was carried out as described below.

6-[N-(2-Methacryloyloxyethyl)-N-methyl]amino-2-(4-nitrophenyl)-1,3-benzoxazol (**9a**). A portion of 4.73 g

(0.015 mol) of **7a** was dissolved in 200 ml of methylene chloride and then 3.14 g (0.03 mol) of methacryloyl chloride was dropped in. Then, 2 ml of triethylamine was added, and stirred at room temperature for 12 h. The reaction solution was poured into water and extracted with methylene chloride. The organic layer was dried with magnesium sulfate and evaporated to yield red crystal-like powder. The product was purified by column chromatography on silica gel using a mixture solvent of THF and hexane, and finally crystallized by THF and hexane to give red crystals. The yield was 4.35 g (76%).

mp 160–162°C; UV-vis: λ_{max} (CHCl$_3$): 432 nm; ^{1}H n.m.r. (CDCl$_3$): δ 1.91 (s, 3H, CH$_3$), 3.10 (s, 3H, NCH$_3$), 3.75 (t, 2H, CH$_2$), 4.39 (t, 2H, CH$_2$), 5.55 (s, 1H, =CH$_2$), 6.07 (s, 1H, =CH$_2$), 6.86–6.9 (m, 2H, ArH), 7.61 (d, 1H, ArH), and 8.31 ppm (s, 4H, ArH–NO$_2$).

Anal. calc. for C$_{20}$H$_{19}$N$_3$O$_5$ (381.39): C, 62.99%; H, 5.02%; N, 11.02%. Found: C, 62.9%; H, 5.04%; N, 11.1%.

9b: Yield: 77%; mp 140–142°C; UV-vis: λ_{max} (CHCl$_3$): 478 nm; ^{1}H n.m.r. (CDCl$_3$): δ 1.90 (s, 3H, CH$_3$), 3.08 (s, 3H, NCH$_3$), 3.70 (t, 2H, NCH$_2$), 4.33 (t, 2H, OCH$_2$), 5.54 (s, 1H, =CH$_2$), 6.05 (s, 1H, =CH$_2$), 6.83 (s, 1H, ArH), 6.88 (d, 1H, ArH), 7.53–7.63 (m, 2H, ArH), and 7.90 ppm (d, 1H, ArH).

9c: Yield: 80%; mp 202–204°C; UV-vis: λ_{max} (CHCl$_3$) 453 nm; ^{1}H n.m.r. (CDCl$_3$): δ 1.89 (s, 3H, CH$_3$), 3.09 (s, 3H, NCH$_3$), 3.73 (t, 2H, NCH$_2$), 4.35 (t, 2H, OCH$_2$), 5.54 (s, 1H, =CH$_2$), 6.05 (s, 1H, =CH$_2$), 6.89–6.92 (m, 2H, ArH), 7.24 (d, 1H, ArH), 7.44 (d, 1H, ArH), and 7.63 ppm (d, 1H, ArH).

9d: Yield: 75%; mp 155–158°C; UV-vis: λ_{max} (CHCl$_3$) 479 nm; ^{1}H n.m.r. (CDCl$_3$): δ 1.90 (s, 3H, CH$_3$), 3.10 (s, 3H, NCH$_3$), 3.73 (t, 2H, NCH$_2$), 4.37 (t, 2H, OCH$_2$), 5.54 (s, 1H, =CH$_2$), 6.06 (s, 1H, =CH$_2$), 6.87–6.93 (m, 2H, ArH), 7.62 (d, 1H, ArH), 7.74 (s, 1H, =CH), 8.01 (d, 2H, ArH), and 8.27 ppm (d, 2H, ArH).

9e: Yield: 81%; mp 140–142°C; UV-vis: λ_{max} (CHCl$_3$) 445 nm; ^{1}H n.m.r. (DMSO-d_6): δ 1.90 (s, 3H, CH$_3$), 3.10 (s, 3H, NCH$_3$), 3.71 (t, 2H, NCH$_2$), 4.38 (t, 2H, OCH$_2$), 5.61 (s, 1H, =CH$_2$), 5.94 (s, 1H, =CH$_2$), 6.85 (d, 1H, ArH), 6.92 (s, 1H, ArH), 7.20–7.74 (m, 3H, =CH and ArH), 8.05 (d, 2H, ArH), and 8.20 ppm (d, 2H, ArH).

Polymerization

Synthesis of **10a** was conducted as below.

PMBz copolymer (**10a**) was synthesized by general radical polymerization. A portion of 1.907 g (5 mmol) of vinyl monomer **9a** and 0.501 g (5 mmol) of methyl methacrylate (MMA) as a comonomer was placed in a vacuum-sealable 25 ml Pyrex tube with magnetic stirrer. Then, 0.016 g (0.1 mmol) of AIBN and 5 ml of dried NMP were added to the tube. The mixture was degassed by a repeated freeze-vacuum–thaw technique and sealed using a gas burner. The polymerization tube was placed in an isothermal oil bath and reacted at 65°C for 48 h. The cooled polymerization solution was poured into methanol to precipitate the polymer. The polymer was purified by reprecipitation in methanol. The yield was 1.8 g (75%).

The other copolymers (**10b–10e**) were synthesized by similar procedures.

Measurement

FT-i.r., and ^{1}H n.m.r. (200 MHz) spectra were recorded on a Mattson Alpha Centauri spectrophotometer and a Varian Gemini 200 n.m.r. spectrometer, respectively. Differential scanning calorimeter (d.s.c.) was performed with a Dupont thermal analyzer DSC 2910 at a heating rate of 20°C/min in nitrogen. Thermogravimetric analysis (t.g.a.) was measured with a Dupont thermal analyzer DSC 2950 at a heating rate of 10°C/min in nitrogen. UV-visible spectroscopy was performed by a Shimadzu UV-240. The polymer film thickness was measured with a Tencor P-10 surface profiler. The second harmonic generation (SHG) coefficients, d_{33} of corona poled films were determined by Maker-fringe method using a fundamental beam (1.064 μm) of a Q-switched Nd:YAG laser. We used a quartz reference (d_{11} = 0.5 pm/V). A detailed SHG measurement is described in the literature[22].

Film preparation and poling

Each copolymer (0.2 g) was dissolved in 4 ml of 1,1,2,2-tetrachloroethane on heating. The cooled solutions were filtered through 0.2 μm filters and then spin cast onto normal glass for SHG measurements. All films were dried at around the glass transition temperature (T_g) of each of the copolymers for 2 h to remove solvent prior to poling. Corona poling of films (about 0.5 μm) was performed at 5–8 kV with a tip-to-plane distance of 1 cm at T_g, respectively, and cooled to room temperatures in the presence of the electric field.

RESULTS AND DISCUSSION

Synthesis of benzoxazole chromophores

The synthetic route of the benzoxazole-based NLO chromophores is presented in *Figure 1*. The key step of this synthesis was the benzoxazole ring formation. It was well known that benzoxazole compounds can be generally synthesized in two steps by the prior formation of an *o*-hydroxy amide through condensation of *o*-aminophenol with an acid chloride derivative at low temperature, followed by thermal cycloaddition at high temperature. We selected a two-step reaction at room temperature to reduce side reactions, which was a benzoxazole ring
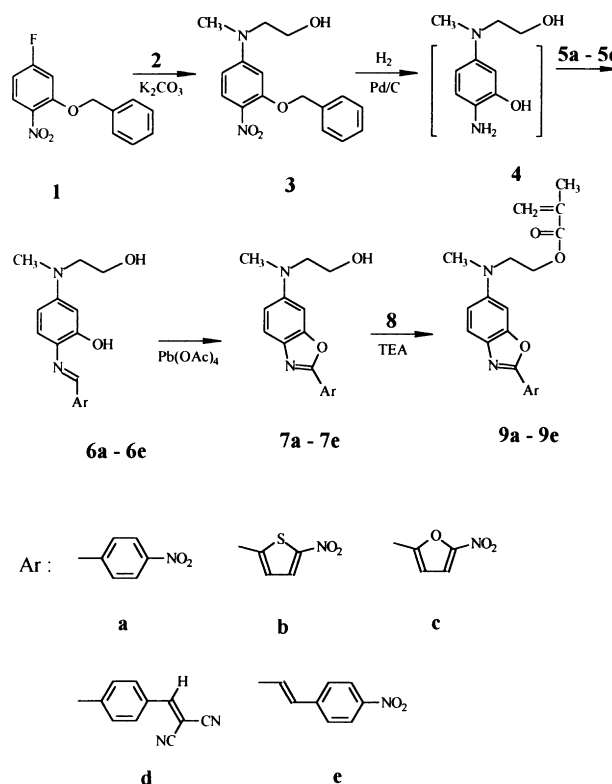

Figure 1 Synthesis of benzoxazole NLO chromophores

formation from oxidation of *o*-iminophenol. A nitro-benzyloxy compound (**3**) was synthesized from the condensation of 2-(methylamino)ethanol (**2**) with 2-nitro-5-fluorophenol (**1**) using potassium carbonate as a acid acceptor. The *o*-aminophenol **4** could be synthesized by the catalytic reduction of compound **3**, which was in situ reacted with aldehyde without separating, because of high air sensitivity of compound **4**, to give iminophenol (Shiff base) **6**. The iminophenol was easily oxidized by treatment with lead tetraacetate in THF at room temperature to give benzoxazole chromophores in high yields[21]. If THF was used as a solvent, one pot reaction without separation of both aminophenol **4** and iminophenol **6** was also available to shorten reaction steps. Although the yields were 70–80% due to recrystallization loss, it was noteworthy that each conversion through overall steps was quite quantitative because both *o*-aminophenol and aldehyde compounds were highly reactive. All products were very easy to separate and purify. Among chromophores **7a**–**7e**, **7c** having a furan ring had the worst solubility in THF. All the compounds were well characterized by ^{1}H n.m.r. spectroscopy. The elemental analysis values of all compounds were generally in good agreement with the calculated values for the proposed structures.

A variety of benzoxazole chromophores could be synthesized by a combination of *o*-aminophenol with commercial aldehydes. Therefore, the molecular design of chromophores for higher hyperpolarizability was easier than that of stilbene-type chromophores. All the benzoxazole compounds had lower λ_{max} values than imine compound. Some benzoxazole chromophores with nitrothiophene, nitrofuran, and dicyanovinylphenyl groups had higher λ_{max} values than that with a nitrophenyl group.

Synthesis of copolymers

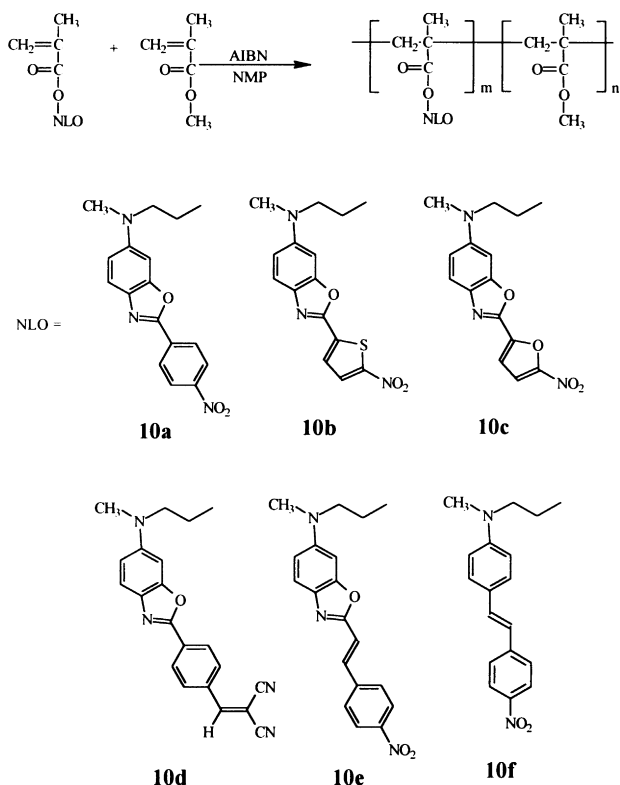All the benzoxazole-based and a stilbene-based vinyl monomer were copolymerized with methylmethacrylate.

Figure 2   Chemical structures of PMMA copolymers in this study

The chemical structures of MMA copolymers (**10a**–**10f**) are shown in *Figure 2*, and their polymerization results are summarized in *Table 1*. Among these copolymers, both copolymers **10b** and **10c** always had a lower molecular weight determined by GPC, and their yields were also quite low (about 30%) compared to that of PMBz (**10a**). This means that nitrothiophene or nitrofuran groups act as free radical trappers. It has been reported that radical polymerization of vinyl monomer with tricyanovinylthiophene was unsuccessful due to the radical trapping by strong electron acceptors[23].

Solubility and thermal properties

Most of benzoxazole-based copolymers were fairly soluble in chlorinated solvents, such as dichloroethane, 1,1,2-trichloroethane, 1,2,3-trichloropropane, and 1,1,2,2-tetrachloroethane (TtCE), and were barely soluble in tetrahydrofuran, chloroform, and 1,1,1-trichloropropane, even on heating. The transparent films of each copolymer for measurements were obtained by spin casting the TtCE polymer solution.

The glass transition temperatures (T_g) of copolymers were in the range of 115–143°C. A copolymer (**10d**) with a dicyanovinyl group had the highest T_g value because of the longest and most rigid chromophore structure. Both copolymers **10b** and **10c** had low T_g values due to their low molecular weight. The thermal decomposition curves of each polymer are presented in *Figure 3*. Most of the copolymers decomposed gradually above 220°C. As expected, copolymers **10b** and **10c**, with the lowest molecular weights, showed inferior thermal stability, while copolymer **10d** had better thermal stability.

To examine the photochemical stability of benzoxazole and stilbene chromophores, both films of PMBz (**10a**) and PMSt (**10f**) were irradiated by ultraviolet (UV) light (365 nm) and the changes of UV-visible spectra observed. The stability against UV light could be compared because the λ_{max} and $\lambda_{cut-off}$ of the two copolymer films were almost the same. As shown in *Figure 4*, the decomposition behavior of two copolymers showed remarkable differences. The absorbance of the PMBz film decreased less than that of PMSt film after the same exposure period to UV light. It was responsible for higher conjugation energy of benzoxazole in comparison with that of phenylenevinylene as a π-conjugated bridge.

All the films were corona poled to have almost the similar order parameters of about 0.30–0.40, which were

Table 1   Polymerization results of PMMA copolymers

Code	Yield (%)	M_n ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	T_g^a (°C)	T_{10}^b (°C)	Solubility^c
10a	75	11.4	22.7	134	280	TCE, TCP, TtCE
10b	27	8.9	13.9	115	270	DCE, TCE, TCP, TtCE
10c	31	8.4	12.3	115	270	DCE, TCE, TCP, TtCE
10d	78	13.2	27.0	143	280	DCE, TCE, TCP, TtCE
10e	80	13.5	23.3	139	280	DCE, TCE, TCP, TtCE
10f	82	12.3	24.6	130	280	THF, CHCl$_3$, CH

^{a}Glass transition temperatures were determined by d.s.c. at a heating rate of 20C/min in nitrogen
^{b}Temperatures of 10% weight loss determined by TG at a heating rate of 10°C/min in nitrogen
^{c}For spin casting: THF, tetrahydrofuran; DCE, 1,2-dichloroethane; TCE, 1,1,2-trichloroethane; TCP, 1,2,3-trichloropropane; TtCE, 1,1,2,2-tetrachloroethane; CH, cyclohexanone
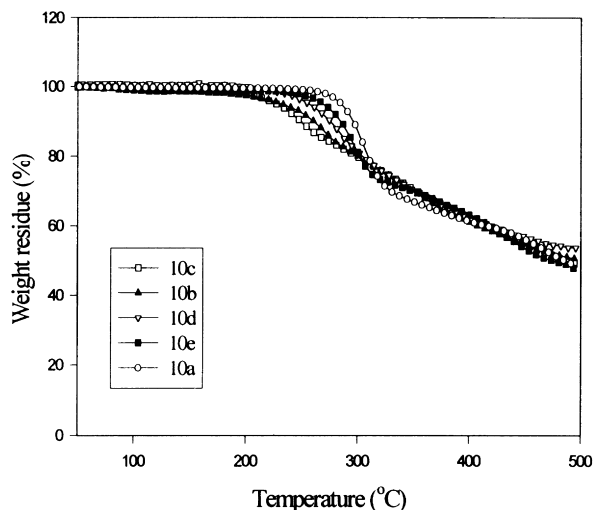
Figure 3 T.g.a. curves of MMA copolymers **10a–10e** with benzoxazole chromophores and a copolymer **10f** with stilbene chromophores measured at a heating rate of 10°C/min

determined by UV-vis spectroscopy. The nonlinear optical coefficients (d_{33}) were measured by Maker-fringe method, and the nonresonant d_{33} values were calculated by a two-level model[24]. The results were summarized in *Table 2*. The SHG coefficients of copolymers were reasonably high, in the range of 65–153 pm/V. The copolymer **10b** containing a thiophene unit had the highest d_{33} (153 pm/V) and nonresonant $d_{33}(0)$ (21 pm/V). Unexpectedly, copolymer **10d** with dicyanovinyl chromophores, having high λ_{max} and μ (dipole moment) $\times \beta$ (hyperpolarizability) value, did not exhibit such a high SHG activity. Moreover, copolymer **10e**, with extended π-conjugated chromophores, which were also expected to have higher d_{33} values than PMBz (**10a**) showed almost the same λ_{max} and SHG activity ($d_{33} = 65$ pm/V). These results may due to an alignment restriction of long and rigid chromophores.

In our previous paper, we reported that PMBz copolymer had better temporal stability of its electro-optic coefficient, r_{33}, than that of general PMSt (**10f**), even if the glass transition temperatures of the two copolymers were nearly similar[16]. To reconfirm the better temporal stability of PMBz, we synthesized another PMBz copolymer (**10a'**) with lower T_g than PMSt (**10f**), and attempted to compare the relaxation behavior of two copolymers. The T_g of **10a'** and **10f** was 121
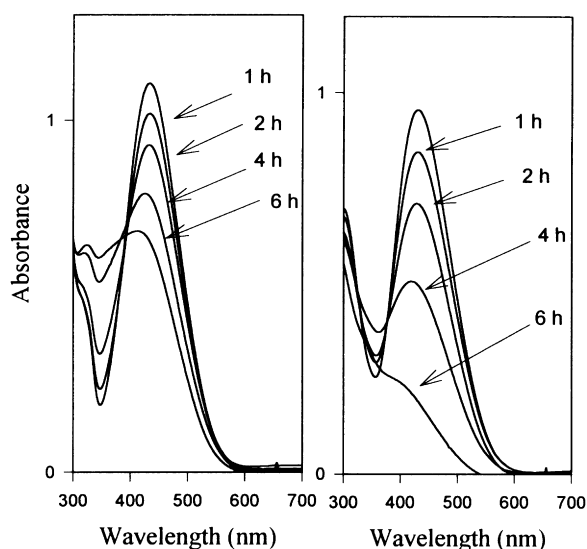
Figure 4 UV–visible spectra of (a) PMBz (**10a**) and (b) PMSt (**10f**) films after UV exposure (365 nm, 470 μW/cm^2) for various times
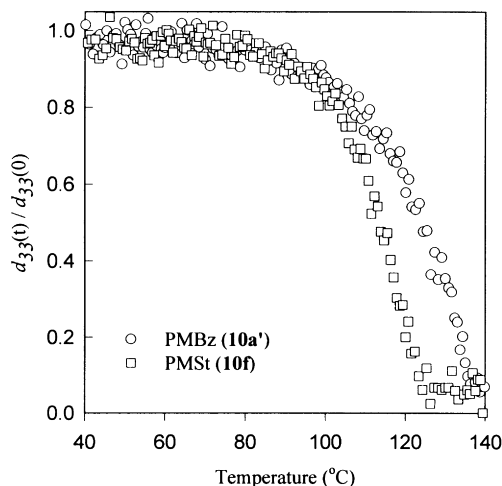
Figure 5 Changes in normalized SHG intensities of (a) PMBz (**10a'**) and (b) PMSt (**10f**) during heat treatment at a heating rate of 1°C/min

and 126°C, respectively. *Figure 5* shows changes in normalized SHG intensities of the two copolymers during heat treatment at a heating rate of 1°C/min. The SHG intensities of copolymers decreased rapidly above 100°C, indicating randomization of the aligned dipole around T_g. In spite of its lower T_g, the PMBz copolymer (**10a'**) showed rather better thermal stability than PMSt (**10f**), with a T_g of 126°C. This means that benzoxazole chromophores were effective for improvement of the thermal relaxation of dipolar alignment.

CONCLUSIONS

We report herein the successful synthesis of a novel series of vinyl monomers bearing benzoxazole NLO chromophores with various electron-withdrawing groups. The PMMA copolymers with these benzoxazole-based chromophores had better thermal stability and UV stability than those with generally well-known stilbene-based chromophores. Moreover, the temporal stability of NLO activity was also improved by introducing rigid benzoxazole chromophores to polymers. High NLO activity was achieved by introduction of benzoxazole–thiophene chromophores. Therefore, NLO polymers with benzoxazole chromophores might be useful candidates for material for actual devices. Subsequent work should be the improvement of NLO coefficients. One of the important advantages of these benzoxazole chromophores is that high NLO active chromophores could be easily synthesized by using commercial or well-designed aldehyde compounds.

Table 2 Benzoxazole-based NLO active PMMA copolymers

Code	λ_{max}^a (nm)	$\lambda_{cut\text{-}off}^a$ (nm)	OD^b	d_{33}^c (pm/V)	$d_{33}(0)^d$ (pm/V)
10a	434	612	0.28	63.4	17.7
10b	483	668	0.39	152.8	21.3
10c	457	655	0.34	73.8	15.8
10d	468	660	0.35	39.7	7.4
10e	440	610	0.34	63.4	16.6

^{a}Film
^{b}Order parameters of poled samples for an SHG measurement calculated by absorbance values at λ_{max} before and after poling
^{c}At 1.064 μm by Maker-fringe method
^{d}Were calculated by a two-level method

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