

## Synthesis and Nonlinear Optical Properties of Novel Polyester with Enhanced Second Harmonic Generation Thermal Stability

You Jin Cho, Mi Sung Kim, and Ju-Yeon Lee\*

Institute of Basic Science, Department of Chemistry, Inje University, Gimhae 621-749, Korea. \*E-mail: chemlly@inje.ac.kr  
Received September 16, 2010, Accepted October 19, 2010

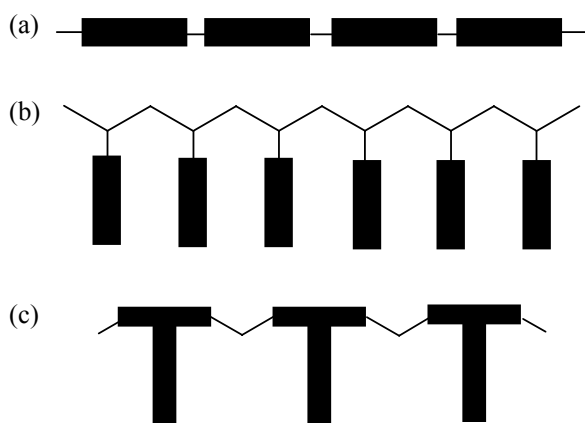
**Key Words:** Nonlinear optics, Polyester, Thermal stability, Second harmonic generation, Relaxation of dipole alignment

Nonlinear optical (NLO) polymers received a great attention in recent years because of their potential applications in the field of electro-optic devices including ultrafast optical switches, high-speed optical modulators, and high-density optical data storage media.<sup>1-6</sup> A potential NLO polymer has to be mechanically very strong and thermally stable with a high glass-transition temperature ( $T_g$ ). In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is one of important criteria; in this context, two approaches have been proposed to minimize the randomization of dipole alignment, namely the use cross-linking method<sup>7-10</sup> and the utilization of high  $T_g$  polymers such as polyimides.<sup>11-16</sup> Various polyesters with NLO chromophores in the main chain<sup>17</sup> or in side chain<sup>18-19</sup> have been prepared and their properties studied. In general, main-chain NLO polymers have good thermal stability of dipole alignments, but they often do not dissolve in organic solvents, and their intractability make them unusable to fabricate stable films. Side-chain NLO polymers have the advantages such as good solubility and homogeneity relative to the main-chain systems, but they often suffer from poor stability of dipole alignments at high temperatures. Recently we have prepared novel polyesters containing dioxy-nitrostilbene<sup>20-21</sup> or dioxybenzylidenemalononitrile<sup>22</sup> as NLO chromophores. The resulting polymers exhibit enhanced thermal stability of second harmonic generation (SHG), which stems from the stabilization of dipole alignment of the NLO chromophore. In this work reported here, we prepared another novel

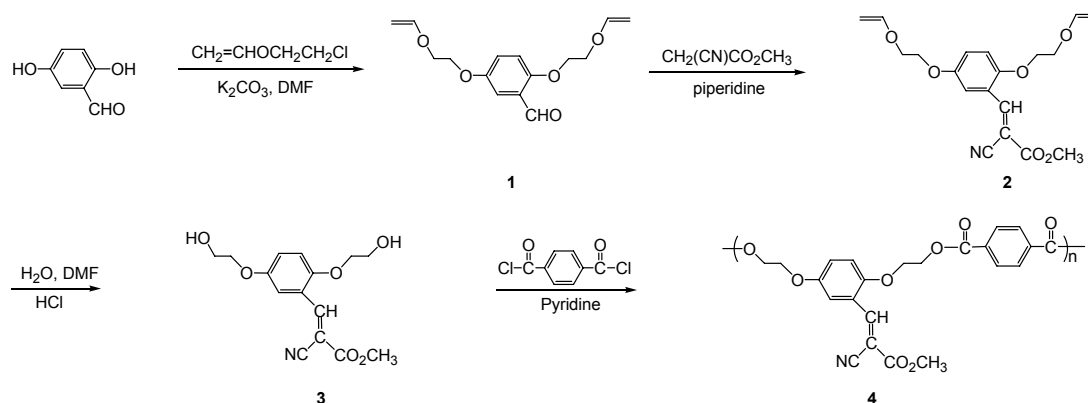
polyester containing 2,5-dioxybenzylidenecyanoacetate groups as NLO chromophores. We selected the latter because they have a large dipole moment and are rather easy to synthesize. Furthermore, 2,5-dioxybenzylidenecyanoacetate group constitutes novel T-type NLO polyester (Fig. 1c), and this T-type NLO polyester has not yet been reported in the literature. Thus, we synthesized a new type of NLO polyester, in which the pendant NLO chromophores are components of the polymer backbone. This T-type NLO polymer is expected to have the advantages of both main-chain and side-chain NLO polymers namely stable dipole alignment and good solubility. After confirming the structure of the resulting polymer we investigated its properties such as solubility,  $T_g$ , thermal stability, second harmonic generation (SHG) activity and relaxation of dipole alignment.

### Results and Discussion

Compound **1** was prepared by the reaction of 2-chloroethyl vinyl ether with 2,5-dihydroxybenzaldehyde. Compound **2** was prepared by the condensation reaction of compound **1** with methyl cyanoacetate. Compound **2** was hydrolyzed to yield acetaldehyde and diol **3**. Monomer **3** was condensed with terephthaloyl chloride in a dry DMF solvent to yield polyester **4** containing the NLO chromophore 2,5-dioxybenzylidenecyanoacetate group. The synthetic route for polyester **4** is presented in Scheme 1. The polymerization yield was 90%. The chemical structure of the resulting polymer was confirmed by <sup>1</sup>H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structure. <sup>1</sup>H NMR spectrum of the polymer showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structure. The IR spectrum of the polymer showed a strong carbonyl peak near 1722 cm<sup>-1</sup> indicating the presence of ester bond. The spectrum also shows a strong absorption peak near 2221 cm<sup>-1</sup> and 1608 cm<sup>-1</sup> due to the nitrile and olefin groups, respectively. These results are consistent with the proposed structure, indicating that the NLO chromophore remained intact during the polymerization. The molecular weights were determined by GPC using polystyrene as the standard and THF as an eluent. The number average molecular weight ( $M_n$ ) of the polymer **4**, determined using GPC, is 16200 ( $M_w/M_n = 1.97$ ). The structural feature of this polymer is that it has pendant NLO chromophores, which are parts of the polymer main chains. Thus the resulting polymer **4** is a mid type of side-chain and main-chain NLO polymer,



**Figure 1.** Main-chain NLO polymers (a), side-chain NLO polymers (b), and T-type NLO polymers (c).



**Scheme 1.** Synthetic scheme and structure of polymer **4**

and is expected to have both of their merits. The polymer **4** is soluble in common solvents such as acetone, DMF, and DMSO, but is not soluble in methanol and diethyl ether. The inherent viscosity is 0.28 dL/g. Polymer **4** shows strong absorption near 391 nm due to the NLO chromophore 2,5-dioxybenzylidenecyanoacetate group. Having obtained the well defined polyester **4**, we investigated its properties.

The thermal behavior of the polymer was investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature ( $T_g$ ). Polymer **4** has a thermal stability up to 250 °C according to its TGA thermogram. The  $T_g$  value of the polymer **4** measured using DSC is near 105 °C. This  $T_g$  value is higher than those of the polyesters containing dioxybenzylidenemalononitrile or dioxynitrostilbene, which are in the range 83 - 95 °C.<sup>23-25</sup> The TGA and DSC studies show that the decomposition temperature of the polymer **4** is higher than that of poling temperature. This indicates that corona poling at 110 °C for a short term is feasible without damaging the NLO chromophore.

The NLO properties of polymer **4** were studied using the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer film was corona-poled. As the temperature was raised to 110 °C, 6.5 kV of corona voltage was applied and this temperature was maintained for 30 min. The refractive index of the sample was measured using the optical transmission technique.<sup>26</sup> The transmittance of thin film gives information on the thickness, refractive index and extinction coefficient. Thus, we could determine these parameters by analyzing the transmittance. SHG measurements were performed at a fundamental wavelength of 1064 nm using a mode locked Nd-YAG laser. NLO properties of polymer **4** are summarized in Table 1.

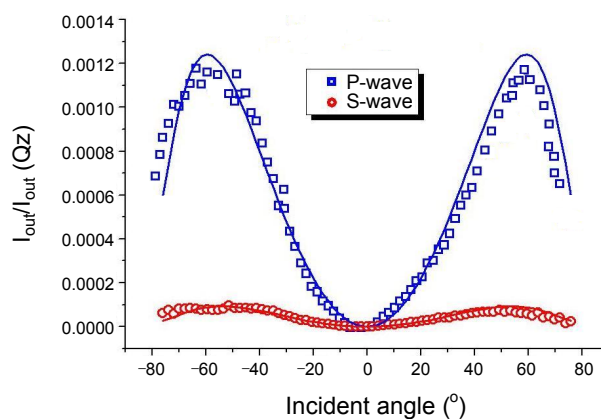
**Table 1.** Nonlinear optical properties of polymer **4**

Polymer	$\lambda_{\max}^a$ (nm)	$d_{33}^b$ (esu)	$d_{31}^b$ (esu)	film thickness <sup>c</sup> ( $\mu\text{m}$ )	$n$
<b>4</b>	391	$3.45 \times 10^{-9}$	$1.33 \times 10^{-9}$	0.53	1.621

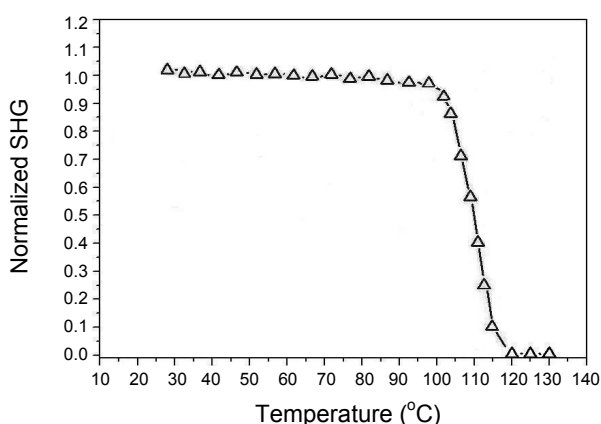
<sup>a</sup>Polymer film after corona poling. <sup>b</sup>SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>27</sup> <sup>c</sup>Film thickness was determined by the optical transmission technique.<sup>26</sup>

In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. Fig. 2 shows the angular dependence of SHG signal for a poled polymer **4**. The SHG values were compared with those obtained from a Y-cut quartz plate. To calculate the  $d_{31}$  and  $d_{33}$  values, both *s*-polarized and *p*-polarized IR laser were directed at the samples. SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure.<sup>27</sup> The values of  $d_{33}$  and  $d_{31}$  for polymer **4** are  $3.45 \times 10^{-9}$  and  $1.33 \times 10^{-9}$  esu, respectively. These  $d_{33}$  value is higher than that of the polyester containing dioxynitrostilbene, which is  $1.42 \times 10^{-9}$  esu,<sup>25</sup> but is lower than those with dioxybenzylidenemalononitrile, which are in the range  $4.46 \sim 6.48 \times 10^{-9}$  esu.<sup>23-24</sup> Since the second harmonic wavelength is at 532 nm, which is not in the absorptive region of the resulting polyester, there is not resonant contribution to this  $d_{33}$  value.

To evaluate the high-temperature stability of the polymer, we studied the temporal stability of the SHG signal. Fig. 3 shows the dynamic thermal stability study of the NLO activity of a film of polymer **4**. To investigate the real time NLO decay of the SHG signal of the poled polymer films as a function of temperature, *in situ* SHG measurements were performed at a heating rate of 3.5 °C/min from 30 °C to 150 °C. The polymer thin



**Figure 2.** Angular dependence of SHG signal for a poled film of polymer **4**.



**Figure 3.** Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 3.5 °C/min.

film exhibits a thermal stability up to  $T_g$  and no significant SHG decay is observed below 105 °C, as shown in Fig. 3. This SHG thermal stability is similar with that of the polyesters containing dioxybenzylidenemalononitrile or dioxynitrostilbene.<sup>23-25</sup> In general, side chain NLO polymers lose thermal stability of dipole alignment around  $T_g$ . Stabilization of dipole alignment is a characteristic of main chain NLO polymers. The high thermal stability of second harmonic generation of polymer **4** is due to the stabilization of dipole alignment of NLO chromophore, which stems from the partial main chain character of the polymer structure. Thus, we obtained a new type of NLO polyester having the merits of both main-chain and side-chain NLO polymers, namely stable dipole alignment and good solubility.

### Experimental Section

**Materials.** Reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2,5-Dihydroxybenzaldehyde, 2-chloroethyl vinyl ether, and tetrahydrofuran (THF) were used as received. Terephthaloyl chloride (TPC) was purified by sublimation under vacuum. Methyl cyanoacetate was distilled under reduced pressure. Piperidine was treated with potassium hydroxide and then distilled over barium oxide to remove trace amounts of water.

**Measurements.** IR spectra were obtained with a Shimadzu FT IR-8201PC infrared spectrophotometer. <sup>1</sup>H NMR spectra were obtained with a Varian 300 MHz NMR spectrometer. UV-vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Elemental analyses were performed using a Perkin-Elmer 2400 CHN elemental analyzer. The glass transition temperatures ( $T_g$ ) were measured using a TA 2920 differential scanning calorimeter in a nitrogen atmosphere. A TA Q50 thermogravimetric analyzer with a heating rate of 10 °C/min up to 800 °C was used for the thermal degradation study of polymers under nitrogen. The number average molecular weight ( $M_n$ ) and weight average molecular weight ( $M_w$ ) of the polymers were estimated using gel permeation (GPC; styragel HR5E4E columns; tetrahydrofuran (THF) solvent).

**Film preparation and SHG measurements.** Polymer films were prepared from a 10 wt % polymer solution in DMF de-

posited on an indium-tin oxide (ITO) covered glass. Prior to film casting, the polymer solution was filtered through 0.45 μm Teflon<sup>®</sup> membrane filter. The films were spin-cast at room temperature in the range 1000 - 1200 rpm. The films were dried for 12 h under vacuum at 60 °C. The alignment of the NLO chromophore of the polymers was carried out using a corona poling method. The poling was performed in a wire-to plane geometry under *in situ* conditions. The discharging wire to plane distance was 10 mm. As the temperature was raised gradually to 5 - 10 °C higher than  $T_g$ , a corona voltage of 6.5 kV was applied and the temperature was maintained for 30 min. The films were cooled to room temperature in the presence of the electric field. Finally, the electric field was removed. The refractive index of the sample was measured using the optical transmission technique.<sup>26</sup> Second harmonic generation (SHG) measurement was carried out one day after poling. A continuum PY61 mode-locked Nd:YAG laser ( $\lambda = 1064$  nm) with pulse width of 40 ps and repetition rate of 10 Hz was used as the fundamental light source and Y-cut quartz was used as reference. A poled polymer film was mounted on the rotator coupled to a step motor. The output signals from the photodiode and PMT were detected as a function of the incident angle. A 3-mm-thick Y-cut quartz crystal (a piece of quartz plate whose plane is perpendicular to the crystalline y-axis and the thickness of the plate is 3 mm, and  $d_{11} = 0.3$  pm/V) was used as a reference for determining the relative intensities of the SH signals generated from the samples. The Maker Fringe pattern was obtained by measuring the SHG signal at 0.5° intervals using a rotation stage. SHG coefficients ( $d_{33}$ ) were derived from the analysis of measured Maker-fringes.<sup>27</sup>

**Preparation of 2,5-(2'-vinylxyethoxy)benzaldehyde (1).** 2,5-Dihydroxybenzaldehyde (13.8 g, 0.10 mol), anhydrous potassium carbonate (36 g, 0.36 mol), and 2-chloroethyl vinyl ether (16.0 g, 0.25 mol) were dissolved in 200 mL of dry DMF under nitrogen. The mixture was refluxed in an oil bath kept at 100 °C for 40 h under nitrogen. The resulting solution was cooled to room temperature and extracted with 300 mL of diethyl ether three times. The organic layer was washed with saturated aqueous sodium chloride solution, and dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielded 23.9 g (86% yield) of pure product **1**. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.98-4.34 (m, 12H, 2 CH<sub>2</sub>=, 2 -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.45-6.58 (m, 2H, 2 =CH-O-), 6.92-6.99 (m, 1H, aromatic), 7.15-7.21 (m, 1H, aromatic), 7.33-7.36 (d, 1H, aromatic), 10.46 (s, 1H, -CHO). IR (KBr) 3096, 3075 (w, =C-H), 2941, 2882 (s, C-H), 1676 (vs, C=O), 1624 (vs, C=C) cm<sup>-1</sup>.

**Preparation of methyl 2,5-di-(2'-vinylxyethoxy)benzylidenecyanoacetate (2).** Piperidine (0.043 g, 0.5 mmol) was added to a solution of 2,5-di-(2'-vinylxyethoxy)benzaldehyde **1** (2.78 g, 10 mmol) and methyl cyanoacetate (1.98 g, 20 mmol) in 30 mL of isopropyl alcohol with stirring at room temperature under nitrogen. After stirring for 10 h at room temperature, the reaction mixture was diluted with 50 mL of water, and extracted with 80 mL of diethyl ether three times. The organic layer was dried with anhydrous magnesium sulfate. Rotary evaporation of diethyl ether gave crude product, which was recrystallized from 1-butanol yielded 2.94g (82% yield) of pure product **2**; mp 66 - 68 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.92 (s, 3H, -CO<sub>2</sub>CH<sub>3</sub>),

3.99-4.28 (m, 12H, 2 CH<sub>2</sub>=, 2 -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 6.46-6.58 (m, 2H, 2 =CH-O-), 6.92-6.97 (d, 1H, aromatic), 7.11-7.17 (q, 1H, aromatic), 7.86-7.89 (d, 1H, aromatic), 8.76 (s, 1H, benzylic). IR (KBr) 3071 (w, =C-H), 2953, 2876 (m, C-H), 2222 (s, CN), 1734 (vs, C=O), 1618, 1589 (vs, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub>: C, 63.50; H, 5.89; N, 3.90. Found: C, 63.58; H, 5.94; N, 3.98.

**Preparation of methyl 2,5-di-(2'-hydroxyethoxy)benzylidenecyanoacetate (3).** Aqueous hydrochloric acid (1.5 M, 30 mL) was slowly added to a solution of methyl 2,5-di-(2'-vinyl-oxyethoxy)benzylidenecyanoacetate (2) (3.59 g, 0.01 mol) in 30 mL of dry DMF with stirring under nitrogen at 0 °C. The mixture was stirred at 0 °C for 12 h under nitrogen. The resulting solution was filtered and washed with to give 2.55 g (83% yield) of 3; mp 70 - 72 °C. <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 2.84 (t, 1H, -OH), 3.90 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 4.02-4.25 (m, 8H, 2 -O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 7.13-7.26 (m, 2H, aromatic), 7.85 (d, 1H, aromatic), 8.76 (s, 1H, -Ph-CH=). IR (KBr) 3337, 3221 (s, O-H), 2953, 2856 (m, C-H), 2222 (m, CN), 1722 (vs, C=O), 1612 (vs, C=C) cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>17</sub>NO<sub>6</sub>: C, 58.63; H, 5.57; N, 4.56. Found: C, 58.71; H, 5.66; N, 4.65.

**Synthesis of polyester 4.** A representative polycondensation procedure was as follows. Terephthaloyl chloride (2.03 g, 0.01 mol) and diol 3 (3.07 g, 0.01 mol) were dissolved in 30 mL of anhydrous pyridine under nitrogen. The resulting solution was heated in an oil bath kept at 80 °C under a nitrogen atmosphere. After heating 12 h with stirring the resulting polymerization solution was poured into 400 mL of methanol. The precipitated polymer was collected and re-precipitated from DMSO into methanol. The polymer was further purified by extraction in a Soxhlet extractor with diethyl ether and dried under vacuum, yielding 3.93 g (90% yield) of polymer 4: η<sub>inh</sub> = 0.28 dL/g (c, 0.5 g/dL in DMSO at 25 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>) δ 3.76 (s, 3H, CO<sub>2</sub>CH<sub>3</sub>), 4.16-4.46 (d, 8H, 2 Ph-O-CH<sub>2</sub>-CH<sub>2</sub>-O-), 7.24-7.43 (d, 2H, aromatic), 7.41-7.52 (s, 1H, aromatic), 7.68-8.05 (d, 4H, aromatic), 8.69-8.75 (s, 1H, -Ph-CH=). IR (KBr) 2954 (m, C-H), 2221 (m, CN), 1722 (vs, C=O), 1608 (s, C=C) cm<sup>-1</sup>. Anal. Calcd for (C<sub>23</sub>H<sub>19</sub>NO<sub>8</sub>)<sub>n</sub>: C, 63.16; H, 4.37; N, 3.20. Found: C, 63.25; H, 4.42; N, 3.14.

**Acknowledgments.** This work was supported by the 2010 Inje University research grant.

## References

- Marks, T. J.; Ratner, M. A. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 155.
- Lee, S. K.; Cho, M. J.; Jin, J.-I.; Choi, D. H. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 531.
- Centore, R.; Riccio, P.; Carella, A.; Quatela, A.; Schutzmann, S.; Stella, F.; De Matteis, F. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 2719.
- Li, Z.; Dong, S.; Li, P.; Li, Z.; Ye, C.; Qin, J. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 2983.
- Jin, F.-L.; Park, S.-J. *Bull. Korean Chem. Soc.* **2008**, *29*, 2521.
- Shrestha, S. P.; Ghimire, R.; Nakarmi, J. J.; Kim, Y. S.; Shrestha, S.; Park, C. Y.; Boo, J. H. *Bull. Korean Chem. Soc.* **2010**, *31*, 112.
- Han, K. S.; Park, S. K.; Shim, S. Y.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1165.
- Zhang, C.; Wang, C.; Yang, J.; Dalton, L. R.; Sun, S.; Zhang, H.; Steier, W. H. *Macromolecules* **2001**, *34*, 235.
- Kim, T.-D.; Luo, J.; Tian, Y.; Ka, J.-W.; Tucker, N. M.; Haller, M.; Kang, J.-W.; Jen, A. K.-Y. *Macromolecules* **2001**, *39*, 1676.
- Liu, Y.-L.; Hsieh, C.-Y. *J. Polym. Sci. Part A: Polym. Chem.* **2006**, *44*, 905.
- Saadeh, H.; Gharavi, A.; Yu, D.; Yu, L. *Macromolecules* **1997**, *30*, 5403.
- Tsutsumi, N.; Morishima, M.; Sakai, W. *Macromolecules* **1998**, *31*, 7764.
- Liu, J.-G.; Nakamura, Y.; Shibasaki, Y.; Ando, S.; Ueda, M. *J. Polym. Sci. Part A: Polym. Chem.* **2007**, *45*, 5606.
- Hoang, M. A.; Kim, M. H.; Cho, M. J.; Kim, K. H.; Kim, K. N.; Jin, J.-I.; Choi, D. H. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 5064.
- Ryu, S.; Kim, J. H.; Lee, S. H.; Lee, M.-H. *Bull. Korean Chem. Soc.* **2008**, *29*, 1689.
- Park, S. J.; Chae, S. W.; Rhee, J. M.; Kang, S. J. *Bull. Korean Chem. Soc.* **2010**, *31*, 2279.
- Lee, J.-H.; Lee, K.-S. *Bull. Korean Chem. Soc.* **2000**, *21*, 847.
- Lee, S.-H.; Kim, Y.-K.; Won, Y.-H. *Macromolecules* **1999**, *32*, 342.
- Ambrosiano, P.; Centore, R.; Concilio, S.; Panunzi, B.; Sirigu, A.; Tirelli, N. *Polymer* **1999**, *40*, 4923.
- Lee, J.-Y.; Jung, W.-T.; Lee, W.-J. *Polym. Int.* **2006**, *55*, 248.
- Lee, J.-Y.; Kim, J.-H.; Jung, W.-T. *Bull. Korean Chem. Soc.* **2007**, *28*, 329.
- Lee, J.-Y.; Kim, J.-H.; Won, D.-S.; Jang, H.-N. *Bull. Korean Chem. Soc.* **2007**, *28*, 1433.
- Won, D.-S.; Lee, G.-Y.; Lee, J.-Y. *Dyes. Pigm.* **2008**, *78*, 225.
- Won, D.-S.; Jung, W.-T.; Lee, J.-Y. *Polym. Bull.* **2009**, *62*, 433.
- Kim, J.-H.; Won, D.-S.; Lee, J.-Y. *Bull. Korean Chem. Soc.* **2008**, *29*, 181.
- Cisneros, J. I. *Appl. Opt.* **1998**, *37*, 5262.
- Herman, W. N.; Hayden, L. M. *J. Opt. Soc. Am. B* **1995**, *12*, 416.