Synthesis and Nonlinear Optical Properties of Novel Polyurethanes with High Thermal Stability for Electro-Optic Applications

Ju-Yeon Lee,* **Sung-Min Park, and Won-Taek Jung**

Institute of Functional Material Chemistry, Department of Chemistry, Inje University, Gimhae 621-749, Korea
*E-mail: chemljy@inje.ac.kr
Received March 6, 2005

A growing research effort has been made for nonlinear optical (NLO) polymers over the past decade because of their potential applications in the field of telecommunications, optical switching, etc.[1-3] In the developments of NLO polymers for electro-optic device applications, stabilization of electrically induced dipole alignment is important considerations. Two approaches to minimize the randomization have been proposed. One is to use cross-linking method[4-6] and the other is to utilize high T_g polymers such as polyimides.[7] Polyurethane matrix forms extensive hydrogen bond between urethane linkage and increases rigidity preventing the relaxation of induced dipoles.[8-11] Recently we reported a novel Y-type NLO polyurethanes with high thermal stability of second harmonic generation.[12-15] This work is now extended to the synthesis of another NLO polyurethanes. In this work we prepared novel polyurethanes (**4-5**) containing 2,3-dioxybenzylidenecyanoacetate group as a NLO-chromophore. We selected 2,3-dioxybenzylidenecyanoacetate group as NLO-chromophore because it will have a large dipole moment and is rather easy to synthesize. Furthermore 2,3-dioxybenzylidenecyanoacetate group constitutes a novel Y-type NLO polyurethanes, and these Y-type NLO polyurethanes are not presented in the literature. Thus, we designed and synthesized a new type of NLO polyurethane, in which the pendant NLO chromophores are parts of the polymer backbones. These mid-type NLO polymers are expected to have both of the merits of main chain- and side chain-NLO polymers; stabilization of dipole alignment and good solubility. After confirming the structure of the resulting polymers we investigated the properties such as morphology of polymer film, second harmonic generation (SHG) activity and relaxation of dipole alignment.

Results and Discussion

Monomer **3** containing NLO chromophore was prepared by hydrolysis of 2,3-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate **2** (see Scheme 1). Polymers **4** and **5** were prepared by the polyaddition reaction between a diol **3** and 2,4-toluenediisocyanate (TDI) and 3,3'-dimethoxy-4,4'-biphenylenediisocyanate (DMBPI) in a dry DMF solvent (see Scheme 2). Polymerization results are summarized in Table 1. The chemical structures of the compounds were identified by ^{1}H NMR, IR spectra, and elemental analysis. Elemental analysis results fit the polymer structures. ^{1}H NMR spectra of the polymers showed a signal broadening due to polymerization, but the chemical shifts are consistent with the proposed polymer structures. The signal at 9.01-9.26 ppm assigned to the amine proton indicates the formation of urethane linkage. The IR spectra of the same polymer samples also show a strong carbonyl peak near 1722 cm^{-1} indicating the presence of urethane bond. The number average molecular weights (M_n) of the polymers were determined to be 14400 ($M_w/M_n = 1.89$) for polymer **4**.
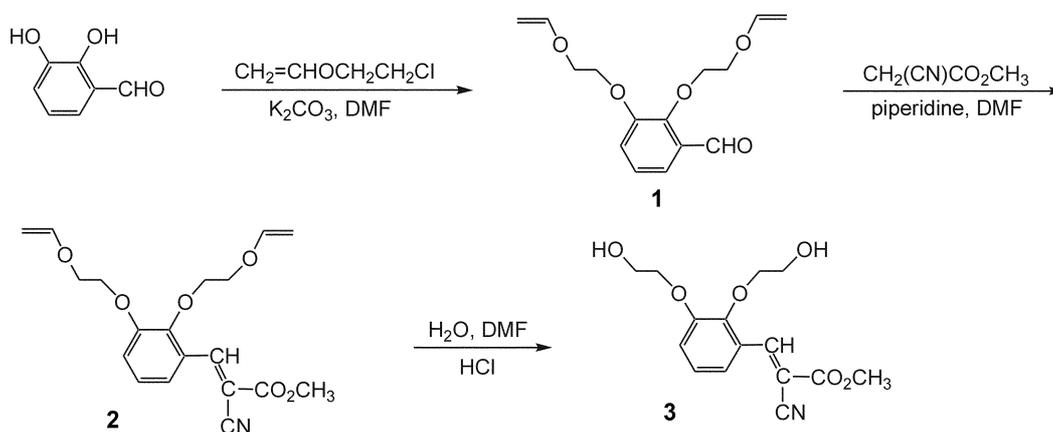
Scheme 1. Synthesis of diol **3**.
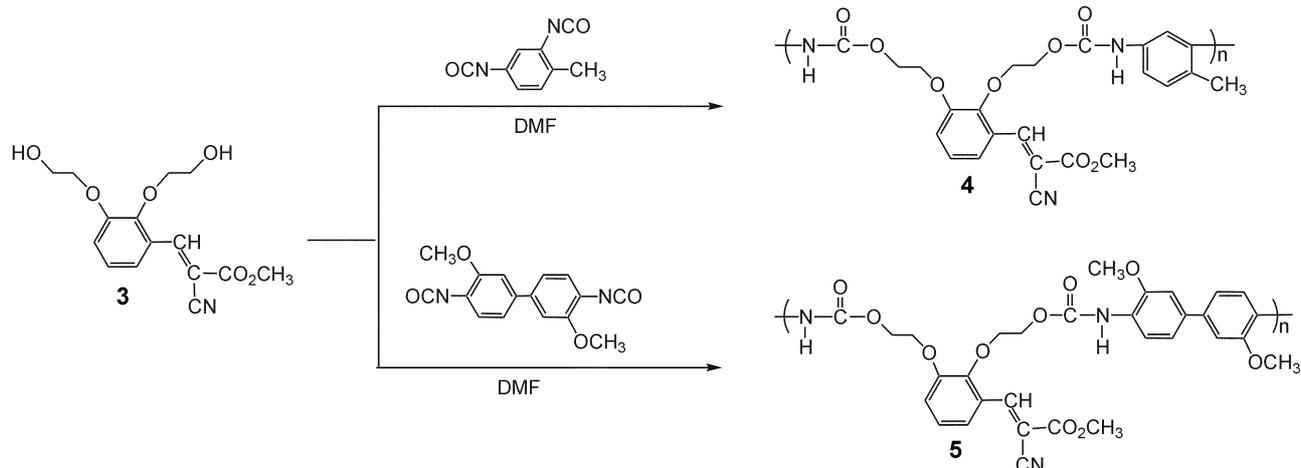
Scheme 2. Synthesis of polymers **4-5**.

Table 1. Polymerization of **3**[a] with TDI[b] and DMBPI[c] in DMF

Monomer	Monomer/ Sovent (mol/L)	Diol **3** to RNCO (mol%)	Time (h)	Yield (%)	η_{inh}[d] (dL/g)	M_n[e]	M_w[e]
3, TDI	0.50	1.0	6	85	0.28	13500	26800
3, TDI	0.80	1.0	8	90	0.30	14400	27200
3, DMBPI	0.50	1.0	6	82	0.24	12800	26500
3, DMBPI	0.80	1.0	8	84	0.25	13400	27600

[a]**3** = Methyl 2,3-di-(2'-hydroxyethoxy)benzylidenecyanoacetate. [b]TDI = 2,4-Toluendiisocyanate. [c]DMBPI = 3,3'-Dimethoxy-4,4'-biphenylenedi-isocyanate. [d]Inherent viscosity of polymer: Concentration of 0.5 g/dL in DMSO at 25 °C. [e]Measured by GPC in THF using polystyrene standard.

Polydispersities were in the range of 1.89-2.07. The polyurethanes **4-5** were soluble in common solvents such as acetone, DMF and DMSO, but were not soluble in methanol and diethyl ether. The inherent viscosities were in the range of 0.25-0.30 dL/g. The striking feature of these polymers is that they have pendant NLO chromophores that are parts of the polymer main chains. Thus, we obtained a new type of NLO polyurethanes with both of side chain and main chain characteristics. These mid-type NLO polymers are expected to have both of the merits of main chain and side chain NLO polymers.

The thermal behavior of the polymers were investigated by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) to determine the thermal degradation pattern and glass transition temperature (T_g). The results are summarized in Table 2. DSC thermograms of the polymers **4-5** are presented in Figure 1. Polymers **4-5** showed a thermal stability up to 260 °C from their TGA thermograms with T_g values around 144-149 °C as shown in Table 2. The initial weight loss in the polymers begins at 259-265 °C.

Nonlinear optical properties of polymers were studied by the SHG method. To induce noncentrosymmetric polar order, the spin-coated polymer films were corona-poled. The UV-Vis absorption spectra of the polymer sample **4** before and after the poling are presented in Figure 2. After the electric poling, the dipole moments of the NLO-chromophores were aligned and UV-Vis spectrum of polymer **4**

Table 2. Thermal Properties of Polymers **4-5**

Polymer	T_g[a], °C	Degradation temp, °C[b]			Residue[b] at 800 °C, %
		5%-loss	20%-loss	40%-loss	
4	144	263	295	321	11.0
5	149	273	306	330	11.3

[a]Determined from DSC curves measured on a TA 2920 differential scanning calorimeter with a heating rate of 10 °C/min under nitrogen atmosphere. [b]Determined from TGA curves measured on a DuPont 951 thermogravimetric analyzer with a heating rate of 10 °C/min under nitrogen atmosphere.
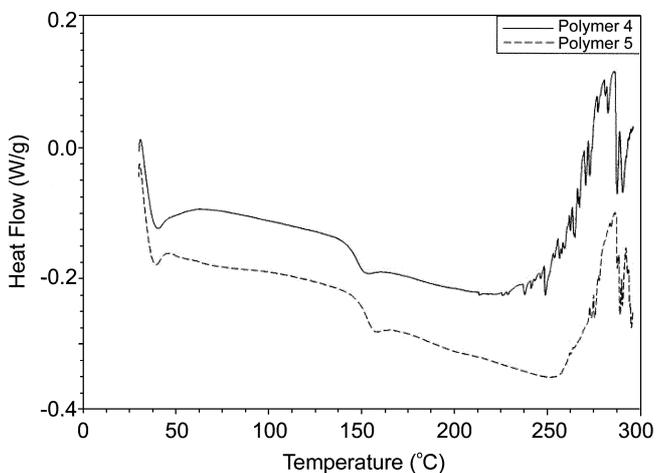
Figure 1. DSC thermograms of polymers **4-5** at a heating rate of 10 °C/min under nitrogen.

exhibited a slight blue shift and a decrease in absorption due to birefringence. From the absorbance change, the order parameter of the poled film could be estimated, which is related to the poling efficiency. The estimated order parameter value Φ was found to have a value of 0.28 for polymer **4** ($\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after poling). The decrease in absorbance after poling is an indicator of the dipole alignment. Domain structures of NLO-chromophores for the poled thin-film samples were obtained using atomic force microscopy (AFM). Figure 3 shows AFM scans of the
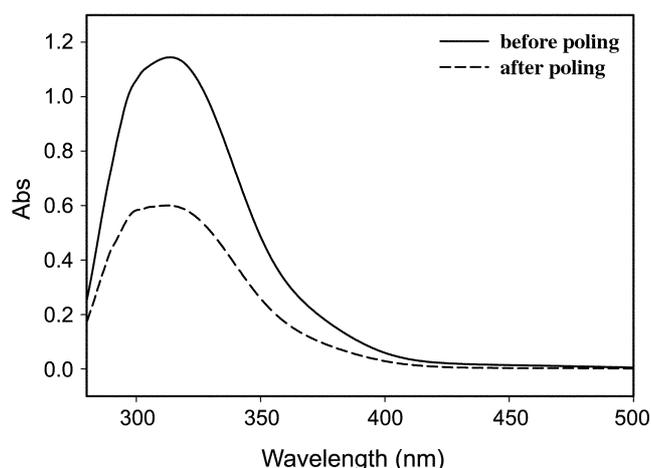
Figure 2. UV-Vis absorption spectra of a film of polymer **4** before and after poling.

spin-coated film before and after poling for polymer **4**. AFM images showed that the surface of the film sample was dramatically changed after poling, resulting in numerous hills and valleys in the surface structure, which were aligned the poling direction. The refractive index of the sample was measured by the optical transmission technique.[16] The transmittance of thin film includes the information of the thickness, refractive index and its extinction coefficient. Thus, we can 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. In order to determine the microscopic second-order susceptibility of the polymer, the angular SHG dependence was recorded. 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 to the samples and recorded. SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes with Pascal fitting program according to the literature procedure.[17] Nonlinear optical properties of polymers **4-5** are summarized in Table 3. The values of d_{31} and d_{33} for polymer **5** were 2.84×10^{-10} and 5.42×10^{-10} esu, respectively. These values are rather small probably because of the short NLO chromophores. Since the second harmonic wavelength was at 532 nm, which is not in the absorptive region of the resulting polymer, there was not resonant contribution to this d_{33} value. To evaluate the high-temperature stability of the polymers, we studied the temporal stability of the SHG signal. In Figure 4, we present the dynamic thermal stability study of the NLO activity of
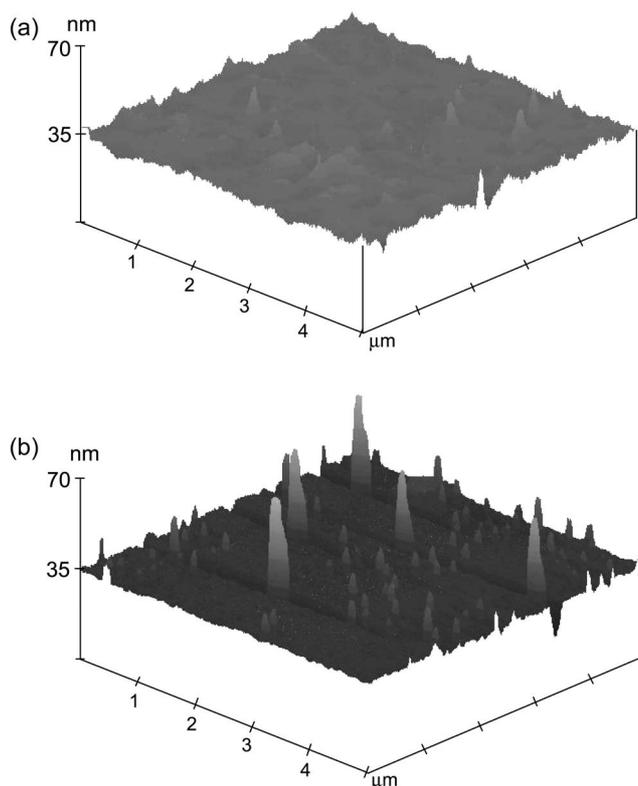
Figure 3. AFM images of spin-coated film of polymer **4**: (a) before corona-poling; (b) after corona-poling.

the film **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 10 ºC/min from 30 ºC to 240 ºC. Poled polymer films exhibited a temporal thermal stability of dipole alignment up to T_g and no SHG decay was observed below 145 ºC. Side-chain NLO polymers usually lose thermal stability of dipole alignment below T_g. Stabilization of dipole alignment is a characteristic of main-chain NLO polymers. The high thermal stability of second harmonic generation of polymers **4-5** was due to the stabilization of dipole alignment of NLO chromophore, which stemmed from the partial main chain character of the polymer struc-ture. The polymers also showed good long-term thermal stability of d_{33} except for the small activity loss within a few days after poling, which are acceptable for NLO device applications. Thus, we obtained a new type of NLO polyurethane having both of the advantages of main-chain and side-chain NLO polymers; stabilization of dipole alignment and good solubility.

Table 3. Nonlinear Optical Properties of Polymers **4-5**

Polymer	$\lambda_{max}{}^a$ (nm)	$d_{33}{}^b$ (esu)	Φ^c	film thickness^d (μm)	$d_{31}{}^b$ (esu)	n^e
4	314	5.42×10^{-10}	0.28	0.53	2.84×10^{-10}	$n_1 = 1.63, n_2 = 1.67$
5	321	3.19×10^{-10}	0.15	0.54	1.72×10^{-10}	$n_1 = 1.61, n_2 = 1.65$

^{a}Polymer film after corona poling. ^{b}SHG coefficients (d_{33}) were derived from the analysis of measured Maker-fringes.[17] ^{c}Order parameter $\Phi = 1 - A_1/A_0$, where A_0 and A_1 are the absorbances of the polymer film before and after corona poling, respectively. ^{d}Film thickness was determined by the optical transmission technique.[16] ^{e}Refractive index was measured at 1064 nm.
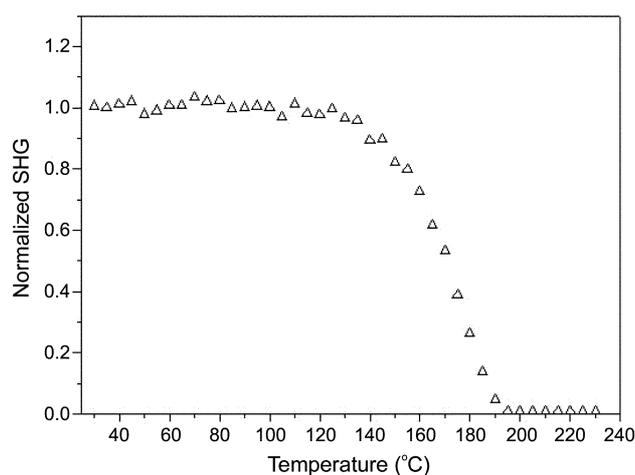
Figure 4. Normalized SHG signal of polymer **4** as a function of temperature at a heating rate of 10 °C/min.

Experimental Section

Materials. The reagent grade chemicals were purchased from Aldrich and purified by either distillation or recrystallization before use. 2,3-Di-(2'-vinyloxyethoxy)benzaldehyde (**1**), methyl 2,3-di-(2'-vinyloxyethoxy)benzylidenecyanoacetate (**2**), and methyl 2,3-di-(2'-hydroxyethoxy)benzylidenecyano-acetate (**3**) were prepared from the corresponding reagents according to a procedure similar to that reported already.[12]

Instrumentation. IR spectra were taken on a Shimadzu FT IR-8201PC infrared spectrophotometer. ^{1}H NMR spectra were obtained on a Varian 300 MHz NMR spectrometer. UV-Vis absorption spectra were measured on a Shimadzu UV-3100S spectrophotometer. Atomic force microscopy (AFM) images were recorded with a Park Science Instrument Autoprobe CP, operated in a contact mode, which measures topography.

Film Preparation and SHG Measurement. The polymer film was prepared from a 10% by weight polymer solution in DMF deposited on an indium-tin oxide (ITO) covered glass. The alignment of the NLO-chromophore of the polymers was carried out by corona poling method. The corona poling was performed in a wire-to plane geometry under in situ conditions. The discharging wire to plane distance was 1.0 cm. As the temperature was raised gradually to 160 °C, 6.5 kV of corona voltage was applied and kept at 160 °C for 30 min. The refractive index of the sample was measured by the optical transmission technique.[16] Second harmonic generation (SHG) measurement was carried out one day after poling. A continuum PY61 mode-locked Nd:YAG laser (λ = 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. The Maker Fringe pattern was obtained from 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.[17]

Synthesis of Polyurethanes 4-5. 2,4-Toluenediisocyanate (1.74 g, 0.01 mol) was added slowly to a solution of 3.07 g

of diol **3** (0.01 mol) in 40 mL of anhydrous DMF. The resulting solution was degassed by a freeze-thaw process under vacuum and placed in an oil bath kept at 80 °C. After heating 6 h with stirring the polymerization tube was opened and the viscous polymer solution was poured into 400 mL of cold water. The precipitated polymer was collected and reprecipitated from DMSO into methanol. The obtained polymer was purified by Soxhlet extraction in diethyl ether for 2 days to give 4.09 g (85% yield) of the pure polymer **4**: η_{inh} = 0.28 dL/g (c, 0.5 g/dL in DMSO at 25 °C). ^{1}H NMR (DMSO-d_6) δ 2.04-2.12 (m, 3H, -CH$_3$), 3.64-3.77 (d, 3H, -COOCH$_3$), 4.29-4.53 (m, 8H, 2 -O-CH$_2$-CH$_2$-O-), 6.97-7.80 (m, 6H, aromatic), 8.58-8.91 (m, 1H, Ph-CH=), 9.29-9.67 (d, 2H, N-H). IR (KBr) 3360 (s, N-H), 2953 (m, C-H), 2222 (m, CN), 1722 (vs, C=O), 1601 (s, C=C) cm^{-1}. Anal. Calcd for (C$_{24}$H$_{23}$N$_3$O$_8$)$_n$: C, 59.87; H, 4.81; N, 8.73. Found: C, 59.98; H, 4.88; N, 8.64. Polymer **5**: ^{1}H NMR (DMSO-d_6) δ 3.73 (s, 3H, -COOCH$_3$), 3.88 (s, 3H, -OCH$_3$), 3.98 (s, 3H, -OCH$_3$), 4.26-4.54 (m, 8H, 2 -O-CH$_2$-CH$_2$-O-), 7.17-7.46 (m, 5H, aromatic), 7.63-7.84 (m, 2H, aromatic), 8.11-8.25 (m, 2H, aromatic), 8.57-8.81 (m, 1H, Ph-CH=), 9.01 (s, 2H, N-H). IR (KBr) 3395 (m, N-H), 2953, 2836 (m, C-H), 2222 (w, CN), 1722 (m, C=O), 1589 (s, C=C) cm^{-1}. Anal. Calcd for (C$_{31}$H$_{29}$N$_3$O$_{10}$)$_n$: C, 61.69; H, 4.84; N, 6.96. Found: H, 61.78; H, 4.92; N, 7.03.

References

1. *Electronic and Photonic Applications of Polymers*; Bowden, M. J.; Turner, S. R., Eds.; American Chemical Society: Washington DC, 1988.
2. *Nonlinear Optical and Elrctroactive Polymers*; Prasad, P. N.; Ulrich, D. R., Eds.; Plenum Press: New York, 1988.
3. *Nonlinear Optical Properties of Polymers*; Heeger, A. J.; Orenstein, J.; Ulrich, D. R., Eds.; Materials Research Society: Pittsburgh, 1988.
4. Han, K. S.; Park, S. K.; Shim, S. Y.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1165.
5. Han, K. S.; Park, S. K.; Shim, S. Y.; Lee, Y. S.; Jahng, W. S.; Kim, N. J. *Bull. Korean Chem. Soc.* **1998**, *19*, 1168.
6. Cho, B. R.; Kim, Y. H.; Son, K. W.; Khalil, C.; Kim, Y. H.; Jeon, S.-J. *Bull. Korean Chem. Soc.* **2002**, *23*, 1253.
7. Kim, M. H.; Jin, J.-I.; Lee, C. J.; Kim, N. J.; Park, C. H. *Bull. Korean Chem. Soc.* **2002**, *23*, 964.
8. Boogers, J. A. F.; Klaase, P. T. A.; Vlieger, J. J. D.; Tinnemans, A. H. A. *Macromolecules* **1994**, *27*, 205.
9. Tsutumi, N.; Yoshizaki, S.; Sakai, W.; Kiyotsukuri, T. *Macromolecules* **1995**, *28*, 6437.
10. Moon, K. J.; Shim, H. K.; Lee, K. S.; Zieba, J.; Prasad, P. N. *Macromolecules* **1996**, *29*, 861.
11. Woo, H. Y.; Lee, K. S.; Shim, H. K. *Polym. J.* **2000**, *32*, 8.
12. Lee, J.-Y.; Park, E.-J. *J. Polym. Sci. Part A: Polym. Chem.* **2002**, *40*, 1742.
13. Lee, J.-Y.; Park, E.-J.; Lee, H.; Rhee, B. K. *Polym. Bull.* **2002**, *48*, 233.
14. Lee, J.-Y.; Bang, H.-B.; Park, E.-J.; Baek, C. S.; Rhee, B. K.; Lee, S. M. *Syn. Met.* **2004**, *144*, 159.
15. Lee, J.-Y.; Bang, H.-B.; Kang, T.-S.; Park, E.-J. *Europ. Polym. J.* **2004**, *40*, 1815.
16. Cisneros, J. I. *Appl. Opt.* **1998**, *37*, 5262.
17. Herman, W. N.; Hayden, L. M. *J. Opt. Soc. Am. B* **1995**, *12*, 416.