

Synthesis of Side-Chain Nonlinear Optical Polymers with Carbazolynitrostilbene Chromophores

Dong Wook Kim, Sung Il Hong, Soo Young Park*, and Nakjoong Kim†

Department of Fiber and Polymer Science, Seoul National University,
San 56-1, Shinlim-dong, Kwanak-ku, Seoul 151-742, Korea

†Division of Polymers, KIST, P.O. Box 131, Cheongryang, Seoul 130-650, Korea

Received November 8, 1996

Two different carbazolynitrostilbene chromophores with second-order nonlinear optical (NLO) activity were newly synthesized by the reaction of 9-(2-hydroxyethyl)-9H-carbazol-3-carbaldehyde with 4-nitrophenylacetonitrile or 4-nitrophenylacetic acid. The NLO monomers were obtained by reaction of these chromophores with methacryloyl chloride. The side-chain nonlinear optical polymers were synthesized by the copolymerization of NLO monomer with methylmethacrylate using a free radical initiator. The chemical structures of the polymers were identified by spectroscopic means and the polymer properties such as molecular weight, T_g , solubility, UV-visible absorption, and second-harmonic generation (SHG) coefficients were investigated.

Introduction

In recent years, much scientific and technological research is directed toward organic polymers possessing nonlinear optical (NLO) properties because of their potential applications in the field of optical communication, optical switching, and optical signal processing.^{1,2} Although prototype optical devices based on inorganic materials such as KTP and LiNbO₃ have already become available, more research interest is focused upon the NLO polymers because of their superior performance and processibility to the inorganic crystals. Among the various NLO polymeric systems, the poled side-chain NLO polymer is currently considered to be the most promising due to the high chromophore content, improved temporal stability, good processibility, and easy structural modification.³ The main issues of side-chain NLO polymers are generally two-fold as follows. First, the NLO chromophores should be designed to have effective π -conjugation capped at one end with electron donor and at the other end with electron acceptor to impart a high molecular hyperpolarizability (β).^{4,5} Second, the NLO polymers should possess high glass transition temperature (T_g) to prevent the dipolar relaxation of poled system.

In this work, we report the design and synthesis of the novel side-chain NLO polymers with carbazolynitrostilbene chromophores, which are likely to satisfy the above-mentioned issues. We incorporated thermally stable carbazole group into the chromophore structure, replacing the traditional aliphatic amine used as an electron donor group, with an additional hope to impart excellent charge transport properties necessary for photorefractivity.⁶ The structures of NLO chromophores and polymers were characterized in detail and the polymer properties such as molecular weight, T_g , solubility, UV-visible absorption, and second-harmonic generation (SHG) coefficients were determined.

Experimental

* To whom correspondence should be addressed

Materials

Organic solvents were purified by distillation over the suitable dehydrating reagents just before use. 9H-carbazole and ethylene carbonate purchased from Aldrich Chem. Co. were purified by recrystallization from ethanol and diethylether, respectively. Commercially available 4-nitrophenylacetonitrile and 4-nitrophenylacetic acid were used as received. Methacryloyl chloride purchased from Aldrich Chem. Co. were purified by distillation at reduced pressure.

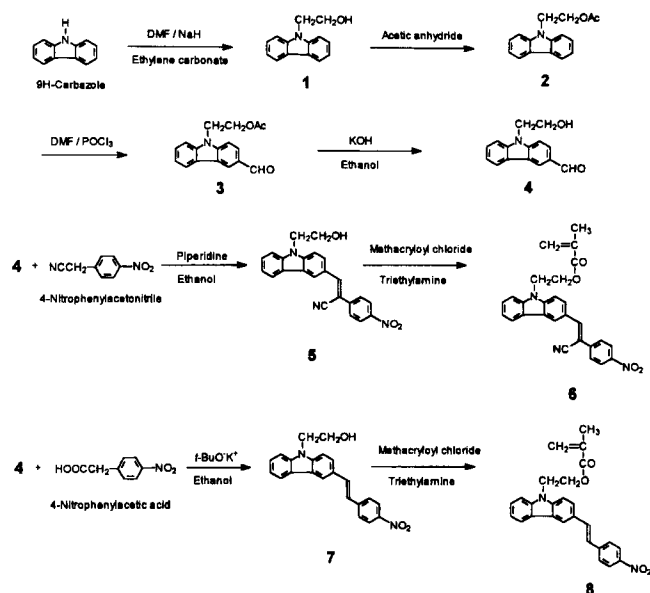
Instrumentation

FT-IR spectra were recorded on a Midac FT-IR spectrophotometer and ¹H NMR spectra were obtained with a Bruker AMX 500 spectrometer. UV-visible spectra were obtained with a Shimadzu UV-2101PC double beam spectrophotometer. Gel permeation chromatography (GPC) analysis of polymers was performed at a flow rate 1.0 mL/min in THF at 30 °C using Waters HPLC component system equipped with five Ultra- μ -styragel® columns (2 × 10⁵, 10⁴, 10³, 500 Å). DSC measurements were performed on a Perkin Elmer DSC7. NLO property of polymer film on quartz plate was measured by the standard Marker-fringe method at 1.064 μ m fundamental wavelength.⁷

Synthesis of the monomers

The synthesis of the monomeric NLO chromophores, **6** and **8** are illustrated in Scheme 1.

2-Carbazol-9-yl-ethanol (1). A solution of 10.0 g (0.06 mol) of 9H-carbazole in freshly distilled DMF (100 mL) was vigorously stirred at 0 °C, and treated with 4.8 g (0.12 mol) of sodium hydride oil dispersion (60%). After 3 h of stirring at 0 °C, 6.38 g (0.07 mol) of ethylene carbonate was added slowly and the mixture was stirred at 0 °C for 1 h and then at 40 °C for 3 h. 10 mL of water was added to the mixture and stirred for 3 h. The resulting mixture was poured into 500 mL of ice water and the precipitate was purified by silica gel column chromatography (ethyl acetate/*n*-hexane=1/2) to give white solid (yield: 67%), mp 80 °C (lit.⁸ mp 81-81.5 °C). IR (KBr pellet, cm⁻¹): 3220 (ν_{O-H}), 2980-2870 ($\nu_{\text{aliphatic C-H}}$). ¹H NMR (DMSO-d₆):



Scheme 1. Syntheses of the monomeric NLO chromophores.

δ 8.1 (d, 2H), 7.6 (d, 2H), 7.4 (t, 2H), 7.2 (t, 2H), 4.9 (t, 1H, OH), 4.4 (t, 2H, OCH₂), 3.8 (t, 2H, NCH₂). Anal. Calcd for C₁₄H₁₃NO: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.23; H, 6.07; N, 7.19.

Acetic acid 2-carbazol-9-ylethyl ester (2). A solution of 5.28 g (0.025 mol) of **1** in 40 mL of acetic anhydride was stirred and heated to reflux for 2 h. After cooling, the excess acetic anhydride was removed at reduced pressure. The residue was poured into 600 mL of ice water and extracted with ethyl acetate. The extract was dried over MgSO₄ and the solvent was removed at reduced pressure. 6.07 g of white solid was obtained. mp 72-74 °C (lit.⁹ mp 74-74.5 °C). IR (KBr pellet, cm⁻¹); 1734 (ν_{C=O}). Anal. Calcd for C₁₆H₁₅NO₂: C, 75.86; H, 5.97; N, 5.53. Found: C, 74.82; H, 5.54; N, 5.53.

Acetic acid 2-(3-formyl-carbazol-9-yl)ethyl ester (3). 5.07 g (0.02 mol) of **2** was dissolved in DMF (20 mL) and phosphorus oxychloride (4.66 mL, 0.05 mol) was added dropwise to the solution at 0 °C. The solution was stirred for 30 min and heated at 100 °C for 2 h. After cooling, the resulting solution was poured into 500 mL of ice water and neutralized to pH 6-8 with sodium hydroxide. The mixture was extracted with ethyl acetate and the extract was dried over MgSO₄. The solvent was removed at reduced pressure and the residue was purified by silica gel column chromatography (ethyl acetate/*n*-hexane=1/2) to give light yellow colored solid (yield: 72%). mp 151-152 °C. IR (KBr pellet, cm⁻¹); 2803 and 2708 (ν_{C-H} of aldehyde), 1686 (ν_{C=O} of aldehyde). ¹H NMR (CDCl₃); δ 10.1 (s, 1H, aldehyde proton), 8.6 (s, 1H), 8.2 (d, 1H), 8.0 (d, 1H), 7.5 (dd, 2H), 7.4 (t, 1H), 7.3 (t, 1H), 4.6 (t, 2H, OCH₂), 4.5 (t, 2H, NCH₂), 1.9 (s, 3H, COCH₃). Anal. Calcd for C₁₇H₁₅NO₃: C, 72.58; H, 5.38; N, 4.98. Found: C, 71.54; H, 5.42; N, 5.31.

9-(2-Hydroxyethyl)-9H-carbazol-3-carbaldehyde (4). 10.0 g (0.036 mol) of **3** was dissolved in ethanol (35 mL) and 4.04 g (0.072 mol) of potassium hydroxide was added into the solution. The mixture was heated to reflux

for 3 h. After cooling, the solvent was removed at reduced pressure and the residue was poured into water. The precipitate was filtered and washed thoroughly with water. After drying under vacuum, yellow colored solid was obtained. mp 123-125 °C. IR (KBr pellet, cm⁻¹); 3490 (ν_{O-H}), 2808 and 2735 (ν_{C-H} of aldehyde), 1670 (ν_{C=O} of aldehyde). ¹H NMR (DMSO-d₆); δ 10.1 (s, 1H, aldehyde proton), 8.7 (s, 1H), 8.3 (d, 1H), 8.0 (d, 1H), 7.8 (d, 1H), 7.7 (d, 1H), 7.5 (t, 1H), 7.3 (t, 1H), 4.9 (t, 1H, OH), 4.5 (t, 2H, OCH₂), 3.8 (t, 2H, NCH₂). Anal. Calcd for C₁₅H₁₃NO₂: C, 75.29; H, 5.48; N, 5.86. Found: C, 74.55; H, 5.50; N, 5.85.

3-[9-(2-Hydroxyethyl)-9H-carbazol-3-yl]-2-(4-nitrophenyl)acetonitrile (5). 2.0 g (0.0084 mol) of **4** and 1.36 g (0.0084 mol) of 4-nitrophenylacetonitrile were dissolved in anhydrous ethanol (100 mL) and 1.2 mL (0.012 mol) of piperidine was added dropwise into the mixture. The resulting solution was heated to reflux for 4 h. The solution was cooled and filtered. The product was washed with ethanol and dried under vacuum to give 3.03 g of red colored solid (yield: 94%). mp 243-245 °C. IR (KBr pellet, cm⁻¹); 3530 (ν_{O-H}), 2210 (ν_{CN}), 1512 and 1336 (ν_{nitro group}). ¹H NMR (DMSO-d₆); δ 8.8-7.3 (m, 12H), 4.9 (t, 1H, OH), 4.5 (t, 2H, OCH₂), 3.8 (t, 2H, NCH₂). Anal. Calcd for C₂₃H₁₇N₃O₃: C, 72.05; H, 4.47; N, 10.96. Found: C, 71.10; H, 4.31; N, 10.87.

2-Methyl-acrylic acid 2-[3-[2-cyano-2-(4-nitrophenyl)vinyl]-carbazol-9-yl]ethyl ester (6). 1.42 g (0.0037 mol) of **5** was dissolved in freshly distilled THF (370 mL). Triethylamine (2.78 mL, 0.02 mol) and a trace amount of 2,6-di-*tert*-butyl-4-methyl phenol (polymerization inhibitor) were added to the solution. The solution was cooled to 0 °C under nitrogen atmosphere and 1.95 mL (0.02 mol) of methacryloyl chloride was added slowly. After stirring at 0 °C for 30 min, the solution was heated at 40 °C for 24 h. The solution was washed with sodium bicarbonate solution and then washed with water. The solution was dried over MgSO₄ and the solvent was removed at reduced pressure. The residue was purified by silica gel column chromatography (chloroform/ethyl acetate=2/1) to give orange colored solid. mp 171-173 °C. IR (KBr pellet, cm⁻¹); 2208 (ν_{CN}), 1716 (ν_{C=O}), 1678 (ν_{C=C} of vinyl group), 1516 and 1338 (ν_{nitro group}). ¹H NMR (CDCl₃); δ 8.7-7.3 (m, 12H), 5.9 (s, 1H), 5.4 (s, 1H), 4.6 (t, 2H, OCH₂), 4.5 (t, 2H, NCH₂), 1.7 (s, 3H, CH₃). Anal. Calcd for C₂₇H₂₁N₃O₄: C, 71.83; H, 4.69; N, 9.31. Found: C, 71.03; H, 4.47; N, 9.19.

2-[3-[2-(4-nitrophenyl)vinyl]-carbazol-9-yl]ethanol (7). 2.00 g (0.0084 mol) of **4** and 3.04 g (0.0168 mol) of 4-nitrophenylacetic acid were dissolved in anhydrous ethanol (120 mL). 0.012 mol of potassium *tert*-butoxide in THF solution was added dropwise to the mixture and heated to reflux for 22 h. The solution was cooled and the precipitate was filtered. The resulting solid was purified by recrystallization from ethanol to give the red colored solid (yield: 43%). mp 183-185 °C. IR (KBr pellet, cm⁻¹); 3410 (ν_{O-H}), 1508 and 1336 (ν_{nitro group}). ¹H NMR (DMSO-d₆); δ 8.5-7.3 (m, 13H), 4.9 (t, 1H, OH), 4.5 (t, 2H, OCH₂), 3.8 (t, 2H, NCH₂). Anal. Calcd for C₂₇H₁₈N₂O₃: C, 73.73; H, 5.06; N, 7.82. Found: C, 72.44; H, 4.81; N, 7.76.

2-Methyl-acrylic acid 2-[3-[2-(4-nitrophenyl)vinyl]-carbazol-9-yl]ethyl ester (8). Triethylamine (0.84 mL, 0.006 mol) and a trace amount of 2,6-di-*tert*-butyl-4-

methyl phenol were added to the solution of **7** (0.50 g, 0.0012 mol) in freshly distilled chloroform (300 mL). The mixture was cooled to 0 °C under nitrogen atmosphere and methacryloyl chloride (0.59 mL, 0.006 mol) was added slowly. The resulting solution was heated at 40 °C for 24 h. After cooling, the solution was washed with sodium bicarbonate solution and then washed with water. The solution was dried over MgSO₄ and the solvent was removed at reduced pressure. The residue was purified by silica gel column chromatography (chloroform/ethyl acetate=2/1) to give red colored solid. mp 147-149 °C. IR (KBr pellet, cm⁻¹); 1722 (ν_{C=O} of ester), 1512 and 1336 (ν_{Nitro group}). ¹H NMR (CDCl₃); δ 8.2-7.1 (m, 13H), 5.9 (s, 1H), 5.4 (s, 1H), 4.6 (t, 2H, OCH₂), 4.5 (t, 2H, NCH₂), 1.7 (s, 3H, CH₃). Anal. Calcd for C₂₆H₂₂N₂O₄: C, 73.23; H, 5.20; N, 6.57. Found: C, 73.07; H, 5.09; N, 6.40.

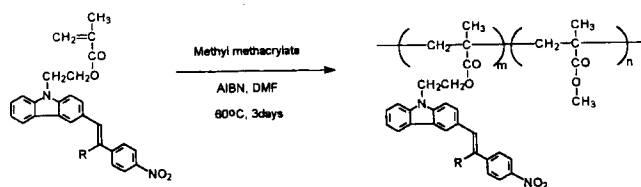
Polymerization

The polymerization of the monomeric NLO chromophores are illustrated in Scheme 2 and the typical procedure of them is as follows. 0.40 g (0.89 mmol) of **6**, 0.27 g (2.67 mmol) of freshly distilled methyl methacrylate, and 5.8 mg (1 mol% to the monomer) of 2,2'-azobis(2-methylpropionitrile) (AIBN) were dissolved in DMF (15 mL). The solution was thoroughly degassed by several freeze-pump-thaw cycles and heated in a sealed ampoule at 60 °C for 3 days. The resulting polymer solution was cooled and poured into vigorously agitated methanol to precipitate the polymer. The product was purified by repeated reprecipitation. After filtration and vacuum drying, an orange colored **P1** was obtained (yield: 45%). IR (KBr pellet, cm⁻¹); 2212 (ν_{CN}), 1734 (ν_{C=O}), 1521 and 1342 (ν_{Nitro group}). ¹H NMR (CDCl₃); δ 8.7-7.3 (aromatic protons), 4.6-4.3 (NCH₂CH₂O), 3.5-3.4 (OCH₃), 1.7 (CH₃), 0.9-0.5 (backbone CH₂). GPC; Mn=17,000, Mw/Mn=1.55.

P2 and **P3** were synthesized by the similar procedure with that of **P1**.

Polymer **P2**: yield; 43%. IR (KBr pellet, cm⁻¹); 2212 (ν_{CN}), 1732 (ν_{C=O}), 1520 and 1342 (ν_{Nitro group}). ¹H NMR (CDCl₃); δ 8.7-7.3 (aromatic protons), 4.6-4.3 (NCH₂CH₂O), 3.5-3.4 (OCH₃), 1.7 (CH₃), 0.9-0.5 (backbone CH₂). GPC; Mn=17,300, Mw/Mn=1.58.

Polymer **P3**: yield; 35%. IR (KBr pellet, cm⁻¹); 1728 (ν_{C=O}), 1514 and 1338 (ν_{Nitro group}). ¹H NMR (CDCl₃); δ 8.2-7.1 (aromatic protons), 4.5-4.3 (NCH₂CH₂O), 3.5-3.4 (OCH₃),



Polymer	R	Feed ratio (mole ratio)	
		NLO monomer	MMA
P1	CN	1	3
P2	CN	1	1
P3	H	1	1

Scheme 2. Syntheses of the side-chain NLO polymers.

1.7 (CH₃), 0.9-0.5 (backbone CH₂). GPC; Mn=10,900, Mw/Mn=1.51.

Results and Discussion

Synthesis of monomers

The compound **1** was synthesized by the reaction of 9H-carbazole with ethylene carbonate using a very strong base, sodium hydride according to the literature.⁸ The compound **1** could alternatively be prepared in a similar yield with 2-chloroethanol instead of ethylene carbonate of this report, which seems to be applied advantageously to the synthesis of longer carbon ω-chloro alcohols. The key material in the synthesis of the monomeric NLO chromophores is the monoaldehyde compound **4**. This compound was found to be synthesized specifically by Vilsmeier formylation of **2** followed by deprotection with base. Figures 1 and 2 show the FT-IR and the ¹H NMR spectrum of **4**, respectively. As shown in Figure 1, the monoaldehyde compound **4** was clearly identified by the strong absorption peak of the aldehyde carbonyl group at 1670 cm⁻¹ and also the characteristic absorption peaks of aldehyde C-H at 2808 cm⁻¹ and 2735 cm⁻¹.¹⁰ The ¹H NMR spectrum in Figure 2 shows the chemical shift of one aldehyde proton at 10.1 ppm and the seven distinct aromatic protons at 8.7-7.3 ppm, conforming to the expected chemical shifts of the carbazole ring protons substituted with one aldehyde group in position 3.

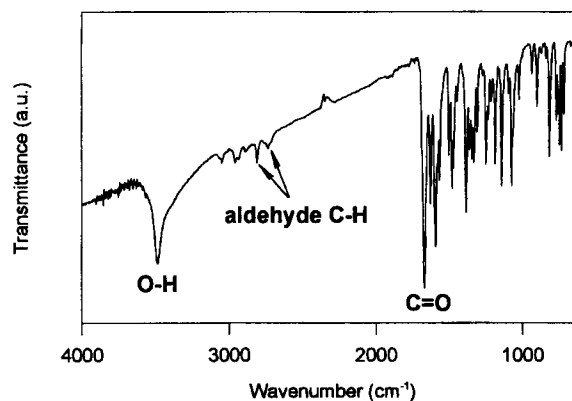


Figure 1. FT-IR spectrum of 9-(2-hydroxyethyl)-9H-carbazol-3-carbaldehyde, **4**.

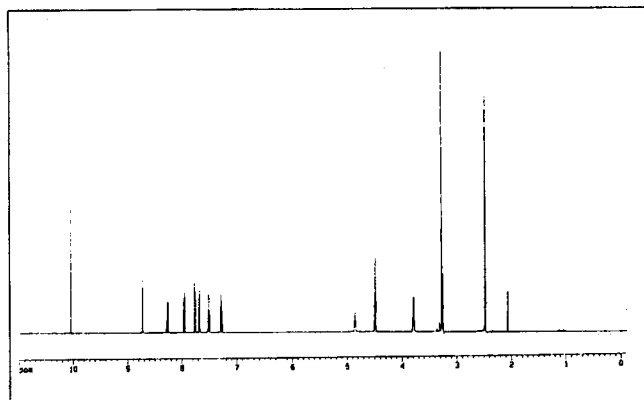


Figure 2. ¹H NMR spectrum of 9-(2-hydroxyethyl)-9H-carbazol-3-carbaldehyde, **4**.

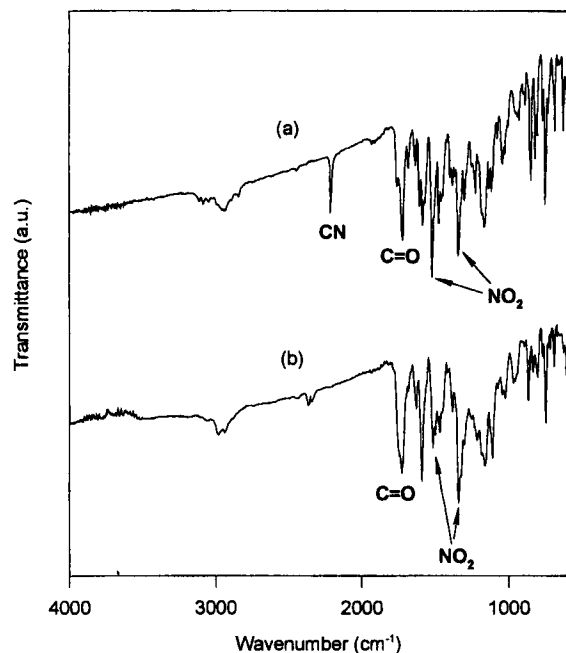


Figure 3. FT-IR spectra of the monomeric NLO chromophores, (a) **6** and (b) **8**.

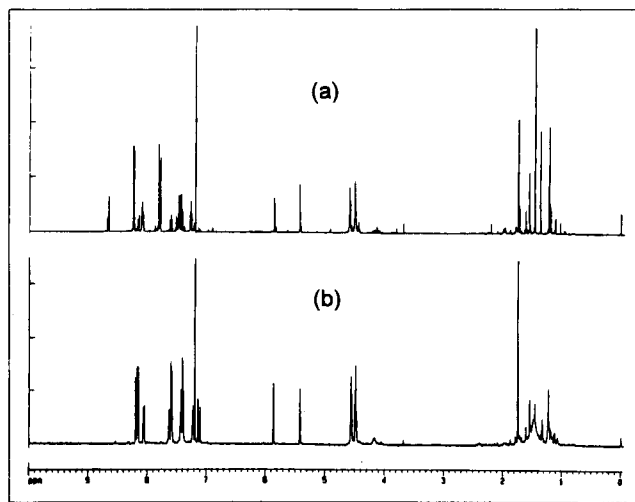


Figure 4. ^1H NMR spectra of the monomeric NLO chromophores, (a) **6** and (b) **8**.

The compound **5**, which was precipitated out in the solution during the reaction, was easily synthesized and purified in good yield (~90%) by Knoevenagel condensation reaction of the aldehyde compound **4** and 4-nitrophenyl acetonitrile. However the synthesis of the compound **7** required relatively severe conditions, because the carboxylic acid group of 4-nitrophenyl acetic acid is the weaker electron withdrawing group than the cyano group of the 4-nitrophenyl acetonitrile. Although we used stronger base (*tert*-butoxide) and longer reaction time (22 h), the reaction yield (~40%) was quite low for compound **7**.

Figures 3 and 4 show the FT-IR and the ^1H NMR spectrum of the monomeric NLO chromophores, respectively. As shown in Figure 3(a), compound **6** was identified by the

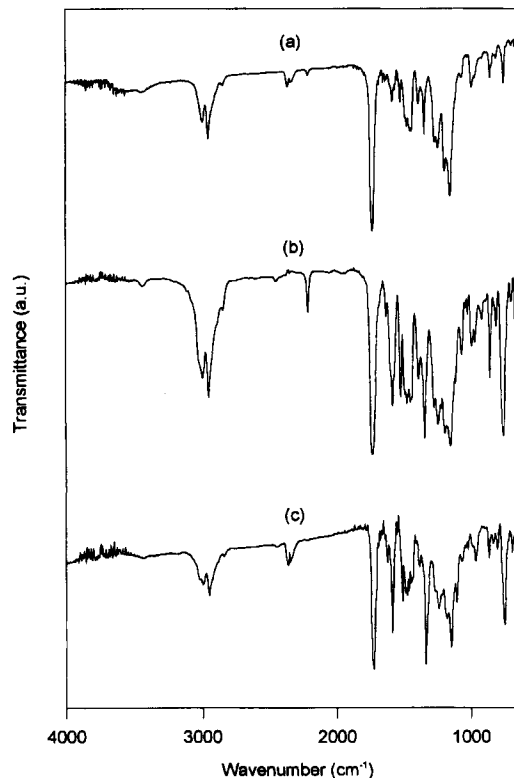


Figure 5. FT-IR spectra of the polymers, (a) **P1**, (b) **P2**, and (c) **P3**.

strong absorption peaks of the cyano group at 2208 cm^{-1} , α,β -unsaturated carbonyl group at 1716 cm^{-1} , and the nitro group at 1516 cm^{-1} and 1338 cm^{-1} . In Figure 3(b), compound **8** shows the similar spectrum to compound **6** except for the absence of cyano group absorption. The ^1H NMR spectrum of the compound **6** shown in Figure 4(a) identifies the chemical shift of aromatic protons at 8.7-7.3 ppm and the vinyl protons at 5.9 and 5.4 ppm. The ^1H NMR spectrum of the compound **8** in Figure 4(b) was very similar to that of the compound **6**.

Properties of polymers

The FT-IR and ^1H NMR spectra of the NLO polymers are shown in Figure 5 and 6. Comparing the spectra of Figure 5(a) and 3(a), it is noted that wavenumber of carbonyl stretching vibration increased by 18 cm^{-1} after polymerization, together with the disappearance of characteristic stretching vibration of vinyl group at 1678 cm^{-1} .¹⁰ Apart from these changes, polymer **P1** shows the strong absorption bands like monomer **6** at 2212, 1521, and 1342 cm^{-1} indicating the intact cyano, and nitro groups, respectively. Polymer **P2** shows the same absorption band as **P1**, but the intensity of absorption peak of cyano and nitro groups is stronger. The spectrum of polymer **P3** is similar to that of **P1** except the absence of cyano group. ^1H NMR spectra in Figure 6 show the chemical shift of aromatic protons, the protons in $\text{NCH}_2\text{CH}_2\text{O}$, OCH_3 , CH_3 , and the protons in backbone CH_2 to clearly identify the copolymers between NLO monomers with MMA.

The glass transition temperatures (T_g) of the polymers were determined to be $125\text{ }^\circ\text{C}$, $140\text{ }^\circ\text{C}$, and $140\text{ }^\circ\text{C}$ for **P1**,

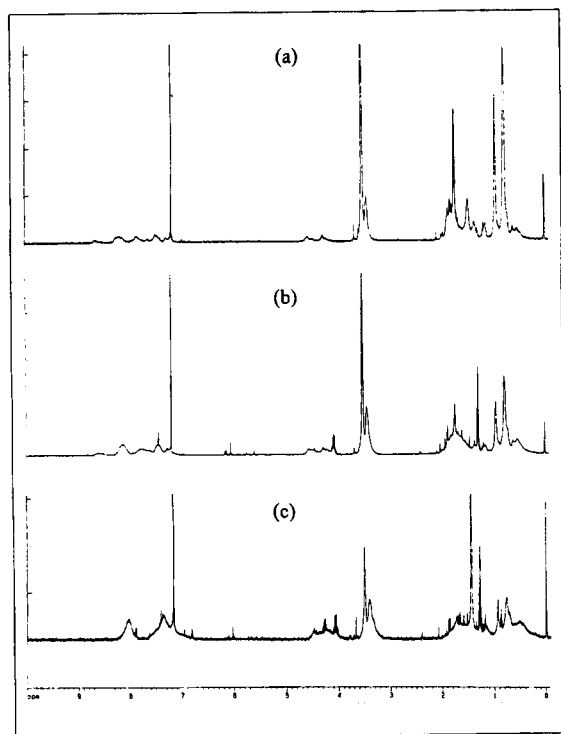


Figure 6. ^1H NMR spectra of the polymers, (a) **P1**, (b) **P2**, and (c) **P3**.

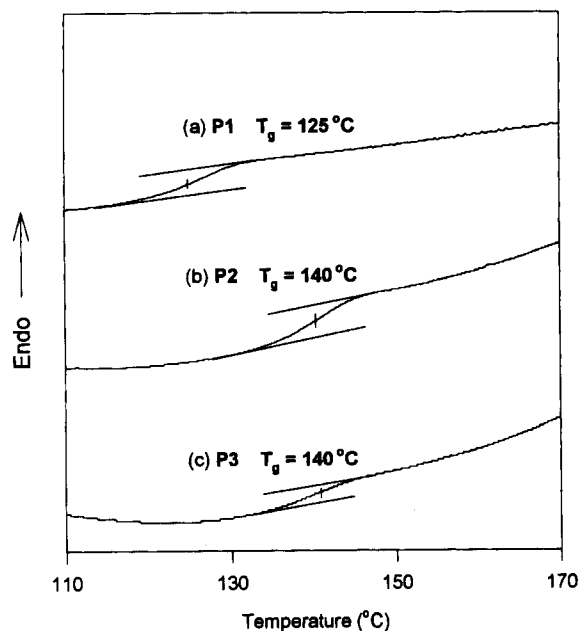


Figure 7. DSC thermograms of the polymers, (a) **P1**, (b) **P2**, and (c) **P3** (heating rate: $10\text{ }^\circ\text{C}/\text{min}$).

P2, and **P3** respectively from the DSC thermograms shown in Figure 7. It is clearly shown that the higher content of the chromophore resulted in the higher T_g of the polymer, indicating the enhanced thermal stability of the polymer due to the carbazole ring. As shown in Figure 7(b) and (c), it seems that the cyano group has no adverse effect on T_g of the polymer.

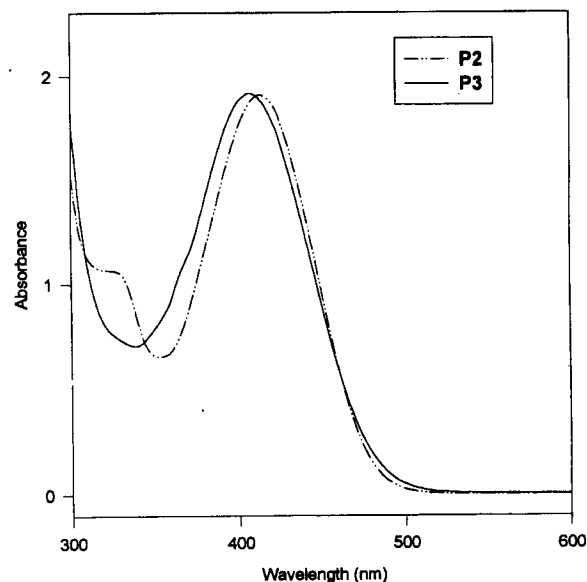


Figure 8. The absorption spectra of the polymers, **P2** and **P3** in chloroform solution.

The number-average molecular weights of the polymers were determined to be 10,000-17,000 by GPC analysis. All the polymers are very soluble in common organic solvents such as chloroform, dichloromethane, THF, and DMF etc. Figure 8 shows the absorption spectra of the polymers in chloroform solution. It is noted that the polymer **P3** shows the absorption maximum at 408 nm and **P2** shows the absorption maximum at more red-shifted region (414 nm) than that of **P3** due to the presence of cyano group. **P1** showed the same absorption spectrum as **P2**. The SHG coefficient (d_{33}) of **P1** determined by the Marker-fringe method at $1.064\text{ }\mu\text{m}$ fundamental wavelength was found as large as $18\text{ pm}/\text{V}$. Detailed measurements of NLO properties are in progress and will be published elsewhere.

Conclusion

We synthesized two different NLO chromophores with carbazole group as an electron donor group and nitrostilbene or nitrocyanostilbene as an electron acceptor. The chromophores were synthesized by the reaction of 9-(2-hydroxyethyl)-9H-carbazol-3-carbaldehyde with 4-nitrophenylacetonitrile or 4-nitrophenylacetic acid. The side chain NLO polymers were synthesized by a common free radical copolymerization of the methacrylate monomer of these NLO chromophores with MMA. The thermal properties of the polymers have been investigated by DSC and T_g s of the polymers were in the range of 125-140 $^\circ\text{C}$. The number-average molecular weights of the polymers were determined to be 10,000-17,000. All polymers could be soluble in common polar solvent and the absorption maxima of **P2** and **P3** were 414 nm and 408 nm, respectively.

Acknowledgment. We thank Prof. S. D. Lee and Mr. J. W. Moon for SHG measurement and Mr. J. C. Cho for GPC analysis. This work was financially supported in part by Ilju Foundation and KIST 2000 Program in 1995-1996.

References

1. Nie, W. *Adv. Mater.* **1993**, 5, 520.
2. Zyss, J. *Molecular Nonlinear Optics*; Academic Press: New York, U.S.A., 1994.
3. Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, 94, 31.
4. Marder, S. R.; Perry, J. W. *Adv. Mater.* **1993**, 5, 804.
5. Buckley, A. *Adv. Mater.* **1992**, 4, 153.
6. Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, 94, 127.
7. Singer, K. D.; Sohn, J. E.; Lalama, S. J. *Appl. Phys. Lett.* **1986**, 49, 248.
8. Uryu, T.; Ohkawa, H.; Oshima, R. *Macromolecules* **1987**, 20, 712.
9. Flowers, R. G.; Flowes, L. W. *J. Chem. Soc.* **1948**, 70, 3019.
10. Socrates, G. *Infrared Characteristic Group Frequencies*; John Wiley & Sons: New York, U.S.A., 1994.

Acid Structure of MgO-SiO₂ Binary Oxide Catalyst and Activity for Acid Catalysis

Jong Rack Sohn*, Eun Hee Park, and Haw Won Kim†

Department of Industrial Chemistry, Engineering College, Kyungpook National University, Taegu 702-701, Korea

†Department of Industrial Chemistry, Kyungil University, Kyungsan 712-701, Korea

Received November 19, 1996

A series of MgO-SiO₂ catalysts were prepared by coprecipitation from the mixed solution of magnesium chloride and sodium silicate. Some of the sample were modified with 1 N H₂SO₄ and used as modified catalysts. The addition of MgO to SiO₂ caused the increase of acidity and the shift of O-H and Si-O stretching bands of the silanol group to a lower frequency in proportion to the MgO content. The acid structure of MgO-SiO₂ agreed with that proposed by Tanabe *et al.*. Catalytic activity for 2-propanol dehydration increased in relation to the increase of acidity and band shift to a lower frequency.

Introduction

In many cases, the components are inactive while their mixtures have a high catalytic activity. Thus, recently many kinds of mixed oxides were reported to show catalytic activity for particular reactions.¹⁻⁶ TiO₂ alone is impractical as a catalyst because of its low catalytic activity. However, mixed oxide systems combining TiO₂ with such oxides as V₂O₅, MoO₃, P₂O₅, SiO₂ and ZnO are known to be effective for various reactions.⁷⁻¹¹ Pure silica gel, which has no catalytic activity with respect to dehydration of isopropyl alcohol, exhibits considerable acidity and catalytic activity on addition of only 0.1% ZrO₂.¹² These combinations seem to induce an unexpectedly great change in the catalytic behavior.

Acid catalyzed reaction is correlated with acid amount and acid strength. In cumene dealkylation the more acidic the catalysts, the higher catalytic activity they show.^{13,14} On the other hand, tert-butanol dehydration takes place on relatively weaker acid sites, while skeletal isomerization of isobutylene requires exceedingly strong acid sites.¹⁵ Thus to incorporate acidity and stronger acid strength, single or binary oxide catalysts are modified with sulfuric acid in many cases.¹⁶⁻²² High catalytic activity of catalyst modified with sulfuric acid is attributed to the enhanced acidic property by the inductive effect of S=O bonds of the complex formed

by the interaction of oxides with sulfate ion.^{21,23}

Pure silica gel shows no acidic property and is used mainly as the support of catalysts, while magnesium oxide is typical solid base catalyst. So far, however, only a small amount of work was done for the MgO-SiO₂ catalyst.^{24,25} In this work, the catalytic activities of MgO-SiO₂ series catalysts prepared by coprecipitation method and their correlations to the acidic properties have been studied. Also the catalytic activities of MgO-SiO₂ modified with H₂SO₄ are compared with those of unmodified catalysts. For this purpose the 2-propanol dehydration was used as test reaction.

Experimental

Catalysts. The coprecipitate of MgO-SiO₂ was obtained by adding aqueous ammonia slowly into the mixed aqueous solution of magnesium chloride and sodium silicate solution at 70 °C with stirring until the pH of the mother liquor reached 8. The ratio of magnesium chloride to sodium silicate was varied. The coprecipitate thus obtained was washed thoroughly with distilled water until chloride ion was not detected and dried at room temperature. The dried coprecipitate was again washed with successive portions of a 5% ammonium nitrate solution and then with hot distilled water to remove sodium ion in the coprecipitate. The dried precipitate was powdered below 100 mesh and was used as catalyst after calcination at 400 °C for 1.5 hr. Some samples were modified by pouring 30 mL of 1 N H₂SO₄ into each 2

*To whom correspondence should be addressed.