Macromolecules **1995,** *28,* 4638–4643

Synthesis and Characterization of Novel Side-Chain Nonlinear Optical Polymers Based on Poly(1,6-heptadiyne) Derivatives

Hyung-Jong Lee,[†] Su-Jin Kang,[†] Hwan Kyu Kim,[‡] Hyun-Nam Cho,[§] Joon T. Park,[†] and Sam-Kwon Choi*[,†]

Department of Chemistry, KAIST, 373-1 Kusung-Dong, Yusung Gu, Taejon, Korea, Department of Macromolecular Science, Han Nam University, 133 Ojung-dong, Taejon, Korea, and Polymer Materials Laboratory, Korea Institute of Science and Technology, P.O. Box 131, Cheongyangri, Seoul, Korea

Received October 27, 1994; Revised Manuscript Received March 8, 1995[®]

ABSTRACT: Novel types of multifunctional polymer that contain a conjugated backbone for both third- and second-order nonlinear optical (NLO) materials have been investigated. We synthesized the 1,6-heptadiyne derivatives bearing NLO chromophores. The resulting monomers were easily homopolymerized and also copolymerized with ethyl dipropargyl(diethoxyphosphoryl)acetate (TDPA) using a metathesis catalyst to give corresponding polymers with large optical nonlinearities. Molecular structural characterizations for the resulting polymers were achieved by ^{1}H- and ^{13}C-NMR, FTIR, and UV–visible spectroscopies. The polymers obtained were found to be amorphous and showed thermal stability up to 250 °C. The homogeneous polymer solutions could be spin coated to the optical quality thin films on the ITO glass substrates. These films have been oriented by an electric contact poling process. The electro-optic coefficients, r_{33}, of the poled polymer films were in the range 1.7–10.1 pm/V, and the nonresonant values of the third-order NLO coefficient, $\chi^{(3)}$, were found to be (2.1–3.3) × 10^{-11} esu.

Introduction

Nonlinear optical materials are being actively studied for such potential optoelectronics applications as second harmonic generation (SHG) and third harmonic generation (THG), holography, frequency up and down conversion, electro-optic modulation, and switching.[1,2] Recently, organic poled polymer systems containing chromophores with large second-order nonlinear susceptibilities have emerged as a promising class of electro-optic material because of their fast response time, modification capability, and ease of processing for integrated assembly.[3] These polymer materials include doping NLO dyes into amorphous polymer matrices (guest–host systems),[4] attaching NLO moieties covalently onto polymer backbone as pendants (side-chain systems),[5,6] incorporating NLO chromophores as part of a polymer main chain (main-chain systems),[7,8] and utilization of sequential synthesis methods (cross-linked systems).[9]

A number of side-chain NLO polymers have been prepared by various polymerization methods.[5,6,10,11] However, a metathesis polymerization technique to synthesize second-order NLO polymers has not been used. In this paper, we describe the synthesis and physical properties of the poly(1,6-heptadiyne)s bearing chromophores as pendant groups, yielding a new type of multifunctional polymer which retains both second-order and third-order NLO properties. Poly(1,6-heptadiyne)s comprise a broad class of cyclopolymers with a conjugated double bond and cyclic recurring unit in the polymer backbone.[12–14] The unique properties of these polymers originate from the structure of fully π-conjugated cyclic polymer backbones, which also possess a large third-order susceptibility along a polymer main chain.[15,16] The rationale in designing these new materials is that conjugated backbone appendaging $\chi^{(2)}$ chromophores play the role of third-order nonlinear susceptibility as well as rigid polymer backbone.

Experimental Section

Instruments. ^{1}H- and ^{13}C-NMR spectra were recorded with the use of a Bruker AM-300 or AM-200 spectrometer, and chemical shifts are reported in ppm units with tetramethylsilane as an internal standard. FT-IR spectra were measured with neat oils or KBr pellets on a Bomem MB-100 spectrometer, and frequencies are given in reciprocal centimeters (cm^{-1}). A Shimadzu UV-3100S spectrometer was used for UV-visible spectral data. The molecular weight and polydispersity were determined in THF solvent with a Waters GPC-150C calibrated with polystyrene standards. Elemental analysis was performed with a Perkin-Elmer 240DS elemental analyzer. Thermal analyses were carried out on a DuPont TGA 9900 thermogravimetric analyzer under nitrogen at a heating rate of 10 °C/min. X-ray diffraction patterns of unoriented samples were obtained on a Rigaku Geigerflex X-ray diffractometer equipped with a flat-plate camera using Ni-filtered Cu Kα radiation at a scan speed of 4°/min.

Materials. Tungsten(VI) and molybdenum(V) chlorides (Aldrich Chemical Co., resublimed, 99.9%) were used without further purification. Palladium(II) chloride and ethylaluminum dichloride (Aldrich Chemical Co.) were used without further purification, and tetrabutyltin was distilled under reduced pressure. 4-(*N*-(6-Hydroxyhexyl)-*N*-methylamino)-4′-nitrostilbene was synthesized according to the published literature procedures.[5] Propargyl bromide (Aldrich Chemical Co., 80 wt % solution in toluene) was dried over calcium hydride and fractionally distilled by recommended procedures.[14] All solvents were used after purification according to conventional methods.

4-[(3-Chloropropyl)sulfonyl]toluene (1). A two-phase system composed of 1-bromo-3-chloropropane (31 g, 0.2 mol) in toluene (60 mL), *p*-toluenesulfinic acid sodium salts (17.8 g, 0.1 mol) in water (60 mL), and 1 g of tetrabutylammonium bromide was stirred overnight at 80 °C. After the reaction mixture was cooled to room temperature, water (200 mL) was added, and the organic layer was extracted three times with toluene. The organic layer was dried over anhydrous MgSO$_4$, and the solvent was removed at reduced pressure to deposit a pale yellow oil that crystallized on trituration with hexane. The product was recrystallized from hexane/toluene to provide 20.8 g (89.4%) of white solid, mp = 143 °C: ^{1}H-NMR (CDCl$_3$)

---

* To whom all correspondence should be addressed.

[†] KAIST.

[‡] Han Nam University.

[§] KIST.

[®] Abstract published in *Advance ACS Abstracts,* May 15, 1995.

0024-9297/95/2228-4638$09.00/0

δ 2.16 (m, 2H), 2.43 (s, 3H), 3.21 (t, 2H), 3.59 (t, 2H), 7.37 (d, 2H), 7.78 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ 21.6 ($-CH_2-$), 25.9 ($-CH_3$), 42.7 ($-CH_2Cl$), 53.6 ($-CH_2SO_2$), 127.9, 130.0, 135.9, 144.9 (phenyl).

4-[(3-Acetoxypropyl)sulfonyl]toluene (2). A mixture of 4-[(3-chloropropyl)sulfonyl]toluene (20 g, 0.086 mol) in toluene (70 mL), 35 g of sodium acetate in water (70 mL), and 3 g of TBAB was stirred at 80 °C for 20 h. The reaction mixture was poured onto 400 mL of water and extracted with ethyl acetate. The organic layer was concentrated after drying over $MgSO_4$. The product was distilled in vacuo to produce 18 g (82%) of a viscous liquid, bp = 155 °C/0.1 mmHg: ^{1}H-NMR ($CDCl_3$) δ 1.99 (s, 3H), 2.0 (m, 2H), 2.43 (s, 3H), 3.12 (t, 2H), 4.08 (t, 2H), 7.35 (d, 2H), 7.78 (d, 2H); ^{13}C-NMR ($CDCl_3$), δ 20.5 ($-CH_2-$), 21.4 ($-CH_3$), 22.3 (CH_3C), 53.0 ($-CH_2SO_2$), 61.8 ($-CH_2O-$), 127.8, 129.8, 135.7, 144.7 (phenyl), 170.4 (CO_2).

4-[(6-Acetoxyhexyl)sulfonyl]toluene (3). A mixture of 4-(methylthio)phenol (44.8 g, 0.36 mol), potassium carbonate (74.5 g), and DMF (250 mL) was treated with 6-chloro-1-hexanol (40.9 g, 0.3 mol) at 25 °C. The reaction mixture was stirred for 1 h at 25 °C and then for 12 h at 70 °C. The solution was poured over 300 mL of water, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with aqueous $NaHCO_3$ and again with water. The organic layer was concentrated after drying over $MgSO_4$. The residue (4-(methylphenyl)-6-hydroxyhexyl sulfide) was dissolved in 27 mL of pyridine and 36 g of acetic anhydride (0.35 mol), and the solution was heated at reflux for 16 h. After cooling, the reaction mixture was poured onto 300 mL of 5% HCl in water, and the resulting mixture was extracted with ethyl acetate. The combined organic extracts were washed with aqueous $NaHCO_3$ and again with water and dried ($MgSO_4$). After evaporation of the solvent, the product (4-(methylphenyl)-6-acetoxyhexyl sulfide) was obtained in 65 g (82%) yield and used without further purification for further reaction: ^{1}H-NMR ($CDCl_3$) δ 1.3−1.6 (m, 8H), 2.0 (s, 3H), 2.29 (s, 3H), 2.85 (t, 2H), 4.02 (t, 2H), 7.09 (d, 2H), 7.24 (d, 2H). A mixture of 4-(methylphenyl)-6-acetoxyhexyl sulfide (65 g, 0.244 mol) and 300 mL of glacial acetic acid was heated to reflux with stirring, hydrogen peroxide (69 g, 30% solution) was added in small portions, and then the resulting mixture was stirred at reflux for 3 h. The reaction mixture was concentrated, and the residue was dissolved in dichloromethane. The solution was washed with water and dried over $MgSO_4$, and then the solvent was removed. The crude product was fractionally distilled under vacuo to yield 61 g (84%) of viscous liquid, bp = 185−190 °C/0.1 mmHg: ^{1}H-NMR ($CDCl_3$) δ 1.3−1.65 (m, 8H), 2.0 (s, 3H), 2.42 (s, 3H), 3.04 (t, 2H), 4.0 (t, 2H), 7.34 (d, 2H), 7.76 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ 20.9, 25.4, 27.9, 28.2 (methylene), 21.6 ($-CH_3$), 22.6 (CH_3C), 56.2 ($-CH_2SO_2$), 64.1 ($-CH_2O$), 128.0, 129.8, 136.2, 144.5 (phenyl), 171.0 (CO_2).

4-[(3-Acetoxypropyl)sulfonyl]benzyl Bromide (4). 4-[(3-Acetoxypropyl)sulfonyl]toluene (50 g, 0.195 mol), *N*-bromosuccinimide (35.6 g, 0.2 mol), and benzoyl peroxide (0.4 g) were dissolved in 200 mL of CCl_4 under a nitrogen atmosphere. The mixture was heated at reflux for 12 h. The reaction mixture was cooled, and the succinimide was filtered off. The filtrate was washed with water and dried over $MgSO_4$, and then the solvent was evacuated. The residue was a mixture of 30% unreacted starting material and 70% brominated product: ^{1}H-NMR ($CDCl_3$) δ 2.0 (s, 3H), 2.03 (m, 2H), 3.1 (t, 2H), 4.07 (t, 2H), 4.47 (s, 2H), 7.57 (d, 2H), 7.86 (d, 2H).

Diethyl [4-[(3-Acetoxypropyl)sulfonyl]benzyl]phosphonate (6). The distilled triethyl phosphite (25 g, 0.15 mol) was heated at reflux, and 33 g (0.1 mol) of 4-[(3-acetoxypropyl)sulfonyl]benzyl bromide was added dropwise with stirring for a period of 10 min; at such a rate a gentle reflux was maintained. When the addition was completed, the reaction was refluxed for an additional 5 h. The mixture was cooled to room temperature and evaporated at reduced pressure (0.5 mmHg) to remove the volatile materials. The residue was purified by column chromatography using first ethyl acetate/hexane (1:1) and then ethyl acetate/methanol mixed solvent as an eluent to yield 27.14 g (81%) of viscous liquid: ^{1}H-NMR ($CDCl_3$) δ 1.21 (t, 6H), 2.0 (m, 5H), 3.1 (t, 2H), 3.25 (d, 2H), 4.0 (m, 6H), 7.5 (d, 2H), 7.83 (d, 2H); ^{13}C-NMR ($CDCl_3$) δ 16.3 (CH_3), 20.7 ($-CH_2-$), 22.3 (CH_3CO_2), 32.5, 35.2 (PCH_2), 53.2 ($-CH_2SO_2$), 61.9 ($-CH_2OAc$), 62.4 ($-CH_2OP$), 128.2, 130.7, 137.4, 138.8 (phenyl), 170.6 (CO_2).

4-(Dimethylamino)-4′-[(3-hydroxypropyl)sulfonyl]stilbene (8). To a vigorous stirred suspension of sodium hydride (1.2 g, 50 mmol, 60% dispersion in mineral oil), (*N*,*N*-dimethylamino)benzaldehyde (3.72 g, 25 mmol), and 50 mL of dry, freshly distilled 1,2-dimethoxyethane (DME) under nitrogen at room temperature was added diethyl [4-[(3-acetoxypropyl)sulfonyl]benzyl]phosphonate (10.2 g, 25 mmol) in 30 mL of DME. The mixture immediately turned yellow. The reaction mixture was heated at reflux for 3 h under nitrogen. The yellow solution was then poured over 400 g of crushed ice. A yellow solid was filtered and air dried. The resulting solid was dissolved in 150 mL of 10% (v/v) HCl in the mixture of ethanol and water (1:1), and the solution was heated at reflux for 10 h. After cooling, the solution was neutralized to pH 7 by the slow and careful addition of sodium carbonate. The yellow solid thus formed was collected by filtration, washed with water, and air dried. Recrystallization from ethanol/pyridine yielded 5.6 g of a yellow solid: ^{1}H-NMR (DMSO-d_6) δ 1.67 (m, 2H), 2.93 (s, 6H), 3.23 (t, 2H), 3.39 (m, 3H), 6.74 (d, 2H), 7.1 (d, 1H), 7.39 (d, 1H), 7.49 (d, 2H), 7.77 (m, 4H); ^{13}C-NMR (DMSO-d_6) δ 26 ($-CH_2-$), 30.1 (NCH_3), 52.3 ($-CH_2SO_2$), 58.6 (CH_2O), 112.0, 121.4, 124.1, 126.2, 128.0, 128.1, 132.6, 135.9, 143.3, 143.3, 150.4 (stilbene).

4-(Dimethylamino)-4′-[[3-(dipropargylacetoxy)propyl]sulfonyl]stilbene (M-1). A stirred mixture of 4-(dimethylamino)-4′-[(3-hydroxypropyl)sulfonyl)]stilbene (3.5 g, 10.1 mmol), distilled pyridine (0.79 g, 10.1 mmol), and 50 mL of dry, distilled THF was treated dropwise with dipropargyl acetic acid chloride[14] (1.9 g, 12 mmol) in 20 mL of THF at 25 °C under nitrogen. The resulting solution was stirred at 50 °C for 48 h and then poured onto 300 mL of aqueous sodium bicarbonate. A yellow solid formed, was filtered off, and air dried. The solid was purified by column chromatography using chloroform as an eluent. The product was recrystallized from ethanol/chloroform to produce 3.5 g (75%) of yellow solid, mp = 142 °C. Anal. Calcd for $C_{30}H_{35}NO_4S$: C, 71.26; H, 6.98. Found: C, 71.31; H, 6.89. ^{1}H-NMR ($CDCl_3$): δ 1.96 (t, 2H), 2.0 (m, 2H), 2.56 (m, 4H), 2.72 (m, 1H), 2.99 (s, 6H), 3.19 (t, 2H), 4.2 (t, 2H), 6.7 (d, 2H), 6.9 (d, J = 16.23, 1H), 7.22 (d, J = 16.27, 1H), 7.44 (d, 2H), 7.62 (d, 2H), 7.83 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ 19.9 ($-CH_2C$), 22.6 ($-CH_2-$), 40.3 ($-CH-$), 43.1 (NCH_3), 53.3 (CH_2SO_2), 62.6 (CH_2O), 70.7 ($\equiv CH$), 80.3 ($\equiv C-$), 112.2, 121.7, 124.2, 126.3, 128.1, 128.2, 133.1, 135.7, 144.1, 150.7 (stilbene), 172.0 (CO_2). IR (cm^{-1}): 1726 (C=O), 3285 ($\equiv CH$).

4-[(6-Acetoxyhexyl)sulfonyl]benzyl Bromide (5). **5** was prepared from 5-[(6-acetoxyhexyl)sulfonyl]toluene (**3**) (61 g, 0.2 mol), NBS (35.6 g, 0.2 mol) and 0.4 g of BPO in 400 mL of CCl_4 solution by the same procedure as described for **4**. Yield = 67%. ^{1}H-NMR ($CDCl_3$): δ 1.3−1.7 (m, 8H), 2.0 (s, 3H), 3.0 (t, 2H), 3.98 (t, 2H), 4.48 (s, 2H), 7.57 (d, 2H), 7.86 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ 20.7, 25.2, 27.6, 28.0 (methylene), 22.3 (CH_3C), 38.7 ($BrCH_2$), 55.9 ($-CH_2SO_2$), 63.9 ($-CH_2O$), 128.4, 129.7, 138.8, 143.6 (phenyl), 170.9 (CO_2).

Diethyl [4-[(3-Acetoxyhexyl)sulfonyl]benzyl]phosphonate (7). **7** was prepared from 4-[(6-acetoxyhexyl]benzyl bromide (**5**) (44 g, 0.12 mol) and triethyl phosphite (27 g, 0.16 mol) by the same procedure as described for **6**. Yield = 81%. ^{1}H-NMR ($CDCl_3$): δ 1.18 (t, 6H), 1.3−1.64 (m, 8H), 1.95 (s, 3H), 3.0 (t, 2H), 3.21 (d, 2H), 4.0 (m, 6H), 7.45 (d, 2H), 7.78 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ 20.8, 25.3, 27.8, 28.2 (methylene), 22.3 (CH_3C), 32.4, 35.1 (PCH_2), 53.4 ($-CH_2SO_2$), 61.8 ($-CH_2OAc$), 62.3 ($-CH_2OP$), 128.3, 137.3, 138.7 (phenyl), 170.7 (CO_2).

4-(Dimethylamino)-4′-[(6-hydroxyhexyl)sulfonyl]stilbene (9). **9** was prepared from 4-[(3-acetoxyhexyl)sulfonyl]benzyl phosphonate (**7**) (21.7 g, 0.05 mol), (dimethylamino)benzaldehyde (7.49 g, 0.05 mol), and sodium hydride in DME solution by the same procedure as described for **8**. Mp = 188 °C. Yield = 57%. ^{1}H-NMR (DMSO-d_6): δ 1.26−1.67 (m, 8H), 2.95 (s, 6H), 3.24 (t, 2H), 3.40 (m, 3H), 6.74 (d, 2H), 7.1 (d, 1H), 7.40 (d, 1H), 7.49 (d, 2H), 7.77 (m, 4H). ^{13}C-NMR (DMSO-d_6): δ 22.6, 25.4, 27.8, 28.2 (methylene), 30.1 (NCH_3), 52.3 ($-CH_2SO_2$), 58.6 (CH_2O), 112.0, 121.4, 124.1, 126.2, 128.0, 128.1, 132.6, 135.9, 143.3, 143.3, 150.4 (stilbene).

4-(Dimethylamino)-4′-[[6-(dipropargylacetoxy)hexyl]sulfonyl]stilbene (M-2). **M-2** was prepared from 4-(dimethylamino)-4′-[(6-hydroxyhexyl)sulfonyl]stilbene (**9**) (5 g, 13 mmol), dipropargylacetic acid chloride (3.7 g, 24 mmol), and 1.9 g of pyridine in THF solution by the same procedure as described for **M-1**. Mp = 145 °C. Yield = 83%. For **M-2**: yield, 87%. Anal. Calcd for $C_{27}H_{29}NO_4S$: C, 69.95; H, 6.30. Found: C, 69.82; H, 6.23. ^{1}H-NMR ($CDCl_3$): δ 1.36−1.71 (m, 8H), 1.97 (t, 2H), 2.60 (m, 4H), 2.73 (m, 1H), 2.99 (s, 6H), 3.09 (t, 2H), 4.12 (t, 2H), 6.72 (d, 2H), 6.93 (d, J = 16.24, 1H), 7.21 (d, J = 16.26, 1H), 7.44 (d, 2H), 7.60 (d, 2H), 7.82 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ 19.9 ($-CH_2C$), 22.6, 25.4, 27.8, 28.2 (methylene), 40.3 ($-CH-$), 43.0 (NCH_3), 56.3 (CH_2SO_2), 64.7 (CH_2O), 70.5 ($\equiv CH$), 80.5 ($\equiv C-$), 112.2, 121.8, 124.4, 126.3, 128.2, 128.4, 132.9, 135.7, 143.8, 150.6 (stilbene), 172.1 (CO_2). IR (cm^{-1}): 1727 (C=O), 3283 ($\equiv$CH).

4-[*N*-[6-(Dipropargylacetoxy)hexyl]-*N*-methylamino]-4′-nitrostilbene (M-3). **M-3** was prepared from 4-[*N*-(6-hydroxyhexyl)-*N*-methylamino]-4′-nitrostilbene (5 g, 14.1 mmol), dipropargylacetic acid chloride (4.3 g, 28.2 mmol), and 2.1 g of pyridine in THF solution by the same procedure as discribed for **M-1**. Mp = 117 °C. Yield = 83%. Anal. Calcd for $C_{29}H_{32}N_2O_4$: C, 73.70; H, 6.83. Found: C, 73.68; H, 6.80. ^{1}H-NMR ($CDCl_3$): δ 1.37−1.64 (m, 8H), 1.99 (t, 2H), 2.60 (m, 4H), 2.64 (m, 1H), 2.96 (s, 3H), 3.34 (t, 2H), 4.13 (t, 2H), 6.66 (d, 2H), 6.91 (d, J = 16.24, 1H), 7.21 (d, J = 16.26, 1H), 7.41 (d, 2H), 7.53 (d, 2H), 8.15 (d, 2H). ^{13}C-NMR ($CDCl_3$): δ 19.9 ($-CH_2C$), 25.7, 26.6, 26.7, 28.5 (methylene), 38.3 ($-CH-$), 43.0 (NCH_3), 52.3 (CH_2N-), 64.9 (CH_2O), 70.5 ($\equiv CH$), 80.4 ($\equiv C-$), 111.7, 121.2, 123.8, 124.4, 125.9, 128.5, 133.6, 145.0, 145.7, 149.6 (stilbene), 172.3 (CO_2). IR (cm^{-1}): 1724 (C=O), 3289 ($\equiv$CH).

Polymerization. Catalyst solution preparation and polymerization were carried out in a dry nitrogen atmosphere. $MoCl_5$ was dissolved in chlorobenzene to make 0.2 M solution prior to use. A typical polymerization procedure was as follows. A solution of **M-1** (0.2 g, 1.3 mmol) and 1,4-dioxane (5 mL, $[M]_0$ = 0.125) was prepared. To this monomer solution was added 0.12 mL of $MoCl_5$ solution (0.02 mmol) at room temperature. The polymerization was carried out at 70 °C for 24 h and terminated with a small amount of methanol. The polymer was precipitated into a large amount of hexane in a blender, and the resulting reddish black powder was filtered and dried in a vacuum oven at 80 °C until constant mass was maintained.

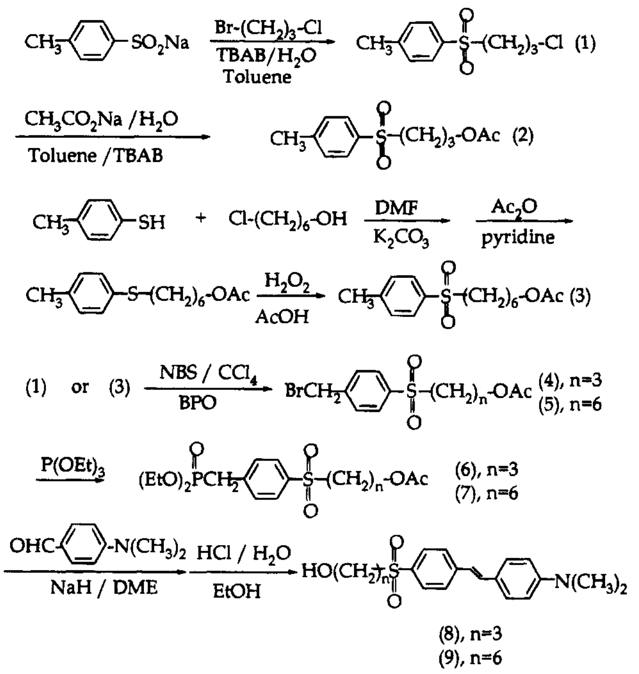
Polymer Film Spin Coating. Polymer was dissolved in 1,1,2-trichloroethane at a concentration range of 5−15 wt % depending on the desired film thickness. The solution was applied to the substrate with a syringe through a Teflon membrane filter (millipore, 0.22 μm Millex-GS) until the substrate was completely covered. The substrate was then spun at 300 rpm for 5 s followed by 1500 rpm for 60 s. After coating, the films were heated to 80 °C at 0.1 mmHg for 10 h to remove residual solvent.

Measurement of the Refractive Index and the Thickness. The refractive index, n, at a wavelength of 1.3 μm and the thickness, d, of the polymer films were measured by determining the propagation constants of at least the two lowest order transverse electric optical guided modes for samples cast on a glass substrate. The modes were excited by a diode laser beam that was prism coupled into the film. Using the propagation constants, the mode equation for a three-layer waveguide was solved for n and d. The thickness was confirmed with an α-step surface or depth profiler.

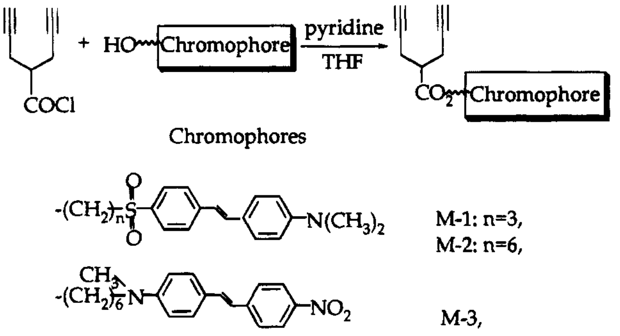
Poling. A polymer film was coated on indium tin oxide (ITO) coated glass. Subsequently, an aluminum electrode was evaporated on top of the polymer film. To align the chromophores, a film was slowly heated to 100 °C and then a positive voltage was applied to the Al electrode. After 1 h, the heater was turned off and the film was allowed to cool below 30 °C, at which point the voltage was turned off.

Electro-optic Measurements. The electro-optic coefficient, r_{33}, of the poled films was measured at wavelength of 1.3 μm using a simple reflection method developed by Teng et al.[17] A Soleil-Babinet compensator was used to bias the dc intensity at the half-maximum intensity. The phase retardation between the p and s waves was modulated at about 170 Hz. The amplitude of modulated intensity was determined using a lock-in amplifier, which can be used to calculate the r_{33} values.

Scheme 1. Syntheses of Chromophores



Scheme 2. Syntheses of Monomers



Third-Order Susceptibility Measurements. The third-order susceptibility, $\chi^{(3)}$, of the films was measured at a fundamental wavelength of 1.907 μm using a third harmonic generation (THG) Maker fringe technique reported elsewhere.[18]

Results and Discussion

Synthesis of Monomers and Polymers. The synthetic routes of the chromophores are shown in Scheme 1. Preparation of the internal sulfone aceptor group (2) was facilitated through the reaction of *p*-toluenesulfinic acid sodium salt and 1-bromo-3-chloropropane with a phase transfer catalyst. The other general synthetic strategy and the preparation of some of the intermediate compounds are described elsewhere.[19,20] The monomers were synthesized by reacting the chromophore with dipropargylacetic acid chloride[14] in the presence of pyridine using THF as a solvent (Scheme 2). The chromophore monomers of **M-1**, **M-2**, and **M-3** were homopolymerized or copolymerized with ethyl dipropargyl(diethoxyphosphoryl)acetate to produce NLO-active polymers. Scheme 3 outlines the cyclopolymerization of the chromophore monomers by transition metal catalysts such as $MoCl_5$-, WCl_6-, and $PdCl_2$-based catalysts.

Scheme 3. Syntheses of Polymers

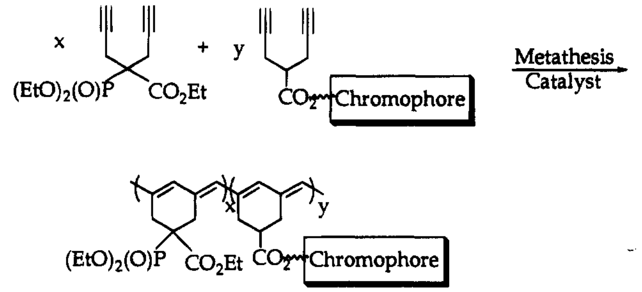


Table 1. Polymerization of the Chromophore-Containing Monomers with Various Transition Metal Catalysts[a]

exp no.	monomer	catalyst syst[b] (mole ratio)	M/C[c]	$[M]_0$[d]	PY (%)[e]
1	**M-1**	$MoCl_5$	50	0.25	trace
2	**M-1**	$MoCl_5/EtAlCl_2$ (1:4)	50	0.25	40
3	**M-1**	$MoCl_5/(n\text{-}Bu)_4Sn$ (1:4)	25	0.25	15
4	**M-1**	$WCl_6/EtAlCl_2$ (1:4)	25	0.25	
5	**M-1**	$PdCl_2$[f]	25	0.25	97
6	**M-2**	$MoCl_6/EtAlCl_2$ (1:4)	20	0.125	45
7	**M-2**	$PdCl_2$[f]	50	0.25	93
8	**M-3**	$MoCl_6/EtAlCl_2$ (1:4)	20	0.125	
9	**M-3**	$PdCl_2$[f]	50	0.25	96

[a] Polymerization was carried out at 60 °C for 24 h in dioxane. [b] The mixture of catalyst and cocatalyst in chlorobenzene was aged for 15 min before use as catalyst. [c] Mole ratio of monomer to catalyst. [d] Initial monomer concentration. [e] The precipitated polymers in methanol were gravimetrically estimated. [f] Polymerization was carried out at 90 °C in DMF.

Table 2. Copolymerization of the Chromophore-Containing Monomers with TDPA by $MoCl_5$[a]

polym	monomer	m_{feed}[b]	$m_{polymer}$[c]	polym yield,[d] %	$\bar{M}_n$[e]	$\bar{M}_w/\bar{M}_n$[e]
PTDPA[f]	TDPA	0	0	96	46k	3.2
P-1a	**M-1**	30	29	79	36k	1.9
P-1b	**M-1**	40	43	78	23k	2.4
P-2a	**M-2**	30	28	93	26k	1.8
P-2b	**M-2**	50	49	94	28k	1.7
P-3a	**M-3**	30	20	74	28k	1.8
P-3b	**M-3**	50	38	59	16k	1.7

[a] Polymerization was carried out at 60 °C for 24 h in dioxane. The mole ratio of monomer to catalyst was 25. The initial monomer concentration was 0.2 M. [b] Mole fraction (%) of chromophoric monomer charge. [c] Mole fraction (%) of chromophoric monomer in copolymer by ^1H-NMR. [d] The precipitated copolymers in hexane were gravimetrically estimated. [e] Values were obtained by GPC analysis with polystyrene standards. [f] Homopolymer of TDPA.

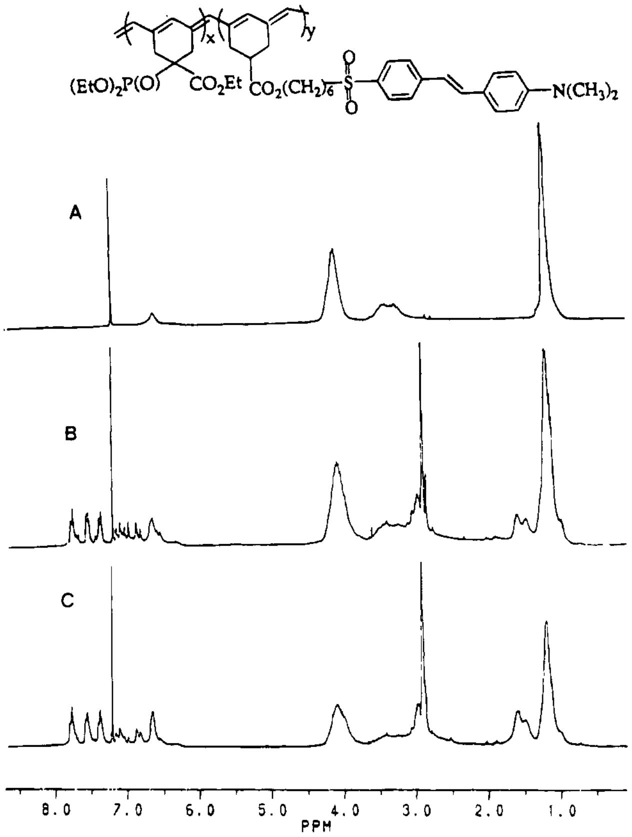


Figure 1. ^1H-NMR spectra of PTDPA (A), **P-2a** (B), and **P-2b** (C) in $CDCl_3$.

In Table 1, the results for the homopolymerization of the chromophore monomers by various catalyst systems are listed. $PdCl_2$ was found to be a very effective catalyst for the polymerization of chromophore monomers. This result was similarly observed for the polymerization of dipropargyl derivatives having a highly polar functional group reported previously.[21] Polymerizations by $PdCl_2$ gave high polymer yields and soluble polymers in chloroform, but relatively low molecular weight polymers were obtained. The polymerization reaction of chromophore monomers using $MoCl_5$-based catalyst, however, produced insoluble and intractable materials. The preparation of soluble polymers containing chromophores was accomplished by the use of the various dipropargyl derivatives as comonomers such as diethyl dipropargylmalonate, 3-(trimethylsilyl)propyl dipropargylmalonate, ethyl dipropargyl(diethoxyphosphoryl)acetate (TDPA),[15] etc. Among them, TDPA bearing a polar phosphonate group was easily copolymerized with chromophore monomers, yielding completely soluble NLO-active polymers and excellent quality thin films, as shown in Scheme 3. Synthetic and characterization data for the copolymers are presented in Table 2. The polymerization of chromophore monomers having a sulfone group by metathesis catalyst led to the formation of polymer yields higher than those with a nitro group as an electron acceptor. The composition of the copolymers **P-1a**–**P-2b** (determined by integration of ^1H-NMR signals) closely matched the composition of the monomer feed mixture except for the copolymers **P-3a** and **P-3b** which were lower in the polymers than in the monomer feed composition for the NLO chromophore monomer. When the concentration chromophore monomer was high, the resulting polymers were partially insoluble. The practical concentration of chromophore monomer was limited up to approximately 50 mol % for the yield of soluble copolymers. The molecular weights ($\bar{M}_n$) and polymer dispersity values of the resulting polymers were estimated to be in the range (1.6–4.3) × 10^4 and 1.7–3.2, respectively.

Structural Characterization. Characterization of chromophore monomers and polymers was achieved by ^1H- and ^{13}C-NMR, FTIR, and UV–visible spectroscopies. All of the stilbene compounds were isolated as pure trans isomers, judging from the values of the ^1H-NMR coupling constants of the vinyl protons (~16 Hz). Figure 1 shows the ^1H-NMR spectra of PTDPA and copolymers of **M-2**. As the polymerization proceeded (Figure 1), an acetylene proton peak at 2.0 ppm disappeared, and new vinylic proton peaks appeared at the region 6.8–7.2 ppm together with aromatic stilbene peaks. For copolymers, the NLO chromophore ratios were estimated by a comparison of the integration of the phenyl resonance at 7.8 ppm with the methyleneoxy resonance at 4.0 ppm (see Table 2).

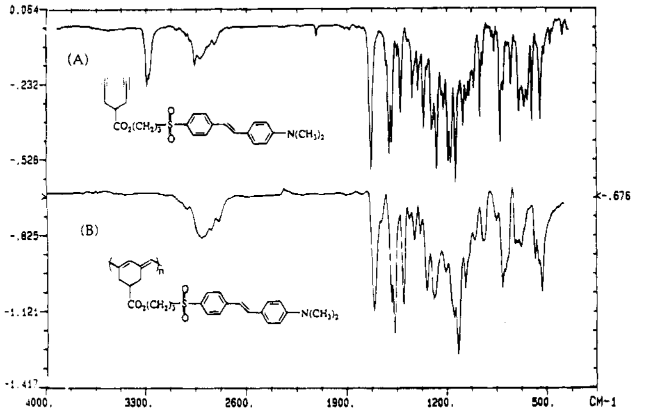


Figure 2. FTIR spectra of **M-1** (**A**) and the **P-1** homopolymer (B) (sample: experiment no. 2 in Table 1).

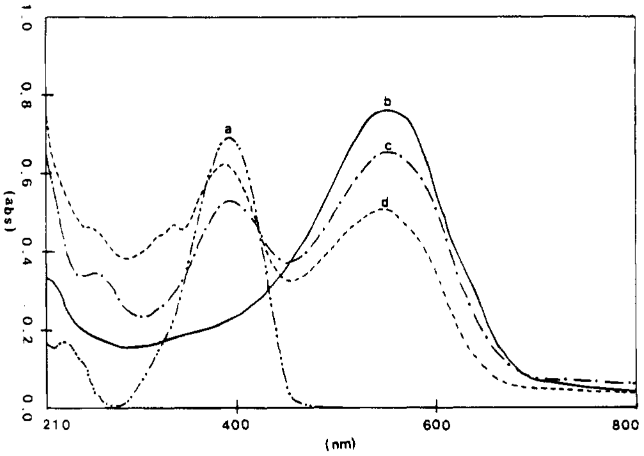


Figure 3. UV–visible spectra of monomer **M-1** in $CHCl_3$ solution (a) and PTDPA (b), **P-1a** (c), and **P-2b** (d) coated films on quartz substrate.

Figure 2 shows the FT-IR spectra of the monomer (**M-1**) and the corresponding polymers. Infrared spectroscopy for all of the polymers shows no absorption at 3285 and 2140 cm^{-1}, which is expected to be present for the acetylene carbon–hydrogen stretching and carbon–carbon triple bond stretching of the monomers. The absorbances for the SO_2 unit around 1378 cm^{-1} and the P=O unit around 1297 cm^{-1} were detected at the copolymers.

Figure 3 shows the UV–visible spectra of the monomer (**M-1**), poly(TDPA), and copolymers. The monomer spectrum was taken in $CHCl_3$, and the polymer spectra were taken in spin-coated films on a quartz substrate. Poly(TDPA) shows the characteristic broad band at 540 nm due to the $\pi-\pi^*$ transition of the conjugated cyclic polyene backbone. The polymers **P-1a**–**P-3b** containing chromophore show two maximum absorption values around 390 and 550 nm due to pendant chromophore and conjugated cyclic polyene backbone, respectively.

From the above spectral data, it is proposed that the polymer structure is believed to be a linearly cyclized form, as described in Scheme 3. Also, it has been known that the resulting cyclized polymers with conjugated double bonds have both five- and six-membered ring structures with a certain ratio, which should depend on the polymerization conditions, monomer structures, and the kinds of catalysts used.[12,22,23]

Physical Properties. As mentioned above, the homopolymers of the chromophore monomers prepared by $MoCl_5$ were insoluble in any organic solvents. However, the copolymers were completely soluble in various organic solvents such as chloroform, methylene chloride, THF, and 1,1,2-trichloroethane, and easily spin coated on the various plate substrates.

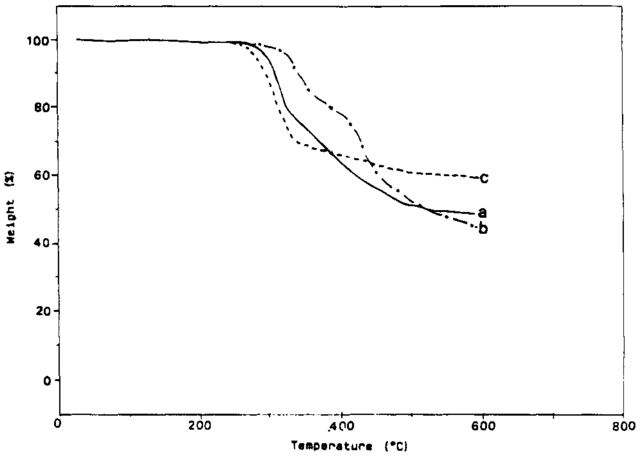


Figure 4. TGA thermogram of **P-1b** (a), **P-2b** (b), and **P-3a** (c) in N_2 (scanning rate = 10 °C/min).

Table 3. Linear and Nonlinear Optical Data for Polymers

polym^a	λ_{max}, nm NLO-phore	λ_{max}, nm backbone	n^b (1.3 μm)	$V_p{}^c$ (V/μm)	r_{33} (pm/V) (1.3 μm)
PTDPA		548	1.584		
P-1a	390	547	1.618	87	1.7
P-1b	389	548	1.633	92	5.2
P-2a	391	549	1.656	120	4.6
P-2b	392	550	1.664	161	10.1
P-3a	461	553	1.665	115	3.2

[a] See in Table 2. [b] Indices of refraction were determined from waveguiding experiments. [c] Electric field during poling. [e] Electro-optic coefficient.

The thermal stability of the resulting polymers was evaluated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. The TGA data (Figure 4) of the copolymer exhibits the initial decomposition temperature above 250 °C. The **P-2b** copolymer exhibits the most thermal stability among the three, and it started its weight loss at about 300 °C. In general, it has been known that the glass transition temperature (T_g) of the side-chain NLO polymers varied with both the loading of the chromophoric side chain and the length of the connecting spacer group.[11] Unfortunately, we could not observe clearly the glass transition temperature of the poly(1,6-heptadiyne)s bearing NLO chromophores by the DSC thermogram. So, we failed to determine the poling temperature. Instead, it was observed that UV–visible spectra of the copolymers did not change upon heating to 100 °C. But, at an elevated temperature of 130 °C, they showed a small blue-shift and hyperchromic shift of the λ_{max} 550 nm due to conformational deformation or air oxidation promoted by heat to the conjugated backbone. These results suggest that these copolymers exhibit conformational stability of at least 100 °C, and so, the poling process was applied at this temperature on the basis of the UV–visible study. In addition, all of these side-chain NLO polymers appeared to be amorphous when examined by polarized optical microscopy and by X-ray diffraction analysis.

The second-order nonlinear optical behaviors of poly(1,6-heptadiyne)s containing NLO chromophores was examined. Table 3 shows the wavelength of maximum visible absorption, λ_{max}, derived from pendant chromophore and π-conjugated backbone, and the refractive

Table 4. Third-Order Nonlinear Optical Susceptibilities of the Polymers[a]

sample	chromophore concn (mol %)	$10^{11}\chi^{(3)}$ (esu)
PTDPA		3.4
P-1b	45	2.6
P-2a	28	2.1
P-2b	49	2.7
P-3a	20	3.3

[a] The third harmonic generation (TGH) measurement was performed using the Maker fringe technique at 1.907 μm.

index, n, measured at 1.3 μm for unpoled polymer film samples. It was found that n of the copolymers gave higher values than that of PTDPA not bearing any chromophore while the values of λ_{max} were similar each other. This result clearly shows the effects of incorporation of chromophore into the polymer backbone. We measured the values of electro-optic coefficients, r_{33}, for poled film samples of **P-1a**–**P-3a** by using the simple reflection technique reported by Teng[12] et al. Table 3 shows the measured electro-optic coefficients of polymer films at 1.3 μm at different poling conditions. It was observed that r_{33} in the present study was 10.1 pm/V for **P-2b** poled at the 161 V/μm. This preliminary result indicates that the orientation of the NLO chromophores in **P-1b** shows no significant relaxation at ambient conditions within 60 days after poling.

The polymers having a delocalized π-electron in the main chain have been expected to possess extremely large third-order optical susceptibility.[24–26] However, such an extended π-electron conjugation generally rendered the polymers insoluble and infusible as well, which has seriously limited the fabrication of practical NLO devices. Recently, we reported the third-order nonlinear optical properties of poly(1,6-heptadiyne)s which were environmentally stable, soluble, and processable. The third-order optical nonlinearities of poly(1,6-heptadiyne)s bearing NLO active chromophores were evaluated for the first time. The third-order nonlinear susceptibility ($\chi^{(3)}$) values of chromophore polymers were measured using the Maker fringe technique at 1.907 μm. Since the polymer films have a very weak absorption in the third-order harmonic wavelength region ($\lambda = 0.62-0.70$ μm) (Figure 3), the third-order susceptibility can be estimated. The $\chi^{(3)}$ values of the polymer films were calculated by comparing the measured THG peak intensity of the films with that of the standard fused silica substrate according to the equation reported elsewhere.[14] It is clear that the $\chi^{(3)}$ values of the poly(1,6-heptadiyne)s bearing a chromophore pendant group are in the $(2.1-3.3) \times 10^{-11}$ esu range depending on the chromophore concentration, as shown in Table 4. It indicates that the $\chi^{(3)}$ values are little affected by incorporating the pendant NLO chromophores, as compared with our previous work.[15,16]

Conclusions

We have presented a new approach to the design of NLO polymers bearing both large second- and third-order nonlinearities at the same time. We have synthesized side-chain NLO polymers based on π-conjugated cyclic polyene backbone by metathesis catalysts. These polymers are amorphous and can easily be processed into thin films of optical quality. The poled films of the **P-2b** polymer exhibit 10.1 pm/V and no significant decay at ambient conditions within 60 days. The third-order nonlinear susceptibilities of the present polymers were evaluated to be about 10^{-11} esu at the incident wavelength of 1.907 μm.

Acknowledgment. We express our appreciation to U. H. Min for measurements of refractive index and electrooptic coefficients. We also thank Dr. Myung-Hyun Lee for helpful discussions.

References and Notes

(1) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic: New York, 1987; Vols. 1, 2.

(2) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley: New York, 1991.

(3) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Optics*; ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991.

(4) Walsh, C. A.; Burland, D. M.; Lee, V. Y.; Miller, R. D.; Smith, B. A.; Twieg, R. J.; Volkson, W. *Macromolecules* **1993**, *26*, 3720.

(5) Robello, D. R. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 1.

(6) Robello, D. R.; Dao, P. T.; Phelan, J.; Revelli, J.; Schildkraut, J. S.; Scozzafava, M.; Ulman, A.; Willand, C. S. *Chem. Mater.* **1992**, *4*, 425.

(7) Xu, C.; Wu, B.; Becker, M. W.; Dalton, L. R. *Chem. Mater.* **1993**, *5*, 1439.

(8) Wright, M. E.; Mullick, S. *Macromolecules* **1992**, *25*, 6045.

(9) Xu, C.; Wu, B.; Dalton, L. R.; Shi, Y.; Ranon, P. M.; Steier, W. H. *Macromolecules* **1992**, *25*, 6714.

(10) Allcock, H. R.; Dembek, A. A.; Kim, C.; Devine, R. L. S.; Shi, Y.; Steier, W. H. *Macromolecules* **1991**, *24*, 1000.

(11) Vanermen, G.; Samyn, C.; S'heernn, G.; Persoons, A. *Makromol. Chem.* **1992**, *193*, 3057.

(12) Gibson, H. W.; Bailey, F. C.; Epstein, A. J.; Rommelmann, H.; Kaplan, S.; Harbour, J.; Yang, X. Q.; Tanner, D. B.; Pochan, J. M. *J. Am. Chem. Soc.* **1983**, *105*, 4417.

(13) Jang, M. S.; Kwon, S. K.; Choi, S. K. *Macromolecules* **1990**, *23*, 4135.

(14) Jin, S. H.; Kim, S. H.; Cho, H. N.; Choi, S. K. *Macromolecules* **1991**, *24*, 6050.

(15) Lee, H. J.; Oh, J. M.; Choi, S. J.; Kim, H. K.; Choi, S. K. *Polym. Bull.* **1994**, *32*, 433.

(16) Park, S. Y.; Cho, H. N.; Kim, N.; Park, J. W.; Jin, S. H.; Choi, S. K.; Wada, T.; Sasabe, H. *Appl. Phys. Lett.* **1993**, *65* (3), 18, 289.

(17) Teng, C. C.; Man, H. T. *Appl. Phys. Lett.* **1987**, *56* (18), 1734.

(18) Kajzar, F.; Messier, J. *Thin Solid Films* **1985**, *132*, 11.

(19) Ulman, A.; Williams, D. J.; Penner, T. L.; Robello, D. R.; Schildkraut, J. S.; Scozzafava, M.; Willard, C. S. U.S. Pat. 4,792,208, 1988.

(20) Nijhuis, S.; Rikken, G. L. J. A.; Havinga, E. E.; ten Hoeve, W.; Wynberg, H.; Meijer, E. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1093.

(21) Gal, Y. S.; Choi, S. K. *J. Polym. Sci., Part A: Polym. Chem.* **1993**, *31*, 345.

(22) Schrock, R. R.; Fox, H. H. *Organometallics* **1992**, *11*, 2763.

(23) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

(24) Rao, D. N.; Chopra, P.; Ghoshal, S. K.; Swiatkiowicz, J.; Prasad, P. N. *J. Chem. Phys.* **1986**, *84*, 7049.

(25) Berkovic, G.; Shen, Y. R.; Prasad, P. N. *J. Chem. Phys.* **1987**, *87*, 1897.

(26) Le Moigne, J.; Hilberer, A.; Strazielle, C. *Macromolecules* **1992**, *25*, 6705.

MA946245B