Synthesis and Characterization of Poly(aryl ether chalcone)s for Second Harmonic Generation

X. T. Tao,[†] T. Watanabe, K. Kono, T. Deguchi, M. Nakayama, and S. Miyata*

Graduate School of Bio-Applications and Systems, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei-shi, Tokyo 184, Japan

Received December 18, 1995. Revised Manuscript Received March 11, 1996[⊗]

The synthesis of a new class of poly(aryl ether chalcone)s is described by a polycondensation reaction of 4,4′-difluorochalcone with various bisphenols in the excess anhydrous potassium carbonate in sulfolane/toluene mixture solvent. Fluoride atoms located at the para position of the chalcone moiety were found to be very activated toward nucleophilic aromatic substitution, and high molecular weight polymers were obtained. These polymers are amorphous and with glass transition temperatures at 150−200 °C and are very soluble in solvent such as chloroform and *N*-methylpyrrolidinone (NMP). The onset decomposition temperatures by thermogravimetric analysis of these materials were all above 330 °C. High optical quality films were obtained by spin-coating the polymer solution of NMP. The cutoff wavelength was shorter than 410 nm. The refractive indexes of these polymers at different wavelengths are reported. The corona poled polymers have different symmetry structures from the reported polymers, both P- and S-polarized SHG have been observed in these polymers.

Introduction

Worldwide research effort has been directed toward pushing organic second-order nonlinear optical (NLO) polymers into practical device applications since their ease in device fabrication and low cost.[1−4] To find practical applications in second harmonic generation (SHG), a number of requirements should be satisfied for a polymeric material, including good temporal and thermal stability of poling-induced orientations, tradeoff between NLO efficiency and transparency, and low optical loss and phase-matching characteristics at the expected wavelengths. Initially, the simplest form of guest−host systems was studied in considering the ease of preparation. However, the poling induced orientations in most of guest−host systems are not stable even at room temperature, and the obtainable NLO coefficients are limited by the low solubility of chromophores in the polymer host. In recent years the materials research effort has centered on polymers with high glass transition temperatures such as polyimides and some exciting results of polymers for electrooptical (EO) modulation applications have been reported.[5,6] Nevertheless, most of the polyimides have strong absorption in the visible region and are not suitable for SHG in the UV and visible regions.

Different from the significant progress in EO polymers, highly efficient SHG has not been realized in poled polymers.[7] This is because, except for the problem of temporal instability of poling-induced orientation, a number of other problems such as the tradeoff between transparency and efficiency; a suitable phase-matching method should also be solved.

We have concentrated our researches on organic NLO materials with two-dimensional charge-transfer chromophores.[8−10] We have pointed out that organic molecules with two-dimensional charge-transfer conformations (2-D CT molecule) easily forming a noncentrosymmetric crystal structure. In addition, in these molecules, the off-diagonal hyperpolarizability component is larger than the diagonal components and increases the effective phase-matched second harmonic generation.[8a−c] When a 2-D CT molecule such as *N*,*N*′-bis(*p*-nitrophenyl)methanediamine (*p*-NMDA) and the one-dimensional charge-transfer molecule (1-D CT molecule) 2-methyl-4-nitroaniline (MNA) were loaded into the same polymer matrix poly(methyl methacrylate) (PMMA) to make guest−host systems, it was found that the system with the 2-D CT molecule has much better temporal stability of poling-induced NLO properties over that system with

---

[†] Permanent address: Institute of Crystal Materials, Shan Dong University, PRC.

* To whom all correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

(1) Chemla, D. S., Zyss, J., Eds. *Nonlinear optical properties of organic molecules and crystals*; Academic Press: New York, 1987.

(2) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; Wiley: New York, 1991.

(3) Burland, D. M., Ed. *Chem. Rev.* **1994**, 94.

(4) Marder, S. R.; Sohn, J. E.; Stucky, G. D. *Materials for nonlinear optics*; ACS symposium series 455; American Chemical Society: Washington DC, 1991.

(5) (a) Verbiest, T.; Burland, D. M.; Jurich, M. C.; Lee, V. Y.; Miller, R. D.; Volksen, W. *Science* **1995**, *268*, 1604. (b) Peng, Z.; Yu, L. *Macromolecules* **1994**, *27*, 2638.

(6) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.

(7) (a) Singer, K. D.; Andrews, J. H. In *Molecular nonlinear optics, materials, physics, and devices*; Zyss, J., Ed.; Academic Press: San Diego, 1992. (b) Penner, T. L.; Motschmann, H. R.; Armstrong, N. J.; Ezenyilimba, M. C.; Williams, D. J. *Nature* **1994**, *367*, 49.

(8) (a) Yamamoto, H.; Katogi, S.; Watanabe, T.; Sato, H.; Miyata, S. *Appl. Phys. Lett.* **1992**, *60*, 935. (b) Nalwa, H. S.; Watanabe, T.; Miyata, S. *Adv. Mater.* **1995**, *7*, 754. (c) Watanabe, T.; Kagami, M.; Miyamoto, H.; Kidoguchi, A.; and Miyata, S. In *Nonlinear Optics, fundamental, device, and applications*; Miyata, S., Ed. Elsevier: Amsterdam, 1991; p 201. (d) Tao, X. T.; Watanabe, T.; Shimoda, S.; Zou, D. C.; Sato, H.; Miyata, S. *Chem. Mater.* **1994**, *6*, 1961.

(9) Tao, X. T.; Watanabe, T.; Zou, D. C.; Ukuda, H.; Miyata, S. *J. Opt. Soc. Am. B.* **1995**, *12*, 1581.

(10) Tao, X. T.; Watanabe, T.; Zou, D. C.; Shimoda, S.; Sato, H.; Miyata, S. *Macromolecules* **1995**, *28*, 2637.

S0897-4756(95)00607-7 CCC: $12.00

a 1-D CT molecule. After drawing and poling main-chain polymers with 2-D CT chromophores, the refractive indexes in different directions can be controlled and phase-matched SHG by birefringence has been realized in poled polymers by us.[9]

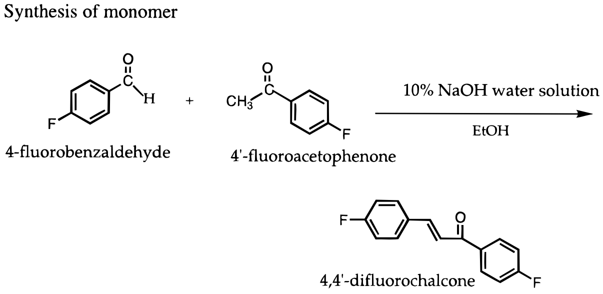
The 4,4′-disubstituted chalcones are molecules possessing a quasi-two-dimensional charge-transfer characteristics. The first hyperpolarizabilities of 4,4′-dimethoxyl chalcone were calculated by the program system MOPAC with the PM-3 parametrization at frequency $\omega = 0$. The β_{xxx} and β_{yxx} are found to be 6.28 $\times 10^{-30}$ and 3.81 $\times 10^{-30}$ esu, respectively, indicating that such types of molecules have both relatively large diagonal and off-diagonal hyperpolarizabilities in considering their transparency (the β_{xxx} of p-nitroaniline was calculated to be -6.27×10^{-30} esu at $\omega = 0$). Chalcone molecules have different charge-transfer characteristics from the traditional one-dimensional and two-dimensional molecules in which β_{xxx} or β_{xyy} is the dominant hyperpolarizability component, respectively.

The powder nonlinear optical effect of chalcone has been reported by Twieg et al.[11] After that, extensive study in searching for an organic single crystal with a wide transparency in the visible region has been reported by Miyata et al.[12] and others.[13,14] It was reported that the 4-bromo-4′-methoxychalcone (BMC)[13] has a powder SHG signal of 11 times that of urea and with a cutoff wavelength of 430 nm. BMC belongs to monoclinic crystal system, with point group m. The NLO coefficients of $d_{13} = 27$ and $d_{33} = 6.3$ pm/V were reported. Another interesting chalcone single crystal is 1-(2-thienyl)-3-(4-tolyl)-propen-1-one (T-17),[14] which shows an effective NLO coefficient of 7.1 pm/V and with a cutoff wavelength of 390 nm. These results indicated that chalcone single crystals have attractive transparency/NLO coefficients tradeoff. Unfortunately, all the reported chalcone single crystals have very poor mechanical properties and thermal properties. These crystals are difficult to use in practice. We think if the chalcone chromophore can be incorporated into a main-chain polymer, the drawbacks of poor thermal and mechanical properties should be improved, and the good balance between transparency and NLO effects would remain. Furthermore, main-chain polymers with such quasi-2-D CT chromophores would have some different NLO behaviors from other polymeric systems. Here we report the synthesis and characterization of a series of novel poly(aryl ether chalcone)s.

Experimental Section

General Method. The IR spectra were recorded with a JASCO FT/IR-5300 spectrometer using KBr pellets. Ultraviolet spectra were recorded with a JASCO V-500 spectrometer using a thin film spin coated on an ITO glass substrate. ^{1}H and ^{13}C NMR spectra were recorded at 400 or 500 MHz using a JEOL λ-400 or λ-500 spectrometer in DMSO-d_6 or $CDCl_3$ with TMS as the internal standard. The T_g's of the polymers and melting point of 4,4′-difluorochalcone were obtained using a Nigaku 220 DSC-TG-DTA instrument at a heating rate of 10 °C/min in nitrogen atmosphere. The T_g was taken from the midpoint of the change in slope of the baseline, while melting temperature was taken from the onset of the change in slope to the minimum of the endothermic peak. The weight loss data were obtained from a Nigaku 220 TG-DTA instrument at a heating rate of 10 °C/min in nitrogen. Elemental analysis was done by using a YANACO MT-5 instrument. Molecular weights were determined on a gel permeation chromatography (GPC) instrument (JASCO, 880-PU) relative to polystyrene standards using chloroform as an eluent at a rate of 0.5 mL/min; a UV detector was set at 254 nm wavelength.

Scheme 1



Synthesis of Monomer. *4,4′-Difluorochalcone (Scheme 1).* A mixture of 4-fluorobenzaldehyde (12.4 g, 0.1 mol), and 4′-fluoroacetophenone (13.8 g, 0.1 mol) in 100 mL of ethanol was stirred at room temperature for 30 min; 10 g of 10% NaOH aqueous solution was added to the mixture which was stirred until a white precipitate was obtained. The precipitate was filtered, washed with water, dried, and recrystallized from acetone. 4,4′-Difluorochalcone (25 g) was obtained as a white solid.

Anal. Calcd for $C_{15}H_{10}F_2O$: C, 73.77; H, 4.10. Found: C, 73.77; H, 4.09. ^{1}H NMR (DMSO-d_6) δ 7.28 (2H, Ar), δ 7.38 (2H, Ar), δ 7.70−7.90 (2H, CH=CH), δ 7.95 (2H, Ar), δ 8.25 (2H, Ar); ^{13}C NMR (DMSO-d_6) δ 188.2, 167.1, 165.0, 163.2, 143.0, 135.0, 131.5, 122.2, 116.5. IR (KBr) 1660.86 (C=O), 1599.13 cm^{-1} (C=C).

Synthesis of Polymers. Polymerization was conducted by a conventional procedure which utilized potassium carbonate as the base to form the phenolate in situ. All the polymerizations were conducted with the same molar concentrations and heating schedule (Scheme 2). A typical process is as follows. A 100 mL three-neck round-bottom flask equipped with a Dean−Stark trap, nitrogen inlet, and magnetic stirrer was charged with 4,4′-difluorochalcone (2.44 g, 0.01 mol), 4,4′-isopropyridenediphenol (bisphenol A, 2.28 g, 0.01 mol), anhydrous potassium carbonate (2.00 g, 0.0145 mol), sulfolane (20.0 mL), and toluene (10.0 mL). Nitrogen was sparged through the reaction mixture with stirring for 20 min, and then the mixture was slowly heated to 150 °C, and the mixtures were refluxed for 4 h. Water generated from the formation of the phenolate was removed as an azeotrope with toluene. The reaction mixture was diluted with 20 mL of N-methylpyrrolidinone (NMP), filtered hot through a G4 glass filter, and precipitated dropwise into 400 mL of methanol with stirring. After suction filtration and drying, the polymer was redissolved in chloroform and precipitated again into methanol to yield a white fibrous polymer after filtration. To ensure salt removal, the polymer was further purified by extraction in a Soxhlet extractor with water then dried at 100 °C under vacuum overnight. After purification, an almost quantitative yield of polymer was obtained.

C-1: Anal. Calcd for $C_{29}H_{24}O_3$: C, 82.85; H, 5.71. Found: C, 81.56; H, 5.60. ^{13}C NMR ($CDCl_3$) δ 188.5, 162.0, 159.5, 153.4, 147.0, 138.8, 132.4, 131.0−128.0, 121.0−115.0, 42.4, 31.0.

C-2: Anal. Calcd for $C_{31}H_{28}O_3$: C, 83.03; H, 6.25. Found: C, 82.60 H, 6.05. ^{13}C NMR ($CDCl_3$) δ 188.5, 162.4, 159.6, 150.6, 147.4, 143.4, 132.0, 131.0−128.0, 125.6, 119.0, 117.4−114.0, 42.5, 31.2, 16.1.

C-3: Anal. Calcd for $C_{35}H_{26}O_3$: C, 85.02; H, 5.26. Found: C, 83.36; H, 5.35. ^{13}C NMR (DMSO-d_6) δ 188.0, 166.1, 162.4,

---

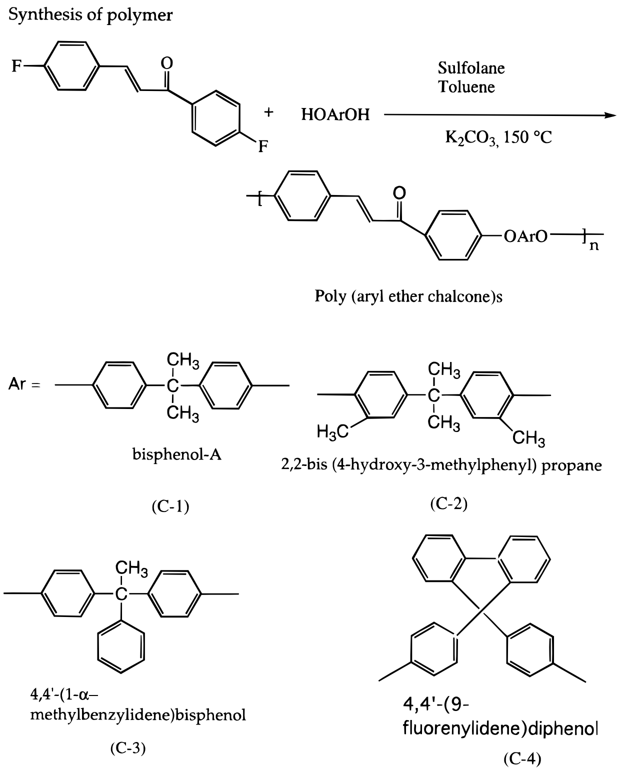
(11) Twieg, R. J.; Jain, K. In *Nonlinear Optical Properties of Organic and Polymeric Materials*; Williams, D. J., Ed.; ACS Symposium Series 233; American Chemical Society: Washington, DC, 1983.

(12) Fichou, D.; Watanabe, T.; Takeda, T.; Miyata, S.; Goto, Y.; Nakayama, M. *Jpn. J. Appl. Phys.* **1988**, *27*, L249.

(13) Zhang, G.; Kinoshita, T.; Sasaki, K.; Goto, Y.; Nakayama, M. *J. Cryst. Growth* **1990**, *100*, 411.

(14) Kitaoka, Y.; Sasaki, T.; Nakai, S.; Goto, Y. *Appl. Phys. Lett.* **1991**, *59*, 19.

Scheme 2



161.0, 158.3, 154.6, 153.2, 148.4, 144.1, 142.0, 138.5, 132.0−125.0, 122.0, 121.1, 118.0−113.0, 51.0, 29.3.

C-4: Anal. Calcd for $C_{40}H_{26}O_3$: C, 86.64; H, 4.69. Found: C, 86.10; H, 4.52. ^{13}C NMR (DMSO-d_6) δ 188.0, 164.5, 162.2, 160.5, 158.6, 156.2, 154.6, 151.0, 142.5−138.8, 135.2, 132.8, 131.0−125.0, 122.2−114.0, 63.2.

Thin-Film Preparation. Polymer films for refractive indexes measurements were prepared by spin coating on glass slides from an NMP solution with a concentration of 20 wt %. The films for absorption measurement were prepared by spin coating on an ITO glass; the spinning rate was in the range 1500−3000 rpm. The spin coated films were dried in a vacuum oven at 160 °C for 2 days. The thickness and refractive indexes of the films were determined by the *m*-line method.

Corona Poling. These main-chain polymers were poled by the corona poling method. The polymers were spin coated on a glass slide, and the evaporated aluminum layer on the other side was used as the ground electrode. Corona poling discharge is a partial breakdown of air and is initiated by a discharge in an inhomogeneous electric field; ions are created and deposited on the top of the surface of polymer films. In the experiment, a 5−8 kV positive electric voltage was set to the tungsten needle which was suspended about 1 cm above the ground aluminum electrode. The corona current was below to 2 μA, the poling temperature was kept near the glass-transition temperature (T_g) of the polymers.

Results and Discussion

Monomer Synthesis. The reason for selecting difluorochalcone as the monomer for the preparation of poly(aryl ether chalcone)s is that fluorine is an easier leaving group in a nucleophilic substitution reaction than other halides. Chalcone derivatives were easily synthesized by the condensation reaction of aldehydes with acetophenones and with high yield. In our experiments, at room temperature, and in very short time, almost quantitative product of 4,4′-difluorochalcone was obtained by the reaction of 4-fluorobenzaldehyde with 4′-fluoroacetophenone in ethanol.

Polymer Synthesis. Numerous poly(aryl ether)s have been synthesized since these polymers possess many desirable properties including excellent thermal stability, high glass transition temperatures, and good mechanical and optical properties.[15−19] The general synthesis method of poly(aryl ether)s is the nucleophilic displacement of an aryl dihalide with a diphenoxide in polar aprotic solvents. The aryl difluoride is activated by electron-withdrawing groups such as a carbonyl, sulfone, or heterocyclic group which increases the electrophilicity of the fluorine-bearing carbon. In addition, these activation groups accept a negative charge by resonance interaction, thus lowering the activation energy for the displacement through a Meisenheimer complex.[17] The stronger the electron-withdrawing group, the easier the reaction takes place.

Two main methods have been used to predict the potential reactivity of activated aromatic dihalide toward phenoxides in nucleophilic aromatic substitution reactions.[15] One is compare the partial positive charge density (δ) at the carbon-bearing fluoride. The larger the value (δ), the higher the reactivity. The other method is comparing the ^1H NMR chemical shifts of the hydrogens ortho to the electron-withdrawing group. A downfield shift generally corresponding to an increase in the reactivity. Here only inductive effects of the activating group have been considered, and the effect of these groups on the stability of the Meisenheimer complex intermediate has not been considered. Therefore, this standard can be used only qualitatively.

The active group in chalcone is an α,β-unsaturated ketone; the carbon−carbon double bond and the carbon−oxygen double bond are separated by just one carbon−carbon single bond, i.e., the double bonds are conjugated. The electronic effect of this group has been evaluated by ^1H NMR. Figure 1 shows the ^1H and ^{13}C NMR spectra of 4,4′-difluorochalcone. Comparison of the ^1H NMR spectral assignments of 4,4′-difluorochalcone shows that the protons ortho to the electron-withdrawing group have a chemical shift of δ 7.95 and 8.25 as compared to the ortho positions δ 7.84 of 4,4′-difluorobenzophenone, a conventional activated dihalide. This result suggests an α,β-unsaturated ketone is a stronger activating group for nucleophilic aromatic substitution and that it should be possible to incorporate it into poly(aryl ether) even more readily. The structure of the unsymmetric ketone monomer is also unique for studying the effects of symmetry on the properties of polymers.[18a] Moreover, the relatively long conjugation system in chalcone will significantly increase its hyperpolarizability over that of benzophenone.

In such types of nucleophilic substitution reactions, polar aprotic solvents are necessary because they effectively dissolve the monomers and solvate the cation, which further activates the phenate anion by making it more nucleophilic. They also dissolve the oligomeric polar intermediates which are initially formed in a step-

---

(15) (a) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1017. (b) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1025. (c) Singh, R.; Hay, A. S. *Macromolecules* **1992**, *25*, 1033. (d) Strukelj, M.; Hay, A. S. *Macromolecules* **1992**, *25*, 4721. (e) Gao, C. P.; Hay, A. S. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, 33, 2347.

(16) (a) Strukelj, M.; Hedrick, J. C.; Hedrick, J. L.; Twieg, R. J. *Macromolecules* **1994**, *27*, 6277. (b) Strukelj, M.; Hedrick, J. C. *Macromolecules* **1994**, *27*, 7511.

(17) Percec, V.; Clough, R. S.; Grigoras, M.; Rinaldi, P. L.; Litman V. E. *Macromolecules* **1995**, *26*, 3650.

(18) (a) Douglas, J. E.; Wang, Z. Y. *Macromolecules* **1995**, *28*, 5970. (b) Zhang, C. H.; Wang, Z. Y. *Macromolecules* **1994**, *26*, 3324.

(19) DeSimone, J. M.; Stompel, S.; Samulski, E. T.; Wang, Y. Q.; Brennan A. B. *Macromolecules* **1995**, *25*, 2546.

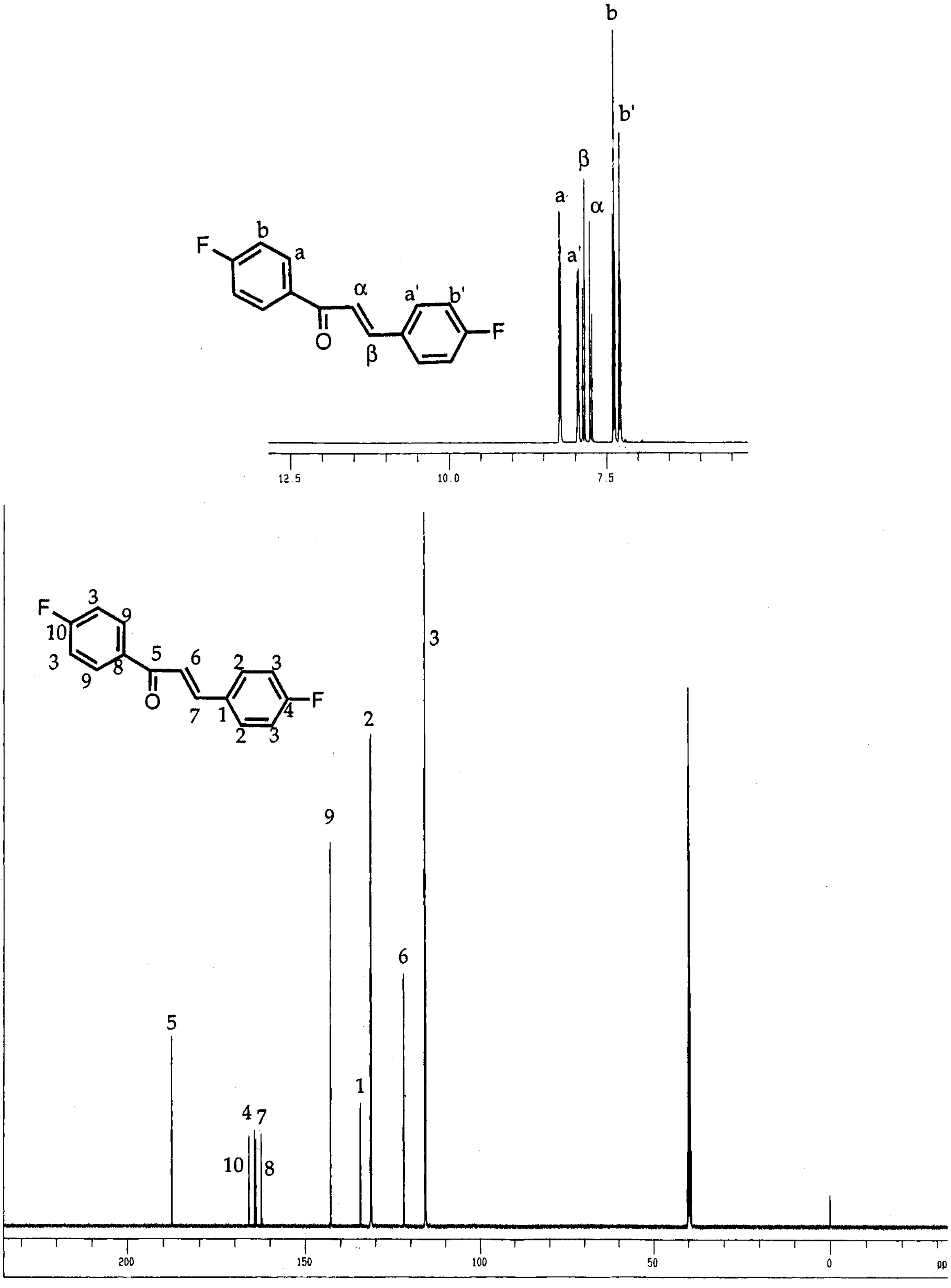


Figure 1. ^{1}H (a, top) and ^{13}C (b, bottom) NMR spectra of 4,4′-difluorochalcone in DMSO-d_6.

growth polymerization and allow reaction to continue to give a high molecular weight polymer. Irrespective of the polymerization solvent, toluene was used as a cosolvent to remove water generated by phenoxide formation as a toluene/water azeotrope. Strukelj et al.[16] have studied the effects of solvents on the polymerization reaction of 4,4′-difluorobenzil with various biphenols. They found when using high-purity commercial NMP and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidine (DMNP) as solvents, an intensive green polymerization mixture, and only low molecular weight poly(aryl ether benzil)s were obtained with long reaction times. The green color of the polymerization mixture was attributed to the impurity in NMP and low molecular weight polymer was due to the polymer degradation after a buildup in molecular weight. In our experiment, sulfolane was used as the solvent, and high molecular weight polymers were obtained. Completion or near completion of polymerization was qualitatively estimated by the point where the viscosity increased dramatically by varying the reaction time for different bisphenols. When the biphenol is bisphenol A, the best

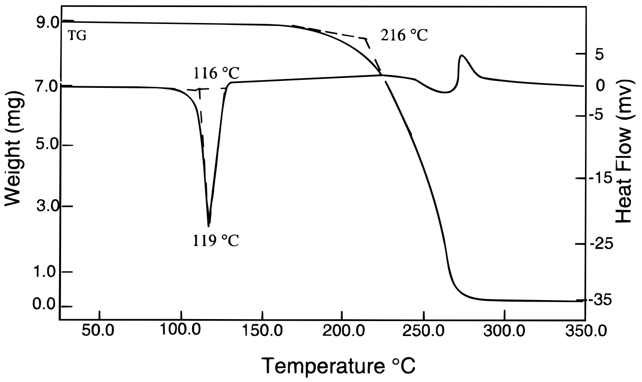


Figure 2. TGA and DTA thermograms of 4,4′-difluorochalcone under an atmosphere of N_2.

Table 1. Molecular Weights of Poly(aryl ether chalcone)s Measured by GPC

code	$10^{-4}M_n$	$10^{-4}M_w$	M_w/M_n	code	$10^{-4}M_n$	$10^{-4}M_w$	M_w/M_n
C-1	3.9	8.0	2.05	C-3	14.6	23.4	1.60
C-2	24.9	69.1	2.77	C-4	30.6	58.2	1.90

reaction time was 4 h, at longer reaction time, the polymers with too large molecular weight were not soluble in any general organic solvents. The best reaction time for C-4 polymer was 8 h. When commercial NMP was used as the solvent, a strong green color was observed in the mixture, and the obtained polymers have relatively low molecular weights.

Several main-chain polymers with chalcone-type groups have been reported by polycondensation of aromatic diacetyl compounds with aromatic dialdehydes.[20] The obtained polymers had low molecular weights and were hard and brittle and with limited solubility in general organic solvents. Malm and Lindberg reported the synthesis of substituted polychalcones by Fridel−Crafts acetylation of vanillin and *p*-hydroxybenzaldehyde in nitrobenzene using $AlCl_3$ as a catalyst, and the molecular weights of their polymers were below 5000.[21] The molecular weights of poly(aryl ether chalcone)s measured by gel permeation chromatography (GPC) related to polystyrene standard using chloroform as an eluent are listed in Table 1. The number-average molecular weights range from 3.9×10^4 to 25.0×10^4 for different bisphenols. The polydispersity factors lie between 1.6 and 2.7. These data indicate very high molecular weight polymers have been synthesized. All the polymers are amorphous and very soluble in chloroform and polar aprotic solvents such as NMP. High-quality thin films have been prepared by spin coating the NMP solution of the polymers.

Thermal Properties. The thermal gravimetrical analysis (TGA) and differential thermal analysis (DTA) curves of 4,4′-difluorochalcone are shown in Figure 2. The melting point of this monomer is 116 °C and the onset weight-loss temperature is 170 °C. Similar to other chalcones, this material has a low melting point, and the poor thermal stability is one main drawback of a chalcone single crystal for NLO applications. A glass transition temperature was observed for all the polymers in differential scanning calorimetric (DSC) curves. Figure 3a shows the DSC curve of a C-3 polymer. Shown in Figure 3b is the TGA curve of the same polymer. The thermal properties of all the polymers are reported in Table 2. These results indicate poly (aryl ether chalcone)s with a range of T_g from 150 to 200 °C and an onset decomposition temperature in the range 330−350 °C have been synthesized, dependent on the bisphenols. Generally, the glass transition temperature increases with increasing steric hindrance, as was observed with other poly(aryl ether ketone)s. However, the decomposition temperature decreases with increasing steric hindrance. These results indicate these polymers have good thermal stability and relatively high glass transition temperature.

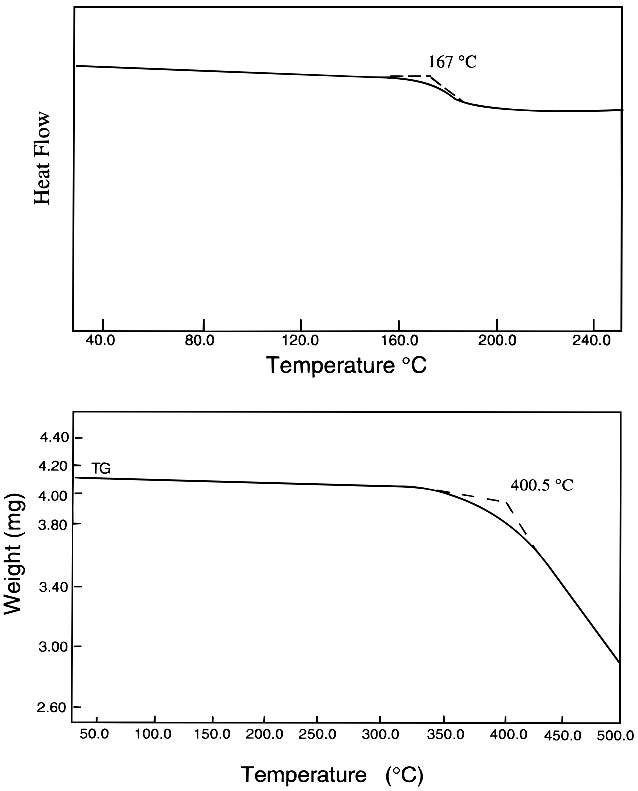


Figure 3. DSC (a, top) and TGA (b, bottom) thermograms of a poly(aryl ether chalcone) C-3 under an atmosphere of N_2.

Table 2. Thermal Properties of Poly(aryl ether chalcone)s

code	T_g (°C)	T_d (onset, °C)	code	T_g (°C)	T_d (onset, °C)
C-1	152	352	C-3	167	340
C-2	157	350qC-4	195	330	

Absorption Spectra. UV−visible absorption spectroscopy is a readily available technique for the evaluation of dipole orientation of chromophores in the polymer subjected to a dc electric field. If the light is propagated along the direction of the poling field (normal to the film plane), one observes a shift in the maximum as well as a reduction in the absorption intensity. Such an effect is called electrochromism. It is due to the alignment of transition dipole moments of chromophores along the poling field direction. The effect of poling is generally expressed as an order parameter as[22]

$$\Phi = 1 - A_p/A_0 \tag{1}$$

where A_p is the absorption intensity of the poled film

---

[20] Cascaval, C. N.; Oleinek, H.; Zugravescu, I.; Schneider, I. A. *Makromol. Chem.* **1973**, *169* 129.

[21] (a) Malm, B. *Makromol. Chem.* **1981**, *182*, 1307. (b) Malm B.; Lindberg J. J. *Makromol. Chem.* **1981**, *182*, 2747.

[22] Page, R. H.; Jurich, M. C.; Reck, B.; Sen, A.; Twieg, R. J.; Swalen, J. D.; Bjorklund, G. C.; Willson, C. G. *J. Opt. Soc. Am. B* **1990**, *7*, 1239.

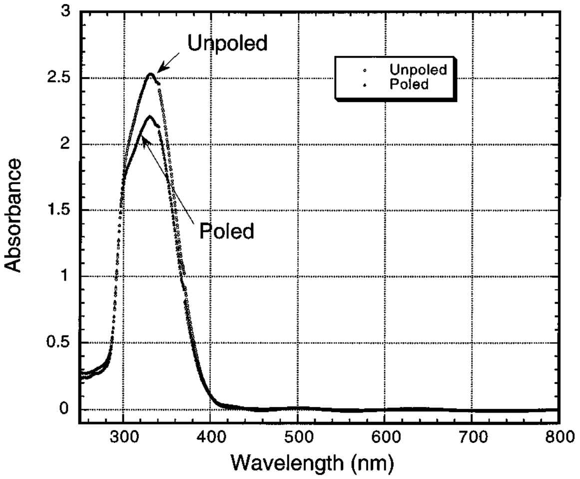


Figure 4. UV−vis absorption spectra of thin C-3 polymer on an ITO glass before and after poling. The spectra are measured with light perpendicular to the poling field.

and A_0 is the absorption intensity of unpoled film. Shown in Figure 4 are the UV−visible absorption spectra of C-2 polymer. After corona poling, an absorption intensity decrease is clearly seen, but there is no apparent shift of absorption maximum. The corona poling-induced order parameter of this polymer is 0.13. The order parameters for other polymers are in the range 0.11−0.20.

Refractive Index. To obtain the nonlinear optical properties of a thin film, such as the NLO coefficients, it is essential to have information about the basic properties of film thickness, refractive indexes at fundamental and harmonic wavelengths. The refractive index can be measured using conventional approaches such as ellipsometry, Brewster angle determination, and spectroscopic interference. Film thickness can be measured either by micrometric or morphological means. However, for a soft film such as a polymeric film, the aforementioned techniques for measuring thicknesses are not nondestructive. We obtained the thicknesses and refractive indexes of the polymeric films by the *m*-line method.[23] This measurement is done by using the prism coupling technique with an optical waveguide. The light beam from a He−Ne laser, an YAG laser, and its second harmonic wave was coupled into the film by a FD21 prism. The coupling angle θ determines the phase velocity in the propagation direction, $V(i) = (c/n_p)\sin\theta$, of the incident waves in the prism (index n_p) and in the gap. Strong coupling of light into the film occurs only when we choose θ so that $V(i)$ equals the phase velocity V_m of one of the characteristic modes of propagation in the polymer wave guide (m = 0, 1, 2, ...). Thus, by determining these synchronous angles θ_m of strongest coupling, we can find experimentally the characteristic propagation constants of a given film and obtain the film thickness and refractive index simultaneously.

Figure 5 shows the refractive index dispersion of C-3 polymer at the selected wavelength of 0.532−1.064 μm. The refractive indexes of all the four polymers are listed in Table 3. From the refractive index dispersion curves and the values of refractive index, we can see all the refractive indexes in the film plane (TE mode) are larger than those in the film normal direction (TM mode). This is because the polymer chains are stretched in the film plane. Similar results have been reported by other researchers as well as in our previous publications.[8,10]

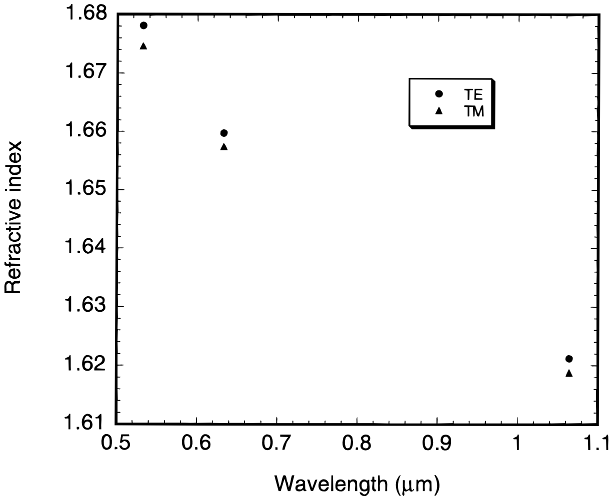


Figure 5. TE and TM mode refractive indexes of C-3 polymer measured in air at room temperature by the *m*-line method.

Table 3. Refractive Indexes of Poly(aryl ether chalcone)s at Different Wavelengths Measured by the *m*-Line Method

polymer	wavelength (μm)	n_{TE}	n_{TM}
C-1	0.532	1.6808	1.6751
	0.6328	1.6666	1.6612
	1.064	1.6240	1.6204
C-2	0.532	1.6634	1.6583
	0.6328	1.6441	1.6390
	1.064	1.6107	1.6069
C-3	0.532	1.6781	1.6746
	0.6328	1.6597	1.6574
	1.064	1.6212	1.6188
C-4	0.532	1.7106	1.6995
	0.6328	1.6862	1.6763
	1.064	1.6534	1.6443

The refractive indexes of C-4 polymer are apparently higher than those of C-1 polymer in whole transparency region; however, the C-2 and C-3 polymers with methyl or phenyl substituents have smaller refractive indexes than C-1 polymer. The change of the refractive index of these polymers can be explained qualitatively in terms of the substituent contributions to the molar refraction and molar volume of the polymer. The molar refraction, according to Lorentz and Lorenz,[24] is expressed as

$$R_{LL} = \frac{n^2 - 1}{n^2 + 2}V \qquad (2)$$

or

$$\frac{n^2 - 1}{n^2 + 2}V = \frac{4\pi}{3}N_A\alpha \qquad (3)$$

where R_{LL} is the molar refraction, V is the molar volume, N_A is Avogadro's number, and α is the polarizability. Thus the refractive index decreases with increasing molar volume and increases with increasing molar refraction (or polarizability). This model allows the calculation of the refractive index of a mixture of noninteracting substances by using the refraction index

---

[23] Tien, P. K.; Ulrich, R. *J. Opt. Soc. Am.* **1970**, *60*, 1325.

[24] Van Krevelen, D. W. *Properties of Polymers: Their Estimation and Correlation with Chemical Structure*; Elsevier: Amsterdam, 1976.

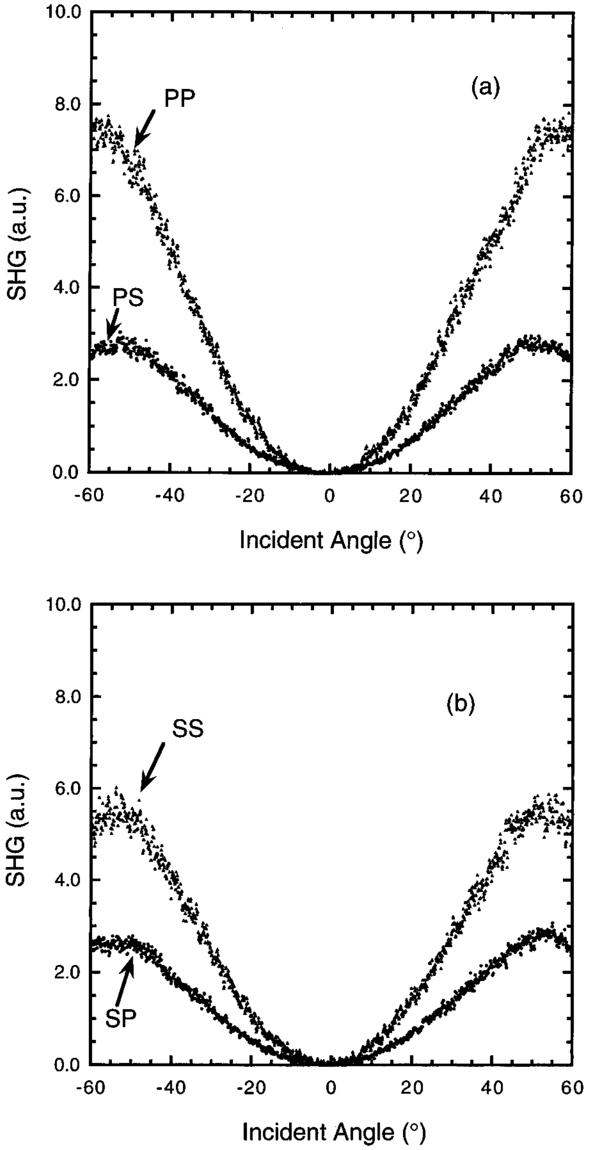


Figure 6. Marker fringes of corona poled C-2 polymer with P (a) and S (b) polarized second-harmonic light.

of the components of the mixture. In the case of polymers, when we neglect the effects of chain orientation and intergroup actions, the structure–refractive index relationships are mainly determined by the competing effects of molar refraction and molar volume. Under this fundamental assumption, this model has also been used to predict the refractive index of a polymer. A number of molar refraction values have been collected in Van Krevelen's book[24] and have been found to predict the refractive index of nonconjugated polymers with good accuracy. However, any significant interaction among groups can invalidate the additivity principle. More recently, Yang and Jenekhe[25] reported a new series of Lorentz–Lorenz molar refraction values after considering the effects of π-electron delocalization and optical dispersion for functional groups commonly found in π-conjugated polymers and dramatic improvement in the accuracy of predicting the refractive index of conjugated polymers has been achieved.

We have calculated the polarizabilities of these polymers by the MOPAC program. On the basis of the calculated polarizabilities, the refractive indexes of these polymers have been calculated by Lorentz–Lorenz mode. We found the calculated values were overestimated compared to the experimental values. However, the trend of the theoretic calculations are in agreement with the experimental measurement. Compared to C-1 polymer, we might have expected that C-2 and C-3 polymers would have larger molar refractions due to the methyl and phenyl substituents. However, the increase of molar volume due to the substituents even more and thus causes a net decrease in refractive index of C-2 and C-3 polymers. On the other hand, although the fluorenylidene group in C-4 polymer is more bulky than the methyl group and hence with larger molar volume, the contribution to the molar refraction due to the bulky group is so large that the refractive indexes of C-4 polymer are substantially higher than those of C-1 polymer.

Nonlinear Optical Properties. Second harmonic generation was employed to study the NLO properties of the polymer films. A Spectro-Physics mode-locked Nd:YAG laser ($\lambda = 1.064\ \mu$m) with pulse width of <10 ns and repetion rate of 10 Hz was used as the fundamental source. A Y-cut quartz crystal was used as the reference. The obtained Maker fringes of the corona onset poled polymers are shown in Figure 6. Different from the generally corona poled polymers, in the present case both P- and S-polarized SH light are observed. Indicating the corona poled films no longer belong to ∞mm symmetry. Such unusual two-dimensional nonlinearity in corona poled amorphous polymers has not been reported in the literature. At present, the origin of this unusal nonlinerity in these polymers is not clearly understood. However, this phenomenon is certainly related to the unique molecular structure of chalcone.

Conclusion. 4,4′-Difluorochalcone has been synthesized, which undergoes polycondensation with various bisphenates to give amorphous high thermal stable poly(aryl ether chalcone)s in excellent yields. The polymerization reactions were conducted in sulfolane in the presence of K_2CO_3 to give high molecular weight polymers. All the spin-coated films are optically clear and transparent in the visible region. The refractive indexes of these polymers have been measured by the *m*-line method. The values are relatively high for organic polymers because the large amount of aromatic structures in these polymers. Chalcone is an α,β-unsaturated ketone, which can be reacted with certain amines, hydroxylamine, phenylhydrazine, etc. to yield β-amino carbonyl compounds. Therefore, many other polymers with better thermal properties can be obtained through the precursor poly(aryl ether chalcone)s.[26] The chromophores in all the polymers can be oriented by corona poling, and unusual two-dimensional asymmetry has been observed for the first time in corona poled polymers. The details on the NLO properties of these polymers will be discussed in a separate paper.

Acknowledgment. This research was partially supported by the Grant-in Aid for Scientific research, Nos. 07246105 and 07750049, from the Ministry of Education, Science, and Culture, Japan.

CM950607S

---

(25) (a) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1995**, *7*, 1276. (b) Yang, C. J.; Jenekhe, S. A. *Chem. Mater.* **1994**, *6*, 196.

(26) Oleinek, H.; Zugravescu, I. *Makromol. Chem.* **1972**, *157*, 179.