

the lowest energy conformers.

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Wholly Aromatic Polyesters Containing NLO Chromophores in the Side Chain

Suck-Hyun Lee, Ki-Cheon Lim, Jong-Taek Jeon, and Seog-Jeong Song*

Department of Applied Chemistry, College of Engineering, Ajou University Suwon 442-749, Korea

*Kolon Group Central Research Institute, Yongin-gun, Kyunggi-do 449-910, Korea

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A series of poly(1,4-phenylene terephthalates) with pendant NLO chromophores was prepared by the solution polycondensation of 2,5-NLO chromophore substituted terephthalic acid with hydroquinone. The polymers obtained gave satisfactory NMR and elemental analysis results when taking into account their expected structures and the inherent viscosity value proved the polymeric character of all polymers. DSC, optical polarizing microscopy and WAXS studies revealed that none of these polymers exhibited liquid crystalline mesophases. Preliminary results on NLO properties of these polymers showed a surprisingly large second harmonic signal relative to a Y-cut quartz plate.

Introduction

There has been a tremendous growth of interest in the field of nonlinear optical (NLO) polymers since polymeric materials offer the attractive combinations of optical, structural and processing properties. Among the NLO properties, second harmonic generation (SHG) is the first observed effect and has also been the most widely studied.¹ It is now well known that this frequency doubling activity requires

a stable non-centrosymmetric macroscopic structure and very few organic materials crystallize into nonsymmetric space groups. Various approaches with polymeric system to create noncentrosymmetric structures have been attempted.

Examples of polymeric materials exhibiting SHG include¹:

- Guest-host polymer systems in which the active molecules are simply dissolved or distributed in the polymer matrix,
- Electro-optic polymers in which the active molecules are covalently bonded either to the polymer side chain or

to the main chain.

c) Network polymers containing chemically reacted or simply dissolved active molecules by thermal, photochemical or sol-gel reactions.

All the above systems need to pole polymers at temperatures near their glass transition with an electric field to achieve a noncentrosymmetric structure which may be frozen into place by cooling or chemically reacting the polymer during poling. In this study, we attempted to make a new class of side chain polymers. Side chain polymers are traditionally prepared by covalently bonding a rigid organic molecule to a flexible polymer backbone *via* a spacer of 4-6 carbon atoms. However, these materials suffer from major deficiencies including chromophore aggregation or pairing during processing at high levels of substituents due to the strong dipole-dipole interactions of NLO active groups.^{2,3} To avoid this undesired effect the NLO chromophores are attached to a rigid type main chain of the polymer. Based on this consideration, we studied wholly aromatic polyesters bearing NLO phores in the side chain, being capable of alignment with minimal aggregation during field poling.

Experimental

Materials and Measurements

Elemental analysis was performed by Perkin-Elmer-Series II 2400. ¹H NMR spectra were obtained using a Varian-Gemini 2000 spectrometer and IR spectra using Nicolet Magna-IR 550 spectrometer. Melting points were measured on a Fisher-Jones melting point apparatus. The inherent viscosity was measured at 30 °C from the solution of 0.1 g/dL in 1,1,2,2-tetrachloroethanol. DSC measurements were made on a Perkin-Elmer DSC-7 instrument at the heating rate of 10 °C/min. Polarizing optical microscopic investigations were carried out with a Leitz laborlux optical microscope equipped with a hot stage. Wide angle X-ray diffraction measurements were carried out on a Rigaku Geiger Flex D-Max IIIa instrument.

Monomer synthesis

N-(4-Nitrophenyl)-L-prolinol (NPP) (1). L-Prolinol (25 g; 0.25 mol) and potassium carbonate (25 g; 0.18 mol) were dissolved in 25 mL of dimethylsulfoxide. 1-Fluoro-4-nitrobenzene (FNB) (33 g; 0.23 mol) was added slowly over the period of 1 h to the mixture, which was heated at 50 °C with stirrer for 24h. The reaction mixture was cooled to room temperature and the product was precipitated in distilled water. The precipitate separated by filtration was recrystallized from toluene yielding a yellow solid. The product yield was 95%, mp 117 °C (lit.⁴ 115-116 °C).

¹H NMR spectrum (CDCl₃); δ (ppm) 2.0 (brs. 1H, OH), 2.0-2.3 (m, 4H, -CH₂-), 3.2-3.8 (m, 4H, N-CH₂, O-CH₂), 3.9-4.2 (quen. H N-CH), 6.6 (d, 2H, meta from NO₂), 8.1 (d, 2H, ortho from NO₂)

IR spectrum(KBr): 3450 (O-H stretching), 3140 (aromatic C-H), 2950 (aliphatic C-H), 1450-1650 (aromatic C=C, N=O), 1100-1300(C-O)

α-[N-(4-Nitrophenyl)-L-prolinoxy]-ω-bromoalkane (2) (Scheme 1). All of the α-[N-(4-nitrophenyl)-L-prolinoxy]-ω-bromoalkanes were prepared using the same method. Representative experimental procedures for the synthesis

of the dibromo hexane (*n*=6) compound are given below. To a solution of the NPP (1) (5 g, 0.023 mol) in 250 mL of THF was added NaH (2.7 g, 0.11 mol) in room temperature. After 30 min of stirring the yellow solution turned brown. To this solution was added excess 1,6-dibromoalkane (36.7 g, 0.16 mol) and the mixture was stirred under nitrogen atmosphere at 60-70 °C for 12h. The resulting solution was filtered and the remaining excess dibromoalkane and THF were distilled off under reduced pressure. Final isolation of the product was made by chromatography on a silicagel column with hexane-ethylacetate (3/1=v/v) as the eluent. A viscous brown liquid 2 (*n*=6) was obtained and the yield was 70%, mp 39 °C.

¹H NMR (CDCl₃); δ (ppm) 1.5-2.4 (m, 12H, -CH₂-), 3.2-3.6 (m, 8H, O-CH₂, N-CH₂, Br-CH₂), 4.0-4.1 (quen, 1H, N-CH), 6.5 (d, 2H, meta from NO₂), 8.2 (d, 2H, ortho from NO₂)

IR (cm⁻¹); 3140 (aromatic C-H str.), 2950 (ali C-H str.), 1512 (N-O str.) 1307 (C-O str.) Anal. calcd: *n*=4 (C, 50.28; H, 6.20; N, 7.82), *n*=5 (C, 51.61; H, 6.51; N, 7.52), *n*=6 (C, 52.85; H, 6.80; N, 7.25), *n*=7 (C, 54.20; H, 7.06; N, 6.99), *n*=8 (C, 55.07; H, 7.31; N, 6.76), *n*=9 (C, 56.07; H, 7.54; N, 6.53), *n*=10 (C, 57.68; H, 7.76; N, 6.33)

Found: *n*=4 (C, 50.23; H, 6.34; N, 7.51), *n*=5 (C, 51.13; H, 6.65; N, 7.31), *n*=6 (C, 53.10; H, 6.68; N, 7.40), *n*=7 (C, 53.10; H, 6.90; N, 6.68), *n*=8 (C, 55.32; H, 7.42; N, 6.61), *n*=9 (C, 55.93; H, 7.69; N, 6.38), *n*=10 (C, 57.07; H, 7.68; N, 6.10)

Diethyl 2,5-di-[6-(N-(4-nitrophenyl)-L-prolinoxy)hexyleneoxy]terephthalate (3, *n*=6). The synthesis of this product was carried out according to the known method.⁵ Diethyl 2,5-dihydroxyterephthalate 5.0 g (1.97×10⁻² mol) and potassium carbonate 5 g (0.15 mol) were dissolved in DMF 20 mL and stirred for 30 min. A solution of 1-[N-(4-nitrophenyl)-L-prolinoxy]-6-bromohexane (2.44 g, 5.91×10⁻² mol) in 10 mL DMF was added dropwise to the above solution. This reaction mixture was stirred at 50 °C for 20h and then K₂CO₃ was removed by filtration and DMF was distilled off *in vacuo*. The residual viscous liquid was recrystallized from DMF/ethanol=1/4(v/v); yield 90%, mp 63 °C.

¹H NMR (CDCl₃); δ (ppm) 1.3-1.4 (t, 6H, CH₃), 1.7-2.3 (m, 24H, -CH₂-) 3.2-3.6 (m, 12H, O-CH₂, N-CH₂), 3.9-4.1 (m, 6H, COOCH₂, N-CH), 4.5 (t, 4H, Ph-O-CH₂), 6.6 (d, 4H, meta from NO₂), 7.8 (s, 2H, Ar.), 8.1 (d, 4H, ortho from NO₂)

IR (cm⁻¹); 3140 (Ar. C-H str.), 2950 (ali. C-H str.), 1512 (N-O str.), 1307 (C-O str.) Anal. calcd: *n*=4 (C, 62.51; H, 6.76; N, 6.94), *n*=5 (C, 63.28; H, 7.02; N, 6.71), *n*=6 (C, 64.01; H, 7.26; N, 6.49), *n*=7 (C, 64.69; H, 7.48; N, 6.28), *n*=8 (C, 65.50; H, 7.65; N, 6.06), *n*=9 (C, 65.93; H, 7.89; N, 5.91), *n*=10 (C, 66.50; H, 8.08; N, 5.74)

Found: *n*=4 (C, 62.26; H, 6.45; N, 6.92), *n*=5 (C, 63.02; H, 7.04; N, 6.78), *n*=6 (C, 63.71; H, 7.15; N, 6.34), *n*=7 (C, 64.53; H, 7.60; N, 6.51), *n*=8 (C, 65.37; H, 7.84; N, 6.04), *n*=9 (C, 65.76; H, 7.87; N, 5.94), *n*=10 (C, 66.49; H, 7.96; N, 5.60)

2,5-Di-[6-(N-(4-nitrophenyl)-L-prolinoxy)hexyleneoxy]terephthalic acid (4). The product (3, *n*=6) 47.62 g (5.8×10⁻² mol) was dissolved in ethanol 6 mL under reflux. To the solution was added a solution of KOH 3.25 g (5.8×10⁻² mol) in ethanol 10 mL and the reaction was conducted under reflux for 3h. After the reaction was completed, the ethanol was distilled off and the residue was dissolved

in distilled water, neutralized with 2 N HCl and then extracted with methylene chloride. The yellow precipitate was then collected, recrystallized from ethanol yield 90%, mp 155 °C.

$^1\text{H NMR}$ (CDCl_3); δ (ppm) 1.7-2.2 (m, 24H, $-\text{CH}_2$), 3.2-3.8 (m, 12H, $\text{O}-\text{CH}_2$, $\text{N}-\text{CH}_2$), 3.9-4.1 (m, 2H, $\text{N}-\text{CH}$), 4.3-4.5 (t, 4H, $\text{Ph}-\text{O}-\text{CH}_2$) 6.6 (d, 4H, meta from NO_2), 7.34 (s, 2H, Ar.), 8.1 (d, 4H, ortho from NO_2)

IR(cm^{-1}); 2400-3600 (O-H, str.), 2950 (ali. C-H str.), 1512 (N-O str.), 1307 (C-O str.) Anal. calcd: $n=4$ (C, 60.78; H, 6.19; N, 7.46), $n=5$ (C, 61.68; H, 6.48; N, 7.19), $n=6$ (C, 62.51; H, 6.76; N, 6.94), $n=7$ (C, 63.28; H, 7.02; N, 6.70), $n=8$ (C, 64.16; H, 7.04; N, 6.50), $n=9$ (C, 64.84; H, 7.27; N, 6.30), $n=10$ (C, 65.64; H, 7.45; N, 6.08)

Found: $n=4$ (C, 60.52; H, 6.43; N, 7.75), $n=5$ (C, 61.96; H, 6.70; N, 6.93), $n=6$ (C, 61.83; H, 6.22; N, 6.79), $n=7$ (C, 63.30; H, 7.19; N, 6.57), $n=8$ (C, 64.79; H, 7.32; N, 6.42), $n=9$ (C, 64.52; H, 7.65; N, 6.69), $n=10$ (C, 65.96; H, 7.28; N, 6.16)

Polymer Synthesis

The following procedure was employed to prepare polymers from terephthalate monomers with different spacer lengths of methylene and hydroquinone.

One example is detailed here.

To a round bottom flask equipped with a stirrer was placed thionyl chloride 1.16 mL (6.0×10^{-3} mol) and added pyridine 6.23 mL (13.0×10^{-1} mol) dropwise under cooling with ice. After the addition was completed, the mixture was stirred for an additional 30 min. When the mixture was cooled in an ice-bath to 2-3 °C, a solution of 4 (1.21 g, 1.5×10^{-3} mol) in pyridine 10 mL was slowly added dropwise to the above mixture and then stirred for 30 min after removing the iced bath. To this mixture was added hydroquinone 0.17 g (1.5×10^{-3} mol) and then the reaction was completed at 80 °C for 24h under dry nitrogen atmosphere. Finally the solution was poured into methanol and the precipitated polymer was washed with methanol and distilled water three times respectively and dried in vacuum at 60 °C to yield the yellow polymer (1.21 g, 92%).

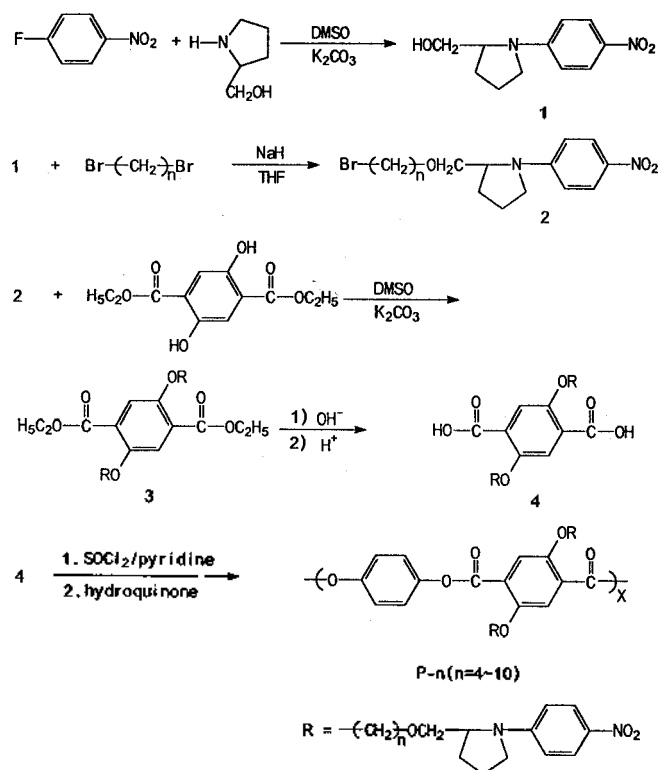
$^1\text{H NMR}$ (CDCl_3); δ (ppm) 1.6-2.2 (m, 24H, $-\text{CH}_2$), 3.1-3.7 (m, 12H, $\text{N}-\text{CH}_2$, $\text{O}-\text{CH}_2$), 3.9-4.1 (m, 2H, $\text{N}-\text{CH}$), 4.2-4.5 (t, 4H, $\text{Ph}-\text{O}-\text{CH}_2$), 6.6 (d, 4H, meta from NO_2), 7.3 (m, 4H, HQ), 7.6 (s, 2H, TPA), 8.2 (d, 4H, ortho from NO_2)

IR(cm^{-1}); 3070 (Ar. C-H str.), 2950 (ali. C-H str.), 1730 (C=O str.), 1620 (Ar. C=C str.), 1512 (N-O str.), 1310 (C-O str.) Anal. calcd: $n=4$ (C, 64.06; H, 5.88; N, 6.79), $n=5$ (C, 64.77; H, 6.16; N, 6.57), $n=6$ (C, 65.43; H, 6.42; N, 6.36), $n=7$ (C, 66.05; H, 6.67; N, 6.16), $n=8$ (C, 66.64; H, 6.90; N, 5.98), $n=9$ (C, 67.19; H, 7.12; N, 5.80), $n=10$ (C, 67.71; H, 7.32; N, 5.64)

Found: $n=4$ (C, 65.25; H, 5.81; N, 6.90), $n=5$ (C, 64.92; H, 6.33; N, 6.36), $n=6$ (C, 65.23; H, 6.22; N, 6.09), $n=7$ (C, 65.96; H, 6.82; N, 6.41), $n=8$ (C, 67.11; H, 6.74; N, 5.98), $n=9$ (C, 67.48; H, 7.03; N, 6.16), $n=10$ (C, 67.40; H, 7.59; N, 5.90)

Film preparation and poling

For the SHG measurements, the polymer solutions were prepared in a mixed solvent of phenol/tetrachloroethane (1 : 2 v/v) with a concentration of 5-10 wt%. The solution was first passed through a 0.50 μm filter (Milipore) to remove



Scheme 1. Synthetic routes of monomers and polymers.

particle impurities. A thin film (~ 2 μm thick) was prepared on a substrate (usually ITO glass) by spinning at 2000-4000 rpm. The spin-coated samples were placed in a vacuum oven at 60 °C for over 24h to obtain solvent free films. The corona discharge method was used to pole the sample, and a positive voltage of 5 kV was applied to a sharp tungsten needle located 10 mm in front of the grounded electrode. Poling was performed for 15 min at $T_g + 15$ °C.

SHG measurements

Second harmonic measurements were made by the Maker fringe method⁸ with an Nd:YAG laser operating at 1.064 μm . The set-up will be fully described elsewhere. A quartz reference, which also monitored the laser power, and the sample were measured simultaneously throughout the course of experiments. The second harmonic intensity was compared with the second harmonic generated by a Y-cut quartz crystal (1 mm thick).

Results and Discussion

Synthesis of Monomers and Polymers. The synthetic scheme of the chromophore monomers and polymers is shown in Scheme 1. All of the intermediate compounds and polymers gave satisfactory NMR and elemental analysis results. The reactions of 1 with dibromoalkanes were carried out easily, but the product 3 ($n=4-6$) was separated using a silica gel preparatory column. All of the polymers were prepared by the direct solution polycondensation instead of melt polymerization to reduce possible side reactions. A chromophore-containing aromatic dicarboxylic acid chloride was obtained by treating thionylchloride, and reacted with hydro-

Table 1. General Properties of the Polymers

Polymer P-n	Yield %	η_{inh} (dl/g) ^a	Tg, °C	Tm, °C
P-4	92	0.38	68	148
P-5	95	0.89	63	90
P-6	92	0.29	56	89
P-7	95	0.67	50	n.o. ^b
P-8	91	0.20	41	n.o.
P-9	90	0.10	34	n.o.
P-10	92	0.33	30	n.o.

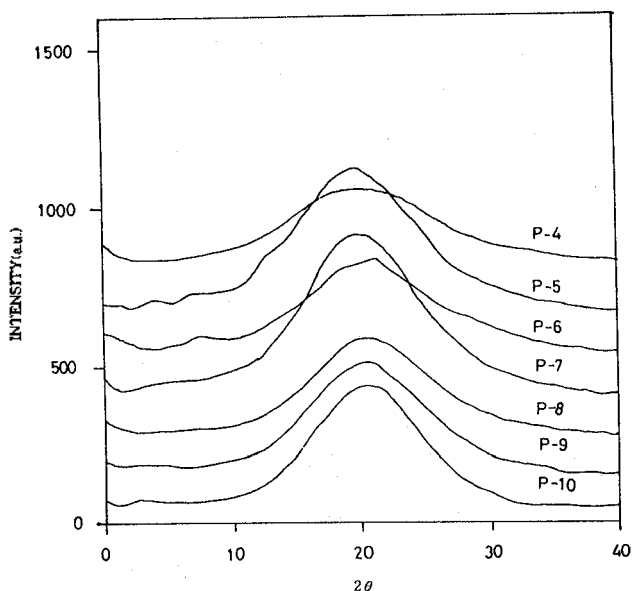
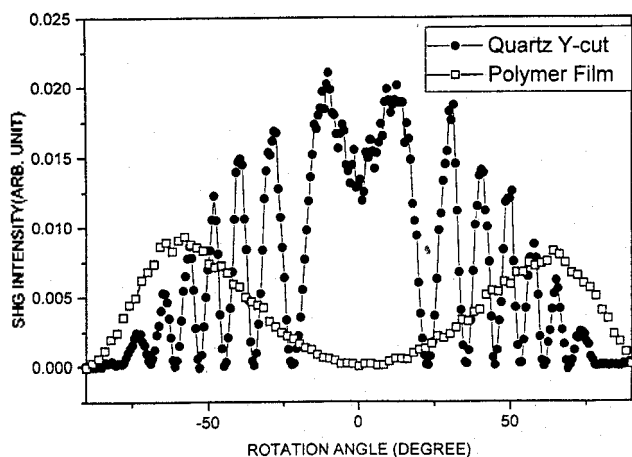
^aTg and Tm represent for the glass transition and melting transition temperature respectively. ^bNot observed.

quinone in pyridine under an atmosphere of nitrogen at 80 °C. The polymer obtained is a yellow powder, soluble in common organic solvents such as tetrachloroethane, CHCl₃ and mixed solvents consisting of phenol and tetrachloroethane. The inherent viscosities of the polymers measured at a concentration of C=0.1 g/dL ranged from 0.20 to 0.89 dL/g and proved the polymeric character of all polymers.

Properties of Polymers. In this report, we present briefly the data on the phase behavior and qualitative SHG properties of the polymers p-4 to p-10 having a spacer of carbon atoms n=4-10, and the quantitative measurements of NLO properties and the other physicochemical studies are currently being made and will be reported in a forthcoming publication.

Phase Behavior of Polymers. It is now well known that the polyesters based on hydroquinone and 2,5-dialkoxy terephthalic acid exhibit a nematic mesophase and layered structures in the solid state as well as in the mesophase depending on the number of carbon atoms in the alkoxy side chain.^{9,10} Contrary to this expectations no liquid crystalline behavior was observed for all the polymers prepared in this study. DSC thermograms showed a glass transition only from 30 °C to 68 °C for the various polymers having different number of methylene spacers (Table 1). Complementary polarizing optical microscopy (not shown here) corroborated the result of DSC experiments. At no temperatures were optical textures indicative of liquid crystalline phases observed in any sample studied. In accord with the above results, the WAXS patterns as shown in Figure 1 resulted in a broad halo typical of a liquid-like short range order. In the material with shorter spacer lengths of n=4-6, a weak melting transition ($\Delta H_m=1-3$ J/mole) was detected by DSC between 100 °C and 150 °C. This result, which is initially surprising, indicates that the strong dipole character of an appended NLO chromophore disturbs mesophase formation and lowers the transition temperatures. In addition, the concentration of rigid main chain relative to side groups is rather low compared to conventional main chain polymers causing side groups break apart significantly the host polymer.

To demonstrate NLO characteristics of the prepared polymers, a comparison of second harmonic intensity obtained from spin coated polymer films and a Y-cut quartz crystal of thickness 1 mm. The second harmonic intensity was measured using p-polarized fundamental and p-polarized second

**Figure 1.** Wide angle X-ray diffractograms of the polymers.**Figure 2.** Maker fringe curve showing SHG intensity vs θ for the reference (Quartz Y-cut 1.0 mm thick) and for the Polymer (P-4).

harmonic light. The thickness of the polymer film ranged from 1 to 3 μm as measured by an M-line waveguide technique. Figure 2 shows Maker fringes of a polymer (n=4) and a reference quartz. Here θ is the angle between the propagation direction and the normal to the film surface. The SHG intensity is zero at 0° and grows around this angle, indicating that after poling the average dipole moment of the polymer is perpendicular to the film surface. The most interesting aspect of these SHG intensities is in their magnitudes. The second harmonic intensity value of this polymer of thickness around 1 μm is comparable to that of a Y-cut quartz ($d_{11}=0.4$ pm/V) whose thickness is 1 mm. The UV-Visible absorption of the polymer at the second harmonic wavelength ($\lambda=532$ nm) is neglectable (Figure 3) and therefore the obtained SHG intensities are essentially not resonance enhanced. This surprisingly high intensities for this system might be attributed to high levels of chromophore substitution and

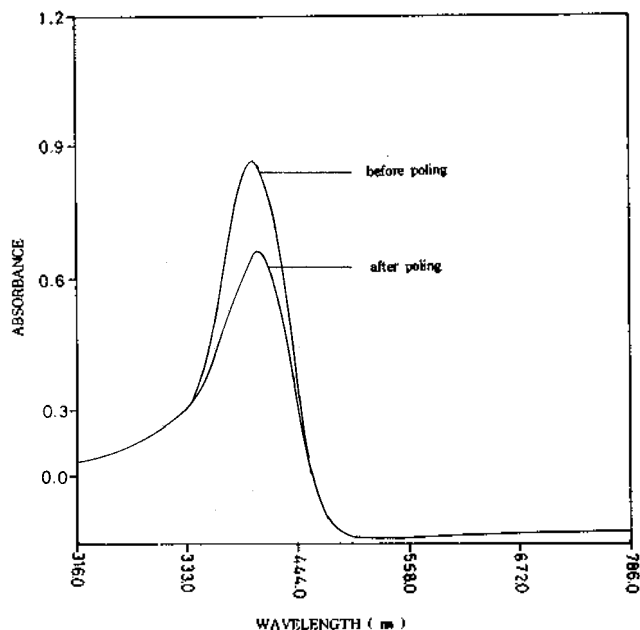


Figure 3. UV-Visible absorption spectra of a polymer film (P-4), before and after poling.

to enhanced ordering of the chromophore due to the semi-rigid nature of the main chain. Note that in a solid solution (guest-host system) in PMMA, the concentration of chromophores is limited by the aggregation problem to about 12 wt%.^{11,12} However the fractional mass of the chromophore in the polymer prepared in this study was estimated to be about 54% ($n=4$). In addition to the chromophore concentration, enhancing factors that cause high SHG intensity values may include minimal dipole pairing due to attachment at the rigid system. At this stage, since very little is known about the exact structures of these polymers, we can only consider that because of their stiffness and shape anisotropy, relatively stiff main chains tend to order themselves in more or less parallel arrays during a spin coating process and impart to the system parallel alignment of dipole and hence a facilitated chromophore alignment in the poling stage. As expected, we observed also that significant SHG signal appeared from unpoled samples not shown here and the fringe patterns as in Figure 2 were not completely symmetric. This indicates that the films are not isotropic in the through-plane direction and the chromophores are preferentially aligned by themselves parallel to the main chains.

Conclusion

A series of fully aromatic polyesters having pendant NLO

chromophores with different spacer lengths was obtained via a solution polycondensation. These polymers were soluble in a common organic solvent and can easily be processed into thin films of optical quality. DSC, optical polarizing microscopy and WAXS analysis showed that none of these polymers exhibit liquid crystalline mesophases. The absence of liquid crystallinity in these polymers may be attributed to the greater randomness arising from the strong dipolar interaction of the chromophores. Preliminary results on the NLO properties of these polymers showed surprisingly large second harmonic signals. This high magnitude of second harmonic intensity value might be attributed to the high chromophore density and order parameters.

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