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Synthesis and Characterization of New Polymers Exhibiting Large Optical Nonlinearities. 3. Rigid-Rod/Flexible-Chain Copolymers

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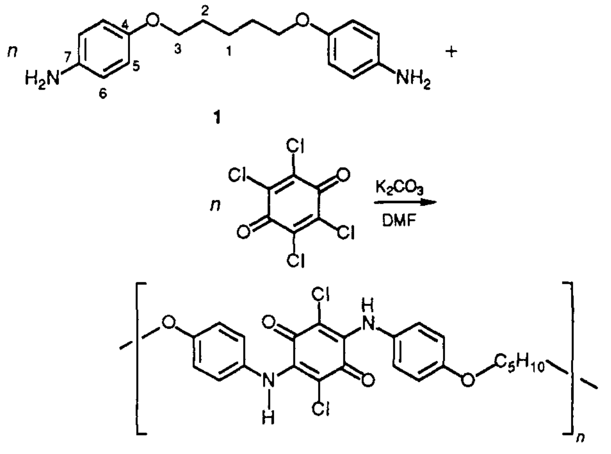
Abstract: As part of a continuing exploration of organic and organometallic polymers as nonlinear optical materials, a new copolymer with triphenodioxazine rigid-rod and aliphatic flexible-chain segments has been synthesized. This copolymer exhibits improved processibility and a defined absorption band edge (with an optical spectrum nearly identical with that of the oligomeric triphenodioxazine model compound) when compared to traditional electroactive polymers, which exhibit poor solubility and a diffuse band edge (partly due to polymer heterogeneity and disorder). Degenerate four-wave mixing (DFWM) measurements for polymer a, an open-chain version of triphenodioxazine, indicate a third-order susceptibility of 4.5×10^{-9} esu, which demonstrates that no significant sacrifice of optical nonlinearity is required to obtain the desired properties. This study reports a limited investigation of both the temporal response and frequency dependence of the observed optical nonlinearity. By control of reaction conditions, the preparation of several versions of the copolymer is demonstrated, providing insight both into structural electronic property relationships and the role that structure plays in determining solubility.

Organic polymeric materials with conjugated π-orbital systems have been shown to exhibit ultrafast, very large nonlinear optical response.[1-3] This rapidly growing area of research may lead to promising applications for polymeric materials in optoelectronic devices such as optical computing, sensor protection, and dynamic holography, etc. The basic requirement for practical applications of these materials is a high nonresonant nonlinear third-order susceptibility, such as $\chi^{(3)}$ of 10^{-8}–10^{-9} esu accompanied by low optical loss, e.g., an absorption coefficiency <1 cm^{-1}. The polymers that have been investigated to date have the disadvantage of polydispersity, which smears the optical absorption band structure. This disadvantage will unavoidably result in resonant contributions to the optical nonlinearity in these polymers, as has been observed.[3] Theoretical studies show that, in polyconjugated systems, π-electron delocalization is limited by electron–phonon and electron–electron interaction.[4-6] Consequently, the third-order NLO response will increase as the conjugation length increases for short conjugation length and then begin to saturate to some finite length. For example, in polyene systems, theory predicts that, after 15 double bonds, the third-order susceptibility begins to saturate.[6] These results suggest that, in order to have a large optical nonlinearity, it is not necessary to have a large conjugated system within the polymer. Incorporation of finite chain length NLO-active units into processible polymers will provide materials with NLO properties similar to those found in extended conjugation polymers. On the basis of this observation, we have synthesized copolymers with rigid-rod and flexible-chain segments. We have shown that ladder polymers with quinodioxaline-type units have large third-order susceptibilities.[7,8] Triphenodioxazine is a well-known dye material,[9] which has an extended π-electron delocalization over a five-fused-ring unit that should be NLO active.[10] We have succeeded in preparing a copolymer with triphenodioxazine and a flexible-chain spacer. This polymer has a clearly defined optical band gap, good processibility, and high thermal stability. Degenerate four-wave mixing (DFWM) measurements reveal unusually large optical nonlinearity: $\chi^{(3)}$ values as high as 4.5×10^{-9} esu for polymer a, an open-chain version of triphenodioxazine, have been observed. In this report, we focus on the synthesis and characterization of this copolymer; a detailed description of NLO measurements will be given elsewhere.[11]

Results and Discussion

The reaction of **1** and chloranil to synthesize the prepolymer (see reaction 1) can be carried out in several different solvents.



(1)

prepolymer

2

Ethanol, pyridine, and DMF have been tested. It was found that the prepolymer will immediately precipitate out of ethanol and pyridine media, and the molecular weights, consequently, are small. DMF is a better choice. The prepolymer so obtained is only partially soluble in DMF and insoluble in ethanol, pyridine, acetone, and chloroform, which probably reflects the effect of hydrogen bonding in the prepolymer.

The FTIR spectrum of the prepolymer shows a peak at 3230 cm^{-1} from >N–H stretching and two peaks at 2937 and 2867 cm^{-1}

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

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

(3) Heeger, A. J.; Orenstein, J.; Ulrich, D. R. *Nonlinear Optical Properties of Polymers*; Symposium Proceedings; Materials Research Society: 1988; Vol. 109.

(4) de Melo, C. P.; Silby, R. *Chem. Phys. Lett.* **1988**, *140*, 537.

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(6) Beratan, D. N.; Onuchic, J. N.; Perry, J. W. *J. Phys. Chem.* **1987**, *91*, 2696.

(7) Yu, L. P.; Dalton, L. R. *Synth. Met.* **1989**, *29*, E-463.

(8) Yu, L. P.; Dalton, L. R., submitted for publication in *J. Am. Chem. Soc.*

(9) K. Venkataraman. *The Chemistry of Synthetic Dyes*; Academic Press: New York, 1952; Vol. II.

(10) Martino, R. Private communication. Unpublished computations from Hoechst Celanese, for example, give γ values of aminonitro-substituted five-fused-ring oligomers of 24.8-64.3 $\times$ 10^{-35} esu, depending on the position of the nitro substituent.

(11) Cao, X. F.; Jiang, J. P.; Hellwarth, R. W.; Yu, L. P.; Dalton, L. R., in preparation.

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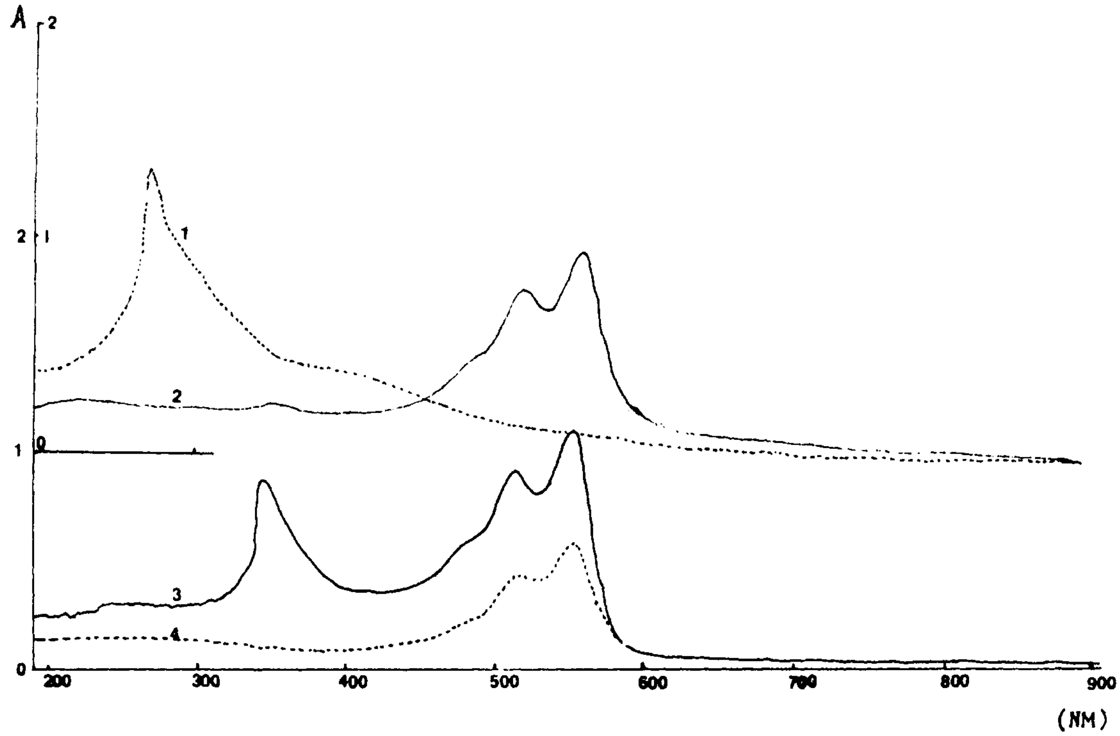
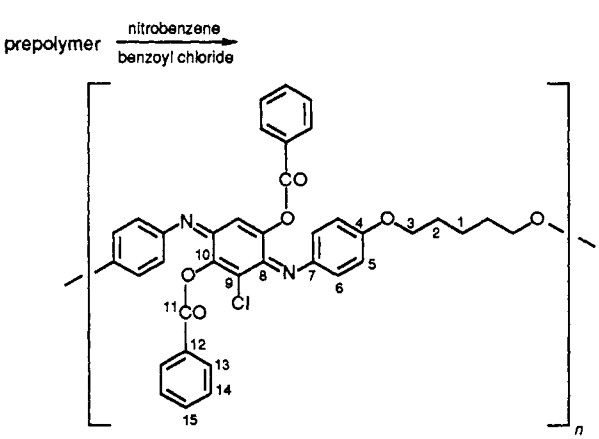


Figure 1. UV/vis spectra of **1**, the prepolymer, **2**, polymer b, **3**, polymer a, and **4**, model compound, 3,10-dimethoxy-6,13-triphenodioxazine.

from $-(CH_2)-$ stretching. The peak at 1600 cm^{-1} due to the quinone carbonyl group and an absorption band around 1250 cm^{-1} due to –O–C– stretching can be observed. The UV/vis spectrum of the prepolymer (see curve 1 in Figure 1) shows two absorption bands at 280 and 405 nm, which correspond to $n-\pi^*$ and $\pi-\pi^*$ transitions of amine and quinone units.

The formation of triphenodioxazine from 2,4-(diarylamino)-3,5-dichloroquinone (**2**) is via a Friedel–Crafts reaction. Many Friedel–Crafts catalysts have been used in the cyclization of **2**, such as $AlCl_3$, P_2O_5, PCl_5, and benzoyl chloride,[11] with high boiling point solvents, such as nitrobenzene and trichlorobenzene. Further condensation of the prepolymer, therefore, has been tested with different media and catalysts. The first run of the reaction was carried out in nitrobenzene with benzoyl chloride as the catalyst (reaction 2). The color of the mixture changed from brown to red, which is the characteristic color of triphenodioxazine. The final polymer is soluble in DMF and 1-chloronaphthalene. Spectroscopic studies and elemental analysis indicate that the polymer is an open-chain copolymer, as shown in reaction 2, instead of cyclized triphenodioxazine copolymer.



(2)

polymer a

The FTIR spectrum of polymer a shows a strong carbonyl absorption at 1775 cm^{-1} from benzoyl groups. The absorption peak from >N–H at 3230 cm^{-1} in the prepolymer disappears, and a new peak around 3060 cm^{-1}, which can be assigned to aromatic proton stretching, appears. A peak at 1674 cm^{-1} due to >C=N– stretching can be observed. A very intense absorption at 700 cm^{-1} is typical of the out-of-plane deformation of monosubstituted benzene ring protons. The ^1H NMR spectrum of polymer a shows a broadened aromatic region accounting relatively for 18 protons. The aliphatic proton peaks are also broadened because of slowed molecular dynamics due to the increased polymer size (polymeric effect). Figure 2 is the ^{13}C NMR spectrum of polymer a. It can be seen that all of the peaks are broadened due to the polymeric effect. The aromatic carbons and carbonyl carbons of benzoyl chloride can be clearly seen. The assignments of the spectra support the proposed structure of polymer a.[12]

Further evidence for the proposed structure of polymer a comes from the UV/vis spectrum (see Figure 1). Curve 4 is the spectrum of the model compound, 3,10-dimethoxy-7,9-dichlorotriphenodioxazine,[13] and curve 3 is the spectrum of polymer a. These curves are identical in the visible region, which means they have similar $\pi-\pi^*$ transitions. Curve 3 is considerably different from the spectrum of the prepolymer (see curve 1 in Figure 1). New features in the UV/vis spectrum of polymer a are due to the introduction of benzoyl groups and the formation of a larger π-system.

Although polymer a is not a fully cyclized triphenodioxazine copolymer, it has these advantages: it is fully soluble in DMF, DMSO, and 1-chloronaphthalene, and optical quality films can be cast from the solutions. GPC measurements in DMF show that the weight average molecular weight of polymer a, MW, is about 22 600 using polystyrene as the standard.

Polymer a is thermally stable up to 480 °C, except for a small percentage (2%), of weight loss at 330 °C, which might be caused by some impurities. DSC shows a T_g transition at 170 °C and a T_m transition around 250 °C.

To get a fully cyclized copolymer, several different reaction methods were attempted. Since it is well-known that this cyclization is an oxidative ring-closure process, we believe that the reaction could be promoted by the addition of oxidative agents.

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[12] Pretsch, E.; Seibl, J.; Simon, W.; Clerc, T. *Tables of Spectral Data for Structure Determination of Organic Compounds*; Springer-Verlag: Berlin, FRG, 1983.

[13] Note that the optical spectra of polymers a and b are similar, indicating comparable conjugations, and that both are similar to the model compound, thus arguing for similar conjugation in all three systems.

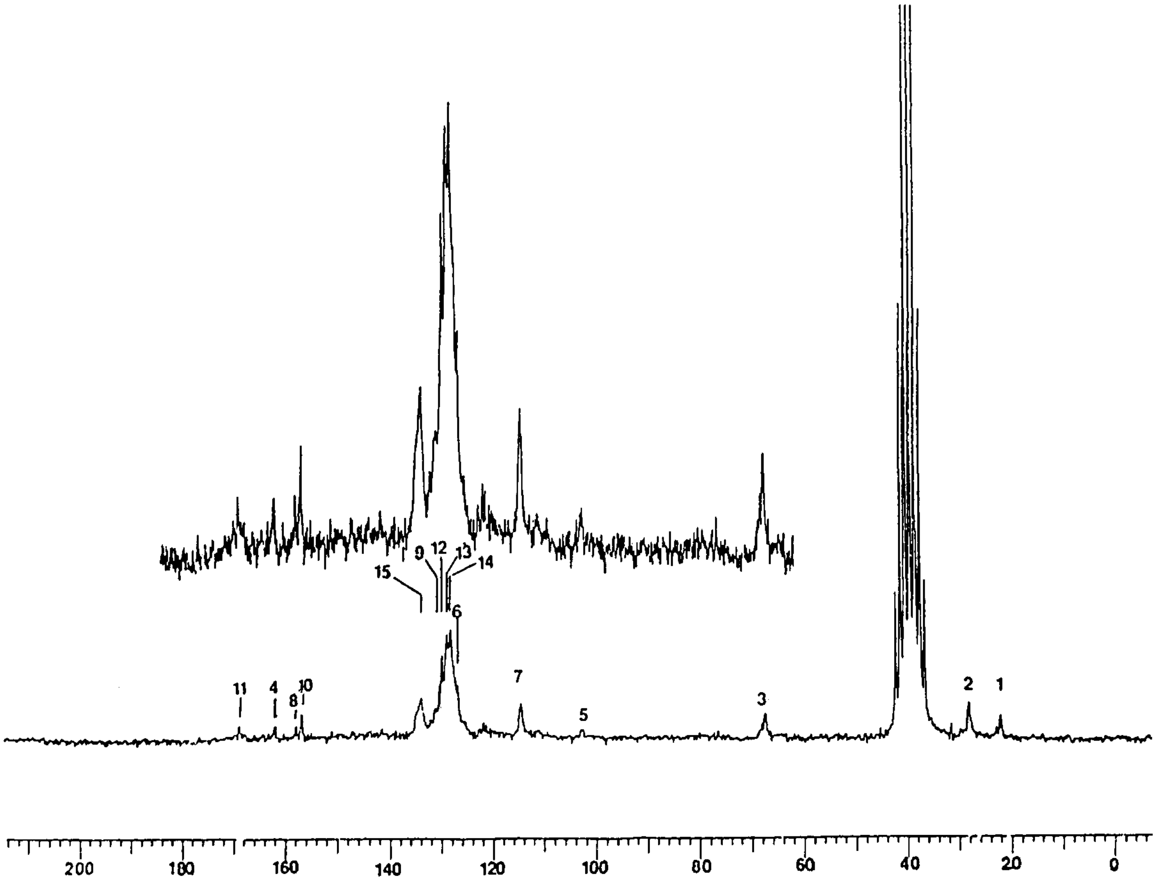


Figure 2. ^{13}C NMR spectrum of polymer a in DMSO-d_6.

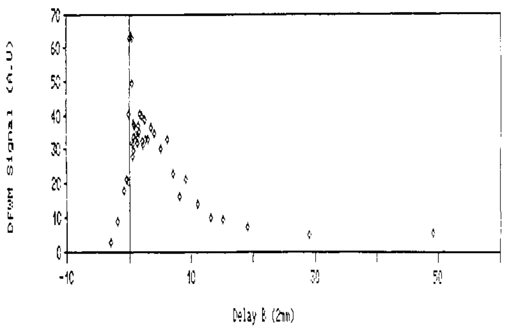
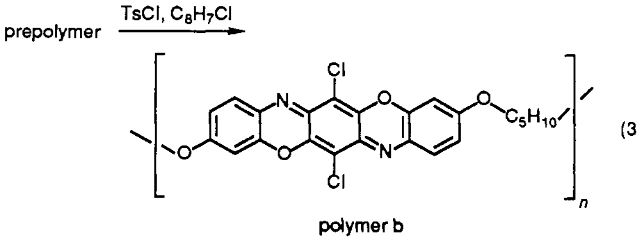


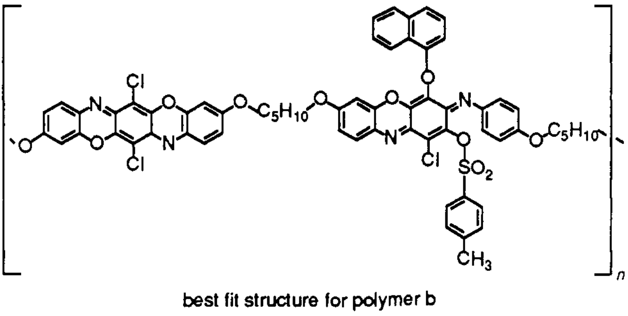
Figure 3. DFWM signal pulse energy vs delay time for polymer a.

Thus, when a small amount of iodine (1%) is added to the nitrobenzene and benzoyl chloride reaction media, the rate of reaction is accelerated. Only 1 h is needed to complete the reaction, but the structure of the final polymer is the same as that of polymer a. P_2O_5 and PCl_5 in nitrobenzene and dichlorobenzene yield intractable black solids. However, when *p*-toluenesulfonyl chloride is utilized as the catalyst in 1-chloronaphthalene, cyclization occurs.

Polymer b is soluble in 1-chloronaphthalene and partially soluble in DMF. The FTIR spectrum of polymer b is similar to that of the model compound and shows a marked change from that of polymer a. The carbonyl absorption at 1775 cm^{-1} in polymer a is absent in polymer b. The peak due to >C=N– appears at 1627 cm^{-1}, and the out-of-plane deformation peaks due to aromatic protons have changed from the 1,4-substituted pattern (831 cm^{-1}) of the prepolymer and polymer a to the 1,2,4-substituted pattern (773, 826, 872 cm^{-1}) of polymer b. Elemental analysis shows a discrepancy between the theoretical and experimental values. This can be reconciled by assuming that the final polymer structure is less perfect than expected and that side reactions might have accompanied the cyclization reaction. The following polymer structure gives a very good fit of elemental analysis data.



(3)



best fit structure for polymer b

The UV/vis spectrum of polymer a is identical with that of the model compound (see curve 2 in Figure 1). Three peaks in the visible region (479, 515, 567 nm) can be observed. It can be seen that both polymer a and polymer b show sharply defined optical absorption band edges at about 585 nm (see Figure 1). This is an advantage for NLO studies, since one can more easily determine the nonresonant contribution to the NLO process.

TGA studies indicate that polymer b is thermally stable up to 360 °C. It was realized that this polymer had the potential to exhibit liquid crystallinity. However, DSC shows that no thermal process occurs below 300 °C. Since this may reflect the length of the flexible-chain spacer groups, synthesis of copolymers with longer spacers is in progress.

GPC study of the soluble portion of polymer b in DMF shows a multipeak distribution pattern with a weight average molecular

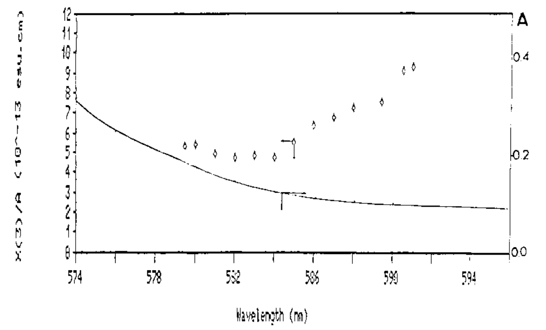


Figure 4. $\chi^{(3)}/\alpha$ and linear absorption spectra.

weight varying from 25 500 to 84 300. Since we use polystyrene as standard, these values seem to be overestimated according to the film quality of this polymer.

DFWM measurements have been performed on both polymer a and polymer b, which were cast on glass plates. Film from polymer b has a large light scattering because the polymer is easy to aggregate when films are prepared due to limited solubility. This results in a DFWM signal for polymer b with a large amount of noise. Accurate results are yet to be determined and will be reported separately. According to our current observation, polymer a and polymer b have similar NLO behavior. Figure 3 shows a plot of the DFWM signal pulse energy versus the delay time of the backward pump beam B for polymer a: each data point is an average over 10–20 pulse energy fluctuations of the order of 20%. In this figure, all polarizations are vertical to the delay beam B. From Figure 3, we can see an extremely fast NLO process at zero delay time and a slower NLO process. The physical meanings of these processes are not fully understood yet, but it can be reasonably assumed that the former process is from the contribution of virtual electronic excitation while the latter one arises from the resonant electronic contribution. Figure 4 shows the linear and third-order DFWM signals as a function of incident laser frequency. It can be seen that the $\chi^{(3)}$ values are very large; the $\chi^{(3)}/\alpha$ value falls into the range of 10^{-12}–10^{-13} esu·cm. In Figure 4, it would appear that $\chi^{(3)}/\alpha$ values may increase at lower frequencies. This observation should be treated with care, because the error in measurements would also be expected to increase due to the lower signal to noise ratio in both the third-order and linear optical measurements. If the phenomenon is real, it is indeed intriguing and deserves further investigation.

Conclusion

The results of the current study of the NLO properties of a rigid-rod/flexible-chain copolymer clearly show that it is possible to improve the processibility of existing conjugated polymers without sacrificing optical nonlinearity, which is consistent with theoretical prediction. It is important to note from this work that incorporation of dye molecules into a polymer backbone is an appropriate research direction to pursue in order to promote the third-order NLO properties of polymeric materials.

Experimental Section

Reagents and solvents are analytical-grade quality, purchased commercially, and used without further purification unless otherwise noted. Chloranil was recrystallized from toluene.

1,5-Bis(4-aminophenylene-1-oxy)pentane (1). This compound was synthesized from the corresponding dinitro compound by hydrogenation at 50 atm using Pd/activated carbon as catalyst in THF. ^{1}H NMR ($CDCl_3$): δ 1.75 (quint, 6 H, $-(CH_2)_3-$), 3.25 (s, 4 H, NH_2), 3.85 (t, 4 H, $-OCH_2-$), 6.65 (d, 8 H, aromatic proton). ^{13}C NMR ($CDCl_3$): δ 22.0 (C_1), 29.0 (C_2), 78.0 (C_3), 115.6 (C_6), 116.0 (C_5), 140.0 (C_7), 152.0 (C_4).

Anal. Calcd for $C_{17}H_{22}N_2O_2$: C, 71.32; H, 7.69; N, 9.79. Found: C, 71.41; H, 7.76; N, 9.72.

3,10-Dimethoxy-7,9-dichlorotriphenodioxazine. 3,10-Dimethoxy-7,9-dichlorotriphenodioxazine is synthesized from 3,6-bis[(*p*-methoxybenzene)amino]-2,5-dichloroquinone (II). Compound II (2 g, 4.77 mmol) and *p*-toluenesulfonyl chloride (2 g, 10.5 mmol) were ground and added to 1-chloronaphthalene (20 mL). The mixture was refluxed for 1 h and then cooled to room temperature and filtered. The residue was washed with methanol, water, and finally methanol and was dried under vacuum.

Anal. Calcd for $C_{20}H_{12}Cl_2N_2O_2$: C, 57.83; H, 2.87; N, 6.75; Cl, 17.11. Found: C, 57.48; H, 3.07; N, 6.65; Cl, 16.93.

Prepolymer. Compound **1** (2 g, 6.993 mmol) was mixed with potassium acetate (3.432 g, 35 mmol) in DMF (10 mL). Chloranil (1.7204 g, 6.993 mmol) in DMF (20 mL) was then added dropwise with vigorous stirring. The resulting green solution was refluxed for 6 h and then poured into methanol (100 mL). A brown solid was collected by filtration and washed by water and then methanol. The final product was dried under vacuum at 60 °C overnight, yielding the prepolymer (2.99 g, 93%).

Anal. Calcd for $(C_{23}H_{20}N_2Cl_2O_4)_n$: C, 60.13; H, 4.35; N, 6.10; Cl, 15.47. Found: C, 60.22; H, 4.42; N, 6.06; Cl, 15.37.

Polymer a. Prepolymer (0.904 g, 1.97 mmol) was mixed with nitrobenzene (15 mL) and benzoyl chloride (3 mL), and then the solution was refluxed. During the first 15 min, the color of the mixture changed from brown to red. After 4 h, the reaction mixture was poured into methanol (50 mL) and the red precipitate was collected by filtration and washed with methanol until the filtrate became colorless, yielding polymer a (1.09 g, 83%). ^{1}H NMR (DMSO): δ 1.6 (broadened, 6 H), 3.9 (broadened, 4 H), 6.5–8.2 (broadened, 18 H). ^{13}C NMR (DMSO): see Figure 4.

Anal. Calcd for $(C_{37}H_{28}N_2Cl_2O_6)_n$: C, 66.56; H, 4.20; N, 4.20; Cl, 10.64. Found: C, 66.12; H, 3.87; N, 3.75; Cl, 11.45.

Polymer b. Prepolymer (0.3 g, 0.65 mmol) was ground with *p*-toluenesulfonyl chloride (0.3 g, 1.57 mmol). The mixture was added to 1-chloronaphthalene, 10 mL), and the solution refluxed for 30 min. The mixture was then filtered hot, and the filtrate was cooled and poured into methanol (50 mL). The red solid was collected by filtration and washed with methanol and acetone, yielding polymer b (0.15 g, 50%).

Anal. Calcd for $(C_{23}H_{16}N_2Cl_2O_4)_n$: C, 60.65; H, 3.52; N, 6.15; Cl, 15.60. Found: C, 64.04; H, 3.86; N, 4.73; Cl, 8.41. Best fit structure: C, 64.42; H, 4.05; N, 4.77; Cl, 9.07.

Characterization of the Polymer. FTIR spectra of pressed KBr pellets were taken using a 1760 Perkin-Elmer FTIR spectrometer. UV/vis spectra were obtained in DMF and 1-chloronaphthalene as noted using a Perkin-Elmer Lambda 4C UV/vis spectrophotometer. Thermal analyses were performed using Perkin-Elmer DSC-7 and TGA-7 systems with a heating rate of 20 °C/min. GPC analysis was performed employing a Hewlett-Packard 1090 liquid chromatograph. NMR spectra were recorded on JEOL FX 90 Q FTNMR spectrometer.

NLO measurements were performed using degenerate four-wave mixing (DFWM). A "phase conjugation" geometry for DFWM is employed in which all four beam polarizations can be varied to give independent data. Three input beams are formed from a dye laser pulse pumped by a Quantel Model YG 471-C Nd:YAG laser. Frequency can be changed by changing the dye molecule.

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Registry No. 1, 2391-56-2; (**1**)(chloranil) (copolymer), 122847-53-4; (**1**)(chloranil) (SRU), 122847-54-5; II, 17123-21-6; a, 122847-55-6; 1,5-bis(4-nitrophenoxy)pentane, 14467-60-8; 3,10-dimethoxy-6,13-dichlorotriphenodioxazine, 21839-60-1.