AD-A280 210

Organic NonLinear Optical Polymers. 6. High Performance

Materials Based on the Poly(*p*-phenylene) Backbone
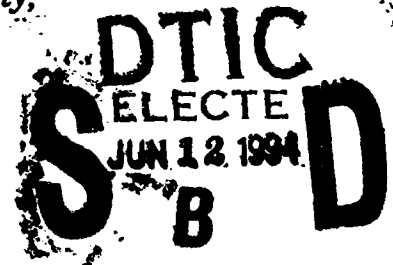
by

Michael E. Wright and Edward G. Toplikar

Department of Chemistry & Biochemistry, Utah State University,
Logan, Utah 84322-0300

Hilary S. Lackritz and Suchitra Subramanyan

School of Chemical Engineering, Purdue University,
West Lafayette, IN 47907-1283

Submitted to

Makromol. Chemie, Rapid Commun.

94-18008

May 28, 1994

DTIC QUALITY INSPECTED 1

94 6 10 117

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 28, 1994	3. REPORT TYPE AND DATES COVERED 1 June, 1993 - 31 May, 1994

4. TITLE AND SUBTITLE
Organic NonLinear Optical Polymers. 6. High Performance Materials Based on the Poly(p-phenylene) Backbone

5. FUNDING NUMBERS
N00014-91-J-1625
R&T 4132051

6. AUTHOR(S)
Michael E. Wright, Edward G. Toplikar, Hilary S. Lackritz, and Suchitra Subrahmanyan

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Utah State University
Department of Chemistry & Biochemistry
Logan, UT 84322-0300

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report #22

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Department of the Navy   ONR Scientific Officer
Office of Naval Research   Dr. Kenneth J. Wynne
800 North Quincy Street   (703) 696-4409
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Submitted to *Makromol. Chemie, Rapid Commun.*

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

This paper describes preliminary work exploring the feasibility of preparing high-performance NLO-materials based on the poly(p-phenylene) (PPP) backbone. Three new monomer/NLO-phores of the general formula: $4\text{-}RSO_2C_6H_4C \equiv C(4\text{-}XC_6H_4)$ [where R = 2,5-dichlorophenyl; **2a**, X = H; **2b**, X = OMe; **2c**, X = NMe$_2$] were synthesized and then homopolymerized using catalytic nickel and stoichiometric zinc to produce the poly(p-phenylenes), **3a-c**, respectively, as low molecular weight materials (M_n = 1800-6000). Both NLO-phores (**2b-c**) dispersed in PMMA displayed good SHG signal stability at ambient temperature (~12% loss/100 h). The oligomeric materials dispersed in PMMA showed a lower magnitude of $\chi^{(2)}$ or no NLO signal. Attempts to induce dipolar asymmetry in the homopolymers **3b** and **3c** by corona poling were unsuccessful.

14. SUBJECT TERMS
NonLinear Optical, Corona Poling, High Performance Polymers, Polyphenylene

15. NUMBER OF PAGES
24 pages

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL

Organic NonLinear Optical Polymers. 6. High Performance Materials Based on the Poly(p-phenylene) Backbone

Michael E. Wright* and Edward G. Toplikar
Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Hilary S. Lackritz* and Suchitra Subrahmanyan
School of Chemical Engineering, Purdue University, West LaFayette, Indiana 47907-1283

[For Chemical Abstracts and Review Purposes]

Summary. This paper describes preliminary work exploring the feasibility of preparing high-performance NLO-materials based on the poly(p-phenylene) (PPP) backbone. Three new monomer/NLO-phores of the general formula: $4\text{-}RSO_2C_6H_4C=C(4\text{-}XC_6H_4)$ [where R = 2,5-dichlorophenyl; **2a**, X = H; **2b**, X= OMe; **2c**, X= NMe_2] were synthesized and then homopolymerized using catalytic nickel and stoichiometric zinc to produce the poly(p-phenylenes), **3a-c**, respectively, as low molecular weight materials (M_n = 1800-6000). NLO-phores **2b-c** and low molecular weight oligomers of **3c** were dispersed in PMMA and films were subjected to corona poling. Both monomer/NLO-phore guest-host systems displayed $\chi^{(2)}$ activity, with **2c** exhibiting a signal of 1.7 pm/V and **2b** exhibiting a signal of 0.9 pm/V. Both NLO-phores displayed good temporal stability at ambient temperature (~12% loss/100 h). The oligomeric materials dispersed in PMMA showed a lower magnitude of $\chi^{(2)}$ or no NLO signal. Attempts to induce dipolar asymmetry in the homopolymers **3b** and **3c** by corona poling were unsuccessful.

[End of Summary]

Introduction

Polymers show great promise in making materials with second order and third order nonlinear optical (NLO) properties and hence are of great importance in making optoelectronic devices.[1] The success of second order NLO materials lies in the temporal stability of $\chi^{(2)}$, the second order nonlinear optical susceptibility. $\chi^{(2)}$ materials, *i.e.* materials that generate second harmonic light, by definition must lack inversion symmetry.[2] Obtaining this dipolar asymmetry is usually accomplished by applying an electric field to orient the dipoles (permanent and induced) of the NLO-phores in the polymer matrix.[3] The issue crucial to obtaining long term stability is to make the polymer matrix very rigid and minimize the local mobility/local free volume so that the orientation of the NLO-phore does not randomize after removal of the applied electric field.[4] Many approaches have been taken to prepare thermally and temporally and stable NLO polymers (NLOPs) with high NLO effeciciency, including guest-host,[5] cross-linked,[6] side-chain,[7] and main-chain functionalized systems.[8] As NLO-polymeric materials are designed to be more rigid to retain NLO-phore alignment following poling, it has a counter-productive effect on the actual alignment process itself.[9] The manner by which the NLO-phore is covalently integrated within a rigid-polymer matrix (*e.g.* main-chain, side-chain, etc...) becomes a critical issue in determining the overall processability of the material.

In a continuing effort to synthesize novel materials which show significant $\chi^{(2)}$ activity and possess excellent temporal stability, we have synthesized the first high-performance, high-T_g NLOP based on the poly(*p*-phenylenes) (PPP) (see cartoon below).[10] The system is poised to utilize additive dipole moments from each NLO-phore to assist (or

2

drive) positioning of the polymer backbones but does not require global (end-on-end)

reorientation of the polymer chains for NLO-phore alignment.[11]
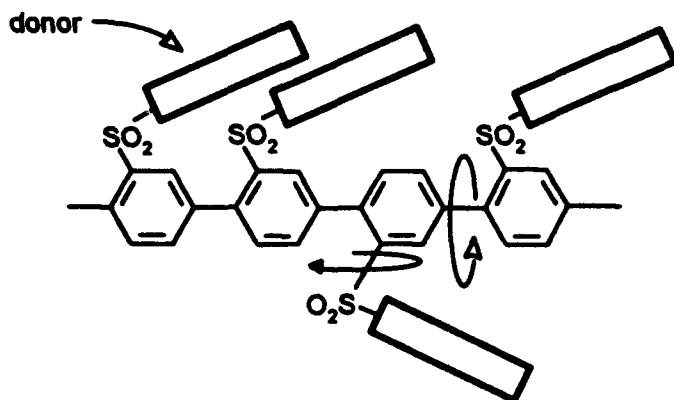
The temporal stability of $\chi^{(2)}$ for these systems has also been examined and characterized

from the polymer physics point of view.[12] Such an understanding of the structure-activity

relationship is very important since it will help polymer chemists to design future

generation materials with specific, tailorable optical or electronic properties. Herein we

present a preliminary report on the synthesis and NLO time-dependent spectroscopy of the

PPP-based NLO materials.

Results and Discussion

Monomer Synthesis and Characterization. Friedel-Crafts acylation of bromobenzene

with 2,5-dichlorobenzenesulfonyl chloride affords compound 1 in high yield.[13] Selective

Pd/Cu catalyzed alkynylation[14] of the aryl bromide functional group produces new NLO-

monomers 2a-c (Scheme 1).

Scheme 1
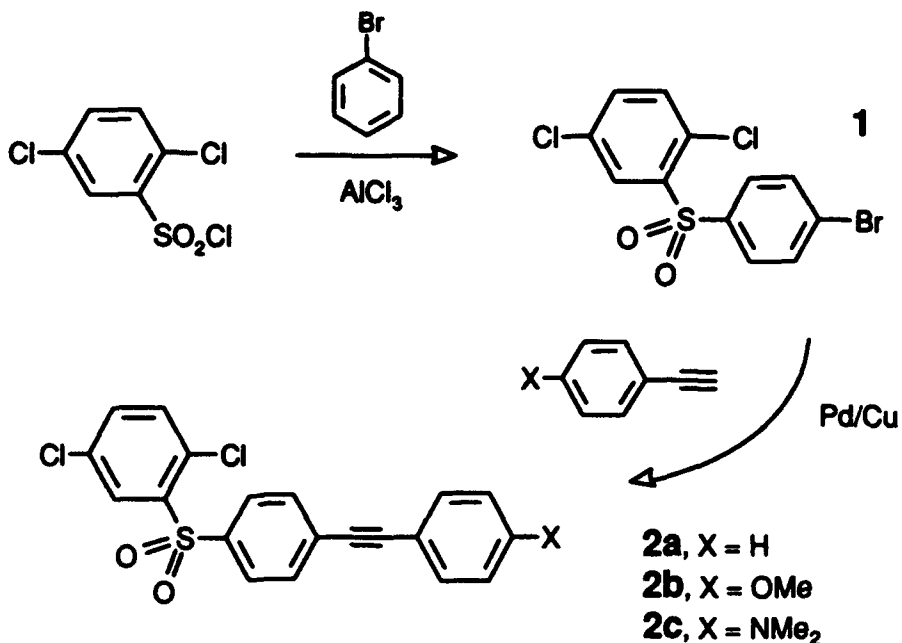
The NLO-phore **2c** has been characterized by a single-crystal x-ray diffraction study.
A drawing of the molecular structure is presented in Figure 1 along with the labeling
scheme employed. The compound crystallizes in the acentric orthorhombic space group
$P2_12_12_1$ with one molecule per asymmetric unit. The aromatic rings and the dimethyl
amino group are all coplanar as expected.[15] No significant averaging of the single (1.435
and 1.425 Å) and triple (1.192 Å) bonds connecting the donor and acceptor aryl rings is
observed.[15] The molecular structure assists in visualizing how the NLO-phore prefers to be
nearly orthogonal to what will become the linear axis of the polymer backbone upon
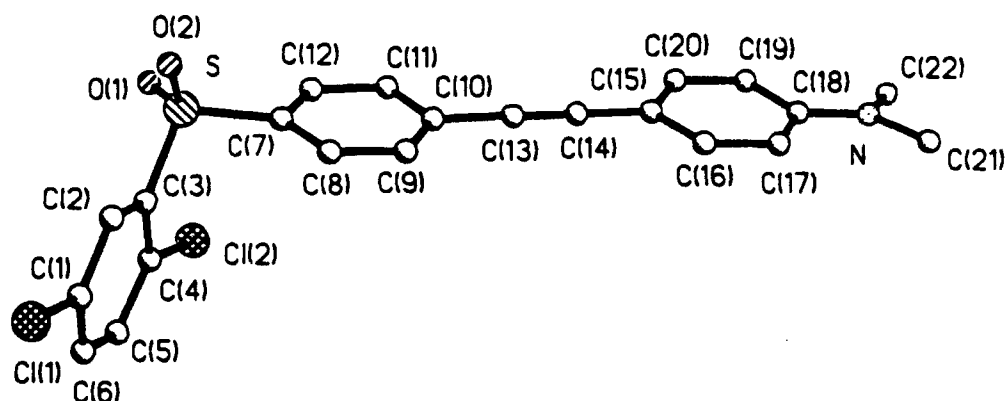polymerization.

4

Figure 1. Drawing of the molecular crystal structure of NLO-phore **2c** including the labeling scheme used.

Polymer Synthesis and Characterization. Homopolymerization of the monomers using a recent modification by Charturvedi and co-workers[16] affords poly(*p*-phenylene) derivatives of moderately low molecular weight. Fortuitously, the monomer containing the best NLO-phore, **2c**, afforded the highest molecular weight polymer (M_n = 6,000, PD = 1.5) and is also very soluble in common organic solvents. The polymerization of **2a** gives soluble oligomeric products (M_n = 1,800) and significant amounts of insoluble material. The insoluble material is most likely high molecular weight polymer. The polymerization of **2b** yields low molecular weight material (M_n= 3,900, PD =1.6). Attempts to increase the molecular weight by various methods, including the addition of more catalyst, have so far proved ineffective. For each polymer there is an absence of the Ar-Cl bond stretch in the infrared spectra.
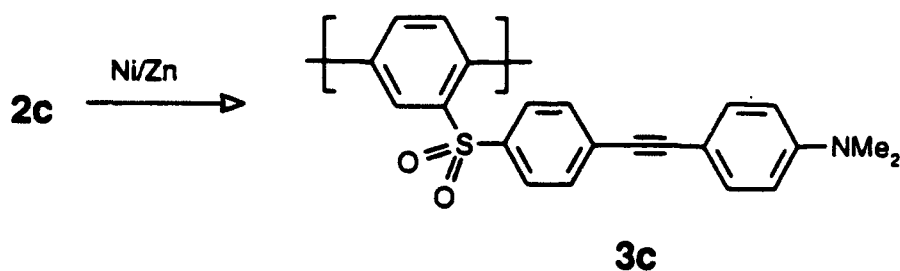
Polymer 3c shows reasonably good thermal stability as shown in the TGA trace and analysis by DSC shows a well defined T_g at 220 °C (Figure 2). The high T_g is indicative of high tacticity for poly(p-phenylenes).[17] To our knowledge this is one of the highest T_g NLOPs and contains an impressive 76 wt-% of the active NLO-phore.
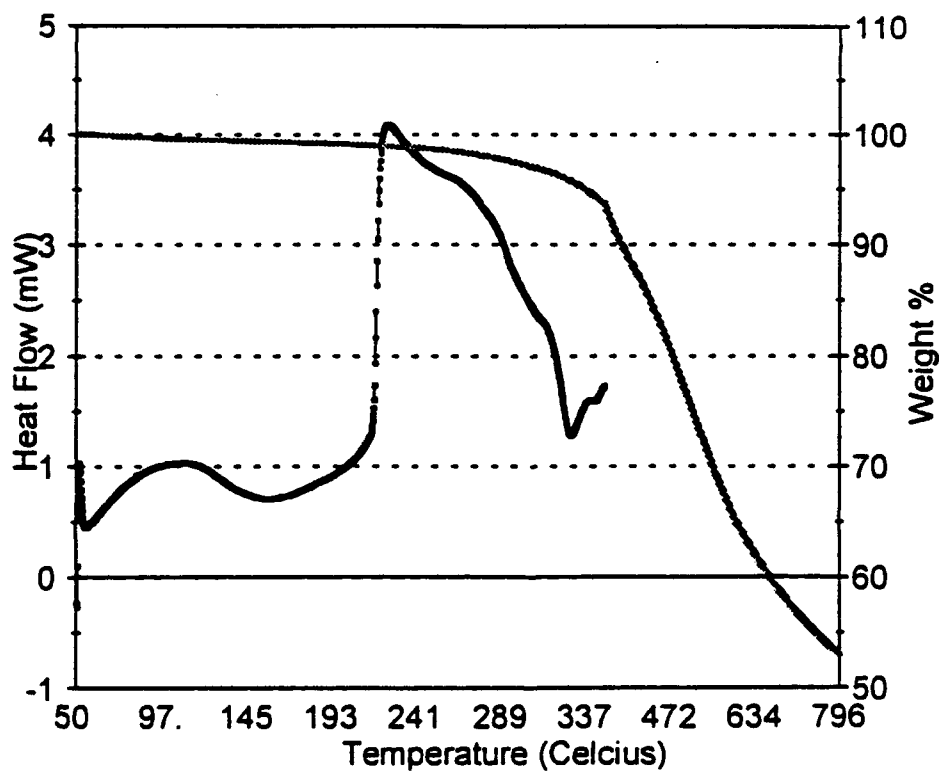

Figure 2. TGA and DSC analysis of polymer 3c under a nitrogen atmosphere. A ramp rate of 10 °C/min was used.

The thermal stability of polymer 3c was explored by recording UV-vis spectra for a film supported on a glass slide which was heated in air at 200 °C over a period of 24 h. Measurements were made by placing the glass slide directly in the spectrometer and using a blank slide for background. The data show a decrease in the absorption intensity (less than 10%) for λ_{max} over a period of 24 h, which indicates that some decomposition of the NLO-phore is taking place. This suggests that the NLOP is reasonably stable at temperatures near the T_g of 220 °C.

Second Harmonic Generation Experiments. The first SHG experiments were performed on systems of NLO-phores 2b-c dispersed in a PMMA polymer host (Figures 3-6). The orientation during poling and the relaxation following poling were studied as a function of time and processing conditions in both systems. A rapid increase in signal is observed as the corona field is applied (V_{pole} = 4.2 kV, T_{pole} = T_g + 10 °C = 120 °C, 1 cm gap dry nitrogen ambient), and excellent temporal stability is observed when the field is removed after the samples are cooled to ambient temperature (Figure 3 and 5). The temporal behavior of the NLO signal during and following corona poling for the sample containing 2c is illustrated in Figure 3. A closer examination of the short time response during poling shows that the signal in the case of the film doped with monomer 2b decays during corona poling above the T_g (Figure 6). This decay has been observed in other polymer systems and arises from the increased polymer mobility which enhances the rotational Brownian motion of the NLO-phore at higher temperatures and competes with the corona field-induced ordering.[4e] The second order susceptibility is a function of both the poling field and temperature as shown by the approximation, $\chi^{(2)} \propto \mu E_{pole}/kT$.[18] Also, the film doped with NLO-phore 2b shows an increase in signal with cooling during corona poling (Figure 6), consistent with

the above argument. The $\chi^{(2)}$ signal drops about 5-10% in the first few minutes following

removal of the applied field, and then remains constant for over 100 h (Figure 3). The

signal drops much more rapidly for the sample containing 2c over the same time period,

with decay of about 11% in the first 5 h (Figure 4). In addition, the magnitude of the $\chi^{(2)}$

signal of 1.7 pm/V for compound 2c is 1.9 times that of compound 2b. The

dimethylamino moiety is a better donor-group, so a larger $\mu\beta$ product can be expected.

This may explain the observed enhanced SHG signal intensity for compound 2c.

Figure 3. Relative second harmonic electric field as a function of time for NLO-phore
2c/PMMA guest-host system: T = 120 °C, no field; (b) corona field applied = + 4.2 kV; (c) T
cooled to below 30 °C, corona field on; (d) corona field off, T = 30 °C.

8

Figure 4. Short-time response during poling and relaxation for NLO-phore 2c/PMMA guest-host system: (b) increased corona field from 3.5 to 4.2 kV; (c) T cooled to below 30 °C, field on; (d) corona field off, T = 30 °C.
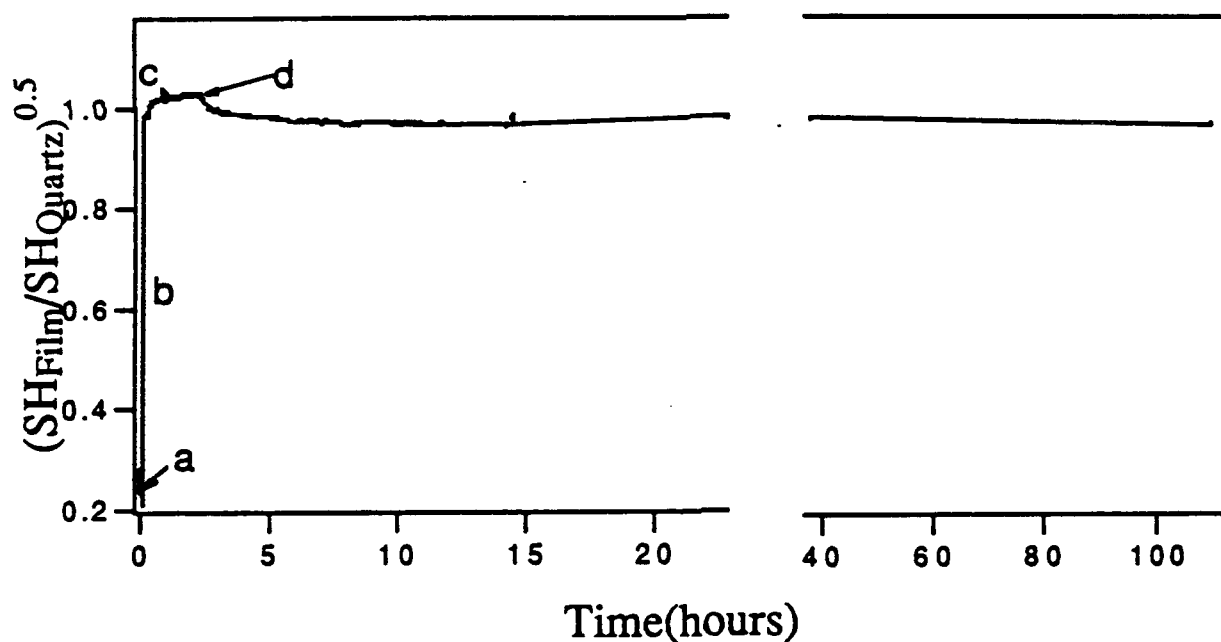

Figure 5. Relative second harmonic electric field as a function of time for NLO-phore 2b/PMMA guest-host system: T = 120 °C, no field; (b) corona field applied = + 4.2 kV; (c) T cooled to below 30 °C, corona field on; (d) corona field off, T = 30 °C.
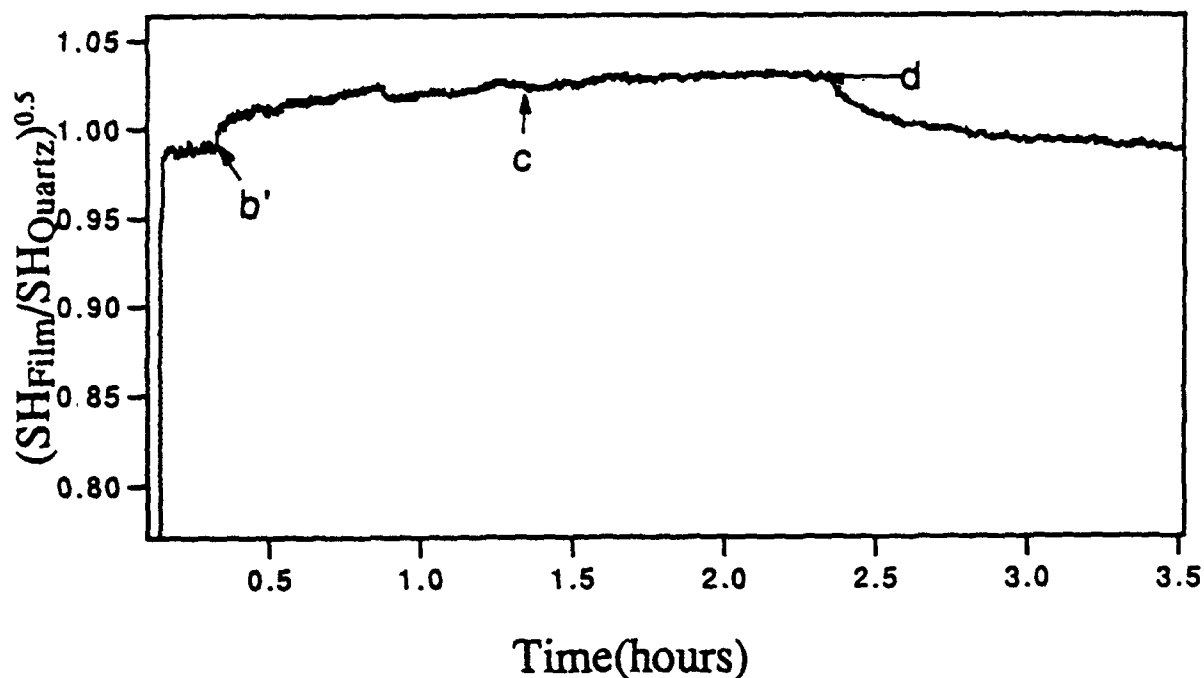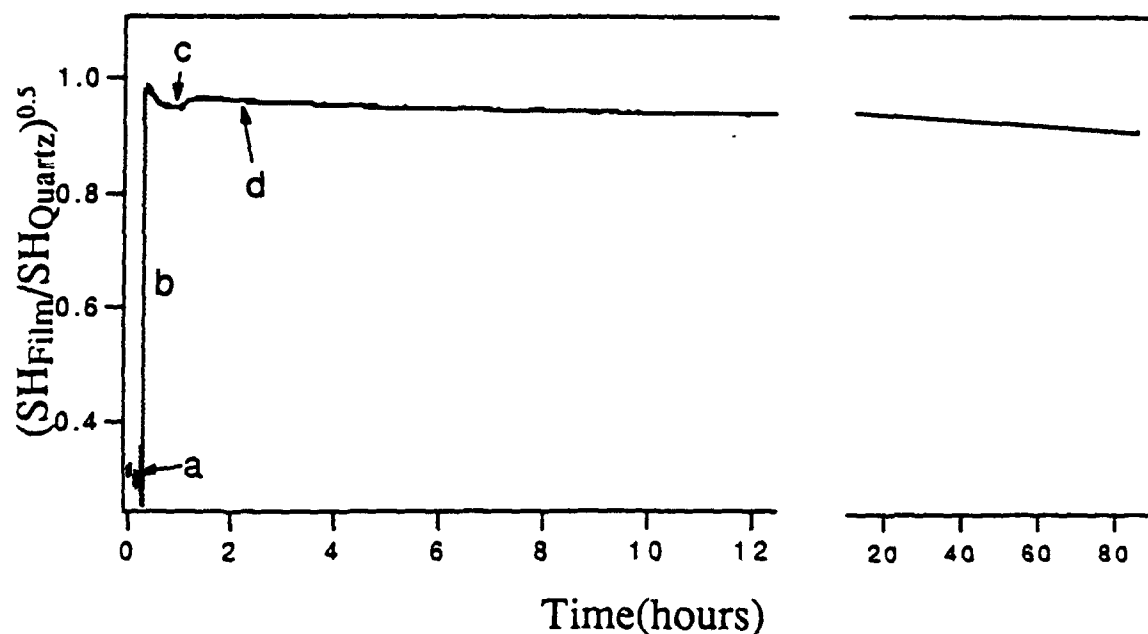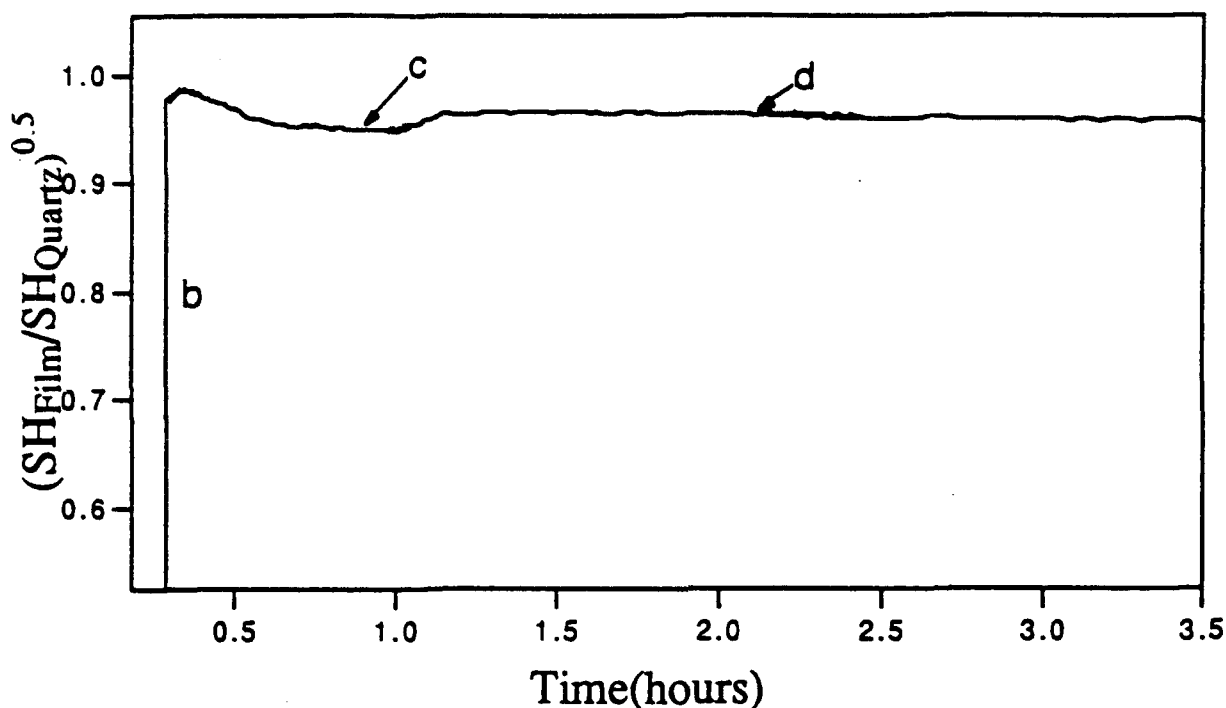
Figure 6. Short-time response during poling and relaxation for NLO-phore 2b/PMMA guest-host system: (b) corona field applied = +4.2 kV; (c) T cooled to below 30 °C, corona field on; (d) corona field off, T = 30 °C.

In order to understand the relaxation behavior in terms of molecular motion, the time- resolved data has been fit to both Williams-Watts (WW) stretched exponential and biexponential forms. It is found that the WW stretched exponential does not adequately describe the observed decay behavior. Others have also noted the inadequacy of the WW fit to describe the short time relaxation behavior of corona poled doped films well below T_g.[4] Using a biexponential of the form $y = \theta_1 \exp(-t/\tau_1) + \theta_2 \exp(-t/\tau_2)$, improved fits to the data were obtained.[4] By using this approximation we are not assuming that there are only two characteristic relaxation times but instead recognizing that "fast" and "slow" characteristic times may approximate the multiplicity of relaxation times. Since τ_2 relates to the long term relaxations, it may be related to the mobility in the polymer matrix. The effect of the surface charge decay is also contained in the calculated parameters for the fit.

10

The solid line in Figure 7 for the films doped with NLO-phores **2b** and **2c** represents this fit. The biexponential fit for the film doped with monomer **2b** yields coefficients $\theta_1 = 0.94$, $\theta_2 = 0.02$ and time constants $\tau_1 = 4.8$ h, $\tau_2 = 2140$ h and similarly the parameters for the sample containing **2c** are $\theta_1 = 0.97$, $\theta_2 = 0.05$, $\tau_1 = 1.6$ h, $\tau_2 = 5620$ h. From the coefficients it can be inferred that in both cases most of the decay is due to the "fast" relaxation component. In addition, the film doped with NLO-phore **2c** shows three times faster relaxation at short times compared to sample containing NLO-phore **2b** but plateaus to a stable signal at longer times. The observation that NLO-phore **2c** relaxes significantly faster in the PMMA host cannot be rationalized on the basis of NLO-phore size, since the molecules are very similar in size.
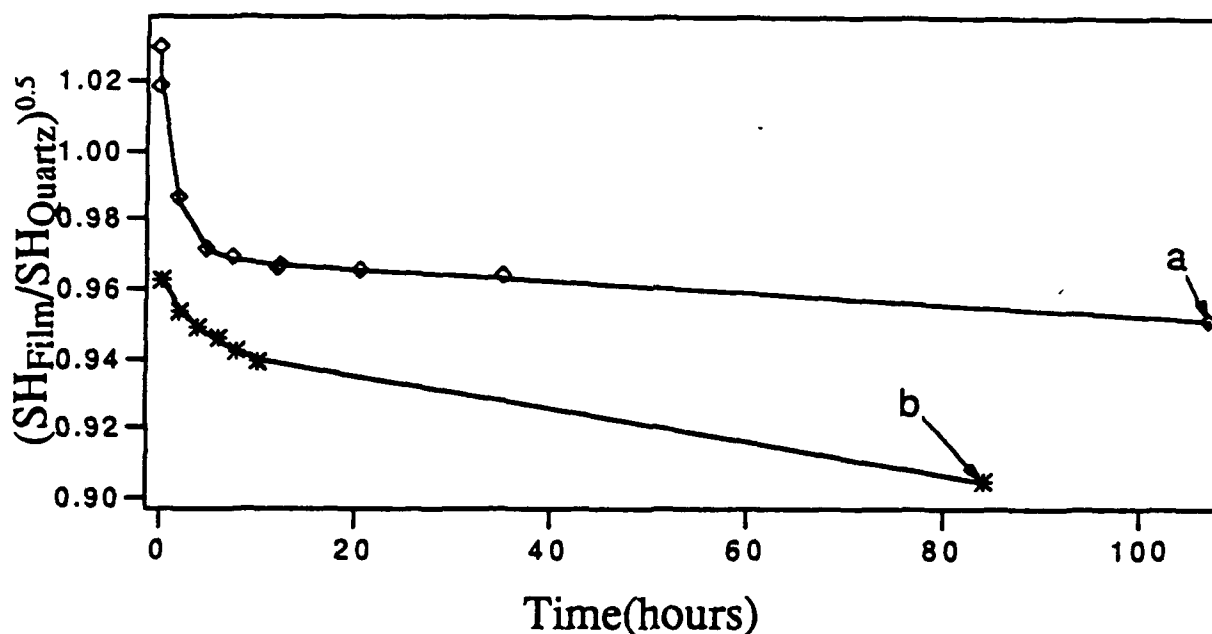

Figure 7. Decay of SH signal with time: (a) **2c**/PMMA; (b) **2b**/PMMA guest-host systems. The solid line represents biexponential fit for each system. For NLO-phore **2b** the time constants are $\tau_1 = 4.8$ h, $\tau_2 = 2140$ h and $\tau_1 = 1.6$ h, $\tau_2 = 5620$ h for NLO-phore **2c**. Fit = a*exp(-t/τ_1) + b*exp(-t/τ_2).

No SHG signal was observed during corona poling (V_{pole} = ~3.5 kV, 1 cm gap, dry nitrogen ambient) of thin films of spin cast polymer 3c for poling temperatures both above and below the T_g. This is probably caused by the difficulty in orienting NLO-phores which are restricted in their mobility by proximity to the stiff polymer backbone, both on an intra- and inter-chain basis. This has been noted previously in unrelated NLOPs.[19] On the other hand, there are recent cases that illustrate how rigid-rod polymers with the NLO-phore placed in a geometry orthoganol to the polymer backbone can in fact be aligned by poling.[20]

The oligomeric material was also prepared and doped into a PMMA host in order to examine the effect of diluting inter-chain packing forces in the hope that the system would then be capable of orienting via poling. Oligomers of 3c at two different molecular weights (2,750 and 3,800) were dispersed in PMMA and investigated. The lower molecular weight oligomer could be poled but the SHG signal from the oligomer is lower than the monomer/NLO-phore dispersed in PMMA (Figure 8). The higher molecular weight oligomer however could not be aligned by poling. This is consistent with the argument that the longer rigid-rod polymer backbone is hindering the alignment process.[19,21]
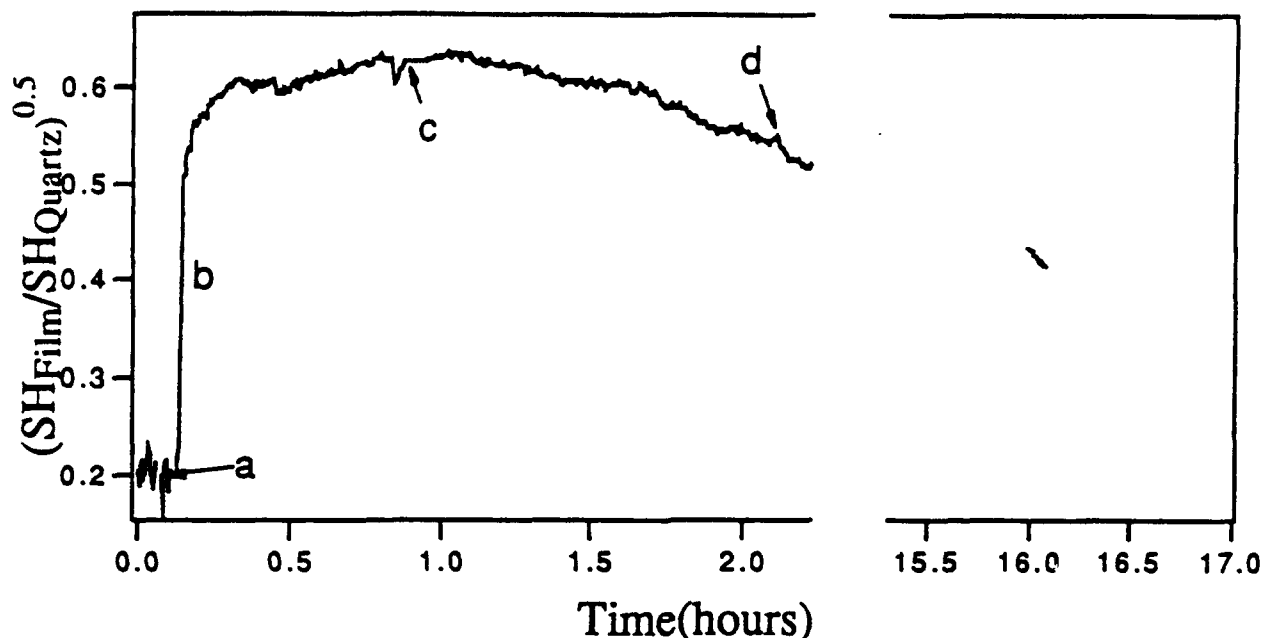
Figure 8. SH signal as a function of time for 10 wt-% of oligomer of 3c (M_n = 2,750) in PMMA: (a) T = 120 °C, no field; (b) poled at -4.5 kV; (c) cooled below 30 °C, field on; (d) field turned off.

Concluding Remarks. The new NLO-phore/monomers prepared in this study were easily aligned by corona poling when dispersed in a PMMA host, however, as the same NLO-phore was incorporated as an integral part of the PPP backbone, some resistance to poling was observed. The higher molecular weight oligomer of 3c (M_n of 3,800) dispersed in PMMA or films of polymer 3c (M_n 6,000) were found to show no SHG activity. The results indicate the rigid PPP backbone is interfering in the alignment process. Studies are continuing to better understand the effects induced by the rigid backbone and use this knowledge to design the next generation of PPP based NLOPs.

13

Experimental part

Methods. All manipulations of compounds and solvents were carried out by using standard Schlenk techniques. Solvents were degassed and purified by distillation under nitrogen from standard drying agents. Spectroscopic measurements utilized the following instrumentation: ^1H NMR, Varian XL 300; ^{13}C NMR, JEOL 270 (at 67.80 MHz) and Brüker 400 (at 100.61 MHz). Infrared, Perkin Elmer 1750 FT-IR; UV-vis, HP-8452A. NMR chemical shifts are reported assigning $CDCl_3$ resonance at $\delta = 7.25$ ppm in ^1H and assigning the $CDCl_3$ resonance at $\delta = 77.0$ ppm in ^{13}C spectra. ^{13}C spectra of the polymers were recorded at 50 °C and only the most intense peaks were assigned. The 1,4-dichlorobenzenesulfonyl chloride, the bromobenzene, N,N-dimethylaniline, CuI, aluminum trichloride, and phenylacetylene were all purchased from Aldrich Chemical Co. and used without further purification. The 4-bromoanisole was purchased from Lancaster and used without further purification. The trimethylsilylacetylene was purchased from Farchan Laboratories Inc. and was used as received. The K_2CO_3 (granular) was purchased from Baxter. The $(PPh_3)_2PdCl_2$ was prepared according to literature procedure.[22] Thermal analysis of the polymers was performed using a Perkin Elmer TGA7 and DSC7 station. GPC data was collected on a Varian 5000 HPLC employing PL size-exclusion column (300 x 7.5 mm, 5μ particle size). Molecular weight data is referenced relative to polystyrene standards. Elemental analyses were performed by Atlantic Microlab Inc, Norcross, Georgia.

Second Harmonic Generation Measurements. The polymers were dissolved in spectroscopic grade chloroform and spin coated on ITO glass slides. They were then air

dried for two days, followed by drying under vacuum and heating to 110 °C for about 48 h to remove solvents and provide erasure of thermal history. The samples were stored in a desiccator under reduced pressure. Samples were mounted in a sample holder containing heaters connected to a temperature controller. The samples were properly grounded and corona poled typically at 4000 V with a needle set 1.0 cm away from the sample. The corona current was limited to < 1 μA to prevent damaging the samples. The sample holder was purged with nitrogen before poling. A typical experimental cycle consisi measuring the baseline (no SHG observed) and then heating the sample to T_g + 10 °C. After equilibrating the sample at that temperature, it was corona poled unitl the SHG signal inreased and leveled off (for about five min). Then the sample was cooled to ambient temperature, following which the poling field is turned off and the SHG signal decay is followed over time.

Details covering the experimental setup for transmission SHG have been published.[23] The sample was mounted vertically on a temperature controlled copper block and the laser was incident at 23 degrees with respect to the surface normal. The signal was averaged by a boxcar integrator and was collected and stored by computer.

2-[1,4-Dichlorophenyl]$SO_2C_6H_4Br$ **(1).** A Schlenk flask was charged with 5.0 g (20.4 mmol) of 2,4-dichlorobenzene sulfonyl chloride, 2.14 mL (20.4 mmol) of bromobenzene and 2.72 g (20.4 mmol) of aluminum trichloride and heated at 125 °C for 6 h with stirring. The reaction mixture was cooled and diluted with 150 mL of methylene chloride and organic layer washed twice with 100 mL of water, once with 100 mL of brine, and then dried over K_2CO_3. The solvent was removed under reduced pressure and the crude

15

product was crystallized from a solution of 10% (v/v) EtOAc/ Hexanes to afford 1 as tan

needles (m.p. 163-164 °C, 4.18 g, 56 % yield). ^{1}H NMR (CDCl$_3$): δ = 8.33 (d, H^2), 7.82 (d,

H^8), 7.68 (d, H^9); $J_{8,9}$ = 8.6 Hz, 7.51 (dd, H^6); $J_{2,6}$ = 2.6 Hz, 7.38 (d, H^5); $J_{5,6}$ = 8.5 Hz. Intensity

ratio: 1:2:2:2:2. ^{13}C NMR (CDCl$_3$): δ = 139.3 (C^4), 138.3 (C^3), 134.7 (C^2), 133.7 (C^7), 133.2 (C^6),

132.3 (C^8), 131.0 (C^1), 130.7 (C^5), 130.2 (C^9), 129.2 (C^{10}). IR (CH$_2$Cl$_2$): 1331 cm^{-1} (s, S=O). UV

(CH$_2$Cl$_2$) λ_{max}/ nm (ε= 1.90 x 10^3/ L·mol^{-1}·cm^1) = 294.

(C$_{12}$H$_7$BrCl$_2$O$_2$S) (366.06)   Calc.   C 39.40   H 1.93
                                              Found   C 39.54   H 2.05

4-[2-[1,4-Dichlorophenyl]SO$_2$]C$_6$H$_4$C≡CPh (**2a**). A Schlenk flask was charged with 3.81

g (10.41 mmol) of 1, 100 mL of triethyl amine, 0.16 g (0.63 mmol) of triphenylphosphine,

0.12 g (0.63 mmol) of CuI, and 0.22 g (0.31 mmol) of (PPh$_3$)$_2$PdCl$_2$. 1.14 mL (10.41 mmol) of

phenylacetylene was added and the resulting solution was heated to reflux and allowed to

stir overnight. The solution was then cooled and the crude product was diluted with 250

mL methylene chloride and the organic layer was washed twice with 100 mL of water,

once with 100 mL of brine, and then dried over K$_2$CO$_3$. The solvent was removed under

reduced pressure and the crude product was subjected to column chromatography (2 x 20

cm) on alumina. The column was eluted with CH$_2$Cl$_2$ to yield a tan band. The solvent was

removed under reduced pressure to yield pure **2a** as a solid (m.p. 149-152 °C, 2.82 g, 70%).

^{1}H NMR (CDCl$_3$): δ = 8.34 (d, H^2); $J_{2,6}$ = 2.5 Hz, 7.92 (d, H^8), 7.65 (d, H^9); $J_{8,9}$ = 8.6 Hz, 7.51

(m, H^6, H^{14}, H^{15}), 7.38 (m, H^5, H^{16}). Intensity ratio: 1:2:2:4:3. ^{13}C NMR (CDCl$_3$): δ = 139.6

(C^4), 138.3 (C^3), 134.6 (C^2), 133.7 (C^7), 133.2 (C^6), 131.9 (C^9), 131.8 (C^{14}), 131.1 (C^1), 130.8 (C^5),

129.3 (C^{10}), 129.1(C^{16}), 128.7 (C^9), 128.5 (C^{15}), 122.2 (C^{13}), 93.8 (C^{11}), 87.6 (C^{12}). IR (CH$_2$Cl$_2$):

1327 cm^{-1} (s, S=O). UV (CH$_2$Cl$_2$) λ_{max} / nm (ϵ = 1.93 x 10^3 / L mol^{-1} cm^{-1}) = 318.

(C$_{20}$H$_{12}$Cl$_2$O$_2$S) (387.28)

	Calc.	C 62.03	H 3.12
	Found	C 62.49	H 3.37

4-[2-[1,4-Dichlorophenyl]SO$_2$]C$_6$H$_4$C=C[4-methoxyphenyl] (2b). A Schlenk flask was charged with 1.66 g (4.54 mmol) of 1, 40 mL of triethyl amine, 0.07 g (0.27 mmol) of triphenylphosphine, 0.05 g (0.27 mmol) of CuI, and 0.10 g (0.14 mmol) of (PPh$_3$)PdCl$_2$. 0.60 g (4.54 mmol) of 4-methoxyphenylacetylene was added and the resulting solution was heated to reflux and allowed to stir at reflux overnight. The solution was then cooled and the crude product was diluted with 250 mL methylene chloride and the organic layer was washed twice with 100 mL of water, once with 100 mL of brine, and then dried over K$_2$CO$_3$. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography (2 x 20 cm) on alumina. The column was eluted with CH$_2$Cl$_2$ to yield a yellow band. The solvent was removed under reduced pressure to yield pure 2b as a solid (m.p. 170-172 °C, 1.21 g, 64%). ^{1}H NMR (CDCl$_3$): δ = 8.33 (d, H^2); $J_{2,6}$ = 2.6 Hz, 7.90 (d, H^8), 7.61 (d, H^9); $J_{8,9}$ = 8.7 Hz, 7.48 (m, H^6 and H^{14}), 7.36 (d, H^5); $J_{5,6}$ = 8.5 Hz, 6.88 (d, H^{15}); $J_{14,15}$ = 9.0 Hz, 3.85 (s, CH$_3$). Intensity ratio: 1:2:2:3:1:2. ^{13}C NMR (CDCl$_3$): δ = 160.3 (C^{16}), 139.6 (C^4), 137.8 (C^3), 134.6 (C^2), 133.6 (C^7), 133.3 (C^8), 133.2 (C^6), 131.6 (C^9), 131.1 (C^1), 130.7 (C^5), 129.7 (C^{10}), 128.7 (C^{15}), 114.1 (C^{13} and C^{14}), 94.1 (C^{12}), 86.6 (C^{11}), 55.3 (CH$_3$). IR (CH$_2$Cl$_2$): 1327 cm^{-1} (s, S=O). UV (CH$_2$Cl$_2$) λ_{max} / nm (ϵ = 3.01 x 10^4 / L mol^{-1} cm^{-1}) = 328.

(C$_{21}$H$_{14}$Cl$_2$O$_3$S) (417.31)

	Calc.	C 60.44	H 3.38
	Found	C 60.30	H 3.49

2-[1,4-Dichlorophenyl]SO$_2$C$_6$H$_4$C=C[4-dimethylaminophenyl] (2c). A Schlenk flask was charged with 6.08 g (16.6 mmol) of 1, 130 mL of triethyl amine, 0.26 g (1.00 mmol) of triphenylphospine, 0.19 g (1.00 mmol) of CuI, 0.36 g (0.50 mmol) of (PPh$_3$)PdCl$_2$, and 2.41 g (16.6 mmol) of 4-(*N*,*N*-dimethyl)phenylacetylene. The resulting solution was heated to reflux and allowed to stir at reflux for 18 h. The solution was allowed to spontaneously cool and the mixture was diluted with 250 mL of methylene chloride. The organic layer was washed twice with 100 mL of water, once with 100 mL of brine, and then dried over K$_2$CO$_3$. The solvents were removed under reduced pressure and the crude product subjected to column chromatography (2 x 20 cm) on alumina. Elution with CH$_2$Cl$_2$ afforded a yellow band which was collected and the solvent removed under reduced pressure to yield pure 2c as a solid (m.p. 223-224 °C, 4.16 g, 58%). ^{1}H NMR (CDCl$_3$): δ = 8.34 (d, H^2), 7.89 (d, H^8), 7.60 (d, H^9); $J_{8,9}$= 8.6 Hz, 7.49 (dd, H^6); $J_{2,6}$= 2.6 Hz, $J_{5,6}$= 8.6 Hz, 7.39 (m, H^5 and H^{14}), 6.66 (d, H^{15}); $J_{14,15}$ = 9.0 Hz, 3.01 (s, NMe$_2$). Itensity ratio: 1:2:2:1:3:2:6. ^{13}C NMR (CDCl$_3$): δ = 150.6 (C^{16}), 139.8 (C^4), 137.1 (C^3), 134.5 (C^2), 133.6 (C^7), 133.1 (C^6), 133.0 (C^8), 131.3 (C^9), 131.1 (C^1), 130.7 (C^5), 130.4 (C^{10}), 128.6 (C^{15}), 111.7 (C^{14}), 108.5 (C^{13}), 95.9 (C^{11}), 86.3 (C^{12}), 40.1 (CH$_3$). IR (CH$_2$Cl$_2$): 1327 cm^{-1} (s, S=O). UV (CH$_2$Cl$_2$) λ$_{max}$ / nm (ε= 4.76 x 10^3 / L mol^{-1}cm^{-1}) = 380.

(C$_{22}$H$_{17}$Cl$_2$NO$_2$S) (430.35)			
	Calc.	C 61.40	H 3.98
	Found	C 61.41	H 4.01

X-ray diffraction study of 2c. Yellow crystals of 2c (0.5 x 0.4 x 0.3 mm) suitable for X-ray analysis were grown from diffusion of pentane into a CHCl$_3$ solution containing 2c. Crystallographic data: orthorhombic, P2$_1$2$_1$2$_1$, *a* 7.786(2), *b* 8.359(3), *c* 31.536(6) Å, *V*

2052.6(8) $Å^3$, $Z = 4$, D_{calcd} 1.393 g cm^{-3}, μ(Mo-K_α) 4.36 cm^{-1}, ambient temperature. Intensity

data [2θ-θ, $3° \leq θ \leq 45°$, variable scan speed of 3.0 to 14.65°/min, 1579 independent

reflections, 1277 with $F_o > 3.0\sigma(F_o)$] were collected on a Siemens R3m/V diffractometer.

The structure was initally solved using direct methods and the remaining nonhydrogen

atoms were located using difference Fourier syntheses. Neutral atomic scattering factors

internal to SHELXTL PLUS/VMS [Version 4.21/V, 1992] were used. Final refinement was

by full-matrix least-squares minimization of $\sum[w(F_o-kF_c)]^2$ with weights, w = 1/[σ^2(F) +

0.0010*F^2]. All nonhydrogen atoms were refined ansiotropically; the hydrogen atoms were

refined as geometrically constrained {"riding" on the carbons to which they are attached}

with constrained isotropic thermal parameters. Final refinement of the structure led to R

3.85%, R_W 4.63%, GOF 1.05, mean Δ/σ = 0.001, N_o/N_v = 5.0, and the largest peak in the

final difference map of 0.21 e $Å^{-3}$.

Polymer Synthesis (3). Monomers 2a-2c were all polymerized by the method

developed by Chaturvedi et al.[16] After the polymerization reaction was complete the crude

reaction mixture was filtered through celite to remove the zinc dust. The celite was

washed with dichloromethane to dissolve any polymer left remaining. The

dichloromethane solution was washed with a 10% NaCN (w/w) solution to remove any

nickel left in solution. The organic layer was dried over $MgSO_4$ and filtered. The solvent

volume was reduced and the polymer was precipitated in ether. The polymer was

redissolved in dichlormethane and precipitated again in ether. This procedure was

repeated three times to afford polymers:

Polymer 3a. ^{1}H NMR (CDCl$_3$): δ = 8.0 - 7.3 (br m, H^2, H^9, H^8, H^{14}, H^{15}, H^{16}), 7.1 - 6.5

(2 br s, H^5, H^6). ^{13}C NMR (CDCl$_3$): δ = 132.7 (C^8), 132.5 (C^{14}), 128.7 (C^{15}), 128.6 (C^9). IR (CH$_2$Cl$_2$): 1327 cm^{-1} (s, S=O). UV (CH$_2$Cl$_2$) λ_{max} / nm (ϵ = 2.56 x 10^3 / L mol^{-1}cm^{-1}) = 316.

Polymer 3b. ^1H NMR (CDCl$_3$): δ = 8.2 - 7.3 (br m, H^2, H^9, H^8, H^{14}), 7.1 - 6.1 (3 br s, H^5, H^6, H^{15}), 3.9 - 3.6 and 3.6 - 3.3 (br s, CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 132.2 (C^8), 128.5 (C^{15}), 112.9 (C^{14}), 55.4 (CH$_3$). IR (CH$_2$Cl$_2$): 1327 cm^{-1} (s, S=O). UV (CH$_2$Cl$_2$) λ_{max} / nm (ϵ = 3.95 x 10^2 / L mol^{-1}cm^{-1}) = 316.

Polymer 3c. ^1H NMR (CDCl$_3$): δ = 8.0 - 7.3 (br m, H^2, H^9, H^8, H^{14}), 7.3 - 5.8 (3 br s, H^5, H^6, H^{15}), 3.1 - 2.6 and 2.6 - 2.2 (2 br s, CH$_3$). ^{13}C NMR (CDCl$_3$): δ = 132.2 (C^8), 131.9 (C^9), 128.5 (C^{15}), 111.8 (C^{14}), 40.3 (CH$_3$). IR (CH$_2$Cl$_2$): 1319 cm^{-1} (s, S=O). UV (CH$_2$Cl$_2$) λ_{max} / nm (ϵ = 1.33 x 10^3 / L mol^{-1}cm^{-1}) = 374.

Collected References

[1] For a general treatment of NLO materials see: *Nonlinear Optical and Electroactive Polymers*, P. N. Prasad and D. R. Ulrich, Eds., Plenum Press. New York. 1988; *Organic Materials for Non-linear Optics*, R. A. Hann, and D. Bloor, Eds., Spec. Publ. No. 69, The Royal Society of Chemistry. London. 1989; *Organic Materials for Non-linear Optics II*, R. A. Hann, and D. Bloor, Eds., Spec. Publ. No. 91, The Royal Society of Chemistry. London. 1991; *Materials for Nonlinear Optics: Chemical Perspectives*, S. R. Marder, J. E. Sohn, and G. D. Stucky, Eds., ACS Symp. Ser 455, American Chemical Society, Washington D.C. 1991; D. M. Burland, R. D. Miller, C. A. Walsh, *Chem. Rev.* **94**, 31 (1994).

[2] N. Bloemberger In *Nonlinear Optics*, W.A. Benjamen, New York 1965; Y. R. Shen, In *Principles of Nonlinear Optics*, John Wiley & Sons: New York 1984; D. R. Robello, C. S. Willand, M. Scozzafava, A. Ulman, D. J. Williams, In *Materials for Nolinear Optics: Chemical Perspectives*, D. R. Marder, J. E. Sohn, and G. D. Stucky, Eds., ACS Symp. Ser 455, American Chemical Society, Washington D.C. 1991, p. 279-293.

[3] K. D. Singer, J. E. Sohn, S. J. Lalama *J. Appl. Phys. Lett.* **49**, 248 (1986); K. D. Singer, M. G. Kuzyk, J. E. Sohn *J. Opt. Soc. Am. B* **4**, 968 (1987).

[4] (a) G. Boyd *Thin Solid Films* **152**, 295 (1987); (b) H. L. Hampsch, J. Yang, G. K. Wong, J. M. Torkelson, *Macromolecules* **21**, 526 (1988); (c) H. L. Hampsch, J. Yang, G. K. Wong, J. M. Torkelson, *Polym. Commun.* **30**, 40 (1989); (d) H. L. Hampsch, J. M. Torkelson, S. J. Bethke, S. G. Grubb, *J. Appl. Phys.* **67**, 1037 (1990); (e) H. L. Hampsch, J. Yang, G. K. Wong, J. M. Torkelson, *Macromolecules* **23**, 3640 (1990); (f) H. L. Hampsch, J. Yang, G. K. Wong, J. M. Torkelson, *Macromolecules* **23**, 3648 (1990); (g) R. Loucif-Saibi, K. Nakatani, J. A. Delaire, M. Dumont, Z. Sekkat, *Chem. Mater.* **5**, 229 (1993) J. A. Osaheni, S. A. Jenekhe, *Chem. Mater.* **4**, 1282 (1992).

[5] See ref. 3 and 4 of this paper; J. R. Hill, P. L. Dunn, G. J. Davies, S. N. Oliver, P. Pantelis, J. D. Rush, *Elec. Lett.* **23**, 700 (1987); W. Köhler, D. R. Robello, C. S. Willand, and D. J. Williams *Macromolecules* **24**, 4589 (1991); J. I. Chen, S. Marturunkakul, L. Li, R. J. Jeng, J. Kumar, S. K. Tripathy *Macromolecules* **26**, 7379 (1993); C. A. Walsh, D. M. Burland, V. Y. Lee, R. D. Miller, B. A. Smith, R. J. Tweig, W. Volksen, *Macromolecules* **26**, 3720 (1993).

[6] M. Eich, B. Reck, D. Y. Yoon, C. G. Wilson, G. C. Bjorklund, *J. Appl. Phys.* **66**, 3241 (1989); M. A. Hubbard, T. J. Marks, J. Yang, G. K. Wong, *Chem. Mater.* **1**, 167 (1989); M. Chen., L. P. Yu, L. R. Dalton, Y. Shi, W. H. Steier, *Macromolecules*, **24**, 5421 (1991); B. K. Mandal, J.

Kumar, J. C. Huang, S. K. Tripathy, *Makromol. Chem., Rapid Commun.* **12**, 63 (1991); C. Xu, B. Wu, L. R. Dalton, P. M. Ranon, Y. Shi, W. H. Steier, *Macromolecules* **25**, 6716 (1992); H. Müller, I. Müller, O. Nuyken, P. Strohriegl, *Makromol. Chem., Rapid Commun.* **13**, 289 (1992); R. J. Jeng, Y. M. Chen, J. I. Chen, J. Kumar, S. K. Tripathy *Macromolecules* **26**, 2530 (1993) and references cited

[7] For some recent examples of side-chain NLOPs see: C. Ye, N. Minami, T. J. Marks, J. Yang, G. K. Wong, *Macromolecules* **21**, 2901 (1987); L. M. Hayden, G. F. Sauter, F. R. Ore, P. L. Pasillas, J. M. Hoover, G. A. Lindsay, R. A. Henry, *J. Appl. Phys.* **68**, 456 (1990); N. Zhende, T. M. Leslie, A. B. Padias, H. K. Hall, Jr., *Macromolecules* **24**, 2100 (1991); D. Jungbauer, I. Teraoka, D. Y. Yoon, B. Reck, J. D. Swalen, R. Twieg, C. G. Wilson *J. Appl. Phys.* **69**, 8011 (1991) M. Zhoa, M. Bautista, W. T. Ford, *Macromolecules* **24**, 844 (1991); H. R. Allcock, A. A. Dembek, C. Kim, R. L. S. Devine, Y. Shi, W. H. Steier, C. W. Spangler, *Macromolecules* **24**, 1000 (1991); M. E. Wright, E. G. Toplikar, R. F. Kubin, M. D. Seltzer, *Macromolecules* **25**, 1838 (1992); D. Morichère, P.-A. Chollet, W. Fleming, M. Jurich, B. A. Smith, J. D. Swalen, *J. Opt. Soc, Am. B* **10**, 1984 (1993); H. J. Winkelhahn, T. K. Servay, L. Kalvoda, M. Schulze, D. Neher, G. Wegner, *Ber Bensenges. Phys. Chem.* **97**, 1287 (1993); T. K. Servay, H. J. Winkelhahn, M. Schulze, C. Boefell, D. Neher, G. Wegner, L. Kalvoda, *Ber Bensenges. Phys. Chem.* **97**, 1272 (1993); D. H. Choi, W. M. K. P. Wijekoon, H. M. Kim, P. N. Prasad *Chem. Mater.* **6**, 234 (1994); M. W. Becker, L. S. Sapochak, R. Ghosen, C. Xu, L. R. Dalton, Y. Shi, W. H. Steier, A. K.Y. Jen, *Chem. Mater.* **6**, 104 (1994); M. E. Wright, E. G. Toplikar, H. S. Lackritz, J. T. Kerney, *Macromolecules* **27**, 0000 (1994)

[8] G. D. Green, H. K. Hall, Jr., J. E. Mulvaney, J. Noonan, D. J. Williams, *Macromolecules* **20**, 716 (1987); G. D. Green, J. I. Weinschenk, J. E. Mulvaney, H. K. Hall, Jr., *Macromolecules* **20**, 722 (1987); W. Köhler, D. R. Robello, P. T. Dao, C. Willand, D. J. Williams, *J. Chem. Phys.* **93**, 9157 (1990); J. D. Stenger-Smith, J. W. Fischer, R. A. Henry, J. M. Hoover, G. A. Lindsay, L. M. Hayden, *Macromol. Chem., Rapid Commun.* **11**, 141 (1990); G. A. Lindsay, J. D. Stenger-Smith, R. A. Henry, J. M. Hoover, R. F. Kubin, *SPIE-The International Society for Optical Engineering* **1497**, 418 (1991); G. A. Lindsay, S. F. Nee, J. M. Hoover, J. D. Stenger-Smith, R. A. Henry, R. F. Kubin, M. D. Seltzer, *Ibid.* **1560**, 443 (1991); M. E. Wright, E. G. Toplikar, in *Materials for Nolinear Optics: Chemical Perspectives* S. R. Marder, J. E. Sohn, and G. D. Stucky, Eds., ACS Symp. Ser 455, American Chemical Society, Washington D.C. 1991, p. 602; F. Fuso, A. B. Padias, H. K. Hall, Jr., *Macromolecules* **24**, 1710 (1991); Z. Ni, T. M. Leslie, A. B. Padias, H. K. Hall, Jr., *Macromolecules* **24**, 2100 (1991); D. R. Robello, J. S. Schildkraut, N. J. Armstrong, T. L. Penner, W. Köhler, C. S. Willand, *Polym. Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **32**(3), 78 (1991); W. Köhler, D. R. Robello, P. T. Dao, C. S. Willand, D. J. Williams, *Macromolecules* **24**, 4589 (1991); M. E. Wright, E. G. Toplikar,

Macromolecules **25**, 6050 (1992); M. E. Wright, M. S. Sigman, *Macromolecules* **25**, 6055 (1992); M. E. Wright, S. Mullick, *Macromolecules* **25**, 6045 (1992); R. Zentel, H. Baumann, D. Scharf, M. Eich, A. Schoenfeld, F. Kremer, *Makromol. Chem., Rapid Commun.* **14**, 121 (1993); M. Moroni, J. Le Moigne, S. Luzzati, *Macromolecules* **27**, 562 (1994). M. E. Wright, S. Mullick, H. S. Lackritz, L.-Y. Liu, *Macromolecules* **27**, 0000 (1994)

[9] W. Gibbons, R. P. Grasso, M. K. O'Brien, P. J. Shannon, S. T. Sun *Macromolecules* **27**, 771 (1994)

[10] M. E. Wright, E. G. Toplikar, *Polym. Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **35(1)**, 368 (1994)

[11] D. J.Williams, *Thin Solid Films* **216**, 117 (1992) and references cited therein.

[12] H. S. Lackritz, J. M. Torkelson, "Polymer Physics of Poled Polymers for Second Order Nonlinear Optics" in *Molecular Optoelectronics: Materials, Physics, and Devices*, J. Zyss, Ed., Academic Press, New York **1993**, Chapter 8

[13] B. Delfort, G. Lucotte, L. Cormier *J. Polym. Sci., Part A* **28**, 2451 (1990)

[14] The alkynylation reaction conditions are taken from: S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara *Synthesis* 627 (1980)

[15] E. M. Graham, V. M. Miskowski, J. W. Perry, D. R. Coulter, A. E. Stiegman, W. P. Schaefer, R. E. Marsh, *J. Am. Chem. Soc.* **111**, 8771 (1989)

[16] V. Chaturvedi, S. Tanaka, K. Kaeriyama, *Macromolecules* **26**, 2607 (1993)

[17] R. W. Phillips, V. V. Sheares, E. T. Samulski, J. M. Desimone, *Polym. Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **35(1)**, 367 (1994); G. Y. Wang, R. P. Quirk, *Polym. Prepr (Am. Chem. Soc., Div. Polym. Chem.)* **35(1)**, 503 (1994)

[18] P. N. Prasad, D. J. Williams *Introduction to Nonlinear Optical Effects in Molecules and Polymers*, Wiley-Interscience, New York (1990)

[19] W. Köhler, D. R. Robello, C. S. Wiland, D. J. Williams, *Macromolecules* **24**, 4589 (1991)

[20] C. Weder, P. Neuenschwander, U. W. Suter, P. Prêtre, P. Kaatz, P. Günter, *Macromolecules* **27**, 2121 (1994)

[21] This has been noted previously for head-to-tail rigid NLO oligomeric materials: H. E. Katz, M. L. Schilling, G. E. Washington, *J. Opt. Soc. Am. B* **7**, 309 (1990); H. E. Katz, M. L. Schilling, *Proc. SPIE* **1147**, 90 (1990); H. E. Katz, M. L. Schilling, *J. Am. Chem. Soc.* **111**, 7554 (1989)

[22] A. O. King, E. Neghishi, F. J. Villani, Jr, A. Silveira, Jr., *J. Org Chem.* **43**, 358 (1978)

[23] M. E. Wright, E. G. Toplikar, H. S. Lackritz, J. T. Kerney, *Macromolecules* **27**, 0000 (1994)