

AD-A280 248



Office of Naval Research

Grant: N00014-91-J-1625

R&T Code: 4132051

Technical Report No. 16

Poly(*p*-phenylene) Derivatives New High Performance

Nonlinear Optical Polymers

by

Michael E. Wright & Edward G. Toplikar

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

Submitted to

American Chemical Society, Polymer Preprints



May 28, 1994

94-17992



300

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.

94 6 10 099

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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 Poly(p-phenylene) Derivatives New High Performance Nonlinear Optical Polymers			5. FUNDING NUMBERS N00014-91-J-1625 R&T 4132051	
6. AUTHOR(S) Michael E. Wright and Edward G. Toplikar				
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 #16	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of Naval Research 800 North Quincy Street Arlington, VA 22217-5000			10. SPONSORING/MONITORING AGENCY REPORT NUMBER ONR Scientific Officer Dr. Kenneth J. Wynne (703) 696-4409 NTIS CRA&I <input checked="" type="checkbox"/> DTIC TAB <input type="checkbox"/> Unannounced <input type="checkbox"/> Justification	
11. SUPPLEMENTARY NOTES Polymer Preprints 1994, 35(1), 0000			By Distribution /	
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 CODES Dist Avail and/or Special A-1	
13. ABSTRACT (Maximum 200 words) NLO polymers (NLOPs) based on the poly(p-phenylene) (PPP) backbone were prepared in the study. The thermal stability for the new materials is presented. The polymer displayed a T _g of 220 deg C. The TGA scan of the material indicated reasonable thermal stability to 300 deg C. A thin film of the material was supported on a glass slide and heated at 200 deg C and monitored by UV-vis spectroscopy. These experiments indicated less than 10% loss of the absorption band due to the NLO-phore (i.e. chromophore) over a period of 24 h.				
14. SUBJECT TERMS NonLinear Optical, Polymers Conjugated Polymers, Polyphenylenes			15. NUMBER OF PAGES 2 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	

Poly(*p*-phenylene) Derivatives: New High Performance Nonlinear Optical Polymers

Michael E. Wright* and Edward G. Toplikar

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

Introduction

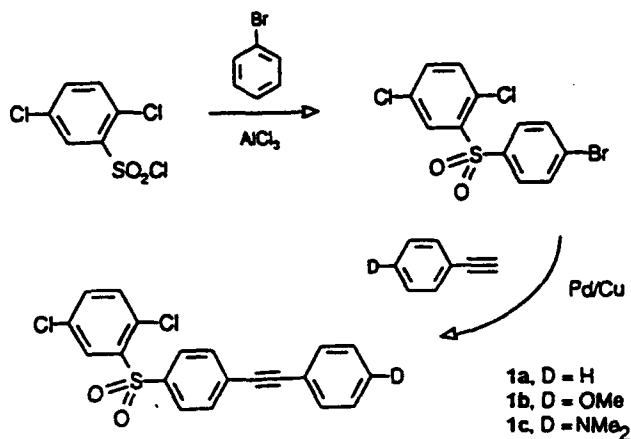
Nonlinear optical (NLO) materials research has become a very mature and sophisticated area of polymer chemistry.¹ The design criteria for NLO active molecules which have $\chi^{(2)}$ activity is well established.² Many of the original criterion applied to $\chi^{(2)}$ NLO materials have changed with the recent discovery of light emitting polymer based devices.³ One current area of focus in NLO materials is the development of photonic devices.⁴ NLO polymers (NLOP) have shown great promise for device applications. NLOP's have large optical nonlinearities, super fast response time (GHz), and often exhibit high damage thresholds ($>10^3$ MW cm⁻²). It appears that NLOP's can match the challenges found in this rapidly developing area of advanced technology.⁵ The thermal stability of NLOP materials is of primary concern and is an issue currently of interest.

In this paper, we will present results from our synthetic studies targeted at preparing high-performance NLO polymers based on poly(*p*-phenylene).

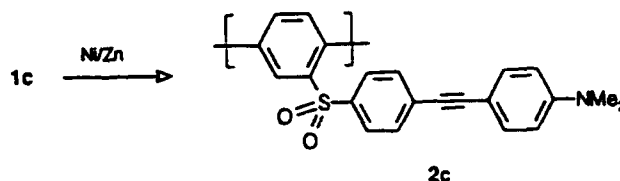
Results and Discussion

We have prepared a series of *p*-dichlorophenylene monomers containing tolane based NLO-phores (Scheme I). These NLO-phores were selected on the basis of their fairly large hyperpolarizability and reasonably good thermal stability.

Scheme I



The monomers were polymerized using the Ni/Zn mediated homocoupling⁶ to afford poly(*p*-phenylenes) in moderate yield with a range of molecular weights. Polymer 2c was produced in the highest yield and molecular weight ($M_n = \sim 8,000$).



DSC analysis of polymer 2c shows a strong T_g at 220 °C. The polymer is soluble in common organic solvents and solutions of 2c can be spin-cast to produce films of high optical quality. Thermal stability of 2c is excellent to 300 °C and above that temperature we see decomposition of the NLO-phore side-chain. Optical studies are underway (Prof. H. Lackritz and Kirk Wilson, Purdue University) and will be briefly discussed in the presentation.

Acknowledgment. We would like to express our sincere gratitude to the Office of Naval Research for funding this research.

References

1. *Materials for Nonlinear Optics: Chemical Perspectives*, Marder, S. R.; Sohn, J. E.; Stucky, G. D. Eds.; ACS Symposium Series 455, American Chemical Society, Washington D.C. 1991 and references cited therein. *Organic Materials for Nonlinear Optics II*, Hann, R. A.; Bloor, D. Eds.; Spec. Publ. No. 91, The Royal Society of Chemistry, London, England 1991 and references cited therein.
2. Marder, S. R.; Beratan, D. N.; Cheng, L.-T. *Science* 1991, 252, 103.
3. Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* 1990, 347, 539. Braun, D.; Heeger, A. *J. Appl. Phys. Lett.* 1991, 58, 1982.
4. Kolinsky, P. V. *Optical Engineering* 1992, 31, 1676 and references cited therein.
5. Lytel, R.; Lipscomb, G. F.; Kenny, J. T.; Ticknor, A. J. *Proc. SPIE* 1991, 1563, 122. Stamatoff, J.; DeMartino, R.; Hass, D.; Khanarian, G.; Man, H. T.; Norwood, R.; Yoon, H. N. *Die Angew. Makromol. Chemie* 1990, 183, 151 and references cited therein.
6. Colon, I.; Kwiatkowski, G. T. *J. Polym. Sci., Part A: Polymer Chemistry* 1990, 28, 367. Kwiatkowski, G. T.; Colon, I. *Polym. Prep.* 1991, 31(1), 342.