

AD-A280 196



Office of Naval Research

Grant: N00014-91-J-1625

R&T Code: 4132051

Technical Report No. 15

**Organic Nonlinear Optical (NLO) Polymers. 4.
Thermally Stable NLO Polymers**

by

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Submitted to

American Chemical Society, Polymer Preprints

94-17993

May 28, 1994



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REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE May 22, 1994	3. REPORT TYPE AND DATES COVERED 1 June, 1993 - 31 May, 1994		
4. TITLE AND SUBTITLE Organic Nonlinear Optical (NLO) Polymers. 4. Thermally Stable NLO Polymers			5. FUNDING NUMBERS N00014-91-J-1625 R&T 4132051	
6. AUTHOR(S) Michael E. Wright, 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 #15	
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	
11. SUPPLEMENTARY NOTES Polymer Preprints 1994, 35(1), 0000				
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) NLO polymers (NLOPs) based on the poly(<i>p</i> -phenylene) (PPP) backbone were prepared in the study. Starting from readily synthesized NLO-phore/monomers, homopolymerization afforded low molecular weight PPPs with the NLO-phore attached to the polymer backbone through a sulfone linkage. The thermal and linear optical behavior of the new materials is discussed in the paper.				
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	

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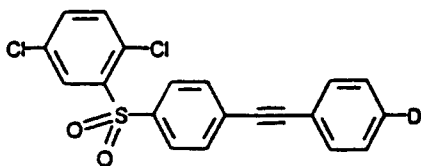
Introduction

The development of polymeric materials for applications in nonlinear optical (NLO) devices continues to be an area of ongoing research.¹ The key for success in the implementation of these materials is retention in alignment of the NLO-phores for long periods of time and at elevated temperatures. Guest-host and side-chain systems suffer in that, in many cases, they fail to retain this alignment over very long periods of time. Guest-host systems rely on hydrogen bonding or electrostatic interactions and these forces prove too weak and alignment is lost rapidly.² Side-chain, or pendant, systems offer the advantage of having the NLO-phore covalently linked to the polymer matrix.³ This helps to restrict some modes of relaxation, however, most polymer backbones for side-chain systems are those which possess poor thermal properties (polystyrene and PMMA). These poor thermal properties result in relaxations in the matrix which are still too rapid for practical device applications. Main-chain systems suffer from an altogether different problem.⁴ In many cases, main-chain systems have not exhibited the local mobility necessary to achieve alignment of the polymer chains. One notable exception is Dalton's random polymerization of an NLO-phore with a diisocyanate.⁵ Therefore, there exists a need for a polymer which can overcome some of the thermal properties that typical side-chain matrices suffer from, in addition to providing sufficient local mobility to allow for alignment of the polymer chains.

Our approach seeks to incorporate a NLO-phore into a thermally stable backbone.⁶ In this case, we have chosen poly(*p*-phenylene)^{7,8} as our polymer backbone. These pendant systems should afford polymers which offer the ease of alignment that side-chain systems possess along with the advantage of excellent thermal properties.

Results and Discussion

We have prepared a series of *p*-dichlorophenylene monomers containing a variety of donor groups.



Monomers:

2a, D = H
2b, D = OMe
2c, D = NMe₂

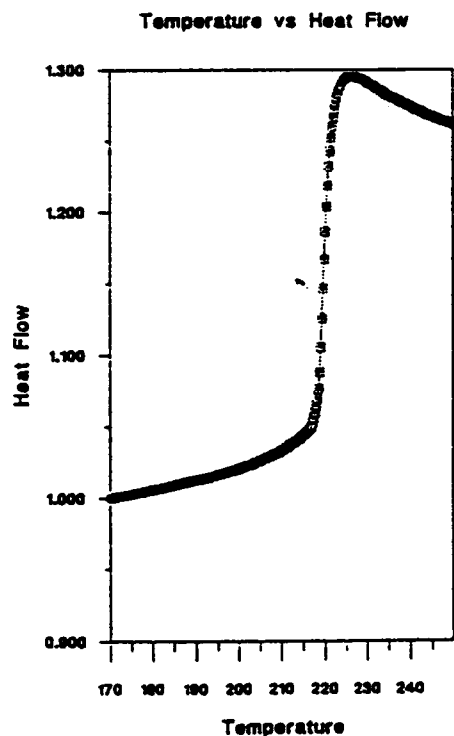
Polymers:

3a, D = H
3b, D = OMe
3c, D = NMe₂

These donor groups were chosen to discern how they effected the thermal and optical properties of the polymers.

The monomers were homopolymerized by use of a Ni/Zn couple.⁹ This procedure afforded polymers of low to moderate molecular weight. Polymerization of monomer 2a afforded oligomeric products along with significant amounts of insoluble materials. We suspect this insoluble material is higher molecular weight polymer. Polymerization of monomer 2b afforded only oligomeric products ($M_n = 1800$). Monomer 2c, which contains the best NLO-phore, afforded the highest molecular weight polymer ($M_n = 6000$). This polymer is soluble in chlorinated organic solvents. All attempts to increase the molecular weight by various methods, including addition of more catalyst, have so far proven ineffective.

The DSC scan for polymer 3c is shown below. This scan shows a T_g at about 220 °C.

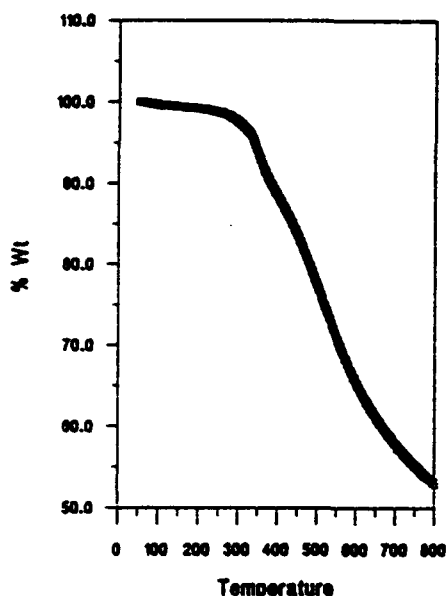


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The TGA scan for 3c is below. The scan shows about a 5% weight loss up to about 280 °C. At temperatures above 280 °C, we see decomposition of the NLO-phore.

Temperature vs % Wt



Concluding Remarks

Several new dichlorophenylene monomers with pendant NLO-phores were synthesized and polymerized to yield soluble polymers of low to moderate molecular weights. This work demonstrates one of the first attempts at incorporation of NLO-phores into thermally stable polymeric backbones. Optical studies are currently underway (in collaboration with Prof. H. Lackritz and Kirk Wilson, Purdue University) and the results will be presented at the meeting.

Acknowledgments

We would greatly like to acknowledge the Office of Naval Research for funding this research.

Experimental Section

4-[2-(1,4-Dichlorophenyl)]SO₂C₆H₄C≡CPh (2a). ¹H NMR (CDCl₃) δ 8.34 (d, *J* = 2.5 Hz, 1 H, H-2), 7.92 (d, *J* = 8.7 Hz, 2 H, H-8), 7.65 (d, *J* = 8.6 Hz, 2 H, H-9), 7.51 (m, 4 H, H-6, H-14, H-15), 7.38 (m, 3 H, H-5, H-16).

4-[2-(1,4-Dichlorophenyl)]SO₂C₆H₄C≡C(4-methoxyphenyl) (2b). ¹H NMR (CDCl₃) δ 8.33 (d, *J* = 2.6 Hz, 1 H, H-2), 7.90 (d, *J* = 8.7 Hz, 2 H, H-9), 7.61 (d, *J* = 8.7 Hz, 2 H, H-8), 7.48 (m, 3 H, H-6 and H-14), 7.36 (d, *J* = 8.5 Hz, 1 H, H-5), 6.88 (d, *J* = 9.0 Hz, 2 H, H-15).

2-[1,4-Dichlorophenyl]SO₂C₆H₄C≡C(4-dimethylamino-phenyl) (2c). ¹H NMR (CDCl₃) δ 8.34 (d, *J* = 2.6 Hz, 1 H, H-2), 7.89 (d, *J* = 8.6 Hz, 2 H, H-8), 7.60 (d, *J* = 8.6 Hz, 2 H, H-9), 7.49 (dd, *J* = 2.6 Hz, *J* = 8.6 Hz, H-6), 7.39 (m, 3 H, H-5 and H-14), 6.66 (d, 2 H, H-15), 3.01 (s, 6 H, CH₃).

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