

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 15, 1996		3. REPORT TYPE AND DATES COVERED FINAL, 10/1/92-2/29/96
4. TITLE AND SUBTITLE New Polymers and Composites with Enhanced Optical Nonlinearity			5. FUNDING NUMBERS	
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AFOSR/ NO NL Building 410, Bolling AFB DC 20332-6448			10. SPONSORING/MONITORING AGENCY REPORT NUMBER F49620-92-J-0536	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT APPROVED FOR PUBLIC RELEASE; DISTRIBUTION IS UNLIMITED.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) New multifunctional monomers and copolymers and/or composites incorporating these monomer subunits have been synthesized and characterized for applications as third-order nonlinear optical materials or as light-emitting diodes. The chromophore units in the copolymer formulations are related to oligomeric segments of such fully conjugated polymers as poly[p-phenylene vinylene], poly[2,5-thienylene vinylene], polythiophene and diphenylaminodiphenylpolyenes. The copolymers could be fabricated into thin-film light-emitting diodes with emission in the blue region of the visible spectrum. These devices exhibit low turn-on voltages and bright emission and are being considered for commercialization. 19960502 034				
14. SUBJECT TERMS Nonlinear optical materials, copolymers, light-emitting diodes			15. NUMBER OF 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	

FINAL TECHNICAL REPORT

Prepared for: Air Force Office of Scientific Research

Title: "New Polymers and Composites with Enhanced Optical Nonlinearity"

Grant Number: F49620-92-J-0536

Grant Period: September 30, 1992 - September 30, 1995
(No-cost Extension to February 29, 1996)

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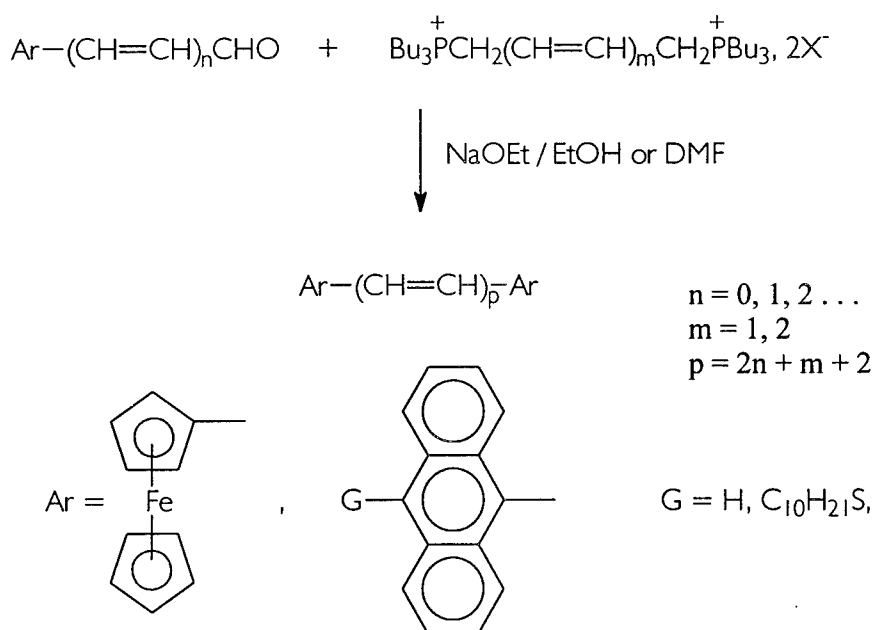
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Introduction

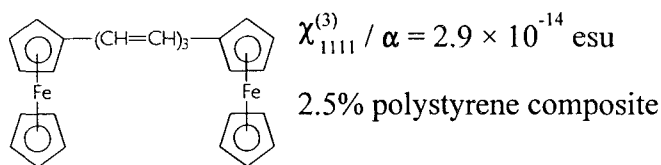
The original goal of this program was the design of new organic polymers and composites with enhanced third-order optical nonlinearity. New organic NLO chromophores were to be designed and synthesized and incorporated into copolymer formulations as alternating repeat units, or into guest-host composite systems.

Synthesis of New Chromophores and Polymers

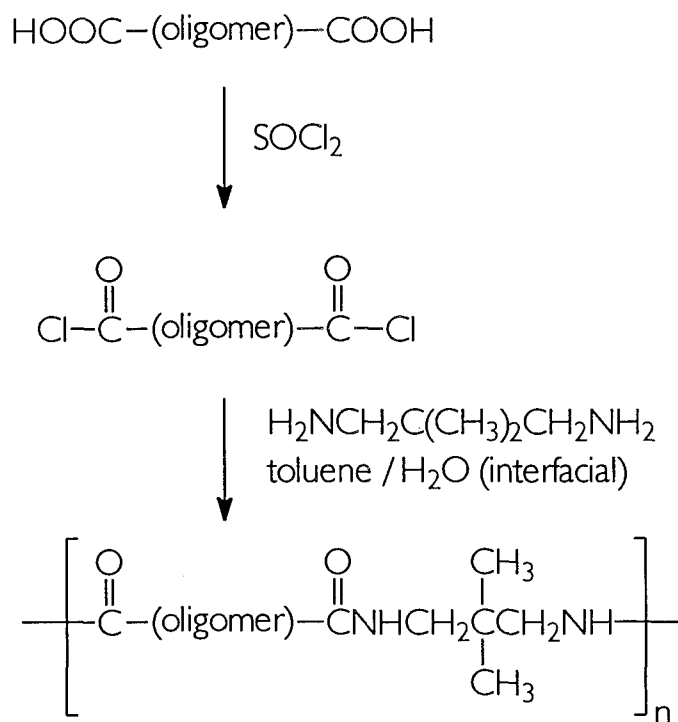
In the first year of this project, the focus was on bis-anthracenylpolyenes and bis-ferrocenylpolyenes. Several new polyenes were synthesized by bis-Wittig condensation:



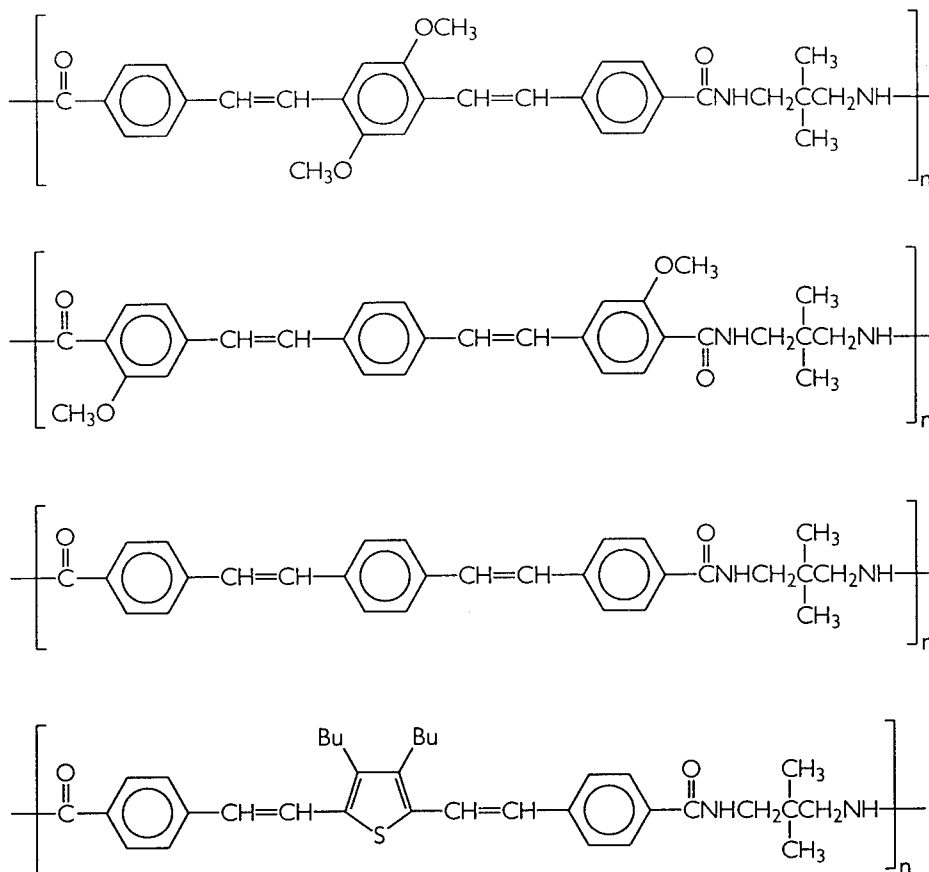
Polyenes with $p > 6$ could not be synthesized due to solubility limitations. Both polyene series were chemically oxidized to stable bipolaron-like dications with SbCl_5 . In both cases, the dications were extremely stable. Polycarbonate composites of the bis-anthracenylpolyenes in both neutral and oxidized form were prepared, and it was determined that no decay in optical absorption for the bipolaron form was found after several months. However, the films did become brittle, probably due to incomplete removal of antimony species (SbCl_5 or SbCl_3). The bis-ferrocenylpolyenes could also be cast as optical quality films in polystyrene composites. However, concentrations greater than 2.5% of the NLO-active species were difficult to prepare due to lack of solubility and/or phase separation. Attempts were made to incorporate both bis-anthracenyl and bis-ferrocenyl moieties into copolymers (polyurethane and polycarbonate formulations). This approach was not very successful due to lack of monomer and oligomer solubility which produced materials of low molecular weight. $\chi^{(3)}$ values for the 1,6-bis-ferrocenylhexa-1,3,5-triene were obtained by degenerate four-wave mixing in collaboration with Professors Robert Hellwarth and Larry R. Dalton at the University of Southern California.



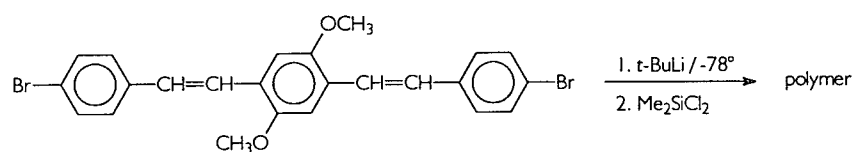
In the second year of the project, we expanded our studies to include NLO-active chromophores which might exhibit multifunctionality. Thus, not only might these new materials display enhanced third-order nonlinearity, but they may also function in such diverse fashions as light-emitting thin-film diodes (LEDs), or as potential polymeric superconductors when in their doped form. We focused on incorporation of the NLO-phores into formal copolymers such as polyamides or as block copolymers alternating with dialkylsilanyl groups. We were able to incorporate polythiophene, poly[p-phenylene vinylene] (PPV), or poly[thienylene vinylene] (PTV) oligomeric repeat units into polyamide structures in excellent yield:



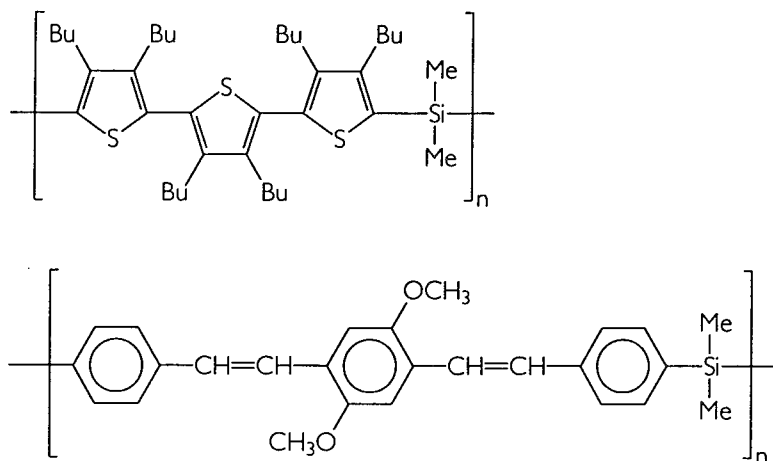
The following polymers were synthesized by this approach:



Silane block copolymers were made by reacting a dilithio derivative of the NLO-phore with the corresponding dichlorodialkylsilane moiety:

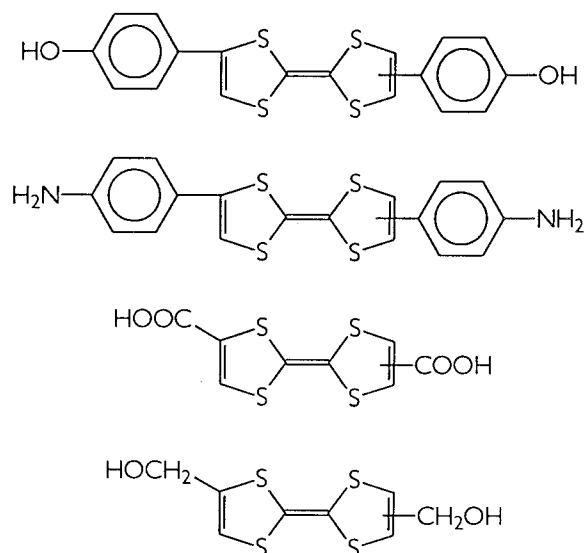


The silane block approach in general yielded lower MW polymers than the polyamide syntheses, however, the following polymers were obtained:

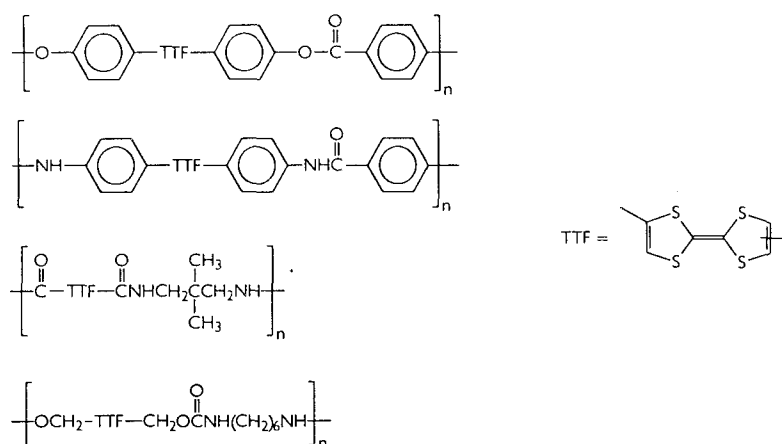


Several of these copolymers have been successfully tested in LED devices. This is discussed in a later section.

As a companion project to our URI-RIP program (AFOSR 49620-92-J-0533), we have been attempting to incorporate TTF subunits into copolymer and pendant polymer formulations. The following monomers have been successfully synthesized:

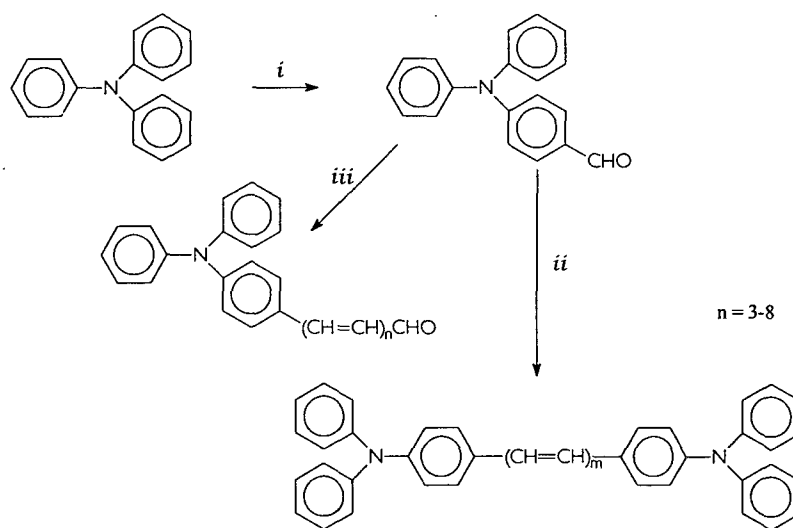


The AASERT fellow working on this project, Mr. John Thurmond, is currently converting these monomers into the following polymer formulations:



Polymer synthesis and characterization will be the final stage of his doctoral thesis.

Finally, two of the undergraduate research assistants associated with this project over the past two years have developed a new approach to the design of thermally stable NLO chromophores based on the diphenylamino moiety. Bis-(*N,N*-diphenylamino)diphenylpolyenes have been synthesized as follows:



- i. $\text{POCl}_3 / \text{DMF} / \Delta$
 ii. $\text{Bu}_3\text{P}^+\text{CH}_2(\text{CH}=\text{CH})_p\text{CH}_2\text{P}^+\text{Bu}_3, 2\text{X}^-$
 iii. $\text{Bu}_3\text{P}^+\text{CH}_2-\text{O}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{O}-\text{P}^+\text{Bu}_3 / \text{NaOEt} / \text{DMF} ; 10\% \text{ HCl} / \text{THF}$

The resulting polyenes are *much more* soluble than those based on Me_2N substituents. They are also more stable thermally. We have been able to synthesize polyenes up to $n = 8$, with no loss in solubility. The polyenes can be oxidatively doped to bipolaron-like dications in solution with SbCl_5 .

to yield extremely stable charged species (no decay in optical signal for several weeks). The absorption characteristics of these materials are shown in Table 1.

Table 1. Oxidative doping of bis(diphenylamino)diphenylpolyenes

n	$\lambda_{\max}$ π - π^* neutral (nm) ^a	$\lambda_{\max}$ BP (nm) ^a
3	424	730
4	438	770
5	449	805
6	462	848
7	464	892
8	485	922

^a10⁻⁵ M solutions in CH₂Cl₂.

At the current time we are extending these syntheses to determine if there are oligomer length or solubility limitations to this synthetic approach to new NLO chromophores with enhanced processibility and thermal stability. In addition, we have recently shown that these moieties can be incorporated into copolymer structures which are being evaluated for their LED and NLO behavior (Figure 1).

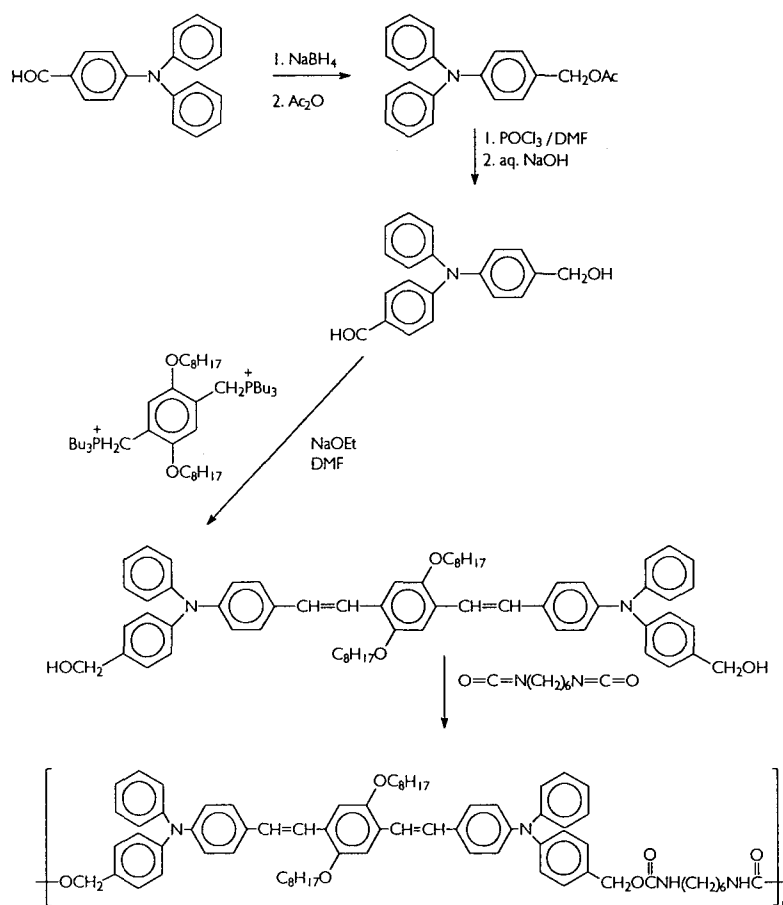


Figure 1. Synthesis of copolymer incorporating diphenyl aminophenyl-PPV subunits.

Interactions/Transitions

An ongoing collaboration with Laser Photonics Technology, Inc., as reported in our last Interim Progress Report (September 30, 1994-September 1, 1995), utilizing several of the polymers developed in this program, is continuing. The copolymers incorporating PPV and PTV segments have been fabricated into LED devices, funded under an SBIR Phase I by the National Science Foundation. A Phase II proposal has been submitted and is still under active consideration. This collaboration is being coordinated by Dr. Ryszard Burzynski, Laser Photonics Technology, Inc., 1576 Sweet Home Road, Amherst, NY 14228. Professor Spangler is a consultant to this project. A summary of the polymer LED characteristics is illustrated in Figures 2-5 and in Table 2.

Personnel Supported

The original appointee to the AASERT fellowship was Ms. Michelle Sachtleben. After working on the above project for one semester, Ms. Sachtleben resigned her position for personal reasons and left graduate school for an industrial position. Mr. John Thurmond replaced her, as reported in our first Interim Progress Report. Mr. Thurmond has since completed all the requirements for the doctoral degree and is scheduled to graduate in May 1997. He has recently been awarded a Dissertation Completion Fellowship by Northern Illinois University. Mr. Thurmond intends to pursue a postdoctoral appointment in NLO materials, followed by a college-level academic position. He will continue the research interests developed during the tenure of his AASERT fellowship. Mr. Thurmond has also been involved in the URI-RIP project on the design of superconducting organic polymers.

Several undergraduates have participated in this project as research assistants. The following list of students also indicates how they are currently involved in chemistry:

1. Mr. William Veldhuyzen, Ph.D. program, University of Illinois
2. Mr. Ken Ifkovits, Ph.D. program, University of Arizona
3. Mr. Hu Li, M.S. program, University of Southern California
4. Mr. Tyson Norlin, current undergraduate research assistant, plans to attend graduate school

New Discoveries, Inventions, or Patent Disclosures

At the current time, no patent disclosures on the LED work have been filed.

Honors/Awards

None.

Presentations/Publications

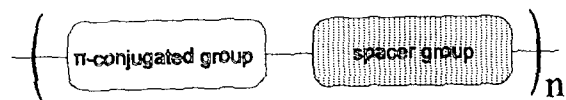
1. C. W. Spangler, "Formation, Stabilization and Nonlinear Optical Properties of Bipolaronic Charge States in Highly Conjugated Systems," invited paper, 50th Southwest Regional Meeting, American Chemical Society, Ft. Worth, Texas, November 1994.

2. L. Zhu, T. Hall, J. Thurmond and Mamatha N., "Studies Toward the Design and Synthesis of Superconducting Organic Polymers Incorporating TTF and BEDT-TTF Subunits," 50th Southwest Regional Meeting, American Chemical Society, Ft. Worth, Texas, November 1994.
3. C. W. Spangler, "The Influence of Charge State Incorporation on the Nonlinear Optical Properties of Conjugated Polyenes," *Handbook of Conducting Polymers*, T. Skotheim, J. Reynolds and R. Eisenbaumer, eds., Marcel Dekker, Inc. (in press).

Three papers have resulted to date involving technology transfer of selected polymers prepared in this program to Laser Photonics Technology. These materials have been utilized to prepare new organic LEDs with controlled predictable emission. This technology transfer project is being funded by the National Science Foundation.

4. C. W. Spangler, H. Li, J. Thurmond, M. He, S. Ghosal, Y. Zhang, M. Casstevens and R. Burzynski, "Organic Copolymers as Materials for Light-Emitting Diodes," Spring Meeting, Materials Research Society, San Francisco, CA, April 1995.
5. C. W. Spangler, J. W. Thurmond, H. Li, M. He, S. Ghosal, Y. Zhang, M. K. Casstevens and R. Burzynski, "New Copolymers for Applications as Organic LEDs," *Proc. SPIE* **1995**, 2528, 46.
6. C. W. Spangler, H. Li, T. Norlin and J. Thurmond, "The Synthesis of New Organic Copolymers for Applications as Light-Emitting Diodes," *Polymer Preprints* **1995**, 36(2), 296.

Three additional papers are currently being prepared for presentation at meetings in 1996.



General structure of the EL compounds studied

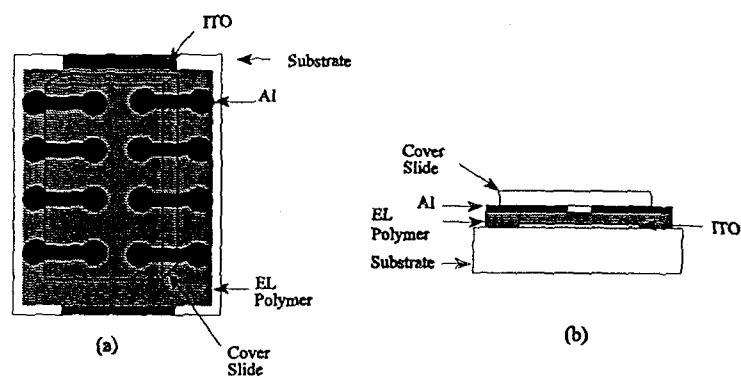


Table 2 : Summary of light emission characteristics obtained from the LED junctions.

Compound	$\lambda_{\max}$ /nm	Color	Quantum efficiency
LED4	440	blue-violet	2.33×10^{-6}
LED1	470	blue	2.07×10^{-4}
LED2	500	blue-green	6.75×10^{-4}

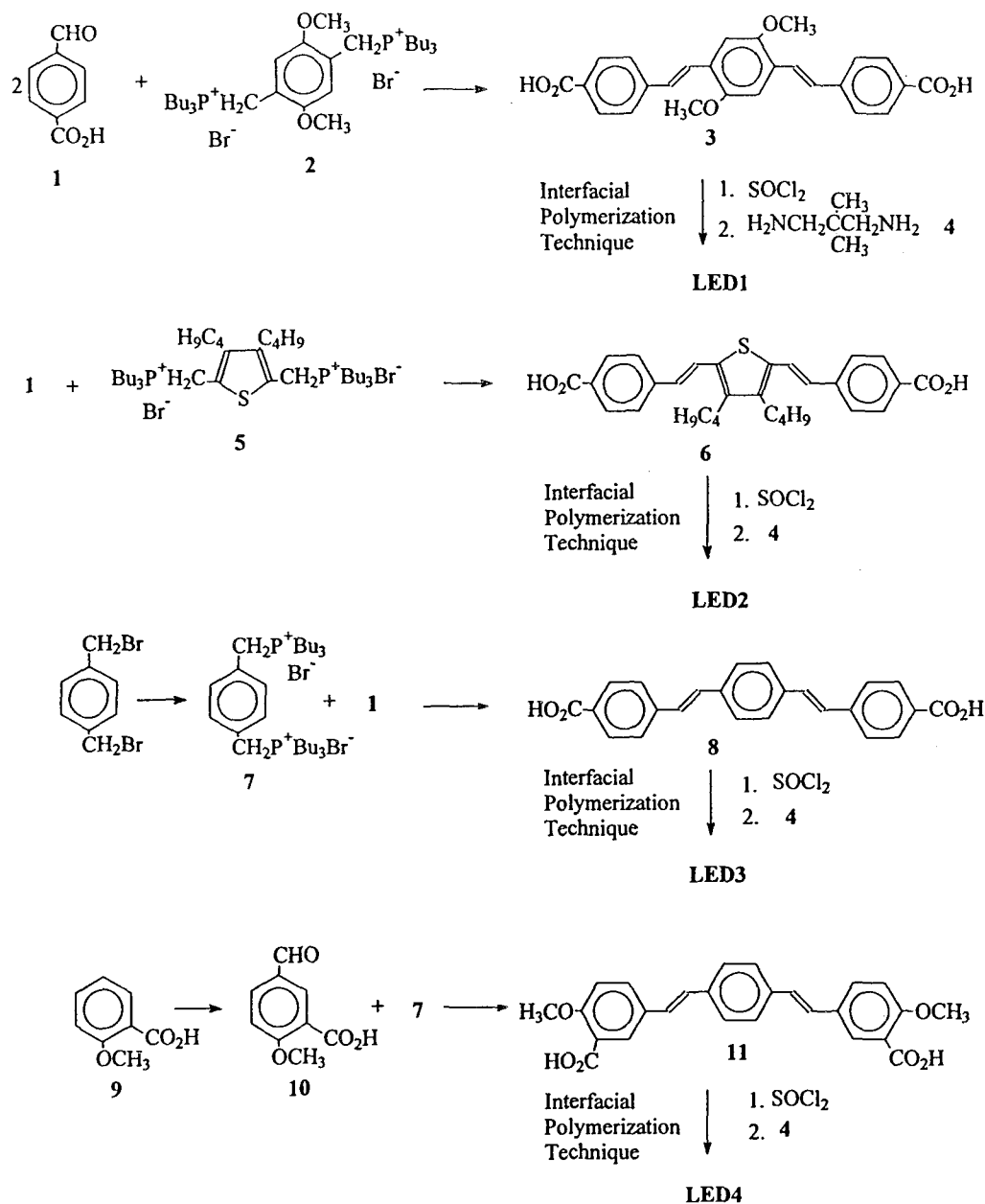


Figure 2: Synthesis of LED1, LED2, LED3 & LED4.

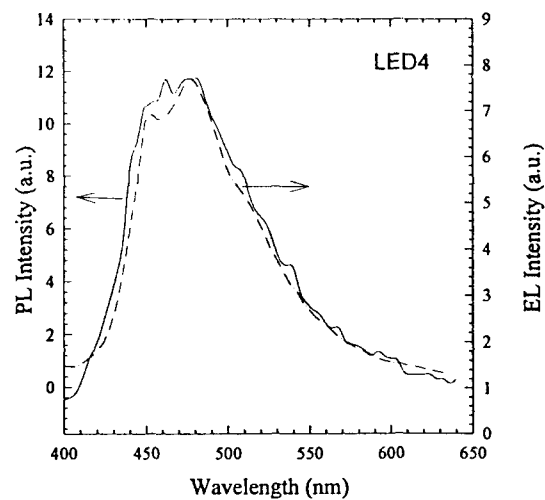
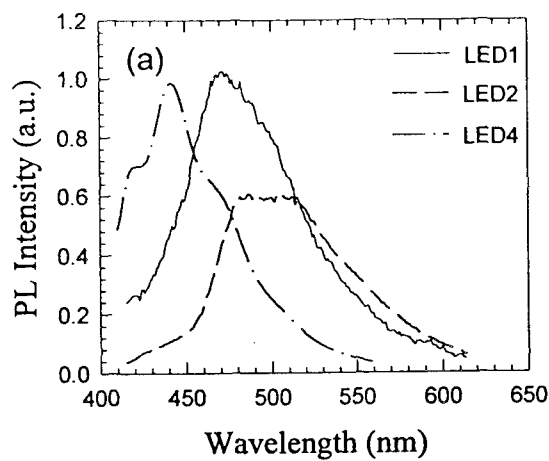


Figure 3: Photoluminescence and electroluminescence spectra for LED4.

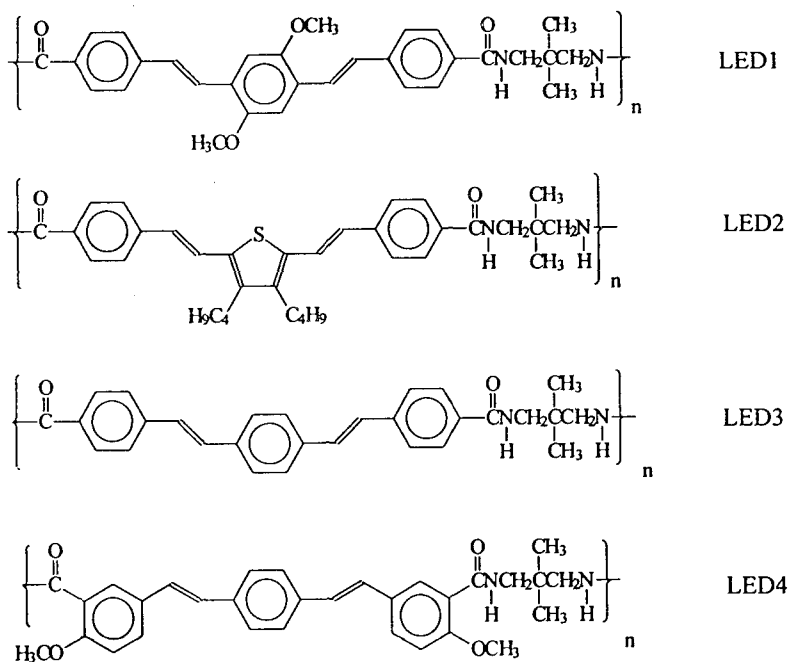


Figure 4: Chemical structures for LED1-4.

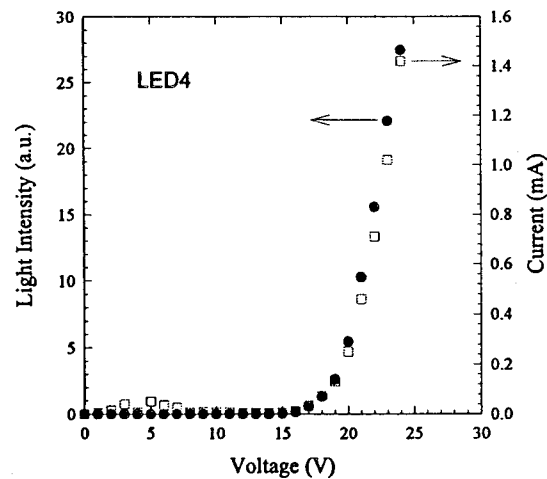
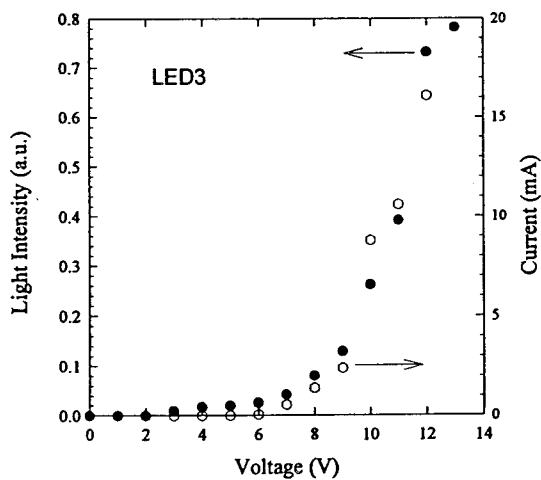
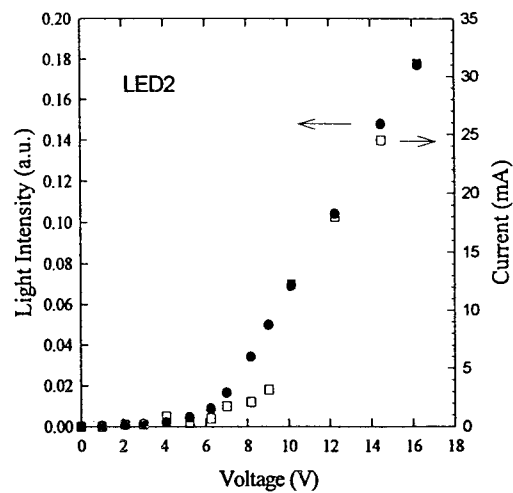
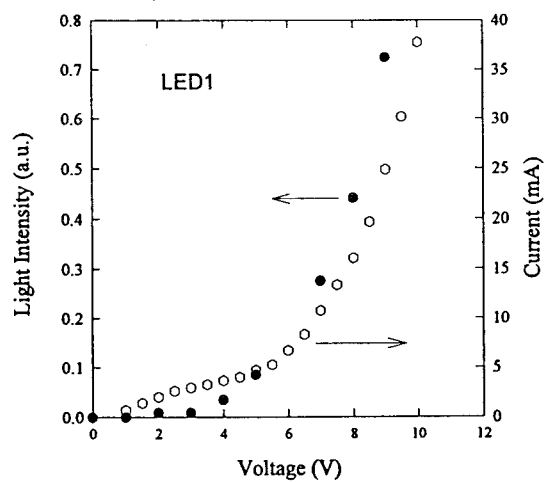


Figure 5: Voltage dependence of light intensity and current for LED1-4.