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Conjugated Polymers From Cyclohexadienediol Monomers

Progress Report
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ROMP polymerization has become an important method for the preparation of polyphenylenevinylene and poly(p-phenylenevinylene). The new route allows the band gap and processing properties of the polymers to be varied by the use of side chains and functional groups. These materials are being used to fabricate electroluminescent devices with tunable colors. New techniques have been developed for the synthesis of the starting arenes and benzobarrelene. These synthesis start from the ICI diol system that was used in the preparation of poly(p-phenylenevinylene). A key to these developments is the availability of well defined catalysts, considerable effort has been devoted to the design and synthesis of new complexes that will catalyze the ROMP polymerization reaction and to develop new procedures which will control the molecular weight and livingness of those systems know. The students involved in this work have gained experience in polymer synthesis, catalyst development and the fabrication of devices.
2. Objectives: no change

3. & 4. Progress and Technical Accomplishments

**Polyarylenevinylene**

The ICI cyclohexadiene monomer has been used to prepare poly(arylenevinylene) derivatives through a precursor route. The polyarylene vinylenes show interesting properties and some derivatives have been used to fabricate photoemitting diodes. A general route to polynaphthalene vinylenes has been developed that is now being expanded into the synthesis of block polymers. A simple route to substituted benzyne precursors (8a,b) was developed and the resulting benzynes were added to the ICI monomer. The adducts could be converted to benzobarrelene analogs by the treatment of the benzaldehyde acetal derivative with a strong base such as LDA.

![Chemical structure](image)

\[ R = -(CH_2)_3CH_3 \text{ or } -(CH_2)_6CH_3 \]

The resulting benzobarrelenes could be polymerized to in high yields with a variety of ROMP catalysts. These living systems could be used to control the molecular weight and molecular weight distribution.

![Chemical structure](image)

The resulting soluble polymers could then converted to the soluble vinlylenenaphthylene with a variety of oxidizing agents, however DDQ was the most effective.
The UV/Vis spectrum of the fully conjugated derivatives displays a strong absorbance at 448-450 nm, which demonstrates the formation of an extended p-conjugation in the oxidized polymer after the dehydrogenation. When excited at 440 nm, the fluorescence emission spectra of the conjugated polymers show strong signals at 583 nm and 572 nm respectively. By visual observation, solutions of the conjugated polymers glow yellow orange under UV irradiation. In preliminary studies, electroluminescence devices have been fabricated by spin coating using these materials. A key finding was that good internal electroluminescence quantum efficiencies of up to 0.05% could be obtained using an air stable Aluminum electrode.

Derivatives that contain halogens as electron withdrawing groups have been prepared and converted to polymers. It has been found that these derivatives can be used to tune the emission spectrum of the resulting polymer for example a polymer with red fluorescence has been reported. With support from another agency, this work has continued as a method for the preparation of a variety of block polymers and related systems. A number of new methods of controlling the polymerizations were uncovered during this work and is now being studied in detail in a mechanistic study supported by the NSF.

Since the monomers that are being prepared are new substrates for ROMP, a method of predicting which compounds will polymerize has been developed and is being applied to a number of new substrates.

**Polyparaphenylene:** The final papers on the synthesis of polyparaphenylene have been published. A collaboration with A. MacDiarmid at U. of Penn has resulted in the conversion of the precursors into extremely stable films of PPP. Samples of the high molecular weight, linear precursor to polyparaphenylene that was prepared were sent to the University of Dayton, Edwards Airforce Base and to other federal laboratories. Other applications in the construction of blue electroluminesence diodes and in the development of a high density battery are being explored.
5. Graduate students supported during this effort:
   Michael Wagaman
   Thomas Wilhelm

6. Publications:


Chapters


7. Interactions/Transitions:

(a) Participation at meetings, conference, seminars, etc.:

209th ACS National Meeting, Anaheim, CA
April 2-6, 1995

210th ACS National Meeting, Chicago, IL
August 20-24, 1995

(b) Consultative and advisory functions to other laboratories and agencies. (Provide subject matter, institutions, locations, dates, and names of individuals involved.

NRC Polymers, Macromolecules Advisory Board,
Material to G. Leissing for fabrication of LED

(c) Transitions.

8. New discoveries, inventions, or patent disclosures. none

9. Honors/Awards.

1995 ACS Award in Polymer Chemistry sponsored by Mobil Chemical Company