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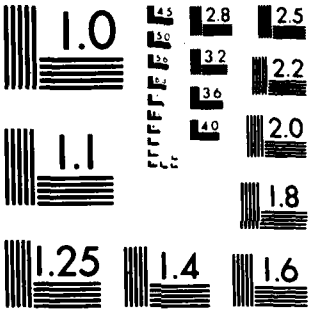

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REPORT DOCUMENTATION PAGE

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1. REPORT NUMBER: 20	2. GOVT ACCESSION NO.: AD-A136955
3. RECIPIENT'S CATALOG NUMBER: (12)	
4. TITLE (and Subtitle): Polymerization of 3-Methyl-2,5-Dibromothiophene Utilizing n-Butyl Lithium and Copper(II) Chloride	5. TYPE OF REPORT & PERIOD COVERED: Technical Report # 20
	6. PERFORMING ORG. REPORT NUMBER:
7. AUTHOR(s): Adel Amer, Hans Zimmer, Kevin J. Mulligan, Harry B. Mark, Jr., Stanley Pons, Jerome F. McAleer	8. CONTRACT OR GRANT NUMBER(s): N00014-83-K-0470
9. PERFORMING ORGANIZATION NAME AND ADDRESS: University of Utah, Department of Chemistry, Salt Lake City, UT 84112	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: Task No. NR 359-718
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Chemistry Program - Chemistry Code 472, Arlington, Virginia 22217	12. REPORT DATE: January 6, 1984
	13. NUMBER OF PAGES:
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Formation of conducting thiophene polymers formed by the use of n-butyl lithium as a dehalogenating agent is descreted.

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S/N 0102-LF-014-6601

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OFFICE OF NAVAL RESEARCH

Contract N00014-83-K-0470

Task No. NR 359-718

TECHNICAL REPORT NO. 20

Polymerization of 3-Methyl-2,5-Dibromothiophene Utilizing n-Butyl Lithium and Copper(II) Chloride

By

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Prepared for Publication in

Journal of Polymer Science and Polymer Chemistry

University of Utah
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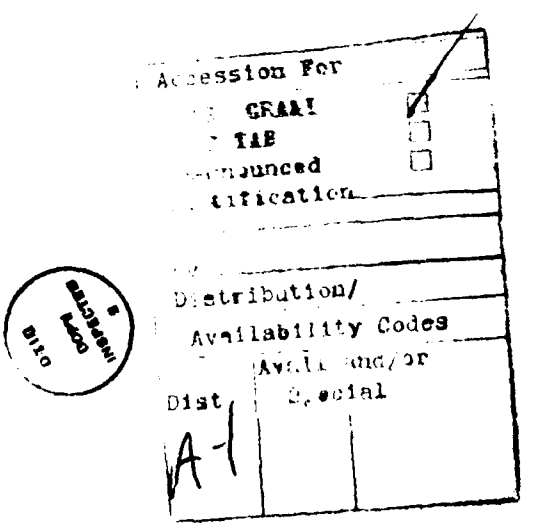
January 6, 1984

Polymerization of 3-Methyl-2,5-Dibromothiophene Utilizing n-Butyl Lithium and Copper(II) Chloride



Introduction

In recent years, there have been extensive research activities focussed on macromolecules with extended π-electron system[1]. Among the many macromolecules studied, conjugated olefinic compounds (polyenes), have been given much attention. Various methods for their synthesis have been reported.

In the heterocyclic category, there are four reports on the synthesis of poly(3-substituted-2,5-thienylene) (substituent = H, CH_3) via coupling of 3-substituted-2,5-dibromothienylmagnesium by nickel salt promoters.[2-5] Recently Afanas'ev, et al. reported also about the preparation of poly(2,5-thienylene) by an electrochemical method.[6]

The ability for charge transport through the thiophene polymer chain is an important criterion for achieving high conductivity. For that reason we began to study the synthesis of polyenes. The present investigation was undertaken to improve the synthesis of poly(3-methyl-2,5-thienylene) and to obtain a magnesium free material. Therefore, we chose to use n-butyl lithium as dehaloginating agent. Cu(II) chloride was utilized to serve as catalyst.

Experimental

Instrumentation

^1H- and ^{13}C-NMR spectra were recorded on a Nicolet NT300 narrow bore spectrometer with 1180 E data system. Chemical shifts are expressed in δ relative to tetramethylsilane as internal standard. Infrared spectra (IR) were recorded using a Perkin-Elmer Model 599 spectrometer calibrated against the 1601 cm^{-1} band of polystyrene.

Materials

3-Methyl-2,5-dibromothiophene was prepared according to the procedure by O. M. Cohn and S. Gronowitz.[7] n-Butyl lithium was obtained as a solution in n-hexane from

Lithium Corporation of America; the anhydrous cupric chloride (golden label), from Aldrich Chemical Company was used as received. Tetrahydrofuran (THF) was distilled from sodium and benzophenone under an argon atmosphere.

Polymer Synthesis

A solution of 7.952 gm (0.031 mole) of 3-methyl-2,5-dibromothiophene in 40 ml of dry THF was treated with 44.4 ml (0.062 mole) of 1·4 N n-butyl lithium in hexane at -55°C under N_2 atmosphere. The resulting colorless suspension was stirred for 10 min. at this temperature, then 8.354 gm of anhydrous cupric chloride followed by 7.952 gm of 3-methyl-2,5-dibromothiophene were added. The reaction mixture was allowed to warm up to -5 to 5°C. Stirring was continued for 20 min. while dry oxygen was bubbled through the suspension for 30 min. The reaction mixture was hydrolyzed with an aqueous solution of 5 gm potassium cyanide in 500 ml of water. The resulting precipitate was filtered off, washed with water and methanol to yield 4 gm of polymeric material. It was first extracted with methanol to remove the low molecular weight polymer, followed by extraction with $CHCl_3$, leaving an insoluble residue. Analysis found for $CHCl_3$-extractable fraction: %C, 51.07; %H, 3.62; %S, 27.26; %Br, 11.68; %Cl, 5.38; %Cu, 0.83 (total 99.86%).

Results and Discussion

n-Butyl lithium/cupric chloride proved successful as a polymerization agent of 3-methyl-2,5-dibromothiophene. The yield of the polymer was found to be dependent on the reaction temperature.

In order to get further information about the stereoselectivity of C-C coupling by the present method, we have prepared the poly(3-methyl-2,5 thienylene) exactly as reported by T. Yamamoto et al.[5] using Mg and $NiCl_2$(bpy) and compared some physical properties of the polymer synthesized by these different methods.

Poly(3-methyl-2,5-thienylene) prepared by the present method is light brown whereas the one prepared by the previously reported method is dark brown.[5] The UV-vis spectra for the $CHCl_3$-extractable polymers (Fig. 1) showed difference in position of λ_{max} and magnitude of absorbance. The polymer synthesized by the present method showed a rather narrow UV absorption band at 415 nm which may be attributed to a fairly uniform range of molecular weight of this polymer. On the other hand, the polymer prepared by the known method[5] exhibited a low absorbance broad band at 420 nm indicating a wide range of molecular weight. ^{1}H-NMR ($CDCl_3$) spectra (Fig. 2) showed two singlet at δ 2.192 and 2.369 (3H, CH_3), and a peak at δ 6.902 (1H, thiophene ring proton) (for the polymer synthesized by n-BuLi/$CuCl_2$, Fig. 2A). For the polymer synthesized by Mg/$NiCl_2$(bpy) Fig. 2 (B) two singlet at δ 2.216 and 2.382 (3H, CH_3) and a singlet at δ 6.944 (1H, thiophene ring proton) were observed. The methyl group protons resonated as two singlet in both cases, however the integration over the area showed that one singlet predominated over the other in the case of the polymer synthesized by the present method. A result which can be explained by the fact that under oxidative coupling of 3-methyl-2,5-dibromo-thiophene mixed with the corresponding di-lithium species, the probability of symmetrical coupling of the aryl species is much lower than the probability of unsymmetrical coupling.[8] A plausible explanation of the ^{1}H-NMR spectrum (A) is the presence of a mixture of transoid and cisoid forms *I* and *II*.

However, ^{13}C-NMR ($CDCl_3$) (Fig. 3) of poly(3-methyl-2,5-thienylene) prepared by our method showed eight different methyl groups by exhibiting peaks at δ 14.763, 14.815, 15.014, 15.173, 15.347, 15.376, 15.531 and 15.669. The IR-spectrum has a strong absorption band at 800 cm^{-1} which is due to the characteristic out-of-plane C-H deformation of the thiophene ring; it also showed bands at 1420 and 1490 cm^{-1} which are caused by the ring stretching of substituted thiophene.[3]

The room temperature conductivity of a compressed pellet showed the polymer to be an insulator. A drastic change in conductivity, however, was observed upon doping with iodine. The polymer-iodine adduct shows electric conductivity of 3.2×10^{-2} S cm^{-1} for the $CHCl_3$ -extract (iodine/polymer = 30 wt percent) which is about equal to the reported value of 2.8×10^{-2} S cm^{-1} which, however, contains much more iodine, namely 94 wt percent.

It is interesting to note that the average polymer chain contains 8 monomer units (calculated on the base of the amount of bromine which is assumed to be present on chain ends only). This seems to confirm recent suggestions that long chains of the polymer are not a necessary condition for good conductivity.[9]

In conclusion, our new method yields an excellent Mg-free polymer. An exploratory investigation utilizing n-BuLi/transition metal complexes as polymerization agents of dibromoarylenes including structural studies and detailed electric properties are in progress.

Acknowledgement

This research was supported in part by the National Science Foundation, Grant No. CHE8205873. S.P. thanks the Office of Naval Research for support of part of this work.

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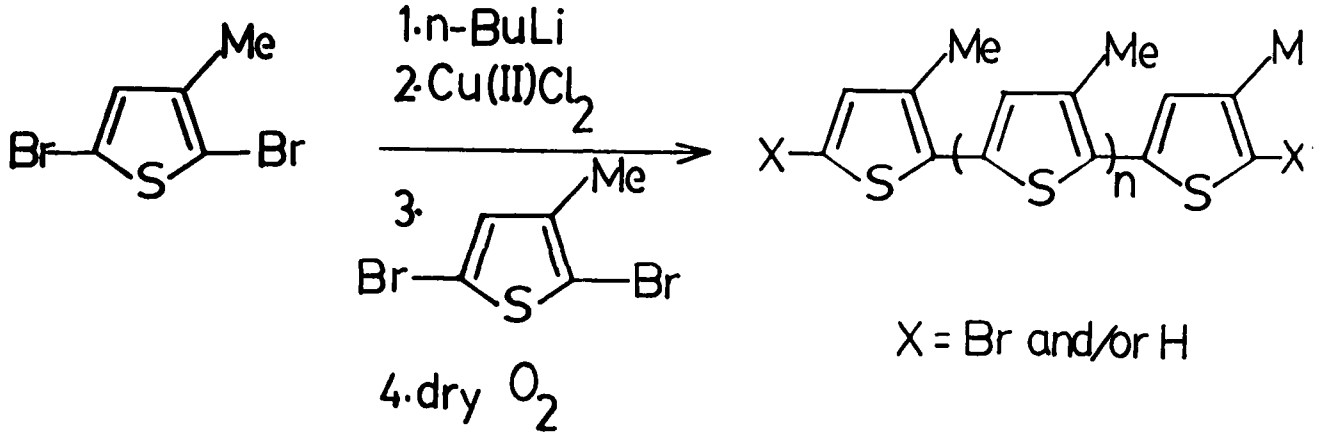
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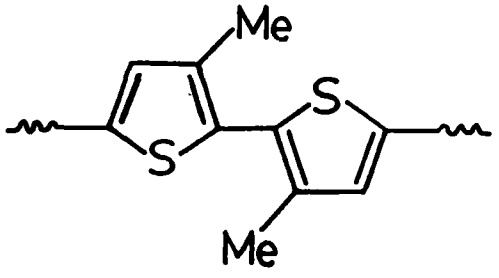
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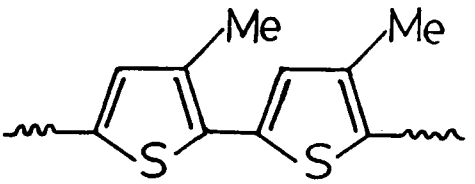
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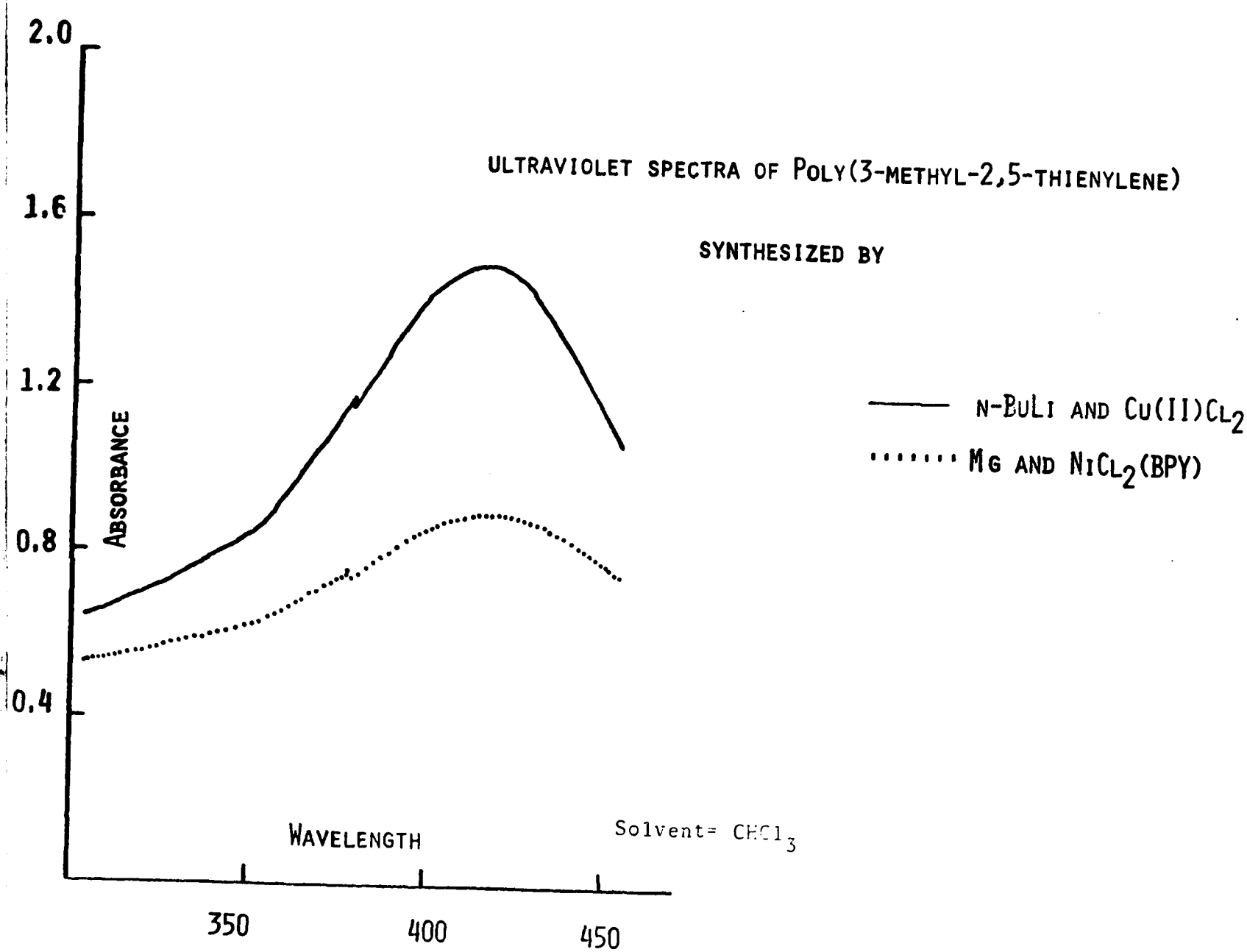
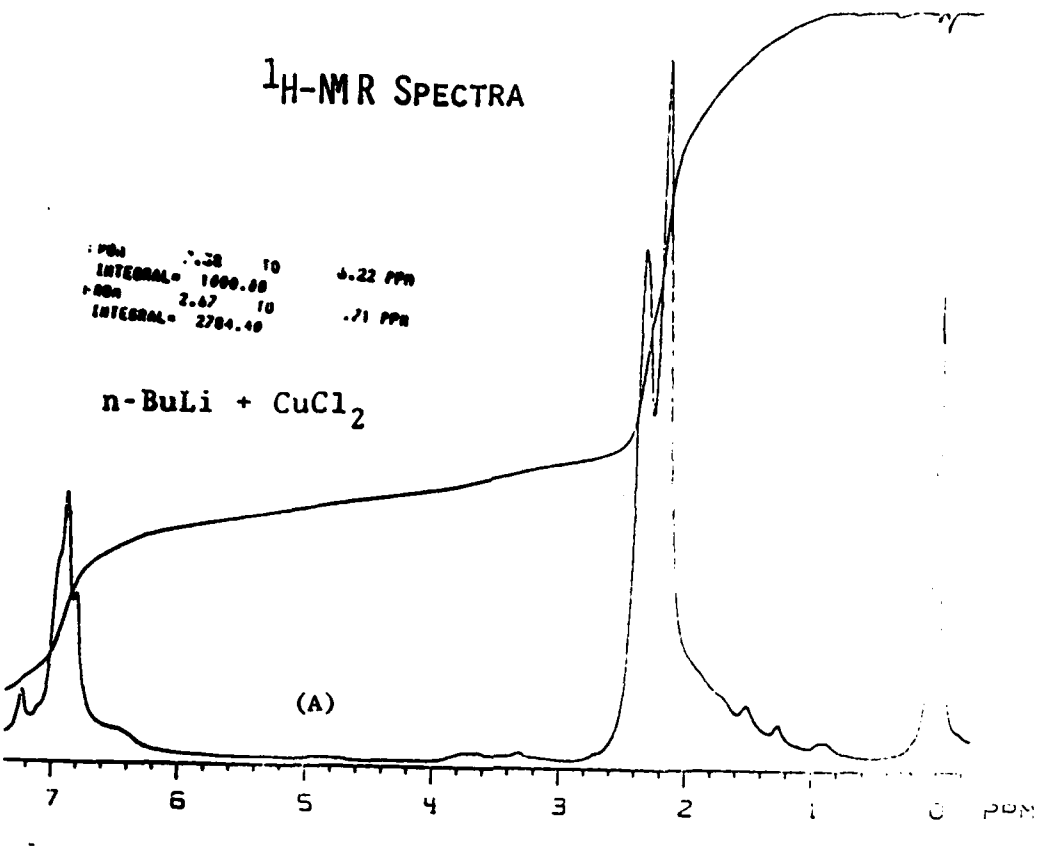
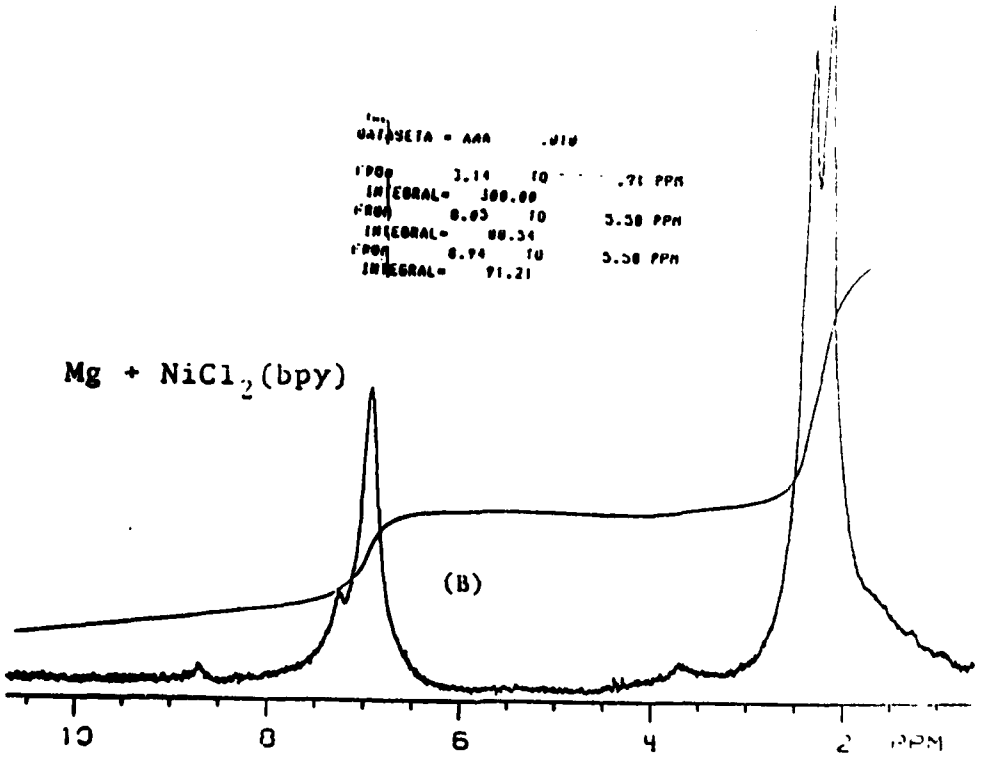

ULTRAVIOLET SPECTRA OF POLY(3-METHYL-2,5-THIENYLENE)
SYNTHESIZED BY
N-BULI AND CU(II)CL2
MG AND NICL2(BPY)
2.0
1.6
1.2
0.8
0.4
ABSORBANCE
WAVELENGTH
350
400
450
Solvent= CHCl3

Fig. 1





Solvent= $CDCl_3$

Fig. 2

Decoupled ^{13}C-NMR Spectrum

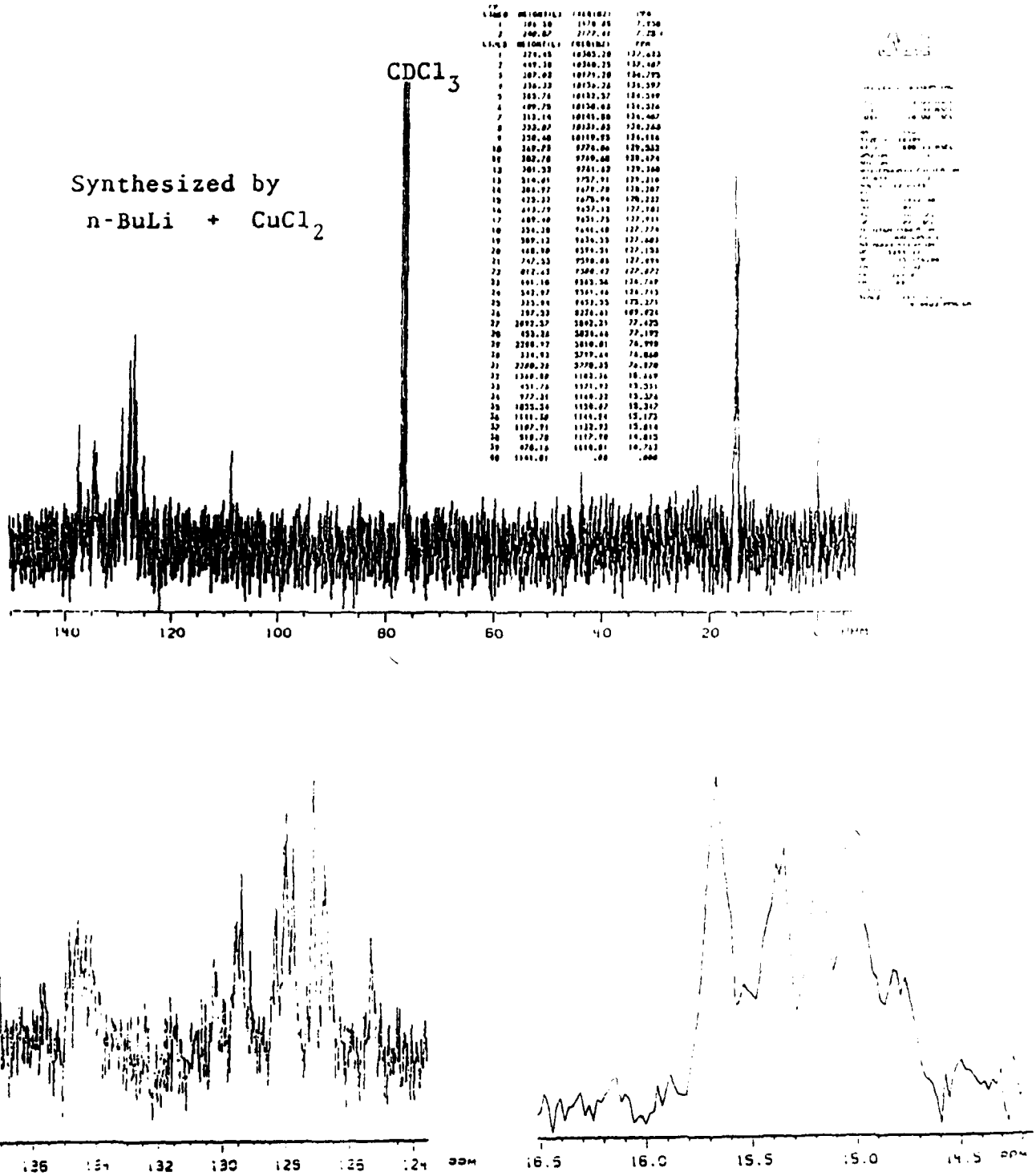


Fig. 3