

AD-A243 641



✓  
②

*Office of Naval Research*

Grant: N00014-91-J-1625

R&T Code: 4132051--01

*Technical Report No. 2*

Organometallic NLO Polymers. Linear Main-Chain NLO Polymers of Ferrocene

by

Michael E. Wright and Edward G. Toplikar

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

DTIC  
S ELECTE D  
DEC 24 1991  
D

Accepted for Publication in

*Polym. Preprints* 1992, 33(1), pp 0000

December 13, 1991

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.

91-18883



91 1225 071

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
1a. REPORT SECURITY CLASSIFICATION <b>Unclassified</b>			1b. RESTRICTIVE MARKINGS		
2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT <b>Approved for public release: distribution unlimited</b>			
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE					
4. PERFORMING ORGANIZATION REPORT NUMBER(S)			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION <b>Utah State University</b>		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION		
6c. ADDRESS (City, State, and ZIP Code) <b>Chemistry and Biochemistry Dept. Logan, UT 84322-0300</b>			7b. ADDRESS (City, State, and ZIP Code)		
8a. NAME OF FUNDING / SPONSORING ORGANIZATION <b>Office of Naval Research</b>		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER		
8c. ADDRESS (City, State, and ZIP Code) <b>800 N Quincy St. Arlington, VA 22217-5000</b>			10. SOURCE OF FUNDING NUMBERS		
			PROGRAM ELEMENT NO <b>N00014-91</b>	PROJECT NO <b>J-1625</b>	TASK NO <b>4132051</b>
			WORK UNIT ACCESSION NO		
11. TITLE (Include Security Classification) <b>Technical Report #2: "Organometallic NLO Polymers. Linear Main-Chain NLO Polymers of Ferrocene"</b>					
12. PERSONAL AUTHOR(S) <b>Michael E. Wright and Edward G. Toplikar</b>					
13a. TYPE OF REPORT <b>Preprint</b>		13b. TIME COVERED FROM <b>4/15/91</b> TO <b>4/15/92</b>		14. DATE OF REPORT (Year, Month, Day) <b>Dec. 13, 1991</b>	15. PAGE COUNT
16. SUPPLEMENTARY NOTATION <b>Polym. Preprints 1992, 33(1), pp 0000</b>					
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) <b>Polymers, Ferrocene, Nonlinear optical materials, Second harmonic generation, Single-crystal, X-ray diffraction, polyesters, condensation polymers, Knoevenagel condensation.</b>		
FIELD	GROUP	SUB-GROUP			
19. ABSTRACT (Continue on reverse if necessary and identify by block number)  <b>Bis(functionalized) ferrocene NLO-phore monomers were prepared. Several ferrocene NLO-phores were characterized by single-crystal molecular structures. The new ferrocene monomers were successfully polymerized using a Knoevenagel polycondensation technique. The polymers were characterized by spectroscopic and GPC data.</b>					
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>		
22a. NAME OF RESPONSIBLE INDIVIDUAL <b>Dr. Kenneth J. Wynne</b>			22b. TELEPHONE (Include Area Code) <b>(703) 696-4409</b>		22c. OFFICE SYMBOL

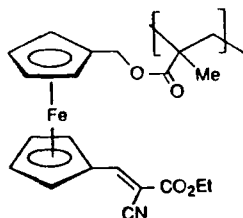
# ORGANOMETALLIC NLO POLYMERS. LINEAR MAIN-CHAIN NLO POLYMERS OF FERROCENE

Michael E. Wright\* and Edward G. Toplikar

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

## Introduction

The discovery of ferrocene over four decades ago marked the beginning of organometallic chemistry.<sup>1</sup> The ferrocene unit has proved itself to be a versatile building block with excellent thermal and photochemical stability.<sup>2</sup> Polymeric materials which contain organometallic moieties have become a well developed and mature subdiscipline of polymer chemistry.<sup>3</sup> The ferrocene unit has been incorporated into polymers as a pendant group<sup>4</sup> and also as part of the polymer backbone.<sup>5</sup>

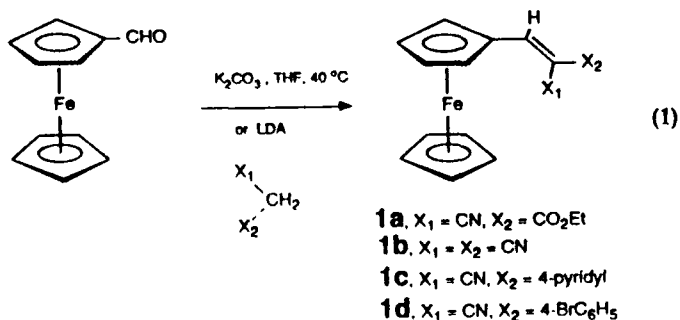


A very recent use of ferrocene complexes has appeared in the area of nonlinear optical (NLO) materials.<sup>6</sup> Based on both theory<sup>7</sup> and experimental<sup>8</sup> data, ferrocene compounds possess large hyperpolarizability values (i.e.  $\beta$ ). These data combined with excellent thermal and photochemical stability make ferrocene systems a top organometallic candidate for use in NLO materials.<sup>9</sup> Our research program has recently demonstrated that a ferrocene complex bound to poly(methyl methacrylate) copolymer can be successfully aligned and exhibit the optical property of second harmonic generation (SHG).<sup>10</sup>

We describe herein the synthesis of several novel ferrocene monomers and their utilization in the preparation of main-chain organometallic NLO polymers.

## Results & Discussion

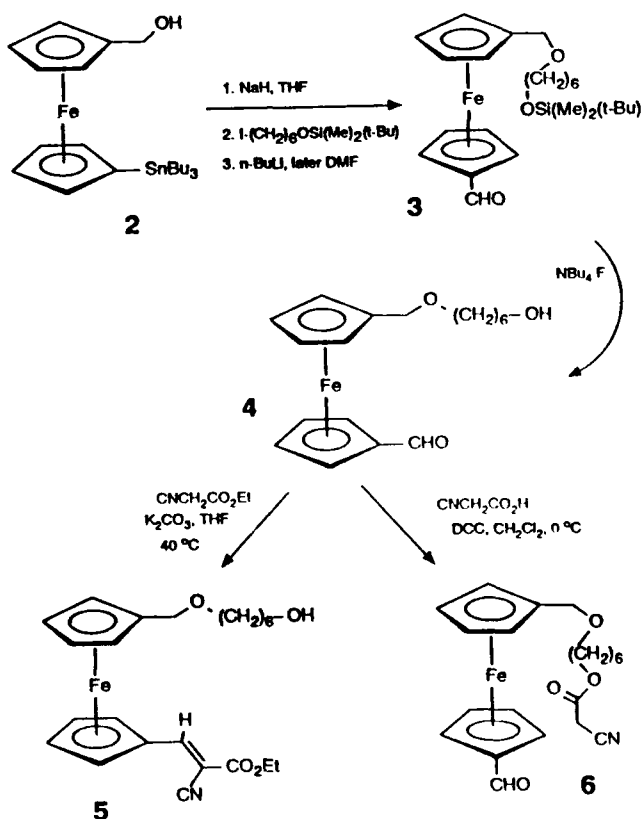
**Crystallographic Study of Ferrocene NLO-phores**  
Treatment of ferrocenecarboxaldehyde with active methylene compounds results in high yields of the condensation product 1 (eq 1).<sup>11</sup> For the preparation of 1c and 1d we employed lithium diisopropylamine in place of K<sub>2</sub>CO<sub>3</sub>. The reactions proceed in nearly quantitative yield with no apparent side reactions.



Four ferrocene NLO-phores have been characterized by single-crystal molecular structure determinations. Several structural features are worth noting. In all the systems we have prepared to date the cyano group is found in a Z-relationship to the ferrocenyl moiety. The coplanarity of the system appears related to the electronic nature of the substituents on the vinyl group. Notably, the *p*-bromophenyl group in 1d is rotated considerably out plane from the  $\pi$ -system; whereas, it can be seen that the 4-pyridyl in 1c is nearly coplanar with the  $\pi$ -system.

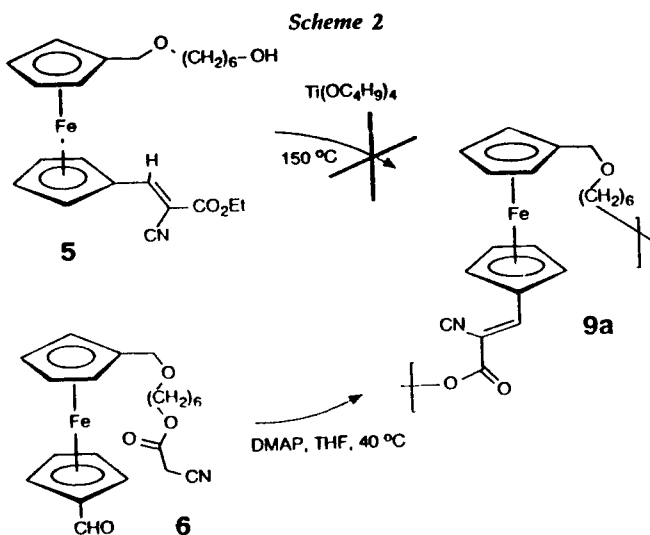
**Monomer Synthesis.** Through chemistry developed in our laboratory we can prepare complex 2 starting from readily available materials. Compound 2 is smoothly O-alkylated and then treated with *n*-BuLi and DMF to afford complex 3 (Scheme 1). Removal of the dimethyl-*tert*-butylsilyl protecting group using tetrabutylammonium fluoride affords complex 4 which serves as a pivotal intermediate in our synthetic strategy. Treatment of 4 with ethyl cyanoacetate in the presence of potassium carbonate affords monomer 5 in high yield. Coupling of 4 with cyanoacetic acid using dicyclohexylcarbodiimide (DCC) affords the AB monomer 6. Monomer 6 is found to be very base sensitive and rapidly undergoes an intramolecular Knoevenagel condensation which makes purification procedures extremely difficult.

Scheme 1



Dist		Author's Report	
A-1			

**Polymer Synthesis & Characterization.** We first attempted to polymerize monomer **5** by treatment with  $Ti(OC_4H_9)_4$  and heating the mixture to 150 °C under a nitrogen atmosphere (Scheme 2). The product of the polymerization reaction was an intractable purple solid. Carrying out the polymerization at 200 °C in a neat melt produced a similar intractable purple solid. In this latter reaction we identified 1,6-hexanediol as volatile by-product of the "polymerization" reaction. We seen similar results when polymerizing monomer **7** in that an intractable purple solid was obtained with spectroscopic (IR and UV-Vis) and analytical analogous to that expected for a polyester.



Treatment of **6** with *N,N*-dimethylaminopyridine (DMAP) at 40 °C produces polymer **9a**. Polymer **9a** is found to be low in molecular weight ( $M_n = \sim 4,500$ ) with both aldehyde and cyanoacetate end-groups. The polymer is soluble in all organic solvents and displays spectroscopic data consistent with the ferrocenyl NLO-phore (*i.e.*  $\beta$ -ferrocenyl- $\alpha$ -cyanoacrylate). Further treatment of polymer **9a** ( $M_n = \sim 4,500$ ) with new monomer produced polymer of higher molecular weight ( $M_n = 6,700$ ). We believe a limiting factor in the polymerization of **6** is an intramolecular Koenenagel condensation which competes with polymer formation. The macrocyclic lactone **10a** has been isolated from the polymerization reaction and fully characterized.

#### Concluding Remarks

Employing the Koenenagel polycondensation reaction affords homopolymers of modest molecular weight. These polymers are tractable materials unlike those obtained through transesterification or neat melt polymerization techniques. Work is continuing on the design of new monomers which are less likely to undergo an intramolecular Koenenagel condensation.

#### Experimental Section

**Polymer 9a** A Schlenk flask was charged with THF (3 mL), **6** (0.34 g, 0.83 mmol), and DMAP (0.10 g, 0.83 mmol). The mixture was heated to 40 °C and allowed to react for 16 h. The reaction mixture was decanted into pentane (100 mL) and the precipitated polymer collected (0.38 g, 43%). The polymer was contaminated with small amounts of lactone **10a**. GPC analysis of the polymer gave an average molecular weight of  $M_n = 4,500$ . A THF solution containing the polymer/lactone

mixture (0.03 g) and **6** (0.91 g, 2.21 mmol) was treated with DMAP (0.27 g, 2.21 mmol) to see if the molecular weight could be increased. GPC analysis of this product showed a peak corresponding to an average molecular weight of  $M_n = 6,700$ . Spectroscopic data for the polymer:  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.13 (s, 1 H, CHO), 4.98 (t,  $J = 2$  Hz, 2 H, Cp), 4.72 (t,  $J = 2$  Hz, 2 H, Cp), 4.29 (t,  $J = 2$  Hz, 2 H, *ipso*-Cp), 4.24 (m, 4 H, Cp and  $CH_2O$ ), 4.13 (s, 2 H,  $CpCH_2O$ ), 3.42 (m, 2 H,  $OCH_2$ ), 1.74 (m, 2 H,  $CH_2$ ), 1.59 (m, 2 H,  $CH_2$ ), 1.41 (m, 4 H,  $CH_2$ );  $^{13}C$  NMR ( $CDCl_3$ )  $\delta$  163.2 ( $CO_2$ ), 158.4 ( $CH=$ ), 116.8 ( $CN$ ), 86.8 (*ipso*-Cp), 77.3 (*ipso*-Cp), 74.6 (Cp CH), 72.2 (Cp CH), 71.2 (Cp CH), 70.8 (Cp CH), 70.4 ( $CpCH_2O$ ), 68.0 ( $CH_2O$ ), 66.1 ( $CH_2O$ ), 29.5, 28.5, 25.7, 25.5 ( $CH_2$ 's).

**Acknowledgment.** Support of this work by the Office of Naval Research is gratefully acknowledged. We also wish express our appreciation to the NSF (CHE-9002379) and Utah State University Research Office for funding the purchase of the Siemens P4 diffractometer.

#### References and Notes

1. Ferrocene was discovered in 1951! Kealy, T. J.; Pauson, P. L. *Nature* 1951, 1039. For a general review of ferrocene chemistry see: Rosenblum, M. "Chemistry of the Iron Group Metallocenes" Wiley, New York, (1965). Watts, W. E. *Organometal. Chem. Revs.* 1967, 2, 231.
2. Harwood, J. W. in "Industrial Applications of Organometallic Compounds," Reinhold, New York (1963). Johnson, J. C., jr. in "Metallocene Technology," Noyes Data Corporation, Park Ridge, New Jersey (1973).
3. Neuse, E. W.; Woodhouse, J. R.; Montaudo, G.; Puglis, C. *Appl. Organomet. Chem.* 1988 2, 53. Neuse, E. W.; Rosenberg, H. *Metallocene Polymers*, Marcel Dekker, New York 1970. *Inorganic and Organometallic Polymers: Macromolecule, Containing Silicon, Phosphorus, and other Inorganic Elements*, Zeldin, M., Wynne, K. J., Allcock, H. R., Eds.; ACS Symp. Ser., Washington D. C., 1987. Pittman, C. U., Jr.; Rausch, M. D. *Pure Appl. Chem.* 1986, 58, 617. Sheats, J. E., Carraher, C. E., Pittman, C. U., Jr., Eds.; *Metal-Containing Polymer Systems*, Plenum, New York 1985.
4. For example see: Zhan-Ru, L.; Gonsalves, K.; Lenz, R. W.; Rausch, M. D. *J. Polym. Sci. A* 1986, 24, 347 and references cited therein.
5. (a) Iwakura, C.; Kawai, T.; Nojima, M.; Yoneyama, H. *J. Electrochem. Soc.* 1987, 134, 791. (b) Singh, P.; Rausch, M. D.; Lenz, R. W. *Polym. Bulletin* 1989, 22, 247.
6. Green, M. L. H.; Marder, S. R.; Thompson, M. F.; Bandy, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *Nature* 1987, 330, 360. Perry, J. W.; Stiegman, A. E.; Marder, S. E.; Coulter, D. R. In *Organic Materials for Nonlinear Optics*, Hann, R. A., Bloor, D. Eds.; *Spec. Publ. No. 69, The Royal Society of Chemistry: London, England* 1989. Coe, B. J.; Jones, C. J.; McCleverty, J. A.; Bloor, D.; Kolinsky, P. V.; Jones, R. J. *J. Chem. Soc., Chem. Commun.* 1989, 1485.
7. For a theoretical (SCF-LCAO MECI formalism) treatment of organometallic NLO materials see: Kanis, D. R.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* 1990, 112, 8203.
8. Cheng, L.-T.; Tam, W.; Meredith, G. R.; Marder, S. R. *Mol. Cryst. Liq. Cryst.* 1990, 189, 137.
9. Marder, S. R.; Perry, J. W.; Tiemann, B. G.; Schaefer, W. P. *Organometallics* 1991, 10, 1896.
10. Wright, M. E.; Toplikar, F. G.; Kubin, R. F.; Seltzer, M. D. *Macromolecules*, submitted for publication.
11. Barben, I. K. *J. Chem. Soc.* 1961, 1827.