

2

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Service, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Project Director (0704-0188), Washington, DC 20503.



1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE April 30, 1993		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Synthesis of Chiral Molybdenum ROMP Initiators and all-Cis Highly Tactic Poly-2,3-R ₂ Norbornadiene (R = CF ₃ or CO ₂ Me).				5. FUNDING NUMBERS C N00014-92-J-1433	
6. AUTHOR(S) David H. McConville, Jennifer R. Wolf and Richard R. Schrock					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Massachusetts Institute of Technology Department of Chemistry, 6-331 77 Massachusetts Avenue Cambridge, MA 02139				8. PERFORMING ORGANIZATION REPORT NUMBER #19	
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 4132038	
11. SUPPLEMENTARY NOTES Journal of the American Chemical Society, in press.					
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) Well-defined molybdenum ROMP catalysts that contain C ₂ -symmetric diolate ligands (tartrates, binaphtholates, or biphenolates) have been prepared and shown to polymerize 2,3-R ₂ norbornadienes (R = CF ₃ or CO ₂ Me) to give, in the most favorable case, >99% cis polymers that are >>99% tactic.					
14. SUBJECT TERMS ROMP (Ring Opening Metathesis Polymerization), tartrates, binaphtholates, biphenolates, cis polymers, norbornadienes				15. NUMBER OF PAGES 11	
				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	

DTIC
SELECTED
MAY 13 1993
S C D

23 5 11 05 8

93-10292



OFFICE OF NAVAL RESEARCH

Contract N00014-92-J-1433

R & T Code 4132038

Technical Report No. 19

Accession For	
NTIS CRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Synthesis of Chiral Molybdenum ROMP Initiators and all-Cis Highly
Tactic Poly-2,3-R₂Norbornadiene (R = CF₃ or CO₂Me)

by

David H. McConville, Jennifer R. Wolf, and Richard R. Schrock

Journal of the American Chemical Society

in press

Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

April 30, 1993

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.

Synthesis of Chiral Molybdenum ROMP Initiators and all-Cis Highly Tactic
Poly-2,3-R₂Norbornadiene (R = CF₃ or CO₂Me).

by

David H. McConville, Jennifer R. Wolf, and Richard R. Schrock*

Contribution from

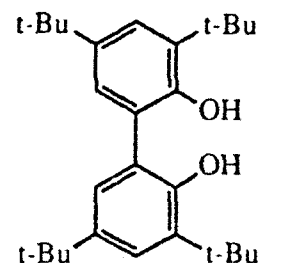
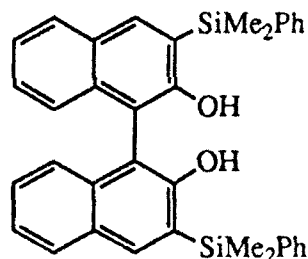
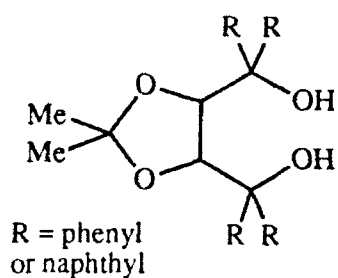
Department of Chemistry 6-331
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Abstract

Well-defined molybdenum ROMP catalysts that contain C₂-symmetric diolate ligands (tartrates, binaphtholates, or biphenolates) have been prepared and shown to polymerize 2,3-R₂norbornadienes (R = CF₃ or CO₂Me) to give, in the most favorable case, >99% cis polymers that are >99% tactic.

Controlling the stereochemistry of polymers prepared by ring-opening of norbornenes and norbornadienes has been a long standing problem,^{1,2} one that ultimately could be solved by employing well-characterized catalysts with known structures and activities. Catalysts of the type $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{OR})_2$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3\text{-}i\text{-Pr}_2$)^{3,4} have been shown to ring-open polymerize 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) to give highly tactic all-trans polyNBDF6 when $\text{OR} = \text{O-}t\text{-Bu}$ (in toluene or THF)⁵ and all-cis polyNBDF6 with a tactic bias of $\sim 74\%$ when $\text{OR} = \text{OCMe}(\text{CF}_3)_2$ (in THF).⁶ We show here that catalysts of this general type can be prepared that contain C_2 -symmetric chiral diolate ligands and that poly-2,3-bis(trifluoromethyl)norbornadiene (polyNBDF6) and poly-2,3-dicarbomethoxynorbornadiene (polyDCNBD) can be prepared using them that are $>99\%$ cis and $>99\%$ tactic.

C_2 -Symmetric tartrate and BINO derivatives (see below) and related C_2 -symmetric ligands have been widely and successfully used for enantioselective organic reactions in the past



decade.⁷⁻²⁰ Addition of (+)- $\text{Ph}_4\text{tartH}_2$ to $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})(\text{OTf})_2(\text{DME})^{21,22}$ ($\text{DME} =$ dimethoxyethane) in diethyl ether in the presence of triethylamine yielded $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[(+)\text{-Ph}_4\text{tart}](\text{S})$ ((+)-**1**; $\text{S} =$ a mixture of NEt_3 and dme ; see Supplementary Material) in 70% yield. $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[(-)\text{-Ph}_4\text{tart}](\text{S})$ ((-)-**1**) and $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[(+)\text{-Nap}_4\text{tart}](\text{S})$ ((+)-**2**; $\text{Nap} = \beta\text{-naphthyl}$) were prepared in an analogous manner. $(\pm)\text{-BINO}(\text{SiMe}_2\text{Ph})_2\text{H}_2$ was prepared in a manner analogous to known SiR_3 derivatives⁷ and treated with two equivalents of $\text{KCH}_2\text{Ph}^{23}$ to give $(\pm)\text{-BINO}(\text{SiMe}_2\text{Ph})_2\text{K}_2$, which when added to $\text{Mo}(\text{CH-}t\text{-Bu})(\text{NAr})(\text{OTf})_2(\text{DME})^{21,22}$ in THF gave crystalline $\text{Mo}(\text{CH-}t\text{-}$

Bu)(NAr)[(±)-BINO(SiMe₂Ph)₂](THF) ((±)-3) in 70% yield.^{24,25} Crystalline Mo(CHCMe₂Ph)(NAr')[(±)-BINO(SiMe₂Ph)₂](THF) ((±)-4; Ar' = 2,6-C₆H₃Me₂) was prepared from (±)-BINO(SiMe₂Ph)₂K₂ and Mo(CHCMe₂Ph)(NAr')(OTf)₂(DME)²⁶ in a manner analogous to that used to prepare (±)-3. NMR spectra of (+)-1, (-)-1, and (+)-2 show an H_α and C_α resonance for a single alkylidene rotamer, while NMR spectra of (±)-3 and (±)-4 suggest that they are mixtures of anti and syn rotamers.^{27,28} (See Supplementary Material.)

The cis/trans ratio in polyNBDF6 is determined readily and accurately by ¹³C NMR,^{5,6} while tacticity can be determined at the triad level by analyzing the resonances for C(7), as shown in Figure 1(a).⁶ The resonance at 38.38 ppm in Figure 1(a) can be assigned to C(7) in a tactic polymer (cc,mm or cc,rr triad), while that at 37.61 ppm can be assigned to C(7) in atactic polymer (cc,mr triad).⁶ The resonance at 36.44 is assignable to C(7) in a polymer whose tacticity is different than that which gives rise to the C(7) resonance at 38.38 ppm, while the minor broad resonances in Figure 1(a) can be ascribed to C(7) in ct triads.

PolyNBDF6 prepared from (+)-2 in DME (97% cis; Table I) precipitates as it is being formed. The fact that the polymer is relatively insoluble in DME, dichloromethane, toluene, and THF (although soluble in acetone) prevented determination of molecular weight and polydispersity by GPC. The C(7) region of the ¹³C NMR spectrum of this polymer in acetone-d₆ (Figure 1(b)) shows primarily one carbon resonance (at 38.31 ppm), consistent with a tacticity of 97% for the all-cis triads (Table I) on the basis of the cc assignments shown in Figure 1(b). PolyNBDF6 prepared from (+)-1 in DME or THF, which was identical to that prepared from (-)-1 in DME or THF, was soluble in THF and had a lower all-cis tacticity (88%; Table I). (A higher enantioselectivity has been observed employing Nap₄tart as a chiral auxiliary instead of Ph₄-tart in organic reactions.^{14,17})

PolyNBDF6 prepared using (±)-3 as the initiator in THF is only ~71% cis, although the tacticity of the all-cis triads is relatively high (86%; Table I). However, polyNBDF6 prepared from 200 equiv of NBDF6 and (±)-4 as the initiator was >99% cis and was soluble only in acetone. Its ¹³C NMR spectrum in the C(7) region is shown in Figure 1(c). The narrow 38.31

ppm resonance is virtually the only C(7) resonance present. The ^1H NMR spectrum of this polymer is also relatively sharp and well-resolved. (See Supplementary Material.) Therefore we propose that this polymer is at least 99% tactic. The vastly improved cis/trans ratio and percent tacticity upon changing from isopropyl groups to methyl groups in the imido ligand of the initiator is striking. An oligomer of polyNBDF6 (28 mer) prepared using (\pm)-**4** is soluble in THF and has a molecular weight (4900 versus polystyrene) and polydispersity (1.09) consistent with a living ROMP polymerization.

In order to test whether tacticity control is possible with other norbornadiene derivatives we prepared samples of poly-2,3-dicarbomethoxynorbornadiene using **1**, **2**, **3**, and **4** as initiators and compared them with polyDCNBD prepared employing $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ in DME^4 as shown in Table II. (^{13}C NMR spectra of polyDCNBD are closely analogous to those for polyNBDF6.) The percent tacticity for polyDCNBD was at least as high as that for polyNBDF6 in every case involving a chiral initiator.

Finally, we prepared $\text{Mo}(\text{CH-t-Bu})(\text{NAr})[\text{Bipheno}(\text{t-Bu})_4]$ (**5**) by adding $\text{Bipheno}(\text{t-Bu})_4\text{K}_2$ to $\text{Mo}(\text{CH-t-Bu})(\text{NAr})(\text{OTf})_2(\text{DME})$ in THF. The $\text{Bipheno}(\text{t-Bu})_4$ ligand has been shown to "flip" rapidly on the NMR time scale in some lanthanide complexes,²⁹ although it is "locked" on the NMR time scale (300 MHz) in **5** at 25°C. We were somewhat surprised to find that polyDCNBD (250 mer) prepared from **5** in THF was >99% cis and 96% tactic.

We have now proven by proton NMR that all cis polymers prepared from enantiomerically pure dicarboalkoxynorbornadienes are isotactic, while the all trans polymer are syndiotactic.³⁰ Therefore we believe that the all cis, tactic polymers prepared here are also isotactic, and that a bias toward isotacticity by chain end control using $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$ as the initiator is being enhanced by site control at a chiral metal center. Future studies will be aimed at determining under what conditions other monomers can be polymerized stereoselectively. One might also consider the possibility that catalysts such as (+)-**1** or (+)-**2**, or enantiomerically pure versions of **3** or **4**, could selectively

polymerize or ring-close^{31,32} one enantiomer in a racemic mixture.

Acknowledgements. R.R.S. thanks the Office of Naval Research and the National Science Foundation (CHE 91 22827) for research support. D.H.M. thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship, and John Oskam for running high field ¹³C NMR spectra.

References

- (1) Ivin, K. J. "Olefin Metathesis"; Academic: New York, 1983.
- (2) Ivin, K. J.; Saegusa, T. "Ring-Opening Polymerization"; Elsevier: London, 1984.
- (3) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.
- (4) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 0000.
- (5) Bazan, G.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.
- (6) Feast, W. J.; Gibson, V. C.; Marshal, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.
- (7) Maruoka, K.; Itoh, T.; Araki, Y.; Shirasaka, T.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 2975.
- (8) Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1989**, *111*, 1940.
- (9) Mikami, K.; Masahiro, T.; Nakai, T. *J. Am. Chem. Soc.* **1990**, *112*, 3949.
- (10) Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310.
- (11) Narasaka, K.; Iwasawa, N.; Inoue, M.; Yamada, T.; Nakashima, M.; Sugimori, J. *J. Am. Chem. Soc.* **1989**, *111*, 5340.
- (12) Narasaka, K.; Hayashi, Y.; Shimadzu, H.; Niihata, S. *J. Am. Chem. Soc.* **1992**, *114*, 8869.
- (13) Schmidt, B.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 99.
- (14) Schmidt, B.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 1321.
- (15) Seebach, D.; Beck, A. K.; Imwinkelreid, R.; Roggo, S.; Wonnacott, A. *Helv. Chim. Acta* **1987**, *70*, 954.
- (16) Toda, F.; Mori, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1245.

- (17) Weber, B.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 84.
- (18) Weidmann, B.; Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1983**, *22*, 31.
- (19) Noyori, R. *Science* **1990**, *248*, 1194.
- (20) Noyori, R.; Takaya, H. *Acc. Chem. Res.* **1990**, *23*, 345.
- (21) Fox, H. H.; Yap, K. B.; Robbins, J.; Cai, S.; Schrock, R. R. *Inorg. Chem.* **1992**, *31*, 2287.
- (22) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. J. *Am. Chem. Soc.* **1990**, *112*, 3875.
- (23) Schlosser, R. R.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.
- (24) BINO ligands have been attached to titanium^{25a} and tungsten^{25b} and the results of several x-ray studies have been published.
- (25) (a) Boyle, T. J.; Barnes, D. L.; Heppert, J. A.; Morales, L.; Takusagawa, F. *Organometallics* **1992**, *11*, 1112. (b) Heppert, J. A.; Dietz, S. D.; Boyle, T. J.; Takusagawa, F. *J. Am. Chem. Soc.* **1989**, *111*, 1503.
- (26) Yap, K. B.; Fox, H. H.; Schrock, R. R., unpublished results.
- (27) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.
- (28) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.
- (29) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124.
- (30) McConville, D. H.; O'Dell, R.; Schrock, R. R., to be published.
- (31) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426.
- (32) Fu, G., C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992** *114*, 7324.

Table I. Poly[2,3-bis(trifluoromethyl)norbornadiene]^a

Catalyst	cis (%)	cis tactic (%)	equiv	M _n ^b	M _w /M _n ^b	yield (%)
Mo(CHCMe ₂ Ph)(NAr)[OCMe(CF ₃) ₂] ^c	97	74	100	19 500	1.05	85
Mo(CHCMe ₂ Ph)(NAr)[(+)-Ph ₄ tar] (+)-1	98	88	100	14 000	1.05	95
Mo(CHCMe ₂ Ph)(NAr)[(+)-Nap ₄ tar] (+)-2 ^d	97	97	100	-	-	85
Mo(CH-t-Bu)(NAr)[(±)-BINO(SiMe ₂ Ph) ₂] (±)-3	71	86	100	11 200	1.06	87
Mo(CHCMe ₂ Ph)(NAr)[(±)-BINO(SiMe ₂ Ph) ₂] (±)-4 ^e	>99	>99	200	-	-	97

^a All polymers were prepared in THF, unless otherwise noted. ^b Determined by GPC in THF versus polystyrene standards. ^c Prepared as described in reference 6. ^d Prepared in DME. ^e A 28 mer was found to be soluble in THF and had M_n = 4900 and M_w/M_n = 1.09.

Table II. Poly[2,3-dicarbomethoxynorbornadiene]^a

Catalyst	cis (%)	cis tactic (%)	equiv	M _n ^b	M _w /M _n ^b	yield (%)
Mo(CHCMe ₂ Ph)(NAr)[OCMe(CF ₃) ₂] ^c	98	73	100	16 400 ^d	1.04 ^d	86
Mo(CHCMe ₂ Ph)(NAr)[(+)-Ph ₄ tar] (+)-1 ^e	93	93	100	23 000	1.60	85
Mo(CHCMe ₂ Ph)(NAr)[(+)-Nap ₄ tar] (+)-2	93	97	100	51 500	2.38	80
Mo(CHCMe ₃ (NAr)[(±)-BINO(SiMe ₂ Ph) ₂] (±)-3	93	97	100	34 000	1.84	94
Mo(CHCMe ₂ Ph)(NAr)[(±)-BINO(SiMe ₂ Ph) ₂] (±)-4	>99	>99	100	28 700 ^f	1.28 ^f	97
Mo(CH-t-Bu)(NAr)[Bipheno(t-Bu) ₄] 5	>99	96	250	56 000	1.33	95

^a All polymers were prepared in THF, unless otherwise noted. ^b Determined by GPC in CH₂Cl₂ versus polystyrene standards. ^c Prepared in DME as described in reference 4. ^d GPC analysis performed in THF. ^e Prepared in DME. ^f Prepared in CH₂Cl₂/THF (4:1).

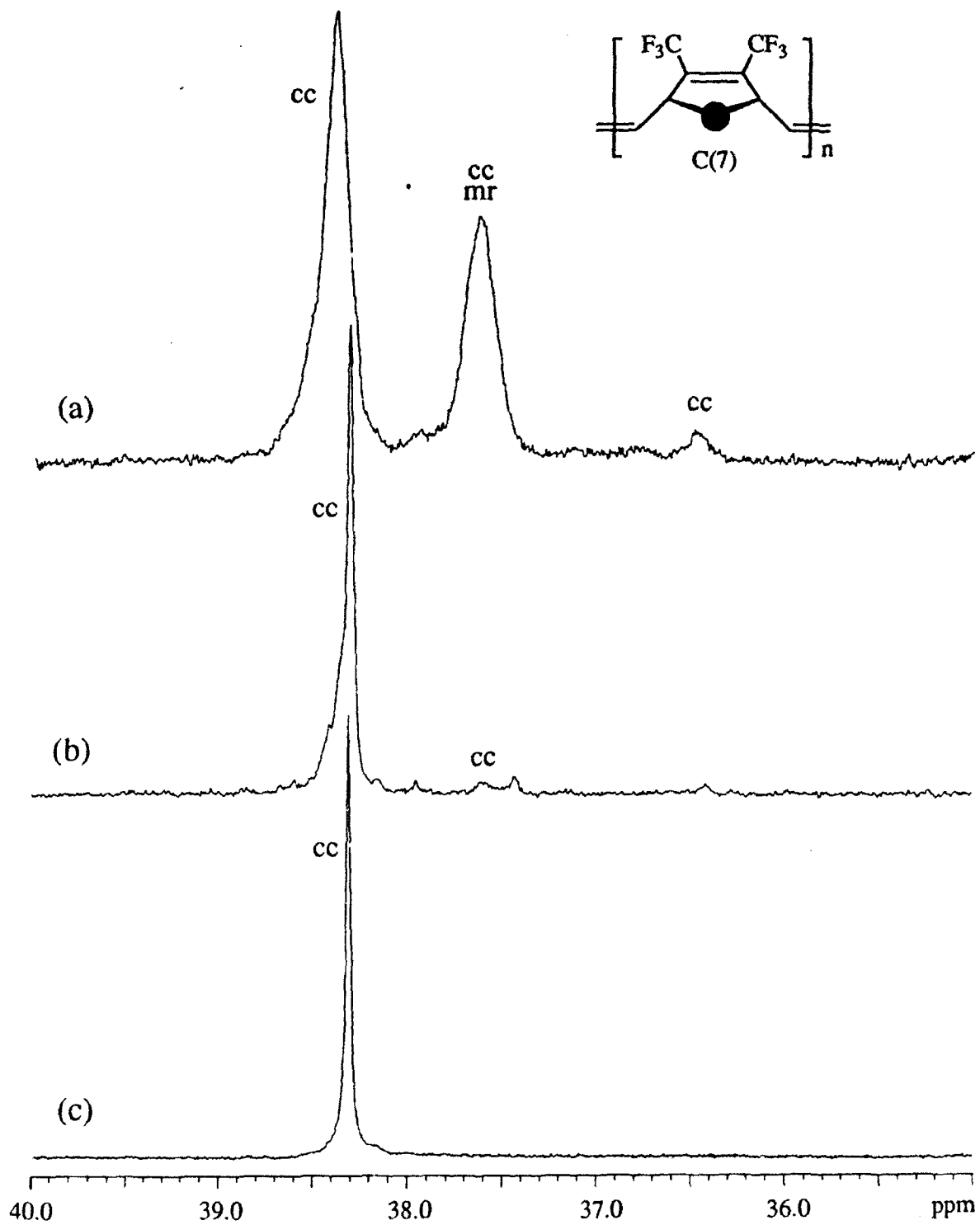


Figure 1. The C(7) region of the 125.69 MHz ^{13}C NMR spectrum in acetone- d_6 of polyNBDF6 prepared with initiator (a) $\text{Mo}(\text{CHCMe}_2\text{Ph})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$; (b) (+)-2; and (c) (\pm)-4.

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Elek Lindner (1)
Naval Command, Control and Ocean
Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

* Number of copies to forward