

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Synthesis of a New Ferrocene-Containing Dithiol and its Reaction with Divinyl Sulfone to Polymers

Oskar Nuyken^a; Thomas Pöhlmann^a; Max Herberhold^b

^a Lehrstuhl für Makromolekulare Chemie I und Bayreuther Institut für Makromolekülforschung (BIMF), Universität Bayreuth, Bayreuth, Federal Republic of Germany ^b Laboratorium für Anorganische Chemie, Universität Bayreuth, Bayreuth, Federal Republic of Germany

To cite this Article Nuyken, Oskar , Pöhlmann, Thomas and Herberhold, Max(1992) 'Synthesis of a New Ferrocene-Containing Dithiol and its Reaction with Divinyl Sulfone to Polymers', *Journal of Macromolecular Science, Part A*, 29: 11, 211 – 220

To link to this Article: DOI: 10.1080/10101329208054585

URL: <http://dx.doi.org/10.1080/10101329208054585>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SYNTHESIS OF A NEW FERROCENE-CONTAINING DITHIOL AND ITS REACTION WITH DIVINYL SULFONE TO POLYMERS

Oskar Nuyken * and Thomas Pöhlmann

Lehrstuhl für Makromolekulare Chemie I und Bayreuther Institut für Makromolekülforschung (BIMF), Universität Bayreuth, Postfach 101251, W-8580 Bayreuth, Federal Republic of Germany

Max Herberhold

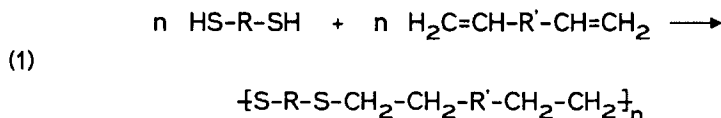
Laboratorium für Anorganische Chemie, Universität Bayreuth, Postfach 101251, W-8580 Bayreuth, Federal Republic of Germany

ABSTRACT

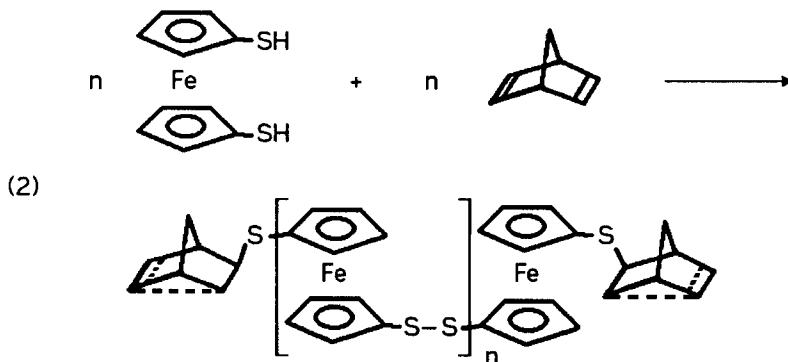
1,1'-Bis(2-mercapto-propylthio)ferrocene (1) was synthesized and converted into a polymer (2) by reaction with divinyl sulfone in a 1:1 ratio. As a result of the *anti*-Markovnikov thiol-addition onto the vinyl groups, the polymer has a regular alternating structure. It is soluble in chloroform and tetrahydrofuran and was characterized by common methods.

INTRODUCTION

During our investigations on the mobility of polymer segments using ^{57}Fe -Mössbauer spectroscopy [1,2] we introduced ferrocene units into the main chain of polymers in order to have a spectroscopic probe. Among several other methods [3] the addition of dithiols to diolefins was used as a synthetic route [4-6] (eq. 1):



However, in contrast to common dithiol/diolefin reactions which lead to alternating structures according to eq. 1, the reaction of ferrocene 1,1'-dithiol with diolefins gives oligomers with disulfide-bridged ferrocene units in the main chain [7,8] (eq. 2):



The formation of disulfide polymers was explained on the basis of a radical mechanism with ferrocenylthiyl radicals as intermediates which are stable enough to terminate the chain growth by radical combination. The stability of these radicals can be ascribed to electronic interactions between the sulfur and the ferrocenyl group [9]. In order to prevent the disulfide formation we have modified the thiol unit by introducing a spacer **R** between the ferrocene nucleus and the SH functional group (Figure 1).

The following route can be used to separate the thiol group from the cyclopentadienyl ring by an alkylthio spacer (Scheme 1).

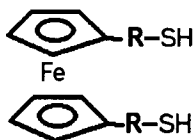
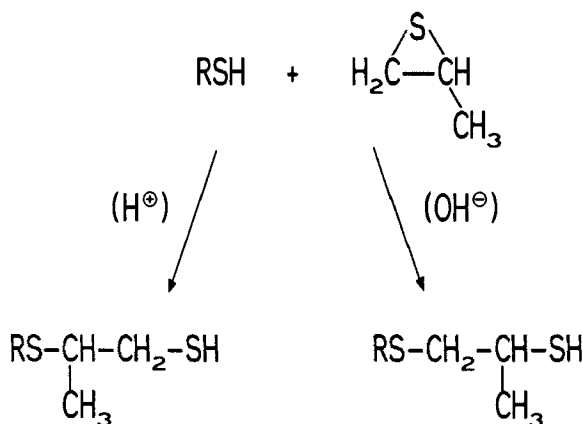


Figure 1: Dimercapto ferrocene derivative containing a spacer **R**



Scheme 1: Reaction of thiols with cyclic sulfides

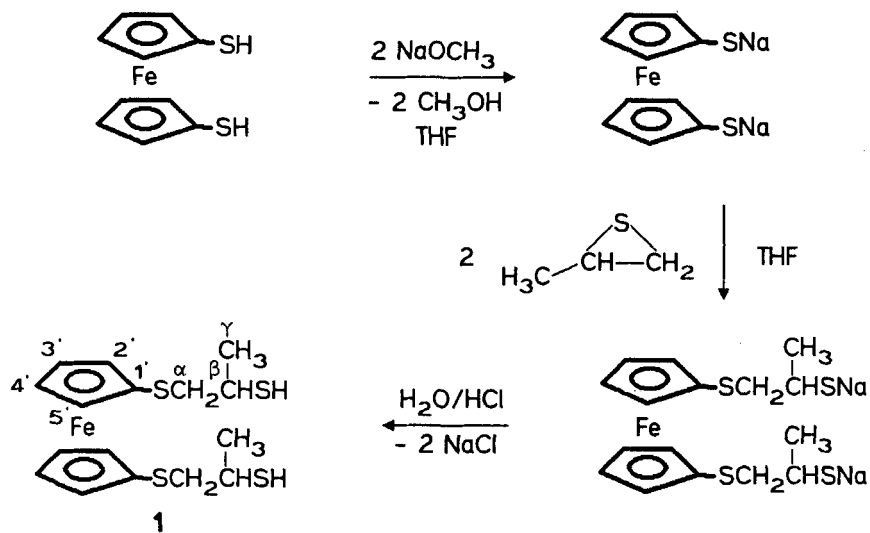
The ring opening of cyclic sulfides by thiols leads to different products, depending on the reaction conditions: Methyl thirane (propylene sulfide) is converted into a secondary thiol in the presence of nucleophiles, whereas a primary thiol is formed with electrophiles [10-12].

RESULTS AND DISCUSSION

a) Synthesis of 1,1'-bis(2-mercapto-propylthio)ferrocene (**1**)

Ferrocene 1,1'-dithiol [13,14] is converted into the corresponding sodium dithiolate by reaction with sodium methylate. Subsequent reaction with two equivalents of propylene sulfide followed by hydrolysis gives **1** as a brownish oil (Scheme 2).

The presence of a chirality center in the 2-mercapto-propyl group is confirmed by the ^1H NMR spectrum. The two protons of the α -methylene group in the substituent appear as separate signals at $\delta = 2.68$ and 2.69 ppm. For the same reason, the ring protons $\text{H}^{2'}$ and $\text{H}^{5'}$ give rise to separate signals at $\delta = 4.23$ and 4.27 ppm. This effect is not apparent in the ^{13}C NMR spectrum where only a single signal at $\delta = 74.7$ ppm is observed



Scheme 2: Synthesis of 1,1'-bis(2-mercapto-propylthio)ferrocene (1)

TABLE 1

NMR data of 1,1'-bis(2-mercapto-propylthio)ferrocene (1)

- ^1H δ = 1.29 (d, 6 H, H^γ , 3J = 6.7 Hz), 1.89 (d, 2 H, SH , 3J = 5.6 Hz), 2.68 and 2.69 (two d, each 2 H, H^α , 3J = 6.0 Hz and 7.7 Hz), 2.90 (m, 2 H, H^β , 3J = 6.6 Hz), 4.18 (vt, 4 H, $\text{H}^{3'}$, $\text{H}^{4'}$), 4.23 (m, 2 H, $\text{H}^{2'}$ or $\text{H}^{5'}$), 4.27 (m, 2 H, $\text{H}^{5'}$ or $\text{H}^{2'}$) ppm.
- ^{13}C δ = 23.1 (C^γ), 34.6 (C^β), 48.4 (C^α), 70.8 ($\text{C}^{3'}$, $\text{C}^{4'}$), 74.7 ($\text{C}^{2'}$, $\text{C}^{5'}$), 80.3 ($\text{C}^{1'}$) ppm.

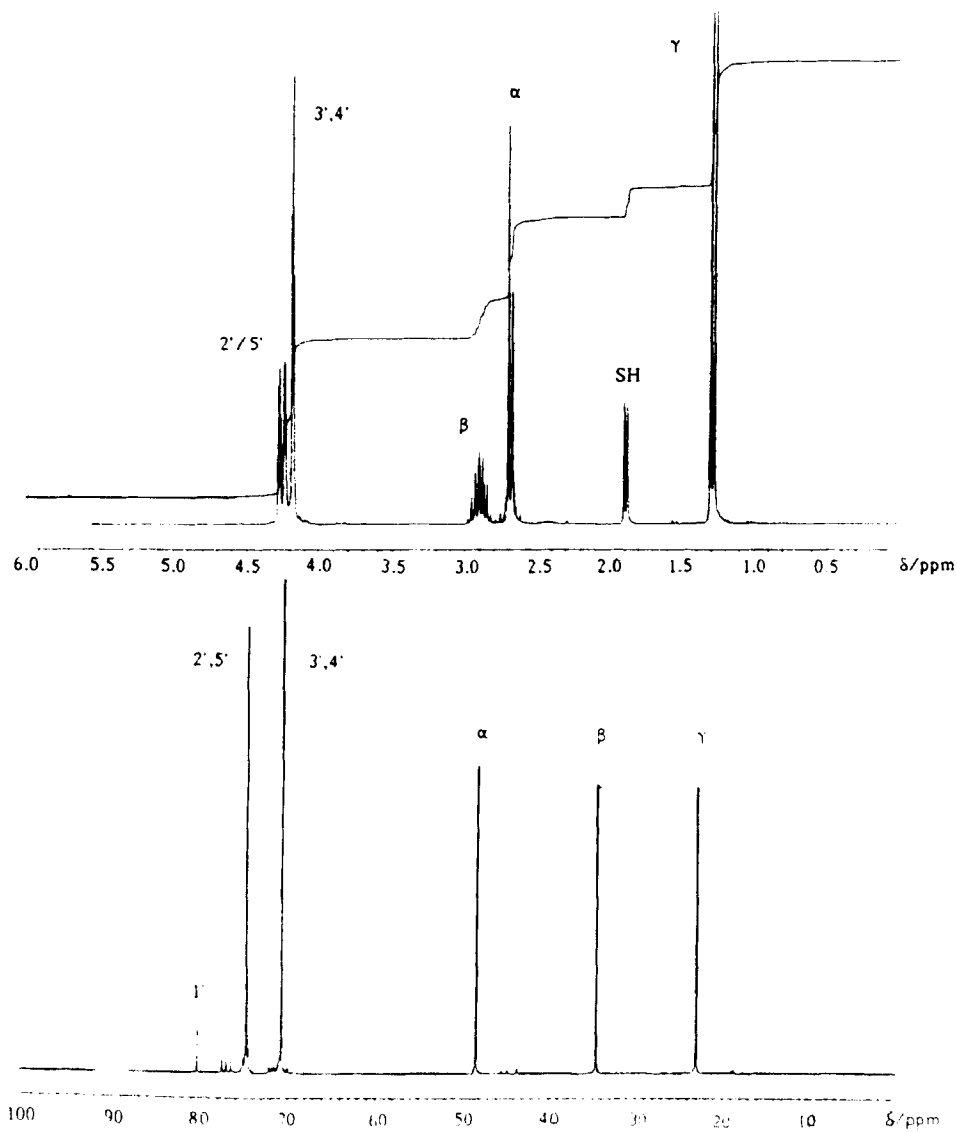


Figure 2: ^1H and ^{13}C NMR spectra of 1,1'-bis(2-mercapto-propylthio)ferrocene (1)

for C^{2'} and C^{5'} (Table 1, Figure 2). In contrast, two separate signals appear for these ring carbon atoms in the case of 3-ferrocenylthio-nortri-cyclane [15].

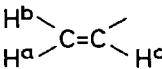
b) Reactions with divinyl sulfone

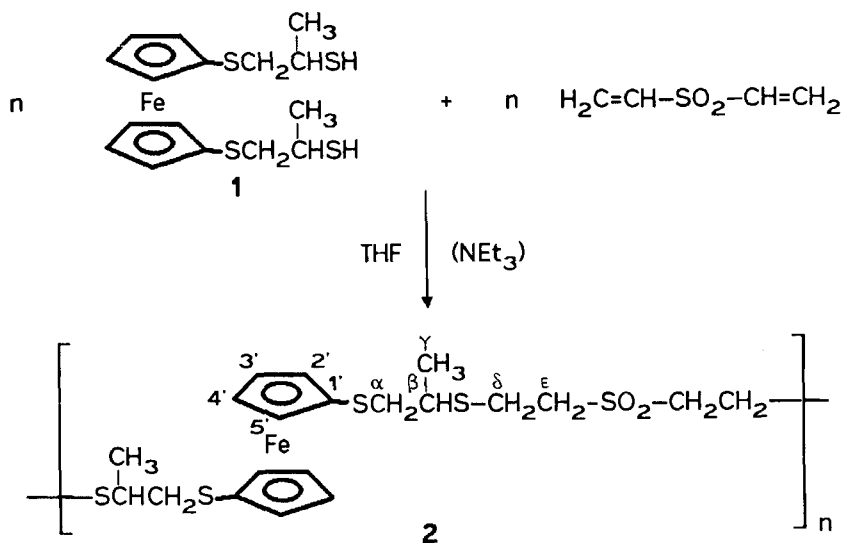
The polyaddition of dithiols to diolefins having electron-withdrawing groups (e.g. keto or sulfone functions) in the neighborhood of the double bonds has been rarely used, up to now, for the synthesis of polymers [5,16-19]. In the course of this Michael-type reaction of α,β -unsaturated sulfones, the thiolate anion initially formed adds to the β -carbon atom of the vinyl component, and the new enolate anion then reacts with a proton to form the *anti*-Markovnikov addition product.

In our investigations we have applied the polyaddition of the new aliphatic dimercapto compound **1** to divinyl sulfone for the synthesis of polymers. Equimolar amounts of the dithiol **1** and divinyl sulfone react in tetrahydrofuran solution with triethylamine as a catalyst to give an orange-coloured polymer which is soluble in tetrahydrofuran and chloroform (Scheme 3). The GPC diagram indicates that the molecular weight (\bar{M}_n) is about 3000 g/mol (calibrated with polystyrene standards). The polymer decomposes at 285°C, as measured by DSC.

Although splitting of the ferrocene signals in the ¹³C NMR spectrum of the dithiol **1** could not be observed, we find such phenomena in the ¹³C NMR spectrum of the polymer. The ring carbon atoms C^{2'}/C^{5'} and C^{3'}/C^{4'} of the substituted cyclopentadienyl rings in the polymer give separate signals at $\delta = 74.86$ and 74.93 ppm and at $\delta = 70.95$ and 71.18 ppm, respectively.

It is also possible to synthesize vinyl- or thiol-terminated telechelics by unstoichiometric use of the educts. The terminal groups can be identified in the ¹H NMR spectrum:

Vinyl group		$\delta = 6.16$ (d, H ^a , ³ J = 10 Hz), 6.41 (d, H ^b , ³ J = 17.2 Hz), 6.59 (dd, H ^c , ³ J = 10 Hz, ³ J = 17.2 Hz) ppm.
Thiol group		$\delta = 1.90$ (d, SH, ³ J = 6 Hz) ppm.



Scheme 3: Polyaddition of 1,1'-bis(2-mercapto-propylthio)ferrocene (1) with divinyl sulfone

TABLE 2

NMR data of the polymer 2

^1H	$\delta = 1.2 - 1.4$ (CH_3), $2.4 - 3.3$ (other alkyl protons), $4.1 - 4.4$ (ferrocene protons) ppm.
^{13}C	$\delta = 20.0$ (C^γ), 22.3 (C^δ), 40.0 (C^β), 44.5 (C^α), 53.5 (C^ϵ), $70.95/71.18$ ($\text{C}^{3'}$, $\text{C}^{4'}$), $74.86/74.93$ ($\text{C}^{2'}$, $\text{C}^{5'}$), 80.73 ($\text{C}^{1'}$) ppm.

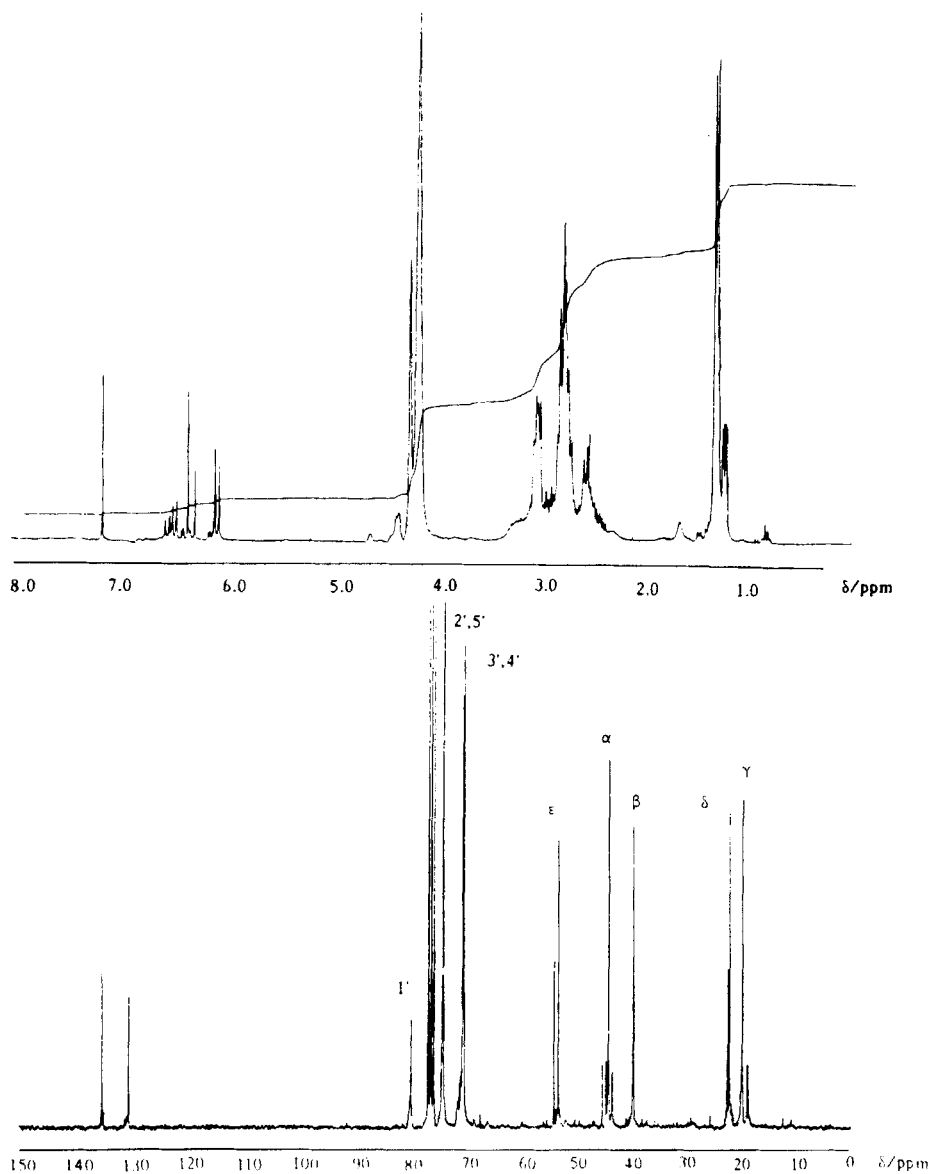


Figure 3: ^1H and ^{13}C NMR spectra of a vinyl-terminated polymer prepared from 1,1'-bis(2-mercapto-propylthio)ferrocene (**1**) and divinyl sulfone

EXPERIMENTAL PART

a) Synthesis of 1,1'-bis(2-mercapto-propylthio)ferrocene (**1**)

To a solution of 634 mg (2.53 mmol) ferrocene 1,1'-dithiol [13,14] in 50 ml THF 274 mg (5.07 mmol) sodium methylate were added at 0°C. 400 μ l (5.07 mmol) propylene sulfide were added at 0°C, and the suspension was allowed to warm up to room temperature under stirring in the course of two hours. Then 5 ml degassed HCl_{conc.} were added and the solvent was removed. The resulting orange-brown oil was further purified by column chromatography over silica using toluene as an eluent.

Yield: 706 mg (70%).

Elemental analysis: Found: C, 48.40; H, 5.07; Fe, 14.26; S, 32.04%.

Calc.: C, 48.23; H, 5.57; Fe, 14.02; S, 32.19%.

b) Synthesis of the polymer **2** from **1** and divinyl sulfone

127 mg (0.32 mmol) of **1** and 32 μ l (0.32 mmol) divinyl sulfone in 1 ml THF were stirred overnight at 40°C with a trace of triethylamine. After dilution with 5 ml THF the orange-brown polymer was preprecipitated in cold methanol, redissolved in THF and again preprecipitated in methanol.

Yield: 150 mg (91%).

c) Instrumentation

¹H and ¹³C NMR spectra: Bruker AC 250, solvent: CDCl₃.

DSC: Netzsch DSC 200.

GPC: Waters, column with PL gel 5 μ , average pore diameter 100 and 500 Å, UV detector 440 and RI detector 410.

Elemental analysis: I. Beetz, Mikroanalytisches Laboratorium, W-8640 Kronach.

ACKNOWLEDGEMENT

We wish to thank the Deutsche Forschungsgemeinschaft (Sonderforschungsbereich 213) for financial support.

REFERENCES

1. F. J. Litterst, R. Feyerherm, O. Nuyken, V. Burkhardt, Hyperfine Interactions, submitted.
2. F. J. Litterst, R. Feyerherm, O. Nuyken, V. Burkhardt, publication in preparation.
3. V. Burkhardt, unpublished results.
4. O. Nuyken, Th. Völkel, Makromol. Chem., Rapid Commun. **11** (1990), 365.
5. O. Nuyken, Th. Völkel, Makromol. Chem. **191** (1990), 2465.
6. O. Nuyken, Th. Völkel, Th. Pöhlmann, Makromol. Chem. **192** (1991), 1959.
7. O. Nuyken, V. Burkhardt, Th. Pöhlmann, M. Herberhold, Makromol. Chem., Macromol. Symp. **44** (1991), 195.
8. M. Herberhold, H.-D. Brendel, O. Nuyken, Th. Pöhlmann, J. Organometal. Chem. **413** (1991), 65.
9. M. Sato, S. Tanaka, S. Ebine, K. Morinaga, S. Akabori, J. Organometal. Chem. **282** (1985), 247.
10. H. R. Snyder, J. M. Stewart, J. B. Ziegler, J. Am. Chem. Soc. **69** (1947), 2675.
11. E. M. Meade, F. N. Woodward, J. Chem. Soc. **1948**, 1894.
12. E. P. Adams, F. P. Doyle, D. L. Hatt, D. O. Holland, W. H. Hunter, K. R. L. Mansford, J. H. C. Nayler, A. Queen, J. Chem. Soc. **1960**, 2649.
13. J. J. Bishop, A. Davison, M. L. Katcher, D. W. Lichtenberg, R. E. Merrill, J. C. Smart, J. Organometal. Chem. **27** (1971), 241.
14. R. Broussier, A. Abdulla, B. Gautheron, J. Organometal. Chem. **332** (1987), 165.
15. M. Herberhold, O. Nuyken, Th. Pöhlmann, J. Organometal. Chem. **405** (1991), 217.
16. Y. Imai, Y. Asamidori, M. Ueda, Makromol. Chem., Rapid Commun. **1** (1980), 659.
17. Y. Imai, Y. Asamidori, T. Inoue, M. Ueda, J. Polym. Sci., Polym. Chem. Ed. **19** (1981), 583.
18. P. Ferruti, E. Ranucci, J. Polym. Sci., Polym. Lett. **26** (1988), 357.
19. P. Ferruti, E. Ranucci, L. Depero, Makromol. Chem., Rapid Commun. **9** (1988), 807.