

This article was downloaded by:

On: 25 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>

Polymeric Ferrocene and Ruthenocene Compounds with Boron in the Main Chain

Eberhard W. Neuse^a

^a Polymer Laboratory, Missile & Space Systems Division Douglas Aircraft Company, Santa Monica, California

To cite this Article Neuse, Eberhard W.(1968) 'Polymeric Ferrocene and Ruthenocene Compounds with Boron in the Main Chain', *Journal of Macromolecular Science, Part A*, 2: 4, 751 – 759

To link to this Article: DOI: 10.1080/10601326808051439

URL: <http://dx.doi.org/10.1080/10601326808051439>

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.

Polymeric Ferrocene and Ruthenocene Compounds with Boron in the Main Chain*

EBERHARD W. NEUSE

*Polymer Laboratory
Missile & Space Systems Division
Douglas Aircraft Company
Santa Monica, California*

SUMMARY

The action of phenylboron dichloride upon ferrocene or ruthenocene in highly concentrated sulfolane solution in the presence of zinc chloride produces soluble polymeric metallocene compounds having phenylboron bridging units in the backbone. Number-average molecular weights are in the approximate range 1200-3500. The polymer structures, which comprise homo- and heteroannularly disubstituted metallocene units and variable populations of cyclopentylene groups in addition to phenylboron bridges, arise as a result of competitive reactions believed to involve electrophilic attack by boron on the metallocene and cleavage of the bonds connecting the central Fe or Ru atom with the cyclopentadienyl rings of the metallocene system, this cleavage reaction being followed by polyalkylation steps via intermediary cyclopentenyl cations. The ruthenocene system undergoes metal-ring bond fission more sluggishly than does ferrocene; hence, the ruthenium-containing polymers possess a lower content of cyclopentylene moieties than determined for the iron-containing counterparts obtained under comparable conditions.

Efforts to incorporate group IV elements into macromolecular ferrocene compounds have led to polymers possessing Si and Sn as

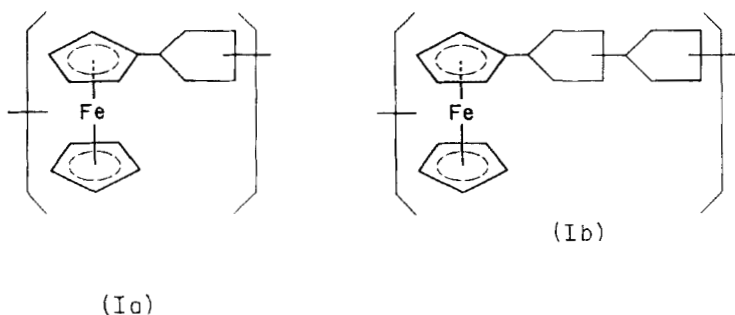
*Metallocene Polymers XXII. For Part XXI, see Ref. [1].

backbone constituents [2-7]. Similarly, group V elements have successfully been introduced as chain links. For example, polymers in which ferrocenylene groups are interconnected by phenylphosphine and phenylphosphoryl bridges were prepared by a Lewis acid-catalyzed polyacylation reaction involving ferrocene and phenyldichlorophosphine as reactants [8, 9], and in an analogous manner polymers possessing nitrophenyl-, chlorophenyl-, and cyanophenyl-substituted arsine bridging groups between ferrocenylene units were obtained* from ferrocene and the corresponding dichloroarsine derivatives. Both condensations proceeded just as well in the melt phase as in solution, and the resulting polymeric compounds had number-average molecular weights ranging from ca. 1000 to 3500.

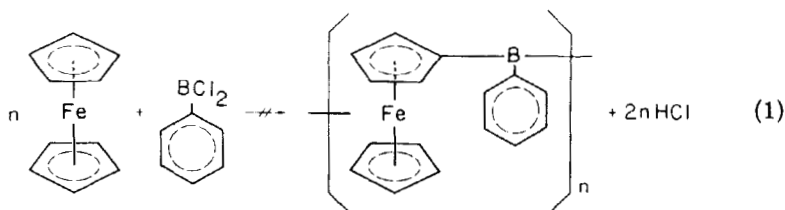
We now wish to report the synthesis of ferrocene polymers containing the group III element boron in the main chain. When ferrocene was reacted over periods of 24-125 hr in highly concentrated sulfolane (tetramethylene sulfone) solution with equivalent or slightly less than equivalent quantities of phenylboron dichloride† and anhydrous zinc chloride at moderately elevated temperatures (60-125°C), polycondensation took place, giving rise to soluble and hence essentially linear polymeric compounds with molecular weights in the approximate range 1500-3500. Analytical results indicate, however, that the polycondensation of Eq. (1), which one might anticipate here by analogy with the interaction of ferrocene and phenyldichlorophosphine, proceeded only to a minor extent. Instead, degradation of the metallocene system, involving both the ferrocene starting material and ferrocenylene units already incorporated into the polymer, constituted the main reaction, this degradation involving rupture of the metal-ring bond under the influence of phenylboron dichloride. In view of the capability of the boron halide to function as a powerful Lewis acid, this cleavage is not altogether unexpected. The efficacy of Lewis acids such as $AlCl_3$, BF_3 , and even $ZnCl_2$ (probably in the form of the respective complexes with H_2O or HCl) in cleaving the metal-ring bond of ferrocene compounds in hydrogen fluoride [10], halocarbon [11-15], benzene [16, 17], or sulfolane [8, 18, 19] solutions as well as in the melt phase [20] had previously been observed; in these earlier investigations, secondary alkylation reactions, probably involving cyclopentenyl and ferrocenylcyclopentyl cationic intermediates [13, 14, 17, 20], had been found to produce monomeric and polymeric cyclopentylene derivatives of ferrocene, the polymeric species typically being composed of such recurring units as (Ia) and (Ib).

* Obtained in an unpublished study in this laboratory.

† An examination of the effect of major reactant ratio variations was not attempted in this work because of the inhomogeneous character of the melt in initial reaction stages, prohibiting accurate control of reactant concentrations.

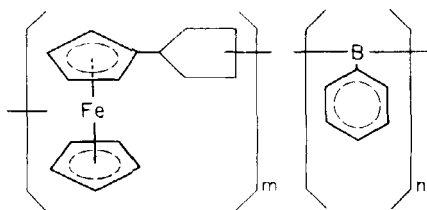


In the present case, this sequence of metal-ring bond fission and subsequent alkylation via cyclopentenyl cations, competing with the anticipated, regular polycondensation course of Eq. (1), gave poly-



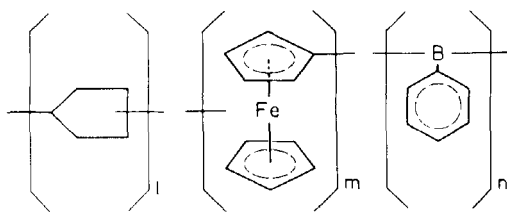
meric structures of considerable complexity, comprising a variable population of ferrocenylene and cyclopentylene groups in addition to the phenylboron unit. Even under very mild experimental conditions (e.g., 12-24 hr at 55-65°C), employing a substantial ferrocene excess, the elemental analyses showed the ratio of cyclopentylene to ferrocenylene units in the polymeric products to approach or slightly exceed unity, the atomic ratios of iron to boron being 2.0-2.5. However, because of considerable heterogeneity of the reaction mass under these mild conditions, the elemental analytical results were not quite reproducible; in addition, polymer yields and molecular weights, as expected, were quite low. In a grossly simplified manner, an exemplifying, idealized structure of this type may be represented by (II) ($m/n = 2$).

At higher temperatures (65-125°C) and longer reaction periods (2-5 days), polymer yields and molecular weights increased. In addition, the cyclopentylene/ferrocenylene ratio increased further, ultimately (that is, under the conditions employed in the present



(II)

study*) to approach a level of about 1.8. In these more advanced stages, apparently, both cyclopentenyl and ferrocenylcyclopentyl cations, arising as primary or secondary cleavage products, participated in the propagation, adding cyclopentylene groups and units (I) to the growing chain of (II); this resulted in structures comprising such types as (II) ($m/n \geq 3$) and (III) ($1/m/n = 3:2:1$) or (III) ($1/m/n = 4:3:1$). At the same time, competitive cleavage of intra-chain-type ferrocenylene groups, increasing in extent with advancing propagation because of increasing populations of such intra-chain ferrocenylene and concomitantly diminishing concentration of free ferrocene, caused further enhancement in the cyclopentylene/ferrocenylene ratio by producing such additional structures as (III) ($1/m/n = 4:2:1$) and (III) ($1/m/n = 5:2:1$), each of these



(III)

*We have abstained from conducting reactions at higher temperatures and over longer periods than indicated because of increased branching and cross-linking under such conditions. Extrapolating the findings presented below, it would appear that continued heating should ultimately produce compounds devoid of metallocene units and exclusively composed of cyclopentylene and phenylboron units.

structures contributing significantly to the average compositions determined analytically.

Four typical experiments illustrating the discussed correlations are summarized in Table 1. The condensations were conducted by stirring the reactants with ZnCl_2 and sulfolane in the molar ratios and under the conditions of time and temperature indicated. The blackish, resinous, and generally somewhat inhomogeneous products were hydrolyzed with ice water, and the resultant crude solids, after removal of unreacted ferrocene and nonpolymeric reaction products by extraction with hexane, were reprecipitated from concentrated and filtered benzene solution by a fourfold excess of 2-propanol containing 10 vol. % water. This gave a small crop of grayish-brown, halocarbon-soluble polymeric product listed as first fraction. (All products were washed with NaHCO_3 soln., 10% aqueous acetic acid, and water, then vacuum dried for 10 days at 100°C over KOH .) A second, considerably larger fraction, essentially composed of oligomeric reaction products, resulted from vacuum evaporation of the filtrate to dryness and washing of the semicrystalline residue with hexane and 2-propanol to remove traces of admixed ferrocene and other monomers.

It is seen that the structural pattern of (II) with equal populations of cyclopentylene and ferrocenylene units is realized only under the mild conditions of expt. 1. In expts. 2-4, requiring increasingly higher temperatures and prolonged heating times, the elemental analyses show a progressive decrease in % Fe and an increase in % H, reflecting the enhanced population of alicyclic constituents in agreement with the assigned structures. A comparison of expts. 3 and 4 also demonstrates the aforementioned effect of intrachain-type ferrocenylene cleavage in highly advanced stages [essentially constant $(l + m)/n$ ratio, but increasing l/m ratio], reflected in the more drastically reduced percentage of iron and slightly increased percentage of boron in expt. 4.

Furthermore, consistent with these structures, the IR spectra* (which, except for minor intensity differences and the appearance of the typical phenyl bands of the $-\text{B}(\text{C}_6\text{H}_5)$ unit†, proved superimposable with those of cyclopentylferrocene [10] and the various ferrocenylene-cyclopentylene polymers of earlier studies [11-14, 20, 21]) exhibited the characteristic alicyclic C-H stretching ($3.40\text{-}3.50\mu$) and deformation ($6.83\text{-}6.92\mu$) doublets in increasingly higher inten-

*The author is indebted to Messrs. R. K. Crossland and W. T. Thompson for recording the NMR and infrared spectra.

†The comparatively low intensity of these bands, consistent with slightly lower phenyl to ferrocenyl ^1H NMR signal ratios than calculated for the various proposed structures, suggests a minor extent of $\text{B}-\text{C}_{\text{phenyl}}$ bond cleavage not otherwise indicated analytically.

Table 1

Expt.	Molar ratio ^a			Time, hr	Temp., °C	Yield, %		Anal. calcd., ^d %			Anal. found, ^c %			Cp/Fe ^e			
	Fc	Rc	PBD ZnCl ₂ S			First fraction	Total ^b	M _n ^c	C	H	B	Fe ^f	C	H	B	Fe ^f	Calcd.
1	1.2 ^g	—	1.0 1.0 1.3	24	60	1.8	6.5	73.01	6.30	1.83	18.86	73.41	6.47	1.66	19.09	1.00	1.1
2	1.2	—	1.0 1.0 1.3	100	65	6.1	13.8	73.58	6.62	1.33	18.48	74.09	6.55	1.19	18.59	1.25	1.3
3	1.0	—	1.0 0.5 0.9	24/10	100/125	9.3	25.2	73.92	6.78	1.31	17.99	73.07	6.58	1.23	18.12	1.38	1.4
4	1.0	—	1.0 1.0 5.0	125	100	16.4	48.8	75.03	7.11	1.37	16.49	74.92	6.92	1.30	15.89	1.71	1.7
5	—	—	1.0 1.0 1.0 ^h	90	65	5.9	14.7	63.34	5.46	1.58	29.62	64.14	5.10	1.39	28.87	1.00	0.9

^aFc, ferrocene; Rc, ruthenocene; PBD, phenylboron dichloride; S, sulfolane.

^bCombined yield of first and second fractions, based on ferrocene.

^cDetermined on first fractions. All compounds additionally containing 1.0-1.5% oxygen (neutron activation analysis), indicating a $-B(C_6H_5)_2OH$ end group.

^dCalculated for structure (II) ($m/n = 2$) in expt. 1; for (III) ($l/m/n = 10:8:3$) in expt. 2; for (III) ($l/m/n = 11:8:3$) in expt. 3; for (III) ($l/m/n = 12:7:3$) in expt. 4; for (V) ($m/n = 2$) in expt. 5. Poor reproducibility in expt. 1 owing to heterogeneity of reaction mass.

^eCyclopentylene/ferrocenyliene proton ratio, calculated for structures indicated in footnote d, and determined from proton signal area ratio in ¹H NMR spectra.

^fRu in expt. 5.

^gNearly identical results with 1.0 mole.

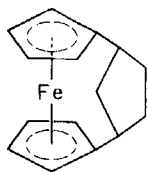
^hEssentially same results with 0.2 mole at 85°C.

sities in going from polymer 1 through polymer 4. Both the 9- μ and 10- μ bands were shown, indicating the presence of unsubstituted ferrocene rings [22] and thus of homoannularly disubstituted (1, 2- and 1, 3) ferrocenylene units in the chain. The two bands, however, invariably appeared in intensities too low to account solely for homoannularly interlinked ferrocenylene units, and the presence of units of the heteroannular (1, 1'-) type must additionally be inferred. Such coexistence of intrachain-type 1, 2-, 1, 3-, and 1, 1'- ferrocenylene groups has generally been observed with ferrocene polymers that arise by polyalkylation mechanisms [20, 23, 24]. A quantitative evaluation of the 9- μ and 10- μ bands [25], taking into account one ferrocenyl end group per chain at the respective molecular weight, gave homoannularities [25] of 50-57% in the present study. This range, several per cent below the homoannularity (~60%) of methylene-bridged polymers of previous investigations [23, 25], may reflect increased steric effects exerted by the bulky alicyclic groups, resulting in enhanced heteroannular substitution orientation.

The ^1H NMR spectra (at 60 MHz, in CDCl_3) of polymers (III), giving broad alicyclic resonances in the τ range 6.5-9.1, allow calculation of the cyclopentylene/ferrocenylene proton signal area ratios; these, as seen from the tabulated data, are well in accord with the structures proposed on the basis of elemental analyses. In addition, the spectra, giving methine to methylene proton signal area ratios (clearly discernible only with fractions having $M_n < 2000$) invariably in the narrow range 0.22-0.25, permit the conclusion that, on the average, 18-20% of the cyclopentylene units in (II) and (III) occur as the gem-disubstituted species (as represented by the non-polymeric model compound, 1, 1-diferrocenylicyclopentane [20]), with the remaining 80-82% being of the 1, 2 and 1, 3 types. Well coincident with the 18-20% range determined in this study, the population of gem-disubstituted cyclopentylene in earlier ferrocenylene-cyclopentylene polymers [20] was reported to be ca. 20%. This finding appears reasonable in view of the fact that cleavage of the metallocene and subsequent alkylation reactions constitute the principal or exclusive mechanism in the two studies compared.

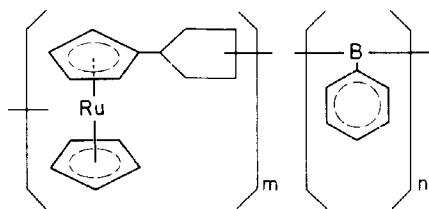
In convincing support of the cleavage mechanism, it was possible to isolate the heteroannularly bridged derivative (IV), 1, 1'-(1, 3-cyclopentylene)ferrocene [17], as a by-product. To this end, the combined and concentrated hexane extracts of the crude reaction products were chromatographed on activated alumina as described [20]. The first band contained unreacted ferrocene (2-10% recovery), and the faint second band, occasionally appearing as the tailing of the first, gave a 0.1-0.2% yield of (IV). No attempts were made in this study to separate from subsequent bands the additional ferrocenyl-substituted cyclopentanes reported previously [20].

To compare the propensity of ferrocene to metal-ring bond fission with that of its next congener, ruthenocene, several experi-



(IV)

ments were conducted using ruthenocene and phenylboron dichloride as the reactants. A typical experiment is included in Table 1 (expt. 5). The polymer fractions were collected as in expts. 1-4 except that chloroform was used as the solvent. The elemental analyses, supported by the cyclopentylene/ruthenocenylylene ratio determined from NMR data, closely correspond to a polymer structure (V) where $m/n = 2$. A comparison with the similar ferrocene run 2 shows a reduced cleavage effect in the ruthenocene case, coupled with enhanced molecular weight. Since the reactivity of ruthenocene in electrophilic substitution reactions is known to be lower than that of ferrocene [26, 27], this enhancement in molecular weight relative to the ferrocene case clearly cannot be the result of an increased rate of substitution (either by boron or by carbon), but may, rather, be due to diminished cleavage of 1, 1'-substituted ruthenocenylylene units of the chain, thus sustaining the integrity of the growing chain to a greater extent than is realized in the ferrocene case. The reduced tendency of the ruthenocene system, relative to ferrocene, toward degradation through bond cleavage between metal and rings, reflected in these results, is well in accord with both the enhancement in metal-ring bond strength [26] and the decrease in nucleophilicity and concomitant increase in resistance toward protonation [28] exhibited by the ruthenium-organic compound.



(V)

REFERENCES

- [1] E. W. Neuse, *Macromolecules*, **1**, 171 (1968).
- [2] V. Azernikov, *Nauka i Zhizn*, 1960, 22.
- [3] H. Rosenberg and M. D. Rausch, U.S. Pat. **3**, 060, 215 (1962).
- [4] E. V. Wilkus and W. H. Rauscher, *J. Org. Chem.*, **30**, 2889 (1965).
- [5] E. V. Wilkus and A. Berger, *Fr. Pats.* **1**, 396, 273; **1**, 398, 255.
- [6] G. Greber and M. L. Hallensleben, *Makromol. Chem.*, **83**, 148 (1965); **92**, 137 (1966); **104**, 77, 90 (1967).
- [7] H. Rosenberg, J. M. Barton, and M. M. Hollander, *Second Intern. Symp. Organometal. Chem., Madison, Wisc., 1965*, Abstr. of Proceedings, p. 42.
- [8] E. W. Neuse and G. J. Chris, *J. Macromol. Sci.*, **A1**, 371 (1967).
- [9] C. H. Pittman, Jr., *J. Polymer Sci.*, (**A1**) **5**, 2927 (1967).
- [10] V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955); U.S. Pat. **2**, 831, 879 (1958).
- [11] A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk SSSR*, **126**, 307 (1959).
- [12] A. N. Nesmeyanov, N. S. Kochetkova, and R. B. Materikova, *Dokl. Akad. Nauk SSSR*, **136**, 1096 (1960).
- [13] S. G. Cottis and H. Rosenberg, *J. Polymer Sci.*, **B2**, 259 (1964).
- [14] H. Valot, *Double Liaison*, **130**, 775 (1966).
- [15] W. G. DeWitt, Ph. D. thesis, University of Illinois, Urbana, 1966.
- [16] S. J. Goldberg, *J. Am. Chem. Soc.*, **84**, 3022 (1962).
- [17] S. G. Cottis and H. Rosenberg, *Chem. Ind. (London)*, 1963, 860
- [18] E. W. Neuse and K. Koda, *J. Macromol. Chem.*, **1**, 595 (1966).
- [19] E. W. Neuse and R. M. Trahe, *J. Macromol. Chem.*, **1**, 611 (1966).
- [20] E. W. Neuse, R. K. Crossland, and K. Koda, *J. Org. Chem.*, **31**, 2409 (1966).
- [21] A. N. Nesmeyanov, N. S. Kochetkova, P. V. Petrovsky, and E. I. Fedin, *Dokl. Akad. Nauk SSSR*, **152**, 875 (1963).
- [22] M. Rosenblum, Ph. D. thesis, Harvard University, 1953.
- [23] E. W. Neuse and E. Quo, *J. Polymer Sci.*, **A3**, 1499 (1965); *Bull. Chem. Soc. Japan*, **39**, 1508 (1966), and refs. therein.
- [24] E. W. Neuse, E. Quo, and W. G. Howells, *J. Org. Chem.*, **30**, 4071 (1965).
- [25] E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **85**, 1952 (1963).
- [26] M. D. Rausch, E. O. Fischer, and H. Grubert, *Chem. Ind. (London)*, 1958, 756; *J. Am. Chem. Soc.* **82**, 76 (1960).
- [27] E. A. Hill and J. H. Richards, *J. Am. Chem. Soc.*, **83**, 3840 (1961).
- [28] T. J. Curphey, J. O. Santer, M. Rosenblum, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960).

Accepted by editor January 15, 1968

Received for publication February 26, 1968