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Notes

X-ray Powder Diffractograms of Some Oligo- and Poly(1,1'-ferrocenylenes)[†]

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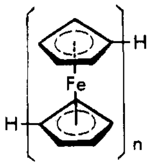
Yamamoto and Collaborators recently described the preparation[1] and properties[2] of a linear, yet benzene-insoluble, poly(1,1'-ferrocenylene) (1) said to possess a molecular mass of 4600 (i.e., $\bar{n} \simeq 25$) and show crystallinity as determined by X-ray powder diffractometry. These findings appeared doubtful in light of the excellent solubility in aromatic solvents observed in extended previous work[3-5] for pure, linear 1 in the molecular mass range 1500–6000 and higher. Because of the overriding importance of solubility for the analytical characterization and use of polymers of this type, we decided to clarify this inconsistency of observations by determining the crystallinity of authentic, soluble poly(1,1'-ferrocenylene) fractions with molecular masses extending up to 5000 for comparison with the diffractometric findings of Yamamoto et al.[2]



Authentic 1 was synthesized by the organolithium–organohalide coupling method as previously described.[5] The crude polymer was fractionated by the earlier established[5] procedure to give, in the order of decreasing degree of polymerization, the polymeric fractions I and II and the oligomer fractions III and IV. Fraction I was further fractionated, by fractionating precipitation,[5] into six subfractions, four of which, labeled Ia, Ib, Ic, and Id, were included in the subsequent evaluation. Molecular mass data and benzene-solubility properties were determined for fractions Ia–d as well as for III and IV. The results are given in Table I. X-ray powder diffractograms (Cu Kα) were recorded within the range $2\theta = 10$–30° for fractions Ia–d and III, as well as for a tetracyanoquinodimethanide (TCNQ$^-$) polysalt of III prepared as described in Yamamoto's paper.[2] Prominent *d* spacings derived from the diagrams for Id (very weak signals) and III (moderately strong signals) are included in Table I, and the well-developed diffractogram of the TCNQ salt of fraction III is summarized in Table III. No signals were detectable for fractions Ia–c.

Next, a poly(ferrocenylene) was synthesized from 1,1'-dibromoferrocene and magnesium in THF–dibromoethane as described in the first paper[1] of Yamamoto's group. The crude product was fractionated by the same procedure as used for the isolation of the fractions in Table I. Low degrees of polymerization and correspondingly poor yields in soluble higher molecular material necessitated per-

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[†] Metallocene Polymers, 42.

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Table I
X-ray Powder Diffractograms of Selected Fractions of 1 Synthesized by Organolithium–Organohalide Polycoupling[a]

fraction[b]	$\bar{M}_n$[c]	solubility in benzene	diffractogram[d] *d* spacing/pm (relative intensity)
Ia	5100	excellent	no signals detectable
Ib	4200	excellent	no signals detectable
Ic	2800	excellent	no signals detectable
Id	1600	excellent	341,[e] 377,[e] 464, 498, 568
III	738, 922, 1106	very poor	329,[e] 413 (19), 442 (32), 540 (100), 760,[e] 880 (24)[f]
IV	500	good	

[a] Poly(1,1′-ferrocenylene) (1) prepared by the method of ref 5 (experiment 7 of that paper). [b] Ia–d obtained by fractionating precipitation of fraction I. [c] By vapor pressure osmometry in benzene at 30 °C (by mass spectrometry for fraction III). Osmometric values rounded off to nearest 100. [d] Cu Kα, λ = 154.18 pm. Signals with intensity <10% of base peak neglected. Signals for Id too weak for intensity assessment. All intensity data are averages of two scans. [e] Variable, peak not always detectable. [f] Almost identical diffractogram recorded for chromatographically separated tetramer/pentamer fraction.

Table II
X-ray Powder Diffractograms of Selected Fractions of 1 Synthesized by Organohalide–Magnesium Polycoupling[a]

fraction[b]	$\bar{M}_n$[c]	solubility in benzene	diffractogram[d] *d* spacing/pm (relative intensity)
Ia′	3600	excellent	no signals detectable
Ib′	2900	excellent	no signals detectable
Ic′	2300	excellent	no signals detectable
Id′	1400	excellent	320,[e] 340,[e] 463, 554, 561, 633[e]
III′	738, 922, 1106	very poor	414 (16), 442 (30), 539 (100), 878 (21)[f]
IV′	500	good	

[a] Poly(1,1′-ferrocenylene) (composition approximating 1) prepared by method of ref 1 (experiment 2 of that paper). [b] Ia′–d′ obtained by fractionating precipitation of fraction I′. [c] By vapor pressure osmometry in benzene at 30 °C (by mass spectrometry for fraction III); presence of traces of monobromo derivatives also indicated. Osmometric values rounded off to nearest 100. [d] Cu Kα, λ = 154.18 pm; signals with intensity <10% of base peak neglected. Signals for Id′ too weak for intensity assessment. All intensity data are averages of two scans. [e] Variable, peak not always detectable. [f] Diffractogram reported in ref 2 for corresponding material ("crystalline poly(1,1′-ferrocenylene)" of that paper): 410 (13), 439 (24), 537 (100), and 870 (26) pm.

forming the polymerization in fourfold scale (relative to the organolithium–organohalide coupling experiment) so as to provide the quantities needed for fractionating precipitation. The respective fractions, given in prime notation, are listed in Table II, which also contains molecular mass, solubility, and X-ray powder diffractometry data. The diffractometric results reported by Yamamoto et al.[2] for their benzene-insoluble material (denoted fraction IV in their preparative paper[1]), which was obtained in a similar fashion as fractions III and III′ of the present study and was assigned[2,6] a molecular mass of 4600, are given in footnote *f* of that table. In confirmation of the original authors' findings,[1] the soluble fractions proved to be impure, containing 2–4% Br in addition to aliphatic segments (IR and NMR) probably introduced via the dibromoethane reagent.[1] Fraction III′ again was transformed into its TCNQ salt and its diffractogram recorded (Table III) together with that of the analogously obtained TCNQ salt of fraction Ib′.

Comparison of Tables I and II reveals virtually identical diffractometric results for the respective nonprimed and primed fractions, and a similar conclusion is reached from inspection of Table III for the diffractograms of the TCNQ salts of fraction III and its primed counterpart. Specifically, the tabulated data show the following: (i) poly(ferrocenylene) fractions possessing molecular masses exceeding 1400–1600 are very soluble in benzene and other aromatics irrespective of the method of synthesis used, thus confirming our earlier observations in this respect;[4,5] (ii) both syntheses afford an oligomeric fraction largely composed of tetra-, penta-, and hexamer, which, while somewhat soluble in boiling toluene and chlorobenzene (the solvents used[5] for its extraction and isolation), is practically insoluble in cold benzene, well in accord with our previous findings; (iii) none of the fractions with $\bar{M}_n$ > 2000, including those in the critical $\bar{M}_n$ range of 4000–5000 reported by Yamamoto et al.,[2] possess crystallinity detectable with the instrumental setup used by us; (iv) the cold benzene-insoluble oligomer fractions III and III′ both possess crystallinity and give virtually identical powder diffractograms. These diagrams, at the same time, are almost identical with that published by Yamamoto et al. for their benzene-insoluble material said to possess $\bar{M}$ = 4600;[2] (v) the TCNQ salts of the oligomeric fraction III and its counterpart III′ are highly crystalline and give practically identical powder diagrams corresponding perfectly to the reported[2] diffractogram of Yamamoto's benzene-insoluble material, while differing distinctly from that of the TCNQ salt of the polymeric fraction Ib′.

It is thus evident that the crystalline, benzene-insoluble poly(ferrocenylene) of Yamamoto's group was not of the high molecular mass (4600) indicated by these authors[2] but rather represented a condensation product composed largely of oligomer fractions with $n \simeq$ 4–6, still sufficiently crystalline to provide a well-defined X-ray powder diffractogram.[7] It is also obvious that the organohalide–magnesium polycoupling reaction proceeds less cleanly, and certainly not with the claimed[2] higher selectivity, than any one of the known coupling procedures involving organolithium intermediates.[4,5]

Experimental Section[8]

Preparation of 1. A. By Organolithium–Organohalide Polycoupling. A palladium(II) chloride catalyzed polycondensation of 1,1′-dilithioferrocene (TMEDA complexed) and 1,1′-diiodoferrocene was performed as previously reported[5] for experiment 7 of that publication, except that double scale was employed (27.4 mmol of diiodoferrocene) and the molar ratio of dilithioferrocene/diiodoferrocene was 1.12. Fractions I (11.6%),

Table III
X-ray Powder Diffractograms of TCNQ Salts of 1, Fractions III and III′

salt[a]	X = TCNQ/Fe[b] in product salt	diffractogram[c] *d* spacing/pm (relative intensity)
III–TCNQ	0.85	744 (100), 655 (50), 583 (75), 505 (75), 393, 392 (40), 358 (16), 342 (12), 320 (25)
III′-TCNQ[d]	0.83	740 (100), 655 (45), 581 (70), 506 (80), 395, 392 (35), 357 (19), 341,[e] 319 (20)[d]
Ib′–TCNQ	0.80	818 (29), 695,[e] 509 (30), 479 (100), 368 (28), 347 (45), 336 (30), 324 (70)

[a] Prepared from fractions III and III′ (Tables I and II) by treatment with TCNQ per procedure of ref 2. [b] Assessed from elemental analysis. [c] Cu Kα, λ = 154.18 pm. Signals with intensity <10% of base peak neglected. [d] Diffractogram reported in ref 2 for corresponding material (TCNQ salt of "crystalline poly(1,1′-ferrocenylene)" of that paper, *X* = 0.81): 734 (99), 651 (51), 575 (86), 501 (100), 389 (53), 354 (20), 338 (14). [e] Variable; peak not always detectable.

II (20.2%), III (29.7%), and IV (24.2%) were collected as described.[5] Fractionating precipitation, by the given procedure,[5] of a 1.2-g sample of fraction I from benzene solution under Ar in the presence of hexane as the nonsolvent afforded six subfractions, the second, third, fourth, and fifth of which were chosen for further evaluation and are listed in Table I as Ia–d, together with fractions III and IV. All fractions gave IR spectra identical with those obtained in the previous work.[5] Excellent solubility in cold benzene was reaffirmed for Ia–d and IV. Fraction III, practically insoluble in cold benzene, dissolved in hot toluene and chlorobenzene. Anal. Calcd for $C_{50}H_{42}Fe_5$ (**1**, $\bar{n}$ = 5): C, 65.12; H, 4.59; Fe, 30.28. Found for III: C, 64.98; H, 5.01; Fe, 29.79.

A sample (0.5 mmol) of III was treated with 2,3,5,6-tetracyanoquinodimethane (TCNQ, freshly recrystallized from deoxygenated benzene, 1.0 mmol) in benzonitrile exactly as described by Yamamoto et al.[2] to give a black TCNQ salt (95%). Anal. Calcd for III-TCNQ (TCNQ/Fe = 0.85): C, 67.77; H, 3.32; Fe, 15.60; N, 13.30. Found: C, 67.11; H, 3.53; Fe, 15.11; N, 12.93.

B. By Organohalide–Magnesium Polycoupling. Crude poly(ferrocenylene) was prepared from 1,1′-dibromoferrocene, 1,2-dibromoethane, and magnesium (1:1:2), catalyzed by $NiCl_2$, as described[1] for experiment 2 of that paper. The crude product was separated into fractions I′ (1%), II′ (3%), III′ (26%), and IV′ (19%) and further into Ia′–d′ (from I′) by the same techniques as employed for the isolation of the nonprimed counterparts under A, above. IR spectra were similar to those of corresponding nonprimed fractions but, as noted before,[1] additional impurity bands appeared at 2900–2850 cm^{-1} and near 870 cm^{-1}. NMR spectra ($CDCl_3$) of Ia′–d′ gave the reported[5] monolithic multiplet at δ 3.8–4.4 and weak impurity resonances[1] in the vicinity of δ 2. Fractions Ia′–d′ and IV′ were readily soluble in cold benzene, and III′ showed the same solubility behavior as its counterpart III. Bromine analyses were performed on a Ia′, Id′, and III′: Found: Br, 2.4 (Ia′), 3.9 (Id′), 2.6 (III′).

Samples (0.5 mmol) of both Ib′ and III′ were converted to the TCNQ salts by treatment with TCNQ (1.0 mmol) in benzonitrile by Yamamoto's procedure.[2] Anal. Found for Ib′-TCNQ (TCNQ/Fe = 0.80): N, 12.48; Fe, 15.47; for III′-TCNQ (TCNQ/Fe = 0.83): N, 12.70; Fe, 15.22.

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Registry No. Poly(1,1′-ferrocenylene) (homopolymer), 55884-62-3; poly(1,1′-dibromoferrocene) (homopolymer), 77979-54-5; (1,1′-diiodoferrocene)·(1,1′-dilithioferrocene) (copolymer), 69153-97-5; poly(1,1′-ferrocenylene) (SRU·TCNQ, 55884-67-8.

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(6) The molecular mass was assessed[1] from elemental analytical data on the assumption that each molecule bears two bromoferrocenyl end groups. This premise is invalidated by our observation that polycoupling in the organohalide–magnesium reaction[1] is accompanied by reductive dehalogenation (formation of bromoferrocene and traces of ferrocene identified by GC).
(7) The oligomeric nature of this crystalline material is also apparent from the thermogram (under N_2) recorded by Yamamoto's group[1] for their best sample, which indicates weight loss to set in near 300 °C and relative residual weight at 600 °C to approximate 75%. The thermogram obtained by us on our fraction Ib (Du Pont Thermogravimetric Analyzer, Model 951, 15 °C min^{-1}, under Ar), in contrast, shows incipient weight loss for this poly(ferrocenylene) to be some 100 °C higher, the relative residual weight at 600 °C being ca. 85%.
(8) Microanalyses were performed in the Analytical Laboratory of this Department; we are indebted to Mrs. S. Heiss for this analytical service. X-ray powder diffractograms were scanned over the range 2θ = 10–28° on a Rigaku Geigerflex diffractometer, D-Max IIIA, at a scan rate of 10 deg min^{-1}.

Carboranylene-Bridged Poly(benzimidazole)

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The icosahedral *meta*-carborane (1,7-dicarba-*closo*-dodecaborane(12)) cluster lends itself, much like the 1,2- and 1,12-dicarba isomers, as an attractive monomer constituent for the preparation of boron-containing macromolecules for a wide range of potential applications as biomedical, nuclear-shielding, or thermostable materials.[1] Our longstanding interest in heteroaromatic polymers prompted us to utilize the recently described[2] 1,7-diformyl-*meta*-carborane for copolymerization with 3,3′-diaminobenzidine (DAB) and subsequent cyclodehydrogenation of the resulting poly(azomethine) **1** to the carboranylene-bridged poly(benzimidazole) **2**. The low-temperature solution polymerization of aromatic dialdehydes with bis(*o*-diamino)-substituted arenes and subsequent oxidative cycloaromatization of the intermediary poly(azomethines) represent a smooth two-stage synthesis of linear, aromatic poly(benzimidazoles).[3] Using this two-stage approach, we first prepared the open-chain poly(azomethine) **1** by anaerobic copolymerization of 1,7-diformyl-*meta*-carborane and DAB (1:1) in *N,N*-dimethylacetamide (DMAC) (6 h at −10 °C, 24 h at 0–25 °C, and then 1 h at 50 °C; Scheme I).

Although a soluble polymeric product was formed under these conditions, the degree of polymerization proved to be unexpectedly low (η_{inh} = 0.08 dL g^{-1}); in addition, the polymer contained sizeable quantities of (unsubstituted) *meta*-carborane. Use of a 5% molar excess of the dialdehyde increased the degree of polymerization only slightly (η_{inh} = 0.09 dL g^{-1}). Extending the reaction time at 50 °C to 6 h did not result in a molecular mass increase as previous experience[3b] would suggest; on the contrary, it caused a dramatic decrease (η_{inh} = 0.02 dL g^{-1}). At the same time, there was enhanced contamination by *meta*-carborane, the latter apparently generated from **1** by cleavage of the C–C bond connecting the azomethine carbon to the carborane carbon atom.[4] In order to suppress this competing backbone fission, it proved necessary to compromise by keeping both the overall reaction time and the upper reaction temperature to a minimum. For example, 6 h at −15 °C and a total of 30 h at 0–25 °C under argon (dialdehyde/DAB = 1.1)[5] gave poly(azomethine) **1** only insignificantly contaminated by *meta*-carborane, although, as would be expected, both the overall polymer yield and the degree of polymerization remained low (first polymer fraction 11% yield, η_{inh} = 0.1 dL g^{-1}; second polymer fraction 56% yield; η_{inh} = 0.07 dL g^{-1}). Surprisingly, even under these mild experimental conditions, electronic absorption spectroscopy indicated that some cyclodehydrogenation (vide infra) had occurred concurrently with polymerization; the spectra (in deoxygenated