Metallocene Polymers. XXI. Polypyrazoles[1]

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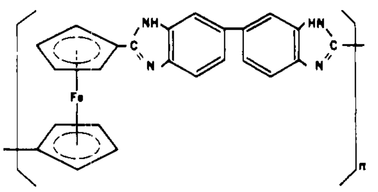
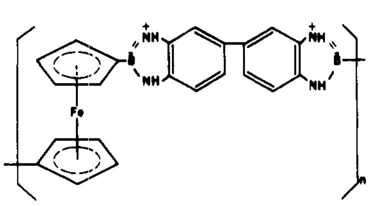
ABSTRACT: The low-temperature solution condensation of 1,1′-bis(diketo)ferrocenes with aromatic or pseudoaromatic dihydrazines produces soluble polyhydrazones with number-average molecular weights of about 1500–2000 and inherent viscosities of about 0.1–0.2 dl g^{-1}. Upon thermal treatment at temperatures of 200–240°, these polyhydrazones undergo cyclodehydration to give polymers containing intrachain pyrazolylene units, these heterocycles being predominantly of the 1,5-disubstituted type. The infusible, largely soluble polypyrazoles show inherent viscosities of 0.15–0.40 dl g^{-1} and exhibit a thermal stability behavior superior to that of other known ferrocene-containing polymers with intrachain heteroaromatic units. The products undergo incipient weight loss at about 400° in argon; relative residual weights are 75–80 and 65–75%, respectively, at 600 and 800°.

Heterocyclic polymers possessing ferrocene groups in the main chain were first investigated by Marvel and collaborators. These authors obtained polybenzimidazoles of structure I by polycondensation of



I

3,3′-diaminobenzidine with 1,1′-di(carbophenoxy)ferrocene at 210–250° in the melt phase, followed by a postheating treatment at 280–290° in the solid state.[2] Analogously, polybenzborimidazolines of type II were



II

synthesized by reacting the same diaminobenzidine derivative with tetrabutyl 1,1′-ferrocenediboronate under similar high-temperature condensation conditions.[3] Both ferrocene polymer types exhibited inherent viscosities, η_{inh}, as low as 0.13–0.20 dl g^{-1} and, contrasting with the analogous benzene–aromatic polyheterocyclics, showed rather unsatisfactory heat stability, thermogravimetric analyses indicating relative weight loss figures of about 20–25% at 400° and 25–30% at 500°.

In the light of the excellent thermostability behavior of ferrocene itself,[4–8] the stability of the ferrocene-containing polymers I and II should be appreciably higher than actually observed by Marvel's group; it was, therefore, of interest to provide additional examples of ferrocene-containing polyheteroaromatics for further study of this question. In previous efforts,[9] the low-temperature solution condensation of bis-β-diketo derivatives of benzene with aromatic dihydrazines had been found to give soluble hydrazone-type prepolymers, from which benzene–aromatic polypyrazoles could be obtained by thermal cyclodehydration. This approach to heteroaromatic polymers appeared attractive in the present case, because the low condensation temperature in the first reaction step should permit relatively smooth control of the primary condensation reaction; this, in turn, should minimize structural irregularities that might lead to incomplete aromatization of the polymeric end product. In addition, the synthesis *via* soluble prepolymers would offer distinct advantages from an application standpoint. In pursuit of these goals, the feasibility of preparing polypyrazoles with ferrocene groups in the main chain through the intermediacy of soluble polycondensation products of dihydrazines with bis(β-diketo)ferrocenes was explored in this laboratory.

Results and Discussion

Polycondensation Reactions. Using in essence the approach outlined previously for the benzene–aromatic series,[9] the three bis-β-diketo compounds 1,1′-bis(formylaceto)ferrocene,[10] 1,1′-bis(acetylaceto)ferrocene,[11] and 1,1′-bis(benzoylaceto)ferrocene[11,12] (reactants A) were condensed in solution with the dihydrazines 1,3- and 1,4-dihydrazinobenzene,[13] 4,4′-dihydrazino-2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl,[14] and 4,4′-dihydrazinodiphenyl sulfone[15,16] (reactants B)

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[1] Part XX: E. W. Neuse and H. Rosenberg, *J. Polym. Sci.*, in press.

[2] L. Plummer and C. S. Marvel, *ibid.*, *Part A-2*, 2559 (1964).

[3] J. E. Mulvaney, J. J. Bloomfield, and C. S. Marvel, *ibid.*, **62**, 59 (1962).

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[7] I. B. Johns, E. A. McElhil, and I. O. Smith, *J. Chem. Eng. Data*, **70**, 277 (1962).

[8] B. Ya. Andreev, L. M. Dyagileva, and G. I. Feklisov, *Dokl. Akad. Nauk SSR*, **158**, 1348 (1964).

[9] E. W. Neuse and R. K. Crossland, *Chem. Ind.* (London), 2005 (1965).

[10] K. Schlögl and H. Egger, *Monatsh. Chem.*, **94**, 1054 (1963).

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[12] C. A. Hauser and C. E. Cain, *ibid.*, **23**, 1142 (1958).

[13] H. A. J. Schoutissen, *J. Amer. Chem. Soc.*, **55**, 4545 (1933).

[14] D. C. Holland, G. J. Moore, and C. Tamborski, *J. Org. Chem.*, **29**, 1562 (1964).

[15] N. Takeda and T. Hattori, Japanese Patent 6916 (1951); *Chem. Abstr.*, **48**, 718 (1954).

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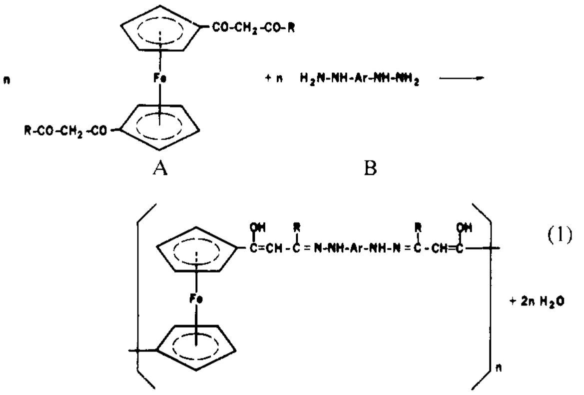
TABLE I
POLYHYDRAZONES III[a]

Polymer	Starting materials: R in reactant A	Starting materials: Ar in reactant B	Yield, %	Mp,[b] °C	η_{inh},[c] dl g^{-1}: DMF	η_{inh},[c] dl g^{-1}: HCOOH	η_{inh},[c] dl g^{-1}: H_2SO_4	M_n[d]	Anal.,[e] %: C	Anal.,[e] %: H	Anal.,[e] %: Fe	Anal.,[e] %: N
IIIa	H	m-C_6H_4	61.1	>300	0.15	0.12	...	1530	61.70 (63.10)	4.71 (4.84)	13.04 (13.61)	13.08 (12.48)
b	H	p-C_6H_4	65.5	>300	0.12	0.10	...	1490	61.70 (62.89)	4.71 (4.68)	13.04 (13.40)	13.08 (12.78)
c	H	p-C_6F_4-p-C_6F_4	69.6	>300	...	0.11[f]	0.11[f]	1720	51.87 (52.13)	2.49 (2.60)	8.61 (8.03)	8.64 (9.34)
d	H	p-$C_6H_4SO_2$-p-C_6H_4	73.6	>300	0.18	0.16	0.15	1850	59.20 (60.17)	4.23 (4.15)	9.82 (10.08)	9.85 (9.25)
e	CH_3	p-C_6H_4	63.9	220–250	0.16	0.15	...	1760	63.18 (63.98)	5.29 (5.30)	12.25 (12.41)	12.28 (11.77)
f	CH_3	p-C_6F_4-p-C_6F_4	74.7	185–230	0.15	...	0.12	2010	53.27 (54.00)	2.98 (2.93)	8.26 (8.62)	8.28 (8.92)
g	CH_3	p-$C_6H_4SO_2$-p-C_6H_4	54.8	180–220	0.15	0.15	0.12	1800	60.41 (60.79)	4.73 (4.42)	9.36 (9.82)	9.39 (8.97)
h	C_6H_5	p-C_6H_4	68.2	>300	0.10	0.09	...	1510	70.35 (71.30)	4.86 (4.75)	9.62 (9.44)	9.65 (9.09)
i	C_6H_5	p-C_6F_4-p-C_6F_4	72.0	270–300	0.11	0.09	...	1690	... ...	... ...	6.98 (7.20)	7.00 (6.77)
j	C_6H_5	p-$C_6H_4SO_2$-p-C_6H_4	57.1	280–300	0.13	0.11	0.10	1730	66.67 (67.03)	4.48 (4.52)	7.75 (8.02)	7.78 (7.56)

[a] Prepared in DMF solution, 3 days at ambient temperature, 1 hr at 90°, with 0.5 mol l.$^{-1}$ of glacial acetic acid; both reactants in 0.1 mol l.$^{-1}$ concentration. For starting materials, see eq 1. Stoichiometric quantities of $NaOCH_3$ added for IIIa, b, e, and h. [b] Range of sintering and partial melting. [c] 0.1% (w/v) at 25°, in DMF, 98% formic acid, and 96% sulfuric acid. [d] In DMF, by vapor pressure osmometry. Additionally in $CHCl_3$ (M_n values in parentheses) on IIIf (2190) and IIIg (1910). [e] Found values in parentheses. Combustion analyses by G. I. Robertson, Jr., Florham Park, N. J. Iron determinations by neutron activation analysis (14 MeV at neutron flux of 10^8 cm^{-2} sec^{-1}). [f] Weight corrected for insolubles.

according to eq 1. Highest purity of all starting materials was a prerequisite for successful polycondensation and subsequent cyclodehydration. The solvents employed were hexamethylphosphoramide, N-methylpyrrolidone, and, preferably, N,N-dimethylformamide (DMF). Preliminary experiments showed that poly-



(1)

IIIa, R = H; Ar = m-C_6H_4
b, R = H; Ar = p-C_6H_4
c, R = H; Ar = p-C_6F_4-p-C_6F_4
d, R = H; Ar = p-$C_6H_4SO_2$-p-C_6H_4
e, R = CH_3; Ar = p-C_6H_4
f, R = CH_3; Ar = p-C_6F_4-p-C_6F_4
g, R = CH_3; Ar = p-$C_6H_4SO_2$-p-C_6H_4
h, R = C_6H_5; Ar = p-C_6H_4
i, R = C_6H_5; Ar = p-C_6F_4-p-C_6F_4
j, R = C_6H_5; Ar = p-$C_6H_4SO_2$-p-C_6H_4

condensation according to eq 1 can best be achieved by using low reactant concentrations and conducting the reactions in the presence of an acidic catalyst, preferably glacial acetic acid, at temperatures not exceeding 30°. However, reaction periods of 1 week and more were required to obtain satisfactory conversion under these conditions. Higher temperatures and concentrations, on the other hand, while improving polymer yields and giving slightly enhanced molecular weights, favored side reactions with the solvent and promoted cyclodehydration of the open-chain segments, thus producing irregularities in the chain structure of polymers III. As a compromise, the conditions summarized in Table I were routinely adopted in this study. Satisfactory conversion was achieved under these conditions, and cyclodehydration, while detectable analytically and spectroscopically on the products, remained irrelevant for practical purposes. The polyhydrazones III, obtained in yields of 55–75%, were tan to reddish brown solids which dissolved in a number of aprotic and acidic solvents. The unsubstituted (R = H) products were infusible up to 300°, while polymers possessing methyl or phenyl side groups melted partially in the 180–300° range.

Table I lists the analytical results, number-average molecular weights, M_n, and inherent viscosities, η_{inh}, for ten typical polyhydrazones III. The rather low degree of polymerization apparent in all cases is in keeping with similarly low viscosity ranges observed in other polymerization reactions involving 1,1′-disubstituted ferrocene derivatives as starting materials[1–3,17–19] and, much as in these earlier cases, may be the result of chain-terminating side reactions involving an intramolecular cyclization to heteroannularly bridged ferro-

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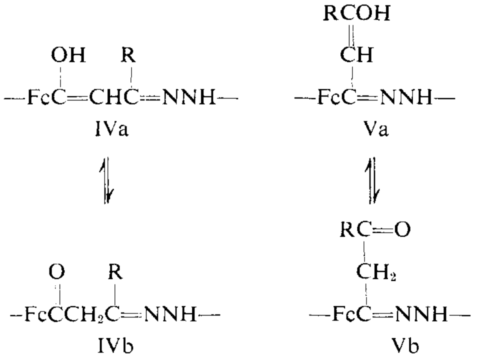
(17) F. W. Knobloch and W. H. Rauscher, *J. Polym. Sci.*, **54**, 651 (1961).
(18) M. Okawara, Y. Takemoto, H. Kitaoka, E. Haruki, and E. Imoto, *Kogyo Kagaku Zasshi*, **65**, 685 (1962).
(19) H. Valot, *Compt. Rend.*, **262**, *Ser. C*, 403 (1966).

cenylene units. Lowest viscosities are apparent for IIIn, i, and j and are doubtlessly accounted for by reduced steric accessibility of the carbonyl groups in the bisdiketone.

Infrared spectroscopic data derived from the polyhydrazones III (on KBr disks) suggest that the enolic structures implied in III, and written as IVa (Fc = 1,1′-ferrocenylene) for the interconnecting open-chain segments, represent an idealized limiting case. Thus, a strong band emerged near 6 μ due to the carbonyl stretching modes of the corresponding tautomeric ketone[20] forms IVb, and, in addition, a moderately strong peak was shown at about 6.88 μ, which may be assigned to the scissoring mode of the methylene group in IVb (partially overlapped by methyl deformation band whenever R = CH_3). The infrared spectra also substantiate the implication of eq 1 that hydrazone formation predominantly involves the γ-carbonyl groups of the bisdiketo starting materials (this implication being based on the expected retardation of nucleophilic attack at the carbonyl carbon in α position to the electron-releasing ferrocene group[21]). All polymers III showed the aforementioned strong carbonyl stretching band within the range 6.02–6.05 μ, that is, at a position which is characteristic of aliphatic acyl derivatives of ferrocene and, hence, must be ascribed to the segment structure IVb possessing an unaffected –FcCO-CH_2– grouping. In cases where R = H, hydrazone formation appears to proceed even exclusively *via* the γ-carbonyl, since no additional carbonyl stretching absorption emerged at 5.75–5.80 μ, where the formyl group of a segment of the type Vb (which should arise as a consequence of hydrazone formation *via* the α-carbonyl) would be expected to absorb. Essentially the same was found to hold for the polyhydrazones with R = C_6H_5, which, at best, showed a very weak shoulder at the position (5.94 μ) typical of the acetophenonyl group of segment Vb. Only in such reactions in which R = CH_3, the extent of α-carbonyl involvement, possibly resulting from the electron-releasing nature of the methyl group, was no longer negligible; the products exhibited an additional, ever so weak, carbonyl stretching peak in the neighborhood of 5.85 μ, pointing to a minor population of segments Vb with acetonyl side groups.



$\text{—Fc}\overset{\text{OH}}{\text{C}}\text{=CH}\overset{\text{R}}{\text{C}}\text{=NNH—}$

IVa

$\text{—Fc}\overset{\overset{\text{RCOH}}{\|}}{\overset{\text{CH}}{\text{C}}}\text{=NNH—}$

Va

$\text{—Fc}\overset{\text{O}}{\text{C}}\text{CH}_2\overset{\text{R}}{\text{C}}\text{=NNH—}$

IVb

$\text{—Fc}\overset{\overset{\text{RC=O}}{|}}{\overset{\text{CH}_2}{\text{C}}}\text{=NNH—}$

Vb

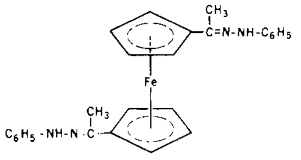
TABLE II

ELECTRONIC SPECTRA OF SOME MONOMERIC AND POLYMERIC HYDRAZONES[a]

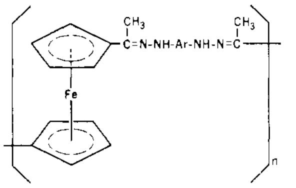
Compound	Wavelength (ε),[b] mμ	
Polymer IIId	461	*c*
Polymer IIIf	465	(1000)
Polymer IIIg	462	(1500)
Dihydrazone VI	450	(1580)
Polymer VII	448	*c*

[a] In $CHCl_3$ solution. [b] Ferrocene ligand-field band (440 mμ); *cf.* ref 22. Molar extinction coefficient, ε, in parentheses (calculated for recurring unit in polymer cases). [c] ε not determined because of incomplete solubility.

The predominance of γ-carbonyl involvement in the polycondensation of eq 1 is also suggested by the electronic spectra recorded for the exemplifying polymers IIId, f, and g. The characteristic, conjugation-sensitive ligand-field band[22] in the high-wavelength region, at 440 mμ in ferrocene, appeared near 460 mμ (Table II), *i.e.*, at the position expected for the polyconjugated system IVa. A less pronounced bathochromic shift of this band, on the other hand, would be anticipated for the hydrazone skeleton V with its shorter domain of conjugation; the band, in this case, should be near the 450-mμ position (Table II) shown by the two model hydrazones VI and VII possessing the same –FcC(R)=NNH– system (R = aliphatic substituent).



VI



VII

Cyclodehydration Reactions. The open-chain polyhydrazones III were converted into the polypyrazoles VIII by thermal treatment under reduced pressure in the absence of oxygen. This cyclodehydration, depicted by eq 2, proceeded at a temperature level appreciably lower than usually required for the cyclodehydration of open-chain polymers to polyheterocyclics, temperatures of 200–240° being sufficient to effectuate essentially complete cyclization. Generally, heating cycles were 8–12 hr at 180°, followed by 12–20 hr at 200° and 5–10 hr at 240°. Use of higher temperatures or drastically prolonged heating periods at the 200–240° level rendered the products increasingly insoluble without producing any further change in elemental composition or spectroscopic behavior. The resultant polypyrazoles VIII, for which the predominantly 1,5-oriented substituent disposition on the pyrazole rings follows from the structure of the precursor polymers III, were infus-

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(20) The coexistence of tautomeric ketone-type segments may also be inferred from the color change to a dark reddish brown observed on alkali treatment of III, indicating conversion to the more deeply colored enolic structures.

(21) K. Schlögl and A. Mohar, *Monatsh. Chem.*, **92**, 219 (1961).

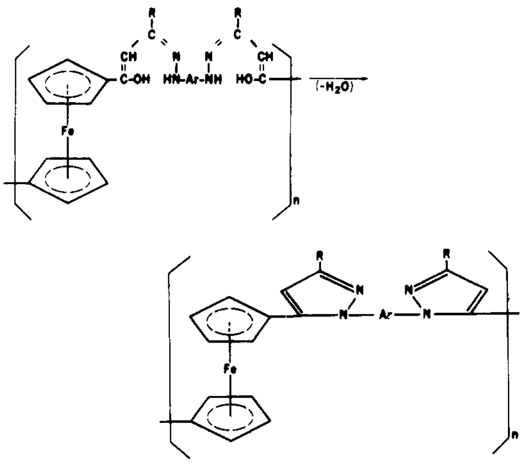
(22) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516, 2246 (1961); *J. Organometal. Chem.*, **4**, 409 (1965).

TABLE III
POLYPYRAZOLES VIII

Poly-pyrazole	Precursor poly-hydrazone	Cyclodehydration conditions[a] Time, hr	Temp, °C	η_{inh}, dl g^{-1} HCOOH	H_2SO_4	Calcd, % C	H	Fe	N	Found,[f] % C	H	Fe	N
VIIIa	IIIa	12/18/7	180/200/240	0.40[b]	0.37	67.37	4.11	14.24	14.28	66.87	4.21	14.11	13.53
b	b	12/18/7	180/200/240	0.33[b]	0.28	67.37	4.11	14.24	14.28	67.13	4.28	14.35	13.88
c	c	9/27[d]	180/200[d]	...	0.22[b]	54.93	1.98	9.12	9.15	54.09	2.19	9.42	8.74
d	d	12/4/16[c]	180/190/225[c]	0.37[b]	0.27	63.15	3.76	10.50	10.55	62.52	4.01	11.10	9.81
e	e	12/18/5	180/200/240	0.27[b]	0.21	68.56	4.79	13.30	13.34	67.83	5.00	12.86	12.78
f	f	12/30/2[d]	180/200/240[d]	0.30[b]	0.26[b]	56.27	2.52	8.72	8.75	56.10	2.62	9.03	8.76
g	g	12/24/8[e]	180/200/240[e]	0.37	0.29	64.29	4.32	9.96	10.00	61.23	4.56	10.33	8.99
h	h	12/15/7	180/200/240	0.19[b]	0.16	...	...	10.50	10.59	...	...	10.11	9.87
i	i	12/15/5[d]	180/200/240[d]	0.20[b]	0.16[b]	62.85	2.64	7.31	7.33	62.29	2.81	7.23	7.02
j	j	12/16/8	180/200/240	0.22	0.18	70.18	4.12	8.16	...	69.51	4.23	7.90	...

[a] From pastes, using DMF solvent (HCOOH for VIIIb, c, and f). [b] Weight corrected for insolubles. [c] Additional heating (2.5 hr at 250°) produced no compositional changes; η_{inh}, 0.29 dl g^{-1} (HCOOH). Further heat treatment rendered product largely insoluble. [d] Additional heating (3–5 hr at 240°) rendered product largely insoluble. [e] Additional heating (4 hr at 280°) gave η_{inh}, 0.42 dl g^{-1} (HCOOH, incompletely soluble); 0.38 dl g^{-1} (H_2SO_4). [f] Carbon and nitrogen analyses frequently erratic; in questionable cases, values listed are average of three runs.

ible and mostly soluble solids. Best solubility, as would be expected, was shown by products containing the flexible biphenylene sulfone segments. In general, polymer solubility was furthermore enhanced by the presence of methyl or phenyl side groups, causing less dense packing of the polymer chains in these cases. Reduced solubility, on the other hand, was observed, irrespective of the nature of the substituent R, with polymers possessing the rigid octafluorobiphenylene bridges. Typical cyclodehydration conditions for the ten precursor polymers of Table I are summarized in Table III, which also lists the analytical data for the resultant polypyrazoles VIII. The analyses, notably the increase in per cent iron and the decrease in per cent hydrogen, in all instances consistent with the compositions of VIII, suggest substantially complete conversion according to eq 2.[23] This reaction course was corroborated by infrared spectroscopy. All polymers VIII with the exception of the fluorine-containing types[24] lacked the characteristic, high-intensity α-carbonyl stretching absorption in the vicinity of 6 μ. (A weak and fairly broad residual shoulder usually observed near this position, and not vanishing upon further heating for 5–8 hr at 280–300°, is probably due to carbonyl-containing end groups.) Instead, there emerged two bands at 6.35–6.44 and 7.10–7.13 μ assignable to ring stretching (mixed C=C, C=N) modes[25] of the pyrazole system; the analogous peaks were exhibited at 6.42 and 7.14 μ by the nonpolymeric model compound, 3-ferrocenylpyrazole[10] (sample kindly furnished by Professor Schlögl). Two more ring-stretching bands generally found in pyrazole spectra at 6.22–6.24 μ and near 7.85 μ[11,12,25–27] were not observable in all types of VIII because of partial superposition by phenyl ring stretching bands and other interferences in this region. A conspicuous pyrazole band was shown at about 10.3 μ by all samples; this absorption, appearing near 10.4 μ in the spectrum of 3-ferrocenylpyrazole and reported near 10.7 μ for other pyrazoles,[27] is likely to be derived from a breathing mode.[25] Other pyrazole bands emerging near 13.3 and 16.3 μ and assignable to ring atom in-plane and out-of-plane deforma-



(2)

VIIIa, R = H; Ar = m-C_6H_4
b, R = H; Ar = p-C_6H_4
c, R = H; Ar = p-C_6F_4-p-C_6F_4
d, R = H; Ar = p-$C_6H_4SO_2$-p-C_6H_4
e, R = CH_3; Ar = p-C_6H_4
f, R = CH_3; Ar = p-C_6F_4-p-C_6F_4
g, R = CH_3; Ar = p-$C_6H_4SO_2$-p-C_6H_4
h, R = C_6H_5; Ar = p-C_6H_4
i, R = C_6H_5; Ar = p-C_6F_4-p-C_6F_4
j, R = C_6H_5; Ar = p-$C_6H_4SO_2$-p-C_6H_4

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(23) Incomplete conversion, however, resulted from cyclodehydration experiments that were conducted with insufficient exclusion of air. The end products from such reactions contained up to 10% O, retained considerable carbonyl stretching infrared absorption in addition to showing strong hydroxyl bands, and, in thermogravimetric analyses, experienced higher weight loss than did the regular products VIII.

(24) VIIIc, f, and i all showed weak or moderate absorption at 6.05 μ likely to be associated with a ring-stretching mode of the polyfluorinated phenyl system. This band appears, for example, in medium intensity at 6.00–6.06 μ in the spectra of pentafluorobenzene and decafluorobiphenyl, as well as in a host of sufficiently unsymmetrical mono- and *para*-disubstituted derivatives of these parent compounds.

(25) A. R. Katritzky, *Quart. Rev.* (London), **13**, 353 (1959).

(26) P. Mirone and M. Vampiri, *Atti Accad. Nazl. Lincei, Rend., Classe Sci. Fis., Mat. Nat.*, **12**, 583 (1952); *Chem. Abstr.*, **46**, 9423 (1952).

(27) C. S. Rondestvedt and P. K. Chang, *J. Amer. Chem. Soc.*, **77**, 6532 (1955).

tion modes,[25] respectively, were found to be of less diagnostic value because of partial merging with phenyl deformation, sulfone bending, and other uncharacterized absorptions.

Concomitantly with the cyclodehydration of eq 2, the heat treatment of the polyhydrazones III caused some chain extension through interaction of the acylaceto and hydrazino end groups, as is indicated by a noticeable viscosity increase in going from the precursor compounds III to their aromatized counterparts VIII. Such linear post-condensation effects are not uncommon in cyclodehydration reactions of open-chain polymers to polyheteroaromatics; typical examples were reported by Marvel's and Levine's groups[28–30] and other workers.[31] The viscosities listed[32,33] show, however, that the chain extension achieved with the ferrocene-containing polypyrazoles is less significant than that attained, for example, in the corresponding benzene–aromatic polypyrazole series, in which inherent viscosities as high as 0.6–1.1 dl g^{-1} were measured. Table IV collects viscosities and some analytical data for the five representative benzene aromatic polypyrazoles IXa–e, which were obtained, as in the previously quoted work,[9] from the appropriate bis-β-diketobenzenes and dihydrazines. The comparatively low degree of chain extension observed on thermal treatment of the ferrocene polymers III suggests that the number of end groups capable of further reaction is severely curtailed in these polymers as compared to the polymeric counterparts of the benzene–aromatic type. This implication bears out the earlier assumption that intramolecular cyclization reactions proceed concurrently with the linear polycondensation reaction of eq 1, producing heterobridged ferrocenylene end units incapable of further post-condensation under the conditions of these experiments.

Thermogravimetric Analyses. In order to obtain a measure of the thermal stability of the polypyrazoles VIII relative to other ferrocene-containing heteroaromatic polymer systems, the products were subjected to thermogravimetric analysis (TGA) in argon atmosphere. The TGA curves obtained demonstrate a remarkably similar behavior for all polypyrazoles investigated. Incipient weight losses generally became observable in the vicinity of 400°; residual weights at 600 and 800° were 75–80 and 65–75%, respectively. Up to temperatures of about 600°, variation of the substituent R from H to CH_3 to C_6H_5 apparently had

TABLE IV

POLYPYRAZOLES IX

Polypyrazole	R in IX	Ar in IX	Cyclodehydration conditions[a]		η_{inh}, dl g^{-1}		η_{inh} of precursor polyhydrazone, dl g^{-1}		Calcd, %			Found,[e] %		
			Time, hr	Temp, °C	HCOOH	H_2SO_4	HCOOH	H_2SO_4	C	H	N	C	H	N
IXa	H	p-C_6F_4-p-C_6F_4	4/7/4[c]	190/200/240[c]	. . .	0.42[b]	0.20	0.18	. . .	. . .	11.11	. . .	. . .	10.35
b	H	p-$C_6H_4SO_2$-p-C_6H_4	12/15/8	170/200/240	1.09[b]	0.47	0.30	0.23	67.91	3.80	13.20	66.82	3.69	12.90
c	CH_3	p-C_6H_4	10/15/4	170/200/230	0.68[b]	0.21	0.22	. . .	. . .	. . .	17.94	. . .	. . .	17.58
d	CH_3	p-C_6F_4-p-C_6F_4	10/24/10	180/200/240	. . .	0.29	. . .	0.14	58.65	2.27	10.52	57.97	2.18	9.59
e	CH_3	p-$C_6H_4SO_2$-p-C_6H_4	10/24/10[d]	180/200/240[d]	0.47	0.33	0.19	0.15	69.01	4.45	12.38	68.84	4.30	12.09

[a] From pastes, using DMF solvent (formic acid for IXa,b). [b] Weight corrected for insolubles. [c] Cyclodehydration not quite complete. Additional heat treatment (3 hr at 240° or 1 hr at 260°) caused further cyclization (ir; found N, 10.76), but rendered product largely insoluble. [d] Additional heating (6 hr at 280°) produced no compositional changes; η_{inh}, 0.62 dl g^{-1} (HCOOH, partially soluble). [e] Carbon and nitrogen analyses frequently erratic; in questionable cases, values listed are average of three runs.

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(28) F. De Schryver and C. S. Marvel, *J. Polym. Sci., Part A-1*, 5, 545 (1967).

(29) P. M. Hergenrother, W. Wrasidlo, and H. H. Levine, *ibid., Part A*, 3, 1665 (1965).

(30) R. D. Stacy, N. P. Loire, and H. H. Levine, *Amer. Chem. Soc. Div. Polym. Chem., Preprints*, 7, 161 (1966).

(31) W. W. Moyer, Jr., C. Cole, and T. Anyos, *J. Polym. Sci., Part A*, 3, 2107 (1965).

(32) A meaningful comparison, obviously, is limited to sets of viscosity values obtained in the same solvent. The differences apparent between data collected in DMF on the one hand and in the two acidic solvents on the other are probably associated with polyelectrolyte formation in the latter case, the strongly protonating sulfuric acid generally giving lowest values. This trend, frequently observed with heteroaromatic systems, is exemplified dramatically in the recently reported[33] polythiazole case, in which inherent viscosities were found to be about four times as high in formic acid as in sulfuric acid.

(33) W. C. Sheenan and T. B. Cole, *J. Polym. Sci., Part A*, 3, 1443 (1965).

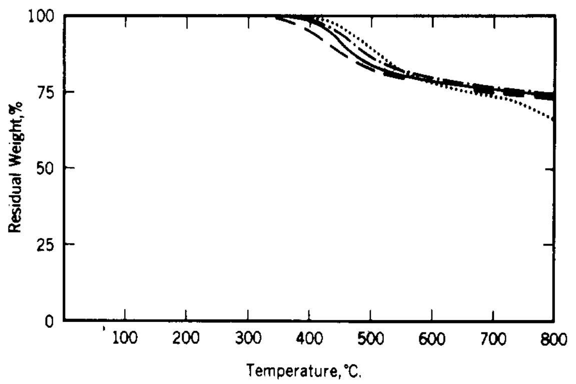


Figure 1. TGA curves of ferrocene–aromatic polypyrazoles (in Ar; heating rate 15° min^{-1}): — · —, VIIIa; ——, VIIIe; · · · · ·, VIIIf; – – –, VIIIg.

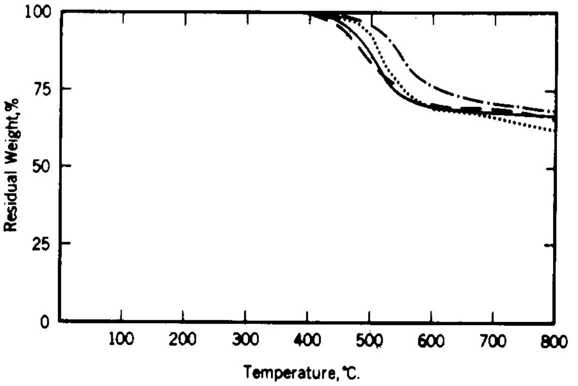
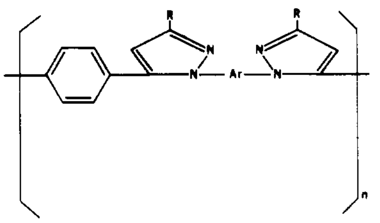


Figure 2. TGA curves of benzene–aromatic polypyrazoles (in Ar; heating rate 15° min^{-1}): — · —, IXa; ——, IXc; · · · · ·, IXd; — — —, IXe.

little effect upon the trend of the thermograms. For example, the curves of polymers VIIIb, e, and h closely approached one another within the 400–600° range, except that, as expected, the unsubstituted VIIIb underwent slightly less weight loss in the 450–550° region than shown by the methyl- and phenyl-substituted compounds, and the same trend held for the analogous groups VIIIc, f, i and VIIId, g, j.[34] At temperatures of about 600° and higher, the phenyl-substituted polymers lost weight somewhat more rapidly than the methyl-substituted and unsubstituted analogs (probably through elimination of benzene moieties), giving comparatively lower (by 5–10%) TGA curves in this region. In comparing polymers with identical substituent R but varying segment Ar, it was observed that the fully aromatic segments, and among these notably the octafluorobiphenylene unit, initially produced enhanced stability relative to the pseudo-aromatic biphenylene sulfone segment. This superior stability, however, was rather marginal and, in general, pertained only to 500–550°. At temperatures exceeding this range, the edge in performance of the fully aromatic polymers vanished for practical purposes; at 700–800°, the perfluorobiphenylene-bridged products even experienced accelerated weight loss and had to be rated somewhat inferior to all fluorine-free polymers in this high-temperature region. Representative TGA curves illustrating the discussed correlations are shown in Figure 1. It is readily evident from these findings that, notwithstanding the minor differences caused by structural variations, the thermostability behavior of the pyrazoles VIII as a group distinctly excels that[2,3] of the polybenzimidazoles I and the polybenzborimidazolines II. This may reflect enhanced control of the initial low-temperature polycondensation reaction of eq 1 relative to the high-temperature reactions leading to I and II.

It is instructive to compare the thermal stability of polymers VIII with that of the corresponding nonferrocene polypyrazoles IX. For the exemplifying polymers IXc, d, and e (Table IV), counterparts to the ferrocene-containing compounds VIIIe, f, and g of Figure 1, the thermograms (in argon) are given in Figure 2; in addition, this figure contains the curve for the unsubstituted polymer IXa. It can be seen that, in the critical range of incipient weight loss up to about 500°, the benzene–aromatic derivatives IX were mostly, but not always, superior, their principal derivative thermogravimetric analysis (DTG) peak[35,36] generally being at a temperature some 50–75° higher than that of the ferrocene analogs. The illustrations further reveal, however, that polymers IX, once breaking down, generally underwent weight loss more rapidly and, in the 600–800° range, had residual weights that for the most part were lower than those of polymers VIII.[37–39]



X a, R = H; Ar = p-C_6F_4-p-C_6F_4
b, R = H; Ar = p-$C_6H_4SO_2$-p-C_6H_4
c, R = CH_3; Ar = p-C_6H_4
d, R = CH_3; Ar = p-C_6F_4-p-C_6F_4
e, R = CH_3; Ar = p-$C_6H_4SO_2$-p-C_6H_4

Experimental Section

Starting Materials. Bis-β-diketo Compounds. The 1,1′-bis(acylaceto)ferrocenes were synthesized from 1,1′-diacetylferrocene by Claisen condensations as described in the literature. Both 1,1′-bis(acetylaceto)ferrocene and 1,1′-bis(benzoylaceto)ferrocene were obtained by the method of Hauser and collaborators[11] (larger quantities purchased from Research Inorganic Chemical Co., Sun Valley, Calif.). The acetylaceto derivative lent itself to ready purification by

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[34] The rather insignificant difference in performance of the unsubstituted polymers on the one hand and of the methyl- and phenyl-substituted compounds on the other must surprise; insufficient purity of the bis(formylaceto)ferrocene starting material may have prevented a more idealized structure build-up and concomitant stability enhancement of the unsubstituted compounds.

[35] DTG represents a plot of the rate of weight change with time or temperature of a sample subjected to TGA. A detailed account of the correlation between TGA, DTG, and related techniques, including instrumentation features, has recently been given.[36]

[36] J. Chiu, *Anal. Chem.*, **39**, 861 (1967).

[37] A similar behavior was reported[38] for a benzene–aromatic, methyl-substituted poly-1,3-pyrazole, which began to break down at about 450° and reached 70% (64%) residual weight near 500° (800°). A related, unsubstituted poly-1,3-pyrazole was found[39] to show the corresponding break near 460°.

[38] J. P. Schaefer and J. L. Bertram, *J. Polym. Sci., Part B*, **3**, 95 (1965).

[39] J. K. Stille and M. A. Bedford, *ibid.*, **B4**, 329 (1966).

repeated recrystallization from chloroform–hexane, mp 142–144° (lit.[11] mp 142.5–144°). The benzoylaceto compound was purified *via* its copper chelate;[12] from the chelate, repeatedly recrystallized from benzene, the bisdiketone was liberated by 20% phosphoric acid as described and was recrystallized three times from acetone, mp 213–214° (lit.[12] mp 213.5–214°). In several instances it became necessary to repeat this purification cycle *via* the Cu chelate in order to attain the proper melting point range. 1,1′-Bis(formylaceto)ferrocene was prepared as the disodium salt following Schlögl's procedure,[10] except that twice the amount of formate was employed and heating extended over 12 hr to complete the reaction. Immediately prior to use, the unstable, free compound was separated by means of gaseous CO_2 from a vigorously stirred aqueous slurry of the sodium salt under an equal volume of ether. The ether layer, washed and dried in the usual manner, was quickly concentrated in a flash evaporator at 0° under light protection, until the ketoaldehyde began to crystallize. The first crop, contaminated with some polymeric material, was discarded, and the main portion crystallizing subsequently (at 0°) was recrystallized from ether in the same fashion. The dark red, fine-crystalline compound, collected in yields generally not exceeding 10–15% (based on diacetylferrocene), gradually decomposed when heated above 180–200° without showing a clear melting point. The compound so prepared was only moderately pure, the molecular weight still indicating the presence of minor higher polymeric contaminants. Further recrystallization from ether or other solvents, however, did not improve the purity. Also, purification *via* the Cu chelate proved to be impracticable because the extended acidification period required to liberate the ketoaldehyde from the complex caused additional polymerization and decomposition.

Anal. Calcd for $C_{16}H_{14}FeO_4$: C, 58.92; H, 4.33; Fe, 17.12; mol wt, 326. Found: C, 58.67; H, 4.46; Fe, 17.74; mol wt, 347, 358.

The corresponding bis(acylaceto)benzene analogs were obtained by similar techniques. The synthesis of 1,4-bis(acetylaceto)benzene (terephthalyldiacetone) from *p*-diacetylbenzene followed an established procedure,[40] mp 185–186° (lit.[40] mp 185–186°). The preparation of 1,4-bis(formylaceto)benzene was analogous to that of 1,1′-bis(formylaceto)ferrocene,[10] involving the condensation of *p*-diacetylbenzene with ethyl formate in the presence of sodium dispersion in benzene. Alternately, sodium hydride was used as the condensing agent. The disodium salt of the ketoaldehyde, arising in 85–90% yield, was acidified with acetic acid under a layer of ether, and the ether phase was worked up as described above for the ferrocene analog, to give in approximately 20% yield (based on diacetylbenzene) the free 1,4-bis(formylaceto)benzene. The compound, more stable than bis(formylaceto)ferrocene, formed light yellow crystals melting at 171–176° (sealed capillary) when placed in the apparatus preheated to about 160°.

Anal. Calcd for $C_{12}H_{10}O_4$: C, 66.05; H, 4.62. Found: C, 66.45; H, 4.98.

Dihydrazines. Both 1,3- and 1,4-dihydrazinobenzene were prepared as the dihydrochlorides from *m*- and *p*-phenylenediamine following the method of Schoutissen.[13] To obtain the compounds in the required purity, it was imperative to achieve complete dissolution at −5° of the sodium nitrite in the sulfuric acid without liberation of nitric oxides in preparing the nitrosylsulfuric acid and to maintain a temperature of maximum −5° (but not lower than −10°, to avoid retardation) throughout the bisdiazotation step. Failure to do so resulted in incomplete diazotation, coupled with the elimination of nitrogen, thus giving products that lacked the required per cent N. It was equally important to conduct the reduction step to completion by stirring the reaction mixture after stannous chloride addition for additional 8 hr at −5 to −10°. For purification, the crude dihydrochlorides of the bases were recrystallized repeatedly from ice-cold aqueous solution by precooled concentrated hydrochloric acid, collecting only the main center fractions. The salts, washed with cold methanol and ether, were dried at ambient temperature *in vacuo*. The purity of the off-white needles thus obtained in 10–20% yield was checked by elemental analysis. Typical samples analyzed as follows.

Anal. Calcd for $C_6H_{12}Cl_2N_4$: N, 26.56; Cl, 33.60. Found for 1,3 compound: N, 26.39; Cl, 33.72. For 1,4 compound: N, 26.35; Cl, 33.90.

4,4′-Dihydrazino-2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl was synthesized as described[14] and was obtained as the pure base by repeated recrystallization from benzene, mp 211–213° (lit.[14] mp 210.5–212.5°).

The preparation of 4,4′-dihydrazinodiphenyl sulfone followed two known procedures;[15,16] the one[16] starting from 4,4′-dichlorodiphenyl sulfone usually gave slightly purer products and was, therefore, preferred. The free base had mp 194–196° dec (lit.[15,16] mp 193°; 195° dec). Again, elemental analysis was used for purity check.

Anal. Calcd for $C_{12}H_{14}N_4O_2S$: N, 20.13. Found: N, 20.06.

Model Hydrazones VI and VII. The reddish brown di(phenylhydrazone) of 1,1′-diacetylferrocene, VI, was prepared in the usual manner from the diacetyl derivative and phenylhydrazine hydrochloride in 50% aqueous ethanol saturated with sodium acetate, mp 96–101° (from ethanol).

Anal. Calcd for $C_{26}H_{26}FeN_4$: C, 69.34; H, 5.82; N, 12.44. Found: C, 69.01; H, 5.98; N, 12.80.

For the preparation of the polyhydrazone VII, equimolar quantities of 1,1′-diacetylferrocene and 4,4′-dihydrazinodiphenyl sulfone were dissolved in DMF (total solute concentration 0.5 mol $l.^{-1}$). After the addition of glacial acetic acid (0.6 mol $l.^{-1}$), the solution was allowed to stand for 48 hr in a stoppered flask under light protection. The polymer was precipitated by excess 2-propanol, was washed with boiling methanol, water and, again, methanol, and was dried for 30 hr at 100° *in vacuo*, yield 65%. The orange-tan, infusible compound was soluble in DMF and hexamethylphosphoramide.

Anal. Calcd for $C_{26}H_{24}FeN_4O_2S$: C, 60.94; H, 4.72; Fe, 10.90; N, 10.93. Found: C, 60.55; H, 4.90; Fe, 10.40; N, 10.69; M_n 1300 (DMF).

Polycondensation Reactions. Condensation of 1,1′-Bis(acylaceto)ferrocenes with Dihydrazines. In a 250-ml round-bottom flask equipped with mechanical stirrer and gas inlet and outlet tubes, 0.01 mol of each of the reactants A and B (Table I) were dissolved in 100 ml of DMF (distilled over P_2O_5). In experiments producing polymers IIIa, b, e, and h, which involved use of the dihydrochlorides of the unstable dihydrazinobenzenes, 1.08 g (0.02 mol) of sodium methoxide was added to the solution of the reactants for neutralization. After the addition of 3.0 g (0.05 mol) of glacial acetic acid, the solutions, protected from light, were stirred under a nitrogen blanket for 3 days at ambient temperature, followed by 1 hr heating at 90°. The solutions, filtered when turbid, were poured into a vigorously stirred mixture of 100 ml of 2-propanol and 200 ml of water containing 1.0 g of ascorbic acid reducing agent. The precipitated polyhydrazones III, ranging in color from a pinkish tan to a light reddish brown, were filtered off, thoroughly washed with water, and briefly digested with three 50-ml portions of boiling methanol. All fluorine-containing products were additionally washed with 0.5 *M* hydrochloric acid, to remove traces of DMF frequently adsorbed, and were washed with water to neutrality. Subsequent drying for 3 days at 100° over P_2O_5 *in vacuo* rendered

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[40] J. P. Wilkins and E. L. Wittbecker, U. S. Patent 2,659,711 (1953).

the products sufficiently dry for analysis and viscometric and M_n determinations. Analytical data and yields for ten representative polymers III are collected in Table I.

Cyclodehydration of Polyhydrazones III. Polypyrazoles VIII. Cyclodehydration was generally accomplished by stirring 0.3–0.5-g quantities of polyhydrazones III with 0.3–0.7 ml of DMF or formic acid to form a sticky, resinous paste, which was placed in a test tube fitted with a tapered joint and vacuum outlet. After removal of most of the solvent at 50° *in vacuo*, the tubes were flushed with nitrogen and reevacuated to remove adsorbed oxygen and were then subjected in a metal bath to the heating cycles given in Table III, raising the temperature to the first heating stage (180°) gradually over a 4-hr period. Throughout the heat treatment, the materials were protected from direct light by covering tubes and bath with aluminum foil. Alternately, concentrated solutions of polymers III in DMF or formic acid were sprayed in repeated passes onto glass plates; the resulting films were predried at 50° under flowing nitrogen and, with their support plates, were subjected to the same heat treatment, using a leakproof vacuum oven. The polypyrazoles obtained by either method were blackish brown, infusible solids. The fluorine-containing types VIIIc, f, and i dissolved only partially in sulfuric acid and formic acid. All other types were completely soluble in sulfuric acid and also largely or completely so in formic acid. Analytical results and viscometric data are collected in Table III.

Polycondensation of Bis(acylaceto)benzenes with Dihydrazines and Cyclodehydration of Resultant Polyhydrazones. Polypyrazoles IX. Polycondensations and subsequent cyclodehydrations to the benzene–aromatic polypyrazoles IXa–e were performed under the experimental conditions described for the ferrocene analogs, employing both the bis-β-diketo compound and the dihydrazine in 0.1 mol $l.^{-1}$ concentration. Thus, 1-4-bis(formylaceto)benzene was condensed with 4,4′-dihydrazino-2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl and 4,4′-dihydrazinodiphenyl sulfone, respectively, to give the hydrazone-type precursor polymers to IXa and b, and the condensation of 1,4-bis(acetylaceto)benzene with 1,4-dihydrazinobenzene, 4,4′-dihydrazino-2,3,5,6,2′,3′,5′,6′-octafluorobiphenyl, and 4,4′-dihydrazinodiphenyl sulfone, respectively, furnished the precursors to IXc, d, and e. The polyhydrazone-type precursor compounds, yellow solids soluble in formic acid, hexamethylphosphoramide, and mostly also in DMF, were heat-treated as described above for the ferrocene analogs (no light protection required). Table IV summarizes exemplifying cyclodehydration conditions and also lists pertinent analytical and viscometric data.

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The Active Oxidation State of Vanadium in Soluble Monoolefin Polymerization Catalysts

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ABSTRACT: The active oxidation state of vanadium in olefin polymerization catalysts prepared from vanadium tetrachloride and dialkylaluminum chlorides was studied. The data suggest two active complexes containing V(III), one much more active but less stable than the other. The more active catalyst evidently came from an inactive V(III) precursor. The origin of the less active V(III) catalyst is unknown. A potentially active V(II) complex was examined under the same conditions as a similar V(III) complex. No conclusive evidence for catalytic activity in the V(II) complex was found. However, theoretical arguments still suggest a V(II) oxidation state can be active in olefin polymerization.

Many investigators have assigned a formal oxidation state to the active state of vanadium in Ziegler polymerization catalysts. For example, Carrick and his coworkers concluded that some divalent vanadium may be a prerequisite for catalytic activity.[1-3] De Liefde Meijer, *et al.*, looked at similar catalysts and concluded that either V(II) or V(III) could be active.[4,5] Other investigators studying different vanadium catalysts concluded that V(III) is the active state.[6-13] Recently even V(IV) and V(V) oxidation states have been suggested.[12]

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