3,4 addition (XIVb) as the bulkiness of the substituent increases. The addition of 1-substituted cyclopentadienes was seen to occur primarily, if not entirely, by 3,4 addition and the rate of this process should be relatively insensitive to the size of the substituent, which is two carbons removed from the polymer chain.

A more exact estimation of the relative amounts of isomers in the monomer mixtures than can be obtained by nmr techniques would require efficient chromatographic conditions under which ACPD and the related dienes studied are stable with respect to isomerization and thermal polymerization. Determination of the isomer ratio in the monomer and subsequent examination of polymer structural units with varying compositions of the monomer feed would then establish the relative importance of isomerization in the polymerization process.

Conclusions

In conclusion, it appears that the cationic polymerization of allyl-substituted cyclopentadienes occurs almost entirely through the double bond in the cyclopentadiene ring. The amount of 1,4 structure increases with increasing steric hindrance around the conjugated double bond system. Although the monomers are obtained as an approximately equimolar mixture of two isomers, some isomerization seems to take place under polymerization conditions. The detailed structure of both monomers and polymers may be established by nmr analysis.

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Poly(ferrocenylazomethines)[1a]

Eberhard W. Neuse,[1b] Harold Rosenberg,[1c] and Robert R. Carlen[1b]

Missile & Space Systems Division, McDonnell Douglas Corporation, Santa Monica, California, and Air Force Materials Laboratory, Wright Patterson Air Force Base, Ohio.

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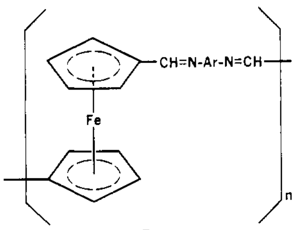
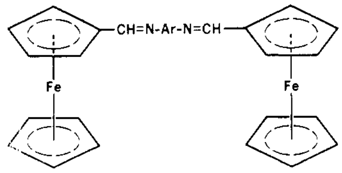
ABSTRACT: Polycondensation of *p*-phenylenediamine with 1,1′-diformylferrocene in N,N-dimethylformamide solution with or without an acidic catalyst leads to soluble polymeric azomethines of the type $[-1,1'\text{-}C_{10}H_8FeCH{=}N\text{-}1,4\text{-}C_6H_4N{=}CH\text{-}]_n$ (I). Inherent viscosities are in the range 10–13 ml g^{-1}. Polymers of the same composition and chain lengths are obtained from the two reactants in glacial acetic acid solution or from the two Schiff bases, $C_{10}H_9FeCH{=}N\text{-}1,4\text{-}C_6H_4N{=}CHC_{10}H_9Fe$ (II) and $C_6H_5N{=}CH\text{-}1,1'\text{-}C_{10}H_8FeCH{=}NC_6H_5$ (III), in a melt exchange reaction at temperatures ultimately reaching 325°. Solid-state postcondensation of these polyazomethines at 350° *in vacuo* produces polymers of unchanged elemental composition, but with inherent viscosities increased to 12–16 ml g^{-1}. Electronic spectral findings indicate that no substantial enhancement in π-electron delocalization is achieved in the polymeric Schiff base I. This confirms earlier reports on 1,1′-ferrocenylene-containing polymers with conjugated substituent links, in which the lack of appreciable conjugation across the central iron atoms was demonstrated spectroscopically. The polyazomethines I exhibit a thermostability behavior only marginally superior to that of ferrocenoyl or ferrocenoylbenzoyl polymers of previous studies; relative residual weights are 70 and 60% at 600 and 800°, respectively.

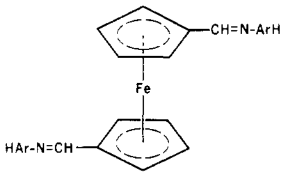
Polyazomethines of the type I (Ar = 1,4-phenylene in all formulas), in which the internuclear connecting segments provide uninterrupted conjugation, should lend themselves well to studies of the problem of electron delocalization across the central metal atom in polyconjugated systems with intrachain type 1,1′-ferrocenylene units. Sonogashira and Hagihara,[2] recognizing this possibility, prepared the polymeric Schiff



I



II



III

$-\!\left[\text{Ar-CH=N-Ar-N=CH}\right]_n\!-$

IV

HAr-CH=N-Ar-N=CH-ArH

V

HAr-N=CH-Ar-CH=N-ArH

VI

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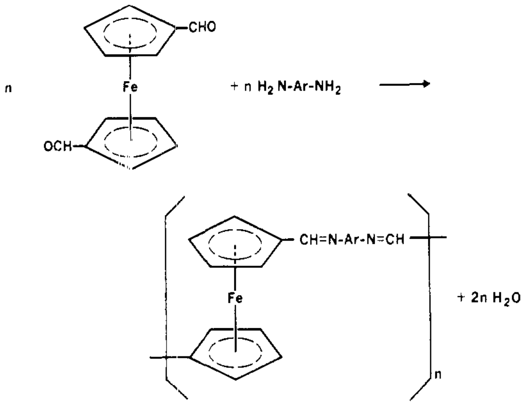
(1) (a) Metallocene Polymers. XXIV. Part XXIII: E. W. Neuse, *J. Org. Chem.*, **33**, 3312 (1968); (b) McDonnell Douglas Corp.; (c) Air Force Materials Laboratory.

(2) K. Sonogashira and N. Hagihara, *Kogyo Kagaku Zasshi*, **66**, 1090 (1963).

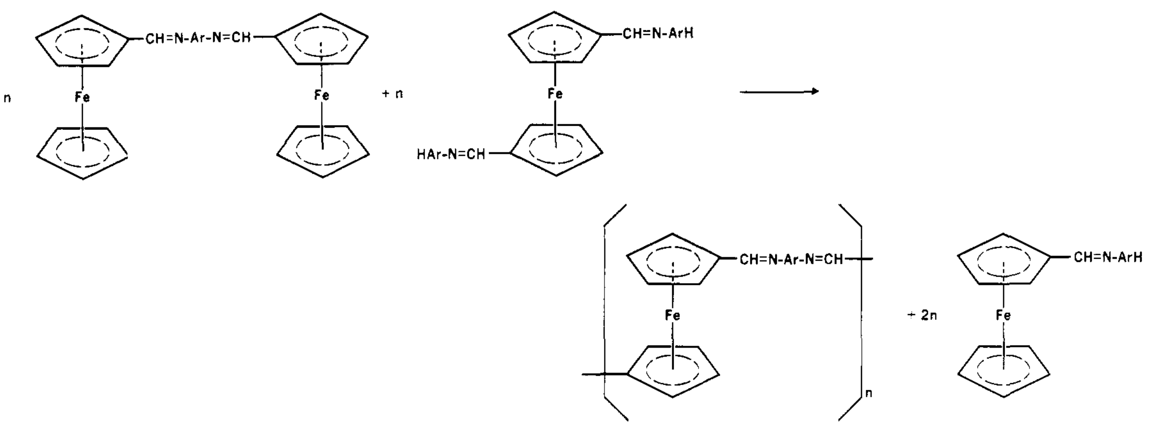
base I and its dinuclear counterpart II by reacting *p*-phenylenediamine in ethanolic solution with 1,1′-diformylferrocene and formylferrocene, respectively. However, the insolubility of the polymer I precluded its characterization by molecular weight or viscosity determinations and prevented the intended spectroscopic evaluation.

In the light of the recent successful syntheses of the analogous, more readily soluble benzene-aromatic polymeric Schiff bases IV and related polymers[3,4] from terephthaldehyde and *p*-phenylenediamine and other dialdehydes and diamines,[5] we have reinvestigated the interaction of *p*-phenylenediamine and 1,1′-diformylferrocene (eq 1) under conditions different from those of Sonogashira and Hagihara. When equimolar quantities of the two components were allowed to react at 25–60° in N,N-dimethylformamide solution, polymerization occurred readily. The deeply colored products were insoluble in the rection medium but soluble in formic acid and partly so in *m*-cresole. When purified by reprecipitation from formic acid solution, the polymers possessed elemental compositions satisfactorily in agreement with structure I and exhibited inherent viscosities, η_{inh}, in the range 10–13 ml g^{-1}, which is roughly in the same order as reported for representative nonferrocene aromatic polyazomethines.[3f,4,6] A comparison in η_{inh} with a related poly(ferrocenylazine) of known molecular weight[7] suggests number-average molecular weights of 2000–3000.



(1)

In attempts to enhance the degree of polymerization of I, longer reaction periods, higher temperatures, or varied reactant ratios were employed in several experiments. Other polycondensations were catalyzed with acetic acid, or the amide solvent was altogether replaced by this acid. Still other experiments employed equimolar quantities of the two nonpolymeric Schiff bases II and III, which were coreacted at temperatures gradually increasing to 325° to give I by the exchange reaction shown in eq 2. The last-named concept followed an approach employed by D'Alelio[4] in the preparation of poly(1,4-xylylidene-1,4-phenylenediamine), IV, from the two complementary Schiff bases V and VI. Apart from the observed acceleration in those reactions that were conducted in the presence of acetic acid,[8] none of these process variations resulted in improvements over the initial, uncatalyzed reaction in dimethylformamide. Since the insolubility of the polyazomethines in the reaction media was believed to be a contributing factor to the comparatively low viscosities



(2)

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[3] (a) C. S. Marvel, S. A. Aspey, and E. A. Dudley, *J. Amer. Chem. Soc.*, **78**, 4905 (1956); (b) C. S. Marvel and N. Tarköy, *ibid.*, **79**, 6000 (1957); **80**, 832 (1958); (c) C. S. Marvel and P. V. Bonsignore, *ibid.*, **81**, 2668 (1959); (d) A. V. Topchiev, V. V. Korshak, Yu. A. Popov, and L. D. Rosenstein, *J. Polym. Sci., Part C*, **4**, 1305 (1963); (e) B. E. Davydov, B. A. Krentsel, Yu. A. Popov, and L. V. Prokofeva, *Vysokomol. Soedin.*, **5**, 321 (1963); (f) E. Dyer and C. C. Anderson, *J. Polym. Sci., Part A-1*, **5**, 1659 (1967); (g) N. Yoda, M. Kurihara, Y. Bamba, and R. Nakanishi, *Kogyo Kagaku Zasshi*, **70**, 2057 (1967).

[4] G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1161 (1967). This paper presents an excellent and most comprehensive account of the synthesis and thermostability behavior of a series of benzene-aromatic polymeric Schiff bases.

[5] The synthesis of insoluble benzene-aromatic polyazomethines has also been reported: (a) J. W. Akitt, F. W. Kaye, B. B. Lee, and A. M. North, *Makromol. Chem.*, **56**, 195 (1962); (b) S. S. Stivala, G. R. Sacco, and L. Reich, *Polym. Lett.*, **2**, 943 (1964); (c) J. Danhäuser and G. Manecke, *Makromol. Chem.*, **84**, 238 (1965); (d) G. F. D'Alelio, R. K. Schoenig, and J. V. Crivello, *J. Macromol. Sci.*, **A1**, 1299 (1967); (e) G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *ibid.*, **A1**, 1321 (1967). See also ref 4.

[6] Ya. M. Paushkin and V. A. Aleksandrova, *Vysokomol. Soedin.*, **8**, 1669 (1966).

[7] K. Hata, I. Motoyama, and T. Masuko, Japan Patent 9679 (1967); *Chem. Abstr.*, **68**, 69582 (1968). These authors found M_n = 1600 for their product. We determined η_{inh} = 5.0 ml g^{-1} (30°, in $CHCl_3$) and M_n = 1360 on a typical polymer of this type.

[8] Acetic acid catalysis of the polycondensation of dialdehydes and diamines was previously observed.[3b,f]

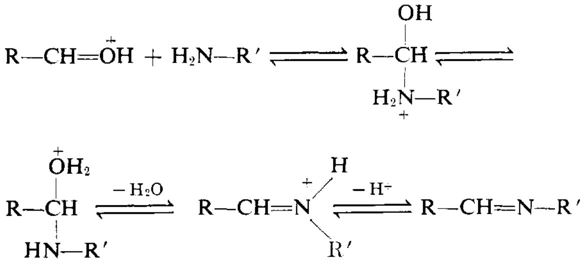
TABLE I

SYNTHESES AND PROPERTIES OF POLYAZOMETHINES I

Expt no.	Molar ratio A/B[a]	Solvent[b]	Catalyst (AA) concn, mol l.$^{-1}$	Reaction conditions, hr (°C)	Yield, %	Anal. Found,[c] % C	H	Fe	N	η_{inh},[d] ml g^{-1}	η_{inh}[d] after post-condn,[e] ml g^{-1}
1	1.0	DMF	...	24 (30) 24 (60)	75.0	67.88	4.41	17.51	8.62[f]	13	16 (15)
2	1.0	DMF	0.6	36 (30)[g]	76.1	67.96	4.51	17.39	9.08	12	14 (14)[h]
3	1.2[i]	DMF	0.5	36 (30)[g]	78.4	68.30	4.63	17.56	9.01	12[i]	16 (14)[j]
4	1.0	AA	...	40 (30)	62.0	67.95	4.66	16.17	8.44	10	...
5	1.0	FA	...	40 (30)	27.9	66.92	5.20	12.55	5.81[k]	14	...
6	1.0	...	...	2 (180) 2 (250) 8 (300) 5 (325)[l]	0.90	68.83	4.77	19.39	6.67	12	...

[a] A = 1,1′-diformylferrocene, B = *p*-phenylenediamine in no. 1–5; A = Schiff base II, B = Schiff base III in no. 6. Combined reactant concentration 0.20 mol l.$^{-1}$ in no. 1, 2; 0.22 mol l.$^{-1}$ in no. 3; 0.60 mol l.$^{-1}$ in no. 4, 5. [b] DMF = N,N-dimethylformamide, AA = glacial acetic acid, FA = 98% formic acid. [c] *Anal.* Calcd for $C_{18}H_{14}FeN_2$: C, 68.81; H, 4.49; Fe, 17.78; N, 8.92. [d] 0.2% (w/v) at 30° in 98% formic acid (96% sulfuric acid in parentheses); rounded off to integral values. [e] 12 hr at 250°, 10 hr at 300°, 5 hr at 350°, 0.7 torr. Selected samples here additionally postheated for 5 hr at 400°, 0.7 torr. [f] *Anal.* Found after postcondensation at max 350°: C, 67.69, H, 4.57; Fe, 17.73; N, 8.37. At max 400°: C, 68.50; H, 4.01; Fe, 18.00; N, 8.79. [g] Similar results if additionally heated for 24 hr at 90°. [h] 15 ml g^{-1} (weight corrected for insolubles) for sample postheated at max 400°. [i] Similar analytical results, but lower η_{inh} (10 ml g^{-1}) at molar ratio 1.3. [j] 16 ml g^{-1} (weight corrected for insolubles) for sample postheated at max 400°. [k] 9.8% O by neutron activation analysis. [l] Last 5 hr at 0.7–1.0 torr.

obtained, several experiments were performed in 98% formic acid, in which the products remained dissolved throughout the polycondensation. The polymers resulting in this case, however, possessed quite unsatisfactory compositions. Low iron contents, coupled with oxygen contents as high as 10%, pointed to considerable oxidation by the solvent; strong ir absorption at the typical carboxyl C=O stretching position (5.95–6.00 μm) and in the carboxyl O–H stretching region (2.9–3.0 μm, with a broad envelope extending from about 2.8 to 3.6 μm) suggested partial conversion of formylferrocenyl into carboxyferrocenyl end groups.[9a] In addition, polymer viscosities, despite the retained solubility of the products in the reaction medium, did not significantly exceed those in the preceding experiments. This may be the result of an unfavorably low concentration of free amine in the equilibrium of the first step in the reaction sequence presented below, which involves nucleophilic attack of the amino nitrogen on the protonated[9b] carbonyl carbon atom (R = 1′-formylferrocenyl or residual polymer chain; R′ = 4-aminophenyl or residual polymer chain).



$$R{-}CH{=}\overset{+}{O}H + H_2N{-}R' \rightleftharpoons R{-}\underset{\underset{+}{H_2N}-R'}{\overset{OH}{CH}} \rightleftharpoons$$

$$R{-}\underset{HN-R'}{\overset{\overset{+}{O}H_2}{CH}} \xrightleftharpoons{-H_2O} R{-}CH{=}\overset{+}{N}\begin{smallmatrix}H\\ \\R'\end{smallmatrix} \xrightleftharpoons{-H^+} R{-}CH{=}N{-}R'$$

Representative polycondensations, including analytical data for the obtained polyazomethines, are summarized in Table I. Some of the products were subjected to a solid state postcondensation at temperatures up to 350° under reduced pressure. This treatment, without substantially affecting the elemental composition or spectroscopic properties, resulted in somewhat decreased solubility. In addition, a minor viscsity increase was produced by further interaction of available formyl and amino end groups under these conditions; after reprecipitation of such postcondensed products from formic acid solution, η_{inh} values of the resultant polymers generally ranged from 12 to 16 ml g^{-1}. Further decreased solubility, coupled with considerable broadening and diffusiveness of the ir absorptions, was shown by polymer samples postheated at 400°; yet no further increase in viscosity of the soluble portions resulted from such treatment. Postheating cycles and analytical data for representative postheated polymers are listed in Table I. The somewhat low hydrogen contents of the products obtained at 400° suggest that the observed decrease in solubility results not so much from linear chain extension but rather from secondary reactions of the azomethine links, such as intramolecular cyclization to phenanthroline moieties, possibly also from cross-linking *via* nuclear hydrogen extraction and recombination of the ensuing free radical sites. Our failure to achieve a substantial increase in viscosity upon postheating to 300–400° is not unexpected in view of the low aldehydic end group concentrations indicated in the untreated I by the extremely low intensity of the formyl carbonyl stretching ir absorption in the vicinity of 6 μm. Partial decarbonylation under the conditions of our experiments may be responsible for the low formyl end group concentrations observed.

Karplus and collaborators, studying the effect of the extent of conjugation upon the ir double bond stretching

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(9) (a) It is not unreasonable to expect such oxidation in view of the previously observed oxidative effects of formic acid solvent on ferrocene-containing polyurethanes: P. Petrovich and H. Valot, *C. R. Acad. Sci., Paris, Ser. C*, **263,** 214 (1966). (b) Formylferrocene protonation occurs readily and is facilitated by stabilization of the resulting conjugate acid through iron d orbital participation: H. E. Rubalcava and J. B. Thomson, *Spectrochim. Acta,* **18,** 449 (1962).

absorption frequency in polyconjugated azines, observed a shift to higher wavelengths with increasing number of double bonds in the polyconjugated system.[10] In an exemplifying series, band positions were found to change from 1635 to 1628 to 1608 cm^{-1} in going from furfuralazine to 3-α-furylacroleinazine to 5-α-furyl-2,4,6-heptatrienalazine. This trend, explicable in terms of decreasing bond order of the C=C and C=N bonds with enhanced electron delocalization over the polyconjugated domain, may thus serve to assess the relative extension of conjugated segments in such systems. The dinuclear II and the polynuclear I both exhibit C=N stretching absorption at the identical position of 6.18 μm. On the basis of Karplus' findings, this observation would seem to suggest the degree of conjugation to be essentially the same in both I and II, which leads to the conclusion that the 1,1′-ferrocenylene group in the polymer chain of I acts as a barrier segment, effectively restricting π-electron delocalization to the extent of the $C_5H_4CH{=}NC_6H_4N{=}CHC_5H_4$ chromophore. The propensity of the ferrocene moiety in heteroannularly disubstituted derivatives to resist, albeit not preclude entirely, the transmission of resonance effects[11] from one cyclopentadienyl ring to the other across the central iron atom has been well documented in the literature for mononuclear derivatives,[12] and several analogous cases in the polymer field have also been reported.[2,13]

For further elucidation of this problem a comparison of the electronic spectra of I and II is in order. The spectra of both compounds are dominated in the near-ultraviolet by a strong, structureless band in the vicinity of 360 nm; in the visible region, a weak band appears near 515 nm. On the basis of its high intensity and half-band width (f[14,15] = 0.61), the 360-nm absorption can be assigned to an allowed $V \leftarrow N$ ($\pi \rightarrow \pi^*$) transition of the polyconjugated system, superimposing upon the symmetry-forbidden, low-intensity ligand-field band[16,17a–c,f,g,18] of the ferrocene molecule in this region. Similarly powerful bathochromic effects were reported[15] for the principal ($\pi \rightarrow \pi^*$) band of a series of nonpolymeric ferrocenylpolyenes and other derivatives with polyconjugated chromophores. The band is shown in high intensities in the same region by the analogous nonferrocene azomethines IV, V, and VI (see following discussion). The weak 515-nm band, near 440 nm in unsubstituted ferrocene, is generally recognized as a ligand-field band arising from a symmetry-forbidden transition of fairly pure d–d character.[17d–i,19] If one assumed unrestricted interannular delocalization of electronic charge in the metallocene system, one would expect the high conjugation sensitivity[12a,d,15b,c,20] of both bands to produce markedly enhanced batho- and hyperchromic shifts in the polymeric compound I (with the entire backbone structure now representing a single unperturbed chromophore) relative to the nonpolymeric azomethine II with its comparatively limited conjugated system.[21] The data in Table II, which lists the two bands for II and a representative sample of I, clearly demonstrate the absence of any such batho- and hyperchromic effects in I relative to II and thus support the conclusion drawn from ir data that resonance effects in the polymer I are

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(10) E. R. Blout, M. Fields, and R. Karplus, *J. Amer. Chem. Soc.*, **70**, 194 (1948). For a similar observation in polyconjugated polyazines, see T. A. Sidorov, L. I. Komarova, Yu. V. Korshak, and B. E. Davydov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 548 (1967).

(11) Appreciable interannular transmission of *inductive* substituent effects, on the other hand, has been observed: N. A. Nesmeyanov and O. A. Reutov, *Dokl. Akad. Nauk SSSR*, **115**, 518 (1957); **120**, 1267 (1958); L. A. Kazitsyna, B. V. Lokshin, and N. A. Nesmeyanov, *ibid.*, **127**, 333 (1959); S. P. Gubin, K. I. Grandburg, E. G. Perevalova, and A. N. Nesmeyanov, *ibid.*, **159**, 1075 (1964); S. A. Butter and H. C. Beachell, *Inorg. Chem.*, **5**, 1820 (1966); K. I. Grandburg and S. P. Gubin, *Izv. Akad. Nauk SSSR., Ser. Khim.*, 551 (1966); S. P. Gubin, *ibid.*, 1551 (1964); R. A. Stukan, S. P. Gubin, A. N. Nesmeyamov, V. I. Goldanskii, and Ye. F. Makarov, *Theort. Eksperiment. Khim.*, **2**, 805 (1966). The commonly recognized interannular deactivating effect of electron-withdrawing substituents in electrophilic substitution reactions of ferrocene falls into this category.

(12) (a) R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962); (b) M. Rosenblum, J. O. Santer, and W. G. Howells, *J. Amer. Chem. Soc.*, **85**, 1450 (1963); (c) E. G. Perevalova, S. P. Gubin, S. A. Smirnova, and A. N. Nesmeyanov, *Dokl. Akad. Nauk SSSR*, **155**, 857 (1964); (d) A. Nakamura, P.-J. Kim, and N. Hagihara, *J. Organometal. Chem.*, **3**, 355 (1965); (e) A. N. Nesmeyanov and E. G. Perevalova, *Ann. N. Y. Acad. Sci.*, **125**, 67 (1965); (f) C. U. Pittman, Jr., *Tetrahedron Lett.*, 3619 (1967).

(13) (a) H. Watanabe, I. Motoyama, and K. Hata, *Bull. Chem. Soc. Jap.*, **39**, 790 (1966); (b) E. W. Neuse and R. K. Crossland, *J. Organometal. Chem.*, **7**, 344 (1967); (c) E. W. Neuse and H. Rosenberg, *J. Polym. Sci., Part A-1*, **6**, 1567 (1968).

(14) Oscillator strength, f, determined by the approximation $f = 4.32 \times 10^{-9} \times \epsilon_{max}\Delta\bar{\nu}$ ($\Delta\bar{\nu}$ = half-band width). See, for example, H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 589. For comparison, 1,4-diferrocenylbutadiene gave[15b] f = 0.60.

(15) (a) G. Drefahl, G. Plötner, and I. Winnefeld, *Chem. Ber.*, **95**, 2788 (1962); (b) K. Schlögl and H. Egger, *Ann.*, **676**, 88 (1964); (c) K. Schlögl and W. Steyrer, *J. Organometal. Chem.*, **6**, 399 (1966).

(16) While the predominant 3d character of this band (near 324 nm in ferrocene) has generally been accepted,[17] appreciable mixing with cyclopentadienyl ring MO's is indicated by its sensitivity to substitution and by the lack of significant temperature effects on band position.[17f,g] Most representations,[17a–c,18] indeed, assign transition levels involving partially ring-localized orbitals.

(17) (a) W. E. Moffitt, *J. Amer. Chem. Soc.*, **76**, 3386 (1954); (b) J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955); (c) A. D. Liehr and C. J. Ballhausen, *Acta Chem. Scand.*, **11**, 207 (1957); (d) F. A. Matsen, *J. Amer. Chem. Soc.*, **81**, 2023 (1959); (e) R. E. Robertson and H. M. McConnell, *J. Phys. Chem.*, **64**, 70 (1960); (f) D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516, 2246 (1961); *J. Organometal. Chem.*, **4**, 409 (1965); (g) A. T. Armstrong, F. Smith, E. Elder, and S. P. McGlynn, *J. Chem. Phys.*, **46**, 4321 (1967); (h) R. Prins, Ph.D. Thesis, University of Amsterdam, 1967; (i) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, **1**, 462 (1967).

(18) M. Yamazaki, *J. Chem. Phys.*, **24**, 1260 (1956); (b) E. Ruch, *Rec. Trav. Chim. Pays-Bas*, **75**, 638 (1956); (c) H. Hennig and O Gürtler, *J. Organometal. Chem.*, **11**, 307 (1968).

(19) That this transition is not entirely localized on the iron atom was emphasized by Armstrong, *et al.*,[17g] and is supported by the observation of other workers[12b,15b,18c] that the substitution sensitivity of the band position is appreciably greater than previously assumed.[17f] Most theoretical treatments, in fact, agree on the involvement in this transition of metal 3d orbitals of e_{2g} symmetry,[17,18c] which, in current thinking (*cf.* M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Part I, John Wiley and Sons, Inc., New York, N. Y., 1965, p 20) are weakly bonding and hence show ever so small overlap with ring MO's.

(20) (a) K. Schlögl, *Monatsh. Chem.*, **88**, 601 (1957); (b) A. N. Nesmeyanov, E. G. Perevalova, and T. V. Nikitina, *Tetrahedron Lett.*, 1 (1960); (c) R. Riemschneider and D. Helm, *Ann.*, **646**, 10 (1962).

(21) Such comparison obviously requires substantial coplanarity of the $C_5H_4CH{=}NC_6H_4N{=}CHC_5H_4$ segments in both compounds. Stuart–Briegleb models suggest that this is readily achievable in all-*anti* structures. In the *syn* forms, resonance is sterically inhibited.

TABLE II

ELECTRONIC SPECTRA OF SOME AZOMETHINES IN THE NEAR-ULTRAVIOLET AND VISIBLE REGIONS[a]

Compound	λ_{max},[b] nm	
	Principal (π–π^*) band	Ligand-field ferrocene band
$\{C_{10}H_8FeCH{=}NC_6H_4N{=}CH\}_n$ (I)[c]	358 (17,000)	517 (1,800)
$C_{10}H_9FeCH{=}NC_6H_4N{=}CHC_{10}H_9Fe$ (II)	360 (15,200)	515 (4,800)
$\{C_6H_4CH{=}NC_6H_4N{=}CH\}_n$ (IV)[d]	386 (13,200)	. . .
$C_6H_5CH{=}NC_6H_4N{=}CHC_6H_5$ (V)[e]	347 (14,500)	. . .

[a] Average of three runs, in *m*-cresole. All solutions allowed to stand for 15 hr in the dark prior to recording. [b] Molar extinction coefficient, ϵ, in parentheses; calculated for I, IV on the basis of recurring unit. [c] Polymer no. 1, Table I; weight corrected for insolubles. Similar results with no. 2–4, 6. [d] Fraction with η_{inh} = 12 ml g^{-1}. Weight corrected for insolubles. [e] Similar results with $C_6H_5N{=}CHC_6H_4CH{=}NC_6H_5$ (VI).

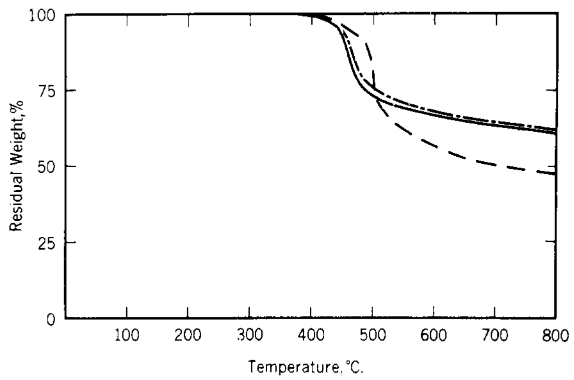

Figure 1. TGA thermograms of polyazomethines I, IV (in argon, at 15° min^{-1} heating rate): ——, I; —·—, I, postheated at 350°; — — —, IV, postheated at 350°.

not significantly transmitted across the iron centers of the metallocene.[22]

It is of interest to compare these results with the spectral behavior of the benzene-aromatic azomethines IV and V. It is seen from Table II that the $\pi \rightarrow \pi^*$ band of the polymer IV, which possesses no electronically isolating metal centers in the chain, indeed experiences a considerable bathochromic shift relative to the $\pi \rightarrow \pi^*$ absorption of the less extended conjugated system in the nonpolymeric Schiff base V (and, likewise, VI).

The spectra discussed in the foregoing were recorded in *m*-cresol solutions. We preferred this solvent, despite its limited dissolving power, over such excellent solvents as formic acid or sulfuric acid. Light-exposed formic and sulfuric acid solutions were found to exhibit appreciable photochromism; the maxima in the near-ultraviolet and visible regions experienced powerful drifting in position and intensity, and even in the dark spectral alterations were rapid enough to render exceedingly difficult a spectral comparison of the azomethines under investigation. The reactions underlying these spectral changes in formic or sulfuric acid solutions are believed to involve protonation (dark reaction) and prototropism (light-induced proton exchange, possibly between Fe- and N-protonated sites of the conjugate acids) with concomitant extensive electronic charge redistribution. *syn–anti* isomerism involving rotation around the C=N double bond undoubtedly represents a factor, albeit minor,[23,24] contributing to the complexity of these reactions. Analogy can be found with other Schiff bases possessing acidic hydrogen atoms in positions favorable for prototropism, in which cases photochromism involving intramolecular proton transfer and rotational isomerism was similarly observed.[24d,e,25] *m*-Cresole, in contrast, although sufficiently acidic for hydrogen bonding with the imino group,[26] lacks the proper acidity necessary to generate the conjugate acid sites[27] required for proton exchange. As a consequence, pronounced photochromism does not exist in this solvent. While minor light induced hyper- and bathochromic shifts, appearently associated with *syn–anti* isomerism, were indeed observed after several hours exposure of the solutions to diffuse daylight, these effects could be obviated by recording the spectra on fresh solutions or, preferably, on solutions that had been allowed to stand for 10–15 hr in the dark so as to ensure attainment of thermal equilibrium between the rotational isomers.

Favorable literature reports on the thermostability of benzene-aromatic polyazomethines[3d,f,4,5b,d,e,28] prompted us to examine the thermal stability behavior of the ferrocene derivative I. Figure 1 shows the

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(22) This electronic behavior of ferrocene finds a parallel in the incapacity of the Mn atom in cymantrene to transmit resonance effects from ring substituents to the carbonyl ligands: A. N. Nesmeyanov, K. N. Anisimov, B. V. Lokshin, N. E. Kolobova, and Yu. V. Makarov, *Dokl. Akad. Nauk SSSR*, **176,** 1082 (1967).

(23) At ambient temperature and above, most azomethines in solution appear to exist in a rapid thermal equilibrium between the rotational (*syn–anti*) isomers,[24a–c] which is unaffected by irradiation with light of variable wavelength or, if affected (*e.g.*, by flash photolysis), is regenerated in a fast thermal dark reaction.[24d] (At low temperatures, photocatalyzed conversion of the predominant, stable form, generally *anti*, to the higher energetic form, generally *syn*, has been reported for a number of aldimines.[24b,c]) For a representative case involving *syn–anti* photoisomerization at room temperature, see ref 24f.

(24) (a) G. M. Wyman, *Chem. Rev.*, **55,** 625 (1955); (b) E. Fischer and Y. Frei, *J. Chem. Phys.*, **27,** 808 (1957); (c) H. A. Staab, F. Vögtle, and A. Mannschreck, *Tetrahedron Lett.*, 697 (1965); (d) G. Wettermark and L. Dogliotti, *J. Chem. Phys.*, **40,** 1486 (1964); (e) R. S. Becker and W. F. Richey, *J. Amer. Chem. Soc.*, **89,** 1298 (1967); (f) R. Kuhn and H. M. Weitz, *Chem. Ber.*, **86,** 1199 (1953).

(25) (a) G. H. Brown and W. G. Shaw, *Rev. Pure Appl. Chem.*, **11,** 2 (1961); (b) G. O. Dudek and E. P. Dudek, *J. Amer. Chem. Soc.*, **86,** 4283 (1964); **88,** 2407 (1966).

(26) H. H. Freedman, *ibid.*, **83,** 2900 (1961).

(27) I. Pavlik and J. Klikorka, *Proc. Int. Conf. Coord. Chem., 9th, St. Moritz-Bad, Switz., 1966*, p 21; quoted by A. N. Nesmeyanov, E. G. Perevalova, S. P. Gubin, and A. G. Kozlovskii, *J. Organometal. Chem.* **11,** 577 (1968).

(28) (a) Yu. A. Popov, B. E. Davydov, M. V. Shishkina, and B. A. Krentsel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 2014 (1963); (b) G. F. D'Alelio, J. V. Crivello, T. R. Dehner, and R. K. Schoenig, *J. Macromol. Sci.*, **A1,** 1331 (1967).

thermograms (in argon) of a representative sample (Table I, no. 1) prior to and after postheating to 350°. Both curves, following almost identical trends, indicate rapid weight loss in the 450–500° temperature range (minimum first derivative peak at ~465°) and relative residual weights near 70 and 60% at 600 and 800°, respectively. These percentages demonstrate that the polyazomethine I, while somewhat more stable thermally than such other polymeric ferrocene compounds as poly(ferrocenoylbenzoyl)[29a] or poly(ferrocenyl ketone),[29b] does not match the stability performance of all-aromatic ferrocene polymers as represented by poly(ferrocenylpyrazole)[29c] and polyferrocenylene.[13b]

A comparison with the dashed line in Figure 1, which represents the analogous, soluble benzene-aromatic polyazomethine IV (also postheated to 350°), demonstrates higher initial stability for the latter. At a temperature slightly above 500°, however, a crossover occurs, and a distinctly inferior performance of IV is indicated in the 550–800° temperature range. These findings[30] on polyazomethine IV are on a par with the thermostability behavior of a related benzene-aromatic polyazomethine reported previously.[3f] Some electrophysical properties of I will be treated in a forthcoming communication.

Experimental Section[31]

Starting Materials and Nonpolymeric Model Compounds. All starting materials for polycondensation reactions must be of high purity to ensure optimal polymer viscosities. *p*-Phenylenediamine, formylferrocene (ferrocenecarboxaldehyde), 1,1′-diformylferrocene, and terephthaldehyde were obtained from commercial sources. *p*-Phenylenediamine was purified by recrystallization from water, followed by vacuum sublimation, mp 140–141° (typical lit.[3f] mp 139–140°). Terephthaldehyde was shaken with 0.5 *M* aqueous KOH to remove oxidized contaminants, washed to neutrality, and recrystallized from water, mp 115–116° (lit.[3f] mp 115–116°). The mono- and dialdehydes of ferrocene were chromatographed on alumina with benzene–chloroform, followed by recrystallization from heptane–dichloromethane (all operations were performed under light protection), mp 124–125° (lit. mp 130–132°,[32a] 124.5°,[32b] 124–125°[32c]) and 179–181° (lit.[33] mp 183–184°), respectively.

The two benzene-aromatic Schiff bases, N,N′-bisbenzylidene-*p*-phenylenediamine (V) and *p*-xylylidenedianiline (VI), were prepared by standard procedures; repeated recrystallization from ethanol furnished products with mp 139–140° (lit.[34] mp 140°) and 165–166° (lit. 164°,[35] 166°[34b,c]), respectively.

N,N′-Bis(ferrocenylmethylidene)-*p*-phenylenediamine (II) was obtained by dissolving 0.010 mol of *p*-phenylenediamine and 0.022 mol of formylferrocene in 30 ml of absolute methanol and refluxing the solution for 1 hr under light protection. The product, crystallizing from the cooled solution in 85% yield, was recrystallized from ethanol–benzene in the dark, mp 252–254° dec (lit.[2] mp >250° dec).

Anal. Calcd for $C_{28}H_{24}Fe_2N_2$: C, 67.23; H, 4.84; Fe, 22.33; N, 5.60. Found: C, 66.97; H, 5.05; Fe, 22.80; N, 5.88.

In an analogous manner, 1,1′-diformylferrocene (0.010 mol) and aniline (0.025 mol, freshly distilled), heated for 4 hr at 100° in 25 ml of glacial acetic acid and precipitated by 75 ml of water, gave ferrocene-1,1′-bis(methylideneaniline) (III) in 65% yield. Purification by chromatography on alumina in chloroform–hexane and recrystallization from ethanol–benzene (all operations were conducted in the dark) furnished the base as blackish red crystals infusible up to 300°.

Anal. Calcd for $C_{24}H_{20}FeN_2$: C, 73.48; H, 5.14; Fe, 14.24; N, 7.14. Found: C, 72.57; H, 4.90; Fe, 14.61; N, 6.57.

Polyazomethine I. From 1,1′-Diformylferrocene and *p*-Phenylenediamine in Dimethylformamide. All reactions conducted in N,N-dimethylformamide (solvent dried over Linde Molecular Sieves, Type 3A) are summarized as No. 1–3 in Table I. Experiment no. 1 is described below.

The solutions of 2.42 g (0.01 mol) of 1,1′-diformylferrocene in 50 ml of dimethylformamide and of 1.08 g (0.01 mol) of *p*-phenylenediamine in 50 ml of the same solvent were combined in a 250-ml round-bottom flask equipped with mechanical stirrer and gas inlet and outlet tubes. The clear, dark red solution, protected from light, was stirred under a nitrogen blanket for 24 hr at 30° and another 24 hr at 60°. The product partially precipitated during the 60° heating period. The suspension was stirred into 150 ml of water. The precipitated polyazomethine was washed with water and methanol and was dried for 24 hr at 100° *in vacuo*, crude yield, 2.90 g (92.4%). For purification, the crude product was dissolved in 40 ml of 98% formic acid. To the filtered solution was added 0.06 g of ascorbic acid dissolved in 8 ml of warm methanol. The mixture was allowed to stand for 5 min to effectuate reduction of any ferricenium sites in the polymer and was then stirred dropwise into 200 ml of 50% aqueous methanol saturated with sodium acetate. The precipitated polymer, separated by filtration, was washed successively with water, 50% aqueous methanol, and meth-

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(29) (a) E. W. Neuse and K. Koda, *J. Macromol. Chem.*, **1**, 595 (1966); (b) E. W. Neuse and R. M. Trahe, *ibid.*, **1**, 611 (1966); (c) E. W. Neuse, *Macromolecules*, **1**, 171 (1968).

(30) It is of interest to compare these results with the outstanding thermostability performance of products IV obtained by D'Alelio[4] at appreciably higher condensation temperatures. For example, polymers synthesized in an exchange reaction at ultimately 400, 600, and 1000° or higher were stable up to approximately 500, 700, and 1100°, respectively.[4,5d,28b] These products all were insoluble, however, and some drastic deviations from the original polyazomethine structures should be expected notably at postcondensation temperatures of 600° and above. Because of the decreased extent of solubility of the ferrocene polymer I when heated at temperatures exceeding 350°, the maximum postheating temperature in the present investigation was restricted to 400°. For comparison with D'Alelio's results, a sample of I postheated at 400° (Table I, footnote *e*) gave a thermogram (in argon) that was positioned about 10% above the solid curve of Figure 1 throughout the 500–800° region; yet the minimum first derivative peak of this thermogram appeared at a temperature only about 25° higher than was found for the sample treated at 350° or below.

(31) Ir spectra, on KBr disks, were measured with a Perkin-Elmer spectrophotometer, Model 521, electronic spectra with Cary spectrophotometer, Model 14. Inherent viscosities, η_{inh}, in 98% formic acid and 96% sulfuric acid (0.2% w/v, at 30°), were measured using Cannon-Fenske viscometers, Series 50 (HCOOH) and 100 (H_2SO_4); no kinetic energy corrections were applied. Thermogravimetric analyses were conducted in argon (gas flow 0.7 l. min^{-1}) at a heating rate of 15° min^{-1} on a Du Pont thermogravimetric analyzer, Model 950; samples were reduced to −100, +200 mesh size. Fe and O determinations were performed by neutron activation analysis; other microanalyses were performed by G. I. Robertson, Jr., Florham Park, N. J.

(32) (a) J. K. Lindsay and C. R. Hauser, *J. Org. Chem.*, **22**, 335 (1957); (b) P. J. Graham, R. V. Lindsey, G. W. Parshall, M. L. Peterson, and G. M. Whitman, *J. Amer. Chem. Soc.*, **79**, 3416 (1957); (c) J. Boichard, J.-P. Monin, and J. Tirouflet, *Bull. Soc. Chim. Fr.*, 851 (1963).

(33) J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 4604 (1961).

(34) (a) A. Ladenburg, *Chem. Ber.*, **11**, 599 (1897); (b) G. F. D'Alelio, J. V. Crivello, R. K. Schoenig, and T. F. Huemmer, *J. Macromol. Sci.*, **A1**, 1251 (1967); (c) G. F. D'Alelio, T. Kurosaki, and R. K. Schoenig, *ibid.*, **A1**, 1279 (1967).

(35) W. Steinkopf and W. Hanske, *Ann.*, **541**, 238 (1939).

anol and was dried for 2 days at 180° *in vacuo*. The reddish brown polyazomethine I did not melt up to 300°; it dissolved readily in formic and sulfuric acids and was partially soluble in *m*-cresole. (The same solubility behavior was shown by all other polyazomethines tabulated.) Freshly prepared, green formic and sulfuric acid solutions turned orange-brown after standing for 1 hr in diffuse daylight; solutions allowed to stand for several hours in the dark turned purplish brown. Yield and analytical data are listed in Table I. In this and other condensations, all operations including the drying step were performed under light protection.

Experiments no. 2 and 3 were conducted in a similar manner. The glacial acetic acid catalyst in these runs was added in aliquots of approximately 0.2 ml over the first 12 hr. The products gave ir and electronic spectra identical with those of polymer no. 1.

From 1,1′-Diformylferrocene and *p*-Phenylenediamine in Glacial Acetic Acid. The reaction variables and analytical results for a representative polycondensation in glacial acetic acid solution are collected in Table I (no. 4). The reactants were dissolved together in the acid. After several hours of stirring under nitrogen, the polymeric product began to precipitate from the solution. After completion of the reaction, the suspension was poured with stirring into the threefold volume of water saturated with sodium acetate, and the precipitated polyazomethine was reprecipitated from formic acid and dried as before. The reddish brown polymer, infusible up to 300°, was identical in spectroscopic behavior with the products from the preceding polycondensations.

From 1,1′-Diformylferrocene and *p*-Phenylenediamine in Formic Acid. The reaction summarized in Table I (no. 5) was conducted as described for the preceding experiment. The polymer remained in solution throughout the condensation period and was precipitated with the fourfold volume of water saturated with sodium acetate. Reprecipitation from formic acid solution was accomplished as before except that the quantity of ascorbic acid used for reduction was increased to 10% by weight of the crude polymer.

By Exchange Reaction from Schiff Bases II and III. The well-ground mixture of 1.000 g (2.0 mmol) of N,N′-bis(ferrocenylmethylidene)-*p*-phenylenediamine (II) and 0.784 g (2.0 mmol) of ferrocene-1,1′-bis(methylideneaniline) (III), after repeated degassing and flushing with argon, was heated in a 30-ml round-bottom flask, employing the heating cycle listed in Table I (no. 6). Up to 300°, this operation was performed under a slow argon stream, and a side arm was attached to the flask to accommodate the subliming monomeric by-products. The final heating step at 325° was conducted under a pressure of 0.7–1.0 torr. The powdery solid mixture sintered somewhat but did not melt during this treatment. The blackish brown product was thoroughly extracted with warm dimethylformamide to remove residual starting materials and monomeric by-products. This was followed by reprecipitation from formic acid solution as before. Analytical results for the dark-brown, infusible polyazomethine are collected in Table I (no. 6).

Postcondensations of Polyazomethines I. Postcondensations of I were carried out at 0.7 torr in Schlenk tubes submerged one-half their length in a low-melting alloy metal (Cerrobend, Cerro Corp.), employing 0.5-g samples of the polymer repeatedly degassed and argon flushed. Heating cycles were as indicated in Table I (footnote *e*). The products, somewhat darkened in color, were removed from the tubes, care being taken to prevent admixture with material sublimed to the upper portion of the vessel. The polymers were no longer completely soluble in formic and sulfuric acids. At 350° postheating temperature, 5–10% of the products were insoluble; at 400°, 20–40% insolubles were found. The soluble portions, after reprecipitation from formic acid and drying at 180° as described, retained their solubility in these acids. Analytical data on the reprecipitated polyazomethines from a representative experiment are given in Table I (footnote *f*).

Polyazomethines IV. Equimolar quantities of terephthaldehyde and *p*-phenylenediamine were condensed in dimethylformamide (total reactant concentration 0.20 mol l.^{-1}) and the products worked up in the same manner as described for the ferrocene polymer no. 1, Table I, except that no reducing agent was employed in the reprecipitation step. The orange-yellow poly(1,4-xylylidene-1,4-phenylenediamine) IV, obtained in 79.5% yield, did not melt or soften below 300°; it was readily soluble in formic and sulfuric acids and partially soluble in *m*-cresole, η_{inh} 17 ml g^{-1} (98% formic acid).

Anal. Calcd for $C_{14}H_{10}N_2$: C, 81.53; H, 4.88; N, 13.59. Found: C, 80.07; H, 5.00; N, 12.87.

Postcondensation of this polymer at 350° in the described manner furnished a light brown product readily soluble in formic acid (η_{inh}, 37 ml g^{-1}) and identical in spectroscopic behavior and elemental composition with the starting material.

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