Journal of Macromolecular Science, Part A

Metallocene Polymers. XVIII. Poly(ferrocenylphosphine oxides)

Eberhard W. Neuse[a]; George J. Chris[a]
[a] POLYMER LABORATORY, MISSILE & SPACE SYSTEMS DIVISION, DOUGLAS AIRCRAFT COMPANY, INC., SANTA MONICA, CALIFORNIA

PLEASE SCROLL DOWN FOR ARTICLE

Metallocene Polymers. XVIII.
Poly(ferrocenylphosphine oxides)*

EBERHARD W. NEUSE and GEORGE J. CHRIS

POLYMER LABORATORY,
MISSILE & SPACE SYSTEMS DIVISION,
DOUGLAS AIRCRAFT COMPANY, INC.,
SANTA MONICA, CALIFORNIA

Summary

The Lewis acid–catalyzed polycondensation of ferrocene with phenyldichlorophosphine is described. Under a variety of conditions, using melt and solution condensation conditions, followed by a mild postoxidation treatment, polymers composed of ferrocenylene units interconnected by phenylphosphoryl groups are obtained. The soluble, but largely infusible, products possess number-average molecular weights up to 3500 (6000 upon subfractionation). Elemental compositions vary with reaction conditions; optimal consistency with the ideal ferrocenylene(phenyl)phosphoryl recurring unit results from use of a moderate ferrocene excess and smallest possible solvent concentrations at temperatures not exceeding 105°. Much as in previously described polyacylations of ferrocene, a minor side reaction is observed which involves rupture of the metal-to-ring bond in ferrocene with subsequent incorporation of cyclopentylene groups into the polymer. This departure, however insignificant, from the purely aromatic polyphosphine oxide composition results in thermal and oxidative stabilities not markedly superior to those of earlier ferrocenylene-methylene polymers.

The promising synthetic results reported on various polymeric systems containing arsine or arsine oxide, phosphine or phosphoryl units in the backbone [for representative publications see (2–9)] has led us to investigate, as part of our efforts in the field of metallocene polymers, the feasibility of synthesizing ferrocene-containing phosphine oxide polymers of type (1). The high aromaticity of

* For Part XVII, see Ref. (1).

$$\left[H-\underset{Fe}{\overset{}{\bigodot}}-PO-OH \right]_n$$

(1)
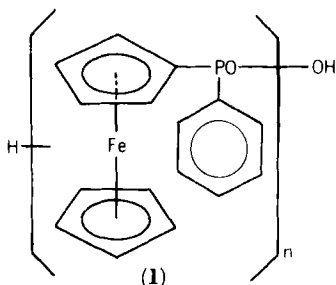
the ferrocene system should permit the preparation of such poly-
mers by direct electrophilic substitution of ferrocene under
Friedel-Crafts conditions much as in the analogous syntheses of
polyferrocenylketones and ferrocenoylbenzoyl polymers described
previously (*1,10*). The present paper discusses the results of this
investigation, which show that under appropriate experimental
conditions, using ferrocene and phenyldichlorophosphine as
reactants, phosphoryl-bridged polymeric compounds can indeed
be prepared.

RESULTS AND DISCUSSION

Polycondensation Reactions and Polymer Structure

The synthetic approach selected for the preparation of (1) in-
volved the condensation of ferrocene with phenyldichlorophos-
phine,* followed by hydrolysis and postoxidation of the primary
polyphosphine. The over-all reaction sequence can be depicted
by Eqs. (1) and (2):

$$n \ \underset{Fe}{\overset{}{\bigodot}} \ + \ n \ Cl-P-Cl \ \underset{\bigcirc}{\overset{}{}} \longrightarrow$$

---
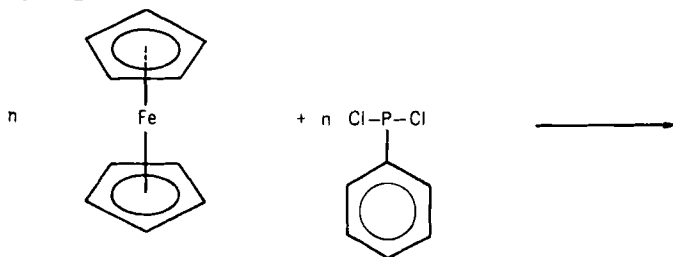
* Earlier attempts to prepare (1) by condensation of ferrocene with phenyldi-
chlorophosphine oxide, thus eliminating the subsequent postoxidation step, gave
unsatisfactory results. Despite long reaction periods and/or high catalyst concen-
trations, polymer yields were low, and the products obtained showed poor solu-
bility characteristics.

$$+ (2n-1)\ HCl \qquad (1)$$

$$\xrightarrow[\text{O}_2,\text{H}_2\text{O}_2]{\text{H}_2\text{O}}$$

$$(2)$$
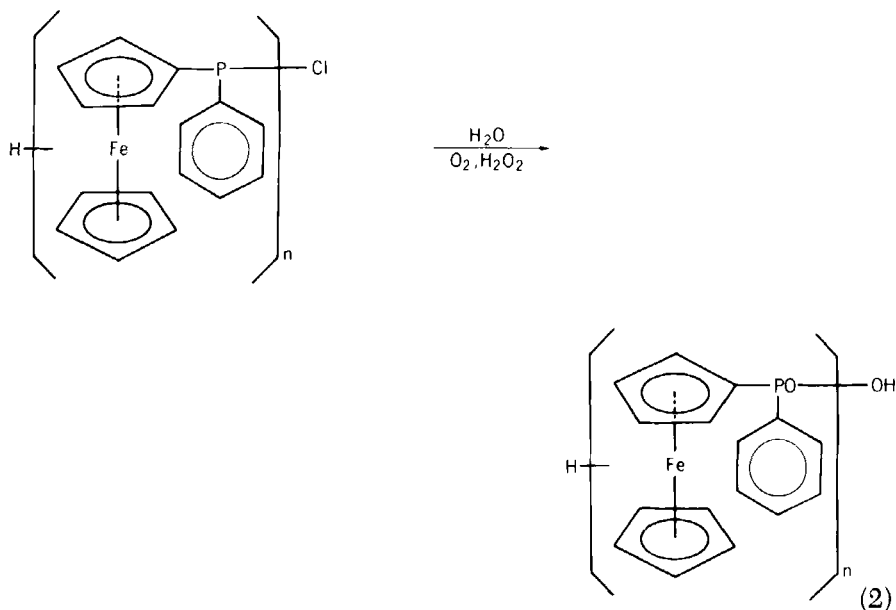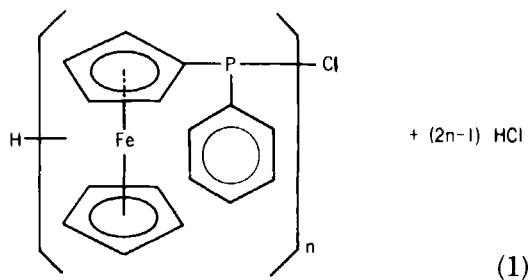
The aluminum chloride–catalyzed reaction of ferrocene with phenyldichlorophosphine had previously been described by Sollott et al. (11). These authors applied experimental conditions (20 hr in refluxing heptane) conducive to the formation of monomeric reaction products, and no polymeric compounds were isolated in their work. [Analogous conditions, with ferrocene and phosphorus trichloride as reactants, were shown by Sollott's (12) and Nesmeyanov's (13) groups to give triferrocenylphosphine; again, no polymers were reported to arise as by-products.]

In the present investigation, in contrast, the condensations were conducted either in the melt phase or in the presence of the di-

polar, aprotic solvent sulfolane (cyclic tetramethylene sulfone), that is, under conditions demonstrated elsewhere (1,10) to favor polymer formation. The catalyst was zinc chloride, which preceding screening experiments had shown to be superior to such other Lewis acids as aluminum chloride, boron tribromide, or boron trifluoride (as etherate), because it required shorter reaction periods and resulted in less cross-linking and decomposition. The sulfolane solvent was generally used in quantities not exceeding equimolarity (relative to phenyldichlorophosphine); in most instances it was added gradually in small portions during advanced stages of the condensations so as to retain melt viscosities sufficiently low for smooth stirring. Solvent quantities markedly larger than stated above resulted in unreasonably long reaction times, thus permitting predominance of detrimental side reactions involving cleavage of the metallocene system. The experiments were conducted at temperatures ranging from 90 to 170° and were generally terminated after conversion had reached 60 to 80%; further "pushing" merely resulted in excessive cross-linking, coupled with increasing insolubility of the polymers without improving polymer yields or properties. The crude reaction products were worked up by thorough hydrolysis, followed by digestion with 0.5% aqueous hydrogen peroxide for conversion of all phosphine to phosphine oxide bridges. This mild postoxidation treatment proved satisfactory, because it was aided by autoxidation during the hydrolysis step.* The polymers (1) so formed were washed with aqueous alkali to extract low-molecular phosphinic acids. Subsequent acid treatment converted phosphinate end groups to free $>P(O)OH$, while extraction with benzene removed oligomeric reaction products and unreacted ferrocene. The polymers were then reprecipitated twice from N,N-dimethylformamide solution by aqueous methanol. The presence of ascorbic acid in these two reprecipitation steps ascertained reduction of ferricenium sites generated in the polymers during the peroxide treatment. Extended vacuum drying of the products at temperatures ultimately reaching 140° was required for complete removal of solvent and other low-molecular impur-

* Smooth air oxidation of triferrocenylphosphine, diferrocenylphenylphosphine, and triphenylphosphine in the presence of aluminum chloride or other impurities was reported by Sollott's group (11,12,14) and other workers (15,16). Similarly, Shen et al. (17) obtained phosphinic acid derivatives from cyclopentadienylmanganese tricarbonyl and phosphorus trichloride in the presence of aluminum chloride.

ities. The polymers thus obtained in yields up to 30% were pinkish-brown solids that dissolvéd in a number of organic solvents and were infusible up to 300°. They could be subfractionated by conventional precipitation techniques, to give subfractions of enhanced monodispersity with M_n values up to 6000.

In each case, the combined mother liquors and benzene extracts, after removal of admixed ferrocene by chromatography or vacuum sublimation, provided oligomeric condensation products in yields of 30 to 50%, thus bringing the total yields in soluble condensation products up to about 80%.

Table 1 summarizes the experimental variables for 10 representative polycondensations. Yields, number-average molecular weights, M_n, and analytical data for the resulting polymers (not, however,

TABLE 1

Polycondensation of Ferrocene with Phenyldichlorophosphine

Expt. no.	Molar concentration[a]			Temp., °C	Time, hr	Polymer yield,[b] %	Total yield,[c] %
	Ferrocene	ZnCl$_2$	Sulfolane[d]				
1	1.5	2.0[e]	—	90	1.0	15.6	45.8
2	1.5	1.0	10.0	75[f]	600[f]	16.0	48.3
3	1.5[g]	1.0	0.3	105/160	9.0/6.0	29.2	69.5
4	1.5[g]	0.5	0.2	105	35.0[h]	16.2	48.5
5	1.4[g]	0.3	0.1	105/160	32.0/0.9	24.9	77.3
6	1.2	0.3	0.1	105/160	31.5/1.0	26.0	71.2
7	1.2	0.5	0.3	105	35.0	17.8	52.1
8	1.2	0.5	0.3	135[i]	7.5[i]	14.2	29.6
9	1.1	0.5	0.9	105/170	35.0/3.0	26.5	79.8
10	1.0	0.5	0.9	105[j]	370[j]	14.1	56.2

[a] Per mole of phenyldichlorophosphine.

[b] Soluble polymers, after two reprecipitations from DMF.

[c] Over-all condensation products including oligomers.

[d] Added in small portions over last 0.5 hr in Nos. 5, 6; over last 3 hr in Nos. 8, 9; over last 10 hr in Nos. 3, 4, 7; after first 50 hr in No. 10.

[e] Similar results with 1.0 ZnCl$_2$ at 2.5 hr.

[f] Similar results after 50 hr at 120°; similar composition, but M_n 760, after 700 hr at 25°.

[g] Initially 1.1 moles. Balance added in small portions over last 5 hr in No. 3; over last 11 hr in Nos. 4, 5.

[h] M_n 2600, % Fe 14.2, after 300 hr.

[i] Reduced total yield and large amounts of insolubles after 3.0 hr at 165°.

[j] Similar yields and composition, but M_n 1160, after 35 hr.

for the oligomeric portions less important for the purpose of the present discussion) are also listed.

The tabulation shows a fairly wide range of compositional variation for the polyphosphine oxides listed. Best agreement in elemental composition with the expected structure (1) can be found in those experiments, exemplified by Nos. 1, 4, and 7, in which the employment of a minimum amount of solvent, if any, was coupled with the use of a moderate ferrocene excess, shortest possible reaction times, and temperatures not exceeding 105°. The molecular weights attained under these conditions, however, generally were below 2000. Drastically extended heating periods or higher temperatures, on the other hand, although giving enhanced molecular weights, invariably resulted in increased phosphorus and correspondingly decreased iron percentages regardless of the ferrocene/phenyldichlorophosphine ratio employed. In general, it proved advantageous to maintain melt temperatures initially at about 105° until the major portion of the dichlorophosphine was consumed, and then continue the reaction at higher temperatures to enhance conversion and molecular weights. Under such conditions, exemplified in Nos. 3, 5, 6, and 9, yields in soluble polymers were optimized, and M_n values were as high as 3500. Failure to employ such low-temperature "conditioning" usually resulted in poor polymer solubility characteristics, thus requiring several additional reprecipitation steps; consequently, the over-all yields in soluble condensation products remained low in such experiments (cf. No. 8 and footnote i).

The high phosphorus and low iron contents found for polymers No. 3, 5, 6, and notably for Nos. 9 and 10, are likely to have resulted from the introduction into the polymer chains of phenylphosphoryl units in excess over the stoichiometry of Eq. (1). This additional incorporation probably involved the reaction of the dichlorophosphine with terminating ferrocenyl groups in (1), giving chains capped at both ends with phosphinic acid groups, and also involved the reaction with intralinear ferrocenylene units, giving variously double-bridged segments. The enhancement of both the phenyl/ferrocenyl proton signal ratio in the PMR spectra and the intensity ratio of the phenyl/ferrocenyl C—H out-of-plane deformation bands in the IR spectra are consistent with the presence of such additional phenylphosphoryl groups in polymers of this type. On the other hand, the chromatographic isolation of diferrocenylphenyl-

phosphine oxide (2) from the oligomeric portions of all reaction products strongly suggests that the polymers, especially those prepared at relatively high ferrocene/phenyldichlorophosphine

(2)
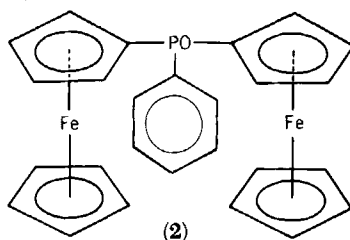
ratios and low temperatures, additionally contained polymeric chains capped at both ends with ferrocenyl groups. The presence of significant chain populations of the latter type in such polymers as Nos. 1, 2, and 4 is supported by the low phosphorus contents of these products.

Another factor responsible for minor compositional deviations from structure (1) is manifested in the invariably high hydrogen contents of all polymers listed. The appearance of weak infrared absorption in the characteristic aliphatic C—H stretching region at 3.45 to 3.50 μ, coupled with very weak, broad alicyclic proton signals at τ 6.8 to 7.3 in the PMR spectra, suggests the high %H to be due to cyclopentylene groups incorporated into the polymers as a result of a cleavage side reaction involving the metal-to-ring bond in ferrocene. In one of the polycondensation reactions, this inference could be verified by chromatographic isolation of the hetero-bridged cyclopentylene derivative (3) (18,19). Since anal-

(3)
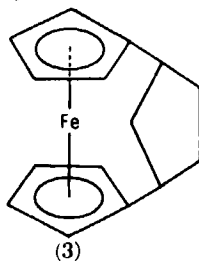
ogous cleavage side reactions were observed in previous condensation reactions of ferrocene with acyl halides (1,10), in which, much as in the present case, the ferrocene reactant was exposed to the combined attack of Lewis acid and hydrochloric acid, the Lewis acid–HCl system apparently exhibits a higher cleavage efficacy

than does the Lewis acid–H_2O system (20) operative, for example, in the polycondensation of ferrocene with aldehydes (21). This leads to the conclusion that, in Lewis acid–catalyzed polycondensations involving ferrocene or ferrocene-containing reactants and products, appreciable incorporation of cyclopentylene or related groups into the polymeric reaction products must be anticipated quite generally whenever hydrogen chloride is liberated as a by-product and the reactions are conducted over extended heating periods at temperatures substantially higher than 40 to 50°.

Spectroscopic Correlations

The infrared spectra (on potassium bromide disks) of the polymers listed in Table 2 and some of their more monodisperse sub-

TABLE 2

Composition of Polymer (1)

Expt. no.	M_n^a	Anal. calcd. for VI				Anal. found			
		C	H	Fe	P	C	H	Fe	P
1	1030	61.24	4.38	17.80	9.87	62.01	5.02	18.02	8.3
2	1850	61.77	4.32	17.95	9.96	59.87	4.80	15.18	8.7
3	2500	61.92	4.30	18.00	—	61.54	5.07	14.10	—
4	970	61.18	4.39	17.78	9.86	61.69	4.88	17.89	8.5
5	2360	61.90	4.31	17.99	9.98	64.71	5.46	12.17	10.2
6	2750	61.97	4.30	18.01	9.99	63.78	5.49	13.11	10.3
7	1090	61.30	4.37	17.82	9.88	61.92	4.89	17.53	9.2
8	2100	61.86	4.31	17.98	9.97	60.63	5.09	14.33	9.8
9	3480	62.05	4.29	18.03	10.00	64.30	5.40	12.84	11.2
10	2960	61.98	4.30	18.01	9.99	65.01	5.38	12.12	11.0

[a] Mean value of duplicate runs, determined in dibromomethane.

fractions showed the characteristic absorption pattern of the ferrocenylphenylphosphoryl recurring unit as exhibited by the phosphine oxide (2) and discussed at some length by Sollott et al. (11). Typical was the relative intensity pattern of the phenyl C=C stretching bands at 6.28 μ (w). 6.75 μ (w), and 6.95 μ (s),* and also

* The last-named band was assigned by several workers (11,22,23) to the P—C_{phenyl} linkage. However, the suggestion (24) of an activated ring vibration appears to be more plausible because of the generally observed appearance of this band in medium to high intensity in a great number of phenyl compounds devoid of phosphorus.

of the C—H out-of-plane deformation bands near 13.4 and 14.3 μ (phenyl) and in the vicinity of 12.2 μ (ferrocenyl), which were utilized earlier in this paper for an assessment of the relative populations of phenyl and ferrocenylene groups in the various reaction products. The P—O stretching mode was represented by very broad and strong absorption near 8.5 μ.* In the spectra of lower molecular samples, this band was resolved into a doublet at 8.45 to 8.60 μ, with a shoulder appearing near 8.3 μ. Another shoulder on the high-wavelength side (8.65 μ), clearly resolved in such monomeric model compounds as diferrocenylphenylphosphine and its oxide (2) (11), as well as in triferrocenylphosphine oxide (12), is probably due to a ferrocene C—H bending mode amplified by the phosphorus substituent. A very strong band near 9.0 μ, merging with the 9-μ ferrocene band, may in part be assigned to the corresponding phosphorus-activated C—H (in-plane) phenyl bending mode; analogous absorption was exhibited at 8.93 to 8.95 μ by triphenylphosphine oxide (22,27) and ferrocenyldiphenylphosphine oxide (11), and at 9.0 μ by diferrocenylphenylphosphine oxide. A contribution from a P—OH bending vibration, however, may be inferred from the conspicuous intercorrelation between this band and the broad, hydrogen-bonded 2.95-μ O—H stretching absorption of the phosphinic acid end group. With another phenyl band of moderate intensity appearing at 10.0 μ (also apparent in the spectra of triphenylphosphine and its oxide), none of the 9-μ and 10-μ bands characteristic of unsubstituted ferrocene rings (28) could be utilized for determination of the per cent homoannularity (29) and, hence, of the relative proportions of homoannularly and heteroannularly substituted ferrocene units in the backbone. However, from the appearance in all spectra of a weak to moderately strong band at 7.08 μ (ferrocene ring-breathing mode), for which a qualitative correlation with the 9-μ and 10-μ bands had

---

* From the frequency of this band (1159 cm^{-1}), accurately determined in bromoform solution, the P—O bond force constant was calculated as $k = 8.37 \times 10^5$ dynes cm^{-1}, using Robinson's approach (25). This indicates the P—O bond in (1) to be more polarized than in (2), for which $k = 8.62 \times 10^5$ dynes cm^{-1} can be determined from the P—O frequency (1178 cm^{-1}). Although the value determined would suggest nearly 75% double-bond character (25), some doubt as to the validity of this inference may arise from the earlier observed (26) invariance of the UV maxima of (2) and triferrocenylphosphine oxide with solvent polarity, which, if also applicable to (1) (insolubility in cyclohexane prevented this test), would rather speak for a predominantly semipolar nature of the P—O bond. Crystallographic bond-length determinations in (2) should aid in resolving this bond order problem.

earlier (30) been established, an appreciable population of homo-annularly interlinked ferrocenylene units can safely be assumed. An examination of the area ratio of the unsubstituted to the substituted cyclopentadienyl ring proton signals in the PMR spectra of representative samples of (1), correcting for ferrocenyl end groups, in fact, permitted the conclusion that nearly one-third of all ferrocene units were of the homoannularly substituted type (with steric effects doubtlessly favoring the 1,3 disposition).

It was demonstrated in an earlier paper (26) that there is no appreciable conjugation between the two ferrocenyl groups in diferrocenylphenylphosphine oxide. One would, therefore, expect a similar lack of electron delocalization along the polymer chain of (1). The UV spectra, measured in the region of the most characteristic allowed transition at 250 to 270 mμ in halocarbon solutions (Table 3),* indeed bear out this expectation, only minor batho-

TABLE 3

UV Maximum in 250 to 270 mμ Region

Compound	M_n	Solvent	Wavelength, mμ
Polymer (1)	2100	CHCl$_3$	258 (9,800)[a,b]
		ClCH$_2$CH$_2$Cl	260 (10,000)[b]
	4800	CHCl$_3$	260 (8,600)[b]
		ClCH$_2$CH$_2$Cl	260 (—)[c]
Diferrocenylphenyl-phosphine oxide (2)	494[d]	CHCl$_3$	255 (11,000)[e]
		ClCH$_2$CH$_2$Cl	255 (9,700)

[a] Molar extinction coefficient in parentheses (average of three samples).
[b] Calculated for repeat unit.
[c] Extinction coefficient not measured because of incomplete solubility.
[d] Mol. wt. calcd.
[e] Taken from (26).

chromic and hyperchromic shifts being noticeable relative to (2). In accord with the absence of substantial resonance domains in the backbone of (1), the polymers were found to be poor semiconductors (32), giving electroconductivities (at 25°) in the same order

* The visible spectra, notably the region from about 330 to 450 mμ comprising forbidden ligand-field bands (31) generally useful in detecting conjugative substituent effects, could not be utilized in this case because of perturbation by solvent effects (possibly involving charge transfer interactions) which produced broad, featureless absorption in this region.

$(10^{-16}$ ohm^{-1} cm$^{-1})$ as shown (32) by such nonconjugated macro-molecular ferrocene compounds as the ferrocenylene-methylene and ferrocenylene-benzylidene polymers of previous studies (29,30,33,37).

Thermal Stability

To obtain a measure of the thermal stability, representative sub-fractionated samples of (1) with molecular weights in the 3000 to 5000 range were subjected to thermogravimetric analysis in argon atmosphere. All samples tested, regardless of the particular degree of monodispersity or molecular weight, showed beginning weight loss somewhat below 300°. The curve fell off gradually to reach 90% (70%, 60%) relative residual weight near 400° (600°, 800°). Analogous runs conducted in air environment, while revealing an initial trend similar to that of the argon runs, showed a steep dropoff at about 450°; residual weights at 500° (600°) were approximately 60% (30%).

These findings suggest only a limited enhancement of the thermal stability, and practically no improvement in oxidative sta-bility, of the poly(phosphine oxides) (1) relative to ferrocene poly-mers of earlier studies (29,30,33) consisting of ferrocenylene units interconnected by methylene bridges. In view of the considerable thermal stability of such model compounds as triphenylphosphine oxide (34,35), it appears that the weak links with respect to thermal (and oxidative) resistance were the alicyclic chain constituents resulting from ferrocene cleavage as noted above.

EXPERIMENTAL

Analytical Procedures, Starting Materials

Temperatures are given in degrees centigrade. Melting points, uncorrected, were taken up to 300°. IR spectra were recorded on KBr disks (in one instance on bromoform solution) with a Perkin-Elmer spectrophotometer, Model 521. UV spectra were taken with a Cary Model 14 recording spectrophotometer. A Varian Associates NMR spectrometer, Model A-60, operating at 60 Mc/sec, was em-ployed for recording the high-resolution proton magnetic resonance (PMR) spectra (chemical shifts, τ, in parts per million relative to tetramethylsilane as internal standard); the solvent was deutero-

chloroform. Number-average molecular weights were measured in dibromomethane with a Mechrolab Vapor Pressure Osmometer, Model 301A, and were recorded as mean values of duplicate runs, rounded off to the nearest 10. Thermogravimetric analyses were performed (at a heating rate of $15°$ min^{-1}) on a du Pont Thermoanalyzer, Model 950, in argon and air environment (200 ml gas flow per min at 1 atm).

Carbon and hydrogen analyses were performed by G. I. Robertson, Jr., Florham Park, N.J. Iron and phosphorus determinations were made by neutron activation analysis, employing a Texas Nuclear Corporation Neutron Generator, Model 9501, coupled with an RCL Multichannel Analyzer. 14 MeV energy at a neutron flux of 10^8 cm^{-1} sec^{-1} was used to induce radioactivity in the sample. Diferrocenylphenylphosphine oxide (2) and triferrocenylphosphine oxide (kindly supplied by Dr. G. P. Sollott, Frankfort Arsenal, Philadelphia) were employed for standardization.

Solvents, chemicals, and reagents were obtained from commercial sources and were further purified as described (10,29). Phenyldichlorophosphine, also available commercially, was redistilled prior to use: b.p.$_{4mm}$ 103 to $105°$.

Polycondensation Reactions

The equipment used was a three-neck, round-bottom flask of 250 to 500 ml capacity, fitted with mechanical stirrer, equalizing dropping funnel, and gas inlet and outlet tubes, the latter protected by a Drierite tube. All experiments were conducted under a blanket of dry nitrogen, and the glassware was oven-dried. The reactions, summarized in Table 1, are exemplified below by the experiment listed as No. 9.

Using the equipment described, the mixture of 40.92 g (0.22 mole) of ferrocene, 35.80 g (0.20 mole) of phenyldichlorophosphine, and 13.63 g (0.10 mole) of anhydrous zinc chloride was heated with stirring at $105°$. Liberal development of hydrogen chloride, accompanied by a gradual increase in melt viscosity, showed the polycondensation to proceed properly. After 35 hr at the temperature indicated, heating was continued for 3 hr at $170°$. During this 3-hr heating period, a total of 21.60 g (0.18 mole) of sulfolane (dried over Linde Molecular Sieves, Type 3A) was added in small portions so as to maintain smooth stirring conditions. The melt, nearly solidified at the end of the reaction, was cooled,

pulverized, and digested with warm water, followed by vigorous agitation, over a 60-min period, with 1000 ml each of 0.5% aqueous hydrogen peroxide, aqueous alkali, and water. It was then taken up in a mixture of 300 ml of warm glacial acetic acid and 30 ml of concentrated hydrochloric acid, and the solution was stirred into 2.5 liters of water. The solid collected by filtration was washed with water, dried for 24 hr over P_2O_5 in vacuo, and was extracted with benzene to remove unreacted ferrocene and oligonuclear phosphine oxides. (In experiments yielding low-molecular end products, e.g., Nos. 1, 2, 4, 7, this extraction was accomplished with a 1:1 benzene-hexane mixture to avoid excessive removal of polymeric constituents.) The residual solid was heated in a high vacuum for 24 hr at 100° and another 24 hr at 140° for removal of residual, coordinated hydrogen peroxide (36) and other volatile impurities and was then dissolved in 65 ml, N,N-dimethylformamide (DMF) containing 3.0 g of ascorbic acid. From the filtered solution, 300 ml of 50% aqueous methanol precipitated the polyphosphine oxide as a yellow-tan solid, which was reprecipitated in the same manner and was dried over P_2O_5 under reduced pressure for 12 hr at 50°, followed by 8 days at 100°. There was thus obtained 16.37 g (26.5%) of tan-brown polymer, for which all analytical data are given in line 9, Table 2. The product did not melt up to 300° and dissolved readily in DMF, pyridine, hexamethylphosphoramide, and dibromomethane. Brittle, transparent films could be cast or sprayed from these solutions. Fractionation by conventional reprecipitation, using chloroform as solvent and hexane as precipitant, gave subfractions in the M_n range 850 to 6100 (first subfraction, only partially soluble, was discarded); fractions with $M_n > 2000$ were infusible up to 300°, whereas those with M_n 800 to 1800 were partially fusible or showed sintering effects. Samples stored for several months occasionally exhibited an aging effect, possibly through oxidation, which reduced their solubility in halocarbons.

From the combined and partially evaporated mother-liquors and washings of the two precipitations from DMF described above, a second polymer portion (17.7 g), of lower molecular weight (a dried sample gave M_n 2130), was salted out by excess water saturated with sodium chloride. Additional quantities of low-molecular products were obtained from the original benzene extract by evaporation to dryness and removal of admixed ferrocene by vacuum sublimation or chromatography (see below), thus bringing the total

yield in soluble condensation products (excluding any material removed by the alkali extraction) to 79.8%.

Chromatographic Separation of Diferrocenylphenylphosphine Oxide (2)

In an experiment duplicated as described above, the benzene extract of the crude product was evaporated to dryness in a rotating evaporator. The resinous residue was extracted with hexane containing 10% (by volume) benzene, and the extract was chromatographed on Alcoa, grade F-20, activated alumina, using the same solvent mixture for elution. Traces of ferrocene (recovery < 1.0%) were eluted first. A second band furnished, in 1.1% yield, crude diferrocenylphenylphosphine oxide (2), which after several recrystallizations from DMF had m.p. 250 to 251° [lit. (11) 239 to 241°].

Anal. calcd. for $C_{26}H_{23}Fe_2OP$ (mol. wt. 494): C, 63.20; H, 4.69; Fe, 22.60. Found: C, 63.57; H, 4.99; Fe, 22.67; mol. wt., 510.

From such other polycondensations as Nos. 1 and 4, phosphine oxide (2) could be isolated in yields up to 9%. When the standard workup procedure of the preceding section was modified so as to omit the postoxidation step with hydrogen peroxide, diferrocenylphenylphosphine, forming an orange band between the bands of ferrocene and (2) on the chromatogram, was isolated in addition in 1 to 7% yield. Repeated recrystallization from hexane gave a product with m.p. 194 to 195.5° [lit. (11) 191 to 193°].

Anal. calcd. for $C_{26}H_{23}Fe_2P$ (mol. wt. 478): C, 65.31, H, 4.85; Fe, 23.36. Found: C, 65.60; H, 5.02; Fe, 23.17; mol. wt., 490

In one experiment, repeated chromatography in hexane solution of the crude ferrocene portion recovered gave a small second band closely following the ferrocene zone. From this band, vacuum sublimation provided a few mg of yellow platelets, m.p. 137 to 139°, undepressed on admixture of authentic (3) (18,19).

Acknowledgments

REFERENCES

1. E. W. Neuse and R. M. Trahe, *J. Macromol. Chem.*, **1**, 611 (1966).
2. T. P. Hobin, in *High-Temperature Resistance and Thermal Degradation of Polymers*, Society of Chemical Industry Monograph No. 13, London, 1961, p. 303; Brit. Pat. 1,015,501 (1962).
3. W. B. McCormack, U.S. Pats. 2,671,077, 2,671,078, 2,671,079 (March 1954).
4. G. M. Kosolapoff, *J. Am. Chem. Soc.*, **77**, 6658 (1955).
5. V. V. Korshak, G. S. Kolesnikov, and B. A. Zhubanov, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1958**, 618.
6. P. R. Bloomfield, U.S. Pat. 3,044,984 (July 1962).
7. V. Gutmann, D. E. Hagen, and K. Utvary, *Monatsh.*, **93**, 627 (1962).
8. E. Steininger and M. Sander, *Proc. Battelle Symp., Thermal Stability of Polymers, Columbus, Ohio*, 1963, S1.
9. A. Y. Garner, U.S. Pat. 3,127,357 (March 1964).
10. E. W. Neuse and K. Koda, *J. Macromol. Chem.*, **1**, 595 (1966).
11. G. P. Sollott, H. E. Mertwoy, S. Portnoy, and J. L. Snead, *J. Org. Chem.*, **28**, 1090 (1963).
12. G. P. Sollott and E. Howard, Jr., *J. Org. Chem.*, **27**, 4034 (1962).
13. A. N. Nesmeyanov, V. D. Vilchevskaya, N. S. Kochetkova, and N. F. Palitsyn, *Izv. Akad. Nauk SSSR Ser. Khim.*, **1963**, 2051.
14. G. P. Sollott and W. R. Peterson, Jr., *J. Organometal. Chem.*, **4**, 49, (1965).
15. D. R. Lyon and F. G. Mann, *J. Chem. Soc.*, **1942**, 666.
16. P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Am. Chem. Soc.*, **83**, 103 (1961).
17. L. M. C. Shen, G. G. Long, and C. G. Moreland, *J. Organometal. Chem.*, **5**, 362 (1966).
18. V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3009 (1955).
19. S. G. Cottis and H. Rosenberg, *Chem. Ind. (London)*, **1963**, 860.
20. E. W. Neuse, R. K. Crossland, and K. Koda, *J. Org. Chem.*, **31**, 2409 (1966).
21. E. W. Neuse, *Nature*, **204**, 179 (1964).
22. L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).
23. D. E. C. Corbridge, *J. Appl. Chem.*, **6**, 456 (1956).
24. C. N. R. Rao, J. Ramachandran, and A. Balasubramanian, *Can. J. Chem.*, **39**, 171 (1961).
25. E. A. Robinson, *Can. J. Chem.*, **41**, 3021 (1963).
26. E. W. Neuse, *J. Organometal. Chem.*, in press.
27. M. Halmann and S. Pinchas, *J. Chem. Soc.*, **1958**, 3264.
28. M. Rosenblum, Ph.D. Thesis, Harvard Univ., 1953.
29. E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **85**, 1952 (1963).
30. E. W. Neuse and K. Koda, *Bull. Chem. Soc. Japan*, **39**, 1502 (1966).
31. D. R. Scott and R. S. Becker, *J. Organometal. Chem.*, **4**, 411 (1965).
32. E. W. Neuse and N. R. Byrd, paper in preparation.
33. E. W. Neuse and E. Quo, *J. Polymer Sci.*, A3, 1499 (1965).
34. C. F. Baranaukas, R. D. Carlson, E. E. Harris, and R. J. Lisanke, *U.S. Dept. Comm. Office Tech. Serv.*, AD **263,891** (1961).
35. I. B. Johns, E. A. McElhill, and J. O. Smith, *J. Chem. Eng. Data*, **7**, 277 (1962).
36. D. B. Copley, F. Fairbrother, J. R. Miller, and A. Thompson, *Proc. Chem. Soc.*, **1964**, 300.
37. E. W. Neuse and D. S. Trifan, paper presented at 148th National Meeting, American Chemical Society, Chicago, Ill., Sept. 1964, p. 5S.

Zusammenfassung

Die durch Lewis-Säuren katalysierte Polykondensation von Ferrocen mit Phenyldichlorphosphin wird beschrieben. Unter verschiedenen Bedingungen, bei Schmelz- und Lösungspolymerisationsbedingungen mit nachfolgender Oxidationsbehandlung wurden Polymere erhalten, die aus Ferrocenyleinheiten bestehen, die durch Phenylphosphorylgruppen miteinander verknüpft sind. Die löslichen, aber zum grössten Teil unschmelzbaren Produkte haben ein Zahlendurchschnittsmittel des Molekulargewichts bis zu 3500 (6000 nach Subfraktionierung). Die elementare Zusammensetzung variiert mit den Reaktionsbedingungen; optimale Übereinstimmung mit der idealen Zusammensetzung von sich wiederholenden Ferrocenylen-(phenyl)phosphoryl Einheiten ergibt sich, wenn man einen geringen Überschuss an Ferrocen anwendet bei geringstmöglichen Mengen an Lösungsmittel, wobei die Temperatur 105° nicht übersteigen sollte. Ebenso wie in früher beschriebenen Polyacylierungsreaktionen des Ferrocens wird zu einem geringen Teil eine Nebenreaktion beobachtet, die eine Sprengung der Metall-Ringbindung im Ferrocen mit nachfolgendem Einbau von Cyclopentylengruppen in das Polymere umfasst. Diese zwar nur geringfügige Abweichung von der rein aromatischen Polyphosphinoxidzusammensetzung resultiert in thermischen und oxidativen Eigenschaften, die nicht merklich jenen überlegen sind, die schon früher von Ferrocenylenmethylenpolymeren gezeigt wurden.

Résumé

Description d'une polycondénsation du ferrocène avec la phényldichlorophosphine, catalysée par les acides de Lewis. Des polymères, composés d'unités ferrocènylèniques, interreliées par des groupes phénylphosphoryls ont été obtenus, dans des conditions variées de condensation en fusion ou en solution, suivie d'un traitement doux de post-oxydation. Les produits, solubles mais en grande partie infusibles out des masses moléculaires moyennes atteignant 3500 (6000 en sousfractionnement). La composition éléméntaire varie avec les conditions de la réaction; le meilleur accord avec une unité idéale répétitive ferrocenylènique(phényl)phosphoryl resulte d'un excès moderé de ferrocene, de la plus petite quantité de solvant possible et des températures ne dépassant pas 105°. Comme dans les polyacylations du ferrocene précédement décrites, on observe une faible réaction secondaire comprenant la rupture de la liaison metal-cycle dans le ferrocene, avec incorporation subsequente des groupes de cyclopentylène dans le polymère. Cet ecart, bien qu'insignifiant, d'une composition purement aromatique en oxyde de phosphine, resulte dans des stabilités thermales et oxydants pas très superieures à celles obtenues avec des polymères du ferrocenylene-methylène précédents.