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History of Organometallic Polymers

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ABSTRACT

In the last 20 years a wide variety of new types of polymers has been prepared containing metals as an integral part of the polymer backbone. This paper summarizes deveopments in the following major areas: vinylic polymers, including vinyl metallocene derivatives and vinylic tin monomers; condensation polymers; polyorganophosphazenes; coordination polymers; mixed valence polymers with electrical conductivity such as $(SN)_x$, polyacetylene and polyphenylene; stacked polymers such as platinum blue, polyphthalocyanines, and TTF-TCNQ. The methods of synthesis and potential applications of these materials in areas such as catalysis, elastomers with low and high temperature stability, metallic conductors, semiconductors, bacteriacides, fungicides, and cancer chemotherapeutic agents are discussed.

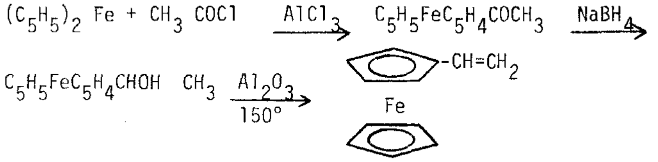
In the past 10-15 years a number of new polymers containing metals as an integral part of the repeating structural unit have been prepared and their properties studied. Three A.C.S. symposia [1] in 1971, 1977, and 1979 have been devoted to these materials and several monographs have been published [2, 3, 7]. Much of the research in this field is still in the very early stages, but in this paper the author will endeavor to focus on key points of interest in six major areas–organotransition metal polymers, condensation polymers, organotin acrylates, polyphosphazenes, coordination polymers, and one-dimensional electrically conductive polymers.

ORGANOTRANSITION METAL POLYMERS

Vinylic Polymers

Interest in polymerization of vinylic organotransition metal monomers commenced with the polymerization of vinylferrocene by Arimoto and Haven [4, 5] in 1955 and has been summarized by C. U. Pittman, Jr. [6], the leading investigator in this field, and by Neuse and Rosenberg [7].

Vinylferrocene, 1, is prepared by Friedel-Crafts acetylation of ferrocene, reduction, and dehydration (1). It is an orange crystalline, slightly air-sensitive material, mp 55°, readily soluble in aromatic and chlorinated solvents. Many other vinylic monomers have been prepared by similar procedures (Table 1).



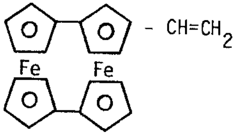
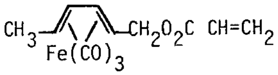
(1)

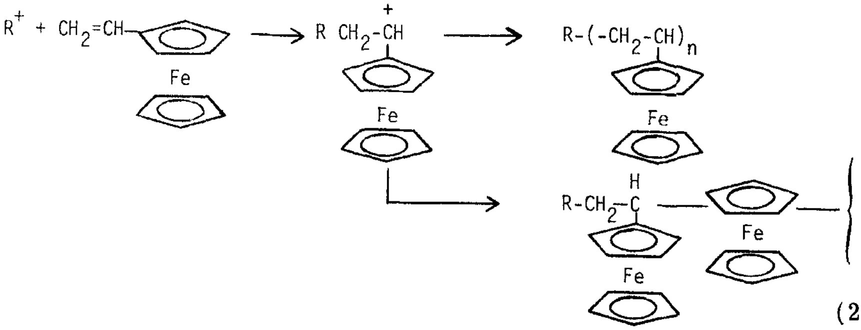
Ferrocene and most other transition metal π-complexes are π-electron donors and show an unusual ability to stabilize carbonium ions in the α-position but not carbanions [12]. Thus the most outstanding characteristic of vinylferrocene and monomers 2-9 is the high electron density in the vinyl group. Cationic and radical polymerization but not anionic polymerization [82] are possible. The ease of oxidation of the central metal atoms places limits on the choice of initiators used and in some cases permits electron transfer between the growing chain and the metal center. The steric bulk of the organometallic group causes a reduction of the reactivity of 1-9 as well as rendering the resulting polymers rigid and brittle.

Cationic polymerization (2) may be initiated by $BF_3 \cdot OEt_2$ or $Et_2AlCl/M(acac)_2$ (M = Ni, Cu, VO) [6]. Attack occurs preferentially on the vinyl group although electrophilic substitution on the ring is also possible. Low molecular weight soluble polymers are obtained, along with some insoluble highly branched or cross-linked materials.

Radical polymerization of monomers 1-9 is summarized in Table 2. Hayes and George [15] have conducted a detailed study of radically induced polymerization of vinylferrocene in benzene and dioxane. In dioxane, typical kinetics for radically induced polymerization were obtained, but in benzene unusual kinetics were obtained which were

TABLE 1. Vinylic Organotransition Metal Monomers

		Refs.			Refs.
			Vinyl Metallocenes		
1	$C_5H_5FeC_5H_4CH{=}CH_2$	6	4	$Fe(C_5H_4CH{=}CH_2)_2$	6
2	$C_5H_5RuC_5H_4CH{=}CH_2$	8	5		9
3	$C_5H_5FeC_5H_4C{\equiv}CH$	6			
			Vinyl Cyclopentadiene and Arene Complexes		
6	$(CO)_3MnC_5H_4CH{=}CH_2$	6	9	$(CO)_2CoC_5H_4CH{=}CH_2$	11
7	$(CO)_2NOCrC_5H_4CH{=}CH_2$	10	10	$(CO)_3CH_3WC_5H_4CH{=}CH_2$	11
8	$(CO)_3CrC_6H_5CH{=}CH_2$	6	11	$Cl(Ph_3P)_2PdC_6H_4CH{=}CH_2$	6
			Acrylates and Methacrylates [6]		
12	$FcCH_2O_2CCH{=}CH_2$		17	$(CO)_3CrC_6H_5CH_2CH_2O_2CCH{=}CH_2$	
13	$FcCH_2O_2CC(CH_3){=}CH_2$		18		
14	$FcCH_2CH_2O_2CCH{=}CH_2$				
15	$FcCH_2CH_2O_2CC(CH_3){=}CH_2$		19	$(C_5H_5)_2TiClO_2CC(CH_3){=}CH_2$	
16	$(CO)_3CrC_6H_5CH_2O_2CCH{=}CH_2$		20	$(C_5H_5)_2TiClOCH_2CH{=}CH_2$	

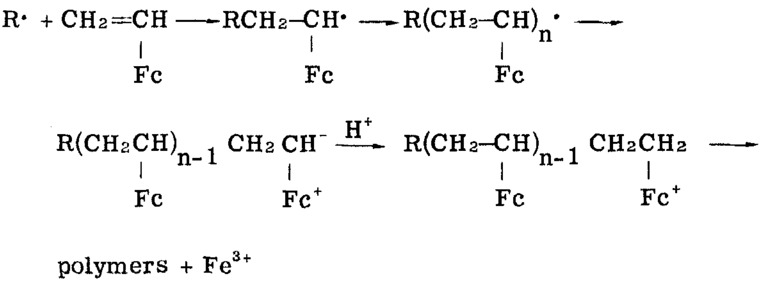


(2)

TABLE 2. Homopolymerization of Vinylic Organometallic Monomers

Monomer	Yield (%)	$\overline{M}_n$	$\overline{M}_w$	[η] (mL/g)	Refs.
1	69	11,400	19,000	6.80	13
2	93	19,660	118,950		8
3	81	2,700			80
5	31	8,000			79
6	25	9,900	17,000		13
7	95	18,500	23,600		78
12	57	20,100	80,000	12.76	13
13	67	35,500	211,000	12.44	81
14	86	36,000	81,000		6
15	89	24,000	65,000		6

attributed to an electron-transfer mechanism of termination (3). Extensive chain transfer to monomer occurred which led to early termination and an apparent maximum possible $\overline{M}_n$ of about 2.5×10^4.



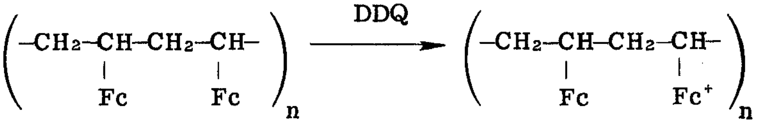
$$R\cdot + CH_2{=}\underset{\textstyle Fc}{\underset{|}{CH}} \longrightarrow RCH_2{-}\underset{\textstyle Fc}{\underset{|}{CH}}\cdot \longrightarrow R(CH_2{-}\underset{\textstyle Fc}{\underset{|}{CH}})_n\cdot \longrightarrow$$

$$R(CH_2\underset{\textstyle Fc}{\underset{|}{CH}})_{n-1}\,CH_2\underset{\textstyle Fc^+}{\underset{|}{CH^-}} \xrightarrow{H^+} R(CH_2{-}\underset{\textstyle Fc}{\underset{|}{CH}})_{n-1}\,CH_2\underset{\textstyle Fc^+}{\underset{|}{CH_2}} \longrightarrow$$

$$\text{polymers} + Fe^{3+} \qquad (3)$$

Polymers of 1 form brittle films soluble in aromatic solvents and chloroform. DSC shows transitions at 170-190° and 225-247° with softening at 280-290°. Torsional braid analysis shows no transitions below 260° with evidence for thermal decomposition above this temperature [17].

Polyvinylferrocene is an insulator (conductivity of 10^{-14} ohm^{-1} cm^{-1}) but when partially oxidized by Ag^+, benzoquinone, or DDQ, it becomes a semiconductor (conductivity of 10^{-8} ohm^{-1} cm^{-1}). Conductivity results from creation of a mixed valence ferrocene-ferricinium polymer in which electrons can hop from one ferrocenyl group to the next:



$$\left(\begin{array}{c}-CH_2-\underset{\displaystyle Fc}{\underset{|}{C}H}-CH_2-\underset{\displaystyle Fc}{\underset{|}{C}H}-\end{array}\right)_n \xrightarrow{DDQ} \left(\begin{array}{c}-CH_2-\underset{\displaystyle Fc}{\underset{|}{C}H}-CH_2-\underset{\displaystyle Fc^+}{\underset{|}{C}H}-\end{array}\right)_n \qquad (4)$$

Similar semiconducting polymers have been prepared from 3 (10^{-7} ohm^{-1} cm^{-1}) and 5 (10^{-3} ohm^{-1} cm^{-1}).

Monomers 1-18 can copolymerize with organic monomers such as styrene, vinylpyrrolidinone, maleic anhydride, acrylate esters, and acrylonitrile and with one another [6, 13] (Table 3). A detailed quantitative study of the reactivities of these monomers based on the Q, e scheme [18] has been undertaken by Pittman [6].

Copolymers of 1-20 show greatly improved mechanical properties. Glass transitions in the range 50-150° are typical and many of the copolymers form peelable films. This improvement of properties, however, has been achieved at the cost of reduced metal content, lowered thermal stability, and greatly reduced electrical conductivity of the mixed valence polymers.

Acrylate monomers such as 12-20 also undergo anionic polymerization [19]. Polymerization of 12-15 initiated by $LiAlH_4$ resulted in linear polymers with $M_n = 1\text{-}7 \times 10^5$ which formed films readily. The glass transition could be lowered from 140-145° to 90° by addition of 1-10% of a plasticizer [17]. Block copolymers with styrene and acrylonitrile also could be obtained, some of which showed separate T_g for the two portions of the chain [17].

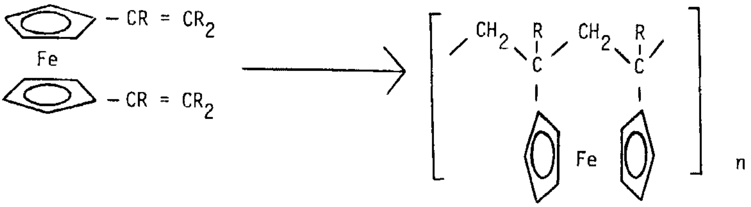
Disubstituted ferrocenes [6] such as 1,1'-divinylferrocene, 4, and 1,1'-diisopropenyl ferrocene undergo vinylic polymerization to produce insoluble cross-linked polymers or cyclopolymerization to produce soluble materials, $M_n = 2\text{-}8 \times 10^4$, when either cationic or radical initiators are employed (5). Cyclic polymerization appears to be favored by slightly polar solvents and lower monomer concentrations.

Monomers with Vinyl-Metal Bonds

Polymerization of monomers containing a vinyl group bound directly to a transition metal has so far not been accomplished. The

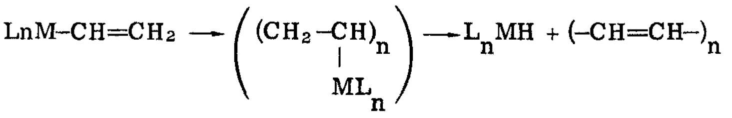
TABLE 3. Copolymerization of Vinylic Organometallic Monomers with Styrene and Methyl Acrylate in Benzene at 70°

Monomer 1 (g)		Monomer 2 (g)		AIBN (g)	Yield (%)	M_1 (mole) % in copolymer)	Refs.
1	3.63	STY	1.03	0.014	22	33	13
	1.82	MA	2.00	0.011	66	27	
2	2.00	STY	1.00	0.020	57	30	8
	1.00	MA	1.00	0.020	76	20	
6	2.28	STY	1.88	0.027	44	14	13
	2.49	MA	1.46	0.020	20	61	
7	2.20	STY	1.08	0.010	30	41	78
8	0.30	STY	0.30	0.01	49	32	13
	0.30	MA	0.26	0.01	44	26	
12	4.32	STY	2.50	0.006	60	24	13
	2.85	MA	2.85	0.014	40	23	
17	1.25	STY	1.01	0.005	77	33	13
	1.25	MA	0.83	0.009	77	29	
18	1.226	STY	0.811	0.0204	29.8	22	6
	2.657	STY	0.094	0.0275	22.2	81	
	1.022	MA	0.559	0.0158	63	33	
	2.541	MA	0.111	0.0265	26	90	



(5)

resulting polymers, if formed, would be highly unstable with respect to elimination of metal hydrides:

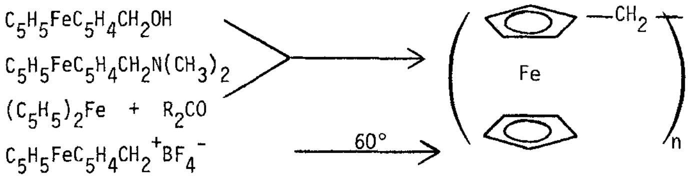


$$\mathrm{LnM{-}CH{=}CH_2} \longrightarrow \left(\underset{\mathrm{ML_n}}{\mathrm{(CH_2{-}CH)_n}} \right) \longrightarrow \mathrm{L_nMH} + (\mathrm{-CH{=}CH-})_n \qquad (6)$$

A series of monomers $CH_2{=}CH{-}M(CH_3)_3$, where M = C, Si, Ge, Sn, and Pb, were homopolymerized and copolymerized using radical initiators [32]. There is a continuous increase in electron deficiency at the vinyl group in passing from C to Sn. It is indeed unusual that the more electropositive the metal becomes, the more electron deficient the vinyl group becomes.

Metallocenylene Methylene Polymers

Polymers analagous to the phenol-aldehyde resins [20, 21] have been prepared by a number of investigators:



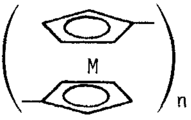
(7)

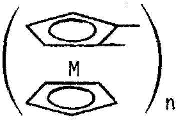
The resulting dark brown to black polymers soften in the range 220-300° and decompose above 300°. The fractions soluble in aromatic or chlorinated solvents show low molecular weight, $\overline{M_n} = 2\text{-}10 \times 10^3$ and varying degrees of branching, depending on the method of synthesis. Insoluble cross-linked material is also produced and is the predominant product when difunctional ferrocene precursors are used.

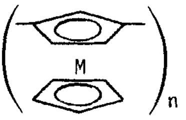
These polymers have been studied by H. Rosenberg and co-workers at the Materials Research Center of Wright-Patterson Air Force Base during 1965-1972, primarily with the hope of creating materials with high thermal stability and resistance to degradation by ultraviolet light. Laminates of a ferrocenylene methylene resin or of polyferrocenylene [28] with fiberglass have great structural stability and when exposed to high temperatures char rather than melt or soften. Use of such materials as ablative heat shields on the nose cones of space capsules was proposed. Before the materials were perfected, however, cheaper ceramic materials were found which performed satisfactorily. The biggest problem, therefore, has been to find applications where the ferrocenyl polymer is sufficiently superior to existing materials to justify its extra cost. So far no large-scale applications have been found.

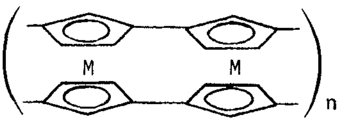
Metallocenylene Polymers

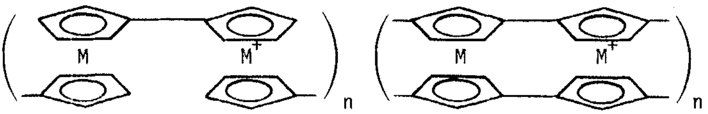
Metallocenylene polymers [22] are of considerable interest because partial oxidation would lead to creation of mixed valence conjugated polymers which would likely be either semiconductors or metallic conductors.


1,1' polymers


1,2 polymer

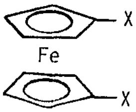

1,3 polymer


1,1', 3,3' polymer


mixed valence polymers

Linking of two different metallocenes such as ferrocene and ruthenocene or osmocene would offer additional possibilities for creating mixed metal-mixed valence polymers.

Attempts at synthesis of 1,1'-polyferrocenylene starting from precursors 21a-f have been reviewed by Neuse and Bednarik [23, 24].



21 a X = I
b X = Br
c X = HgCl
d X = Li
e X = Cu
f X = Li (TMEDA)

The most successful procedure to date [21] involves coupling of highly purified 21a and a slight excess of 21f in THF or DME. Soluble linear 1,1'-polyferrocenylene with $\overline{M}_n$ up to 10,000 with no undesirable end groups is obtained. Polyruthenocenylene with $\overline{M}_n$ up to 1500 has been prepared by a similar procedure. Attempts to increase molecular weight and to prepare copolymers of ferrocene and ruthenocene are currently in progress.

Ferrocene-arylene polymers [25] have also been prepared by a similar procedure (8). Molecular weights were in the range of 1-2 × 10^3 but application of the techniques described by Neuse and Bednarik may produce substantial increase in both yield and $\overline{M}_n$.

$$(C_5H_4Li)_2\ Fe + C_6F_6 \longrightarrow (-C_5H_4FeC_5H_4-C_6F_4-)_n \qquad (8)$$

Direct polymerization of ferrocene with a stoichiometric amount of di-t-butyl peroxide has been reported [26]. Copolymerization with p-dichlorobenzene, naphthalene, and other aromatic hydrocarbons is also possible [30]. Soluble polymers with $\overline{M}_n$ up to 10^5 can be obtained. Subsequent investigations showed the presence of methyl groups, t-butoxy groups, and incorporation of up to 30% of aliphatic linkages between the rings [27-29]. Polymers of this type are much simpler to prepare than linear polyferrocenylene but show greatly reduced thermal stability. The aliphatic linkages would also destroy the conjugation between the rings necessary for electrical conductivity.

Properties of Polyferrocenylene

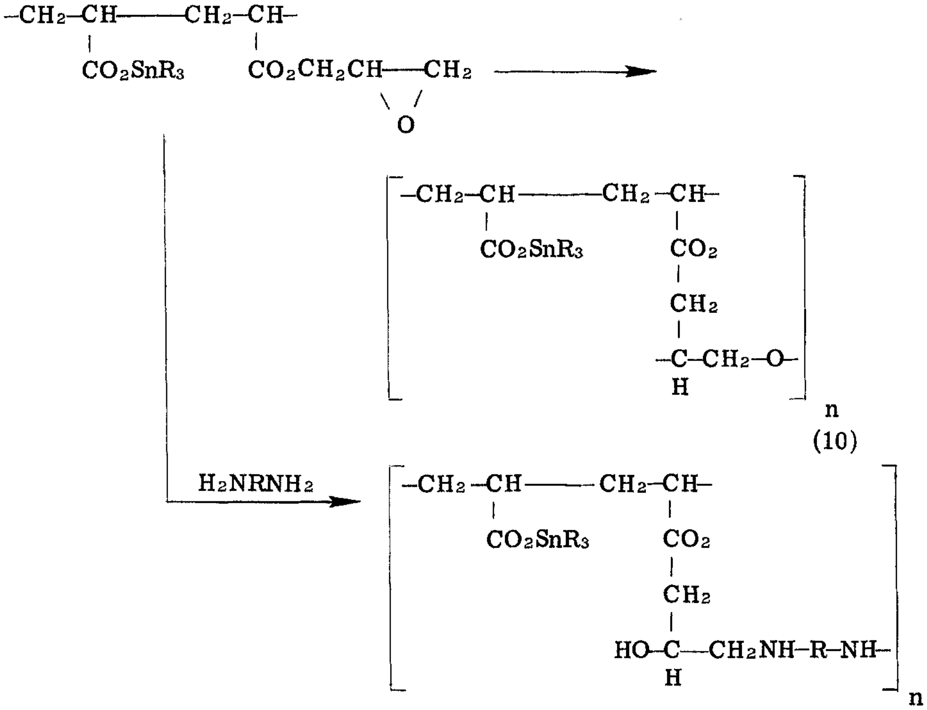
Linear polyferrocenylene is a brittle orange crystalline material soluble in aromatic solvents. It undergoes thermal degradation only above 400° with 85% weight retention at 650° and 75% at 850°. In contrast to p-phenylene polymers, little change in infrared, ultraviolet, or Mössbauer spectra is observed as molecular weight increases. Thus the ferrocenylene units are apparently not coplanar, and extensive conjugation between rings does not take place. Oxidation of the polymer with benzoquinone produces a Class II mixed-valence polymer [24] with a charge transfer band at 1800 nm. Similar behavior was observed by Cowan in detailed studies of ferrocenylene oligomers [31]. Investigations of the conductivity, magnetic susceptibility, dielectric constant, and other properties of mixed-valence polyferrocenylenes are currently in progress.

POLYMERIZATION OF TRIALKYLTIN ACRYLATES

Trialkyltin acrylates and methacrylates may be prepared by esterification of acrylic or methacrylic acid with R_3SnCl [33, 34]. The resulting monomers readily undergo polymerization by radical or anionic initiation. Polymeric material may also be prepared by esterification of polyacrylic acid or polymethacrylic acid:

$$\begin{tikzcd}
CH_2{=}CRCO_2^- + R_3SnCl \arrow[r] & CH_2{=}CRCO_2SnR_3 \arrow[d] \\
(CH_2{-}CRCO_2^-)_n + R_3SnCl \arrow[r] & (CH_2{-}CRCO_2SnR_3)_n
\end{tikzcd} \qquad (9)$$

The resulting polymers are soluble in organic solvents, but if glycidyl acrylate is copolymerized with the tin polymers, cross-linking may be introduced either by base-catalyzed polymerization of the epoxide functions or by addition of aromatic or aliphatic diamines:



(10)

The result is a tough, insoluble film suitable for use as a coating or, if pigment is included, as paint.

Interest in polymers of this type has arisen from the need to find a coating which would inhibit the formation of barnacles on ship bottoms and shore installations [35]. Barnacles greatly increase friction as the ship passes through the water and add unnecessary weight, resulting in increases in fuel consumption up to 30%. The tin polymers hydrolyze slowly to release R_3SnOH which inhibits barnacle growth. Extensive testing is under way to develop paint formulation which can prevent growth of barnacles without releasing toxic material into the water in sufficient amounts to be hazardous to other marine life. Large-scale manufacture of tin-containing paint seems likely soon.

CONDENSATION POLYMERS

Synthesis by Interfacial Techniques

The synthesis and properties of organometallic condensation polymers have been reviewed by Charles Carraher, the leading investigator in the field [36, 37]. Condensation polymers are formed when

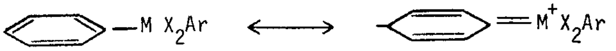
TABLE 4. Components for Synthesis of Organometallic Condensation Polymers

	Lewis Acids		
$(C_5H_5)_2MX_2$	M = Ti, Zr, Hf		X = Cl, Br, I, OH
R_2MX_2	M = Si, Ge, Sn, Sb, Pt R = alkyl, aryl		X = halogen
R_3MX_2	M = As, Sb, Bi R = alkyl, aryl		
MoO_2Cl_2			
$UO_2(H_2O)_2{}^{2+}$			
	Lewis Bases		
Dihydrazines	Diamines		Dithiols
Hydrazines	Dihydrazides		Dicarboxylate salts
Ureas			Dioximes
Thioureas			Diamidoximes
	Lewis Bases Containing Metallocenes		
22	$(HOCR_2C_5H_4)_2M$	23	$(HON = CR{-}C_5H_4)_2M$
24a-d	$(^-O_2CC_5H_4)_2M$	M = Fe, Ru, Co^+, Rh^+	

a Lewis acid containing a metal, usually in Groups IVA, IVB, or VA, interacts with a difunctional Lewis base, which may also contain a metal. The Lewis acids and bases employed are shown in Table 4.

Attempts to synthesize polymers of this type in homogeneous solution have frequently led to production of low molecular weight oligomers by cyclization or degradation of the starting materials. These problems may be avoided by interfacial polymerization in which the polymer is formed under nonequilibrium conditions. In a typical procedure the Lewis acid is dissolved in a nonpolar solvent such as benzene or hexane and the Lewis base in water or a polar organic solvent such as methanol, acetonitrile, nitrobenzene or tetramethylthiophene-1,1-dioxide. If the monomers are particularly susceptible to hydrolysis, both solvents must be anhydrous. Rapid stirring at $1\text{-}5 \times 10^4$ rpm permits rapid mixing and formation of the product at the interface. The reaction is usually complete in 15-120 s and further stirring leads to degradation.

The yield and properties of the polymers formed are highly dependent on the initial concentration of the reagents, solvent, stirring rate, time, and temperature. Yields generally follow the pattern $Pb > Sn \sim Sb > Ge \gg As \sim Si$, while solubility follows the reverse order. Yields are generally higher for bulky aliphatic R groups than for aromatic R, possibly because of diminished reactivity of the metal caused by dπ-pπ conjugation.



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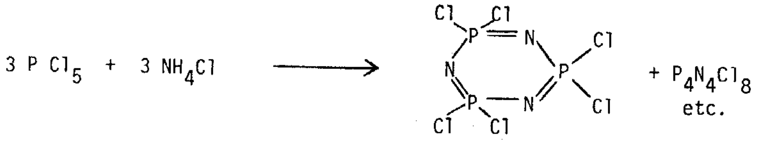
Condensation Polymers with Group IVB Elements

Group IVB condensation polymers are sparingly soluble in solvents such as 2-chloroethanol and show somewhat greater resistance to hydrolysis than Group IVA polymers. Titanocene polyethers often dry to give coherent flexible films, and the titanocene dicarboxylate polymers show a unique tendency to form fibers spontaneously upon scratching. Measurement of molecular weight has proven difficult because of low solubility. The most unusual property of these polymers is their unusual thermal stability, Ti > Zr > Hf. Thermal degradation of the Ti polymer under nitrogen begins at 300-350° but weight loss is only 30% at 800° and substantial organic matter is retained up to 1100° [38].

POLYPHOSPHAZENES

Polyphosphonitrilic chloride, "inorganic rubber," has been known since the early 1900s but had been dismissed as too unstable and intractable for commercial use. It is largely due to the efforts of H. R. Allcock [39, 40] at Pennsylvania State University, N. S. Schnieder, R. E. Singler, and G. Hagnauer working at the U.S. Army Materials Research Center [41, 42] and several industrial firms [43, 44] that it has been developed into a material with widespread applications. The synthesis of polyphosphazenes is outlined in Schemes (12) and (13). Allcock's key contributions were to purify the monomer carefully, reduce the temperature, and discontinue heating while the material still consisted largely of linear chains. Soluble polymers with molecular weight in excess of 10^6 were obtained. The next key step was to replace the easily hydrolyzed chlorine with alkoxides or amines.

Attempts to prepare alkyl or arylphosphazene polymers by reacting $(-PCl_2-N-)_n$ with alkyl lithium reagents or Grignard reagents led



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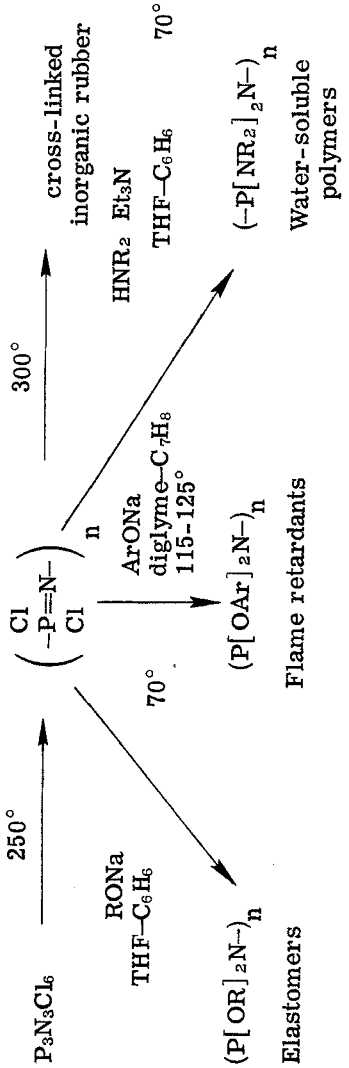

P3N3Cl6
250°
(Cl –P=N– Cl)n
300°
cross-linked inorganic rubber
RONa THF–C6H6
70°
ArONa diglyme–C7H8 115-125°
HNR2 Et3N THF–C6H6 70°
(P[OR]2N–)n
Elastomers
(P[OAr]2N–)n
Flame retardants
(–P[NR2]2N–)n
Water-soluble polymers

(13)

to extensive chain cleavage. Attempts to polymerize substituted trimers were also unsuccessful [45]. Up to 70% substitution can be obtained, however, if polyfluorophosphazene is used [48]. The remaining fluorines may be replaced with alkoxy groups (14). The resulting materials possess greater thermal stability than the alkoxyphosphazenes while still possessing desirable mechanical properties.

$$P_3N_3Cl_6 \xrightarrow{NaF} P_3N_3F_6 \longrightarrow (-PF_2N-)_n \xrightarrow{RLi} (-PR_{1.4}F_{0.6}N-)_n$$

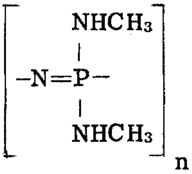
$$\xrightarrow{NaOR} (-PR_{1.4}(OR)_{0.6}N-)_n \qquad (14)$$

Properties and Applications of Polyphosphazenes

The properties of the polymers formed are highly dependent on the nature of the substituents used. The $PNCl_2$ chain is highly flexible, even at low temperatures, T_g = -63°, partly because the nitrogen atoms in the chain have no substituents [46]. Replacing the chlorine atoms with low molecular weight aliphatic alkoxides retains the flexibility and superior elastomers are formed. One of the best, T_g = -77°, contains a random 50:50 mix of trifluoroethoxy and heptafluorobutoxy groups. The fluorines impart a high degree of hydrophobicity and also retard combustion [44].

Alkoxyphosphazenes can be formulated with fillers, laminated with fiberglass, vulcanized, and in other ways fabricated like hydrocarbon or silicone rubbers. They show great resistance to oxidation, organic solvents, gasoline, or lubricating oil. They do not hydrolyze and they retain their tensile strength after prolonged stress at 150° [50, 51]. They ignite with difficulty and when ignited produce little smoke. In overall performance they are superior to the hydrocarbon rubbers and competitive with the silicones in applications which require stability over a broad temperature range, such as fuel lines and gaskets for jet engines. They are fully biocompatible [47] and less likely to interact with fatty tissue than the silicones, so applications as biological implants are being studied.

The amino polyphosphazenes are more hydrophilic. Polymers prepared from low molecular weight amines, 25, amino acids and amino esters, 25, 27, are water soluble and also biodegradable. Polymers containing amines are useful as flame retardants for fabrics, particularly children's pajamas [43]. The amino acid and ester polymers offer potential as controlled release agents in pharmacology. The polyphosphazene chain is capable of binding to cis platinum complexes useful in cancer chemotherapy [48], 28, 29, and releasing the platinum slowly. Thus treatment still can be effective while toxicity is reduced.


$\left[-N=P(NHCH_3)_2-\right]_n$

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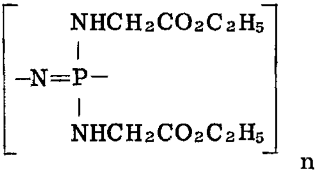
$\left[-N=P(NHCH_2CO_2C_2H_5)_2-\right]_n$

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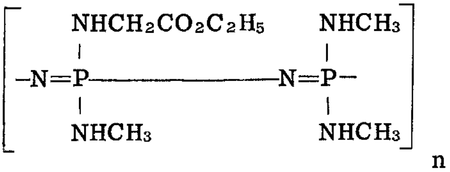
$\left[-N=P(NHCH_2CO_2C_2H_5)(NHCH_3)-N=P(NHCH_3)_2-\right]_n$

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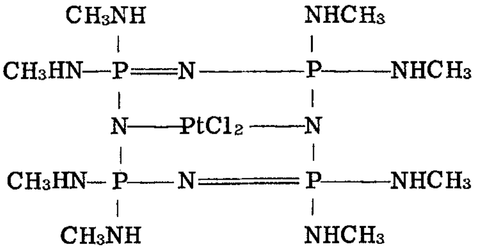

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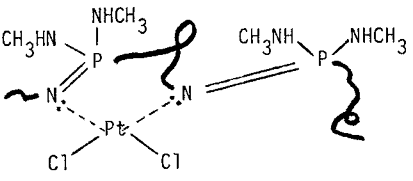

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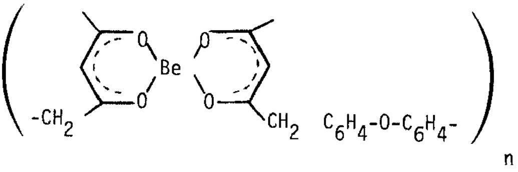
COORDINATION POLYMERS

During World War II, the U.S. Air Force investigated polymeric coordination complexes heavily in an effort to find polymers with thermal stability up to 600°. Leaders in this field at that time and since have been J. C. Bailar, Jr., and B. P. Block. Efforts in this direction had limited success. Polymeric complexes proved to be brittle and insoluble. When organic links were added between the metal sites to improve flexibility, the chains became no stronger than the organic links. A wide variety of polymers was prepared [52-56], however, from three basic approaches.

Polymers from Bis-Chelating Agents

Any type of chelating agents could theoretically be used to form polymers if two molecules were linked. Common examples are β-diketones, 1,2-dioximes, diamines, amino acids, hydroxyquinolines, hydroxy Schiff bases, and thiopicolinimides.

Polymer 30 is an example of a soluble polymer with molecular weight up to 10^5. Unfortunately, it tends to depolymerize at temperatures only slightly above those needed for its formation [57, 58].



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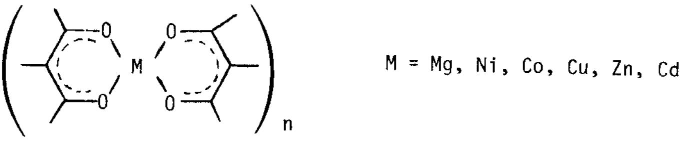
Polymer 31 can be prepared from tetraacetylethane. TGA studies show decomposition in the range 225-350° and stability in the order Mg > Ni > Co > Cu > Zn > Cd [59].



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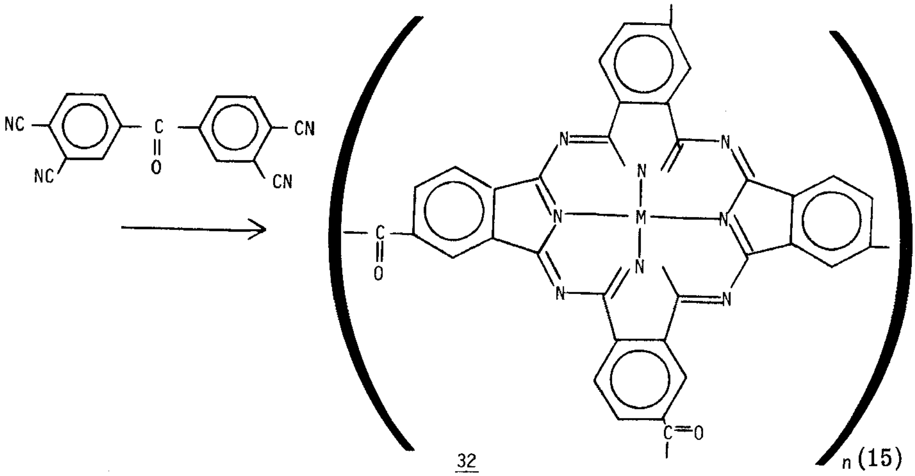
Phthalocyanine polymers can be prepared from 1,2-dinitriles (15) [60]. In general, polymers of this type are insoluble, brittle, highly colored, and show great thermal stability. Compound 32, for example, is stable up to 450° [61]. Many of these materials have potential use as semiconductors although not possessing the conductivity of the stacked polymers which will be discussed later.



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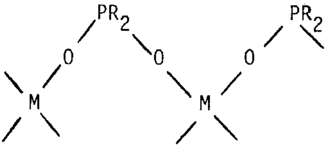
(15)

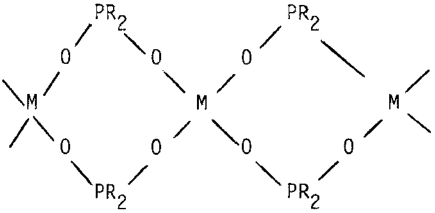
Bridging Ligands

The most extensively studied polymers prepared from bridging ligands are the polymeric metal phosphinates [62]. Polymeric materials have been prepared containing one, two, or three bridging phosphinate units. Metals, such as Al, Be, Co, Cr, Ni, Ti, and Zn have been employed.

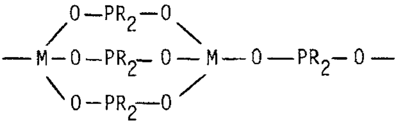
Single bridged



Double bridged



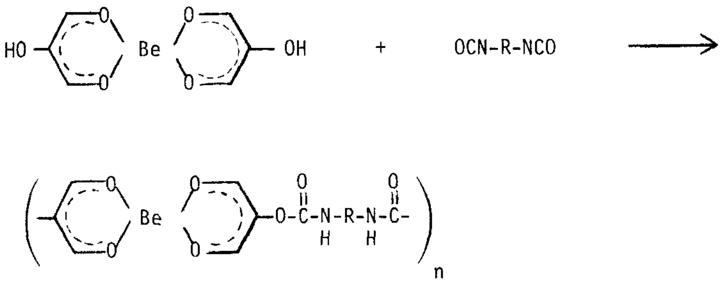
Triple bridged



Polymers with molecular weights up to 1.5×10^5, soluble in organic solvents, and capable of forming flexible films have been obtained. The best materials [63] contain Cr and are pale green flexible film-forming polymers which show thermal stability up to 400°. Thermomechanical properties and glass transition temperatures have been measured by TBA. Applications as viscosity stabilizers for greases, antistatic agents, or as corrosion-resistant coatings have been proposed [52, 62].

Polymers from Complex Monomers

Monomeric metal chelate units such as β-diketone complexes, prophyrins, or phthalocyanines which have pendant functional groups can be linked [64]. One such example is



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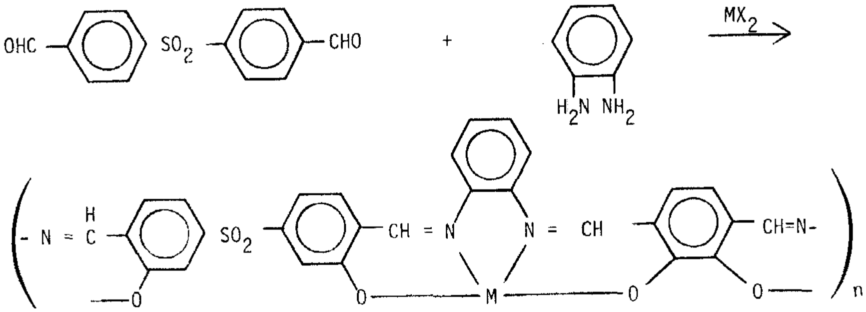
(16)

Incorporation of Metals into Polymer Films

A wide variety of cross-linked or cross-linkable polymeric films has been prepared which contain coordinated metal atoms. The metal is usually incorporated during formation of the film. Three such examples [65-67] are



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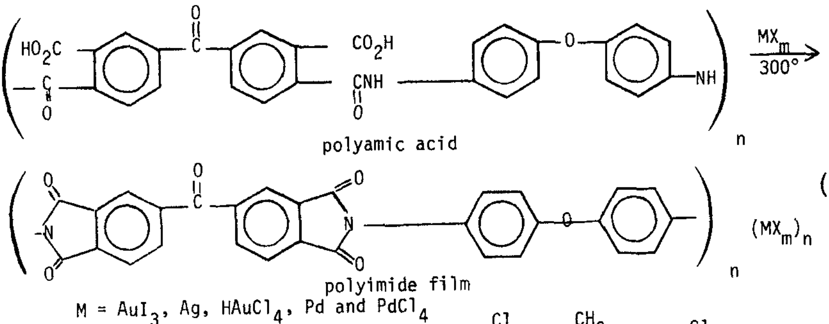

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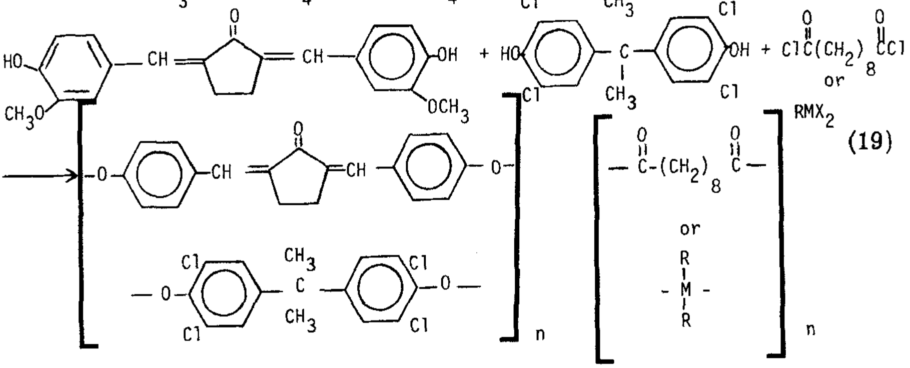


(19)

Applications of these films as electrical conductors or semiconductors, antistatic coatings, or shields against UV radiation have been proposed. The photocross-linkable films have potential applications in the preparation of printed circuits.

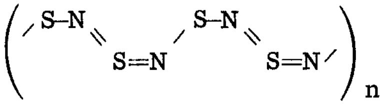
ONE-DIMENSIONAL ELECTRICALLY CONDUCTING POLYMERS [68]

Sulfur Nitride

Poly(sulfur nitride) is prepared by passing S_4N_4 over silver wool at 100-300°. The resulting S_2N_2 condenses onto cooled surfaces and polymerizes to form lustrous brittle metallic crystals of $(SN)_x$, 34. X-ray crystallography shows the existence of zig zag S—N chains. The polymer possesses a mixed valence state with one 4+ sulfur and one 2+ sulfur.

Although $(\text{—SN—})_x$ has been known since 1910, its electrical properties were not investigated until 1973 when M. Labes [69] and later

$$S_4N_4 \xrightarrow[Ag]{100\text{-}300^\circ} S_2N_2 \longrightarrow (\text{-}SN\text{-})_x \xrightarrow{Br_2} (SNBr_{0.4})_x \qquad (20)$$

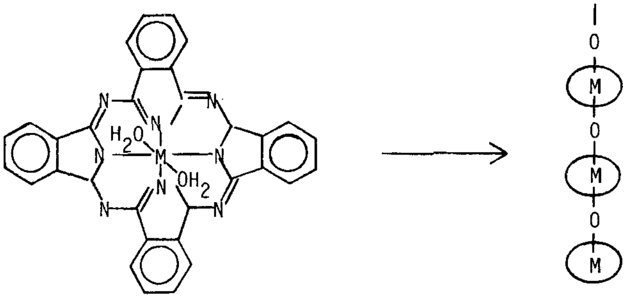


34

workers [70-71] began their studies. Aligned crystals of $(SN)_x$ could be formed which exhibited conductivity along the axis of the chains of $0.01\text{-}3.7 \times 10^3$ (ohm cm)$^{-1}$ at room temperature. Conductivity crosswise was a factor of 50-500 less. At 0.3 K, $(\text{-}SN\text{-})_x$ becomes a superconductor, the first compound of nonmetallic elements to exhibit this property. When $(SN)_x$ is exposed to bromine vapor, oxidation occurs and bromide ions become intercalated between the cationic polymeric chains. The resulting material, $SNBr_{0.4}$, undergoes an increase in density from 2.30 to 2.67 g/cm^3 and an increase in volume of 46%. Electrical conductivity increases by a factor of 10 to a maximum of 9.4×10^4 (ohm cm)$^{-1}$, slightly greater than that of metallic lead. The material retains its fibrous structure. Conductivity perpendicular to the axis is only 8 (ohm cm)$^{-1}$, a factor of 10^4 less. Thus a true one-dimensional conductor has been created.

Stacked Phthalocyanine Polymers

Great progress with phthalocyanine polymers has been made recently by Tobin Marks [72, 73] and his colleagues at Northwestern University. Marks had shown that metal phthalocyanine complexes could be oxidized with bromine or iodine to form a mixed valence state material which acts as a semiconductor. Although the phthalocyanine unit, which resembles graphite structurally, should conduct electricity, difficulty was encountered in passing electrons from one unit to the next. This problem could be avoided if the units were stacked face to face. Dehydration of silicon, germanium and tin phthalocyanines 35 produces such a stack, 36. When the stacked phthalocyanines are oxidized with iodine, a mixed valence polymeric cation is formed with I_3^- ions intercalated in the channels between the chains. Conductivity of up to 2×10^{-1} (ohm cm)$^{-1}$ for $[SiPcOI_{1.40}]_n$ and 1×10^{-1} (ohm cm)$^{-1}$ for $[GePcOI_2]_n$ were observed but only 2×10^{-4} (ohm cm)$^{-1}$ for $[SnPcOI_{5.5}]_n$. Thus in the Sn polymer the phthalocyanine units are too far apart for good conductivity. Perfect small crystals of these materials when prepared should have



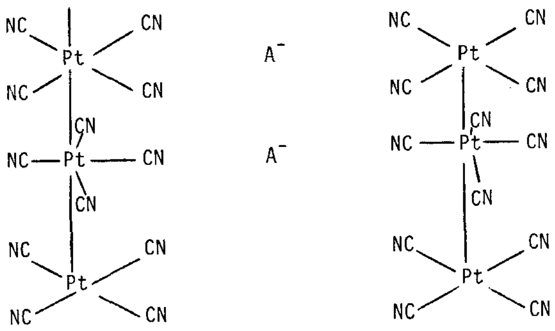
M = Si, Ge, Sn (21)

35 36

conductivity several powers of 10 greater. Conductivity should also be far greater along the axis than crosswise.

Tetracyanoplatinate Complexes

The unusual electrical properties of partially oxidized tetracyanoplatinate complexes were first investigated by K. Krogman in 1968 [74]. Since then, a number of authors have studied them [75-77]. Briefly, one example of a stacked tetracyanoplatinate complex can be prepared by electrolysis of a solution of Rb_2SO_4 and $Rb_2Pt(CN)_4$. Reddish brown crystals of $Rb_3Pt(CN)_4(SO_4{\cdot}HSO_4)_{0.49}{\cdot}H_2O$ form at the electrodes. The material exists as stacked $Pt(CN)_4$ units with the anions in a channel down the middle. The CN groups are staggered along the chains. Compounds of this type act as one-dimensional conductors with conductivity above 1 (ohm cm)$^{-1}$.



37

Polyacetylene

Polymers of acetylene had long been known but had been dismissed as intractable. The first high quality polycrystalline films were prepared by Shirakawa [83, 84] in 1971 by Ziegler-Natta polymerization of acetylene in toluene. Later investigations of its electrical properties have been conducted by Alan MacDiarmid, A. J. Heeger, and coworkers at the University of Pennsylvania [85].

Polyacetylene exists as cis, 38, and trans, 39, forms. If polymerization is conducted in toluene at -78°, the film is completely the cis isomer. At 150° in decane, the trans isomer is formed. The cis isomer can be converted to the trans by heating at 200° for 1 h.

cis polyacetylene

38

trans polyacetylene

39

Both cis and trans isomers appear as silvery flexible films. Electron microscopy shows that the $(CH)_x$ films exist as randomly oriented fibrils which fill about one-third of the space. Partially aligned films may be prepared, but fully aligned material has not yet been prepared.

Pure polyacetylene, either cis or trans, acts as an insulator [conductivity = 10^{-14} $(\text{ohm cm})^{-1}$]. Treatment of the film with Br_2, I_2, AsF_5, H_2SO_4, or $HClO_4$ causes partial oxidation (23). Conductivity rises rapidly and levels off at 5-10% oxidation. The maximum oxidation obtained so far is about 25%. The best cationic conductor so far obtained is cis $[CH(AsF_5)_{0.10}]_x$ at 1.2×10^3 $(\text{ohm cm})^{-1}$. Anionic conductors can also be obtained by reaction with alkali metals (24). The best is $(Li_{0.30}CH)_x$ at 2.0×10^2. Thus n- and p-type conductors can both be prepared.

$$C_2H_2 \xrightarrow[\substack{(C_4H_9O)_4Ti \\ \text{toluene}}]{Et_3Al} (CH)_x \tag{22}$$

$$-(CH-)_x \xrightarrow{AsF_5} (CH[AsF_5]_{0.10})_x \tag{23}$$

$$(CH)_x \xrightarrow{Li} (CHLi_{0.30})_x \tag{24}$$

Development of these materials is still in its infancy. Fully aligned films should have far greater conductivity and should be anisotropic. The conductivity could be controlled by the choice of dopant. The films have far lower density, 0.4-1.5 g/cm^3, than any known metal, show greater flexibility, and are inexpensive to prepare. Thus possible uses abound.

Polyphenylene

Polyacetylene, while useful for forming flexible films, does not have either great structural strength or high thermal stability. R. H. Baughman and co-workers at Allied Chemical Co. have shown that polyphenylene may also be doped to produce electrically conductive materials [86]. The best obtained so far is $C_6H_4(AsF_5)_{0.42}$, conductivity 460 (ohm cm)$^{-1}$. The doped material is far less sensitive to air and moisture than the corresponding polyacetylene derivatives. Doping with alkali metals is also possible, with conductivities up to 7 (ohm cm)$^{-1}$ obtainable. Doping with halogens does not produce highly conducting materials because of the greater difficulty in oxidizing the phenylene units as compared to acetylene units.

Since investigation of these materials is only in its early stages, no immediate applications have been found. It is felt that these complexes are good candidates for the first organic superconductor. If superconductivity can be developed at elevated temperatures, applications will be widespread.

CONCLUSION

In this review the author has tried to summarize the efforts of hundreds of workers in a new field with possible widespread applications. In view of the progress in the last 10 years, it will be exciting to see what happens in the next 10 years in this dynamic field.

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