

科技资料

**INORGANIC AND  
METAL-CONTAINING  
POLYMERIC MATERIALS**

# **INORGANIC AND METAL-CONTAINING POLYMERIC MATERIALS**

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## PREFACE

Research on metal-containing polymers began in the early 1960's when several workers found that vinyl ferrocene and other vinylic transition metal  $\pi$ -complexes would undergo polymerization under the same conditions as conventional organic monomers to form high polymers which incorporated a potentially reactive metal as an integral part of the polymer structures. Some of these materials could act as semiconductors and possessed one or two dimensional conductivity. Thus applications in electronics could be visualized immediately. Other workers found that reactions used to make simple metal chelates could be used to prepare polymers if the ligands were designed properly. As interest in homogeneous catalysts developed in the late 60's and early 70's, several investigators began binding homogeneous catalysts onto polymers, where the advantage of homogeneous catalysis - known reaction mechanisms and the advantage of heterogeneous catalysis - simplicity and ease of recovery of catalysts could both be obtained. Indeed the polymer matrix itself often enhanced the selectivity of the catalyst.

The first symposium on Organometallic Polymers, held at the National Meeting of the American Chemical Society in September 1977, attracted a large number of scientists interested in this field, both established investigators and newcomers. Subsequent symposia in 1977, 1979, 1983, and 1987 have seen the field mature. Hundreds of papers and patents have been published. Applications of these materials as semiconductors and one-dimensional conductors, as radiation shields or as photo-resists, as catalysts, as controlled release agents for drugs and biocides and a wide variety of applications have been studied (see Chapter 1).

This book is an expanded version of the papers presented at the Symposium on Inorganic and Organometallic Polymers at the National Meeting of the American Chemical Society in Miami Beach in September 1989. It is designed to give the reader an introduction to the wide varieties of structures that can be created and the many novel applications that can arise when traditional polymer science, involving primarily compounds of C, H, N, O, S, Si and the halogens is combined with the rest of the periodic table. Three review chapters give an overview of the entire field in the United States, Japan, and Western Europe (Chapter 1), the Soviet Union (Chapter 2), and the People's Republic of China (Chapter 3). Topics such as conductive polymers (Chapters 4,5,6), coordination polymers (Chapter 10), condensation polymers (Chapters 17-21), polyphosphazenes (Chapter 16), carborane siloxanes (Chapter 14), polymer bound catalysts (Chapters 3 and 6), and biopolymers (Chapters 19-20) have been covered in previous monographs cited in Chapter 1. Two new fields, pre-ceramic polymers and polysilanes have emerged since publication of our previous monograph in 1985. Polysilanes (Chapters 13 and 15) had been long sought after but were considered not to be stable. The first example of this class of compounds was reported in 1984. At the fall 1990 ACS

meeting, there were 143 papers on these materials. Pre-ceramic materials (Chapters 11-12) have emerged as a means of taking soluble, tractable polymeric materials which can be spun into fibers, woven into fabrics, cast into films, or fabricated into various shapes and pyrolyzing them to form inorganic materials such as metal oxides, carbides, nitrides, sulfides, or selenides which retain their original shape or else become highly porous, permitting their possible applications as catalysts. The discovery of "high temperature" superconductors in 1986 has given a further impetus to this field.

In summary, the possibilities for research and for new useful materials is as diverse as properties of the elements these materials contain. It is exciting to anticipate how this field will continue to develop in the coming years.

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Charles E. Carraher, Jr.  
Charles U. Pittman, Jr.  
Martel Zeldin  
Brian Currell

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## INORGANIC AND METAL-CONTAINING POLYMERS. AN OVERVIEW

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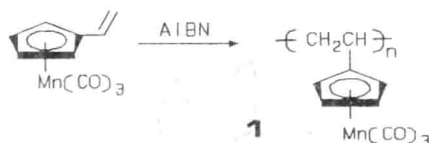
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### INTRODUCTION

Research on organometallic and inorganic polymers has increased enormously since about 1970. This chapter will give the reader an introduction to the variety of structures and applications which have been studied without any attempt to be comprehensive. Good recent reviews of organometallic<sup>1-8</sup> and inorganic polymers<sup>8-19</sup> are available and the reader is referred to them for a more complete introduction. The purpose of this chapter is to stimulate the reader to think about what might result if organic and inorganic chemistry are combined in polymer science. What interesting materials might result. To this end we will first look at some organometallic polymers and then examine some inorganic polymers. The division between these classes is somewhat arbitrary so the authors' prejudices will show.

Organic polymers generally are made from fewer than 10 elements (C, H, N, O, S, P halides) but with organometallic polymers well over 40 additional elements can be included. Polymers might include those with main group metals, such as silicon or germanium, or they could contain transition metals or rare earth elements the variety of structural variations seems endless. The metals may be pendant, as in poly( $\eta^5$ -vinylcyclopentadienyltricarbonylmanganese),<sup>20,21</sup> **1**, formed by the addition polymerization of its vinyl precursor. Metals may be present in the main chain as is found in titanium polyether, **2**, a product of interfacial polycondensation (see Scheme 1).



A large number of polycondensations have been performed as indicated in Scheme 1 (next page) to produce polymers with such metals as Zr, Hf, Ge, Sn, Pb and Bi in the main chain.<sup>22-26</sup>

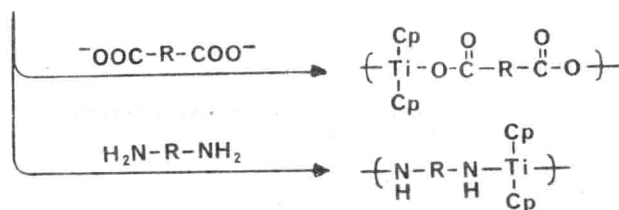
Similarly, a wide range of  $\eta^5$ -vinylcyclopentadienyl monomers containing various transition metals have been both homo- and copolymerized.<sup>20,21,27-42</sup> The aromatic cyclopentadienyl ring behaves as an extremely strong electron donating substituent (Alfrey-Price values of  $e = -1.9$  to  $-2.1$  for such monomers versus  $-0.80$  for styrene,  $-1.37$  for *p*-N,N-dimethylaminostyrene and  $-1.96$  for 1,1'-dianisylethylene).<sup>43</sup> Copolymers with styrene, acrylonitrile, methyl methacrylate, N-vinylpyrrolidone and other monomers have been made for such ( $\eta^5$ -vinylcyclopentadienylcarbonylmetal) systems and for metal containing acrylates, methacrylates and related systems.

$$\begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{Ti} \\ | \\ \text{C}_6\text{H}_5 \end{array} \begin{array}{c} \text{Cl} \\ | \\ \text{Cl} \end{array} + \text{HO}-\text{C}_6\text{H}_4-\text{OH} \xrightarrow[\text{CONDENSATION}]{\text{INTERFACIAL}} \left[ \begin{array}{c} \text{C}_6\text{H}_5 \\ | \\ \text{Ti} \\ | \\ \text{C}_6\text{H}_5 \end{array} \text{O}-\text{C}_6\text{H}_4-\text{O} \right]_n$$

CARRAHER, 1974, 1977

**2**

CARRAHER, 1974, 1977



Carraher 1973  
1983

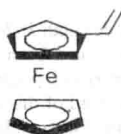
$$R_2ZrX_2$$


with

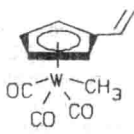


DIOLS  
DITHIOLS  
DIAMINES  
HYDRAZINES  
DITHIOAMIDES  
DIOXIMES

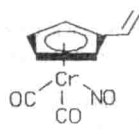
DITHIOHYDRAZIDES  
HYDRAZIDES  
UREA



Ref. 27-29



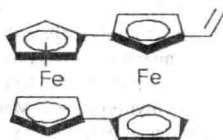
Ref. 33-34



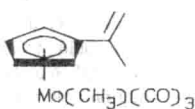
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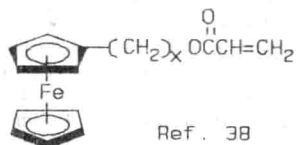
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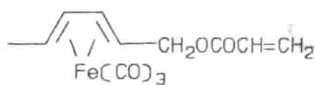
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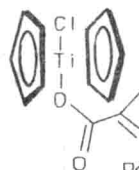
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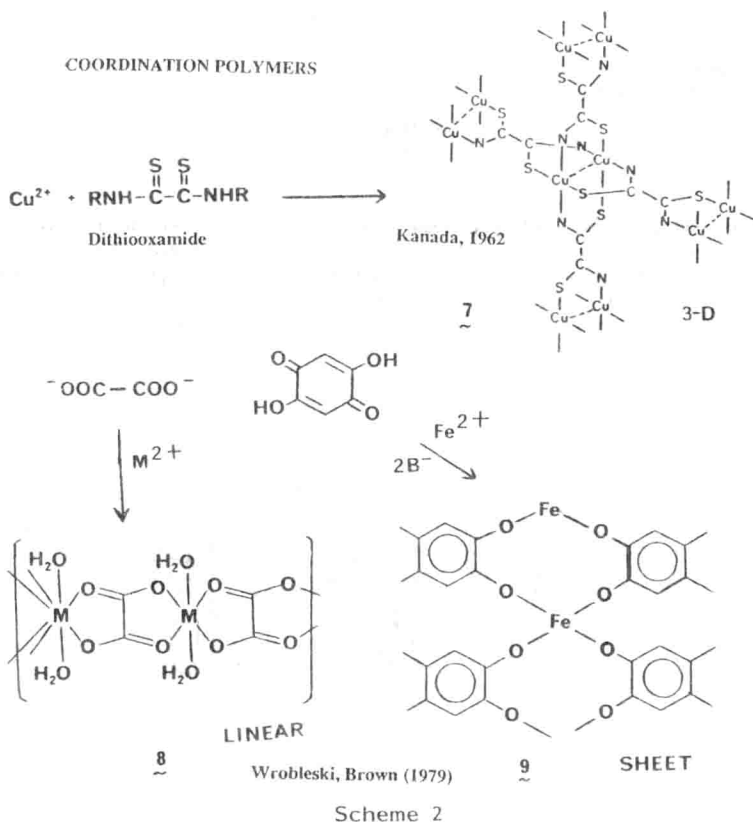
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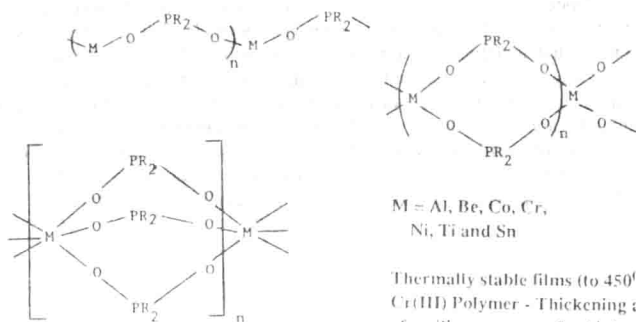
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Scheme 1

The  $\eta^5$ -vinylcyclopentadienyl metal monomers are polymerized by radical initiation<sup>27,42</sup> and they are inert to anionic initiation.<sup>43,44</sup> Cationic initiators have given low molecular weights or no polymers<sup>41,44,45</sup> except for 1,1'-divinylferrocene<sup>46</sup> which undergoes cycloliner polymerization and molecular weights up to 35,000 have been obtained using  $\text{BF}_3 \cdot \text{OEt}_2$ . Radical initiation has led to unusual homopolymerization kinetics in all systems studied carefully so far. Due to the propensity of metals to oxidize, peroxide initiators have not usually been suitable but azo initiators are satisfactory. Unlike vinylcyclopentadienyl monomers, ferrocenylmethyl methacrylate (and acrylate) are readily initiated with anionic systems<sup>43,47</sup> and the molecular weight may be varied regularly using  $\text{LiAlH}_4$ .<sup>47</sup>  $\text{LiAlH}_4$ /TMEDA produced living polymers of these ferrocene acrylic monomers from which block copolymers were achieved with acrylonitrile and MMA.<sup>47</sup>



Organometallic polymers come in a huge variety of structures. Coordination polymers illustrate this phenomena. For example, iron complexes of the dianion of oxalic acid are linear chain structures (see Scheme 2). However, if 2,5-hydroxyquinone is used as the chelating agent, a 2-dimensional planar sheet network is formed.<sup>48</sup> Coordination polymers may also form in three-dimensional networks as represented by the catana- $\mu$ -(N,N'-di-substituted dithiooxamido)copper complex which results from the reaction of  $\text{Cu}(\text{II})$  with dithiooxamides.<sup>49</sup> Such materials are insoluble. The polymeric metal phosphinates shown in Scheme 3 can have single, double or triple-bridged structures. They have been made using Al, Be, Co, Cr, Ni, Ti and Sn as the metal.<sup>14</sup> They form films with thermal stabilities as high as  $450^\circ\text{C}$  and the chromium(III) species have been used as thickening agents for silicone greases for high pressure uses.

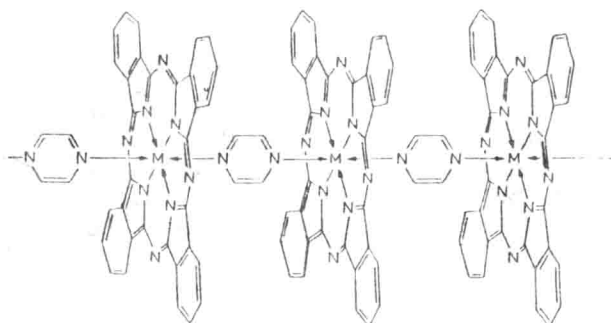


Thermally stable films (to 450<sup>0</sup>)  
Cr(III) Polymer - Thickening agent  
for silicone greases for high  
pressure uses.

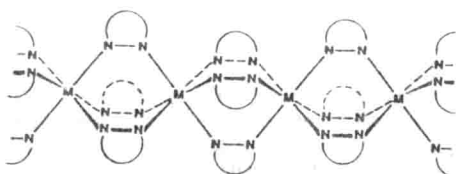
POLY(METAL PHOSPHINATES)  
BLOCK (1970)

Scheme 3

Other wonderful shapes can also be found. The metal phthalocyanine structure with its bridging pyrazine units, shown in Scheme 4, resembles a shiskabob.<sup>50</sup> The metal and pyrazine chain forms the "skewer" which "pierces" the phthalocyanine groups. A braided structure is also represented in Scheme 4. 5-Phenyltetrazolate reacts with metals from all three transition metal series to give the loops shown. The Ni(II) and Fe(II) adducts give extremely viscous aqueous solutions from which both flexible sheets and threads have been made.<sup>51</sup>



DIEL, MARKS, 1984

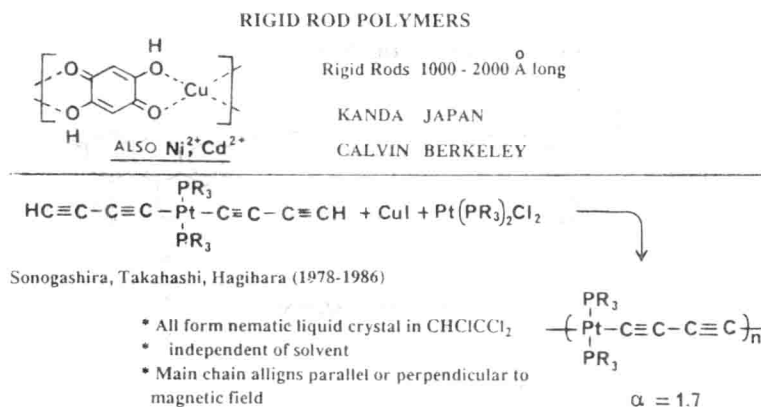


THREADS AND FLEXIBLE SHEETS  
FROM VISCOUS SOLUTIONS

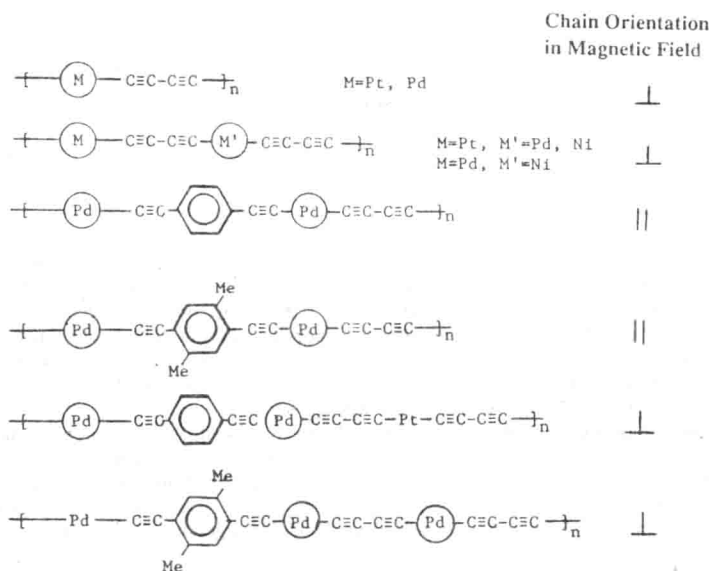
RICHARDS ET AL., 1985

Scheme 4

Rigid rods are another shape into which coordination polymers and organometallic polymers with metals in the main chain have been made. One-to-one complexes of 2,5-dihydroxy-p-benzoquinone with Cu(II), Ni(II) and Cd(II) form polymers (see Scheme 5). The Cu(II) polymers were rigid rods 1000-2000 Å long.<sup>5, 53</sup> Transition metal-polyene polymers have been prepared with rod-like structures,<sup>54-60</sup> as illustrated in Scheme 5, by the reaction of cuprous iodide with *trans*-bis(tri-*n*-butylphosphine)platinum. The linear structures result from all-*trans* configurations at Pt or Pd atoms. This class of polymers, further illustrated in Scheme 6, form nematic liquid crystals. Some of them align their main chain in a direction perpendicular to an applied magnetic field while others align parallel to the field.<sup>55,56</sup> The nature of the transition metal within the chain determines its magnetic properties. The rigid rod structure is indicated by large Mark-Houwink exponents, the independence of  $[\eta]$  values from solvent and the agreement of sedimentation-equilibrium experiments with parameters derived from an ellipsoid revolution model for rigid rods.



Scheme 5

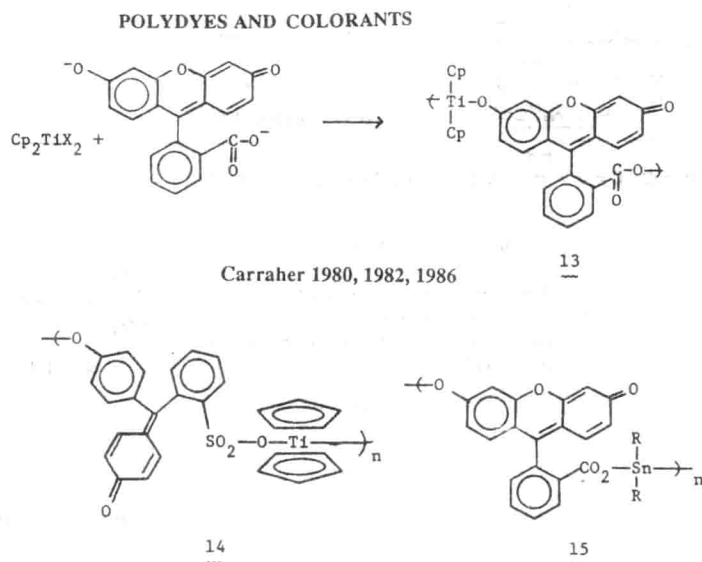


Scheme 6

## ORGANOMETALLIC POLYMERS WITH UNUSUAL PROPERTIES AND APPLICATIONS

In order to convey to the reader just a small portion of the vast diversity of known structures and applications a few examples have been selected. These examples are not necessarily representative of the field in any systematic way but they are selected to provide a flavor of what the field has to offer.

Organometallic condensation polymers have been used as dyes or pigments which resist bleeding, blooming or plateout.<sup>61-63</sup> An example, shown in Scheme 7, is the reaction product of fluorescein or sulfonphthalein dyes with dicyclopentadienyldichlorotitanium or organostannanes. Degrees of polymerization or excess of 100 have been claimed for such polydyes. Such polymers should adhere to surfaces far better than the monomeric analogs.

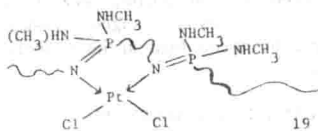


Scheme 7

Coordination complexes of platinum are under study as medicinal agents. For example, polyphosphazenes have nitrogen atoms with unshared electron pairs in the main chain. These nitrogens can chelate platinum dichloride as shown in Scheme 8. The poly[bis(methylamine)phosphazene], shown in Scheme 8, has tumor-inhibiting activity against mouse P388 lymphocytic leukemia and was active in the Ehrlich ascites tumor-regression test.<sup>61</sup> The reaction of  $\text{K}_2\text{PtCl}_4$  with pyrimidines, purines, hydrazines and diamines produces coordination polymers. An example of such a polymer which represses the replication of Poliovirus I and L RNA virus at a level of 10-20  $\mu\text{g/mL}$  is shown in Scheme 8.<sup>62</sup>

Vinyl addition polymers of styrene, substituted in the para position with a europium chelate, have been made by Okamoto.<sup>63</sup> These polymers are being studied as active species in the electronic energy-transfer processes of lasers (see Scheme 8). Absorbed energy from xenon flashlamp pulsing is efficiently transferred to europium and the resulting polymers showed superfluorescence.<sup>63</sup> Even more bizarre was the use of poly(vinylruthenocene) and poly(vinylsomoecene) as preheat shields for targets in inertial-confinement nuclear fusion experiments.<sup>64</sup> Temperatures of  $50 \times 10^6$  °C are needed and this is achieved by focusing high intensity laser beams ( $8 \times 10^{12}$  W/cm.) on spheres of  $^2\text{H}_2$  and  $^3\text{H}_2$ . The release of suprathermal electrons from the target is moderated by polymer layers having 1 to 4 atom % of high Z ( $Z=50-85$ ) species and this permits higher fusion efficiencies. Poly(vinylruthenocene) and poly(vinylsomoecene) were used in some of these experiments.

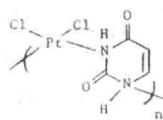
# MEDICINAL AGENTS



19

Tumor-inhibiting against  
mouse P388 lymphocytic leukemia  
and in Ehrlich ascites tumor-test

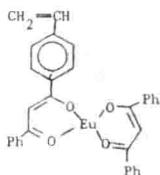
ALLOCK



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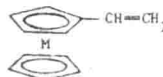
Represses poliovirus I  
and L rna virus replication  
tumoral cell growth stopped  
CARRAHER

## LASER - RELATED



21

Laser electronic energy  
transfer processes  
OKAMOTO 1985  
mma-copolymer superfluorescence  
when pulsed by xenon flashlamps



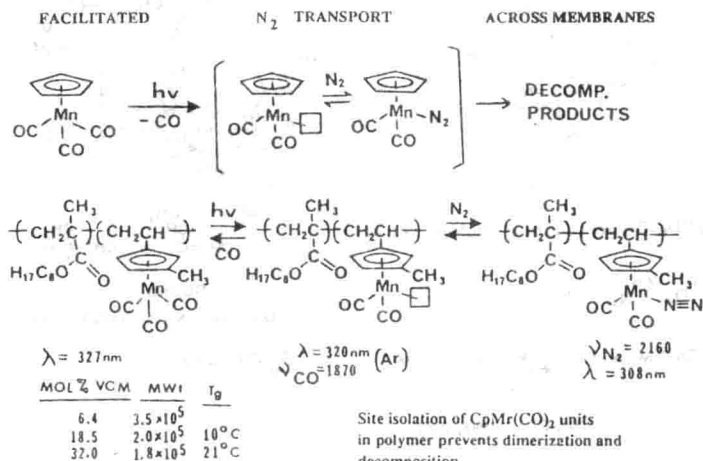
22a M = Ru  
22b M = Os

SHEATS  
KOOL  
PITTMAN

Preheat shields for laser  
targets in inertial-confinement  
nuclear fusion  
 $8 \times 10^{12} \text{ W/cm}^2$   $50 \times 10^6 \text{ }^\circ\text{C}$

## Scheme 8

A most interesting application of organometallic polymers involves the concept of "site isolation" in a polymer with "facilitated transport" through a membrane. In a series of papers the selective transport of oxygen or nitrogen through membranes containing organometallic polymers was examined.<sup>65-69</sup> Cyclopentadienyltricarbonylmanganese, upon irradiation with UV light, loses carbon monoxide and generates a coordinatively unsaturated complex which binds nitrogen reversibly (Scheme 9). However, the unsaturated species is unstable and rapid decomposition occurs by self-reaction in solution. However, when an octyl methacrylate copolymer of the 1-vinyl-3-methyl manganese complex is made and irradiated, the resulting coordinatively unsaturated complex is stable since these sites are isolated from one another and can't react. New carbonyl bands are seen in the IR (Scheme 9). Exposure to nitrogen generates the corresponding nitrogen

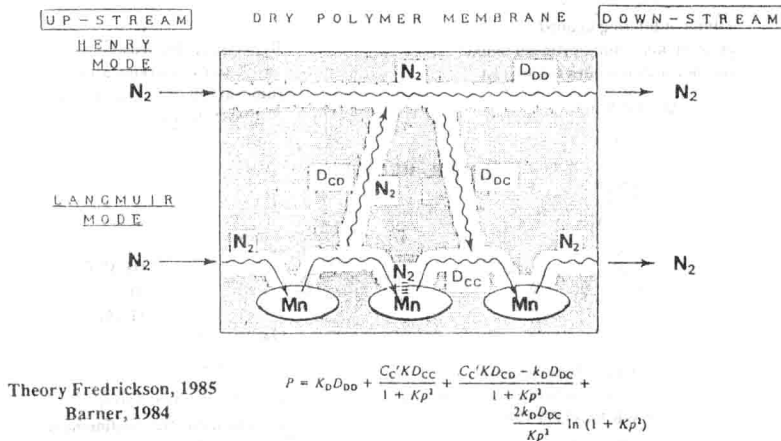


Tsuchida, Nishide 1986-89  
Pittman, 1977

## Scheme 9

complex ( $\nu_{N_2} = 2160\text{cm}^{-1}$ ) reversibly. A membrane composed of this polymer will facilitate the transport of nitrogen as shown in Scheme 10. Dual transport modes, both Henry and Langmuir modes, operate. Nitrogen reversibly jumps from one manganese atom, containing a vacant coordination site, to another. The copolymer compositions and properties can be varied over a range of properties.

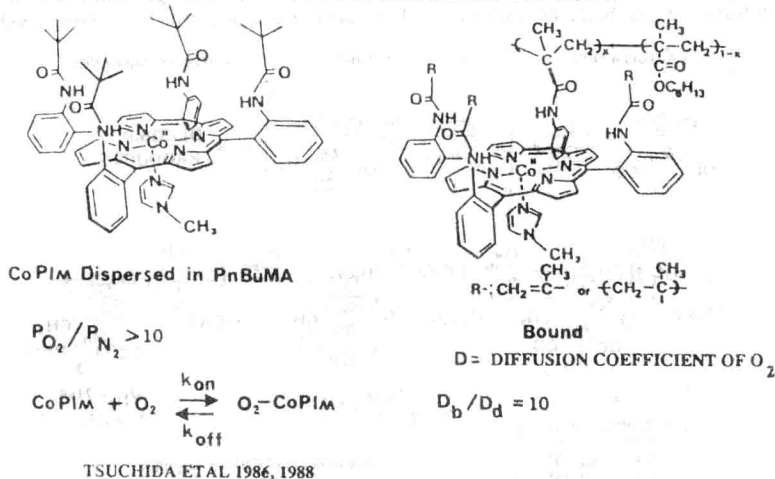
#### DUAL-MODE TRANSPORT (LANGMUIR AND HENRY)



Scheme 10

Oxygen transport has received considerable attention.<sup>65-69</sup> "Picket fence" cobalt porphyrin complexes are selectively blocked at the hindered face so that imidazole bases may only coordinate from the open side. As seen in Scheme 11, the imidazole-coordinated picket fence complex has a vacant coordination site at the top. The small linear oxygen molecule can traverse the "fence" to coordinate reversibly with cobalt from the top side. By dispersing such complexes in films one can build membranes which facilitate oxygen transport. This type of chemistry is one approach to making artificial blood.

#### OXYGEN BINDING AND TRANSPORT THROUGH MEMBRANE



Scheme 11

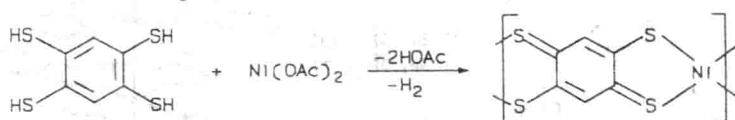
Organometallic and inorganic polymers have frequently been investigated as possible conducting polymers. An early trick was to look for extended conjugation and then introduce mixed valence states. This most often led to charge-hopping type semiconductors. Thus, both poly(ferrocenylacetylene) and poly(vinyl-



ferrocene) were semiconductors which give highest values of conductivity at about 50/50 ferrocene: ferricenium ratios.<sup>70</sup>

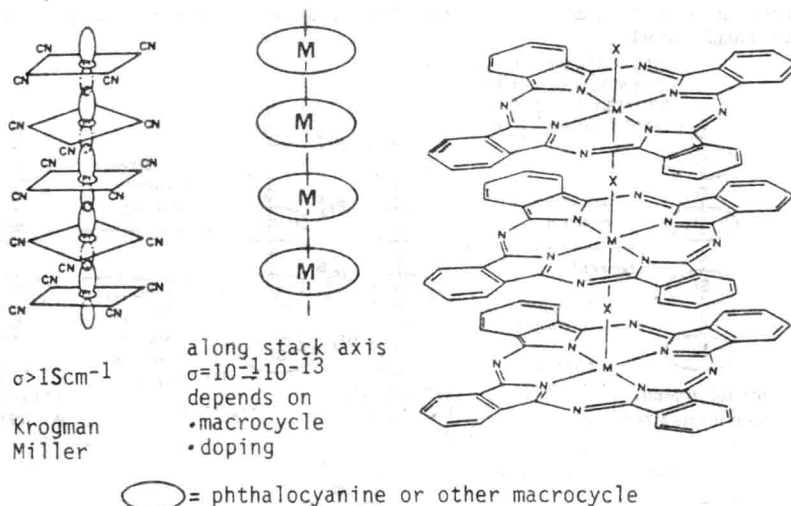


A large number of conjugated coordination polymers of regular structure have been made over many years. Though frequently insoluble amorphous powders, they have, in some cases exhibited, encouraging conductivities. An example of this class is the metal poly(benzodithiolenes) which have been prepared by the reaction of benzene-1,2,4,5-tetrathiol with Ni(II), Fe(II) and Cu(II).<sup>71</sup> They were paramagnetic conductors with conductivities ranging from  $10^{-4}$  to  $10^{-1}$  Scm<sup>-1</sup>. A systematic study of structure versus conductivity in this area has proved very difficult so we will turn our attention to the stacked polymers where structure versus property advances have been forthcoming.



Example stacked polymers are shown in Scheme 12. These can be stacks giving metal chains or metal atoms may alternate with, for example, oxygen atoms. Tetracyanoplatinate stacked complexes are of interest because they have continuous metal-metal orbital overlap down the stack axis.<sup>72-74</sup> The stacks of square-planar Pt(CN)<sub>4</sub> units contain anions in spaces between the stacks. The cyano groups are staggered with respect to those coordinating adjacent Pt atoms. These, so-called Krogmann complexes, are one-dimensional conductors with conductivities greater than 1 Scm<sup>-1</sup>. Work on the Krogmann complexes seems to have stimulated interest on phthalocyanine stacks also represented in Scheme 12. Here the ellipses represent the stacked macrocycles with direct metal-metal interactions down the chain. A variety of such stacked polymers have been made by the reaction of transition metal salts with tetranitriles<sup>75,76</sup> 1,2,4,5-tetracyanobenzene,<sup>77</sup> pyromellitic dianhydride<sup>78</sup> or tetracarboxylic acid derivatives.<sup>79</sup> These systems are semiconducting, typically, with pressed pellet conductivities ranging from  $10^{-1}$  to  $10^{-13}$  Scm<sup>-1</sup>.

#### STACKED POLYMERS



Scheme 12