

## CHAPTER II

### FERROCENE POLYMERS AND TECHNIQUES OF PREPARING CONDUCTIVE POLYMERS

#### A. Review of ferrocene-containing polymers (1955-1984)

This section will review important research into ferrocene-containing polymers covering the period from 1955 to 1984.

From 1955 to 1970, a large variety of polymers containing ferrocene were prepared and reviewed [24].

It has been found that ferrocene is readily oxidized to the stable ferricinium ion at a potential of  $-0.56$  volts [25]. Free radicals, such as benzoyl peroxide, oxidize ferrocene instead of initiating polymerization; and cations, such as nitronium ion, oxidize ferrocene instead of attacking the cyclopentadienyl rings electrophilically. In strong acids, ferrocene is protonated at iron [26]. Thus, in some cases normal cationic polymerization of ferrocene derivatives will be thwarted. Furthermore, initial free radical polymerization of ferrocene derivatives can be precluded if the iron atom catalyzes either preferential decomposition of the initiator, or reduces growing chain radicals.

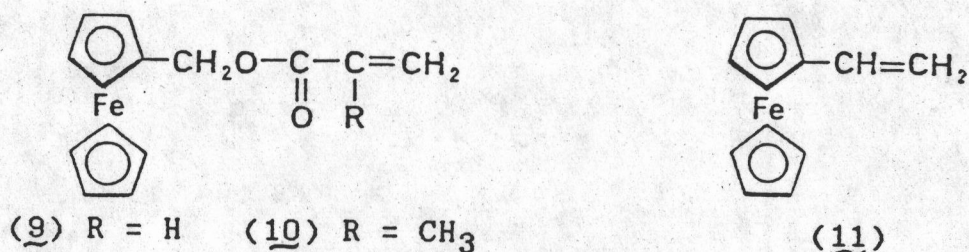
Richards [27] and Hammond [28] have demonstrated that ferrocene functions as a very efficient quencher of photo-

chemically generated triplet states in anthracene, as well as a sensitizer in the photochemical dimerization of isoprene and the isomerization of cis- to trans-piperylene.

Thus, coating made from co-polymers which include the ferrocene nucleus could exhibit special stability to many photochemical degradation reactions brought about by exposure to sunlight. This is an especially attractive possibility when one considers ferrocenes to have low toxicity and high absorption of ultraviolet [29] and gamma radiation [30].

Also, ferrocene might serve as an internal catalyst to promote certain curing reactions. The easy oxidation of ferrocene might lead to polymers containing ferricinium units useful in special adhesive roles.

The AIBN catalyzed solution polymerization of ferrocenyl methyl acrylate (9), ferrocenyl methyl methacrylate (10) and vinylferrocene(11) and the characterization of these polymers have also been investigated [31].



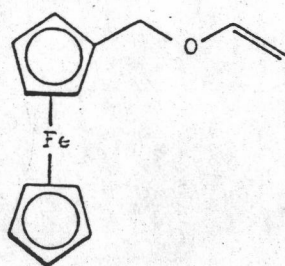
Radical copolymerization of vinylferrocene and 2-vinylnaphthalene gave a copolymer, the composition of which indicated

Mayo-Lewis reactivity ratios of 0.08 and 5.5 respectively [32].

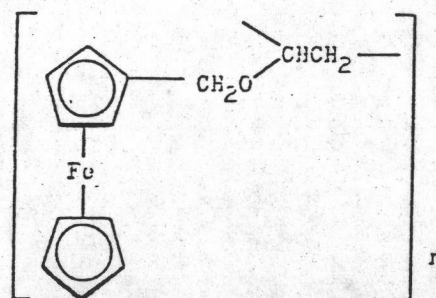
The gamma radiation initiated free radical copolymerization of ferrocenyl methyl methacrylate with styrene, methyl methacrylate and ethyl acrylate in benzene has been investigated [33].

Furthermore, the gamma ray induced polymerizations of ferrocenyl methyl methacrylate and 1,1'-ferrocenyldi(methyl methacrylate) have been investigated [34].

Ferrocenyl methanol was converted to the vinyl ether (12) by heating with  $\text{BuOCH}=\text{CH}_2$  in the presence of mercury (II) acetate. The vinyl ether was then polymerized with boron trifluoride etherate to the linear macromolecule (13 ;  $n=10-11$ ) [35].



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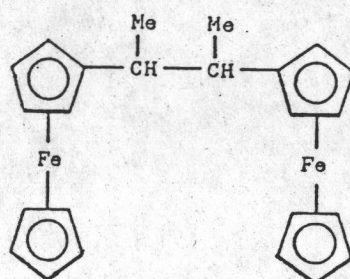
Ferrocenylacetylene has been heated at 190-300°C in the presence of tri-iso-propylborane to form poly(ferrocenyl acetylene) in 80% yield [36].

Ferrocenyl methyl acrylate was homopolymerized in the presence of lithium aluminiumhydride and ethyl magnesium bromide at  $-78^{\circ}\text{C}$  [37].

Plasma polymerization of vinylferrocene has been used to produced a stable coating of an electroactive polymer on pyrolytic graphite electrode surfaces. The electrochemical properties of the polymer film were investigated by cyclic voltametry and the film was found to be electrocatalytically active in the oxidation of ascorbic acid in aqueous acid solution [38].

Vinylferrocene was polymerized in a radio frequency argon plasma to create thin adherent films of polymer on glass, carbon and platinum electrodes. The electrochemistry of the modified electrodes was investigated [39].

Acylation, reduction and dehydration of 2,3-diferrocenyl butane (14) resulted in 2-ferrocenyl-3-(vinyl ferrocenyl)butane which was polymerized with the presence of boron trifluoride etherate and copolymerized with methyl methacrylate to give a copolymer of molecular weight 7700 [40].



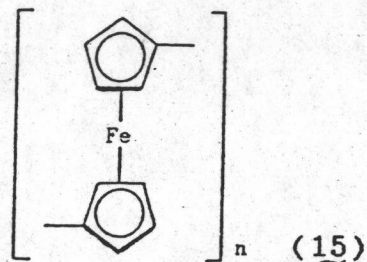
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The condensation of p-ferrocenylaniline, acetylferrocene oxime and p-ferrocenylphenol with  $P(S)Cl_3$  gave insoluble dark brown polymeric products which were thermally stable in air at temperature less than  $200^\circ C$  [41].

The radical copolymerization of  $\alpha$ -cyclopentadienylidene ethylferrocene with butadiene or isoprene gave brown rubbery polymers containing up to 3.02% iron and with molecular weights up to 28,840 [42].

The copolymerization of isopropenylferrocene, 1-ferrocenyl-1,3-butadiene and vinylferrocene with butadiene, chloroprene or isoprene resulted in low molecular weight liquid prepolymers containing carboxyl end groups. These prepolymers underwent subsequent chain extension to give products suitable for use as polymeric binders [43].

1,1'-Dibromoferrocene and 1,1'-diiodoferrocene underwent dehalogenation and polymerization with magnesium to form poly-(1,1'-ferrocenylene)(15) in yields of up to 77%. The polymer had high thermal stability and was converted to a semiconductor by doping with acceptors such as TCNQ and iodine [44].



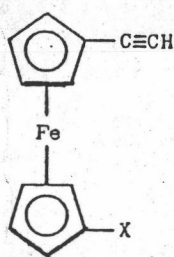
Chemical oxidation, irradiation or electrochemical oxidation of polymers with ferrocenyl groups, or other low ionization potential groups, gave cationic polymers. These were potentially useful as polymer-modified electrodes, as semiconducting polymers and as resists for high resolution electron beams [45].

Ferrocenes are popular for redox polymer-coated electrodes just as they were in monolayer attachments. Poly(vinylferrocene) has been dip coated [46], droplet evaporated [47-48], spin coated [49], oxidatively electrochemically deposited [46, 50-52], and oxidatively photochemically deposited [48] on Pt.

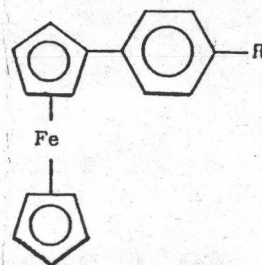
Moessbauer's evidence for the structure of linear, saturated polymers formed by radical polymerization of 1,1'-divinylferrocene was consistent with cyclopolymers containing a three-carbon bridged ferrocene group in the main chain. Polymers formed in the presence of cationic initiators appeared to contain unstrained ferrocene groups consistent with five-carbon bridged bicyclic units or a ladder structure [53].

Dicarbonylferrocenes have been polymerized with biuret to form poly(ferrocenyleniminoimides) and with aromatic diamines to form poly(ferrocenylenazomethines). These new ferrocene polymers have been studied by DTA and thermogravimetry and it was found that the poly(ferrocenylene azomethines) displayed good thermal stability at 200°C [54-55].

Polyenes, polyiminoimides and Schiff polybases containing ferrocene residues have been obtained by polymerization and by polycondensation. Among the monomers used were ethynylferrocene (16; X= H), 1-chloro-1'-ethynyl ferrocene (16; X= Cl), the ferrocenylstyrene (17; R= CCl=CHCHO), the phenylacetylene (17; R= C=CH) and the aceto phenone (17; R= COMe). Polymers with linear or three-dimensional structures were obtained and exhibited good thermal stability and semiconducting properties [56].

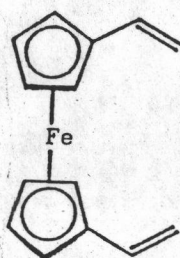


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(17)

Radical polymerization of 1,1'-divinylferrocene (18) produced a homopolymer which was shown by  $^{13}\text{C}$  NMR and Moessbauer spectroscopy to be a cyclopolymer containing a three-carbon bridged ferrocene unit [57].



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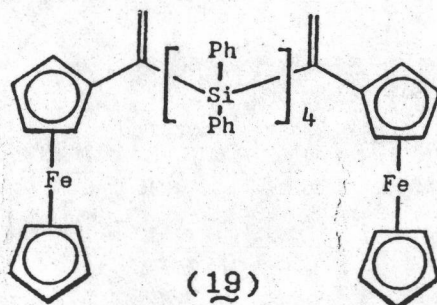
When cationic polymerization is used, then the polymer had an acyclic structure. Divinylbenzene and vinylferrocene have been copolymerized at 680°C and 125 MPa and the resulting copolymer was subjected to pressure pyrolysis to give carbon containing finely dispersed iron. Electroactive plasma polymerized vinylferrocene (PPVF) films have been deposited on glassy carbon electrodes for use in electrochemical X-ray photoelectron spectroscopic and ellipsometric studies [58].

1,1'-Diisopropenylferrocene underwent cationic homopolymerization in the presence of trifluoroacetic acid or boron trifluoride etherate to give a polymer with a number average molecular weight of 8100-14700 [59].

Adducts of crystalline poly(1,1'-ferrocenylene) with various electron acceptors such as iodine, 2,2'-(2,5-cyclohexadiene-1,4-diylidene)bispropanedinitrile and tetracyanoethylene have been prepared. The electrical conductivities of the resulting adducts are relatively high [60].

The preparation and polymerization of the monomers  $RR'C=CH_2$  and  $(H_2C=CR')_2Z$  (R= ferrocenyl, R'= m-carbonyl, Z= 1,7-m-carboranediyl) have been investigated. Treatment of acetylferrocene with  $Li(SiPh_2)_4Li$ , followed by dehydration, produced the monomer (19). The polymerization of this monomer was also studied [61].





A series of vinylferrocene-methyl methacrylate copolymers has been prepared and their absorption from toluene and chloroform onto pyrogenic silicas was measured [62].

Copolymers of vinylferrocene with acrylonitrile, maleic anhydride, N-vinylnaphthalene and acenaphthylene were coated on platinum and semiconductor electrodes such as  $\text{SnO}_2$  and  $\text{In}_2\text{O}_3$ . The photochemical properties of these copolymer films were investigated [63-64].

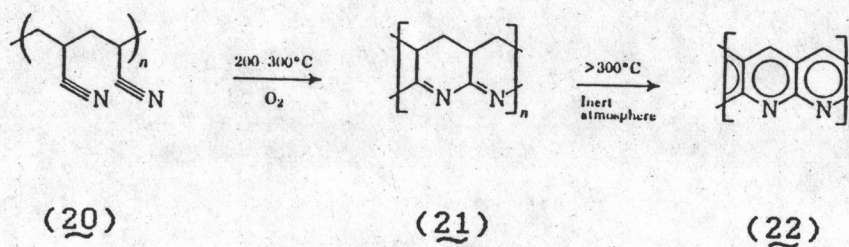
Electrically conducting polymers have been obtained from insulating polymer in solution with its concurrent precipitation. Thus anodic oxidation of a solution of poly(vinylferrocene) gave a deep blue polymeric precipitate containing a partially oxidized mixed-valence salt with ferrocene and ferrocenium ion groups [65].

Semiconducting 1,1'-ferrocenylene polymers have been prepared by doping the polymer with, for example, arsenic(V) fluoride [66].

## B. Pyrolysis System [21]

The pyrolysis system, which is the preparation of conductive polymers, consists of eliminating heteroatoms, e.g. halogen, oxygen, and nitrogen, from the polymer by heating and forming extended aromatic structures approaching that of graphite. Graphite is a prototypical synthetic metal when treated with certain dopants. It is believed that pyrolysis increases charge-carrier mobilities by virtue of producing extended conjugation and increases in the number of charge carriers by the formation of free radicals, which can act as donors to form hole carriers (cations) and as acceptors to form electron carriers (anions).

Polymer pyrolysis is the oldest method of generating conductive organic materials. One system that has been extensively studied is polyacrylonitrile (20). Pyrolysis occurs in three stages. The first stage is achieved by heating the polymer to 200-300°C in the presence of oxygen. This process results in closure of six-membered rings by formation of conjugated imino functionalities (21).

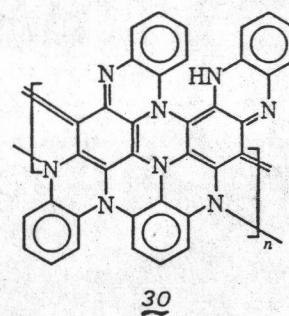
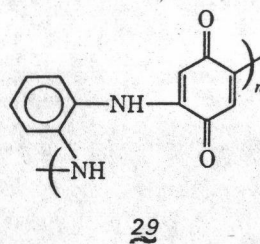
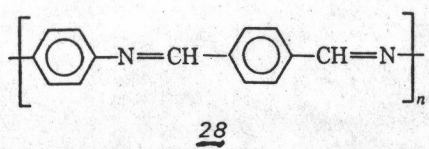
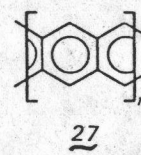
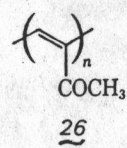
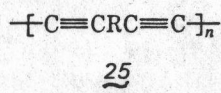
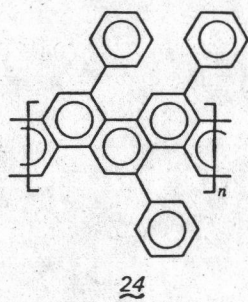
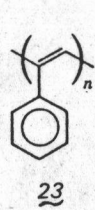


The second stage consists of heating the adduct to 300°C in an inert atmosphere and results in dehydrogenation of the backbone, which leads to a fully conjugated ladder polymer structure (22). Extended planar graphite structure is believed to form above 600°C by loss of NH<sub>3</sub> or HCN. The conductivity can be controlled by temperature of the third stage of pyrolysis. At 400-500°C, conductivities of 10<sup>-12</sup>-10<sup>-3</sup> S/cm can be achieved. If the third stage is carried out in the presence of AlCl<sub>3</sub> at 900°C, a conductivity of 20 S/cm characterizes the resultant black Orlon.

Pyrolysis of a number of other polymers yields materials with conductivities in excess of 10<sup>-10</sup> S/cm. Some representative examples are cited in Table 1.

Table 1. Conductive Polymers Formed by Pyrolysis of Polymers

Starting polymer ( $\sigma_{25^\circ\text{C}}$ ), S/cm	Structure no.	Pyrolysis conditions, °C	Proposed product	$\sigma_{25^\circ\text{C}}$ , S/cm
polyphenylacetylene, 10 <sup>-13</sup>	<u>23</u>	300-700	<u>24</u>	$\leq 5 \times 10^{-2}$
polyynes, 10 <sup>-6</sup> -10 <sup>-14</sup>	<u>25</u>	200-600		$\leq 2$
polyacetylacetylene	<u>26</u>	400-870	<u>27</u>	$\leq 10^{-2}$
metal-containing ion exchange resins		700-1200		$\leq 100$
polymeric Schiff base, 10 <sup>-13</sup>	<u>28</u>	500		$6 \times 10^{-2}$
polyaminoquinones, 10 <sup>-13</sup>	<u>29</u>	350	<u>30</u>	10 <sup>-7</sup>



### C. Polymer Composite System [2]

The polymer composite system is the system obtaining modest conductivity values ( $\sigma = \text{ca } 0.001 \text{ S/cm}$ ) with the electrical properties which can be achieved by filling inert polymer with conductors, e.g., metals or carbon black. The conductivity depends upon contact between the particles of the conductor. If properly chosen, the filler can also improve the electrical properties of the composite relative to those of the polymer.

The electrical conductivity occurs by interparticle contact of the filler species. Therefore, a very steep dependence of the conductivity upon the filler load level result is indicated in Fig.1. for a typical case in which the conductivity changes by ca  $10^3$  over a range of ca 5 wt% change in filler loading. Filler loadings of 10-40 wt% usually are employed. The geometry of the filler particles is also significant. Use of extended fibers as opposed to flakes yields higher conductivity at a given loading level. The higher the aspect ratio (i.e., length to width or length to diameter), the greater the effect.

This is shown schematically in Fig.1 as a shift in the conductivity curve to lower loading levels. The use of high aspect ratio fillers, in some instances, leads to significant improvements in certain tensile and flexural properties. Processing techniques, e.g., low shear techniques, that preserve the

high aspect ratio are required to preserve these qualities in the final product.

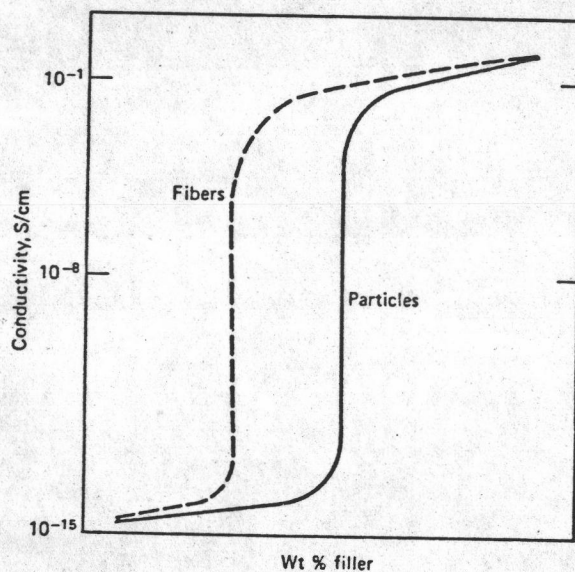


Fig. 1. Typical curve of conductivity as a function of composition for polymer composites. The line for filler flakes is displaced to higher loadings than the dashed line for extended fillers because the fibers yield more filler-filler contacts than the flakes at equivalent loadings.

The filler material must be characterized by high conductivity. Other criteria determine the cost of the materials and are used in order of increasing current costs on a weight basis: carbon black; metals; metallized glass fibers; pitch-derived carbon fibers; and polyacrylonitrile-derived carbon fibers. Some representative conductive polymer composites are indicated in Table 2 .

Table 2 - Data for Typical Commercially Available Conductive Polymer Composites

Composite	Tensile strength, MPa	Tensile elongation, %	Flexural strength, MPa	Flexural modulus $\times 10^4$ , MPa	Izod impact strength, J/m	$\sigma_{25^\circ\text{C}}$ , S/cm
polycarbonate (PC)	65	94	82.1	2.5		$10^{-16}$
PC + 20 wt % Al flake	47	5	77.9	3.99	84.4	$10^{-15}$
PC + 30 wt % Al flake	41	3	74.5	4.54	107	1
PC + 25 wt % metallized glass	82.1	4	113	6.61	59.8	$10^{-7}$
PC + 40 wt % metallized glass	86.9	5	123	9.79	72.6	$10^{-1}$
PC + 10 wt % PAN carbon fiber <sup>d</sup>	78.6	6	123	5.59	58.2	$10^{-8}$
PC + 40 wt % PAN carbon fiber <sup>d</sup>	181	6	232	21.5	101	$10^{-2}$
PC + 25 wt % pitch carbon fiber	69.7	5	101	5.97	59.8	$10^{-6}$
PC + 40 wt % pitch carbon fiber	83.4	5	120	10.1	57.1	$10^{-2}$
nylon-6,6 (N-6,6)	52	78	68	2.56	52	$10^{-14}$
N-6,6 + 40 wt % metallized glass	87.6	4	132	9.79	55	$10^{-7}$
N-6,6 + 25 wt % metallized glass	71.0	4	97.2	6.22	33	$10^{-13}$
N-6,6 + 5 wt % carbon black	41	4	55	1.85	21	$10^{-12}$
N-6,6 + 15 wt % carbon black	26	8	27	1.19	23	$10^{-3}$
N-6,6 + 20 wt % pitch carbon fiber	61	3	170 <sup>d</sup>	0.7 <sup>d</sup>	69	$10^{-4}$
N-6,6 + 40 wt % pitch carbon fiber	100	5	167	13.7	32	$10^{-2}$
N-6,6 + 10 wt % PAN carbon fiber	86	8	135	5.46	28	$10^{-7}$
N-6,6 + 40 wt % PAN carbon fiber	190	4	280	23.9	72	5

#### D. Molecularly Doped System [21]

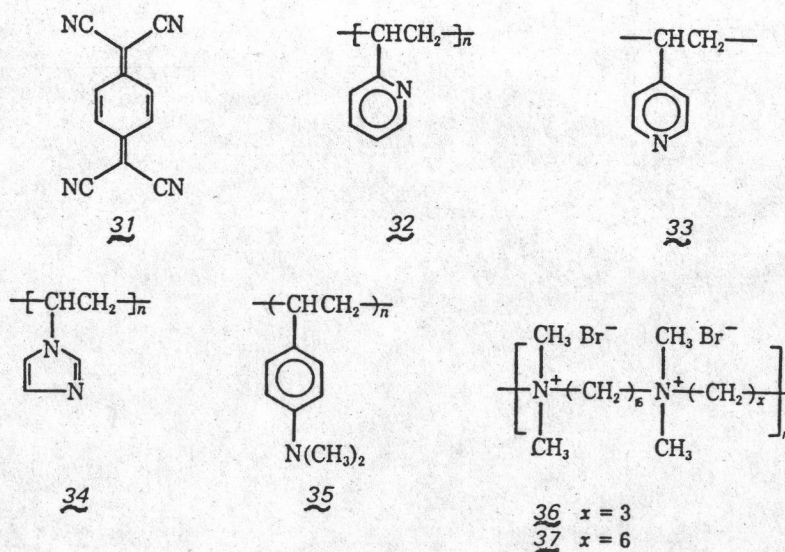
The primary strategy in the design of molecularly doped polymers for synthetic metals is to increase the conductivity of conjugated polymer systems, which are characterized by conductivities of ca  $10^{-12}$ - $10^{-5}$  S/cm and, therefore, possess some charge carriers. The greater number of charge carriers which are increased by doping and extension of the conjugated length increase the mobility of the carriers. However, doping also increases the degree of disorder in the composite doped polymer. This disorder tends to localize the carriers, thereby reducing their mobility. Therefore, it is possible that the conductivities exhibit a maximum value of  $\sigma_{250C}$  at ca 100 S/cm at moderate doping levels. At lower doping levels, the carrier densities decrease; at higher levels, the mobilities can decrease faster than the carrier densities increase. Consequently, the structure of the doped polymeric solid state exerts a decisive influence on the achievable values of the conductivity.

This class of polymers is characterized by relatively high dark conductivity,  $>10^{-5}$  S/cm, after doping. This particular field is rapidly evolving. The main parameters being sought for practical application are high but variable conductivity, processability, stability to ambient conditions, and good mechanical properties. To date, the electrical properties and



conductivity in particular have received the most attention. The conductive systems are mostly insoluble. Interest in polymers of high conductivity has fluctuated over the past several decades. A number of systems were investigated in the early 1960s.

Polymeric quaternary ammonium salts can be converted to highly conductive state by complexation with tetracyanoquinodimethane(TCNQ)(31). In analogy to studies of monomeric TCNQ complexes, poly(2-vinylpyridine)(32), poly(4-vinylpyridine)(33), poly(N-vinylimidazole)(34), poly(4-dimethylaminostyrene)(35), and ionene polymers, e.g., (36) and (37), can be complexed with TCNQ to yield polymers with conductivities as high as  $10^{-2}$ S/cm. Moreover, these systems can form continuous films.



Interest in these systems has diminished, although elastomeric ionenes of (38) have been reported recently. The conductivities for a representative sampling of these systems are given in Table 3. The conductivities are related to the nature of the polymer. They depend primarily upon the ratio of neutral TCNQ to its radical anion. Therefore, conduction in these systems probably occurs through charges associated with the TCNQ moieties. Molecular doping of other polymers to high electrical conductivity was rare prior to 1974. The few reports in the literature are summarized in Table 4.

Table 3 Conductivities of TCNQ-Doped Quaternary Ammonium Polymers

Structure no. of starting polymer	$\sigma_{25^\circ\text{C}}$ , S/cm
<u>36</u>	$10^{-3}$
<u>37</u>	$10^{-3}$
<u>38</u>	$10^{-3}$
<u>39</u>	$10^{-2}$
<u>40</u>	$10^{-2}$
<u>41</u>	$10^{-2}$

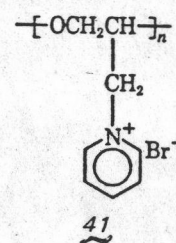
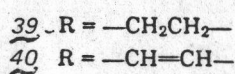
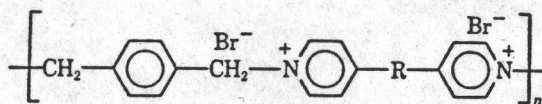
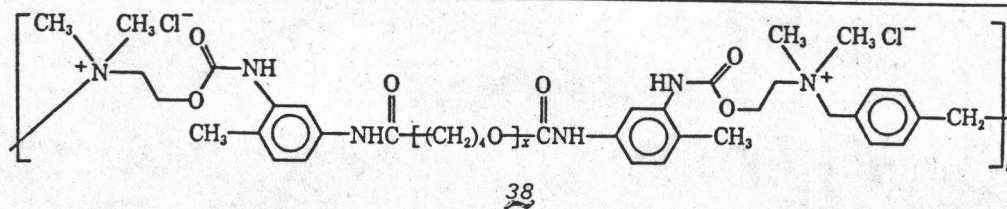
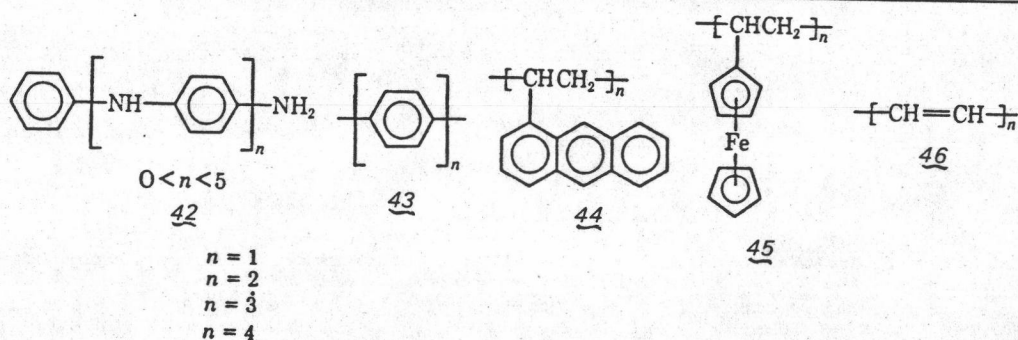
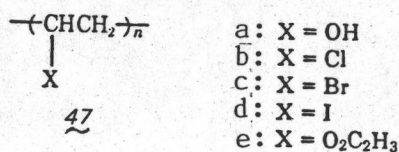


Table 4 Molecular Doping of Neutral Polymers Prior to 1974

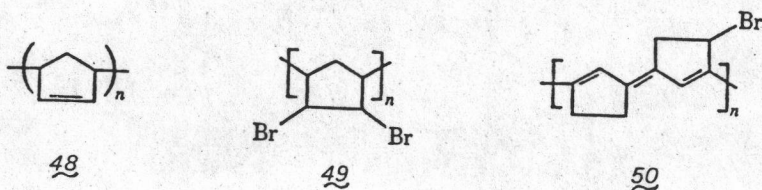
Structure no. of starting polymer, [ $\sigma_{25^\circ\text{C}}$ (S/cm)]	Dopant	Doped polymer, $\sigma_{25^\circ\text{C}}$ , S/cm
<u>42</u>	I <sub>2</sub>	10 <sup>-1</sup>
<u>33</u>	I <sub>2</sub>	10 <sup>-4</sup>
<u>43</u> [10 <sup>-16</sup> ]	I <sub>2</sub>	10 <sup>-4</sup>
<u>44</u>	I <sub>2</sub>	10 <sup>-6</sup>
<u>45</u> [10 <sup>-14</sup> ]	<i>o</i> -chloranil	10 <sup>-6</sup>
<u>46</u> [10 <sup>-6</sup> ]	BF <sub>3</sub>	10 <sup>-3</sup>
<u>46</u> [10 <sup>-6</sup> ]	BCl <sub>3</sub>	10 <sup>-4</sup>
<u>46</u> [10 <sup>-6</sup> ]	NH <sub>3</sub>	10 <sup>-9</sup>
<u>46</u> [10 <sup>-6</sup> ]	CH <sub>3</sub> NH <sub>2</sub>	10 <sup>-10</sup>



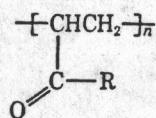
Previous literature contains reports of the direct and indirect syntheses of a number of polyenes. The indirect methods include elimination of water or hydrogen halides from polymers, e.g., (47). In general, the conjugation length is limited, and this is reflected in the relatively low conductivities,  $\sigma < 10^{-6} \text{S/cm}$ .



Another interesting polymer can be derived from polycyclopentadiene (48). Bromination of polymer in solution causes a series of color changes from yellow to yellow-green to blue-black as hydrogen bromide evolves. The reaction is believed to involve the initial formation of the dibromide adduct (49), followed by spontaneous dehydrobromination to the conjugated polyene (50). The conductivity of the insoluble black polymer is  $10^{-6} \text{S/cm}$ .

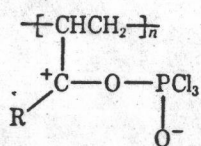


Reaction of films or solutions of poly(alkyl vinyl ketones)(51) with phosphoryl chloride leads to the formation of polymer films with conductivities of  $10^{-2}$ - $10^{-5}$  S/cm.

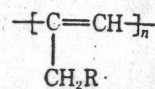


(51)

Formation of a conjugated polyene backbone (53) was proposed for synthesis, presumably occurring by way of (52).

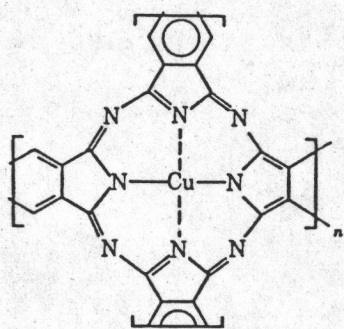


(52)

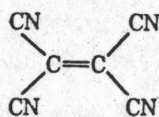


(53)

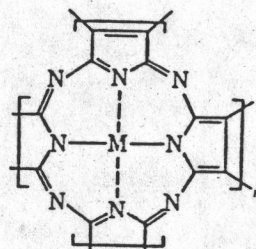
A class of polymers that may be considered doped is the metal-containing group of systems, e.g., polyphthalocyanines; an example is (54), conductivity =  $10^{-1}$  S/cm. These are powders. However, solution-phase deposition of tetranitriles, e.g., tetracyanoethylene (55) onto metal surfaces at ca. 200°C yields black adhesive films with conductivities of up to 10 S/cm. They are believed to have structures such as (56).



(54)



(55)



(56)

From the early 1960s until the late 1970s very few works appeared on conducting polymers. However, the polymerization of acetylene in situ to a free-standing insoluble, flexible film was reported in 1974. Previously, this material had been available only as an insoluble, infusible powder. The availability of polyacetylene (57) in film form sparked a renaissance in efforts to prepare conductive polymers, especially by molecular doping. Free-standing polyacetylene films (58) are prepared by exposure of acetylene to films of concentrated solutions of a Ziegler-Natta catalyst  $\text{Ti}(\text{O}-n\text{-C}_4\text{H}_9)_4\text{-Al}(\text{C}_2\text{H}_5)_3$  on glass surfaces. The thickness of the film can be controlled by the amount of acetylene utilized. At low temperatures, the cis isomer (57) ( $\sigma \approx 10^{-9} \text{ S/cm}$ ) predominates; at high temperatures, it is converted to the more stable trans isomer ( $\sigma \approx 10^{-5} \text{ S/cm}$ ). The films have metallic luster and they consist of fibrils of 20-60 nm diameter. The cis-rich films are flexible and can be stretched over three times their original length.



57



58

Previously, doping of polyacetylene powder by a variety of dopants led to altered conductivity, as noted in Table 5. The recent work on polyacetylene film has extended the number of dopants and the level of conductivity; the results for a number of dopants are given in Table 5. Doping techniques include exposure of the films to the vapors of dopants, e.g.,  $I_2$ ,  $H_2SO_4$ ,  $AsF_5$ , and  $SbCl_5$ , or to solutions of dopants, e.g.,  $I_2$ , sodium naphthalene, and  $NO_2SbF_6$ . Electrochemical oxidation of polyacetylene is also a useful doping technique. The counterion incorporated is the anion in the electrolyte solution, e.g.,  $ClO_4^-$ ,  $I^-$ , and  $BF_4^-$ . Metal-like conductivities are achievable from either the cis or trans isomers.

Table 5. Doping of Polyacetylene Films<sup>a</sup>

Dopant	Equivalents per double bond	$\sigma_{25^\circ C}$ , S/cm <sup>b</sup>
none	none	cis, $1.7 \times 10^{-9}$ trans, $4.4 \times 10^{-5}$
$I^c$	0.50	cis, 360
$I^c$	0.40	trans, 160
$AsF_5^d$	0.28	cis, 560
$AsF_5^d$	0.20	trans, 400
$IBr^d$	0.30	cis, 400
$IBr^d$	0.24	trans, 120
$SbF_6^e$	0.10	cis, 400
$ClO_4^f$	0.13	cis, 970
$Na^g$	0.42	cis, 25
$Na^g$	0.56	trans, 80

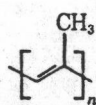
<sup>a</sup> Ref. 2<sup>b</sup> cis and trans denote preponderant starting isomer and do not imply the geometry of the doped polymer.<sup>c</sup> Gas phase  $I_2$  doping.<sup>d</sup> Gas phase.<sup>e</sup> Treatment with  $NO_2^+SbF_6^-$  solution in nitromethane-methylene chloride.<sup>f</sup> Electrochemical oxidation using  $(n-C_4H_9)_4N^+ClO_4^-$  as the electrolyte.<sup>g</sup> By treatment with a tetrahydrofuran solution of sodium naphthalene.

Other polyenes also can be converted to a highly conductive state by treatment with appropriate acceptors and donors as presented in Table 6.

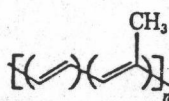
Table 6. Doping of Other Polyenes

Structure no. of polyene [ $\sigma_{25^\circ\text{C}}$ , S/cm]	Dopant	Equivalents per double bond	Doped polymer, $\sigma_{25^\circ\text{C}}$ , S/cm
<u>59</u>	AsF <sub>5</sub>		10 <sup>-3</sup>
<u>60</u>	AsF <sub>5</sub>		40
<u>43</u> [10 <sup>-10</sup> ]	AsF <sub>5</sub>	0.13	500
<u>43</u> [10 <sup>-10</sup> ]	Na	0.19	3000
<u>61</u>	AsF <sub>5</sub>	0.33	10 <sup>-3</sup>
<u>62</u> [10 <sup>-10</sup> ]	AsF <sub>5</sub>	0.19	3
<u>63</u> [10 <sup>-12</sup> ]	I	0.5	0.1
<u>64</u> [10 <sup>-12</sup> ]	AsF <sub>5</sub>	0.33	1
<u>65</u>	AsF <sub>5</sub>	0.33	10 <sup>-2</sup>
<u>66</u>	AsF <sub>5</sub>	0.13	10 <sup>-3</sup>
<u>21</u>	I	>0.05	70
<u>67</u>	I	0.15	0.1
<u>68</u>	BF <sub>4</sub> <sup>a</sup>	0.25	100

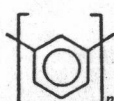
<sup>a</sup> Cationic sites formed electrochemically during synthesis; counterion BF<sub>4</sub>.



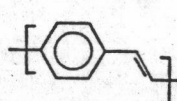
59



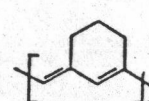
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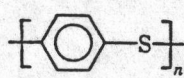
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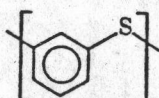
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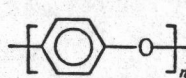
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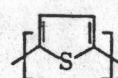
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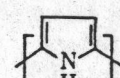
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66



67



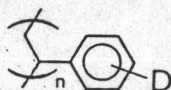
68



Polypropyne (59) is synthesized in a manner similar to polyacetylene and it is a soluble polymer. Poly (p- and m-phenylene)s, (43) and (61), respectively, are formed by a variety of methods from benzene, poly(1,3-cyclohexadiene)s, dihalobenzene, or by Diels-Alder polymerizations. The para isomer is insoluble polymer and is not heat processable; the meta isomer is soluble and heat processable. Poly(p-phenylenevinylene) (62) is synthesized in oligomeric form as a powder by a Wittig reaction. Poly(1,6-heptadiene) (63), an insoluble free-standing film, is synthesized by polymerization of the monomer on films of concentrated Ziegler-Natta catalyst solutions. Poly(p-phenylene sulfide) (64) that is made by bromination and oxidation of thiophenol is commercially available as fiber, film, or powder of high crystallinity. It is soluble and heat processable. The meta isomer (65) is prepared by reaction of m-benzenedithiol and m-di-bromobenzene. Coupling of 2,5-dibromothiophene with organometallic catalysts yields poly(2,5-thienylene) (67). Poly(pyrrole-2,5-diyl) (68) is formed as an insoluble film by electrolysis of pyrrole. Approximately 25% of the pyrrole units are oxidized, and the anion of the electrolyte becomes the counterion.

### E. Chemically Attached System [3]

In contrast to the previous systems, the chemically attached system involves polymers where the donor species, D, is chemically attached to a polymer chain by a covalent linkage.



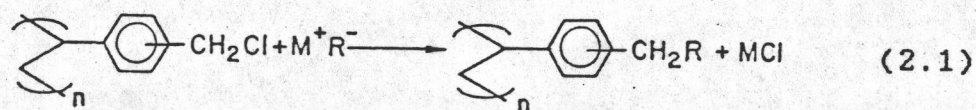
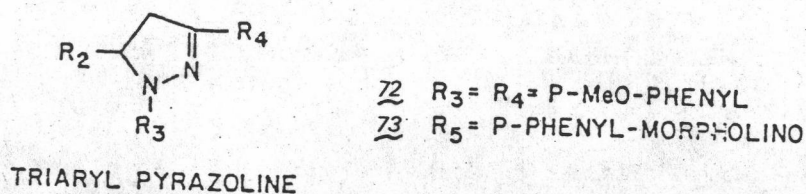
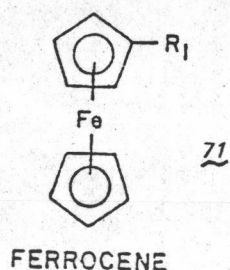
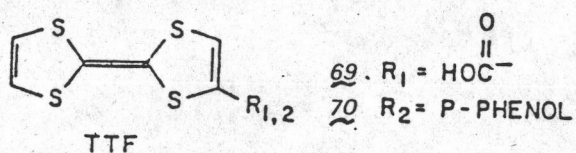
D: Donor species

The density of the bound donors in a polymer is determined in details such as molecular weight, copolymer composition and chain stereochemistry. As might be expected, this enables considerably higher donor densities to be achieved than in the doping case. In addition, problems due to solubility or migration of the donor species are avoided because the donors are chemically anchored to the polymer chain.

Introduction of ion-radicals into the polymer matrix is accomplished by oxidation of the bound donor species. Typical pi-donor molecules can be oxidized using chemical oxidants, photochemically or electrochemically. And these methods can also be used to oxidize the polymer-bound donors, both in solution and in solid film form.

This kind of donor polymers has been prepared by reacting alkali salts of the monofunctionalized pi-donors (69-73) with a poly(vinylbenzyl chloride) backbone as presented in equation (2.1) in high yield ( > 60 % ), the experimental

conditions of which are shown in Table 7.



From the result of the experiments, the polymers are stable, and very soluble in typical organic solvents such as THF, DMF,  $\text{CH}_2\text{Cl}_2$  etc. This high solubility of the product polymer is useful in purification and solution characterization. In addition, their high solubility allows films to be prepared by using common spin-coating procedures, and good quality films

can always be formed in thicknesses from 100 Å to several microns.

TABLE 7

Monomer <sup>a</sup>	M <sup>b</sup>	Experimental Conditions <sup>c</sup>		Polymer <sup>e</sup> Coverage	
		Solvent	Reactant Ratio <sup>d</sup>	Temp. (Time)	
TTF (R <sub>1</sub> )	Cs	DMF	1.1	80°C (24hrs.)	87%
TTF (R <sub>1</sub> )	Cs	DMF	0.30	80°C (24 hrs.)	30%
TTF (R <sub>2</sub> )	K	THF	1.1	Reflux (24 hrs.)	69%
Ferrocene (R <sub>1</sub> )	Cs	DMF	1.1	80°C (24 hrs.)	60%
Triaryl Pyrazoline (R <sub>2</sub> R <sub>3</sub> = 4)	K	THF	1.1	Reflux (24 hrs.)	85%
"	"	"	0.55	"	51%
(R <sub>2</sub> , R <sub>3</sub> , 5)	"	"	1.1	"	65%
"	"	"	0.55	"	47%

<sup>a</sup>For substituents in parenthesis cf. Figure

<sup>b</sup>Cs. salt prepared from CsOH; K salt prepared from KH, by reaction with donor. cf. ref.

<sup>c</sup>Salt and poly(vinylbenzyl chloride) stirred in solution at temperature and time indicated, followed by repeated reprecipitations into H<sub>2</sub>O.

<sup>d</sup>Mole ratio of salt to polymer used.

<sup>e</sup>Percent reaction as determined by elemental analysis.