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Incorporation of Metal Related Materials into Electrically Neutral Polymers

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Incorporation of Metal Related Materials into Electrically Neutral Polymers

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ABSTRACT

Metal containing polymers are numerous and highly diverse.
Such systems include ionomers, polymer-bound coordinating
ligands, organometallic polymers wherein the metal may be
a part of the polymer "backbone", metal-polymer composites
and metal incorporated neutral polymers. The latter system,
which is reviewed herein, is normally concerned with the
modification of polymer properties which may range from
electrical conductivity to polymer flammability. Metallic
additives may be a metal atom vapor, organometallic compounds,
coordination complexes and simple hydrated or anhydrous salts.
Representative polymer systems include polyamides, polyimides,
polyalcohols, polyesters, polyacetylene, polyethylene and
polysiloxane. Each metal is almost a case unto itself regarding
a specific polymer property (i.e. different metals produced
different properties). The chemical state of the metal and
the ligand environment of the metallic species are extremely
important concerning polymer and metal compatibility. The
literature cited, while not exhaustive, is representative
of this rapidly expanding area of polymer research.

SCOPE

The incorporation of metallic species into polymers is an
extremely active area of research. As evidence for this ob-

servation, a search of Chemical Abstracts during the period
1977–1979 revealed over a thousand references to polymers con-
taining metals. Obviously this review cannot attempt to deal
with the entire area of polymer-metal systems. It, however,
will prove useful to outline the various research areas which
we perceive to compose the general field of metal-containing
polymers.

These studies may be roughly subdivided into five categories.
One group would be represented by polymers that have an ionic
group covalently attached which, in most cases, is neutralized.
by a metallic counterion.[1] Incorporation of the metal ion may
occur after formation of the ionic polymer as in the binding of
copper(II) to poly(methacrylic acid)[2] or a metal salt monomer
may be employed for conducting the polymerization. The latter
situation is best illustrated by the use of magnesium or calcium
salts of mono(hydroxyethyl)phthalate as an ionic monomer[3] in the
production of metal-containing polyesters via reaction with
various anhydrides and bisepoxides. The reaction scheme I is
outlined below where the divalent metal cross-links the adjacent
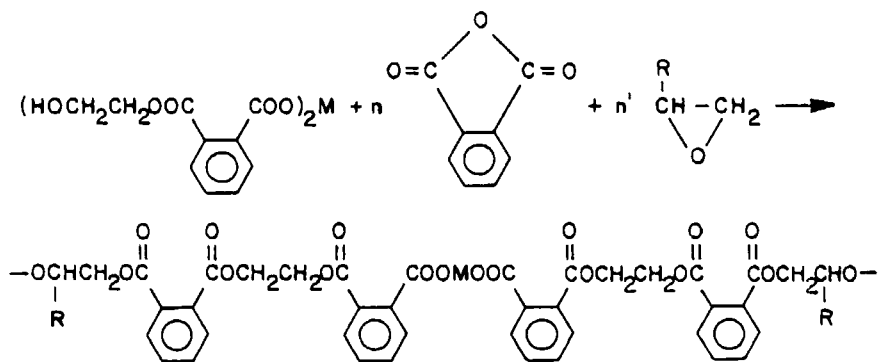
SCHEME   I

carboxyl groups. The field of ionomers has reached an advanced
level of maturity; yet, it continues to develop at a rather fast
rate.

A second very large area of metal-polymer studies is
represented by those polymers which have organically bonded
(i.e. through carbon) metals. These metals are generally part
of the monomer and appear in the polymer "backbone". In the
truest sense of the word these would be organometallic polymers.
Several groups[4-6] have been quite active in this area during the
past decade. Common commercial monomers would include vinyl-
ferrocene, ferrocenylmethylmethacrylate and tricarbonylbenzyl-
acrylate chromium. Reaction scheme II outlines a typical
organometallic polymer. For a much more expanded discussion of
this field the reader is referred to several other chapters of
this monograph.
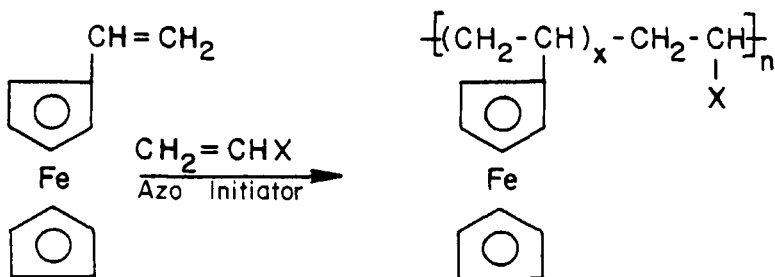
SCHEME   II

A somewhat related group of polymers which would constitute
a third area of metal-polymer systems is represented by
neutral chelate resins or neutral polymer ligands. This field
has received much attention due to the wide variety of uses for
such polymer complexes. Applications include (1) sequestering
of metal ions[7,8] in general or sequestering of one of several

specific metals, (2) models for enzymic and other biological
reactions such as the decomposition of hydrogen peroxide[9] and
(3) homogeneous catalytic reactions whereby the precious-metal
catalyst is "heterogenized" by being anchored to a polymer.[10]
This class of polymer normally is synthesized by taking strong
coordinating ligand monomers such as 4-vinylpyridine[11] and
4'-vinylbenzo-18-crown-6[12] (Structures I and II) or utilizing a
more classical polymer system which has been chemically modifed

$$CH = CH_2$$

I

$$CH_2$$

II
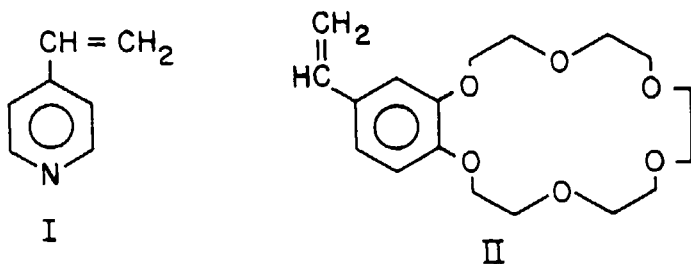
by appending known ligands to the polymer matrix. Reaction
schemes III and IV are known examples of the latter approach.[13,14]
Studies such as mentioned above have focused on the extent of
metal binding to the polymer (i.e. stability constants) or the
reactivity of the metal bound polymer. Many fine reveiws
already exist on this topic.[15]

Other less explored polymer-metal areas include polymer
film laminates and metal-filled polymers. The former[16] would
be represented by the vapor deposition of metals onto polyester
films for the purpose of producing electroconductive films. The
laminate includes the polymer substrate and a metal layer bonded
to the substrate by a polymeric coupler. No doubt some metal
ion could be incorporated into the polymer. The use of "so-
called" inorganic fillers with preformed polymers has received
some attention. Adhesive studies with polyimides have been

$Co(DH)_2 Py$
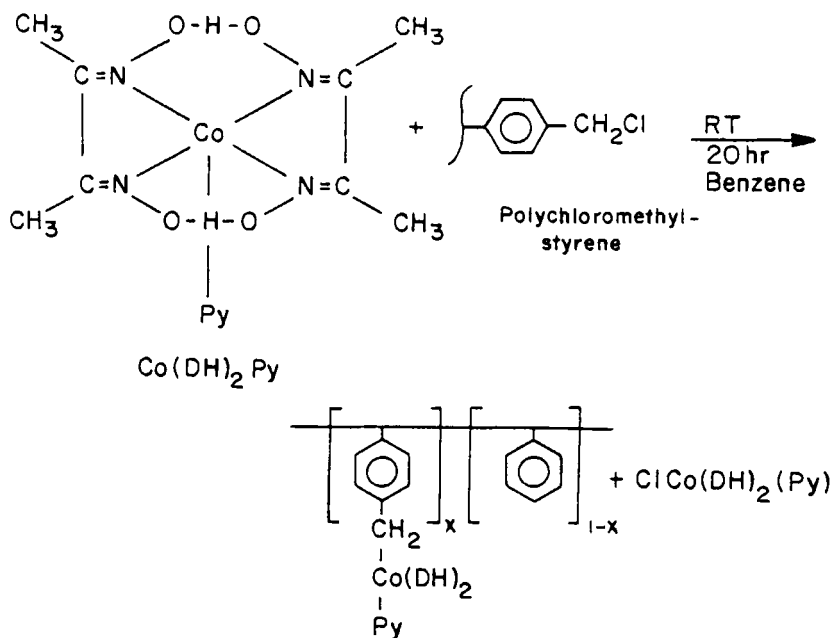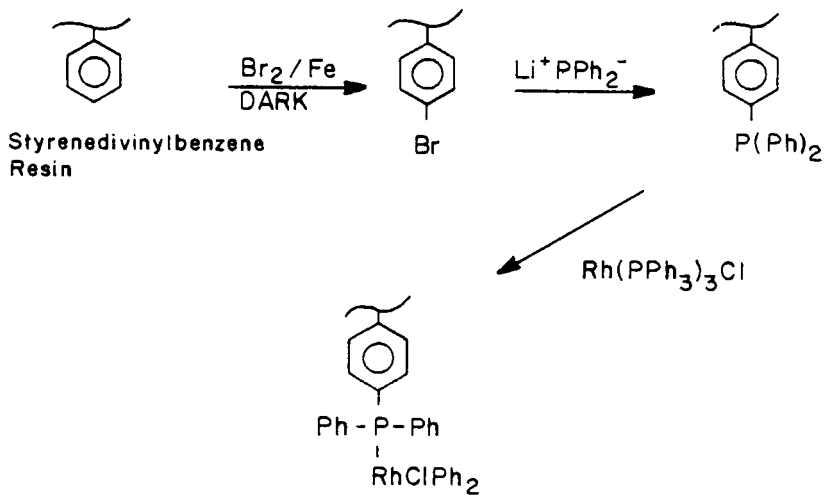
SCHEME III

SCHEME IV

conducted wherein the resin contained 5-40% metal or metal oxide filler.   Enhanced adhesive properties with titanium adherands have been noted with aluminum powder in this regard.[17]   Another study has examined the mechanical properties of polyurethane rubber filled with various fractions (0-50%, v/v) of sodium chloride.[18]

The final area of metal-polymer systems would consist of neutral polymers to which have been added dissolved metal salts, metal complexes, organometallic compounds and metals.   This area has probably received the least study and constitutes the focus of this review.   While this division of metal-polymer studies may seem quite arbitrary, we believe it is readily identifiable, rapidly expanding and (as this review hopefully will attest) highly fascinating.   The uniqueness of this area of metal-containing polymers rests on two observations: (1) the polymer systems employed are electrically neutral and have no readily ionizable groups; and (2) investigations are normally concerned with adding metals for the purpose of modifying polymer properties such as increasing the glass transition temperature (T_g), decreasing the melt temperature (T_m), enhancing adhesive properties, or increasing the electrical conductivity.   Numerous reports have appeared which describe the incorporation of "non-metal" species such as oxygen[19], iodine[20], arsenic pentafluoride[21], and tetracyanoquino-dimethane salts[22] to modify electrical properties of polymers. However, this review shall deal exclusively with "metal" related dopants.   As will become evident, a number of polymer properties have been measured for a large variety of neutral polymers con-taining metal dopants.   The discussion which follows has been arranged into categories of neutral polymers.

REVIEW

Polyamides

Polyamides constitute one of the most common polymer systems to which have been added a large variety of metal salts.   Poly-

(caproamide), Structure III, has received considerable study in
several Italian Laboratories. A decade ago it was observed that

$$-\left[(CH_2)_6 - NH - \overset{\overset{O}{\|}}{C} - (CH_2)_4 - \overset{\overset{O}{\|}}{C} - NH\right]_x$$
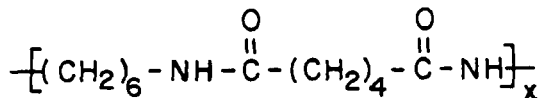
III

aqueous solutions of inorganic salts altered the crystalline
structure of biological macromolecules. Subsequently, the effect
of added KCl, LiCl, LiBr and $CaCl_2$ on the melting behavior of
Nylon 6 as determined by differential scanning calorimetry was
reported. Small amounts of these salts in the complete absence
of water caused a melting temperature depression in excess of the
theoretically predicted temperature depression.[23] Intimate mixing
of the polymer and dopant at approximately 260°C was crucial in
order to obtain large temperature depressions. The extent of
depression depended on the type of metal salt. Potassium chloride
(a salting-out agent) showed no effect; while, the depression noted
with LiCl (a salting-in agent) increased with increasing concen-
tration. Available data at the time suggested a strong direct
interaction between Nylon 6 and salting-in agent in the absence
of water. A serious problem arises in this approach in that
thermal polymer degradative effects occur during metal ion in-
corporation. Nevertheless, the authors believe the investigation
has certain implications for the processing of high melting polymers.

The search for further proof regarding the occurrence of a
direct interaction between salt and Nylon 6 was detailed several
years later.[24] The T_m of Nylon 6 was decreased upon the addition
of metal salts in the order KCl < LiCl < LiBr in the composition
range 0-12%, w/w. X-ray analysis indicated that LiCl and LiBr
tend to favor the crystallization of the γ form of Nylon 6 over
the more common α form. The crystallization rate of Nylon 6
is drastically lowered by LiCl and LiBr; and the melt viscosity

at 250°C is considerably increased in the presence of LiCl. The
nature of the salt polymer interaction was postulated to be
between the amide group of the amorphous polymer and the salt.
Several questions exist in this study regarding which part of
the amide unit (i.e. nitrogen or oxygen) is involved. Also,
it has yet to be decided whether the lithium ion alone or the
ion pair interacts with the polymer.

Stabilized Nylon 6 has been substituted[25] in this work in
an effort to minimize thermal degradation. Depression of the T_m
was comparable to data obtained on unstabilized Nylon 6. Added
lithium salts, however, had no effect on polymer morphology, but
there was a reduction in the rate of crystallization. Further
investigation[26] surprisingly revealed the T_g ($\sim$50°) remained un-
affected by salt additions or concentration. All three salts
caused an increase in melt viscosity. The increase with KCl was
believed to be due to its insolubility in Nylon 6 in which the
KCl acts as an inert filler. Lithium bromide resulted in higher
viscosities than LiCl.

The T_g independence of added salt to poly(caproamide) has
more recently been shown[27] to be incorrect because the effect of
water absorption. When strict precautions to exclude moisture
are taken, the addition of 4% LiCl has been shown to raise the
T_g by 25°C. T_g's of salted and unsalted Nylon 6 are lowered in
the presence of moisture. The amount of moisture absorbed at
equilibrium by Nylon 6 doped with 4% LiCl is double. The bene-
ficial effect in T_g is lost when samples equilibrate with moisture.
It was also observed that the elastic modulus of oriented samples
increases with added salt provided all moisture is absent.
Severe restrictions are thus placed on the practical use of this
system.

A somewhat earlier study was conducted with various nylons
regarding the effect of metal salts on the stress cracking of
polyamides.[28] Halides were found to be most effective; while,
acetates and sulfates did not promote cracking. Later work

revealed that thiocyanates and nitrates[29] were suitable sub-
stitutes. The preparation of specimens for stress cracking was
performed in several ways. These were (1) treatment of the
stretched film with a concentrated solution of metal salts, (2)
immersion of polymer films in solutions of the active salts or
(3) cast film of the nylon-metal salt mixture. The mechanism
of rupture does not appear to be one of simple hydrolysis or
of metal catalyzed hydrolysis. Metal haldies which were found
to be active stress cracking agents induce characteristic changes
in the IR and NMR spectra of nylons. Two types of changes were
observed[30] depending on the metal halide involved which were
attributed to complex formation between the metal and amide
group. Type I metal halides such as Zn(II), Co(II), Cu(II), and
Mn(II) form complexes in which the metal atom is bonded to the
carbonyl oxygen (Structure IV). These agents are believed to
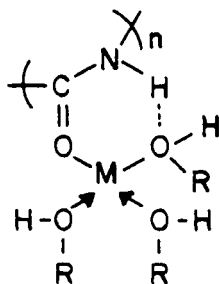

IV

cause stress cracking by interference with the hydrogen bonding
in the polyamide. Type II halides such as Li(I), Ca(II) and Mg(II)
are believed to form proton donating, solvated, species which act
as direct solvents for nylon in a manner similar to phenols and
formic acid. In other words, Type II halides cause simple solvent
cracking. Additional work in this area is not available.

Polyacrylamides

Polyacrylamides (PAA) (Structure V) are another group of
polymers which has received significant study. Tough films of
PAA with less than 50% (w/w) $CuCl_2$ have been produced from aqueous
solution.[31] The Cu(II) doped PAA was not conductive (surface
resistivity = 10^9 ohms). The PAA-Cu(II) film when combined with
iodine, however, exhibited good conductivity (surface resistivity
$\sim 10^3$ ohms). The iodine treated film was prepared first by mixing

$$\left[CH_2 - \underset{\underset{NH_2}{\overset{|}{C}}=O}{\overset{|}{C}H} - CH_2 - \underset{\underset{NH_2}{\overset{|}{C}}=O}{\overset{|}{C}H} \right]_n$$
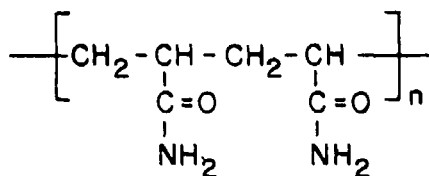
$$\underline{V}$$

aqueous solutions of PAA and $CuCl_2$, casting a film of the resulting
viscous solution, drying at 100°C followed by dipping the film in
an iodine-acetone solution and drying further at 100°C to remove
solvent and excess solvent. Optimum surface conductivity was
achieved for 20-40% (w/w) $CuCl_2$ and more than 1% of iodine. Higher
concentrations of Cu(II) ruined the film flexibility and other
properties. Although the highest conductivity was obtained with
$CuCl_2$, similar results were produced using $Cu(NO_3)_2$, $CuSO_4$, and
$Cu(C_2H_3O_2)_2$. Films prepared under both non-oxygenated and
oxygenated conditions exhibited the same surface conductivities.

Treatment of the PAA-Cu(II)-I_2 polymer with KOH significantly
increased the electrical conductivity[32] of films, and a maximum
conductivity was achieved using an equimolar amount of hydroxide
to the Cu(II) salt. No conduction was observed when the chelate
solution was treated with twice the equimolar amount of hydroxide.
The authors claim that the conductivity of the PAA-Cu(II) film
modified with iodine was dependent on the structures of the

chelate in solution. Structures VI and VII were believed to be
particularly effective; while, Structure VIII was thought not to
participate in the conduction. A very limited ESR study of these
films has been performed[33] in an effort to ascertain the specific
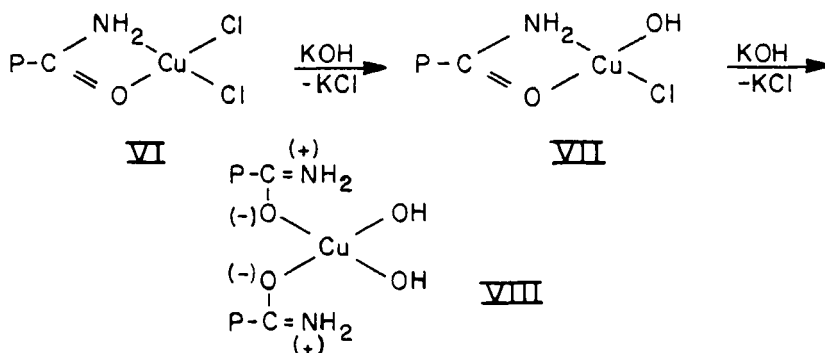
PAA-Cu(II) interaction. A mononuclear Cu(II) coordinated with
two water molecules and chelated with two oxygen or nitrogen
atoms attached to the polymer has been suggested. Optical and
scanning electron microscopy have been performed[34] on films of
PAA-Cu(II)-I_2 in hopes of discovering the reason why semi-conduct-
ive behavior is produced after treatment with I_2. Highly coagu-
lated states of PAA-Cu(II)-I_2 appear to favor the higher surface
conductivity. SEM shows a new reaction product after treatment
with I_2. Iodine is believed to attack those parts of the poly-
mer which are rich in Cu(II). Optical absorption spectra proved
the existence of γ-CuI on the film surface which is believed
to be responsible for the enhanced conductivity.

    Although our discussion is focused along polymer types, it
seems appropriate to mention here a very closely related
effort[33-35] to the PAA work involving poly(vinylalchol) (PVA).
A PVA-Cu(II) film had surface resistivity of 10^{13} ohm, but
after dipping the film in iodine/acetone and drying at 80°C
surface resistivity decreased to 10^3 ohm. For comparison PVA-I_2

with no Cu(II) yielded 10^9 ohm indicating the need for Cu(II).
Satisfactory results were given by more than 15% (w/w) of
copper(II) salt and about 4% (w/w) of iodine. Again KOH was
observed to be effective with the maximum conductivity being
reached at a 1:1 mole ratio. Several structures of PVA-Cu(II)
have been postulated such as deprotonated, $[Cu(RO_2)_2]^{-2}$ and
$[Cu(RO_2)R(OH)_2]^\circ$, and non-ionized species where $R(OH)_2 \equiv PVA$. No
mention of γ-CuI was made. Absorption spectra of the PVA-Cu(II)-
I_2 after washing the film to remove adsorbed I_2 revealed the
presence of I_3^- and multilayer iodine. This observation suggested
that iodine in the chelate film participated in the conduction
in forms of I_3^- and/or miltilayer iodine. Other metal salts
capable of forming chelates with PVA such as Fe(III), Zn(II),
Sn(IV) and Cr(II) salts did not give favorable results, the
resistivities being greater than 10^9 ohm.

Polyimides

Approximately twenty years ago Angelo[36] patented the synthetic
procedure for the addition of metal ions to numerous types of
polyimides (Structure IX depicts an aromatic-type polyimide) along
with the results of selected physical measurements on these
mixtures. The object of the invention was a process for forming
particle-containing (< 1μ) transparent polyimide shaped structures.
Unlike the work discussed previously all of the metals were added
in the form of coordination complexes (e.g. β-diketone and
β-ketoester chelates) rather than as simple anhydrous or hydrated
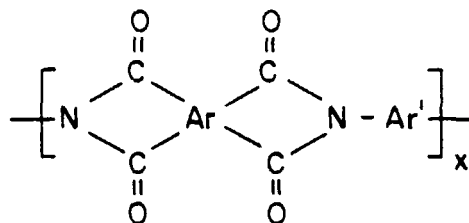

IX

salts. This offers the advantage that the coordination complex
may be more soluble in the polymer solution, more compatible
with the bulk polymer and more evenly distributed throughout
the polymer.

The process employed in this study involved (1) forming the
polyamic acid, (2) adding the metal to the polyamic acid, (3)
shaping the polymer-metal ion mixture and (4) converting to the
metal-containing polyimide. The starting materials for polymer
formation were aromatic or aliphatic diamines and aromatic or
aliphatic tetracarboxylic acid dianhydrides. The major goal of
the invention was the production of polyimide films for use as
decorative or electrically conductive tapes and packaging
materials. Few properties of the films are available from the
patent and no comparison with films cast from the neat polymer
solutions was discussed. The room temperature properties
of a film cast from an N,N-dimethylformamide (DMF) solution of
4,4'-diaminodiphenyl methane, pyromellitic dianhydride and bis-
(acetylacetonato)copper(II) are given below: Percent copper,
3.0%; dielectric constant, 3.6; dissipation factor, 0.004-0.01;
and volume resistivity, 8×10^{12} ohm-cm. No data was given regarding
the glass transition temperature, thermal stability, adhesive
properties, mode of interaction between metal and polyimide, state
of the metal, thermal conductivity, surface resistivity, etc.
Unfortunately further patents or published work in this area are
not available.[37]

More recent work[38] with polyimides and metal compounds con-
cerns polymers derived from 3,3', 4,4'-benzophenone tetracarboxy-
lic acid dianhydride (BTDA) (Structure X), and 3,3'-diaminobenzo-
phenone (m,m'-DABP) and 4,4'-diaminobenzophenone (p,p'-DABP)
(Structure XI) in DMF, N,N-dimethylacetamide (DMAC) or diethylene-
glycol dimethylether. Approximately twenty metals in a variety
of forms were added to polyamic acid solutions. In many cases
films could then be cast and thermally converted to the cor-
responding polyimide. Non-brittle polyimide films were subjected
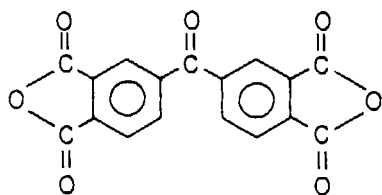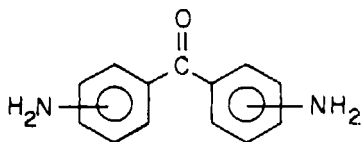
X   XI

to thermomechanical analysis, thermogravimetric analysis, weight
loss on prolonged heating and infrared analysis. Relatively large
positive and negative changes in thermal properties of the metal
ion containing polymers have been noted with different metals.
Predictive trends with certain polymers, however, were not pos-
sible with specific metals.

The best system studied in this regard involves tris(acetyl-
acetonato)aluminum(III), $Al(acac)_3$, addition to the above two
polymer systems. Table I compares a few physical measurements on
the BTDA + m,m'-DABP polyimide alone and the $Al(acac)_3$/polyimide
mixture. An inspection of the data reveals that the T_g of the
$Al(acac)_3$/polyimide is increased without sacrificing any polymer
thermal stability. These effects work together to improve the
high temperature adhesive properties of the polyimide with
respect to bonding titanium surfaces.

The choice of metal, its chemical state, and the counterion
were critical in this investigation as evidenced by the typical
data shown in Table I regarding $NiCl_2 \cdot 6H_2O$ incorporation. As
further proof of this, experiments with $AlCl_3$, $AlCl_3 \cdot 6H_2O$ and
$Al(NO_3)_3$ apparently caused immediate crosslinking (rubber-like
formation) of the polyamic acid such that no film could be cast.
The T_g's were more dramatically increased with the p,p'-DABP
polyimide but at the expense of considerable loss in thermal
stability (Table I). No changes in chemical functionality in
the polyimide were apparent as judged by infrared spectral

TABLE I

COMPARISON OF PURE POLYIMIDE AND METAL

ION-INCORPORATED POLYIMIDES

Polyimide Film	$T_g{}^a$ (°C)	TGA^b (°C)	Adhesive Lap Shear Strength at 275°C^c (psi)
BTDA + m,m'-DABP	251	570	440
BTDA + m,m'-DABP + Al(acac)$_3{}^d$	271	555	1640
BTDA + m,m'-DABP + NiCl$_2$·6H$_2$O^d	279	495	610
BTDA + p,p'-DABP	283	525	-
BTDA + p,p'-DABP + CaCl$_2{}^d$	360	475	-

^{a}Apparent glass transition temperature from thermomechanical analysis

^{b}Thermogravimetric analysis polymer decomposition temperature

^{c}Performed on 50 mil titanium adherends

^{d}Metal complex to polyamic acid mole ratio = 1:4 in DMAc

comparisons of polyimide and polyimide-metal films regardless
of the metal employed.

Incorporation of Al(acac)$_3$ into the polyimide disappointingly
showed no significant reduction in volume resistivity relative
to the polymer alone. Similar results were obtained on NiCl$_2$·6H$_2$O
filled polyimides. Numerous efforts to prepare high quality films
incorporating other metal ions into BTDA + m,m'-DABP were not
satisfactory because metal ion addition resulted in a decreased
solution viscosity. These results suggest that during the film
curing process, the non-conducting Al(acac)$_3$ and NiCl$_2$ maintain
their integrity rather than being converted to the more con-
ducting aluminum or nickel metal as originally envisioned. X-ray

photoelectron spectroscopic (XPS) measurements have confirmed
this hypothesis.

Simultaneous with the above work, superior antistaic
properties were reported[39] for newly available soluble polyimide
(DAPI-Polyimide) film loaded with either LiNO$_3$ or LiCl. Physical
properties and film smoothness remained unchanged except that
electrical resistance was sharply lowered. Conductivity was
increased about 20-fold or 2000% over the standard unfilled
polyimide. Additional tests showed that the films were very
slightly hygroscopic in the presence of lithium ions. This
phenomenon may, in fact, account for the lowered resistivity. It
also was not clear from the NASA brief whether the enhancement
was in surface or volume conductivity.

A more recent effort to incorporate metal species into poly-
imides for the purpose of decreasing polymer resistivity has
appeared.[40,41] Palladium-filled polyimide films have been pre-
pared using the following dianhydride-diamine pairs: BTDA + DABP,
BTDA + 4,4'-oxydianiline (ODA) (Structure XII), and BTDA + 3,3'-
diaminodiphenylcarbinol (DADPC) (Structure XIII). A number of
palladium additives were screened, many of which proved unaccept-
able because of insufficient solubility in DMAc or in the polymer-
DMAc solution. While good quality films containing evenly dis-
persed palladium could be produced with slightly soluble PdCl$_2$
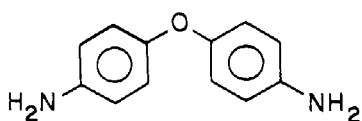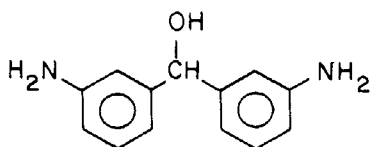
XII   **XIII**

and Na$_2$PdCl$_4$, only minor modifications were realized in polymer
properties. Best results have been obtained with Li$_2$PdCl$_4$ and

$Pd(S(CH_3)_2)_2Cl_2$ as additives. Flexible, dark red-brown films
have been fabricated for the three monomer pairs noted above.

The synthetic procedure involves formation of the polyamic
acid (Structure XIV) in DMAc, intimate mixing of the palladium
complex and polyamic acid, and thermal imidization in air to the
palladium-filled polyimide film. An alternate in situ method
whereby polymerization to the polyamic acid was performed in the
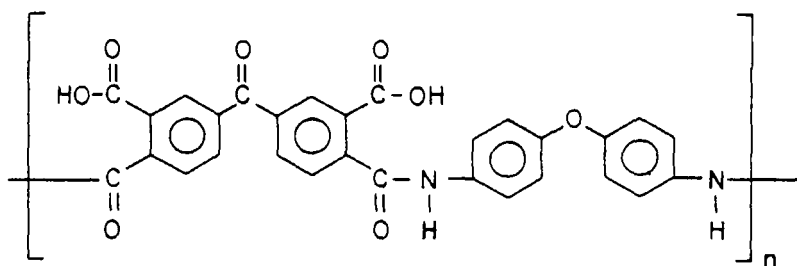
XIV

presence of the palladium complex also proved satisfactory. Several
films possessed noticeably different surfaces depending upon
whether the film had been exposed to the glass or to air during
the imidization procedure. This difference was very noticeable
for the two films containing $Pd(S(CH_3)_2)_2Cl_2$ (BTDA + ODA and
BTDA + DABP). While the glass side had a dark red-brown appear-
ance, the air-side possessed a definite silvery metallic appearance.
The presence of oxygen during the imidization process appears
crucial, since BTDA + ODA and BTDA + DABP doped with
$Pd(S(CH_3)_2)_2Cl_2$ do not give rise to metallic surfaces when
cured in either a dry N_2, Ar, N_2/H_2 or moist Ar atmosphere.

The primary purpose for this study was to ascertain whether
or not the addition of palladium would lower the electrical
resistivities of the polyimides. Table II outlines the results.
Four different combinations of dianhydrides, diamines, and metal

TABLE II

SURFACE AND VOLUME RESISTIVITIES OF CONDUCTIVE PALLADIUM-CONTAINING BTDA-DERIVED POLYIMIDES[a,b]

METAL COMPLEX	ODA	DABP	DADPC	CURING ATMOSPHERE
Li_2PdCl_4	9.5×10^5 ohm[c] 2.0×10^6 ohm-cm[d]	$NC^{[e]}$	1.3×10^7 ohm 1.0×10^7 ohm-cm	Air
$Pd(S(CH_3)_2)_2Cl_2$	$<10^5$ ohm $<10^5$ ohm-cm	$<10^5$ ohm $<10^5$ ohm-cm	NC	Air
Li_2PdCl_4	5.1×10^7 ohm 8.9×10^7 ohm-cm	NC	2.1×10^{10} ohm 1.4×10^{11} ohm-cm	N_2
$Pd(S(CH_3)_2)_2Cl_2$	NC	NC	NC	N_2

[a] Resistivity values are quoted for the best quality films. Values for replicate films do not differ by more than one order of magnitude.

[b] Polymer alone surface and volume resistivities are 10^{17} ohm and 10^{17} ohm-cm, respectively.

[c] Surface resistivity

[d] Volume resistivity

[e] NC = No change in resistivity relative to the polymer alone.

additives yielded polyimides with dramatically lowered resis-
tivities when cured in an air atmosphere. Conductive BTDA + ODA
films were produced using both palladium additives. Surprisingly
Li_2PdCl_4 gave lowered resistivity values with BTDA + DADPC;
while $Pd(S(CH_3)_2)_2Cl_2$ with the same monomer pair exhibited values
equivalent with the polymer alone. The results with BTDA + DABP,
however, were reversed. The metallic surface on the air side
displayed by the two conductive $Pd(S(CH_3)_2)_2Cl_2$ films, no doubt,
lowers resistivity   ($<10^5$ ohm-cm). This metallic surface is
apparently not a necessity, since conductive Li_2PdCl_4 films do
not display a metallic surface. However, as Table II attests,
electrical resistivities are higher for the Li_2PdCl_4 film
(with non-metallic surface).

The results on curing the films in a non-oxygenated atmos-
phere are equally interesting, Table II. No metallic surfaces
are produced with $Pd(S(CH_3)_2)_2Cl_2$ as an additive and no resis-
tivity lowering is observed. Moist argon and forming gas (N_2/H_2)
give the same unchanged results. A nitrogen curing atmosphere,
however, does not change the resisitivity results appreciably for
the air-cured, conductive Li_2PdCl_4 films. It is significant that
in each case, with Li_2PdCl_4, the resistivity values are always
one to three orders of magnitude higher for nitrogen cured films.

X-ray photoelectron spectroscopy (XPS) has proven valuable in
studying some of these palladium-containing polyimides. Measured
XPS binding energies (Pd $3d_{5/2,3/2}$) indicate that an appreciable
amount of palladium has been reduced to the elemental state in
each film. In other words, during the imidization process re-
duction of palladium has occurred. Those films which have low-
ered resistivities exhibit the most reduced palladium. Dif-
ferences between conductive film surfaces exposed to air versus
glass are very apparent here again, since a larger quantity of
reduced palladium always accompanies the side of the film
exposed to the air.

XPS for non-conductive films differs in several respects
from the above. First of all, the palladium signals are relative-
ly weak and the measured binding energies fall between those for
Pd metal and $PdCl_2$. Secondly, an additional pair of photopeaks
are observed at approximately 10 eV higher energy (349.8 and
346.1 eV). The relative intensity of the two pair of peaks has
been found to vary depending upon what place on the film was
being sampled. Conductive films do not show this extra higher
energy pair of photopeaks. This phenomenon is attributed to
differential charging of the surface palladium. Some islands of
palladium are more insulated than other islands by the non-con-
ductive polyimide and cannot dissipate the photo-charge produced
by the x-ray beam. High resistivity films, therefore, appear to
be highly heterogeneous insofar as palladium is concerned. If
palladium is the charge-carrier as we expect, an unequal dis-
tribution of palladium can result in an interruption of the charge
transfer mechanism. The addition of higher amounts of palladium
to these films does not produce the desired results. After curing
for three hours at 300°C the XPS spectrum clearly shows evidence
for Pd(II) and Pd(0) on the surface for 2:4 metal to polymer ratios.
Longer heating times result in more complete palladium reduction
but with significantly more polymer thermal degradation.

Extension of this work to other metals is currently in progress.
Preliminary results suggest that no resistivity lowering is
achieved with those Ag, Pt, Au, Cu and Li complexes which have
been tried to date. High quality films have been produced;
and in the case of Ag, Pt and Au, reduction to the metallic state
has occurred. These results, however, have not been fully
explained.

A much earlier report[42] appeared concerning Ag incorporation
into the polyamic acid derived from pyromellitic dianhydride
(PMDA) (Structure XV) and ODA. Both Ag metal and $Ag(C_2H_3O_2)$
were added to PMDA + ODA; and films containing 0.25-1.00 gram-
atom silver per repeat unit were obtained. Electroconductivity
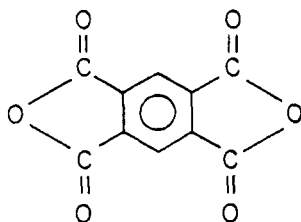
was studied as a function of temperature and Ag content. Thermal
and electrical conductivities were increased 3-7 times for the
polyimide film containing dispersed Ag metal; but no change in
properties was noted for the film containing $Ag(C_2H_3O_2)$.

In 1963 a patent was filed[43] covering very similar work
(e.g. PMDA, 4,4'-methylenedianiline and $Ag(C_2H_3O)$).   The Ag
containing polyamic acid complex was converted to the polyimide
and Ag metal by heating at 300°C in vacuo for 30 minutes. The
film was stated to be tough, flexible, opaque and metallic. At
this stage the film was not conducting. Further heating at 275°C
in air for 5-7 hours rendered it conducting although no resis-
tivity data was reported.

A different kind of metal involvement with polyimides has
recently been reported.[44] This project was concerned with provid-
ing a room temperature bonding process for the purpose of producing
heat resistant bonds. A series of very thin polyimide films under
1 mil in thickness were vacuum metalized with various high melting
metals such as gold. These samples were put in a fixture and
successfully bonded at low pressure to test samples of indium
coated polyimide. The system is believed to make use of the
adhesion of metal films to the organic substrate by the formation
of ligands. Kapton polyimide has been the polymer of choice to
date. The process uses the principle of forming high-melting
solid solutions by the diffusion mixture of two metals where the

minor component may be a low-melting malleable oxidation resis-
tant metal or composite.

Poly(alkylbenzimidazoles)

A series of metal salts having poly(alkylbenzimidazoles)
(Structure XVI for example) as the parent ligand have been
synthesized[45] by mixing dimethylsulfoxide solutions of the
polymer and metal salt in stoichiometric proportions. This
experimental operation gave three results depending on the metal
ion employed. The polymer-metal complex precipitated [Co(II),
Ce(III), Ni(II), Cu(II), Zn(II), Cd(II)], precipitation occurred
on dilution with acetone [Cr(III), Fe(II), Sn(II), Ca(II), Ba(II),
Mg(II), W(VI), V(VI)] or no precipitate appeared [Al(III), Na(I),
K(I)]. Values for the electrical resistivity did not significantly

XVI
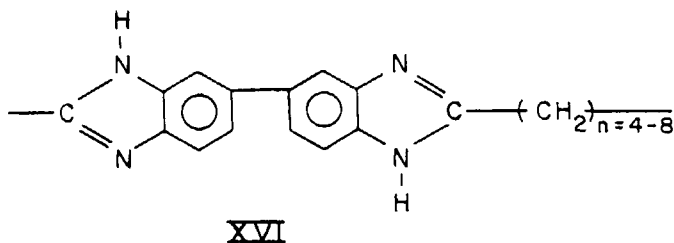
change upon doping the polymer with either $CrCl_3 \cdot 6H_2O$, $CoCl_2 \cdot 6H_2O$
or $Ni(C_2H_3O_2)_2 \cdot 4H_2O$. In contrast, treatment of the polymer with
HCl thereby forming the polymer acid conjugate changed the volume
resistivity from 10^{13} ohm-cm to 10^6 ohm-cm. The nature of the
polymer metal complexes was elucidated using x-ray photoelectron
spectroscopy. Spectra of the core levels of nitrogen, chlorine
and the various metals indicated the formation of polybenzimidazole/
metal salts. In addition it was concluded that the complexes of
Co and Ni were high spin thus ruling out a planar geometry for
the Ni(II) complex.

Poly(vinyl alcohol)

Investigations into poly(vinyl alcohol) (Structure XVII)
have dealt primarily with copper doping. The reader is referred
to the earlier discussion regarding PVA-Cu(II)-I_2 and to "ion-
omeric" type studies with PVA wherein deprotonation of the

$$\left[CH_2-\underset{\underset{OH}{|}}{C}H-CH_2-\underset{\underset{OH}{|}}{C}H\right]_n$$

XVII
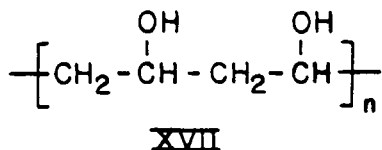
alcoholic group is followed by Cu(II) interaction.[46] One study[47]
which falls into the metal-polymer area as we have defined it
deals with the photoconductivity of PVA films containing Cu(II)
complexes. Well-dried PVA films containing either the nitrate,
sulfate, chloride or bromide salt of Cu(II) have been prepared.
When the ratio $[Cu^{+2}]/[MU]$ (where [MU] denotes the concentration
of PVA monomer residues) is greater than 0.015, illumination at
the charge transfer UV band produces a strong photocurrent in
PVA-$CuCl_2$ and PVA-$CuBr_2$ but not PVA-$Cu(NO_3)_2$ or PVA-$CuSO_4$. Drying
of the films is believed to effect replacement of water molecules
by two halide ions in the copper coordination sphere which is
supported by optical spectra of the film. Nitrate and sulfate
do not appear to enter the first coordination sphere. Tempera-
ture dependent ESR spectra indicate the existence of antiferro-
magnetic superexchange interaction between Cu(II) ions via
intervening halide ions. The exchange interaction is greater for
PVA-$CuBr_2$ than PVA-$CuCl_2$. A network structure is proposed which
is believed to be responsible for photoconduction (Structure XVIII).
When the PVA-$CuCl_2$ film is illuminated at the charge transfer
band the following reaction is believed[46] to occur. The halogen

$$PVA-Cu^{+2} \cdot 2Cl^{-} \xrightarrow{\ h\gamma\ } PVA-Cu^{+} \cdot Cl^{\circ} \cdot Cl^{-}$$
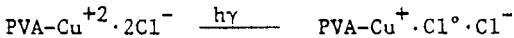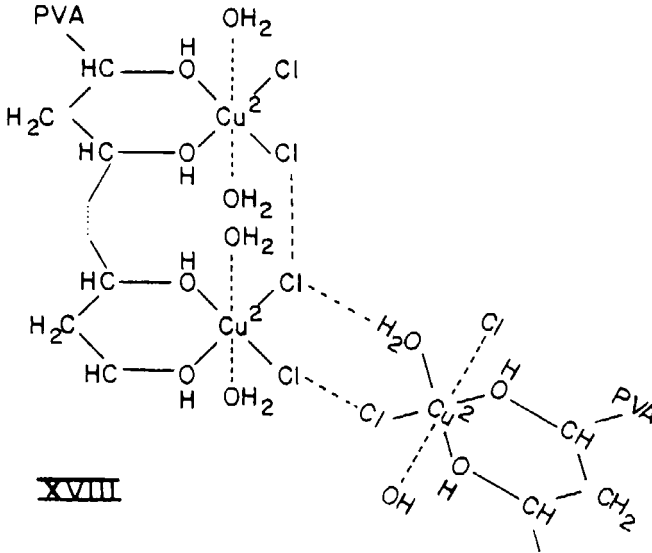
atom abstracts a hydrogen atom from PVA thereby producing a free radical. The authors show some ESR evidence to support this on irradiation. When the ratio $[Cu^{+2}]/[MU]$ is large the halogen atoms interact more with neighboring halide ions. At this point the reduction reaction involves the production of holes in the network of halide ions. The photocurrent is observed when an external electric field is applied to the film. These holes in the network structure are believed to be responsible for the photoconduction. A direct metal-to-metal interaction is stated to not occur.

Polyethers

Glassy polymers have been produced from[48] solutions of $Ca(NCS)_2$ and the polymer derived from Bisphenol A (Structure XIX) and epichlorohydrin (Structure XX). $Ca(NCS)_2$ was appreciably soluble in the "phenoxy" polymer and films containing up to 25% dopant

$$HO-\langle O \rangle- \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} -\langle O \rangle-OH \qquad\qquad Cl-CH_2-CH-CH_2$$
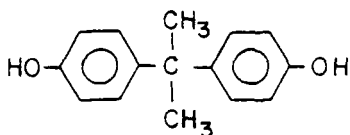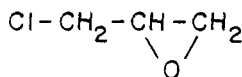
XIX   **XX**

were clear. The anhydrous salt (25% w/w) increased the T_g from 91° to 126°, but the tetrahydrate salt increased the T_g from 162° to 174°. There is an increased resistance to stress cracking by polar organic liquids with the doped polymer. This may be related to the T_g increase or to changes in the solubility parameter, as indicated by insolubility of the salt solutions in solvent for the pure polymer. Increased water sorption and electrical conductivity were found to result from salt incorporation into the polymer. Surface and volume resistivities for the polymer alone were 1×10^{15} ohm and 5×10^{13} ohm-cm; whereas, for "phenoxy" polymer with 13% $Ca(NCS)_2$ by weight the values were 1×10^{10} ohm and 4×10^{10} ohm-cm, respectively. The decrease in resistivity was attributed to the high equilibrium water content accompanying calcium ion addition.

The addition of $ZnCl_2$ and $CoCl_2$ to high (10^5) and low (2000) molecular weight poly(propylene oxide)(PPO) has been reported.[49] Samples were prepared by dissolving PPO and metal salt in methanol or acetone followed by removal of the solvent *in vacuo* at room temperature. $ZnCl_2$ was found to increase the T_g of both high and low molecular weight polymers, but $CoCl_2$ increased the T_g of the low molecular weight polymer only. A single phase system in the $ZnCl_2$ case was indicated; while, a two phase system was apparent in the case of the PPO/$CoCl_2$ with $CoCl_2$ acting as a filler. In the zinc case, elevation of the T_g is believed to result from the formation of five-membered chelate rings by coordination of two adjacent oxygen atoms in the polymer chain with a $ZnCl_2$ molecule.

In an analogous situation, $ZnCl_2$ was added to poly(tetramethylene glycol) with similar results albeit the T_g was raised less for a given amount of metal chloride. Intermolecular coordination with ether oxygen atoms from two neighboring chains was postulated since intramolecular bonding to zinc(II) would involve the formation of a less stable seven-membered chelate ring.

Much earlier[50] the elastomeric properties of PPO mixed with $LiClO_4$ were investigated. Volume contractions were observed and viscoelastic properties were altered which were attributed to strong interaction forces between the Li^+ and polarizable ether oxygens. The glass transition temperature was raised from -70° to 40°C for 25% (w/w) $LiClO_4$ - low molecular weight PPO. Below 15% (w/w) $LiClO_4$, various low molecular weight polymer properties could be interpreted as resulting from the superposition of free polyether segments with those nearest to the $LiClO_4$. Above 15%, no free segments of PPO are believed to remain. The behavior of the high molecular weight PPO was similar, except that below 15% $LiClO_4$ the T_g observed for low molecular weight PPO was split into two transitions, T_g for PPO at -65°C and another at -10°C. The latter is believed to be a transition for polyether helices stabilized by $LiClO_4$ situated in the helix core.

A rather different type study has been performed with water soluble poly(ethylene oxide) (PEO) and various mercuric halides.[51] Fibers of PEO were exposed to saturated anhydrous ether solutions of the mercuric halides for about four weeks. Complexes were formed with a monomer unit (CH_2CH_2O) to mercuric halide ratio of 4:1 for the chloride and bromide and the monomer iodide ratio was 5:1. Examination of the fibers before and after mercuric ion doping with a polarizing microscope and by x-ray diffraction revealed that the chloride fibers remained highly oriented. The bromide fiber was much less oriented; while, the iodide fiber showed no signs of orientation. Although the polymer is water soluble, the polymer complex is not and shows no sign of swelling

in contact with water. The infrared spectrum of the polymer
complex was observed[52] to contain a larger number of absorption
bands over that of the original polymer. This fact suggested
that one of the two C-O bonds per monomeric unit changed from
the trans to the gauche form.

The structures of both the 4:1 (Type I) and 1:1 (Type II)
PEO polymer-HgCl$_2$ complexes have been determined[53] by x-ray
diffraction. For the Type I fiber, four chains pass through
the lattice and four monomeric units are contained in the fiber
identity period. The conformation of PEO in the complex has been
found to be $T_5GT_5\bar{G}$; that is where G and $\bar{G}$ mean the right and
left-handed gauche forms, respectively. The bond length between

$$-CH_2\{O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2\}_n$$

T T   T   T T   G   T T   T   T T $\bar{G}$
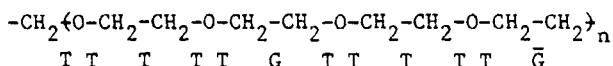
Hg and Cl in the complex (2.30Å) is a little longer than that of
HgCl$_2$ in the crystal (2.25Å). This was consistent with the fact
that the infrared absorption band associated with the antisymmetric
stretching vibration of HgCl$_2$ shifts to 353 cm^{-1} in the complex from
367 cm^{-1} in the crystal. The crystal structure of the Type II
complex was also determined[54] by x-ray diffraction and infrared
absorption methods. For the Type II fiber, two PEO chains pass
through the lattice. The conformation of PEO was near to $TG_2T\bar{G}_2$.
In both cases of Type I and Type II, it was found that the HgCl$_2$
molecule is slightly distorted from its normal linear form.
Coordination to the oxygen atoms of PEO may account for this.
The packing of HgCl$_2$ in Type II is much closer than in Type I.
The nearest Cl---Cl distance is 3.40Å which is smaller than the
sum of the van der Waals radii of the chlorine atoms. The Hg-Cl
distance in the Type II fiber is equal to the distances in the
crystalline state. In this study it was considered that each
oxygen atom of the PEO molecule coordinates to two mercury atoms
with an equivalent distance and angle (<HgOHg=85°).

Polyesters

The interaction of $Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ca(NO_3)_2$ and $Cd(NO_3)_2$ with various polar polymers most of which were polyesters has been investigated.[55] Specifically cellulose acetate, poly(vinyl-acetate), poly(methyl methacrylate) and poly(methyl acrylate) (Structure XXI) were studied. Metal incorporation into the polymer was achieved by mixing solutions of polymer and nitrate followed by casting the solutions onto a KBr plate for infrared measurements or onto a glass plate for T_g measurements. Compatibility of the additive and polymer was tested by noting the clarity of the cast film after evaporation of the solvent. Complete clarity was indicative of solution of the salt in the polymer. Salts were most readily soluble in cellulose acetate with calcium and cadmium nitrates being more soluble than the more covalent zinc and copper salts. Glass transition temperatures varied depending on the salt and polymer system. The absolute magnitude of the shift of T_g with salt concentration did not always continuously increase or decrease (i.e. it maximized or minimized).

Large shifts in the IR spectra of both nitrate and in the polymer carbonyl and ester ether frequencies have been observed. These observations suggested complex formation between polymer and metal salt in the solid state. The carbonyl frequency decreased and the ether frequency increased. The model for the polymer salt

$$-[CH_2-CH]_n$$
$$\quad\quad |$$
$$\quad\quad COOCH_3$$
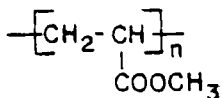
XXI

complex is shown below (Structure XXII). The metal ion is believed to have its nitrate counterions near as well as several solvent molecules since 4 or 6-coordination is anticipated for this metal. A more highly hydrated system was predicted for the ionic salts.

$$
\begin{array}{c}
R \\
| \\
O = C \\
\end{array}
\quad O - R'
$$
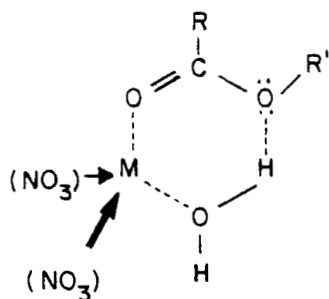
XXII

Differences in properties of the four polymer systems were stated
to be due to interaction and steric effects. The smallest T_g
effects were shown by poly(methyl methacrylate) since the salts
were least readily soluble in this polymer.

Polyacetylene

A major concentrated research effort is now being devoted
to the synthesis and properties of highly conducting derivatives
of polyacetylene (Structure XXIII). Studies have been most
extensive where nonmetal species (eletron acceptors) serve as the
dopant such as I_2, ICl, IBr, AsF_5[56], $(FSO_2O)_2$, H_2SO_4 and $HClO_4$.[57]
Overall increases in conductivity range up to eleven orders of
magnitude with the highest conducting films exhibiting room
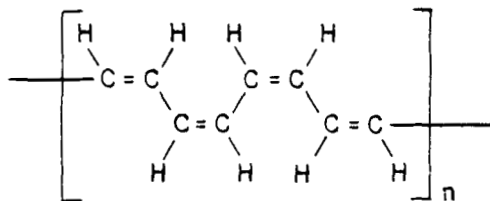
XXIII

temperature values of several hundred ohm^{-1} cm^{-1}. Since this
review is designed to cover only metal doping, the reader is
referred to several treatises[58,59] covering nonmetal species
addition to polyacetylene.

Less effort appears to have been expended toward incorporating
metal species (electron donors) into polyacetylene. Sodium doped
polyacetylene films have been prepared[60] by treating the polymer
with a solution of sodium naphthalide, $Na^{+}(C_{10}H_{18})^{-}$, in THF
whereupon electron transfer from the naphthalide radical anion
to the $(CH)_{x}$ was believed to occur. Employing the trans form,
a film of composition $[Na_{0.28}CH]_{x}$ was produced with conductivity
at 25°C equal to 8×10^{1} ohm^{-1} cm^{-1}. The trans polyacetylene
alone exhibited a conductivity of 4.4×10^{-5} ohm^{-1} cm^{-1}. Lithium
and potassium dopants under similar experimental conditions
yielded comparable results. The general features of electrical
conductivity with eiter donor or acceptor doping are the same,
although detailed differences in the saturation values and the
critical concentration for the metal-insulator transition vary.
In addition donors and acceptors can dope polyacetylene to n-type
and p-type conductors respectively.

Compensation of n-type material by acceptor. doping has been
successfully demonstrated[61] using Na(donor) and I_2 (acceptor).
The conductivity of the n-type material gradually decreases to a
minimum on exposure to an iodine atmosphere. Starting with a film
of initial composition $(CHNa_{0.27})_{x}$ the compensation (minimum con-
ductivity) point occurred at $(CHNa_{0.27}I_{0.28})_{x}$. Continued I_2
doping led to a p-type material where the iodine was believed to
act as a polyanion in the presence of the now positively charged
donor species (D^{+}). The charge transfer need not be complete.
The resulting electron on the polymer chain is weakly bound to the
D^{+}. Compensation in the case of iodine (A) was stated to occur
through formation of $(D^{+}A^{-})$ leaving the polymer chain essentially
neutral and without electronic carriers.

When polyacetylene films are dipped into a solution of $AgClO_4$ or $AgBF_4$ in toluene[62], incorporation of the silver salt takes place to an extent which varies with both the concentration of the toluene solution and the exposure time. Complexes varying in stoichiometry from $(CHAg_{0.006})_x$ to $(CHAg_{0.018})_x$ have been investigated. Striking changes in the film conductivity are produced by silver salt incorporation (i.e. polymer alone, 10^{-5} ohm^{-1} cm^{-1}; $(CHAg_{0.018})_x$, 3 ohm^{-1} cm^{-1}). X-ray diffraction data suggest that (1) $(CH)_x$ remains unchanged, (2) no silver salt is observed and (3) free silver is present. Ammonia vapor causes a rapid decrease in film conductivity; yet, x-ray peaks corresponding to free silver remain unchanged. The enhanced conductivity in the doped film is concluded to not be due to silver metal. Electron microscopy and infrared data suggest that the silver ions are acting as oxidants to give free silver, immobile perchlorate anions and conducting polyolefinic cations according to the following equation:

$$(CH)_x + yAgClO_4 \rightarrow [(CH)_x^{y+}(ClO_4)^-_y] + yAg°$$
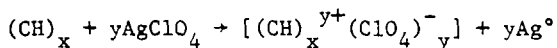
Effects similar to those described for silver are stated to be achieved using the salts of iron and copper; however, no data is available.

Poly(p-phenylene)

Results similar to those obtained with polyacetylene have been realized with poly(p-phenylene) (Structure XXIV) on doping with either electron acceptors or electron donors.[63] The advantage
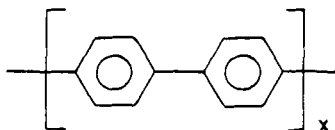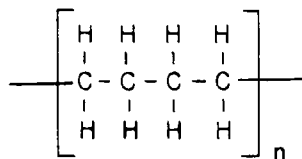

XXIV

of the latter polymer system lies in the fact that $(C_6H_4)_x$ is more thermally stable (e.g. above 450°C in air and 550°C inert) and does not rapidly degrade in air when doped with AsF_4 which exhibits the highest conductivities.

Poly(p-phenylene) can be doped with alkali metals to provide highly conducting n-type materials which have a metallic-gold appearance. Sodium or potassium naphthalide solutions in THF increase conductivity from less than 10^{-10} ohm^{-1} cm^{-1} to a plateau value of 720 ohm^{-1} cm^{-1}. Increases in conductivity are believed to be due to the formation of charge-transfer complexes wherein the metal dopant donates a mobile electron to the polymer chain. Chemical compensation of the potassium doped poly(p-phenylene) can be accomplished with AsF_5 in a manner similar to donor doped polyacetylene.

The effect of moisture, air and halogens on poly(p-phenylene) have been investigated. The alkali metal doped polymer is much more sensitive to air exposure than the AsF_5 doped polymer.[64] Rapid tarnishing of the metallic gold appearance of the doped polymer along with a major decrease in conductivity results. While sodium and potassium dopants produce similar effects with poly(p-phenylene) and polyacetylene, halogens do not provide conducting complexes with the former.[65]

Polyethylenes

Several reports regarding polyethylene and its derivatives with various metal species have appeared, although no extensive studies have been communicated. The effect of salts of carboxylic acids (e.g. metal stearates) on the oxidation of polyethylene (Structure XXV) melts has been studied.[66] For example, zinc

$$\left[\begin{matrix} & H & H & H & H & \\ & | & | & | & | & \\ -\!\!\!-\!\!\!- & C - C - C - C & -\!\!\!-\!\!\!- \\ & | & | & | & | & \\ & H & H & H & H & \end{matrix}\right]_n$$

__XXV__

stearate accelerated the oxidation. The greater the amount of zinc stearate introduced, the greater the oxidation. Copper and lead stearates in low concentrations accelerated polyethylene oxidation. At higher concentrations catalysis of oxidation is observed in the early stages of thermoprocessing, but then in-hibition occurs. Active metals were found to have a similar effect on oxidation. It was concluded that metal containing compounds are formed which diffuse into the melt and control the oxidation rate of the polymer.

Poly(tetrafluoroethylene) (PTFE) is by nature insoluble and highly immiscible with most solids and liquids. This serves as an obstacle to its development into a useful composite mat-erial. Metal-organic substances of low solubility have been found[67] to be miscible with poly(tetrafluoroethylene) (Structure XXVI). Iron pentacarbonyl has been absorbed into PTFE and subsequently transformed into iron oxide applying this principle. The PTFE samples are soaked in a 10% solution of $Fe(CO)_5$ in ethanol at room temperature. Under these conditions the carbonyl

$$\left[\begin{array}{cccc} F & F & F & F \\ | & | & | & | \\ C - C - C - C \\ | & | & | & | \\ F & F & F & F \end{array}\right]_n$$
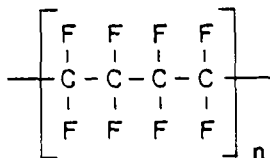
XXVI

is absorbed by the polymer but ethanol is not. Irradiation of the doped PTFE yields non-volatile $Fe_2(CO)_9$; after which, the samples are allowed to undergo air oxidation for three days to yield an Fe_2O_3-PTFE composite. Iron oxide contents range from 0.34 to 1.50%, (w/w). Fe_2O_3 particles are large and close to spherical on the PTFE surface. A dramatic change in adsorbent properties of PTFE occurred on incorporation of Fe_2O_3. The doped polymer is stable at room temperature showing no tendency toward phase separation or embrittlement. The authors suggest that

the oxide may be used to anchor other chemicals and incorporate
them into PTFE leading to other derivatives.

    Thermal pyrolysis and oxidative pyrolysis of poly(propylene)
(PP) (Structure XXVII) with and without chromium have been
recently compared in an effort to improve flame retardancy of
PP.[68] PP was swollen in CCl_4 and then reacted with chromyl
chloride, CrO_2Cl_2, dissolved in CCl_4 at room temperature. The

$$\left[\begin{array}{c} CH_3 \quad\quad CH_3 \quad\quad CH_3 \\ | \quad\quad\quad\quad | \quad\quad\quad\quad | \\ CH-CH_2-CH-CH_2-CH-CH_2 \end{array}\right]_n$$
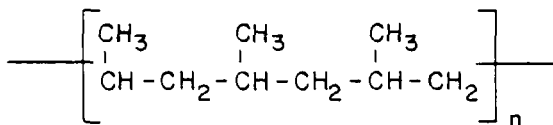
XXVII

product after drying at 60°C for 40 hours contained approximately
2% chromium. Between 388 and 438°C the thermal pyrolysis of PP
and chromium containing PP have comparable reaction rates.
Doping the polymer, however, lowers the thermal pyrolysis act-
ivation energy of PP from 51 to 44 KCal/mole while increasing
the temperature of the maximum pyrolysis endotherm by 15°C. The
effect of chromium on oxidative pyrolysis is more substantive by
comparison. Chromium suppresses the formation of all major
products although no new product was detected. It also increases
the activation energy of oxidative pyrolysis by 10 KCal/mole,
promotes char formation and becomes self-extenguishing with
about 1% of covalently bonded chromium. This behavior suggested
to the investigators that chromium possibly catalyzes termination
processes. Chromium is believed to accelerate the chain term-
ination reaction by providing a nonradical pathway for the
destruction of the reactive hydroperoxide intermediate. The
remarkable efficacy of chromium is emphasized by the fact that
at only 1.5% level of chromium PP has a limiting oxygen index
of 26.4 and a self-ignition temperature of 400°C in air as com-
pared to 17.4 and 250°C respectively for normal PP. The polymer

also contained about 0.6% chlorine, but its presence was not
believed to make any significant contriubtion to flame re-
tardancy.

Poly(methylphenylsiloxane)

The above liquid polymer system provides a unique tech-
nique whereby metal species may be introduced. The employment
of metal vapor-liquid polymer synthetic techniques has been
successfully employed to control the competing processes of
metal atom diffusion, metal atom aggregation and metal atom
anchoring. Francis[69] has demonstrated that Ti, V, Cr and Mo
vapors can be deposited into a liquid poly(methylphenylsiloxane),
(Structure XXVIII) Dow Corning 510, containing a methyl:phenyl
ratio of 17:1. The reactions were carried out in a rotary
reactor in the temperature range 0 to -20°C. Organometallic
polymers in which two phenyl groups are coordinated to the
metal to give an anchored bis(arene) complex are produced.
The reaction scheme V shown below was suggested after spectro-
scopically monitoring the decay of the absorbance due to free

XXVIII
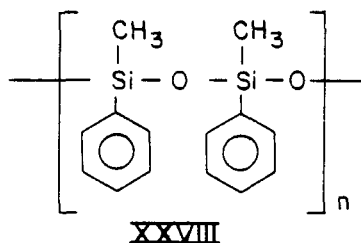
phenyl groups (214 nm) and the corresponding growth of the
absorbances due to products. Polymer-stabilized few-atom
clusters in this system were believed to arise from either
phenyl group solvation effects or bis(arene) metal cluster
complexation. Metal-arene interaction was suggested to
gradually diminish as the cluster nuclearity increased until

Ph of DC 510   A   B
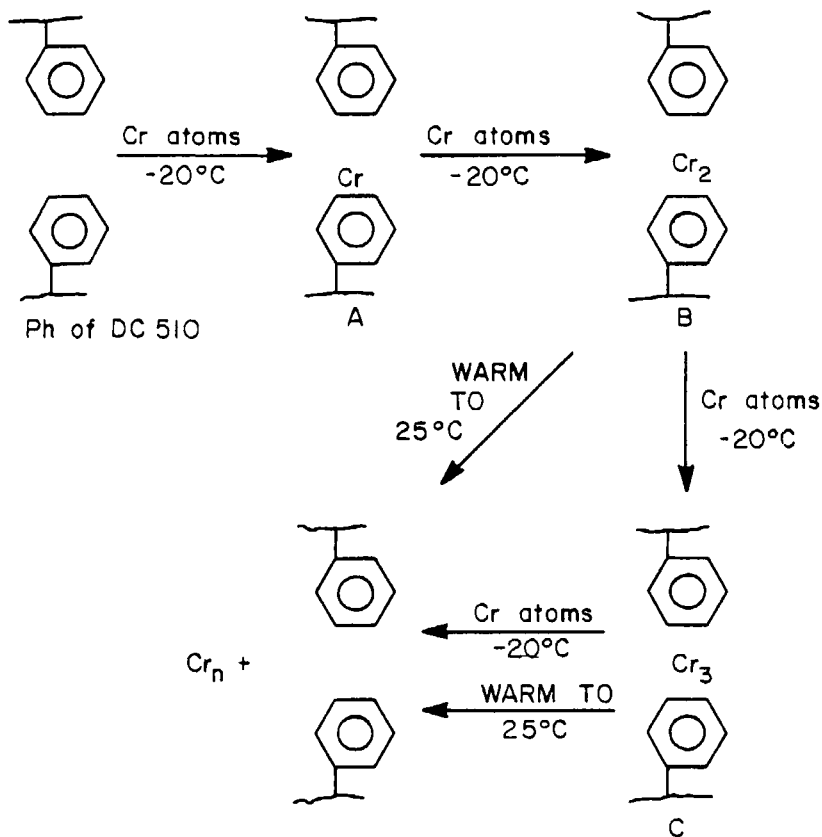
SCHEME $\underline{\text{V}}$

at values of n greater than 3, metal cluster desolvation
occurred to release clusters containing on the order of four
to six metal atoms.

    Attempts[70] to prepare systems containing two different
metals have been reported recently. The bimetallic system
was investigated by means of the following reactions: (1)
sequential Ti and Cr vapor deposition, (2) simultaneous Ti/Cr
vapor deposition, (3) saturation of the phenyl groups on
poly(methylphenylsiloxane) followed by reaction with Cr atoms

and (4) saturation with Cr vapor followed by reaction with Ti
atoms. Bimetal Ti/Cr depositions at low metal loadings led
to polymer-supported bis(arene) complexes with two different
mononuclear metal sites attached to the same polymer. At
high metal loadings binuclear sites containing polymer-stabilized
Ti_2 and Cr_2 as well as TiCr clusters are formed. Very high
Ti/Cr loadings are suggested to lead to unsolvated Cr_xTi_y bi-
metallic clusters approaching colloidal dimensions (Scheme

LOW
METAL
LOADING

TOWARDS
SATURATION

PAST
SATURATION
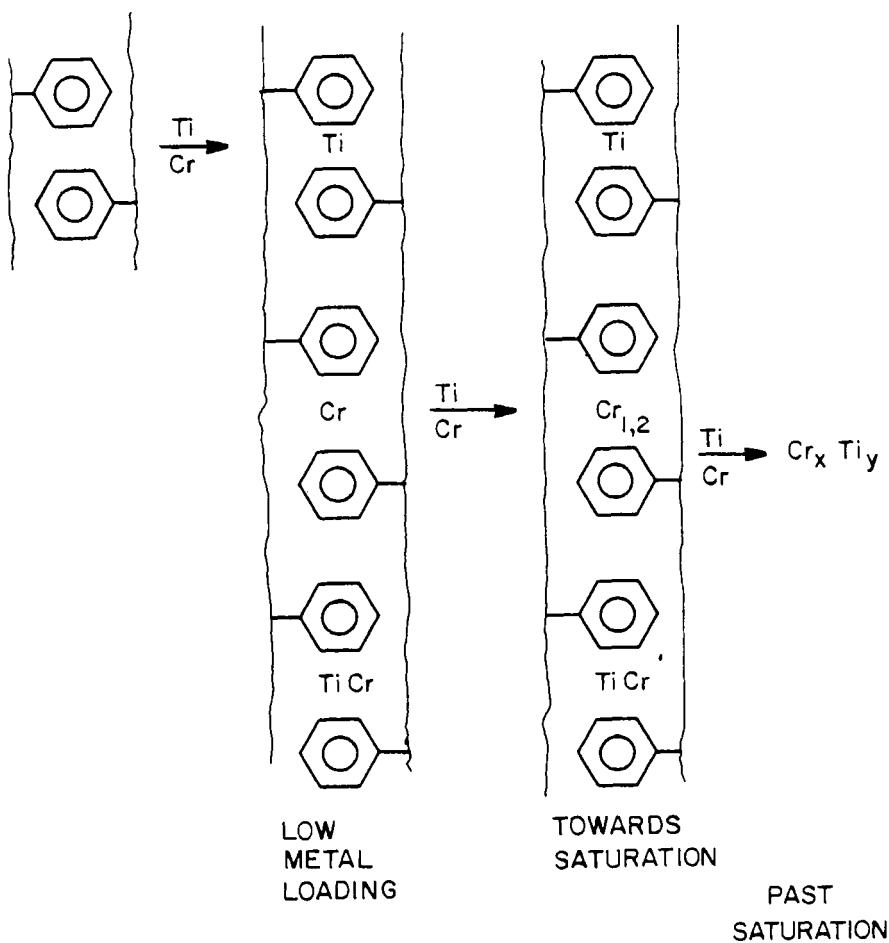
SCHEME VI

VI). Saturation by Ti followed by reaction with Cr indicated that the Ti-containing species are kinetically unstable. For example, the bis(arene) titanium complex appears to yield the TiCr cluster species. Questions regarding the mechanism of Ti displacement by Cr and vice versa were not addressed.

In conclusion, the incorporation of metal related materials into electrically neutral polymers is an active and highly diverse research pursuit. The metallic species and polymer systems which have been explored todate are highly varied. The impetus for such studies is generally the modification of polymer properties; however, the specific properties of interest vary greatly. Modification of adhesive properties, thermal behavior, electrical conductivity, polymer flamability and mechanical properties have been studied for example. The literature cited is by no means meant to be exhaustive; but, we believe it to be well representative of the research area. The area no doubt will continue to expand as investigators explore other metal related dopants and polymer systems in an effort to understand and synthesize materials which posses specific and highly desirable properties.

REFERENCES

(1) E. P. Otocka, J. Macromol. Sci. - Revs. Macromol. Chem., C5, 275 (1971).

(2) E. G. Kolawole and S. M. Mathieson, J. Polym. Sci. Polym. Chem. Ed., 15, 2291 (1977).

(3) H. Matsuda, J. Appl. Polym. Sci., 23, 2603 (1979) and references therein.

(4) C. Carraher and J. Lee, J. Macromol. Sci. Chem., A9, 191
     (1975).

(5) C. U. Pittman, O. Ayers and S. McManus, Macromolecules,
     7, 737 (1974).

(6) C. U. Pittman, Chem. Tech., 416 (1971).

(7) H. Nishikawa and E. Tsuchida, J. Phys. Chem., 79, 2072
     (1975).

(8) A. J. Varma and J. Smid, J. Polym. Sci. Polym. Chem. Ed.,
     15, 1189 (1977).

(9) N. Hojo, H. Shirai, Y. Chujo and S. Hayashi, J. Polym. Sci.
     Polym. Chem. Ed., 16, 447 (1978).

(10) C. U. Pittman, L. R. Smith and R. M. Hanes, J. Amer. Chem.
     Soc., 97, 1742 (1975).

(11) H. Nishide, J. Deguchi and E. Tsuchida, J. Polym. Sci. Polym.
     Chem. Ed., 15, 3023 (1977).

(12) J. Pitha and J. Smid, Biochim. Biophys. Acta, 425, 287 (1976).

(13) H. Nishikawa, E. Terada and E. Tsuchida, J. Polym. Sci.
     Polym. Chem. Ed., 16, 2453 (1978).

(14) C. U. Pittman and L. R. Smith, J. Amer. Chem. Soc., 97,
     1749 (1975).

(15) E. Bayer and V. Schwrig, Chem. Tech., 212 (1976).

(16) J. C. Anderson, U. S. Patent #4,109,052, Aug. 22, 1978.

(17) D. J. Progar and T. L. St. Clair, Preprints, 7th National
     SAMPE Technical Conference, 7, 53 (1975).

(18) C. W. Van Der Waal, H. W. Bree and F. R. Schwargl, J.
     Appl. Polym. Sci., 9, 2143 (1965).

(19) J. M. Pochan, H. W. Gibson and F. C. Bailey, J. Polym.
     Sci. Polym. Lett. Ed., 18, 447 (1980).

(20) Y. W. Park, A. Denensten, C. K. Chiang, A. J. Heeger and
     A. G. MacDiarmid, Solid State Commun., 29, 745 (1979).

(21) T. C. Clarke, R. H. Geiss, W. D. Gill, P. M. Grant, J. W.
     Macklin, H. Morawitz, J. F. Rabolt, D. Sayers and G. B.
     Street, J. C. S. Chem. Comm. 332 (1979).

(22) K. Mizoguchi, T. Kamiya, E. Tsuchida and I. Shinohara, J.
      Polym. Sci. Polym. Chem. Ed., 17, 649 (1979).

(23) A. Ciferri, E. Bianchi, F. Marchese and A. Tealdi,
      Makromol. Chemie, 150, 265 (1971).

(24) B. Valenti, E. Bianchi, G. Greppi, T. Tealdi and A. Ciferri,
      J. Phys. Chem., 77, 389 (1973).

(25) E. Bianchi, A. Ciferri, A. Tealdi, R. Torre and B. Valenti,
      Macromolecules, 7, 495 (1974).

(26) D. Acierno, E. Bianchi, A. Ciferri, B. DeCindio, C. Migliaresi
      and L. Nicolais, J. Polym. Sci. Symposium No. 54, 259 (1976).

(27) D. Acierno, F. P. LaMantia, G. Titamanlio and A. Ciferri,
      J. Polym. Sci. Polym. Phys. Ed., 18, 739 (1980).

(28) P. Dunn and G. F. Sansom, J. Appl. Polym. Sci., 13, 1641
      (1969).

(29) P. Dunn and G. F. Sansom, J. Appl. Polym. Sci., 14, 1799
      (1970).

(30) P. Dunn and G. F. Sansom, J. Appl. Polym. Sci., 13, 1657
      (1969).

(31) H. Kakinoki, O. Sumita, C. S. Cho and F. Higashi, J. Polym.
      Sci. Polym. Lett. Ed., 14, 407 (1976).

(32) F. Higashi, C. S. Cho, H. Kakinoki and O. Sumita, J. Polym.
      Sci. Polym. Chem. Ed., 15, 2303 (1977).

(33) O. Sumita, A. Fukuda and E. Kuze, J. Polym. Sci. Polym. Phys.
      Ed., 16, 1801 (1978).

(34) O. Sumita, A. Fukuda and E. Kuze, J. Appl. Polym. Sci.,
      23, 2279 (1979).

(35) F. Higashi, C. S. Cho, H. Kakinoki and O. Sumita, J. Polym.
      Sci. Polym. Chem. Ed., 17, 313 (1979).

(36) R. J. Angelo and E. I. DuPont DeNemours & Co., U. S.
      Patent, No. 3,073,785 (1959).

(37) R. J. Angelo, Private Communication.

(38) L. T. Taylor, V. C. Carver, T. A. Furtsch and A. K. St.
      Clair, ACS Symp. Ser., 121, 71 (1980).

(39) M. N. Sarboluki, NASA Tech. Brief, 3(2), item 36, Oct.,
      1978.

(40) A. K. St. Clair, V. C. Carver, L. T. Taylor and T. A.
      Furtsch, J. Amer. Chem. Soc., 102, 876 (1980).

(41) L. T. Taylor, V. C. Carver, T. A. Furtsch and A. K. St.
      Clair, PREPRINTS, Org. Coat. and Plas. Chem., 43, 635
      (1980).

(42) N. S. Lidorenko, L. G. Gindin, B. N. Yegorov, V. I.
      Kondratenkov, I. Y. Ravich and T. N. Toroptseva, AN SSSR,
      Doklady, 187, 581 (1969).

(43) A. L. Endrey and E. I. DuPont DeNemours & Co., U. S. Patent,
      No. 3,073,784 (1963).

(44) R. E. Frazer, NASA Tech Brief, 4(1), item 101, Aug., 1979.

(45) S. M. Aharoni and A. J. Signorelli, J. Appl. Polym. Sci.,
      23, 2653 (1979).

(46) N. Hojo, H. Shirai and S. Hayashi, J. Polym. Sci. Symp. No.
      47, 299 (1974).

(47) O. Sumita, A. Fukuda and E. Kuze, J. Polym. Sci. Polym.
      Phys. Ed., 18, 877 (1980).

(48) M. J. Hannon and K. F. Wissbrun, J. Polym. Sci. Polym.
      Phys. Ed., 13, 113 (1975).

(49) R. E. Wetton, D. B. James and W. Whiting, J. Polym. Sci.
      Polym. Lett. Ed., 14, 577 (1976).

(50) J. Moacanin and E. F. Cuddihy, J. Polym. Sci., C14, 313
      (1966).

(51) A. A. Blumberg and J. Wyatt, Polym. Lett., 4, 653 (1966).

(52) A. A. Blumberg, S. S. Pollack and C. A. J. Hoeve, J. Polym.
      Sci., A2, 2499 (1964).

(53) R. Iwamoto, Y. Saito, H. Ishihara and H. Tadokoro, J. Polym.
      Sci. Part A-2, 6, 1509 (1968).

(54) M. Yokoyama, H. Ishihara, R. Iwamoto and H. Tadokoro,
      Macromolecules, 2, 184 (1969).

(55) K. F. Wissbrun and M. J. Hannon, J. Polym. Sci. Polym.
      Phys. Ed., 13, 223 (1975).

(56) R. H. Baughman, S. L. Hsu, L. R. Anderson, G. P. Pez and
     A. J. Signorelli, "Molecular Metals", NATO Conference
     Series, W. E. Hatfield, Ed., Plenum Press, New York, 1979,
     pp. 187.

(57) S. C. Gau, J. Milliken, A. Pron, A. G. MacDiarmid and
     A. J. Heeger, J. C. S. Chem. Comm., 662 (1979).

(58) A. G. MacDiarmid and A. J. Heeger, "Molecular Metals",
     NATO Conference Series, W. E. Hatfield, Ed., Plenum Press,
     New York, 1979.

(59) T. C. Clarke, R. H. Geiss, W. D. Gill, P. M. Grant, H.
     Morawitz, G. B. Street and D. E. Sayers, Synthetic Metals,
     1, 21 (1979/80).

(60) C. K. Chiang, M. A. Druy, S. C. Gau, A. J. Heeger, E. J.
     Louis, A. G. MacDiarmid, Y. W. Park and H. Shirakawa,
     J. Amer. Chem. Soc., 100, 1013 (1978).

(61) C. K. Chiang, S. C. Gau, C. R. Fincher, Y. W. Park, A. G.
     MacDiarmid and A. J. Heeger, Appl. Phys. Lett., 33, 18
     (1978).

(62) T. C. Clarke, R. H. Geiss, J. F. Kwak and G. B. Street,
     J. C. S. Chem. Comm., 489 (1978).

(63) D. M. Ivory, G. G. Miller, J. M. Sowa, L. W. Shacklette,
     R. R. Chance and R. H. Baughman, J. Chem. Phys., 71, 1506
     (1979).

(64) R. H. Baughman, D. M. Ivory, G. G. Miller, L. W. Shacklette
     and R. R. Chance, PREPRINTS, Org. Coat. and Plas. Chem.,
     41, 139 (1979).

(65) L. W. Shacklette, R. R. Chance, D. M. Ivory, G. G.
     Miller and R. H. Baughman, Synthetic Metals, 1, 307 (1979/80).

(66) N. I. Egorenkov, D. G. Lin and V. A. Bely, J. Polym.
     Sci. Polym. Chem. Ed., 13, 1493 (1975).

(67) F. Galembeck, C. C. Ghizoni, C. N. Inpe, C. A. Ribeiro,
     H. Vargas and L. C. M. Miranda, J. Appl. Polym. Sci.,
     25, 1427 (1980).

(68) J. C. W. Chien and J. K. Y. Kiang, Macromolecules, 13,
     280 (1980).

(69)   C. G. Francis and P. L. Timms, J. Chem. Soc. Chem. Commun.,
       466 (1977).

(70)   C. G. Francis, H. Huber and G. A. Ozin, J. Amer. Chem. Soc.,
       101, 6250 (1979).