

Organometallic polymers

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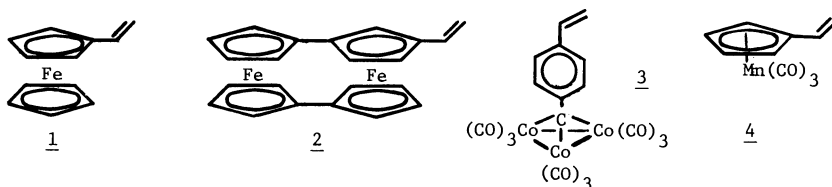
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Abstract - The preparation of a variety of (η^5 -vinylcyclopentadienyl)metal type monomers including (η^5 -vinylCp)M(CO)₂, where M = Co, Rh, Ir, (η^5 -vinylCp)W(CO)₃CH₃, (η^5 -vinylCp)M(CO)₂NO, where M = Cr, Mo, W, (η^5 -vinylCp)(η^5 -Cp)TiCl₂, (η^5 -vinylCp)CuPEt₃ and (η^5 -isopropenylcyclopentadienyl)metal type monomers including (η^5 -isopropenylCp)M(CO)₂NO, where M = Cr, Mo, W, (η^5 -isopropenylCp)M(CO)₂, where M = Co, Rh, (η^5 -isopropenylCp)M(CO)₃CH₃ and (η^5 -isopropenylCp)₂Sn have been prepared. The homopolymerization kinetics of (η^5 -vinylCp)W(CO)₃CH₃ and (η^5 -vinylCp)Cr(CO)₂NO were studied. Copolymerization of several η^5 -vinylCp monomers with styrene, methyl acrylate, acrylonitrile and N-vinylpyrrolidone were conducted using radical initiation. From the reactivity ratios, values of the Alfrey-Price Qe parameters were obtained, illustrating that all of the metallic monomers studied were exceptionally electron rich. Cationic initiation of the (η^5 -isopropenylCp)-metal type monomers gave low molecular weight homopolymers and copolymers at best. The syntheses of 1,1'-bis(β -aminoethyl)ferrocene and 1,1'-bis(β -hydroxyethyl)ferrocene and their interfacial polycondensation with both diacid chlorides and diisocyanates was conducted. These two monomers were compared to their corresponding 1,1'-bis(α -substituted)ferrocene analogs which had been previously studied in polycondensations.

INTRODUCTION

Organometallic polymers are useful in a variety of applications ranging from antifouling agents to catalysts to semiconductors (ref.1-3). The synthesis of organometallic polymers can proceed by modifying known polymers with organometallic units or by preparing organometallic monomers and then polymerizing (or copolymerizing) them. Monomers 1 - 4 represent organometallic monomers previously prepared and polymerized in our laboratory (ref. 4). In each case the organometallic group can electronically interact with the polymerizing center.



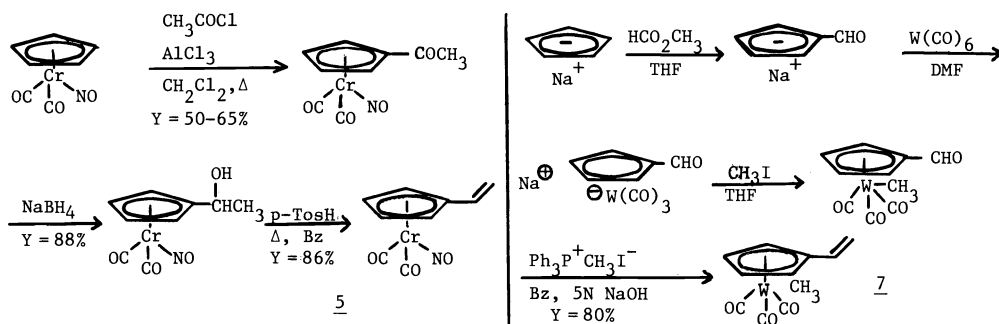
In the radical initiated homopolymerization of both vinylferrocene, 1, in benzene and vinylcymantrene, 4, unusual homopolymerization kinetics were observed (ref. 11, 12). The polymerization of 1 was first order both in monomer and in initiator (AIBN) exhibiting: $V_p = 5.64 \times 10^{-4} [1]^{1.12} [AIBN]^{1.11}$ due to a novel monomolecular termination mechanism caused by electron transfer from iron to the radical center followed by termination (ref. 11). Unlike most vinyl monomers, the molecular weight of poly(vinylferrocene) does not increase with a decrease in $[In]$ but it does increase with an increase in $[1]$ (ref. 7). This is the result of the high chain-transfer constant of 1 ($C_m = 8 \times 10^{-3}$). Vinylcymantrene, 4, also exhibited unusual radical homopolymerization kinetics (ref. 12). In benzene, acetone and benzonitrile $V_p \propto [4]^{1.5} [In]^{0.5}$. This illustrated the initiator (AIBN) efficiency was low and initiation rate is proportional to $[4]$ (ref. 12). In such cases one derives $DP = V_p/V_i = [k_p/(2f' k_t k_d)^{0.5}] ([4]/[In])$ and molecular weight measurements verified this relationship. Copolymerizations of both 1 and 4 with styrene and other monomers were carried out to give the reactivity ratios r_1 and r_2 from which the Alfrey Price e values were calculated (ref. 5, 6, 8, 13, 14). For vinylferrocene and vinylcymantrene the values of e were 2.1 and 1.99 respectively.

The cationic polymerization of organometallic monomers is not well studied. Kunitake and coworkers obtained only very low molecular weights in vinylferrocene homo- and copolymerizations (ref. 15). Korshak et al (ref. 16) and Jablonski and Christl (ref. 17) were not able to make high molecular weight materials from 1,1'-diisopropenylferrocene. However, in view of the well known facile polymerizations of isobutylene and α -methylstyrene under cationic initiation, we investigated the cationic polymerizations of several isopropenyl organometallic monomers.

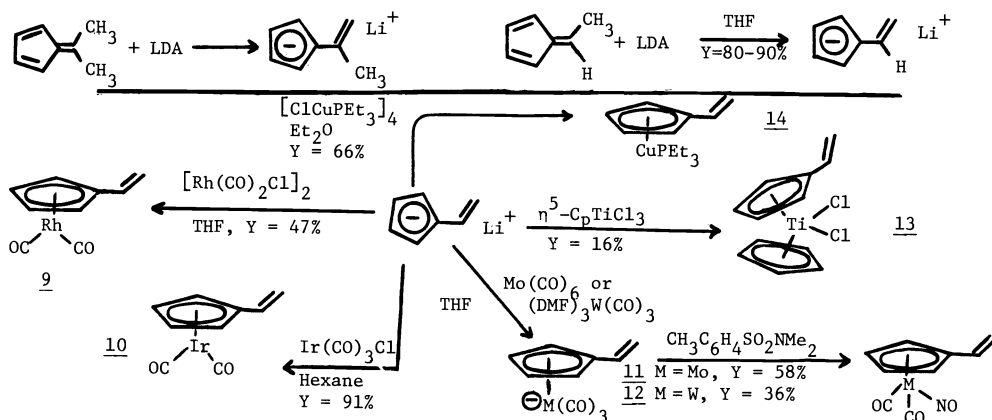
Many previous condensation polymerizations of difunctional ferrocene monomers have emphasized the use of $-\text{COOH}$, $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{NH}_2$ groups at the 1 and 1' positions (ref. 18-20). Thus, during polycondensations (frequently conducted under forcing conditions) steric effects can retard rates. Also, the great stability of α -ferrocenyl carbenium ions could facilitate cleavage of the chain and subsequent side reactions. Thus convenient routes were developed to the 1,1'-bis(β -aminoethyl)- and 1,1'-bis(β -hydroxyethyl)ferrocene monomers to minimize these effects during polymerizations (ref. 21).

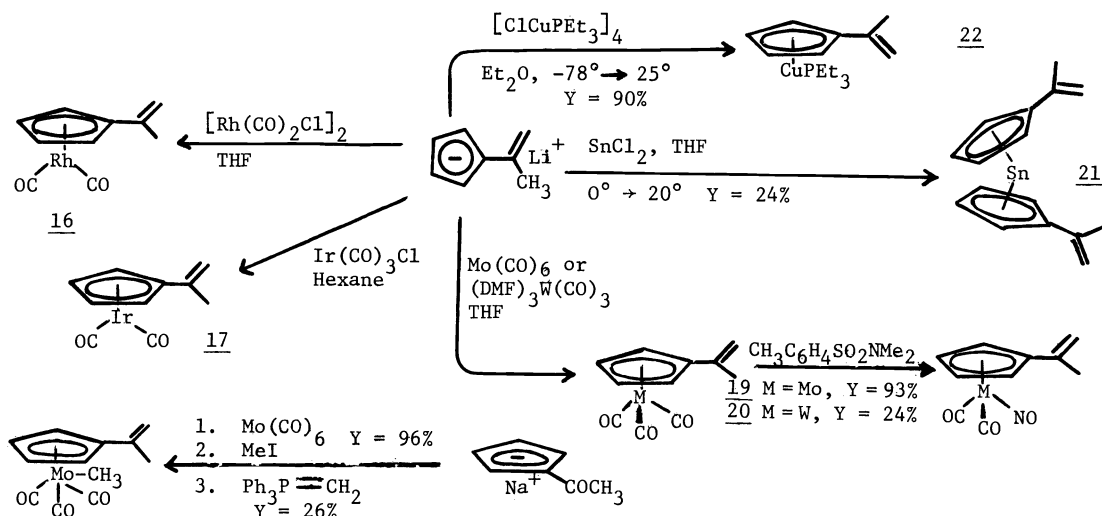
MONOMER SYNTHESSES

(η^5 -VinylCp)Cr(CO)₂NO, **5** was prepared by Friedel Crafts acylation of (η^5 -Cp)Cr(CO)₂NO followed by NaBH₄ reduction to the alcohol and acid catalyzed dehydration (ref. 22-24). While this general method works well for the synthesis of **1**, **2**, **4**, and **5** it is severely limited in scope. Thus, in another approach, sodium cyclopentadienide was reacted with ethylformate to give **6**. This reagent permits the generation of a number of (η^5 -CpCHO)metal derivatives such as (η^5 -CpCHO)M(CO)₂ where M = Co or Rh, and (η^5 -CpCHO)W(CO)₃CH₃, respectively, upon reaction with Co₂(CO)₈/I₂, [Rh(CO)₂Cl]₂ or W(CO)₆ followed by CH₃I (ref. 25-27). However, Wittig chemistry is then required to convert the formyl group to a vinyl moiety. This reduces the scope and convenience of this method. The synthesis of (η^5 -vinylCp)W(CO)₃CH₃, **7**, is illustrated below using this route (ref. 25, 26).

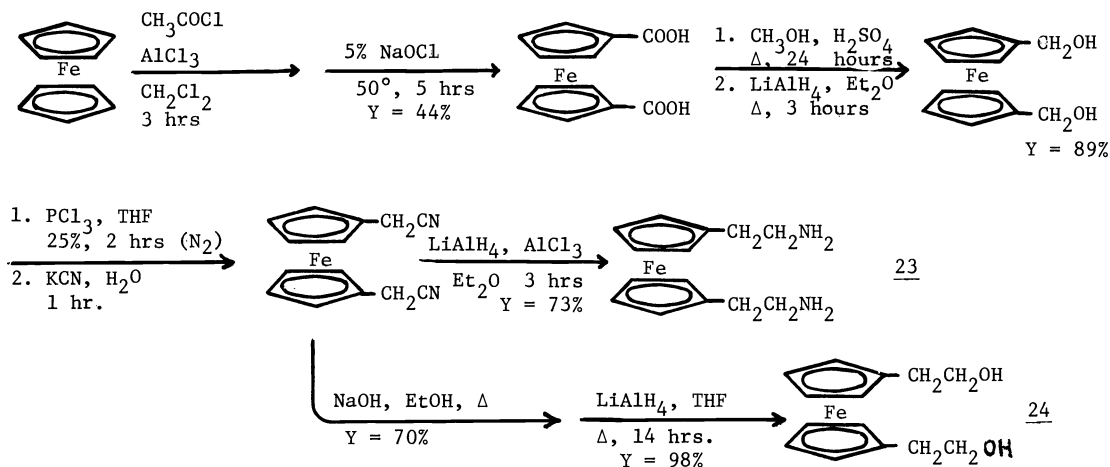


A more general synthesis of the (η^5 -vinylCp)-metal type monomers was developed using 6-methylfulvene (ref. 28, 29). Treatment of 6-methylfulvene with LDA in THF at 25° gave vinylcyclopentadienyl lithium. Likewise reaction of 6,6-dimethylfulvene with LDA gave isopropenylcyclopentadienyl lithium. Both these salts react with a variety of organometallic compounds to directly afford the η^5 -vinyl- and η^5 -isopropenylcyclopentadienyl metal monomers **8** - **22**. This is a convenient means of introducing both vinyl- and isopropenylcyclopentadienyl moieties into organometallic systems incapable of undergoing electrophilic substitution.





The preparation of 1,1'-bis(β -aminoethyl)ferrocene, **23**, and 1,1'-bis(β -hydroxyethyl)ferrocene, **24**, followed conventional paths as shown below (ref. 31).



HOMOPOLYMERIZATION KINETICS OF $(\eta^5\text{-VINYL C}_5\text{H}_4)\text{W}(\text{CO})_3\text{CH}_3$ and $(\eta^5\text{-VINYL C}_5\text{H}_4)\text{Cr}(\text{CO})_2\text{NO}$

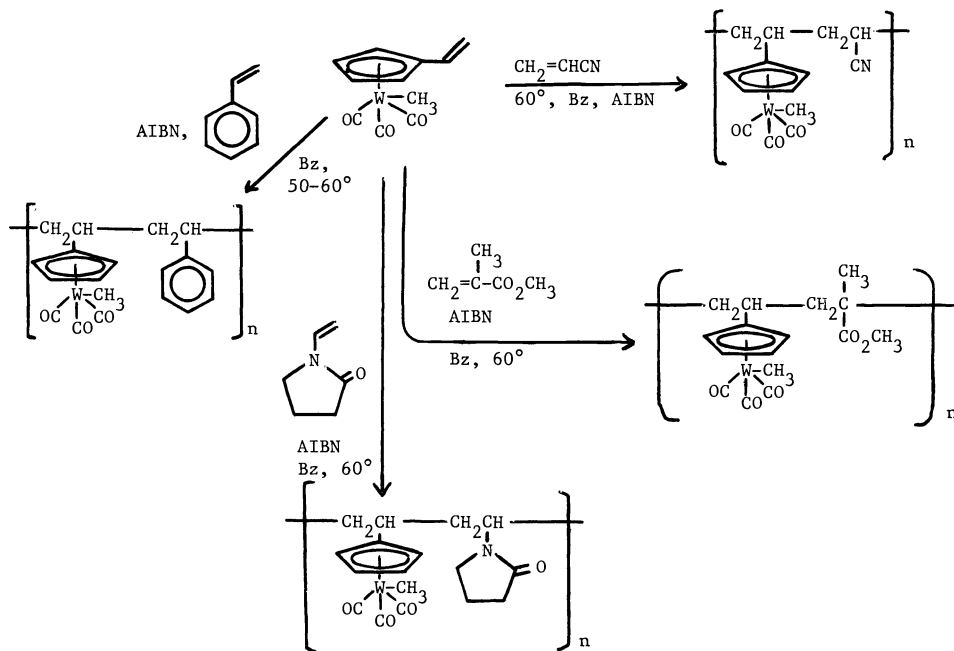
$(\eta^5\text{-VinylCp})\text{W}(\text{CO})_3\text{CH}_3$, **7**, homopolymerized sluggishly in benzene using AIBN initiation at 60° (ref. 26, 32). The rate law: $r_p = 1.13 \times 10^{-2} [\text{7}] [\text{AIBN}]^{2.3}$ emerged. Several reinitiations were usually needed to get good homopolymer yields. Chain transfer via hydrogen abstraction from W-CH₃, the Cp ring or backbone methine positions was ruled out. The polarity of the solvent did not strongly influence homopolymerization of **7**.

Homopolymerizations of $(\eta^5\text{-VinylCp})\text{Cr}(\text{CO})_2\text{NO}$, **5**, in ethyl acetate using AIBN as the initiator were slow. They followed the equation $r_p = 1.70 \times 10^{-4} [\text{AIBN}]^{1/2} [\text{5}]^1$ and gave relatively low molecular weights ($\bar{M}_n = 20,000$ or less) (ref. 23, 24). At constant $[\text{5}]/[\text{AIBN}]$ ratios the molecular weight increased as the $[\text{5}]$ increased. Molecular weight also increased as $[\text{5}]/[\text{AIBN}]$ increased with mol. wt. approximately $\propto ([\text{5}]/[\text{AIBN}])^{1/3}$. When homopolymerized neat at 100°C low yields were obtained unless multiple initiations were used (reminiscent of **1** and **4**). In benzene the $r_p \propto [\text{5}]^{1.5}$ illustrating the similarity of this monomer to **4** and pointing out the low initiation efficiency of **5**.

COPOLYMERIZATIONS OF $(\eta^5\text{-VINYL C}_5\text{H}_4)$ ORGANOMETALLIC MONOMERS

Vinyl monomers **5** and **7-14** have been copolymerized using AIBN initiation with a variety of comonomers such as styrene, methyl acrylate, methyl methacrylate, acrylonitrile N-vinylpyrrolidone etc (ref. 33, 34 and others cited). This is illustrated below for **7**. Space precludes much discussion but typically more extensive studies were made with styrene. Copolymerizations at a variety of M_1/M_2 ratios were fitted (using the nonlinear least

squares method of Mortimer and Tidwell (ref. 35)) to the integrated form of the copolymer equation via our own computer programs to give the reactivity ratios, r_1 and r_2 . From r_1 and r_2 the Alfrey Price Q_e values were calculated using: $r_1 = (Q_1/Q_2 \exp[-e_1(e_1-e_2)])$ and $r_2 = (Q_2/Q_1 \exp[-e_2(e_2-e_1)])$. From this treatment a semiquantitative picture of the electron 'richness' of the monomers' vinyl groups and their propagating radicals' resonance stability arises.



The values of e for several organic monomers are summarized below together with their reactivity ratios in styrene copolymerizations (styrene = M_2). What clearly emerges from this treatment is that all the η^5 -vinylCp-metal monomers are exceptionally electron rich.

	<u>1</u>	<u>4</u>	<u>5</u>	<u>11</u>	<u>7</u>	<u>10</u>
r_1	0.09	0.098	0.30	0.31	0.16	0.29
r_2	2.91	2.50	0.82	0.83	1.55	0.68
e	-2.1	-1.99	-1.98	-1.98	-1.98	-2.08
Q	1.03	1.1	3.1	3.1	1.66	4.1
e	-1.96	-0.80	-0.80	0.39	-0.78	+2.25
Q	1.46	2.86	1.00	1.63	0.002	0.23

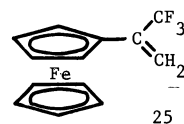
For comparison, their e values show they have vinyl groups similar to 1,1'-dianisylethylene in this respect. Varying the nature of the other metal-bonded ligands or changing the metal atom does not change this result and the values of e are all close to -2.

The values of Q indicate substantial resonance stabilization of the α -organometallic propagating radical exists in each case. Thus, the electron deficient radical center is delocalized into the ring. As one would expect, each of these monomers resists homo- or copolymerization via anionic initiation. The Q_e scheme holds for a variety of electron rich comonomers. Thus, similar e -values are obtained using N-vinyl-2-pyrrolidone ($e = -1.14$, $Q = 0.14$) as M_2 . However, when electron attracting monomers such as methyl acrylate or acrylonitrile are used the results vary substantially. This is the result of a contribution into the copolymerization mechanism of charge-transfer complexes between the very electron rich organometallic monomers with the electron attracting comonomer.

Cobalt monomer 8 was not successfully homo- or copolymerized due to competitive decomposition under radical conditions. Its iridium analog 10 was quite stable. Similar to 8, some radical initiated copolymerizations of cobalt monomer 3 with styrene and MMA also involved competitive decomposition precluding accurate r_1, r_2 determinations. Homopolymers of 10 when treated with NaHBET_3 gave active hydrogenation catalysts while styrene copolymers of 7 were active olefin metathesis catalysts when treated with iBuAlCl_2 .

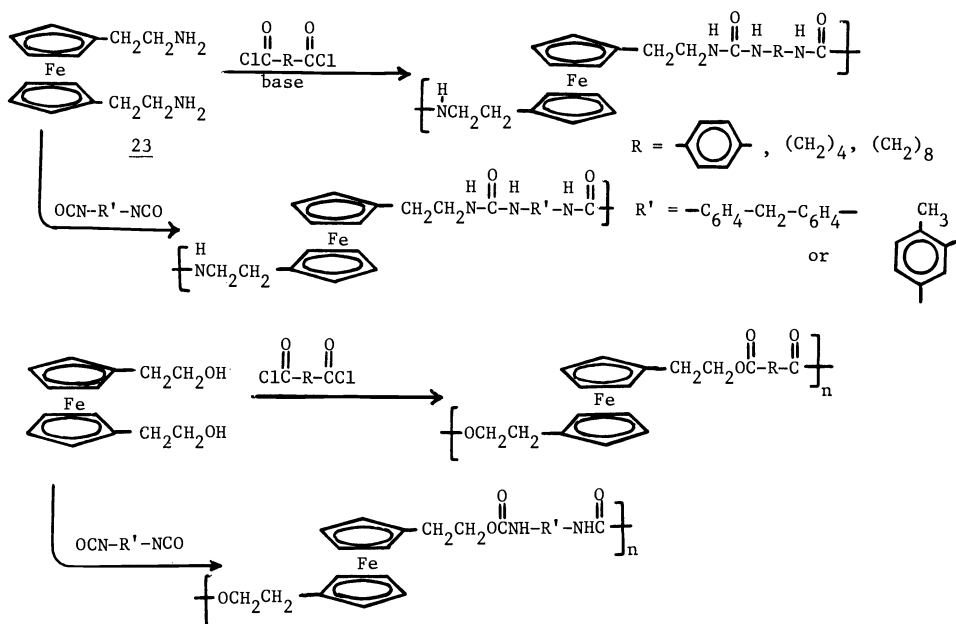
Isopropenyl monomers 15-22 can be looked upon as analogs of α -methylstyrene. However, under cationic polymerization conditions they were not readily homo- or copolymerized (ref. 36). Isopropenylferrocene gave only low molecular weight, predominantly syndiotactic polymers (Mwt max. = 3900 using $\text{BF}_3 \cdot \text{OEt}_2 / \text{CH}_2\text{Cl}_2$, 20°) and no polymers at temperatures below -40° . NMR evidence for termination via internal cyclization has been presented. Stanocene monomer 21 does not polymerize perhaps because the lone pair on tin may act like a Lewis base deactivating the cationic initiators. Likewise 18 resisted any cationic polymerization while 19 gave low mwt products or products where CO stretching absorptions were absent.

If the exceptional α -carbonium ion stability in these systems is causing low polymerization reactivity, a destabilized system might be more reactive. Thus 25 was prepared but it did not homopolymerize with SnCl_4 or $\text{BF}_3 \cdot \text{OEt}_2$. However a 5:1 styrene/25 mixture gave a copolymer, $M_n=4200$ containing 45 mole % 25.



NEW CONDENSATION POLYMERS FROM 23 AND 24

Interfacial polycondensation of 1,1'-bis(β -aminoethyl)ferrocene, 23, with diacid chlorides and diisocyanates gave new polyamides and polyureas (ref. 31). Polymerizations could be conducted at ambient temperatures in contrast to earlier high-temperature polymerizations. Likewise, 1,1'-bis(β -hydroxyethyl)ferrocene, 24, reacts with diacid chlorides and diisocyanates to form ferrocene-containing polyesters and polyurethanes, respectively. Since the reactive groups (NH_2 , OH) are two methylene units removed from the ferrocene nucleus, steric effects are reduced and the instability found in polymers of α -functional ferrocenes, due to the α -ferrocenyl carbonium ion stability, is removed. The polyamide obtained with adipoyl chloride was elastomeric and the polyureas were hard powders.

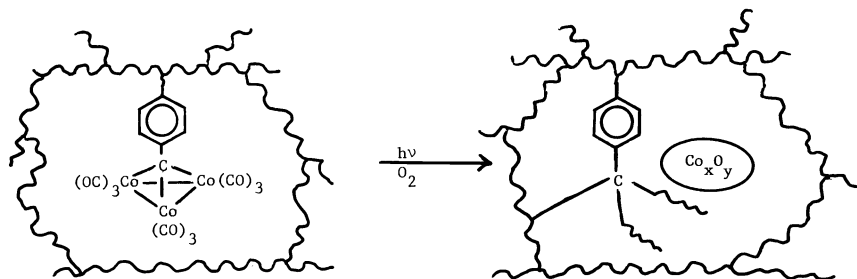


At 300°C the polyamides showed negligible weight loss under nitrogen, whereas polyesters, polyureas and polyurethanes exhibited substantial weight loss. Polyamides with $[\eta]$ values to 1.5 dL/g (m-cresol, 32°) were obtained. Polyurethanes exhibited lower $[\eta]$ values due to premature precipitation from solution and, in the case of 23 + toluenediisocyanate, decreased reactivity due to steric effects.

Further studies involving the polymerization of 23 and 24 and their ruthenium and osmium analogs for thermoplastic block copolymers and for surface modified electrode films is underway.

An interesting possible use of organometallic polymers involves their use in preparing highly dispersed metal or metal oxides within polymer films. By decomposing an organometal-

lic moiety which is chemically attached along the polymer chain one might be able to prepare very tiny metal or metal oxide particles within the polymer matrix. Highly dispersed metal oxide particles are of interest in a variety of materials applications. Since homopolymerization and copolymerization of cobalt monomer **3** led to decomposition of a fraction of **3** in some cases, we undertook the incorporation of **3** into styrene-divinylbenzene resins under mild conditions (ref. 37). Both solution and latex terpolymerizations of **3** with styrene and divinylbenzene were carried out at temperatures of 25°C or below. The resulting resins exhibited IR spectra with carbonyl stretching frequencies the same as pure **3**. Thermal and photolytic decompositions of the $-\text{CCo}(\text{CO})_3$ moiety, in air, within the resins resulted in very fine dispersions of cobalt oxides within the resins.



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