Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Catalysis by Transition Metal Derivatives Bound to Structurally Ordered Polymers

Carlo Carlini[a]; Glauco Sbrana[a]
[a] Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica Industriale, Università di Pisa, Pisa, Italy

To cite this Article Carlini, Carlo and Sbrana, Glauco(1981) 'Catalysis by Transition Metal Derivatives Bound to Structurally Ordered Polymers', Journal of Macromolecular Science, Part A, 16: 1, 323 — 355
To link to this Article: DOI: 10.1080/00222338108082055
URL: http://dx.doi.org/10.1080/00222338108082055

J. MACROMOL. SCI.-CHEM., A16(1), pp. 323-355 (1981)

Catalysis by Transition Metal Derivatives Bound to Structurally Ordered Polymers

Carlo CARLINI and Glauco SBRANA

Centro di Studio del C.N.R. per le Macromolecole Stereordinate ed Otticamente Attive, Istituto di Chimica Organica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa, Italy.

INTRODUCTION

It is well known that metalloenzymes are able to catalyze chemical reactions with a very high activity and selectivity|1-3|. Therefore the synthesis of complexes between transition metal derivatives and structurally ordered macromolecular ligands to give catalytic systems having high activity and stereoselectivity is of large interest from both applicative and speculative point of view. In this connection the main aim of this article is to emphasize the role of the constitutional and configurational order of the macromolecular ligand in determining the properties of the corresponding complexes with transition metal derivatives. This is of particular importance for designing catalytic systems displaying peculiar features as far as activity, selectivity and stereochemistry are concerned. Moreover a better insight into environment and coordination sphere of the polymer attached metal derivative can be of great help for mechanistic studies of the reactions involved.

COMPLEXES OF TRANSITION METAL DERIVATIVES WITH POLY(α-AMINO ACID)S

A large amount of work has been carried out dealing with complexes of transition metal ions and synthetic low and high molecular weight peptides|1,4|. However, few cases have been investigated up to now concerning complexes of transition metal derivatives with poly(α-amino acid)s, looking at possible relations between catalytic, stereochemical properties and primary as well as secondary structure of the polymer ligand.

Pecht et al. have reported|5,6| that poly(L-histidine)-Cu(II) |PLHCu(II)| complexes are catalytically active in the homogeneous oxidation of ascorbic acid(I), (2,5-dihydroxyphenyl)acetic acid(II) and *p*.hydroquinone(III)(Scheme 1) in the range of pH 4.3-5.0, depending on the substrate used. PLHCu(II) complexes exhibited higher catalytic activity than the aquo copper(II) complex, the activity ratio being in the range 6.2-172 (Table 1).

The structure proposed by the authors|6,7|, on the basis of potentiometric titrations and circular dichroism data, for the PLHCu(II) complex formed at pH< 5 involves, in addition to three imidazole nitrogens, at least one deprotonated peptide nitrogen at the square planar coordination positions of Cu(II) ion. Recently|8| Peggion et al. have better defined such structure showing that it is not compatible with the β structure of poly(L-histidine) but with a random coil polypeptide chain. According to these last results the higher activity of PLHCu(II) complexes seems to be attributed not to a peculiar ordered conformational environment of the

TABLE 1

Catalytic Oxidation and Hydrolysis by Water Soluble Complexes of Copper(II) with Different Poly(α-amino acid)s

Catalyst	Reaction	pH	Substrate	Stereoselectivity index[a]	Activity ratio[b]	Ref.
PLHCu(II)	Oxidation	4.3	ascorbic acid	-	6.2	6
		5.0	(2,5-dihydroxyphenyl)-acetic acid	-	172	6
		4.8	*p*.hydroquinone	-	95	6
PLLCu(II)	Oxidation	10.5	DL- and L-3,4dihydroxy-phenylalanine	1.53	7[c]	9,10
		6.9		1.00	2.9[d]	9
PLLCu(II)	Hydrolysis	7.0	D- and L-phenylalanine methyl and ethyl esters	2.41	552[e]	13

[a] Expressed as the ratio between initial oxidation rate or pseudo first order hydrolysis constants of D and L enantiomers.

[b] With respect to the aquo copper(II) complex.

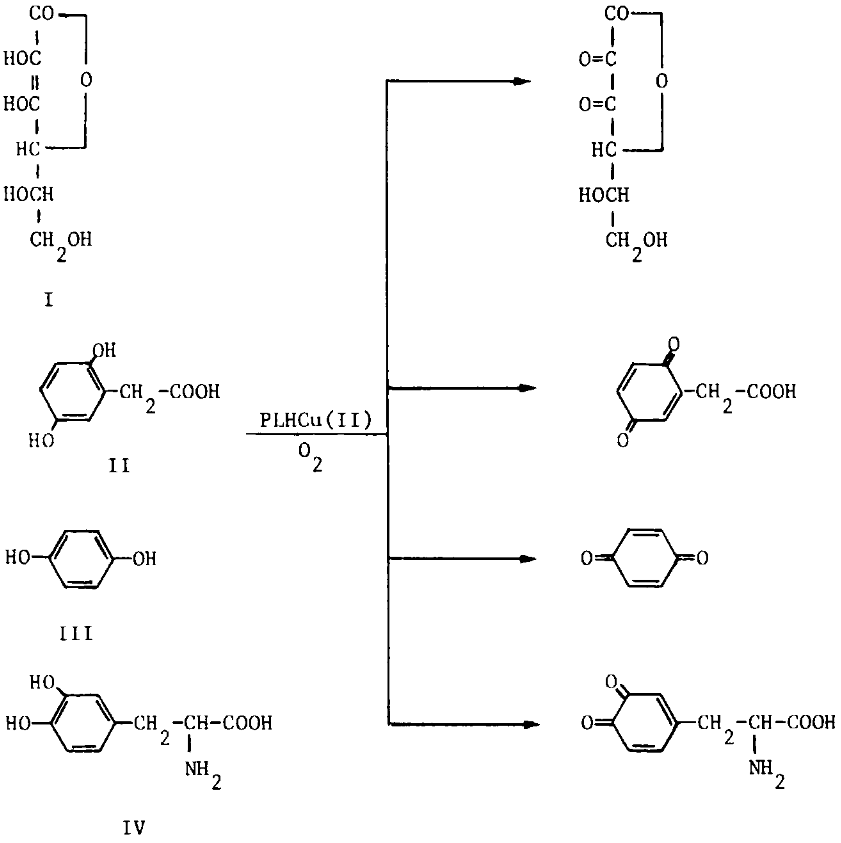
[c] With respect to the $Cu(ethylendiamine)_2$ complex.

[d] With respect to the $Cu(n.butylamine)_4$ complex.

[e] With respect to the $Cu(bipyridyl)_2$ complex.

active sites but to the fact that the polyelectrolyte behaves as a second phase in which the concentration of the reagents is higher than that in the bulk of solution|6|.

Scheme 1



Hatano et al. showed that poly(L-lysine)-Cu(II)|PLLCu(II)| complex exhibits catalytic activity|9,10| in the homogeneous oxidation of 3,4-dihydroxy-phenylalanine(IV) (Scheme 1).

The oxidation rate of PLLCu(II) complex was found to be larger than that of the corresponding complexes with ethylendiamine or butylamine at both pH of 6.9 and 10.5. However, only at pH 10.5 PLLCu(II) complex behaves as an asymmetric selective catalyst for the oxidation of D-IV (Table 1).

The higher catalytic activity displayed by the PLLCu(II) complex with respect to the corresponding derivatives with low molecular weight amines at pH 10.5 was related by the authors|9| to the fact that the former can maintain cupric ions in solution, whereas in the latter case insoluble $Cu(OH)_2$ is formed. In addition the polymer chain may affects the electrostatic field around Cu(II) ions with an enhancement of the oxidation rate; this last effect might play an important role when the reaction is performed at pH 6.9 .

The investigation of the structure of the PLLCu(II) complex shows that it is depending on the pH value|11,12|. In fact at $pH < 8.5$ the cupric ion is coordinated to four side chain amino groups, whereas at pH 10.5 the coordination of peptide nitrogens to the cupric ion occurs with displacement of protons.

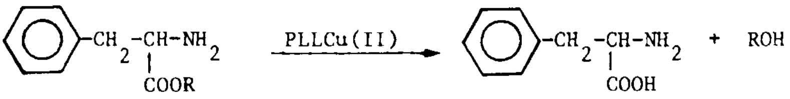
The above authors reported also that at pH 10.5 the main chain of the polymeric ligand is arranged in helical conformation and the asymmetric selectivity in the oxidation of D-IV is proportional to the content of α-helix in the polymer. Accordingly the complex of Cu(II) ions with poly(L-α,γ-diaminobutyric acid), which does not assume one screw sense helical conformations, does not display any stereoelectivity in the oxidation of D-IV|10|.

The α-helix structure of the polymer ligand is necessary, but not sufficient, to explain the stereoelectivity observed in the above catalytic process, the distance between coordinated Cu(II) ions along the main chain of PLL being also very important.

Therefore it was suggested|10| that two or more Cu(II) ions bound to PLL in a relative fixed disposition could act cooperatively with a bifunctional catalysis. According to this hypothesis IV may coordinate to PLLCu(II) through both amino acid and cathecol groups at the same time. This bifunctional activation could allow to bind preferentially D-IV with respect to its enantiomer.

Hatano et al.|13,14| have also reported that the catalytic activity of the PLLCu(II) complex at pH 7 for the hydrolysis of phenylalanine methyl and ethyl esters(V) (Scheme 2) is higher of two order of magnitude with respect to the corresponding $Cu(bipyridyl)_2$ complex and aquo copper(II) ion (Table 1).

Scheme 2



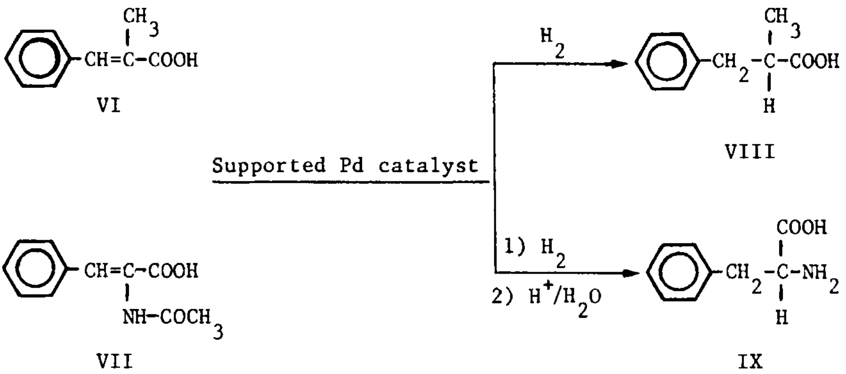
V($R=CH_3$, C_2H_5)

The PLLCu(II) complex is also able to hydrolyze preferentially D-V isomer, the activity ratio between D and L isomers being 2.41 (Table 1). Circular dichroism data suggested that PLLCu(II) gives with D-V a complex more stable than with L-V, the difference of stereoelectivity being ascribed to the different affinity between the enantiomeric substrate and the catalyst|14|.

The effect of chain conformation on asymmetric induction has been also observed with heterogeneous catalysts obtained by supporting metallic palladium on different optically active poly(α-amino acid)s.

Supported metallic palladium on poly(L-leucine), poly(γ-benzyl-L-glutamate), poly(β-benzyl-L-aspartate) and poly(L-valine) is reported by Beamer et al.|15-17| to be catalytically active for the asymmetric hydrogenation of α-methylcinnamic acid(VI) and α-acetoamidocinnamic acid(VII) to give (R)- or (S)-dihydro-α-methylcinnamic acid(VIII) and (S)- or (R)-phenylalanine(IX), respectively(Scheme 3), the optical yield being in the range of 1-6% (Table 2).

Scheme 3



The authors concluded that the asymmetric induction observed was mainly connected with the preferential helical screw sense of the main chain(secondary structure) and not with the configuration of the asymmetric carbon atoms present in the amino acid residues (primary structure) of the optically active polymeric support |16|.

Complexes of ruthenium and rhodium derivatives with poly(L-glutamic acid) (PLGA) and its alkaline salts (PLGNa or PLGK) have been recently obtained in our Institute |18,19|. Analytical and infrared data did not allow to suggest a well defined coordinative situation for these systems, probably due to the different binding properties of the polymer ligand. These polymer-bound complexes have been used as catalysts for the asymmetric hydrogenation, in water medium, of ethylacetoacetate to give 3-hydroxy-ethylbutyrate, the optical purity of which being in the range 0.1-2.6% (Table 3). The low asymmetric induction observed seems to indicate that the

TABLE 2

Stereospecific Hydrogenation of α-Methylcinnamic (VI) and α-Acetamidocinnamic (VII) Acids by Palladium Supported on Poly(α-amino acid)s[a]

Polymeric support	Substrate			
	α-Methylcinnamic acid		α-Acetamidocinnamic acid	
	Predominant enantiomer formed in VIII	Optical yield %	Predominant enantiomer formed in IX	Optical yield %
Poly(γ-benzyl-L-glutamate)	R	4.1	S	6.0
Poly(γ-benzyl-L-aspartate)	S	1.4	R	1.0
Poly(L-leucine)	R	1.5	S	5.4
Poly(L-leucine)	R	1.2	S	5.2
Poly(L-valine)	S	0.9	R	4.3

[a] Hydrogen starting pressure : 4.2 atm .

TABLE 3

Asymmetric Hydrogenation in Water of Ethylacetoacetate by Catalytic Systems Based on Poly(L-glutamic acid)/Ruthenium or Rhodium Derivatives [a]

Catalytic system	T (°C)	Conversion %	3-hydroxy-ethylbutyrate $\lvert\alpha\rvert_D^{25}$	3-hydroxy-ethylbutyrate Optical purity[b] %
PLGA/$RuCl_3$	80	96.4	+0.037	0.20
PLGK/$RuCl_3$	80	100	+0.024	0.13
PLGA/$RhCl_3$	50	42.5	+0.05	0.27
PLGK/$RhCl_3$	25	18.6	$\simeq 0$	-
PLGNa/$\lvert RuBr_2(CO)_3\rvert_2$	100	18.4	+0.48	2.57
PLGA/$Ru(CH_3COO)_2$	80	12.8	$\simeq 0$	-

[a] Hydrogen starting pressure : 80 atm .

[b] Assuming $\lvert\alpha\rvert_D^{25} = 18.7$ for the optically pure 3-hydroxy-ethylbutyrate.

chiral environment of the polymer chain on the active sites is not sufficient to affect markedly the stereochemical pathway of the involved reaction. This fact could be explained taking into account the distance between the metal centers and the polymer backbone.

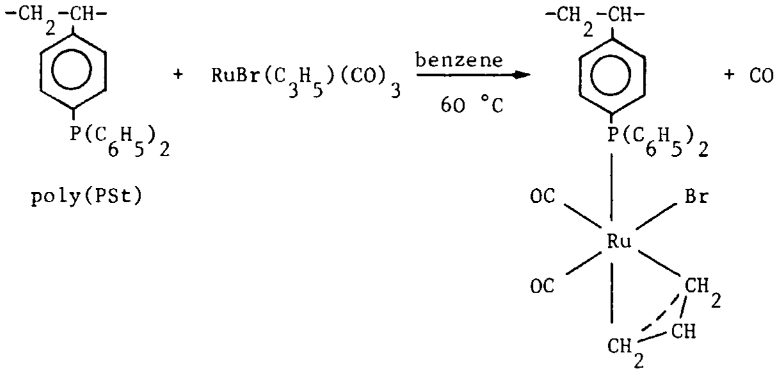
COMPLEXES OF TRANSITION METAL DERIVATIVES WITH STEREOREGULAR SYNTHETIC POLYMERS

Atactic polymers have been largely used in the recent years as macromolecular ligands for anchoring catalytically active metal complexes, with the aim of obtaining heterogeneous catalysts with the high activity and selectivity of the corresponding low molecular weight homogeneous systems. On this subject excellent reviews have been recently reported |20-22|. In general, crosslinked polymers were used and no attempt was done to examine possible effects of polymer microstructure on activity, selectivity and stereochemistry of the reactions involved.

As isotactic vinyl polymers are known to assume stereordered conformations, not only in the crystalline state but also in solution |23,24|, metal complexes bound to these macromolecular matrices could be suitable for controlling the stereochemical pathway of the catalyzed reactions. In this contest macromolecular complexes with definite structure were prepared by reacting both isotactic and atactic phosphenated poly(styrene)s such as poly|(*p*.diphenylphosphino)styrene| |poly(PSt)| and poly|styrene-*co*-(*p*.diphenylphosphino)styrene| |poly(St/PSt)| with $RuBr(C_3H_5)(CO)_3$ |25| (Scheme 4).

All the complexes showed the *cis*-structure X and were insoluble in the most common organic solvents. According to the elemental analysis the percentage of PSt units coordinated to the metal was in the range 85-95%, independently of stereoregularity, molecular weight and content of phosphenated units in the macromolecular ligand.

Scheme 4



poly(PSt)

X

These polymeric complexes were catalytically active for the isomerization of 1-butene in liquid/solid system under nitrogen at 100 °C using toluene as liquid phase |25|. The homogeneous analog with triphenylphosphine displayed higher catalytic activity than the polymeric systems. However, for these last the isomerization rate was strongly affected by the characteristics of the polymer ligand, decreasing with increasing molecular weight and tacticity (Table 4). This behaviour could be explained according to the corresponding decrease of the swelling extent of the polymer matrix, thus giving a lower availability of the active sites to the substrate. A confirmation to this explanation is given by the 1-butene isomerization experiments carried out with the same catalysts in

TABLE 4

Isomerization of 1-butene in Liquid/solid and Gas/solid Systems at 100 °C in the Presence of Catalysts Based on $RuBr(C_3H_5)(CO)_3$ and Phosphenated Poly(styrene)s

	Catalyst			Reaction rate[a] (mole l^{-1} h^{-1} g at. Ru^{-1})	
	Polymer ligand		Ru		
PSt units (mol %)	Tacticity	Molecular weight	%	liquid-solid system[b]	gas-solid system[c]
47.0	isotactic	very high[d]	9.37	840	33.6
23.7	atactic	high[e]	7.62	3,000	44.0
100	atactic	low[f]	17.05	5,100	17.5
29.6	atactic	low[g]	11.14	9,200	19.0

[a] Average in the first two hours.

[b] 1-butene: 4.14 M in toluene; 1-butene(mole)/Ru(g at.): 660.

[c] 1-butene: 15.6 mmoles; catalyst: 6.8×10^{-5} g at. Ru .

[d] Isotactic poly(styrene) used as starting material had $\bar{M}_v \simeq 1{,}200{,}000$.

[e] Atactic poly(styrene) used as starting material had $\bar{M}_v \simeq 187{,}000$.

[f] $|\eta| = 0.28$ dl/g in toluene at 30 °C .

[g] $|\eta| = 0.20$ dl/g in toluene at 30 °C .

gas/solid system (Table 4). In these experiments a large decrease of catalytic activity was observed with lost of any effect of polymer ligand microstructure|25|.

A further approach to evidence the role of primary and secondary structure of the macromolecular ligand in determining the catalytic properties of polymer-bound metal complexes is based on stereoregular optically active polymers.

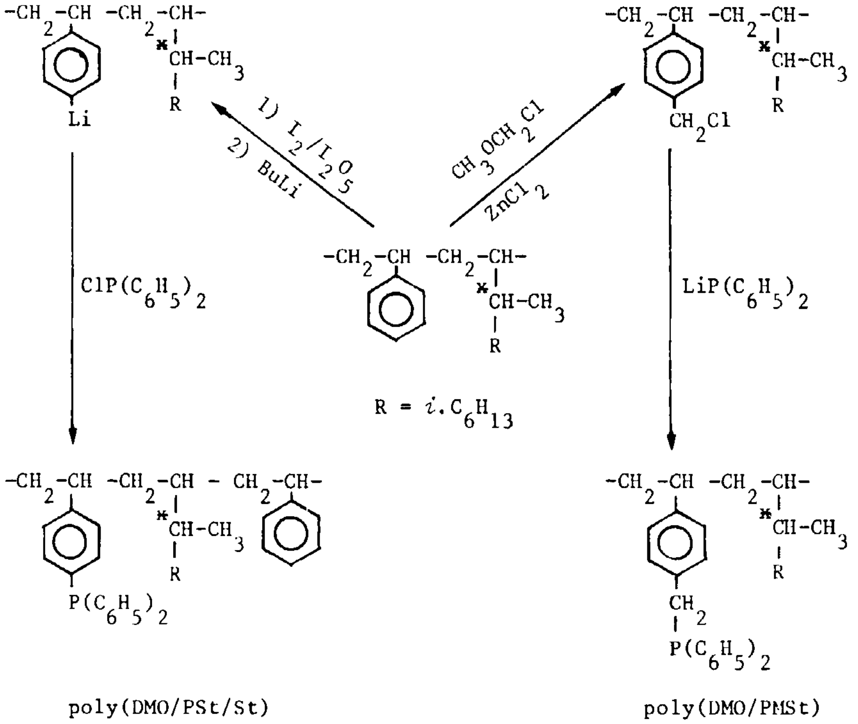
Structurally simple macromolecules with definite configurational and conformational characteristics can be obtained by stereospecific polymerization of chiral vinyl monomers. When the side chain asymmetric carbon atom is in the α or β position with respect the main chain, the macromolecules assume a preferential screw sense helical conformation|23,24|, thus providing an evidence of conformational analogy with poly(α-amino acid)s and proteins.

Therefore coisotactic copolymers of chiral α-olefins such as (R)- or (S)-3,7-dimethyl-1-octene(DMO) with styrene were submitted to the chemical transformations reported in Scheme 5. Thus chiral stereoregular DMO/(*p*.diphenylphosphinomethyl)styrene copolymers |poly(DMO/PMSt)| and DMO/(*p*.diphenylphosphino)styrene/styrene terpolymers |poly(DMO/PSt/St)| having a high conformational homogeneity were obtained|26|. Such P-donor polymers were used as ligands for different ruthenium and rhodium derivatives|27-29|.

The insoluble macromolecular complexes derived from poly(DMO/PSt/St) or poly(DMO/PMSt) and $RuBr(C_3H_5)(CO)_3$ showed for the metal complexed units the structures X and XI, respectively.

Starting with different rhodium compounds such as $|Rh(CO)_2Cl|_2$, $RhH(CO)(PPh_3)_3$ and $RhCl_3 3H_2O$ and the overmentioned optically active phosphenated polymeric materials, polymer-bound rhodium derivatives with complexed metal units XII, XIII, XIV, XV, and XVI were obtained, respectively.

Scheme 5



The above complexes were employed as catalysts in reaction involving racemic or prochiral substrates in non aqueous medium (Table 5).

In the isomerization of racemic 4-methyl-1-hexene, carried out at 100 °C using toluene as reaction medium, in the presence of η-allyl ruthenium derivatives bound to the optically active poly(DMO/PSt/St) or poly(DMO/PMSt), a *cis* and *trans*-4-methyl-2-hexene mixture was obtained with a very low optical yield (≈ 0.1%)|27|.

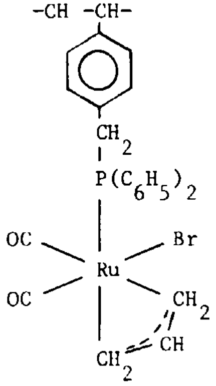
TABLE 5

Ruthenium and Rhodium Complexes Bound to Optically Active Stereoregular Phosphenated Polymers and Their Catalytic Activity in Asymmetric Syntheses

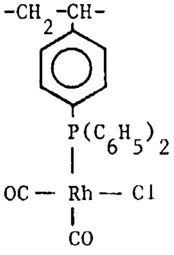
Catalyst		Catalyzed reaction	Substrate	Substrate	Product	
Polymer ligand (composition)	Metal complexed unit			(mole) / Metal (g at.)	Type	Optical yield %
Poly(DMO/PSt/St) (0.49/0.27/0.24)	X	Isomerization[a]	(R)(S)-4-methyl-1-hexene	430	4-methyl-2-hexene(*cis+ trans*)	< 0.1
Poly(DMO/PMSt) (0.52/0.48)	XI	"	"	670	"	< 0.1
Poly(DMO/PSt/St) (0.49/0.27/0.24)	XV	Hydroformylation[b]	Styrene	4,750	Hydratropic aldehyde	< 0.1
Poly(DMO/PSt/St) (0.32/0.28/0.40)	XII	"	"	2,030	"	≃ 0
Poly(DMO/PSt/St) (0.32/0.39/0.29)	XIII	"	"	1,700	"	≃ 0
Poly(DMO/PMSt) (0.52/0.48)	XIV	Hydrosilylation[c]	Acetophenone	210	1-phenyl-ethanol	0.2
Poly(DMO/PSt/St) (0.49/0.18/0.33)	XVI	"	"	170	"	2.5

---

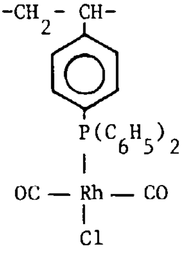
[a] (R)(S)-4-methyl-1-hexene: 2.5 M in toluene; [b] Styrene: 3.5 M in benzene; [c] Acetophenone: 1 M in benzene, diphenylsilane(mole)/acetophenone(mole): 2.



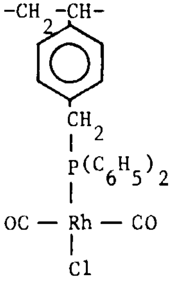
XI



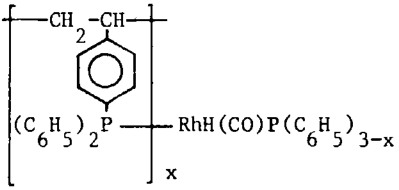
XII



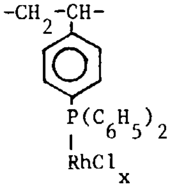
XIII



XIV



XV



XVI

Asymmetric selectivity of the same order of magnitude was obtained in the hydroformylation of styrene to hydratropic aldehyde at 80 °C and 90 atm of CO/H_2 (1/1), using catalysts based on rhodium complexes attached to optically active poly(DMO/PSt/St) having different compositions |29|.

In the reaction of a prochiral ketone such as acetophenone with diphenylsilane at 20 °C in the presence of catalysts obtained from $RhCl_3 \cdot 3\ H_2O$ or $|Rh(CO)_2Cl|_2$ and chiral poly(DMO/PSt/St) and poly-(DMO/PMSt), respectively, optically active 1-phenylethanol was obtained having the same absolute configuration as DMO units and optical purity in the range 0.2-2.5%|27| (Table 5).

These results, even if indicating that the asymmetric polymer support affects the reaction stereochemistry, also show that the dissymmetric environment of the polymer main chain is not sufficient to induce in a large extent the chiral perturbation of the coordination sphere of the metal, probably due to the large distance between polymeric backbone and metal sites in the systems examined up to now. The low values of optical yield could be also related to the substrates used, the nature of which might not be suitable for evidencing local asymmetric environment of the active sites. Accordingly also rhodium complexes with low molecular weight chiral-P phosphine ligands display low asymmetric induction(1-2%) in the hydrogenation of prochiral substrates having similar structure to those mentioned above|30,31|. In this contest the results obtained by Hirai and Furuta|32,33| in the homogeneous asymmetric hydrogenation of prochiral ketones by poly(L-methylethylenimine)/$RuCl_3 \cdot 3H_2O$ in water at pH 5.5, indicate that the substrate may play an important role in determining the stereochemistry of the reaction involved. In fact, in spite of the close vicinity of the metal sites to the backbone of the chiral stereoregular polymer ligand, only in the case of bifunctional ketones such as methylacetoacetate and methyl-*i*.butenyl-ketone an asymmetric induction, even if in low extent, occurred (Table 6).

COMPLEXES OF TRANSITION METAL DERIVATIVES WITH ALTERNATING COPOLYMERS

The results described in the previous section suggest the necessity of reducing as far as possible the distance between the macromolecular backbone and the metal atom in order to improve the in-

TABLE 6

Asymmetric Hydrogenation of Prochiral Ketones by Poly(L-methylethylenimine)/Ru(III) Catalytic Systems at 80 °C and 80 atm [a]

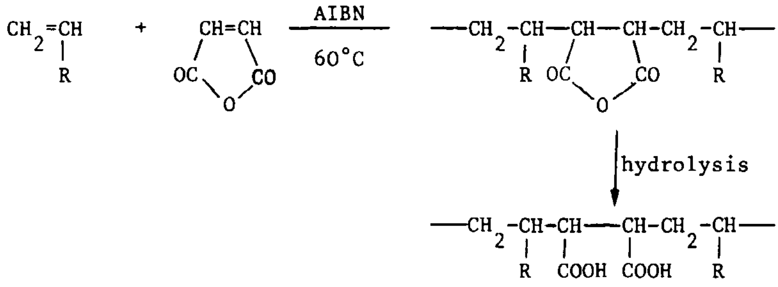
Substrate	Ligand/Ru(III) molar ratio	Total yield %	Hydrogenation product Type	Hydrogenation product Optical yield %
Methylacetoacetate	2.5	54	Methyl(-)(R)-3-hydroxybutyrate	0.5
	10.0	26		5.3
Methyl-*i*.butenyl-ketone	2.5	32	(-)(R)-4-methyl-2-pentanol	0.4
	5.0	22		0.5
Methyl-*i*.butyl-ketone	5.0	65	(R)(S)-4-methyl-2-pentanol	0.0

[a] Substrate(mole)/Ru(g at.) in the range 400-465.

fluence of the primary and secondary structure of the polymer ligand on activity, selectivity and stereochemistry of the catalytic systems. A further improvement can be achieved by designing structurally ordered polymeric ligands where each attached metal atom is at a suitable distance from a peculiar functional group able to assist either the coordination step of the substrate or its successive transformation. Finally using side chains with different hydrophilic properties it should be possible to modify in a large extent the interactions between the liquid reaction medium and the polymeric ligand, thus affecting polymer swelling and availability of the metal sites to the substrate.

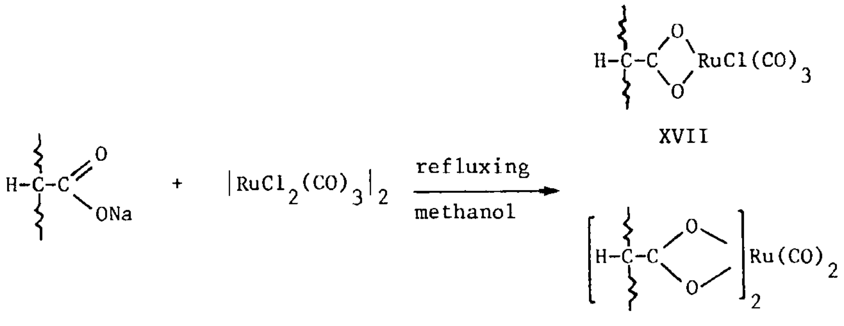
Copolymers of ethylene(Et) or alkyl vinyl ethers with maleic acid(MAc)|34,35|, obtained according to Scheme 6, appeared to possess the above requirements.

Scheme 6



In fact these systems have an alternating structure and the metal binding units(MAc units *via* carboxylic groups) are inserted between two counits bearing one R group, the nature of which can be varied in a large extent. Furthermore the anchoring of the transition met al derivative to the carboxylic groups guarantees a close vicinity to the polymer backbone. In this connection alternating copolymers of MAc with Et |poly(Et/MAc)|, benzyl vinyl ether|poly(BVE/MAc)| and 2-methylbutyl vinyl ether|poly(BuVE/MAc)| as well as vinyl alcohol/BVE/MAc terpolymers|poly(VA/BVE/MAc)| with different content of VA units, obtained by ether cleavage reaction with dry gaseous HBr|36| of the corresponding poly(BVE/MAc), were used as ligands to coordinate ruthenium(II) and rhodium(I) derivatives. By reaction of $|RuCl_2(CO)_3|_2$ with the sodium salts of the copolymers and terpolymers (Scheme 7), insoluble polymer-bound ruthenium derivatives containing different amount of sodium and ruthenium carboxylate groups, were obtained|37|.

Scheme 7



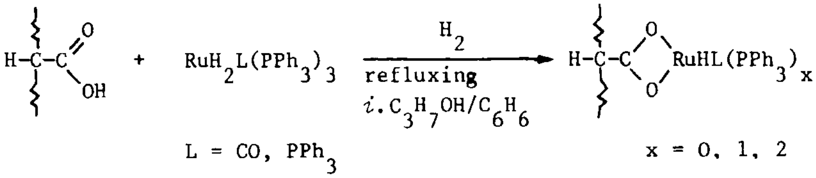
XVII

XVIII

On the basis of elemental analysis and I.R. data, the structures XVII and XVIII could be assigned to the metal containing moieties.

The above macromolecular ligands have been also allowed to react with $RuH_2(PPh_3)_4$ and $RuH_2(CO)(PPh_3)_3$ under the same conditions as used to prepare low molecular weight carboxylate analogs |38| (Scheme 8).

Scheme 8



XIX

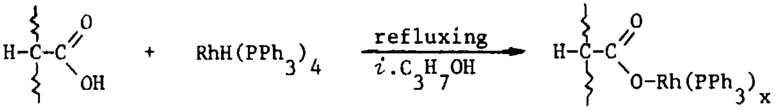
The I.R. spectra indicate for these last insoluble complexes the presence of a ruthenium-hydrogen bond and of a bidentate coordination of the carboxylate group (structure XIX) |37, 39|.

It is of interest to note that the P/Ru ratio is in the range of 1.4-1.8, lower than that theoretically expected (x = 2) and actually observed in the case of poly(acrylic acid) |poly(AA)|. This indicates that, on the average, more than one triphenylphosphine molecule per ruthenium atom is displaced with consequent formation of "coordinatively unsaturated" metal species. This could be due both to the presence in MAc units of two carboxylic groups directly bound to adjacent carbon atoms and to the bulkiness of triphenylphosphine ligands of the metal derivative |39|.

An analogous route was followed |39| to prepare poly-carboxylate-triphenylphosphine rhodium(I) complexes (Scheme 9).

In this case the metal complexes obtained have no hydridic nature and the carboxylate group functions as unidentate ligand as for the corresponding derivatives with low molecular weight carboxylic acids |40|. Thus the metal complexed moieties show the structure XX, where x, that is P/Rh ratio, assumes average values in the range 1.5-1.9, according to the presence of "coordinatively unsaturated" metal species also in this case |39|.

Scheme 9



x = 1, 2, 3

XX

All the polymeric metal complexes obtained from different ruthenium and rhodium derivatives and the overmentioned macromolecular carboxylic ligands have been tested as heterogeneous catalysts for the isomerization and hydrogenation of 1-pentene in the presence of a liquid medium.

The polymer-bound catalysts derived from $|RuCl_2(CO)_3|_2$ and polymeric sodium carboxylates containing different amount of sodium and rhutenium carboxylate groups (Table 7), isomerize 1-pentene at 100 °C under nitrogen in the presence of toluene and a small amount of ethanol, which is necessary for the formation of active ruthenium-hydride species|37|. The catalytic activity of such systems markedly increases with decreasing the content of sodium carboxylate groups . This trend has been related to the contemporary decrease of the swelling extent of the polymeric ligand by the liquid reaction medium, with consequent lower availability of the active sites to the substrate. The effect of the polymer ligand on the swelling extent is better evidenced by the large difference in catalytic ac-

TABLE 7

Isomerization of 1-pentene at 100 °C in the Presence of Polycarboxylate Ruthenium(II) Catalysts Obtained from $|RuCl_2(CO)_3|_2$ and Polymeric Sodium Carboxylates[a]

Complex	Polymer ligand (composition)	$\frac{\text{-COONa}}{\text{total carboxylate groups}}$ %	Heterogeneity of the catalysis[b] %	Initial reaction rate (mmol l^{-1} h^{-1})
1	Poly(AANa)	73	99.9	42
2	Poly(VA/BVE/MAcNa) (0.33/0.17/0.50)	34	93.0	150
3	Poly(Et/MAcNa) (0.5/0.5)	28	67.0	636
4	Poly(VA/BVE/MAcNa) (0.25/0.25/0.50)	27	97.6	1,150
5	Poly(BuVE/MAcNa) (0.5/0.5)	26	95.0	828
6	Poly(AANa)	6	87.0	1,038

[a] 1-pentene: 0.83 M in toluene/ethanol (25/1); 1-pentene(mole)/Ru(g at.): 365.

[b] Evaluated as % of the total ruthenium present in the insoluble residue after the catalytic reaction.

tivity (about one order of magnitude) between the two complexes (2 and 4 , Table 7) containing about the same content of sodium carboxylate groups, but different extent of VA hydrophilic counits |37, 41|.

The systems derived from $RuH_2(PPh_3)_4$ and different polycarboxilic matrices exhibit, in the isomerization and hydrogenation of 1-pentene at 50 °C, catalytic activity much lower than that of the closely related homogeneous models |39| (Table 8).

On the contrary, the catalysts obtained from the same polymeric materials and $RuH_2(CO)(PPh_3)_3$ show a comparable or higher activity than that of their homogeneous counterparts |39|. This behaviour has been related to the presence, in the polymeric catalysts, of "coordinatively unsaturated" metal species to which the substrate may be easily coordinated without displacement of ligands. Accordingly the polymeric catalyst with the lowest P/Ru ratio (complex 14, Table 9) displays the highest activity (about one order of magnitude with respect to its homogeneous analog 13). A confirmation to these results derives from the very low catalytic activity of the system 17, prepared from poly(AA) (Table 9), the metal species of which are almost coordinatively saturated(P/Ru= 1.9). The higher activity due to the "coordinative unsaturation" may be related to the mechanism, generally proposed for isomerization of olefins, also in the presence of carboxylate ruthenium complexes|38|. Accordingly the olefin coordination occurs through displacement of a triphenylphosphine group and/or cleavage of one of the two ruthenium-oxygen bonds of the bidentate carboxylate ligand (Scheme 10). Generally soluble carboxylate carbonyl triphenylphosphine complexes obtained from low molecular weight carboxylic acids are less active than the corresponding carboxylate triphenylphosphine derivatives

TABLE 8

Isomerization and Hydrogenation of 1-pentene at 50 °C in the Presence of Polycarboxylate Ruthenium(II) Hydrido-triphenylphosphine Catalysts Obtained from $RuH_2(PPh_3)_4$ and Their Low Molecular Weight Analogs[a]

	Catalytic system (polymer composition)	$\frac{P}{Ru}$	Heterogeneity of the catalysis[b] %	Initial reaction rate ($mmol\ l^{-1}\ h^{-1}$) Isomerization	Hydrogenation
7	$\|RuH(PPh_3)_3\|_2\|O_2C(CH_2)_2CO_2\|$	3	0	332	232
8	$RuH_2(PPh_3)_4$/poly(Et/MAc) (0.5/0.5)	1.83	97.0	3.5	0.4
9	$RuH(O_2CCH_2OH)(PPh_3)_3$	3	0	224	176
10	$RuH_2(PPh_3)_4$/poly(VA/BVE/MAc) (0.25/0.25/0.50)	1.38	98.0	5	0.4

[a] 1-pentene: 0.83 M in hydrocarbon solvents; 1-pentene(mole)/Ru(g at.): 365; p_{H_2} : 1.06 atm .

[b] See note b, Table 7

TABLE 9

Isomerization and Hydrogenation of 1-pentene at 50 °C with Polycarboxylate Ruthenium(II) Hydrido-triphenylphosphine Catalysts Obtained from $RuH_2(CO)(PPh_3)_3$ and Their Low Molecular Weight Analogs[a]

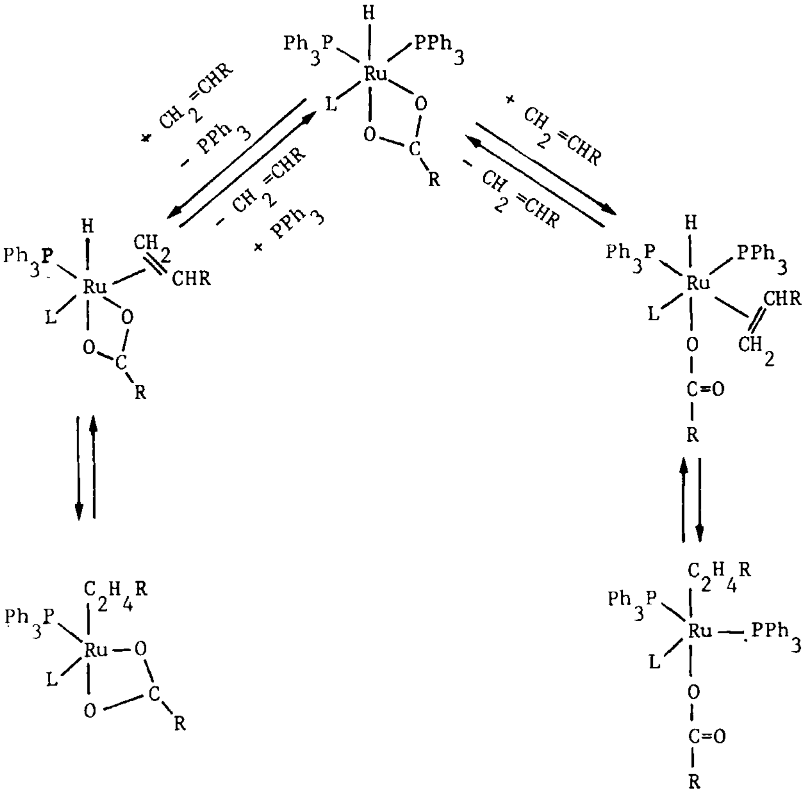
	Catalytic system (polymer composition)	$\frac{P}{Ru}$	Heterogeneity of the catalysis[b] %	Initial reaction rate ($mmol\ l^{-1}\ h^{-1}$) Isomerization	Initial reaction rate ($mmol\ l^{-1}\ h^{-1}$) Hydrogenation
11	$|RuH(CO)(PPh_3)_2|_2|O_2C(CH_2)_2CO_2|$	2	0	38	1.7
12	$RuH_2(CO)(PPh_3)_3$/poly(Et/MAc) (0.5/0.5)	1.38	100	22	0.5
13	$RuH(CO)(O_2CCH_2OH)(PPh_3)_2$	2	0	36	0
14	$RuH_2(CO)(PPh_3)_3$/poly(VA/BVE/MAc) (0.25/0.25/0.50)	1.35	97.0	295	20
15	$RuH_2(CO)(PPh_3)_3$/poly(VA/BVE/MAc) (0.33/0.17/0.50)	1.76	96.0	175	17
16	$RuH(CO)(PPh_3)_2|O_2CCH(CH_3)_2|$	2	0	25	0
17	$RuH_2(CO)(PPh_3)_3$/poly(AA)	1.9	95.0	3	0

[a] See note a, Table 8.

[b] See note b, Table 7.

|compare for example the activities of the catalysts 11 and 13 (Table 9) with those of the catalysts 7 and 9 (Table 8), respectively| as the triphenylphosphine displacement is more difficult when a π-acceptor carbonyl group is coordinated to the metal|38|.

Scheme 10



In the case of the polymeric complexes the opposite behaviour is observed, as shown by the catalysts 10 (Table 8) and 14 (Table 9), derived from the same macromolecular ligand and having comparable

P/Ru ratio. According to Scheme 10, this result can be explained |39,42| considering that, due to the presence of "coordinatively unsaturated" metal species the triphenylphosphine displacement is no longer necessary to activate the olefin and thus this step does not affect the reaction rate. On the other side the carbonyl group present in the above "coordinatively unsaturated" species favours the Markownikoff insertion of the olefin which is the active step for the isomerization process.

Also for the polymeric systems based on rhodium derivatives the catalytic activity, in the isomerization and hydrogenation of 1-pentene at 50 °C, was found to be dependent on the P/Rh ratio, connected with the relative amount of "coordinatively unsaturated" metal species|39|(Table 10).

Recently such species, able to react with O_2 to give paramagnetic Rh(II)O_2^- derivatives, have been detected in the polymeric catalysts by e.s.r. spectroscopy and quantitatively determined. A linear dependence of the overall initial 1-pentene conversion rate (isomerization + hydrogenation) on the content of paramagnetic species was observed and strictly related to the P/Rh ratio|43|, confirming the model previously proposed.

In the above systems the effect of the swelling extent of the catalyst on the activity was finally evidenced using solvents having different affinity with the polymeric matrices as reaction medium. Accordingly the overall catalytic activity strongly increases using 2-propanol in the place of toluene|39|(Table 10).

FINAL REMARKS

The aim of the present review is to call attention of research people to the enormous potentiality offered by polymer/metal complexes in catalysis provided more attention is given to introduce

TABLE 10

Isomerization and Hydrogenation of 1-pentene at 50 °C with Polycarboxylate Rhodium(I) Catalysts Obtained from $RhH(PPh_3)_4$ and Their Low Molecular Weight Analog[a]

Catalytic system (polymer composition)	$\frac{P}{Rh}$	Reaction medium		Heterogeneity of the catalysis[b]	Initial reaction rate (mmol l^{-1} h^{-1})	
		type	ml	%	Isomerization	Hydrogenation
$Rh|O_2CCH(CH_3)_2|(PPh_3)_3$	3	toluene ethanol	24 1	0	482	450
$RhH(PPh_3)_4$/poly(AA)	3	toluene ethanol	24 1	86	53	78
$RhH(PPh_3)_4$/poly(Et/MAc) (0.5/0.5)	1.5	toluene ethanol	24 1	98.5	85	196
$RhH(PPh_3)_4$/poly(VA/BVE/MAc) (0.25/0.25/0.50)	1.9	toluene ethanol	24 1	96	87	121
$RhH(PPh_3)_4$/poly(VA/BVE/MAc) (0.25/0.25/0.50)	1.9	2-propanol ethanol	24 1	92	245	171
$RhH(PPh_3)_4$/poly(BVE/MAc) (0.5/0.5)	1.6	toluene ethanol	24 1	95	65	104
$RhH(PPh_3)_4$/poly(BVE/MAc) (0.5/0.5)	1.6	2-propanol ethanol	24 1	95	240	100

[a] 1-pentene: 0.83 M; 1-pentene(mole)/Rh(g at.): 365; p_{H_2} : 1.06 atm .

[b] See note b, Table 7 .

useful characteristics in the polymer ligand. The use of organic resins to heterogenize homogeneous transition metal complexes is certainly of interest but reduces the polymer ligand to a very modest role which can be better interpreted, at least from economical view-point, by inorganic supports. The use of polymers with definite structure, binding the transition metal in a very definite way to give catalysts working with a known and controllable mechanism, can justify more work in the area as it may offer peculiar possibility in special cases. The work done up to now in this connection is certainly not sufficient to disclose all this potentiality and the examples reported up to now in the literature and described here indicate lines along which future studies should move. In spite of the limited results reached we think to have shown how high selectivity and in particular catalytic activity under very mild conditions and without sophisticated solvents and atmosphere can be approached with polymer/metal complexes provided polymer structure is planned looking at the expected application.

REFERENCES

|1| P. L. Luisi, in Charged & Reactive Polymers: Optically Active Polymer, E. Sélégny, Ed., Vol. 5, Reidel, Dordrecht,1979,p.357

|2| R. J. P. Williams, Pure Appl. Chem., 40, 38 (1975).

|3| A. E. Dennard and R. J. P. Williams, Transition Metal Chemistry, R. L. Carlin, Ed., Dekker, New York, Vol. 2, 1966, p. 116.

|4| S. Inone, Adv. Polymer Sci., 21, 78 (1976).

|5| A. Levitzki, I. Pecht, and M. Anbar, Nature, 207, 1386 (1965).

|6| I. Pecht, A. Levitzki, and M. Anbar, J. Am. Chem. Soc., 89, 1587 (1967).

|7| A. Levitzki, I. Pecht, and A. Berger, J. Am. Chem. Soc., 94, 6844 (1972).

|8| M. Palumbo, A. Cosani, M. Terbojevich, and E. Peggion, Macromolecules, 11, 1271 (1978).

|9| M. Hatano, T. Nozawa, S. Ikeda, and T. Yamamoto, Makromol. Chem., 141, 11 (1971).

|10| T. Nozawa and M. Hatano, Makromol. Chem., 141, 31 (1971).

|11| M. Hatano, T. Nozawa, S. Ikeda, and T. Yamamoto, Makromol. Chem., 141, 1 (1971).

|12| T. Nozawa and M. Hatano, Makromol. Chem., 141, 21 (1971) .

|13| T. Nozawa, Y. Akimoto, and M. Hatano, Makromol. Chem., 158, 21 (1972).

|14| T. Nozawa, Y. Akimoto, and M. Hatano, Makromol. Chem., 161, 289 (1972).

|15| R. L. Beamer, C. S. Fickling, and J. H. Ewing, J. Pharm. Sci., 56, 1029 (1967).

|16| R. L. Beamer, R. H. Belding, and C. S. Fickling, J. Pharm. Sci., 58, 1142 (1969).

|17| R. L. Beamer, R. H. Belding, and C. S. Fickling, J. Pharm. Sci., 58, 1419 (1969).

|18| G. Bini, Thesis, University of Pisa, June 1975.

|19| F. Ciardelli, C. Carlini, and E. Chiellini, Abstracts of XXIVth IUPAC Internat. Symposium on Macromolecules, Jerusalem, 1975, p. 63.

|20| Y. Chauvin, D. Commereuc, and F. Dawans, Progr. Polym. Sci., 5, 95 (1977).

|21| F. R. Hartley and P. N. Vezey, Advances in Organometallic Chemistry, F. G. A. Stone and R. West, Eds., Academic Press, New York, Vol. 15, 1977, p. 189.

|22| G. Manecke and W. Storck, Angew. Chem. Int. Ed. Engl., 17, 657 (1978).

|23| P. L. Luisi and F. Ciardelli, in Reactivity Mechanism and Structure in Polymer Chemistry, A. D. Jenkins and A. Ledwith, Eds., Wiley, London, 1974, p. 471.

|24| F. Ciardelli, C. Carlini, E. Chiellini, P. Salvadori, L. Lardicci, R. Menicagli, and C. Bertucci, in Preparation and Properties of Stereoregular Polymers, R. W. Lenz and F. Ciardelli, Eds., Reidel, Dordrecht, 1979, p. 353.

|25| C. Carlini, G. Braca, F. Ciardelli, and G. Sbrana, J. Mol. Catal., 2, 379 (1977).

|26| E. Chiellini and C. Carlini, Makromol. Chem., 178, 2545 (1977).

|27| F. Ciardelli, E. Chiellini, C. Carlini, and R. Nocci, A.C.S. Polymer Preprints, 17, 188 (1976).

|28| L. Pardini, Thesis, University of Pisa, 1974.

|29| L. Pacchiarini, Thesis, University of Pisa, 1976.

|30| J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. Phillips, J. Am. Chem. Soc., 93, 1301 (1971).

|31| P. Bonvicini, A. Levi, G. Modena, and G. Scorrano, J.C.S. Chem. Commun., 1188 (1972).

|32| H. Hirai and T. Furuta, J. Polym. Sci. B, 9, 459 (1971).

|33| H. Hirai and T. Furuta, J. Polym. Sci. B, 9, 729 (1971).

|34| S. Machi, T. Sakai, M. Gotoda, and T. Kagiya, J. Polym. Sci. A-1, 4, 821 (1966).

|35| E. Chiellini, M. Marchetti, C. Villiers, C. Braud, and M. Vert, Europ. Polym. J., 14, 251 (1978).

|36| H. Yuki, K. Hatada, K. Ohta, I. Kinishita, J. Polym. Sci., 7, 1517 (1969).

|37| G. Braca, C. Carlini, F. Ciardelli, and G. Sbrana, Proc. VIth Int. Congr. Catalysis, G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds., The Chemical Society, London, Vol. 1, 1977, p. 528.

|38| G. Sbrana, G. Braca, and E. Giannetti, J. Chem. Soc., Dalton, 1847 (1976).

|39| G. Sbrana, G. Braca, G. Valentini, G. Pazienza, and A. Altomare, J. Mol. Catal., 3, 111 (1977/1978).

|40| S. D. Robinson and M. F. Uttley, J. Chem. Soc., Dalton, 1912 (1973).

|41| G. Braca, F. Ciardelli, G. Sbrana, and G. Valentini, Chim. Ind. (Milan), 59, 766 (1977).

|42| G. Braca, G. Sbrana, G. Valentini, and F. Ciardelli, Chim. Ind.(Milan), 60, 530 (1978).

|43| G. Braca, G. Sbrana, G. Valentini, A. Colligiani, and C. Pinzino, J. Mol. Catal., 457 (1980).