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→ Styrene-divinylbenzene resins have been functionalized with phosphine ligands and these phosphinated resins have been used to immobilize Rh(I), Ir(I), and Pd(O) catalysts. The selectivity of Rh(I)-catalyzed hydroformylations and the optical yields in styrene hydroformylations have been examined as a function of ligand loading and P/Rh ratios. The rates of Ir(I)-catalyzed hydrogenations of 1,5-cyclooctadienes and Pd(O)-catalyzed

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→ butadiene dimerization-methoxylations were studied. In all cases the resin-catalyzed reactions were compared to their homogeneously catalyzed analogs. All the results appear to be explained in terms of the influence of the resin matrix on metal-ligand equilibria which play important roles in the reaction mechanisms. ↖

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TECHNICAL REPORT NO. 20

Catalytic Reactions Promoted by
Homogeneous Catalysts Attached to
Polystyrene Matrices

by

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February 24, 1978

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INTRODUCTION

Transition metals have played an enormous role in synthetic organic chemistry during the past century. Heterogeneous metal and metal oxide catalysts¹ are widely used in such industrial processes as oxidations, hydrogenations, oligomerizations, carbonylations and decarbonylations, hydrodesulfurization and reforming.² Recently, transition metal compounds have begun to assert a major role in organic synthetic thinking.^{3,4} These homogeneous compounds are already in use in industrial processes such as Wacker oxidation of ethylene to acetaldehyde,⁵ hydroformylation using both cobalt⁶ and rhodium⁷ catalysts, and the carbonylation of methanol to acetic acid catalyzed by $\text{Rh}(\text{CO})_2\text{I}_2^-$.⁸⁻¹⁰

Because homogeneous catalysts often operate at milder conditions and give high selectivities, which may be tailored by choice of solvent and ligand,¹¹ there has been an increase in research activity aimed at overcoming the traditional bias against homogeneous processes.¹²⁻¹⁴ The obvious problems involved with using homogeneous complexes involve separation of products from the catalyst and recycling the catalyst. Since the original reports appeared from a Mobil Research group^{15,16} on anchoring rhodium complexes to macroreticular resins for use in hydroformylations, the use of both organic polymers and inorganic supports to immobilize homogeneous catalysts has grown at a rapid pace.¹²⁻¹⁴ This was evidenced by the First International Symposium on this

topic held in Brussels in October 1974¹⁷ and is further emphasized by the special issue of the Journal of Molecular Catalysis which was devoted entirely to the contributed papers of this 2nd International Symposium here in Lyon.¹⁸

At this symposium we have heard Halpern¹⁹ suggest that the use of polymer ligands offers no real advantage over the homogeneous use of such metal complexes as catalysts, if one does not count the obvious advantage of easy catalyst separation from products. In particular, Halpern argued that based on his group's detailed dissection of the complex mechanism of olefin hydrogenation by Wilkinson's catalyst, $\text{Rh}(\text{PPh}_3)_3\text{Cl}$,²⁰ polymer-anchoring this specific catalyst could never succeed in generating a catalyst which would catalyze olefin hydrogenation at a faster rate than the homogeneous catalyst. However, in this presentation I hope to counter this generally pessimistic view, and point out several chemical advantages to be gained by polymer-anchoring. First, one only has to examine the enhanced substrate selectivities observed by Grubbs et al.²¹ in catalytic hydrogenations using styrene-divinylbenzene-anchored Wilkinson's catalyst to realize that the polymer matrix can exert a major effect on the course of the reaction, relative to the homogeneous use of the catalyst. For example, in homogeneous hydrogenations using $\text{Rh}(\text{PPh}_3)_3\text{Cl}$, the relative rate of hydrogenating cyclohexene versus 2-cholestene was 1.0/0.72 whereas using the polymer-bound catalyst

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gave a relative rate of 1.0/0.03.²¹ Similarly, Pittman and Hanes²² showed polymer-bound $\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}$ gave higher normal/branched product ratios in hydroformylations of 1-pentene than the corresponding homogeneous reactions did. Likewise, polymer-bound $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$, after reduction with NaBH_4 , catalyzed the highly selective dimerization of butadiene to (E,E)-1,3,6-octatriene while the corresponding homogeneous catalyst was far less selective.²³

Furthermore, the literature already demonstrates that polymer-attachment can be used to enhance the rates of certain catalytic reactions. For example, Grubbs and Brubaker have convincingly demonstrated that a fraction of titanocene groups, generated while attached to the surface of macroreticular styrene-divinylbenzene resins, are "matrix-isolated" from one another.^{24,25} Therefore, these resin-bound species are far more active in catalytic hydrogenations than are homogeneous solutions of this complex. In homogeneous solutions, titanocene dimerizes to a catalytically inactive form. Pittman et al., showed that polymer-bound Vaska's complex, $\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}$, more rapidly catalyzed hydrogenation of vinylcyclohexene than did the homogeneous catalyst.²⁶ As will be argued in this manuscript, this was the result of shifts in the position of certain phosphine dissociation equilibria influenced by the swollen polymer matrix. Finally, it has been shown that multistep sequential reactions

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may be performed with different polymer-anchored catalysts in the same reactor.²⁷⁻²⁹ In one of these studies, Gates et al.²⁹ demonstrated that definite rate enhancements could be achieved by using a polymeric multifunctional catalyst for the aldol process.

A very important consideration in the design of polymeric catalysts or reagents is the type of polymer to be used. Soluble uncrosslinked polymers may be used.^{30,31} In this case the reactions will be truly homogeneous and all catalyst sites will be equally available to reagent because diffusion barriers will be eliminated. However, ultrafiltration or precipitation must be used to separate the catalyst. Randomly, crosslinked polymers of very low crosslink density are swellable and allow solvent and reagents to easily penetrate. As the crosslink density increases, sharp increases in diffusional restrictions and sharp decreases in exclusion limits and internal chain mobilities occur.^{32,33} Macroreticular (macro-porous) resins with variety of properties can be used as supports. These are highly crosslinked. They have dimensional stability and a high surface area. They only swell slightly. They can be functionalized only in a thin surface layer. It is known that their surfaces are less crosslinked than their interior.^{34,35} The importance of both macro- and microstructure of the polymer support in the design of a catalyst is exceedingly important and the use of polymer design, scope, and limitations have now been reviewed by Heitz.³⁶ In the work reported here, swellable micro-

porous styrene-1%-divinylbenzene resin supports were used in all cases. Furthermore, the smallest bead size available was used (200-400 mesh). These resins allow the easy permeation of large molecules. Figure 1 emphasizes the difference in structure between swollen microporous and macrorecticular (macroporous) resin structure. In swollen microporous resins, the mobility of the polymer chain segments will often play an important role in the mechanism of catalytic reactions where the metal is attached to bound ligands such as phosphines. This, in turn, affects the chemistry observed. Defining this role is a goal of this study.

Insert
Fig. 1

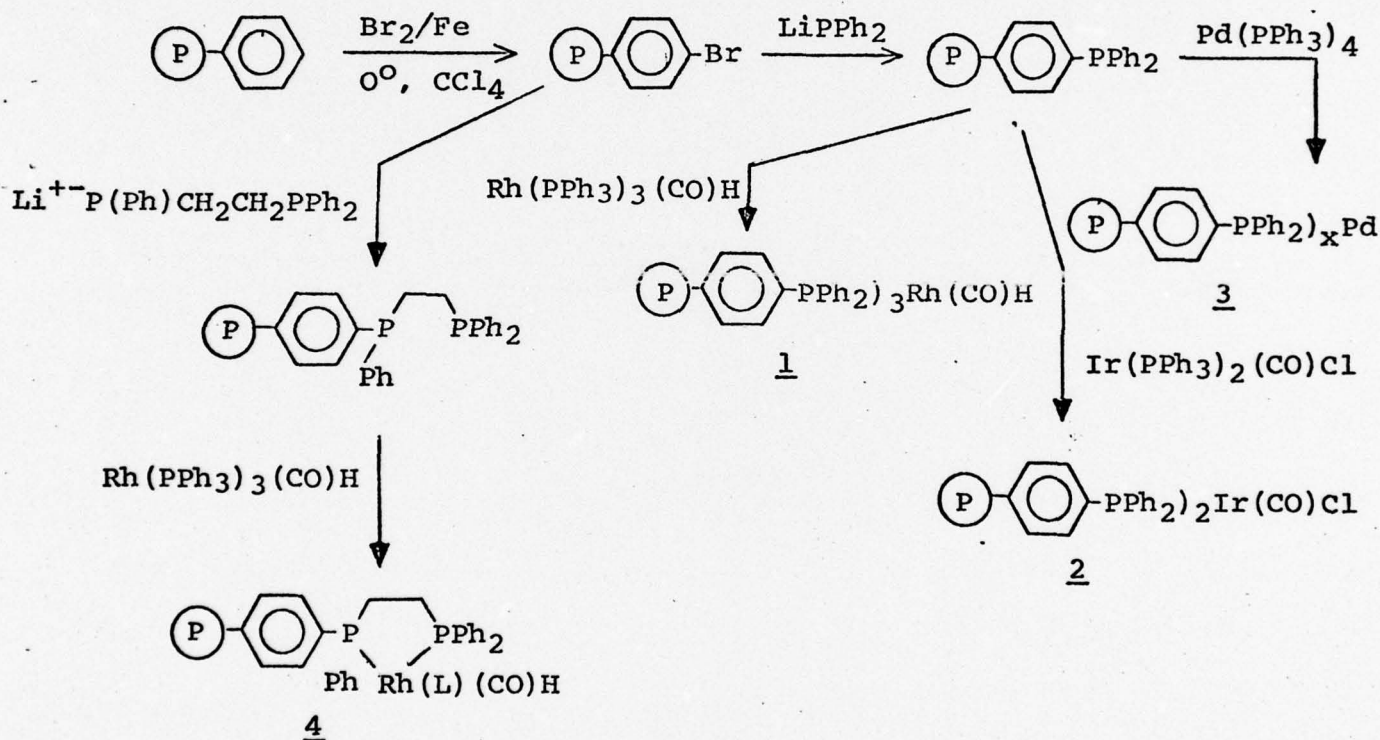
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RESULTS AND DISCUSSION

We have examined the effect of anchoring catalysts to polymers, using bound phosphine ligands, in the following reactions: (1) hydroformylations of 1- and 2-pentene (2) hydrogenation of cyclooctadiene (3) linear dimerization-methoxylation of butadiene (4) asymmetric hydroformylation of styrene and (5) several multistep sequential reactions involving butadiene oligomerizations. In Scheme I the synthesis of the bound catalysts is summarized. In every case, 1% divinylbenzene-crosslinked polymers (Biorad SX-1 resin beads, 200-400 mesh) were employed. They had been thoroughly washed and extracted with benzene, tetrahydrofuran, acetone, ethanol, dilute aqueous HCl and dilute aqueous NaOH in sequence described elsewhere.³⁷ As can be seen, simple ligand exchange was used to bind the metal complexes to the resins.

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By using resins which had different amounts of bromine, the phosphine loading of the resins (that percentage of the polymer's original phenyl rings which were substituted with diphenylphosphino groups) could be varied widely. Finally, by varying the amount of metal complex used in the exchange reaction, the ligand-to-metal ratio could be varied over a wide range. Four extreme cases are envisioned in Figure 2. Cases A and B show two swollen

Scheme 1



resins with low phosphine loadings (PL). Case A has a high P:Rh ratio while case B has a lower P:Rh ratio. Cases C and D represent resins with a high phosphine loading. In Case C the P:Rh ratio is high while in Case D it is low. As will become apparent, these

two variables play a major role in the metal-ligand dissociation equilibria so important in catalytic processes.

Insert
Fig. 2 →

The swollen resin is a dynamic environment. Chain segments move. Chain rotations are continuously taking place. In resin catalysts such as 1-4 (Scheme 1) ligand dissociation equilibria occur. In a homogeneous solution, $\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}$ undergoes the reversible dissociation of PPh_3 . In a swollen polymer this same dissociation will occur. However, one can readily imagine that the intervention of polymer backbone conformational restrictions and mobility limitations will effect the position of this equilibrium. This concept is illustrated in Figure 3. In this hypothetical microsection of resin 1, the reversible dissociation of a polymer-attached diphenylphosphino group is shown. If one pictures the trisphosphine structure on the left as in an unfavorable polymer conformation, it is easy to imagine that the dissociation shown would release a polymer chain segment to move out of this unfavorable conformation. In moving to the more favorable conformation shown at the left, the phosphine is now positioned so that it may not collide with the rhodium. In such a situation, it is easy to see how the resin matrix could increase the value of the equilibrium constant relative to its position in a homogeneous solution. This will also be a function of swelling.

Any attempt to "rigorously" define and compare such equilibria inside resins with the corresponding processes in a homogeneous

solution is fraught with difficulties of definition. First, only a small fraction of total phosphines within a given resin bead are actually available to a specific metal atom (see Figure 2). Imagine that only those phosphines that are in the same microfraction of the polymer as a rhodium atom are available to that rhodium. Secondly, it is possible to imagine that the solvation shell about a given metal atom within the resin is not identical to that in a homogeneous solution. One cannot rigorously avoid these problems. Therefore, for the purposes of this study and in the interest of developing conceptual models which are ultimately useful in the design of catalyst systems, we have chosen the following conventions to compare a polymer-bound catalyst with its homogeneous analog. First, the concentration of metal inside the swollen resin is calculated remembering all that metal is inside the volume of the resin beads (as opposed to the total volume of the reaction mixture). It is this concentration which is used in the analogous homogeneous reactions from which comparisons are made with the resin-catalyzed reactions. Likewise, the concentration of phosphine within the resin beads is the concentration used in homogeneous reactions for comparison with resin-catalyzed reactions. Reactions using polymer-bound catalysts are always compared to the corresponding homogeneous reactions at equal P:metal ratios as well as at equal phosphine and metal concentrations. Furthermore, we have employed either benzene

or toluene as the solvent for both the homogeneous and resin-containing reactions. These solvents fully swell the styrene-divinylbenzene matrix and avoid solvent gradients into the resin. Since the resins were highly swollen and only slightly crosslinked (i.e., 1%), they imbibe a large amount of solvent in the environment within the resin. Thus, (from a solvation shell standpoint) they may not be too different from the environment of the homogeneous reaction. One should keep these "definitions" in mind when the positions of equilibrium inside resin beads are discussed relative to those analogous equilibria in homogeneous solutions.

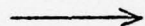
Hydroformylations of 1-Pentene Using $(\text{P}-\text{C}_6\text{H}_4\text{PPh}_2)_3\text{RhH}(\text{CO})$

1-Pentene was hydroformylated to n-hexanal and 2-methylpentanal using $\text{Rh}(\text{PPh}_3)_3(\text{CO})\text{H}$ and its resin-bound analog, 1. Before comparing the two catalyst systems, it is instructive to examine the mechanism of this reaction favored by Wilkinson and coworkers (Scheme 2).³⁸⁻⁴¹ After initial dissociation of phosphine, $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{H}$ coordinates a mole of carbon monoxide. The resulting bisphosphine species, $\text{Rh}(\text{PPh}_3)_2(\text{CO})_2\text{H}$ may undergo the loss of another phosphine giving monophosphine species $\text{Rh}(\text{PPh}_3)(\text{CO})_2\text{H}$. The monophosphine and bisphosphine species are in equilibrium and each is thought to be capable of adding rhodium hydride across an olefin. These additions can occur in both Markovnikov and anti-Markovnikov fashion, but the bisphosphine species gives a higher

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fraction of antiMarkovnikov addition. Subsequent steps, which include carbon monoxide insertion, hydrogen oxidative addition, and reductive elimination of aldehyde, occur to give both normal (n) and branched (b) aldehydes. The n/b ratio, however, depends upon the position of the equilibrium between $\text{Rh}(\text{PPh}_3)(\text{CO})_2\text{H}$ and $\text{Rh}(\text{PPh}_3)_2(\text{CO})_2\text{H}^*$. For steric reasons $\text{Rh}(\text{PPh}_3)_2(\text{CO})_2\text{H}$ is more selective in the addition of rhodium to the terminal carbon. Thus, as the concentration of PPh_3 is raised, the dissociation equilibrium shifts to the right causing, ultimately, a higher n/b product ratio to be observed.

Insert
Scheme 2



What role might the polymer matrix play in hydroformylation?

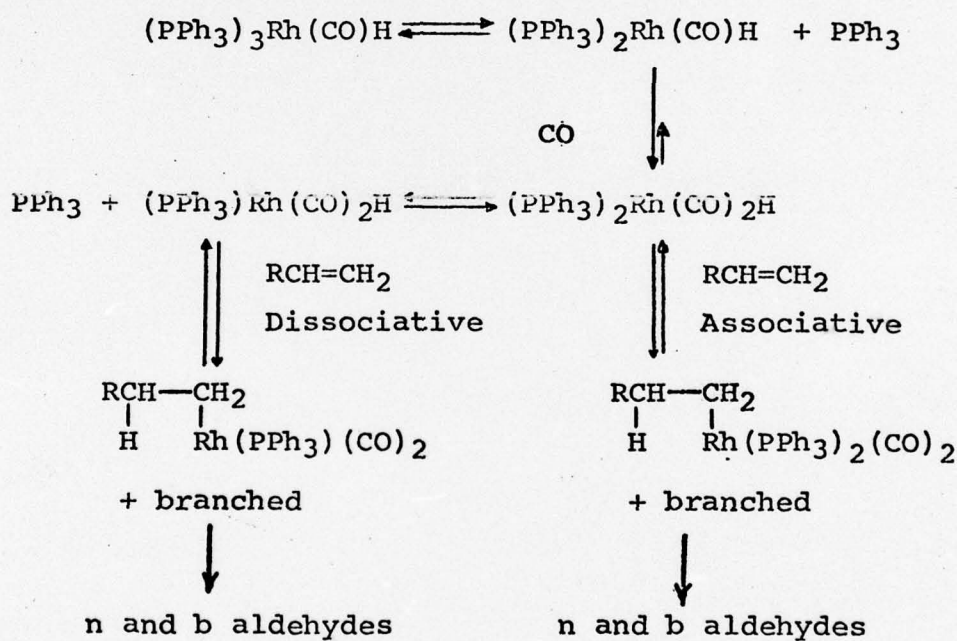
Figure 4 pictures the $\text{RhP}_2(\text{CO})_2\text{H} \rightleftharpoons \text{RhP}(\text{CO})_2\text{H} + \text{P}$ equilibrium within the matrix. It shows two situations. First, upon dissociation of one phosphine, another phosphine readily coordinates the rhodium. This situation will be favored at high phosphine

* It seems more likely to us that the critical equilibrium would actually be: $\text{Rh}(\text{PPh}_3)(\text{CO})_2\text{H} + \text{PPh}_3 \rightleftharpoons \text{Rh}(\text{PPh}_3)_2(\text{CO})\text{H} + \text{CO}$.

Thus, both rhodium species are 16-electron complexes which could readily coordinate olefin prior to rhodium hydride addition.

However, regardless of which view is correct, all the following arguments remain the same concerning the influence of the polymer matrix or added phosphine on n/b selectivity. In this case steric effects and electronic effects would cause more terminal addition of the rhodium with $\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{H}$ than with $\text{Rh}(\text{PPh}_3)(\text{CO})_2\text{H}$.

Scheme 2



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loadings in the resins (high PL) and high P/Rh ratios. On the other hand, phosphine may dissociate without capture of the rhodium by another phosphine. This would be favored at low PL and low P/Rh ratios. In those cases it may be impossible for another phosphine to physically reach the rhodium atom in question. Additional effects may exist. For example, proximity effects may operate. A high frequency factor may exist for phosphine association with rhodium. Such a situation may be imposed by the conformational arrangement of different polymer chains or stereochemistry within a given chain. Likewise, dissociation may be promoted if the original bound $\text{RhP}_2(\text{CO})\text{H}$ species is very unfavorable due to steric factors that cause the chain segments (to which each P is attached) to interact repulsively.

Insert
Fig. 4

→ With these concepts in mind, we predicted that resins with high phosphine loadings (PL) and large P/Rh ratios should give high n/b ratios. In other words, the associative route (Scheme 2) would be favored. At low PL and low P/Rh ratios, low n/b ratios were predicted. Finally, we thought that when the polymer-bound catalysts were compared to their homogeneous analogs (at equal concentrations of Rh, phosphine, equal P/Rh ratios, and all other conditions equal) it might be possible to observe special matrix induced effects on selectivity resulting from changes in the position of the phosphine-rhodium equilibria.

For the purpose of this study four resins are selected for

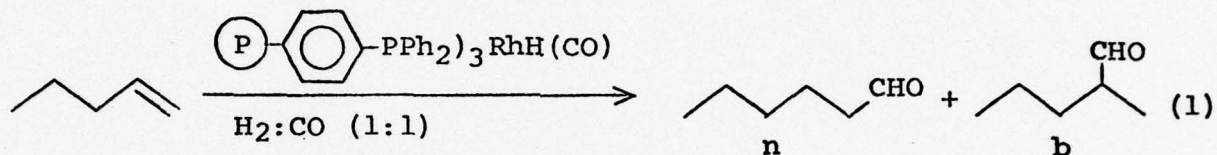
comparison as listed below. Resins 1A and 1B have high

Resin Number	Phosphine Loading (PL)	P:Rh
<u>1A</u>	40	19
<u>1B</u>	40	12
<u>1C</u>	20	23
<u>1D</u>	8.5	3.6

phosphine loadings, but 1A has a higher P:Rh ratio. Resin 1C has an intermediate phosphine loading with a high P:Rh ratio.

Resin 1D has a low phosphine loading and low P:Rh value.

Hydroformylation studies were carried out using these catalysts



on the model olefin, 1-pentene.

The results are plotted in Figure 5. At 100 psig and 400 psig the trends are the same. Resin 1A, as expected, gave the highest selectivities. Lowering the phosphine loading (1C) or the P:Rh ratio (1B) resulted in lower selectivities. At much lower phosphine loadings and P:Rh ratios (i.e., 1D) the selectivity was still lower. This was true over the entire 60-140° temperature range. Clearly, the mechanistic picture and rationale given above does work in the design of the catalyst system.

Polymer-anchored rhodium hydroformylation catalysts frequently gave curved plots of selectivity versus temperature which have no precedent in the homogeneous use of the catalyst. The reason for this has not been determined.

Insert
Fig. 5



The next question to be studied is: how do these resins compare to their analogous homogeneous reactions? Figures 6-8 answer this question for resins 1A-D. At high phosphine loadings and P:Rh ratios the resins are far more selective than the analogous homogeneous reactions. Figure 6 shows how selectivities induced by resin 1A compare with corresponding homogeneous reactions at temperatures from 40° to beyond 140°. Similarly, Figure 7 shows the same phenomenon for resins 1B and 1C. Notice that, at quite low phosphine loadings and P:Rh ratios (i.e., with resin 1D), the corresponding homogeneous reaction is more selective than the resin-catalyzed reaction (Fig. 8). Here, the phosphines must be, to a degree, matrix isolated from one another on the resin. Thus, $(P) - PPh_2)_1 RhH(CO)_2$ must be favored to some extent and the selectivity drops for reasons discussed before.

Insert

Fig. 6,7&8

The resin catalysts also exhibit a different dependence of selectivity upon pressure than the homogeneous catalysts do. This is illustrated for reactions carried out at 100° using 1:1 (H₂:CO) in Figure 9. The pressure dependence of the selectivity is steeper using the resin catalysts from 800 to 100 psi. Decreases in pressure lead to increases in selectivity. The homogeneous catalyst's dependence of selectivity on pressure begins to increase sharply below 80 psi. This phenomena has practical design implications.

Insert

Fig. 9

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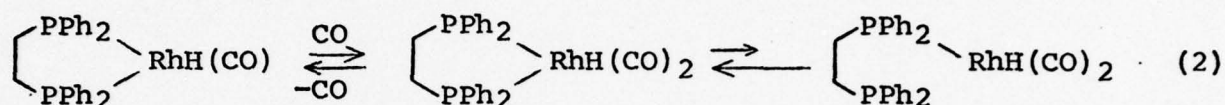
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Fig. 9

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Hydroformylation of 2-Pentene Using
Polymer-Attached Diphos-Rhodium

In studies of the chelating ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, it was found the rhodium-catalyzed hydroformylation of internal olefins took place much faster with this ligand than with PPh_3 .^{7b} This may be due to the necessary cis orientation of the phosphines. Under hydroformylation conditions, the equilibria shown (equation 2) can be suggested. The effect of this as ligand geometry



on the selectivity of 1-pentene hydroformylations was studied^{7b} and only low n/b ratios were obtained (i.e., ~2 at 100-800 psi and 60-100°). The selectivity decreased at 120° and 140°. The rhodium-catalyzed hydroformylation of 2-pentene using polymer-attached diphos (i.e., resin 4) was then studied.

Two different resins were prepared, 4a and 4b. Resin 4a contained a 22% ligand loading level and P/Rh=21 while 4b had a 5.7% ligand loading and P/Rh=2.1 (i.e., almost all the diphos units are bound to a rhodium). Hydroformylations of 2-pentene using resin 4a were conducted at pressures of 100 to 800 psi (1:1, H₂:CO) over the temperature range from 60 to 120°. These results are summarized in Figure 10. The terminal selectivity is low (n/b = <0.3) throughout this range, but it should be noticed that the selectivity to the terminal product increases as the temperature rises. The larger n/b ratio resulted because the

rate of isomerization to 1-pentene increased faster than the increase in the rate of 2-pentene hydroformylation as the temperature was raised. Studies of the product distributions as a function of conversion showed the presence of very small amounts of 1-pentene. This confirmed fast isomerization.

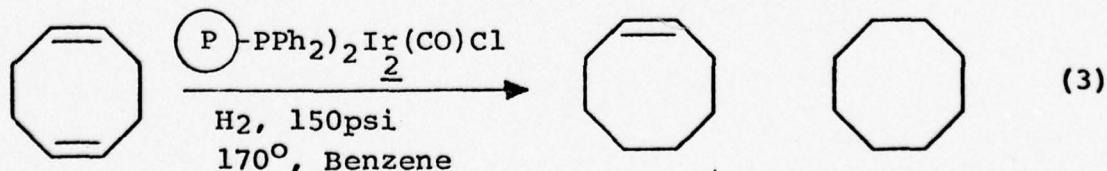
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Fig. 10 →

When excess ligand was not available in the resin, the n/b ratios at higher temperatures were increased. For example, when resin 4b was employed, the values of n/b = 0.6 to 0.7 at temperatures above 100°. These studies are summarized in Figure 11 and a 43% yield of n-hexanal was routinely achieved from 2-pentene at 140° and 100-800 psi. However, these catalysts will not be as selective as the less active phosphine-modified cobalt carbonyls, such as $\text{Co}_2(\text{CO})_8(\text{PBU}_3)_2$.⁴²⁻⁴⁴

Insert
Fig. 11 →

Activation of Polymer-Attached $\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2$ by the Matrix. Hydrogenations of 1,5-Cyclooctadiene.

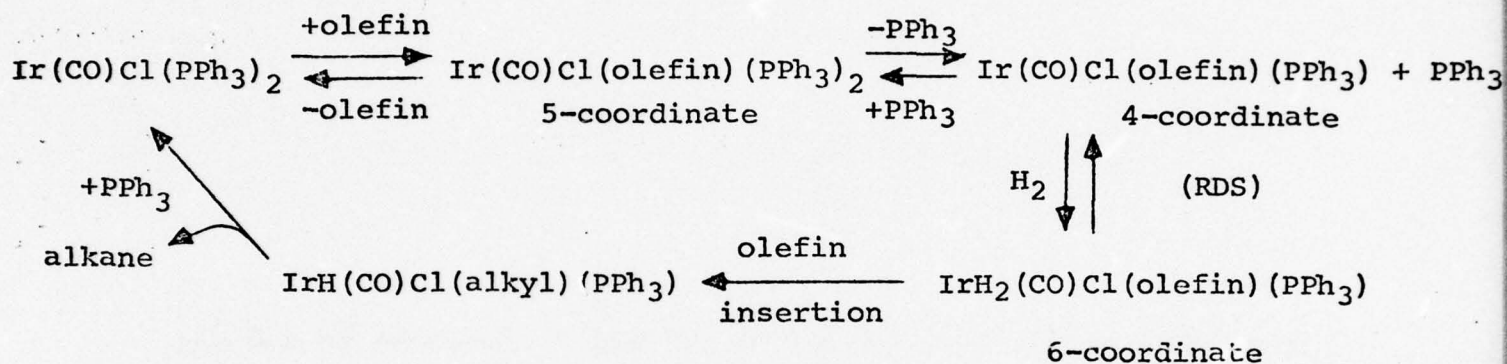
Vaska's complex, $\text{Ir}(\text{CO})(\text{Cl})(\text{PPh}_3)_2$, catalyzes the hydrogenation of olefins^{45,46} and the selective reduction of vinyl cyclohexene to ethyl cyclohexene.²⁶ We have studied the hydrogenation of 1,5-cyclooctadiene to cyclooctene (major product) and cyclooctane when catalyzed by polymer-attached Vaska's complex. Scheme 1 illustrates the synthesis of this resin catalyst (i.e., 2)



and equation 3 illustrates the reaction.

Before discussing the results, it is instructive to review the mechanism of olefin hydrogenation in the presence of $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$. Several investigations^{45,46} have reached the same conclusions about this reaction, and the mechanism is outlined in Scheme 3. Olefin coordination occurs first to generate the 5-coordinate adduct, $\text{Ir}(\text{CO})\text{Cl}(\text{olefin})(\text{PPh}_3)_2$, which

Scheme 3



then loses a mole of PPh_3 reversibly. The resulting 4-coordinate complex, $\text{Ir}(\text{CO})\text{Cl}(\text{olefin})(\text{PPh}_3)$, then may oxidatively add hydrogen in the rate determining step to generate the 6-coordinate dihydride. This is followed by olefin insertion into the iridium-hydride bond and reductive elimination of alkane. We reasoned that a resin matrix having a low P/Ir ratio might increase the rate of hydrogenation. This would be the expected result if the position of equilibrium between $\text{Ir}(\text{CO})\text{Cl}(\text{olefin})(\text{PPh}_3)_2$ and $\text{Ir}(\text{CO})\text{Cl}(\text{olefin})(\text{PPh}_3) + \text{PPh}_3$ was shifted by the matrix toward the 4-coordinate complex. Thus, a higher concentration of the 4-coordinate complex would be

available to oxidatively add hydrogen in the rate determining step. This is illustrated in Figure 12 for a hypothetical section of the resin catalyst. Alternatively, the mechanism might change to one involving initial formation of $(P)-PPh_2Ir(CO)Cl$ (3-coordinate) in the polymer when the P/Ir ratio was low. Then olefin would rapidly add to give the 4-coordinate precursor to hydrogen addition.

Insert
Fig. 12 →

In order to test this idea, three different resins of the type 2 were prepared (2a, b, and c). They had P/Ir ratios of 3, 4, and 22 respectively. Each of these resins was then used to catalyze the reduction of 1,5-cyclooctadiene at 170° under 150 psi of hydrogen. Then the analogous homogeneous reactions were also run at the same conditions. Some of the results are tabulated in Table 1. These results provide a remarkable agreement with the original postulate! At low P/Ir ratios in the resin, the rates of hydrogen uptake were greatly increased.

For example, the amount of hydrogenation was greater in 15 minutes using resin 2a (P/Ir = 3) than when the corresponding homogeneous reaction was run for 33 hrs! Similarly, the amount of hydrogen uptake was greater in 15 minutes using resin 2b (P/Ir = 4) than in the homogeneous reaction after 48 hrs. These are large rate enhancements. As the P/Ir ratio in the resin increased, the rate advantage given by the resin catalysts disappeared. For example, when resin 2c (P/Ir = 22) was employed, the rates of the homogeneous and resin-catalyzed reactions were almost identical.

TABLE 1. Comparison of the Activity of $\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$ with $(\text{P})\text{-PPh}_2)_2\text{Ir}(\text{CO})\text{Cl}$ in the Catalytic Hydrogenation of 1,5-Cyclooctadiene at 170° and 150 psi in Benzene

Catalyst	P:Ir	Time	Conversion to Products		Selectivity Cyclooctene Cyclooctane
			%Cyclooctene	%Cyclooctane	
<u>2a</u>	3 ^a	0.25	57	4	14.3
$\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	3	33.0	37	3	12.3
<u>2b</u>	4 ^b	0.25	69	5	13.8
$\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	4	48.0	44	3	14.7
<u>2c</u>	22 ^a	93	18	1.5	12
$\text{Ir}(\text{CO})\text{Cl}(\text{PPh}_3)_2$	22	72	15	1	15

^a4.03% P in resin

^b10.2% P in resin

Matrix-Activation and Stabilization of Palladium(O)-Catalyzed Dimerization-Alkoxylation of 1,3-Butadiene.

The use of homogeneous platinum and palladium catalysts

is often plagued by precipitation and agglomeration of metal or other catalyst decomposition products. For example, Haag and Whitehurst¹⁵ noted that a black metallic precipitate was formed during the carbonylation of allyl chloride when $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ was used as the catalyst. We chose to study the linear dimerization-methoxylation of butadiene (equation 4), catalyzed by $\text{Pd}(0)$, as an ideal test of the ability of a resin matrix to (a) prevent catalyst agglomeration and (b) activate the catalyst by promoting the formation of coordinatively unsaturated $\text{Pd}(0)$ species. This reaction was selected because it has frequently been cursed by catalyst agglomeration and deactivation.

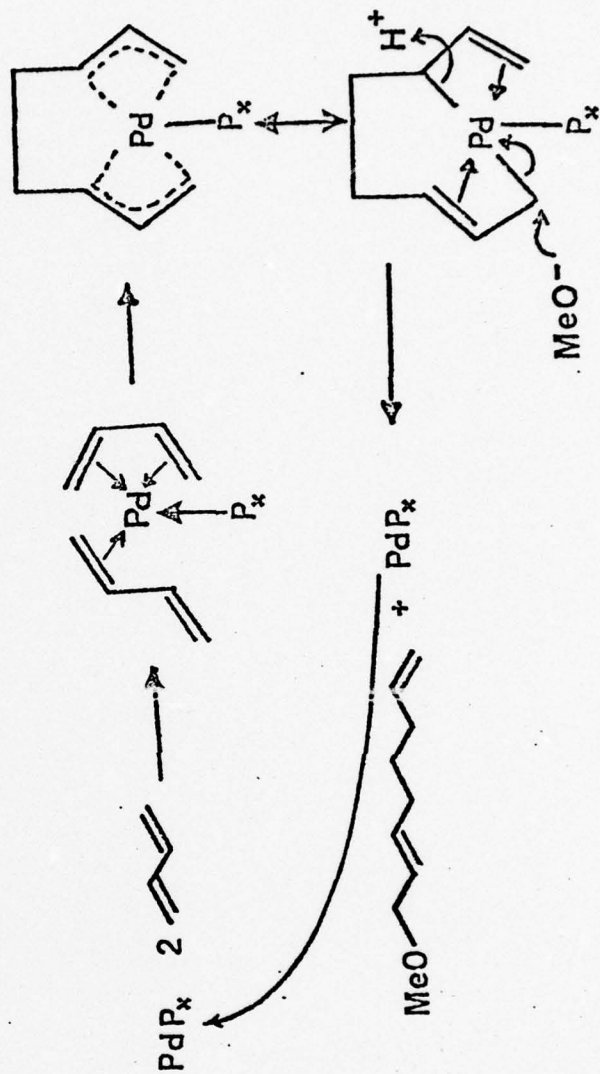
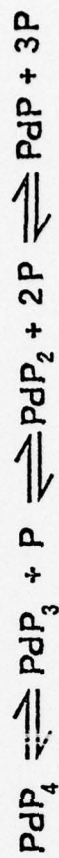


Previous studies by Smutny,⁴⁷ Takahashi,⁴⁸ Tsuji,⁴⁹ Shields,⁵⁰ and Berger⁵¹ have appeared. While some detailed aspects of the mechanism are still subject to controversy, the general features are known and include the phosphine dissociation equilibria and butadiene coordination processes shown in Scheme 4. Halpern studied the analogous dissociation with $\text{Pt}(\text{PPh}_3)_4$ and the first dissociation constant was very large and the second was $1.6 \times 10^{-4} \text{ M}$.⁵² Berger⁵¹ showed that the maximum rate of the palladium-catalyzed dimerization-alkoxylation of butadiene occurred when $\text{P}:\text{Pd}=2$. At

Insert
Scheme 4 →

Scheme 4

MECHANISTIC CONSIDERATIONS



higher phosphine concentrations and P:Pd ratios the rate became very slow, and at low P:Pd ratios the catalyst system becomes unstable and palladium precipitation occurs.

We reasoned that a phosphinated styrene-divinylbenzene resin could be used to "activate" palladium(0) complexes within the resin matrix. In particular, it seemed likely that up to two anchored phosphines would readily coordinate with palladium. However, further coordination of a third and fourth anchored phosphine site to a given palladium atom should become highly unfavorable, relative to the equivalent homogeneous solution equilibria shown in Scheme 4. The coordination of three or four anchored phosphine sites to a given palladium, during the ligand exchange reaction which fixes the palladium complex to the polymer, would require a great increase in the density of polymer chain segments in the vicinity of the metal atom. This should result in steric crowding and entropically unfavorable chain conformations. Even if three or four phosphines did coordinate to palladium (Fig. 13), swelling the polymer in the presence of butadiene remove should cause the dissociation of one or two of the coordinated phosphines. Such dissociations should be strongly favored relative to the same situation in the homogeneous solution (see Figure 13). The net effect should be to generate a more coordinatively unsaturated palladium within the resin matrix than would be found using the corresponding homogeneous catalyst. This would be the case even

though the phosphine concentration within the resin is very high. As the average degree of coordinative unsaturation increases, faster catalytic rates, per palladium atom, should be obtained.

Insert

Figure 13

→ The polymer should also act to "matrix isolate" palladium atoms from one another within the polymer relative to the high agglomeration tendency in homogeneous solutions. While chain mobility is significant,^{53,54} and metal migration within the resin would certainly be expected, the encounter rate of such anchored metal sites is expected to be far slower than similar processes in solution.^{28,55} Therefore, one would expect the polymer-anchored palladium catalysts would not only be more active, but they also would be more stable than the corresponding homogeneous complexes. Further, they should be able to be used in far higher concentrations in the reaction solutions. Overall, this should permit the use of smaller reaction vessels and facilitate longer catalyst lifetimes.

Kinetic studies of the homogeneous dimerization-methoxylation reaction were carried out using excess butadiene to determine the order in methanol and in palladium complex. The disappearance of methanol and the appearance of dimers were monitored by glc (internal standard technique). Plots of $t = (1/k) \ln \frac{[\text{CH}_3\text{OH}]}{[\text{CH}_3\text{OH}-X]}$, where X is the amount of methanol consumed at time=t, were straight lines. Rates were evaluated as the reciprocal of the slope over the first 80% conversion.

The pseudo first order rate constants from this treatment were then plotted as a function of the concentration of $\text{Pd}(\text{PPh}_3)_4$ for the homogeneous reactions. These plots are summarized in Figure 14 for P:Pd ratios of 4, 6, and 8 as dashed curves. When P:Pd is 8, an additional four moles of PPh_3 has been added. As the concentration of homogeneous $\text{P}(\text{PPh}_3)_4$ is increased above 0.004M, the rate rapidly levels off in all three homogeneous cases. This is characteristic of an equilibrium-limited upper concentration limit of the active catalytic species. It was observed throughout these studies for the homogeneous use of palladium(0) catalysts. Figure 14 also illustrates that the limiting homogeneous catalyst concentration is increased somewhat as the P:Pd ratio is lowered. Finally, the rates exhibited by several polymer-anchored catalysts as a function of the amount of catalyst added are also shown in Figure 14.

Insert
Figure 14 →

A series of polymer-anchored catalysts, $(\text{P}-\text{PPh}_2)_x\text{Pd}$, was prepared according to Scheme 1. Three different diphenylphosphinated styrene-divinylbenzene resins were prepared by this procedure. Specifically, phosphine loading levels of 15%, 47%, and 74% were used in this study (resins 3A, 3B, and 3C respectively). The phosphinated resins were then reacted with $\text{Pd}(\text{PPh}_3)_4$ in refluxing benzene to anchor palladium by phosphine exchange. A range of P:Pd ratios from 2.5 to 5.7 was employed. The catalytic resins used in this work are summarized in Table 2 along with their

Table 2. Resin-Anchored Palladium Catalysts Employed in the Dimerization-Methoxylation of Butadiene

Catalyst No.	Phosphorous Loading	Analysis			Swelling Factor ^a
		%Pd	%P	P: Pd	
3A-1	15	3.0	1.8	5.7	
3A-2	15	2.9	2.4	4.3	2.7
3B-1	47	7.7	7.1	3.7	1.8
3B-2	47	7.2	7.9	3.1	
3B-3	47	5.7	7.8	2.5	
3C	74	8.1	6.2	4.5	1.1-1.2

^aThe ratio of the swollen resin's volume in benzene to its dry volume.

numbering system.

Insert
Table 2 →

At 100° the rates of these reactions, catalyzed both by homogeneous and anchored catalysts, were all quite slow. These conditions were purposely chosen to allow the kinetics to be conveniently followed and to avoid complications due to diffusion limitations of the reaction rates. Grinding polymer beads 3A-2 and 3B-2 did not lead to rate enhancements.

The actual concentration of palladium complexes within the swollen resin must be considered. Calculations, which have corrected the volume of the swollen beads based on the appropriate packing factors, indicate the concentration of palladium with resin 3C is about 6.1×10^{-1} molar. For resins 3B-1 and 3A-2 these concentrations are 3.6×10^{-1} and 0.9×10^{-1} molar, respectively. Therefore, the actual concentrations of palladium complexes within the resins are a factor of ten to several hundred times greater than those in homogeneous solution.

To compare the catalytic behavior of the anchored catalysts to homogeneous $\text{Pd}(\text{PPh}_3)_4$, dimerization-methoxylation reactions were carried out using each resin in Table 2 over the same range of conditions and stoichiometries employed for homogeneous runs. Rate constants were then determined in the same manner as for the homogeneous reactions for several different amounts of resin charged to each reaction. This corresponds to obtaining rates for several different concentrations of the homogeneous

system. However, it is not proper to think of the catalyst concentration as specifically increasing when more resin is added, because the palladium complex is present at a constant concentration within the swollen resin matrix. As more resin is added, the amount of palladium complex catalyst available within the reactor goes up, but its concentration remains the same within the resin. More catalyst is available within the same total reaction volume. These studies are summarized, in part, in Figure 14 where homogeneous and heterogeneously catalyzed reactions are compared.

Figures 14 and 15 show the increases in rate which were obtained as more resin catalyst was added to the reaction (holding other variables constant). At first glance, the abscissa in Figure 14 might be confusing when compared to Figure 15. The abscissa in Figure 14 plots the concentration of homogeneous $\text{Pd}(\text{PPh}_3)_4$. In Figure 14 the concentration read from the abscissa does not apply directly to the resin catalysts. Instead, one simply should note that the total amount of palladium within the 50 ml reaction solution was the same for the homogeneous and resin catalysts at any point along the abscissa. In Figure 15, the same abscissa scale is used but the total amount of palladium complex is expressed as mmole of Pd present in each reaction volume (always 50 ml).

Insert
Figure 15 →

Several features of the reactions catalyzed by the anchored

catalysts differ distinctly from the homogeneous reactions. At all concentrations, the resin-anchored catalysts were more active than their homogeneous counterparts at comparable P:Pd ratios. Rate enhancements were obtained by adding more anchored catalyst, even when large amounts of catalyst were already present. For example, resins 3B-2, 3B-3, 3A-1 and 3A-2 can be added until more than 1.2×10^{-2} moles of Pd are present in the reaction solution without loss of rate enhancement as more catalyst is added. This contrasts sharply with the homogeneous reactions where limiting rates are reached when from 4 to 6×10^{-3} moles liter⁻¹ of catalysts has been added. This is even more remarkable when one considers that the actual concentrations of palladium complex with the resin are much higher than those in any of the homogeneous studies.

The rates are lowered as the phosphine loading (PL) in the resins is increased. Figure 15 illustrates this principle. For example at PL=74% the rate is very slow compared to PL=47% or 15%. The P:Pd ratios also play a major role in the rate. As P:Pd increases in the resins (holding PL constant) the rate decreases. This is shown in Figure 15 by comparing P:Pd ratios of 2.5, 3.1, and 3.7 (solid lines) at 47% phosphine loading. Furthermore, at 15% phosphine loading (dashed lines) the rate decreases as P:Pd is raised from 4.3 to 5.7. Finally, the rate is faster at PL=15% when P:Pd is 4.3 than when P:Pd is 3.7 for the higher phosphine loading of 47%.

Another difference between anchored and homogeneous catalyst systems is the far greater stability of the anchored catalysts. For example, resin 3B-3 could be recycled despite the fact it had a low (2.5) P:Pd ratio. The use of a 2.5 P:Pd ratio in homogeneous reactions leads to the formation of a block precipitate during the reactions. This coincides with a decrease in catalytic activity during the reaction. Another resin (PL=47%, P:Pd=4.0) was recycled twice and remained yellow-brown. After these reactions, the rate at which the recycled resin catalyzed dimerization was, within experimental error, the same as that of a fresh aliquote of the same resin. Apparently, site isolation is occurring in the resins which, in turn, allows a higher fraction of the palladium to remain active, even after long reaction periods. Recycle lifetimes and molar turnover limits have not been established for these catalysts, but even cursory observations clearly established that these limits are far higher using the resin catalysts.

The rate enhancements achieved by anchoring Pd(O) to resins are actually more dramatic than it appears in Figures 14 and 15. This follows from a consideration of the actual palladium and phosphine concentrations inside the resin beads. With the swollen polymeric catalysts, the bead volume always occupies less than 10% of the total solution volume. Thus, the actual concentration of palladium and phosphine within the swollen resin spheres is a minimum of ten times greater than is indicated on the abscissas of Figure 14. Therefore, resins 3B-2, 3B-3, 3A-1, and 3A-2 show

no curvature at real catalyst loadings of at least 0.12 moles/liter (0.6 mmol. per 50 ml. in Figure 15). The importance of this observation is that very high catalyst concentrations remain active when anchored to polymer matrices. This fact will permit the use of smaller reactors for this process.

The product selectivity (ratio of 1-methoxy-2,7-octadiene to 3-methoxy-1,7-octadiene) remained constant at about 3.5 as the catalyst concentration was increased in the homogeneous runs. This was true over the catalyst concentration range from 1×10^{-3} to 16×10^{-3} M. Homogeneous selectivity did not change as the P:Pd ratio was increased from 4 to 8. However, the selectivity was higher using resin catalysts 3A-1 and 3A-2 which had a 15% PL and P:Pd ratios of 5.7 and 4.3, respectively. In these cases, the selectivity was in the range of 5.7 to 7. As the phosphine loading was increased in the resin, the selectivity decreased. For example, at PL=47% the selectivity was 3 to 4 when P:Pd was 2.5 or 3.1 (resins 3B-2 and 3B-3). Further, selectivity decreased to 2.5-3.0 at 47% PL when P:Pd reached 3.7 (resin 3B-1). Finally, using highly phosphine loaded resin 3C (PL=74, P:Pd=4.5), the selectivities were lowered to about 1.8. It therefore appears possible to use the resin anchoring to modify catalyst selectivity. Selectivity increases as the resin's phosphine loading decreases and it increases as the P:Pd ratio decreases.

Asymmetric Hydroformylation of Styrene Using Resin-Anchored (-)DIOP.

One of the most important advances in synthetic chemistry in recent years has been the emergence of asymmetric catalytic syntheses using chiral organometallic complexes.⁵⁶⁻⁵⁸ However, only a few studies have commented on the topic of immobilizing asymmetric catalysts on polymeric substrates.^{59,60} Kagan⁵⁹ attached the chiral ligand (-)2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane (i.e., (-)DIOP) to a styrene-divinylbenzene resin and then made a Rh(I) complex with the resin. This resin was used successfully in asymmetric hydrogenations and hydrosilylations. Stille⁶⁰ attached DIOP to a hydrophilic styrene/2-hydroxyethylmethacrylate resin, and after complexing Rh(I) to the resin, it was used in asymmetric hydrogenations of water-soluble amino acid precursors.

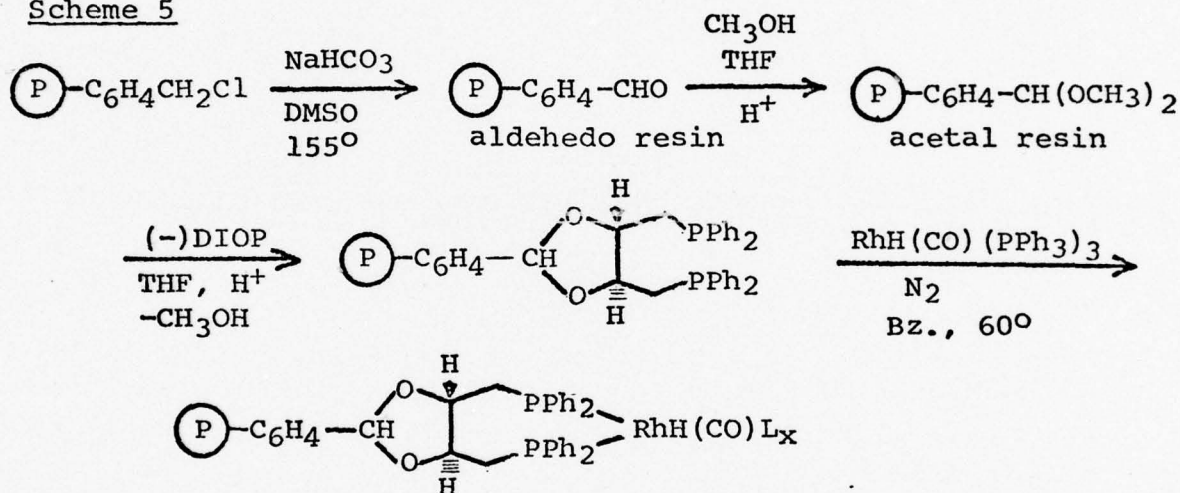
We now report the use of a (-)DIOP Rh(I) complex, attached to styrene-divinylbenzene resins, to catalyze the hydroformylation of styrene. Styrene was used as the model substrate in our work because Pino⁶¹ had already shown optical yields as high as 25% could be obtained in homogeneous rhodium-catalyzed styrene hydroformylations using (-)DIOP at 40° and 1 atm. In surprising contrast, Bayer and Shurig⁶² reported that (-)DIOP-Rh(I), attached to a soluble linear polystyrene, achieved only a 2% maximum optical yield in styrene hydroformylations. Therefore, it seemed necessary

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to do a critical study of how the polymer matrix would affect asymmetric induction using resin attached (-)DIOP-RhI complexes.

Styrene-divinylbenzene resins (both 1% and 2%DVB) were functionalized with (-)DIOP according to Scheme 5. This method is superior to Kagan's method which first added a ditosylate to the aldehyde resin. Using this method, six different resins were prepared where the (-)DIOP loading was varied from 18 to 61%. Also the (-)DIOP/Rh ratio was varied from 3.3 to 24. These

Scheme 5



polymers are listed in Table 3. This Table also summarizes the results of the styrene hydroformylations.

Styrene was hydroformylated in benzene at 40° and 400 psi 1:1, H₂:CO. Under these very mild conditions the optical yields showed a remarkable dependence upon the ligand loading in the polymer. For example, at 18% (-)DIOP loadings only low optical yields (5-6%) were obtained even at high (-)DIOP/Rh ratios. However, at 43% (-)DIOP loading the optical yield was 21.6% when (-)DIOP/Rh

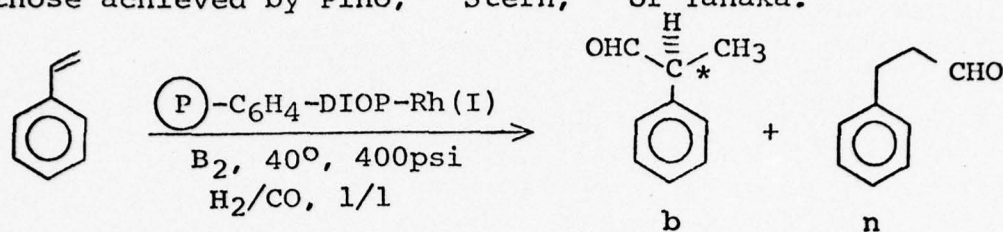
TABLE 3. The Effect of (-)DIOP Loading and the (-)DIOP/Rh Ratio on Optical Yields in the Hydroformylation of Styrene.^a

DVB ^b %	(-)DIOP LOADING	(-)DIOP Rh	b/n	OPTICAL YIELD %
1	18	13	5.0	6.2
1	18	24	6.2	5.1
2	25	3.3	10	5.2
2	25	10	1.8	15.6
1	43	7.1	4.3	21.6
1	61	17	3.8	34.8

^aConditions: 40°, 1:1, H₂:CO, 400 psi, solvent=benzene. Each reaction employed 0.027 mequiv. Rh, 7.9 mmol styrene, and 8 ml of dry benzene.

^bDVB = divinylbenzene

was 7. At a 61% (-)DIOP loading and a (-)DIOP/Rh ratio of 17, the optical yield was 34.8%. This optical yield is higher than than those achieved by Pino,⁶¹ Stern,⁶³ or Tanaka.⁶⁴



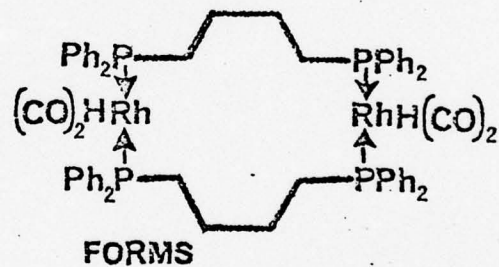
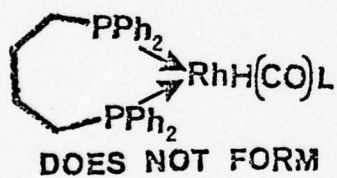
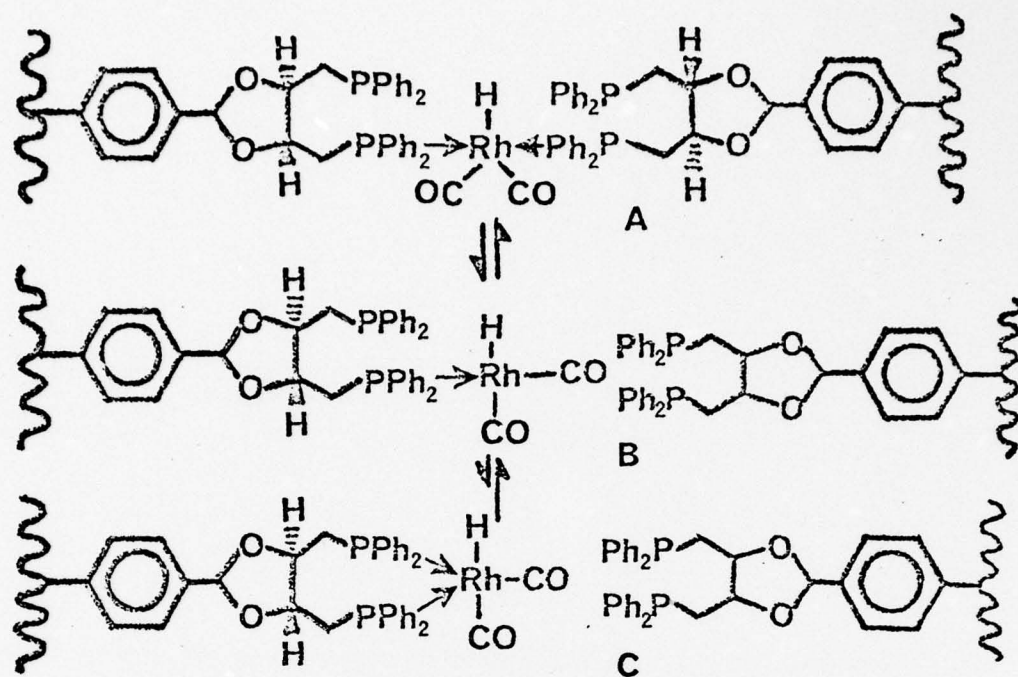
As the (-)DIOP loading and (-)DIOP/Rh ratio were varied, the branched/normal product ratio (b/n) varied widely. However, the branched product was always the major product. The large tendency toward branched product has been noted previously.⁶¹ The dependence of the b/n ratio on pressure, temperature, ligand/Rh ratio, and H₂/CO ratio has not been defined. However, this function has been shown to be complex for both 1- and 2-pentene hydroformylations when the ligand is Ph₂PCH₂CH₂PPh₂.^{7b}

The reason for the variation in optical yield with changes in the (-)DIOP loading and the (-)DIOP/Rh ratio is not known. However, it seems very likely that ligand equilibria again play a major role in these reactions. It is unlikely that the (-)DIOP-Rh(I) complex exists solely (or even largely) as a chelate such as the structure shown in Scheme 5. This structure has a seven-membered ring. Sanger has shown that both 1,3-bis(diphenylphosphino)-propane and 1,4-bis(diphenylphosphino)-butane give bridged dimeric rhodium complexes.⁶⁵ This is illustrated at the bottom of Scheme 6. We suggest, therefore, that ligand equilibria within the resin, of

the type shown in Scheme 6, play a role in determining the b/n ratios and the optical yields. This Scheme is, of course, greatly simplified but it does show both the bisphosphine biscarbonyl and monophosphine biscarbonyl complexes used in the Wilkinson hydroformylation mechanism. As the ligand density in the resin increases, the amount of the bisphosphine species A should increase relative to B and C (Scheme 6). This might play a role in increasing the optical yield.

Insert →
Scheme 6

Scheme 6



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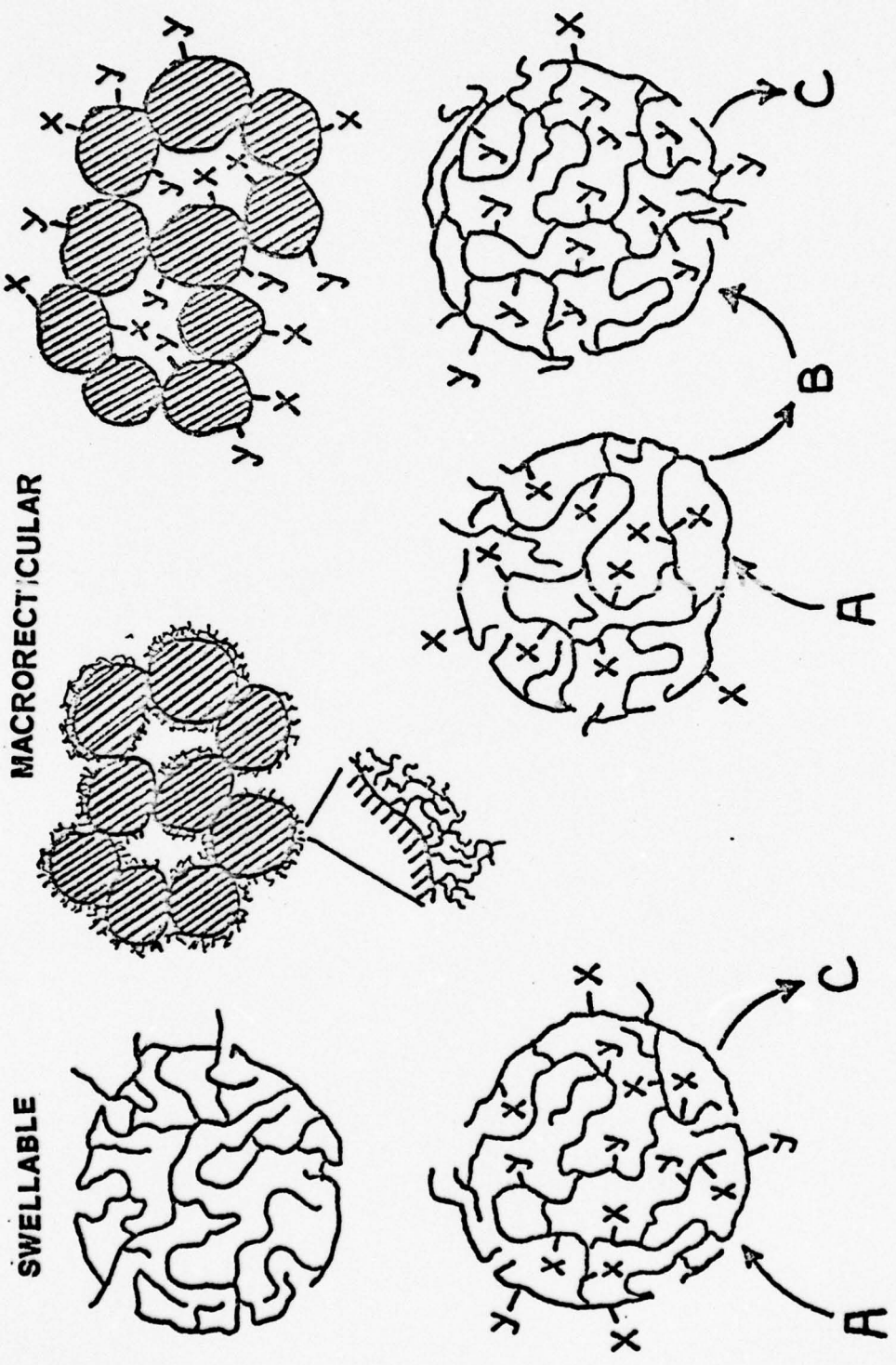
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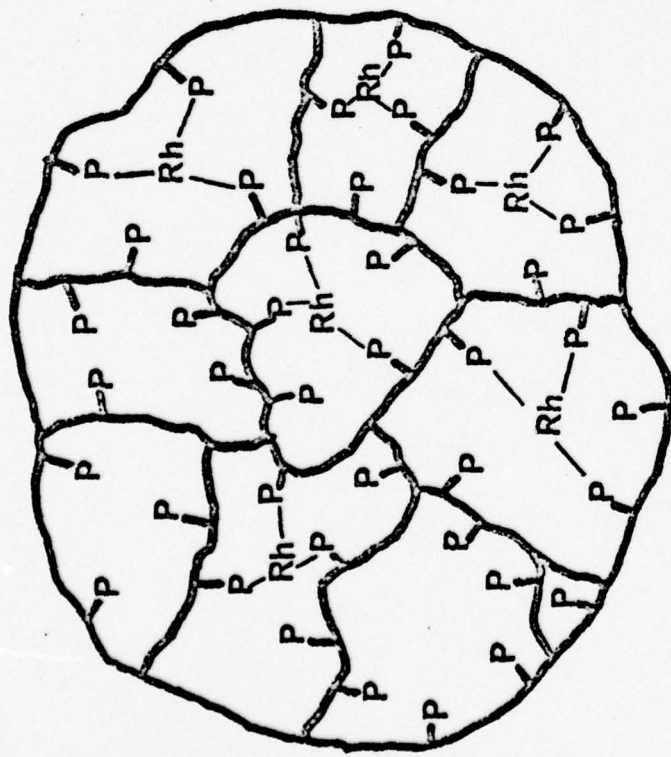
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Captions For Figures

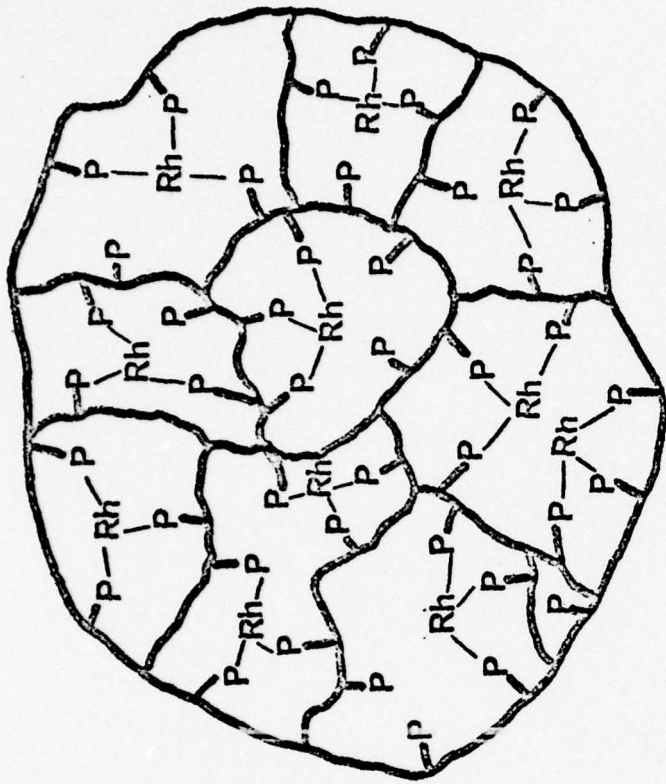
- FIGURE 1. Swellable (Microporous) and Macroreticular Resins. Concept of Catalyst Immobilization.
- FIGURE 2. A Representation of the Phosphine Loading and the Phosphorous to Rhodium Ratio in Swollen Resins.
- FIGURE 3. Ligand Dissociation Equilibria Inside a Swollen Resin.
- FIGURE 4. Suggested Ligand Equilibria which Effect the Selectivity in Hydroformylations Catalyzed by Polymer-Anchored Rh(I).
- FIGURE 5. Selectivity of Polymer-Attached Catalysts as a Function of Phosphine Loading and P/Rh Ratio.
- FIGURE 6. The Greater Selectivity of a Polymer-Anchored Rh(I) Catalyst Relative to Its Homogeneous Analog in 1-Pentene Hydroformylations. $[\text{Rh}] = 4.6 \times 10^{-3} \text{M}$.
- FIGURE 7. The Greater Selectivity of a Polymer-Anchored Rh(I) Catalyst Relative to Its Homogeneous Analog in 1-Pentene/Rh = 400 in Benzene. $[\text{Rh}] = 4.58 \text{mM}$.
- FIGURE 8. The Lower Selectivity of a Resin-Anchored Rh(I) Catalyst Relative to Its Homogeneous Analog at Low Phosphine Loadings.
- FIGURE 9. Pressure Dependence of the Selectivity in Rhodium-Catalyzed 1-Pentene Hydroformylations. Comparison of Resin-Anchored Versus Homogeneous Catalysts. 1-Pentene/Rh = 400. $[\text{Rh}] = 4.58 \times 10^{-3} \text{M}$ for the Resins 1A and 1C and $4.45 \times 10^{-3} \text{M}$ for the Homogeneous Case.
- FIGURE 10. Selectivity in 2-Pentene Hydroformylations Catalyzed by cis-Chelating Phosphine Resin 4a. (Rh = 0.09mmol., 1ml of 2-Pentene and 8ml of Benzene).
- FIGURE 11. Selectivity in 2-Pentene Hydroformylations Catalyzed by cis-Chelating Phosphine Resin 4b. (Rh = 0.09mmol., 1ml of 2-Pentene and 8ml of Benzene).

- FIGURE 12. Postulated Equilibria Contributing to Rate in the Hydrogenation of 1,5-Cyclooctadiene Catalyzed by Resin-Attached Vaska's Complex.
- FIGURE 13. Phosphine-Palladium Dissociation Equilibria Proposed to Account for Palladium Site Activation and Stabilization in the Dimerization-Methoxylation of Butadiene.
- FIGURE 14. The Rates of Dimerization-Methoxylation of Butadiene as a Function of Catalyst Concentration. Comparison of Resin-Attached and Homogeneous Pd(O) Catalysts.
- FIGURE 15. The Rates of Dimerization-Methoxylation of Butadiene Catalyzed by Resin-Attached Pd(O) as a Function of Increasing Catalyst Addition. Variation of Rate with Phosphine Loading and Phosphine/Palladium Ratio.

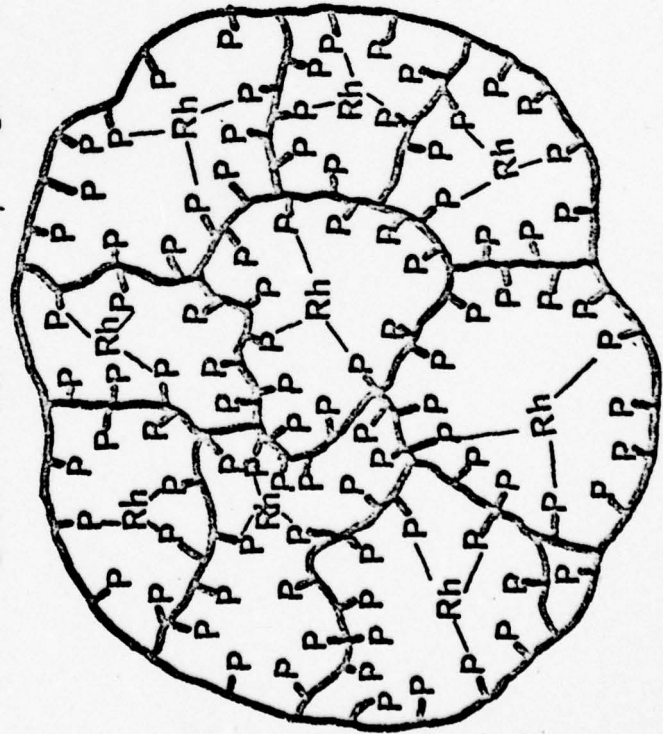




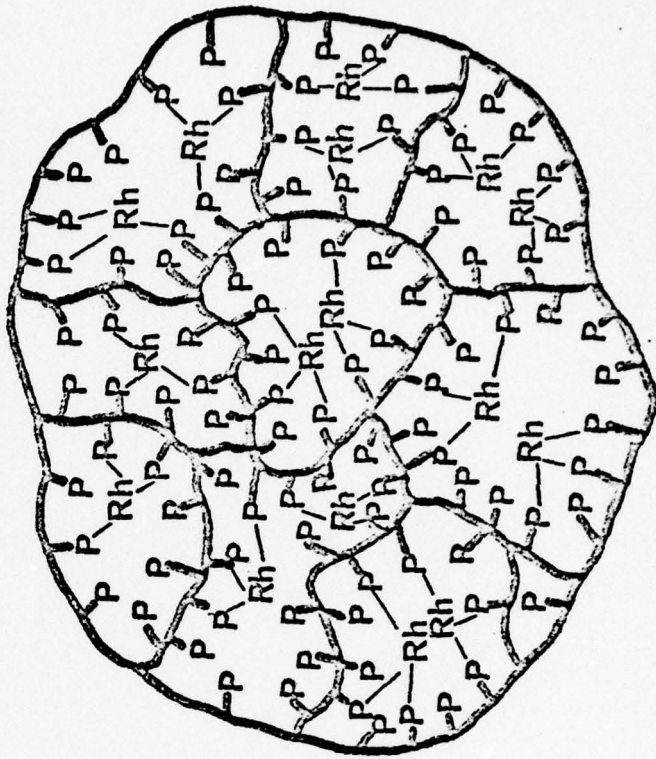
Case A: Low % PL; High P:Rh



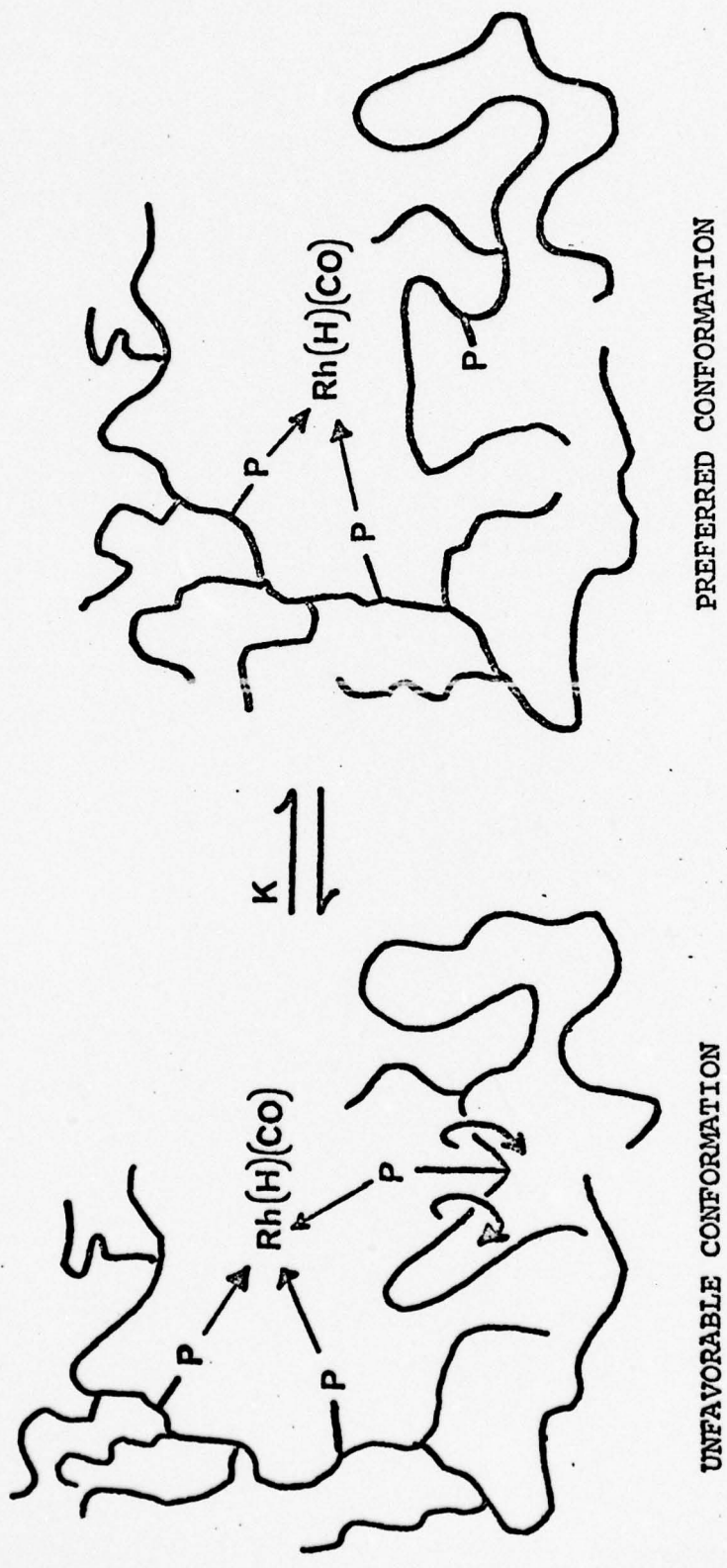
Case B: Low % PL; Low P:Rh



Case C: High % PL; High P:Rh



Case D: High % PL; Low P:Rh



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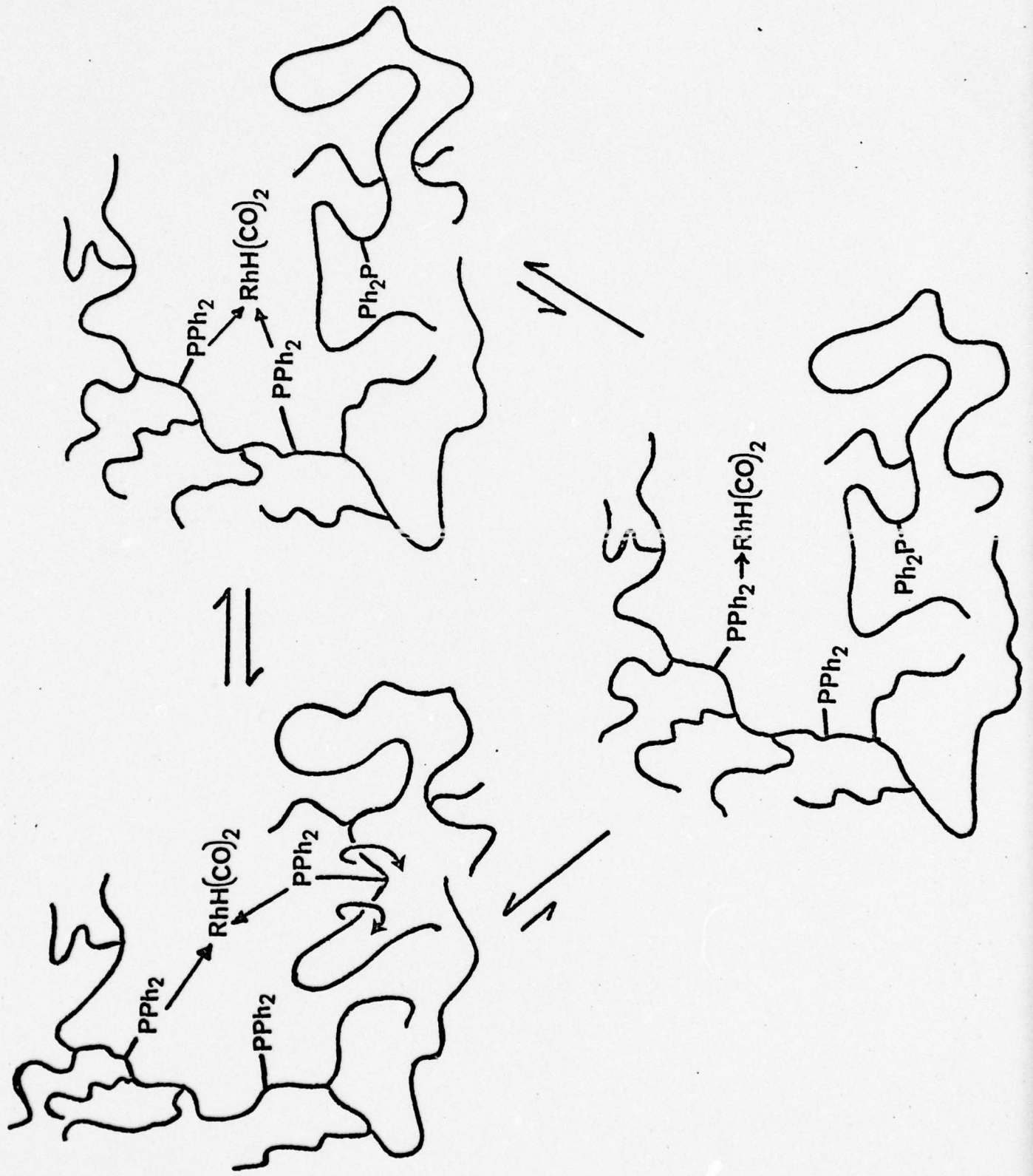
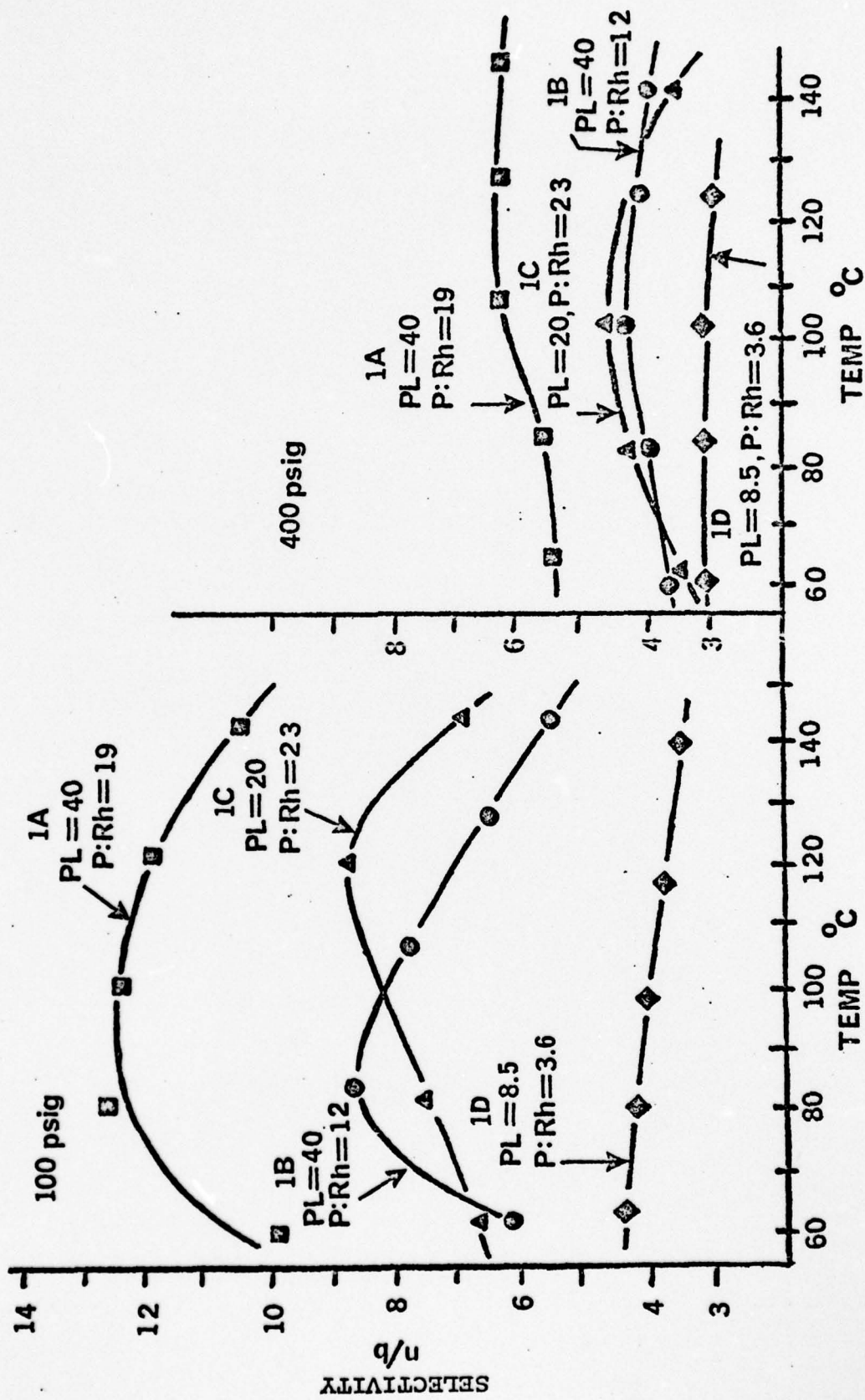
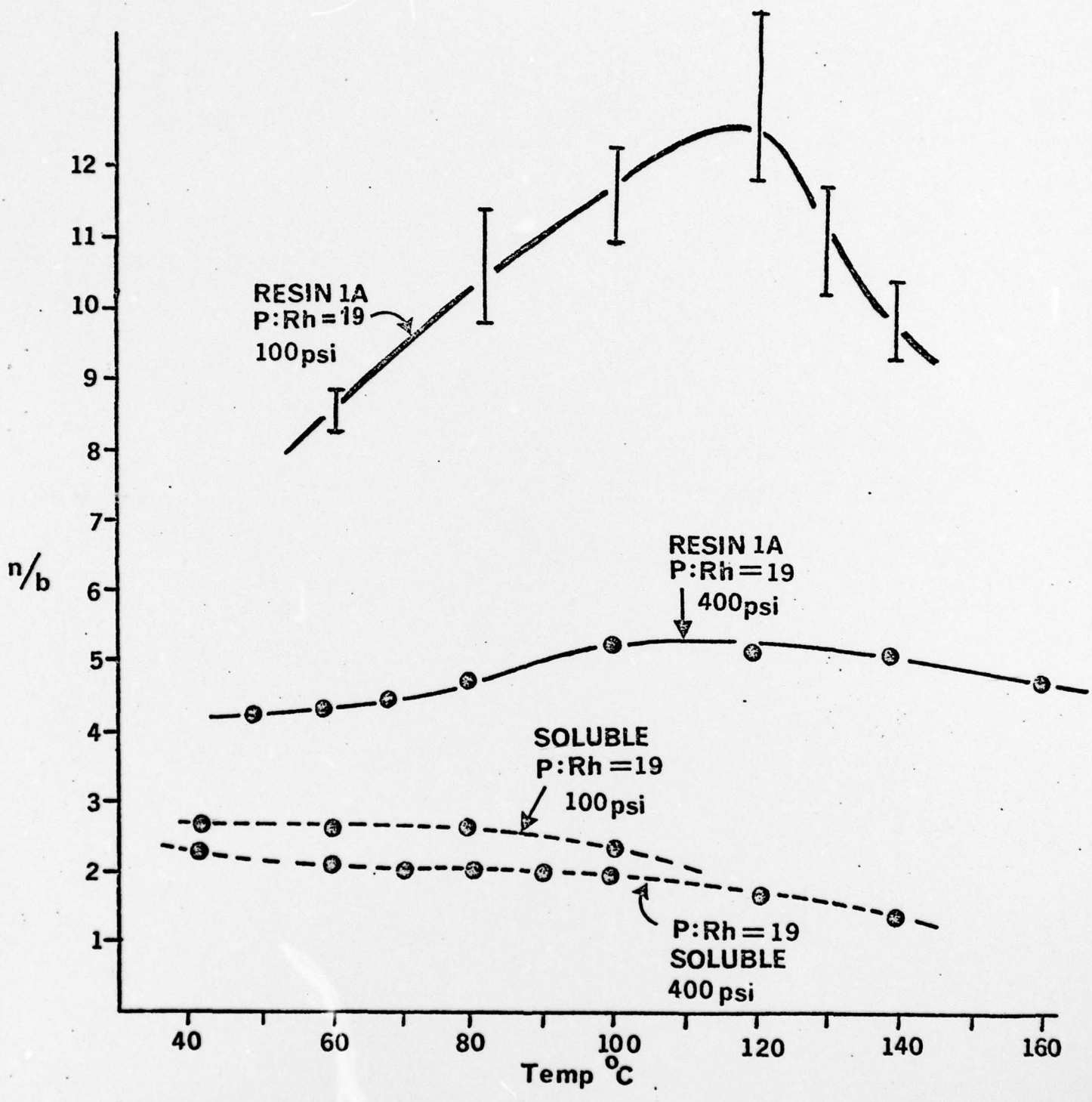
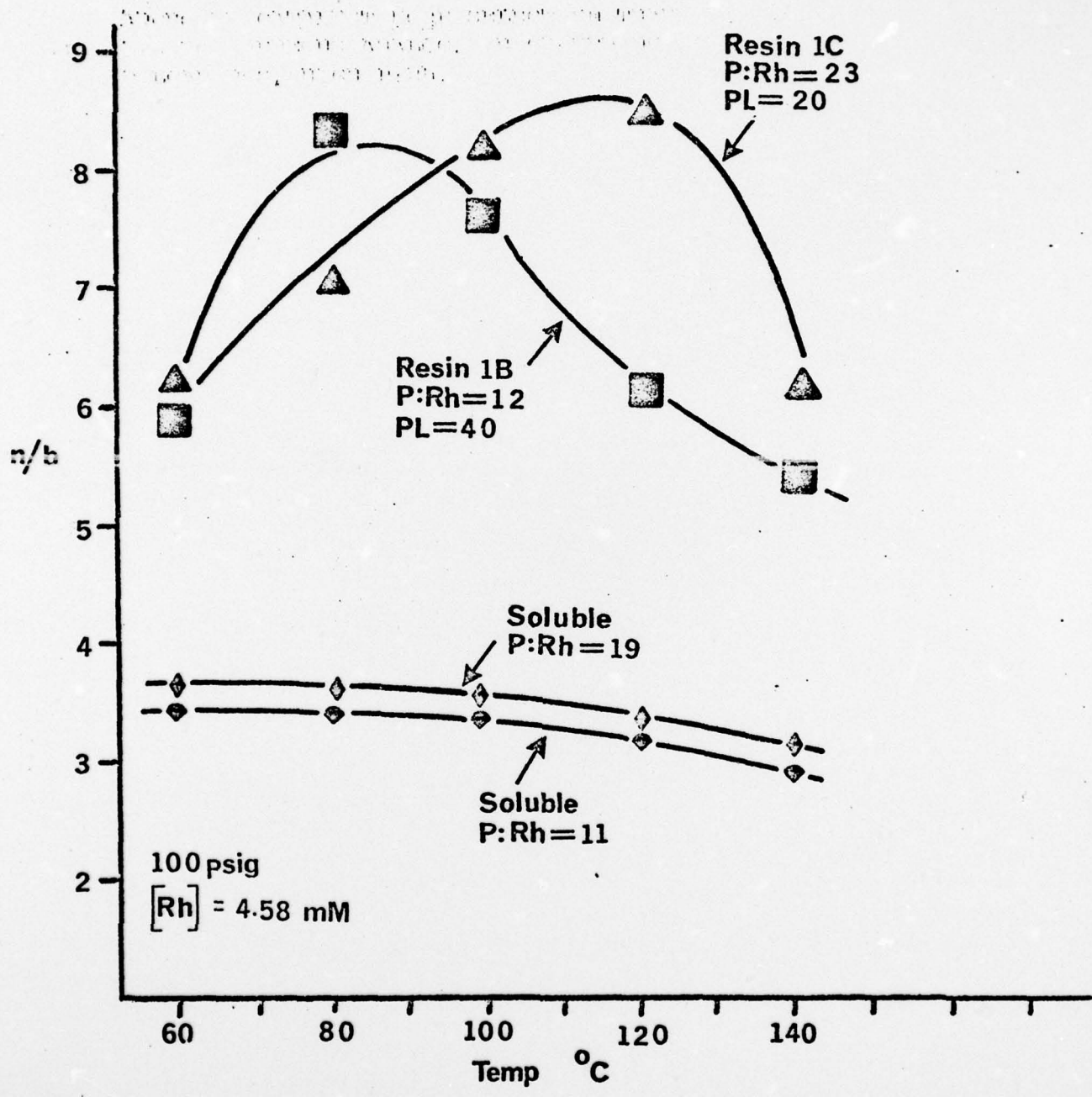
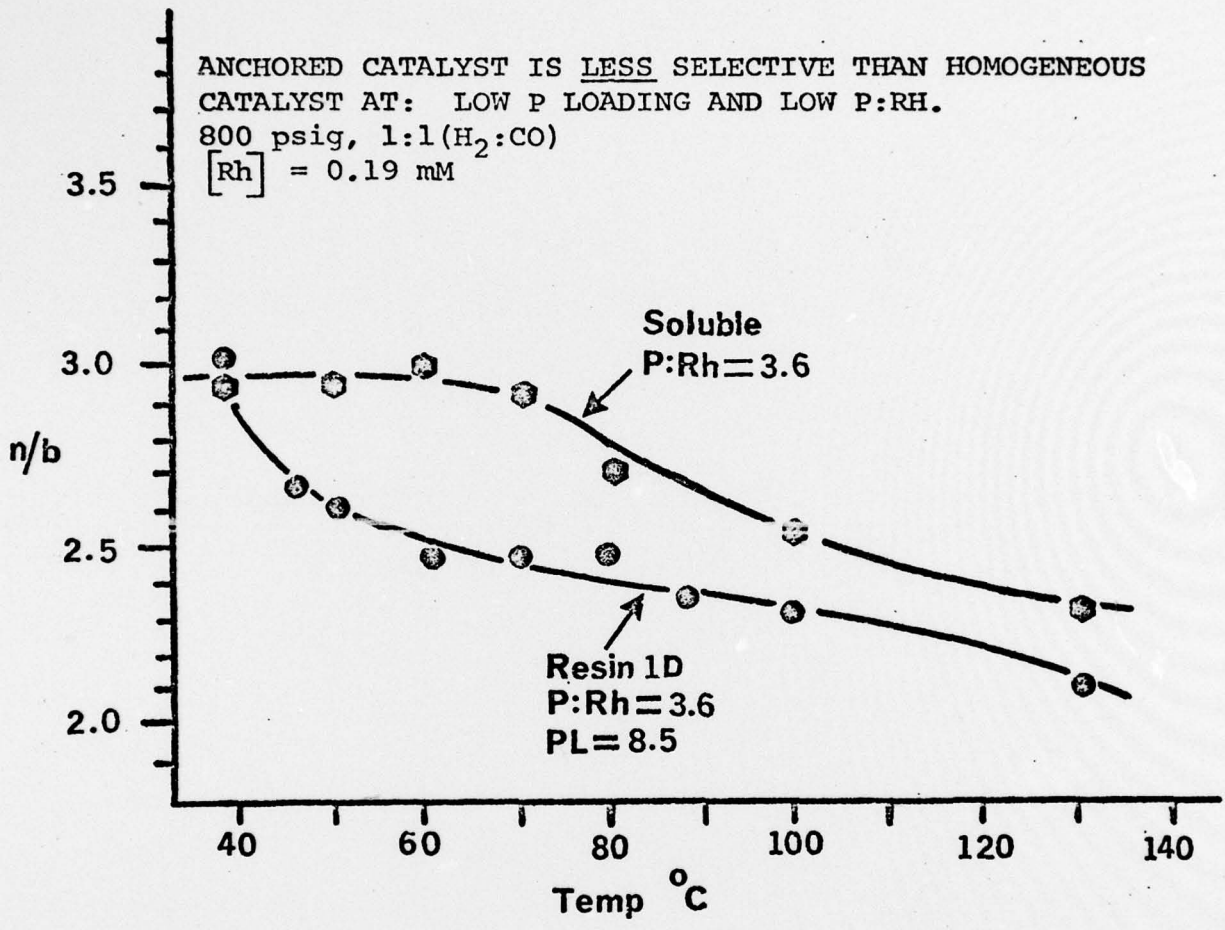


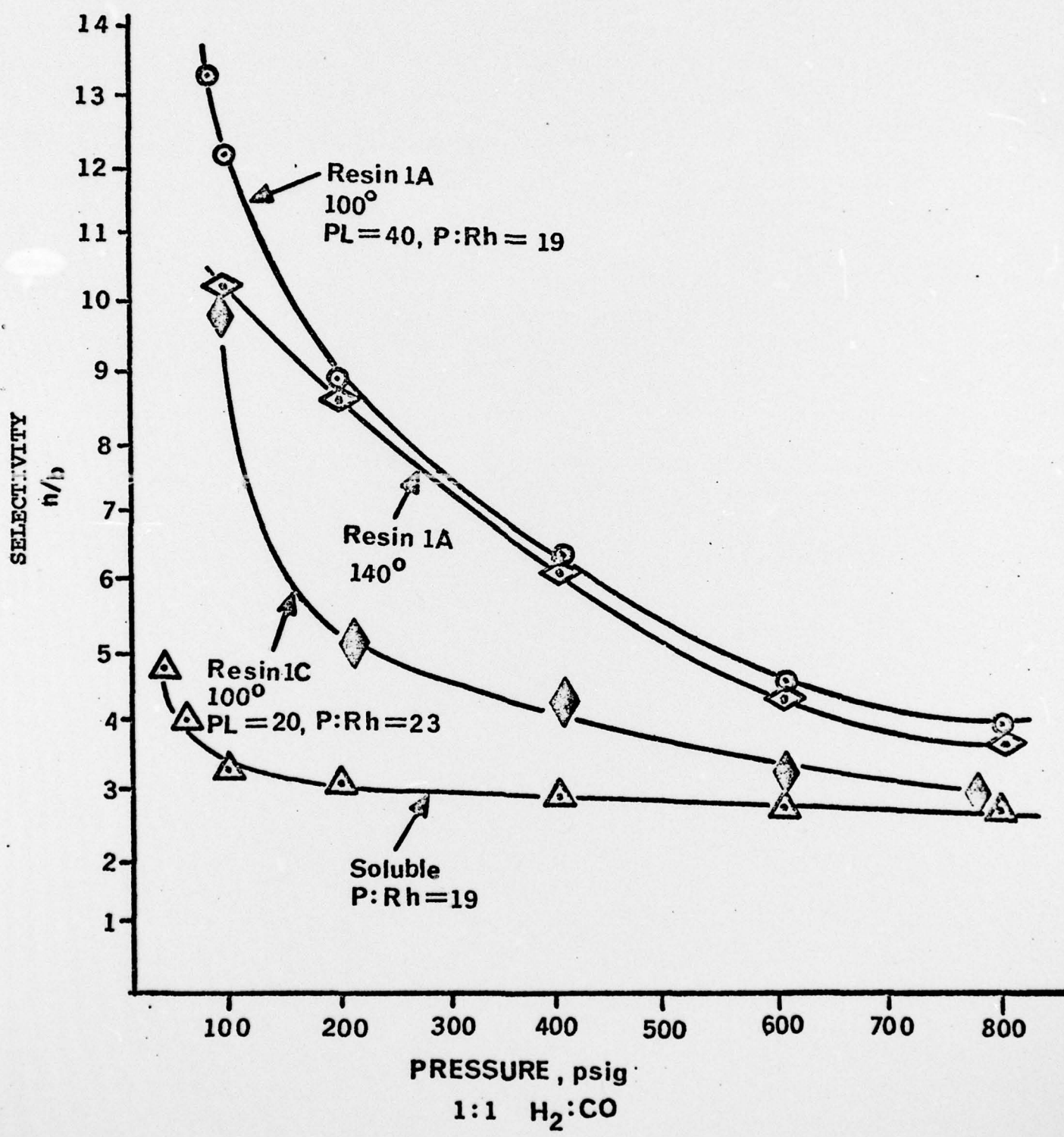
FIGURE 5

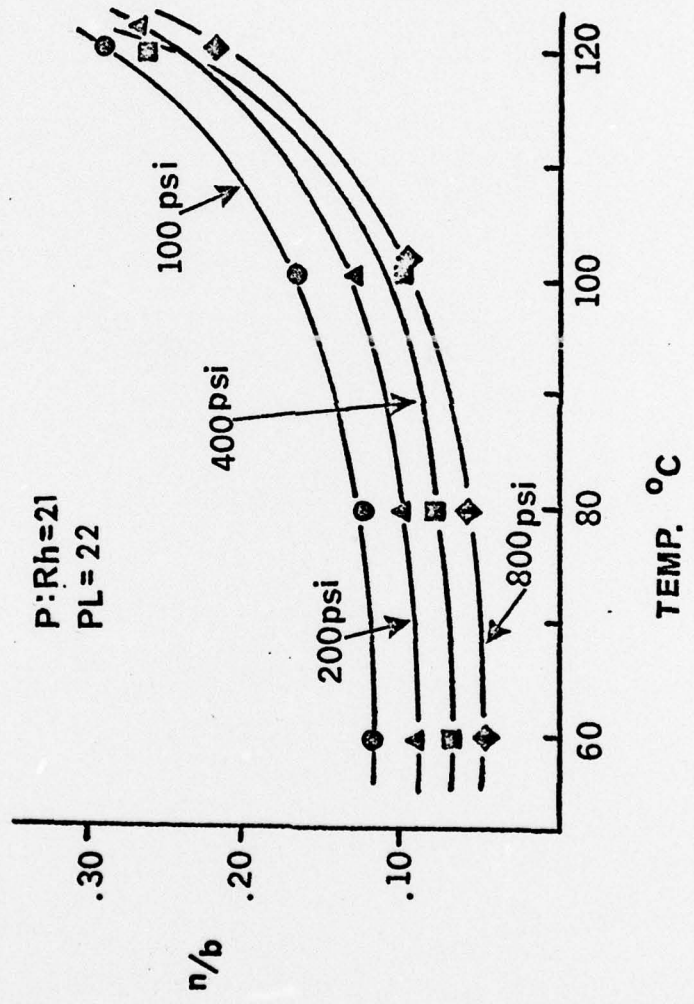
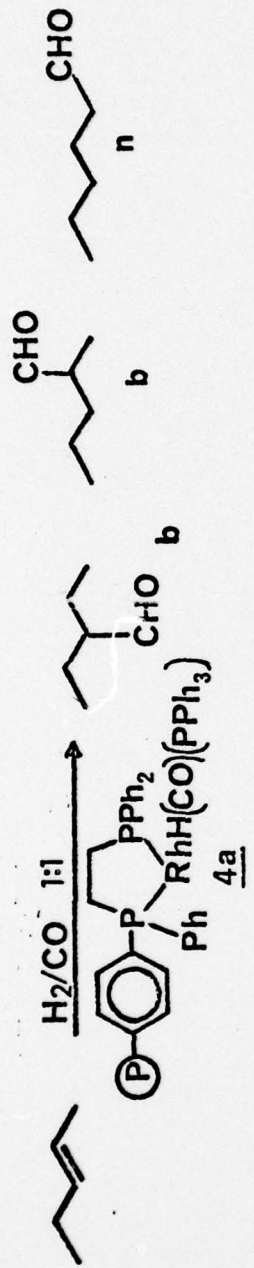


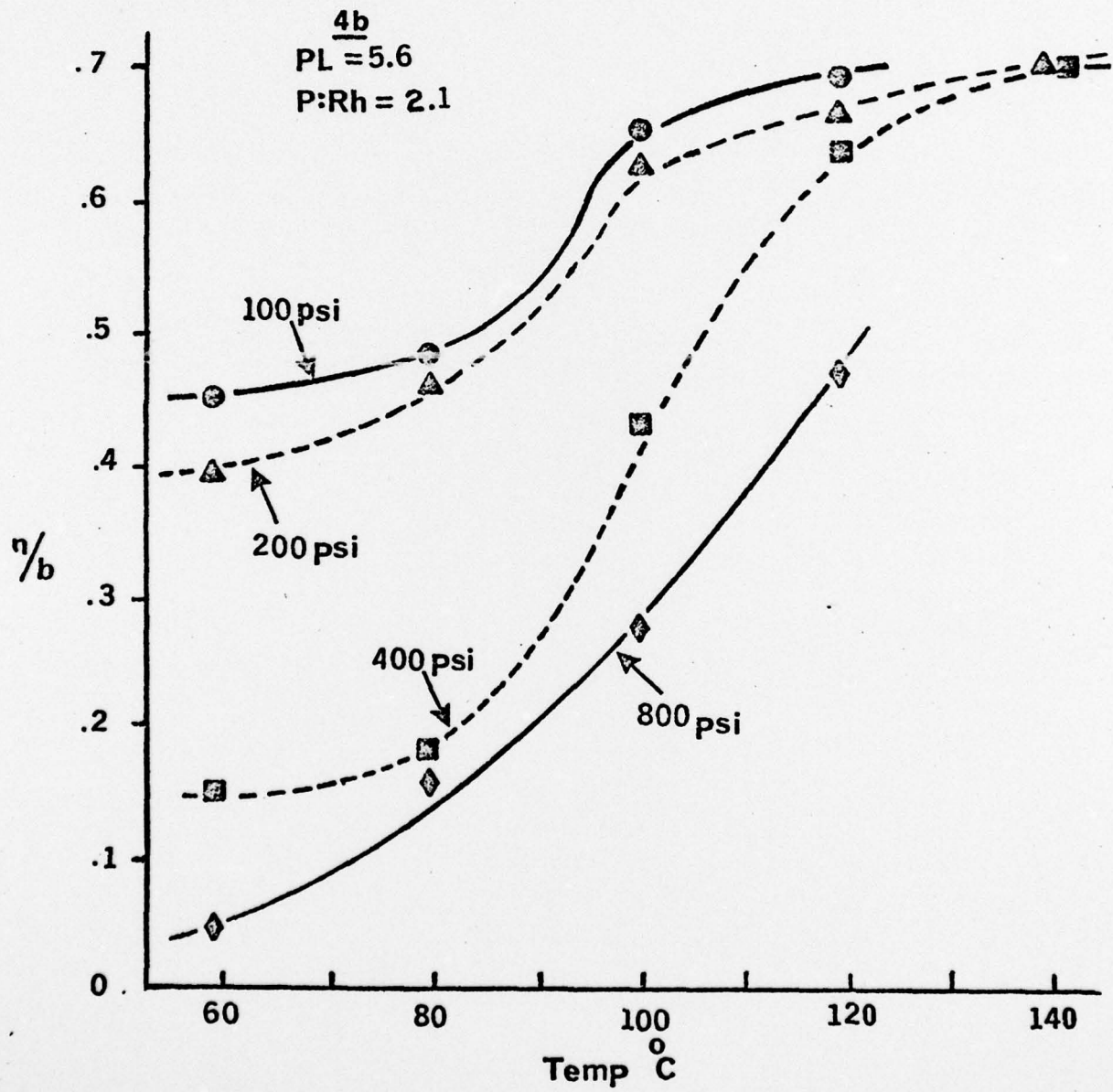


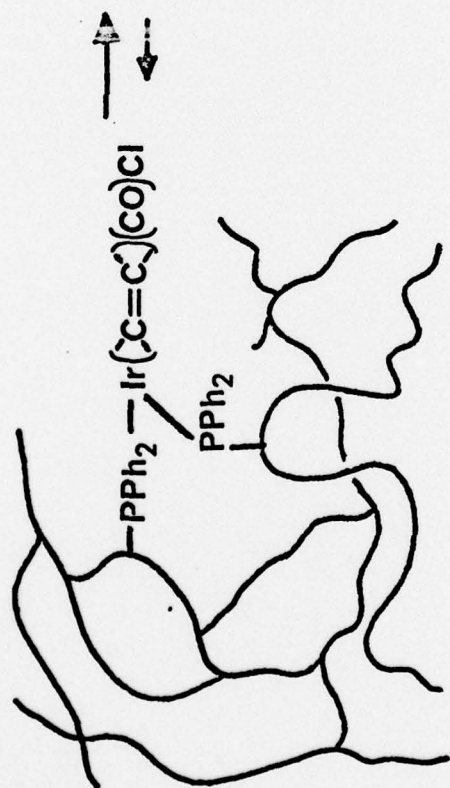
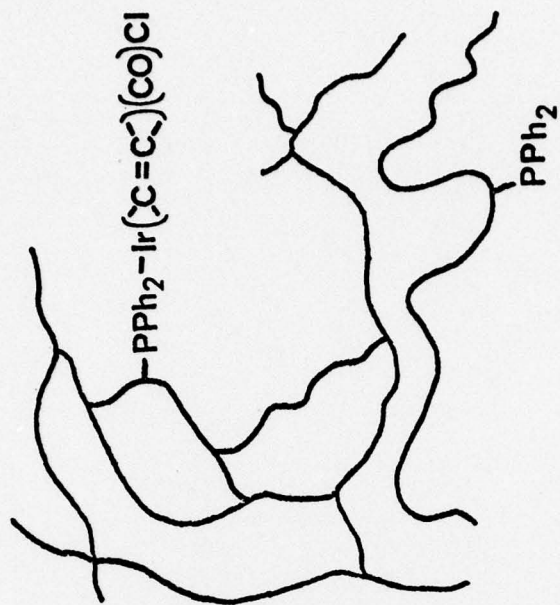




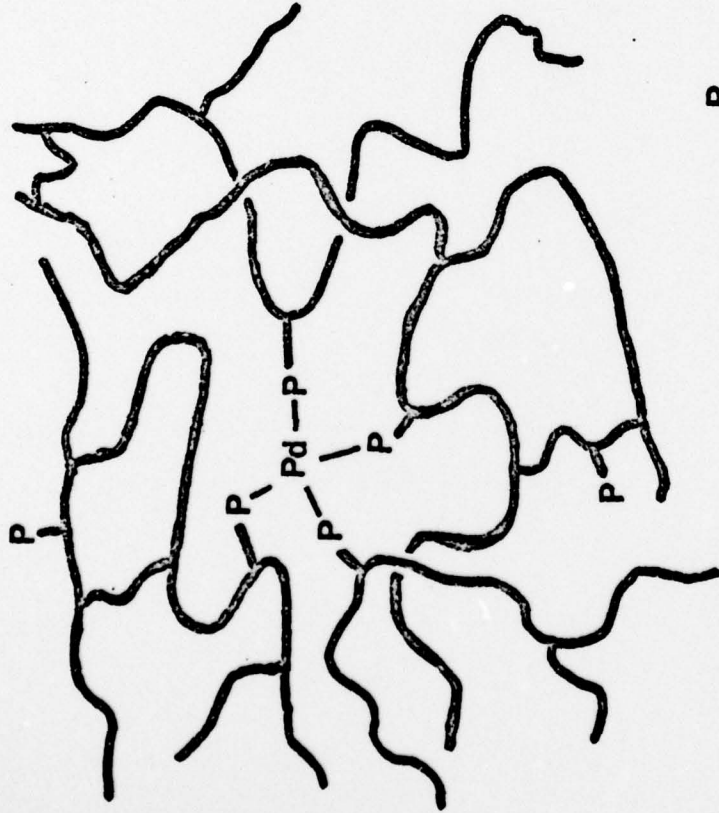
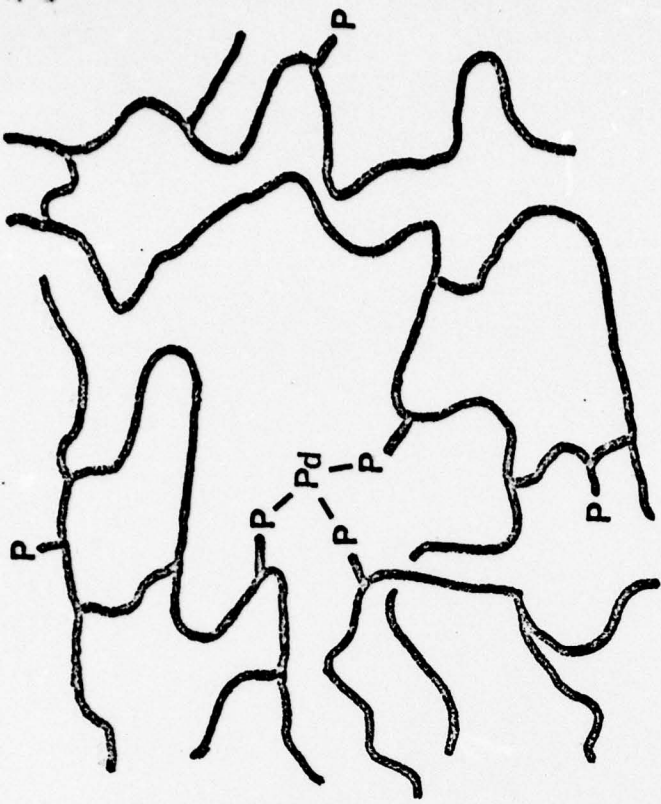




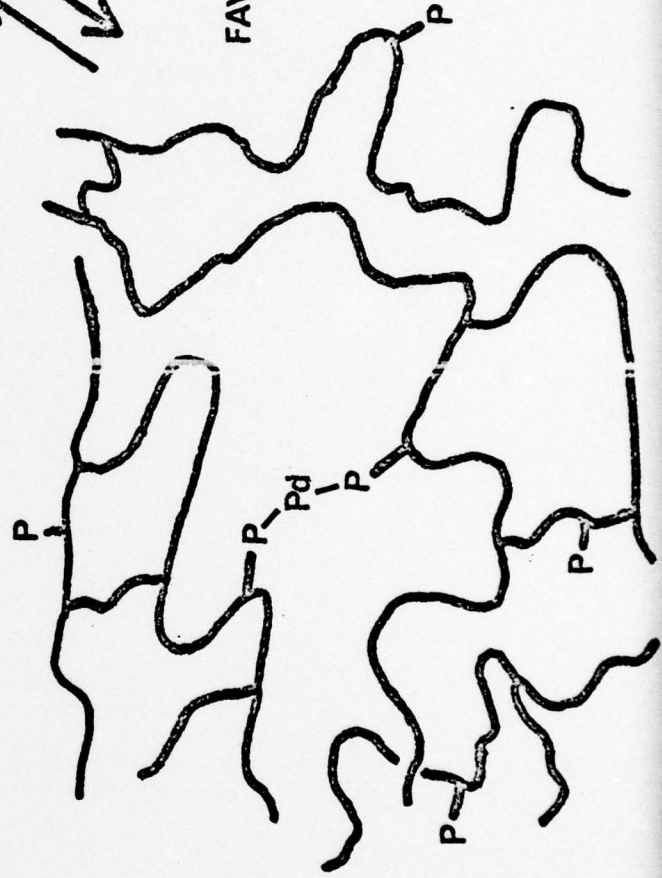




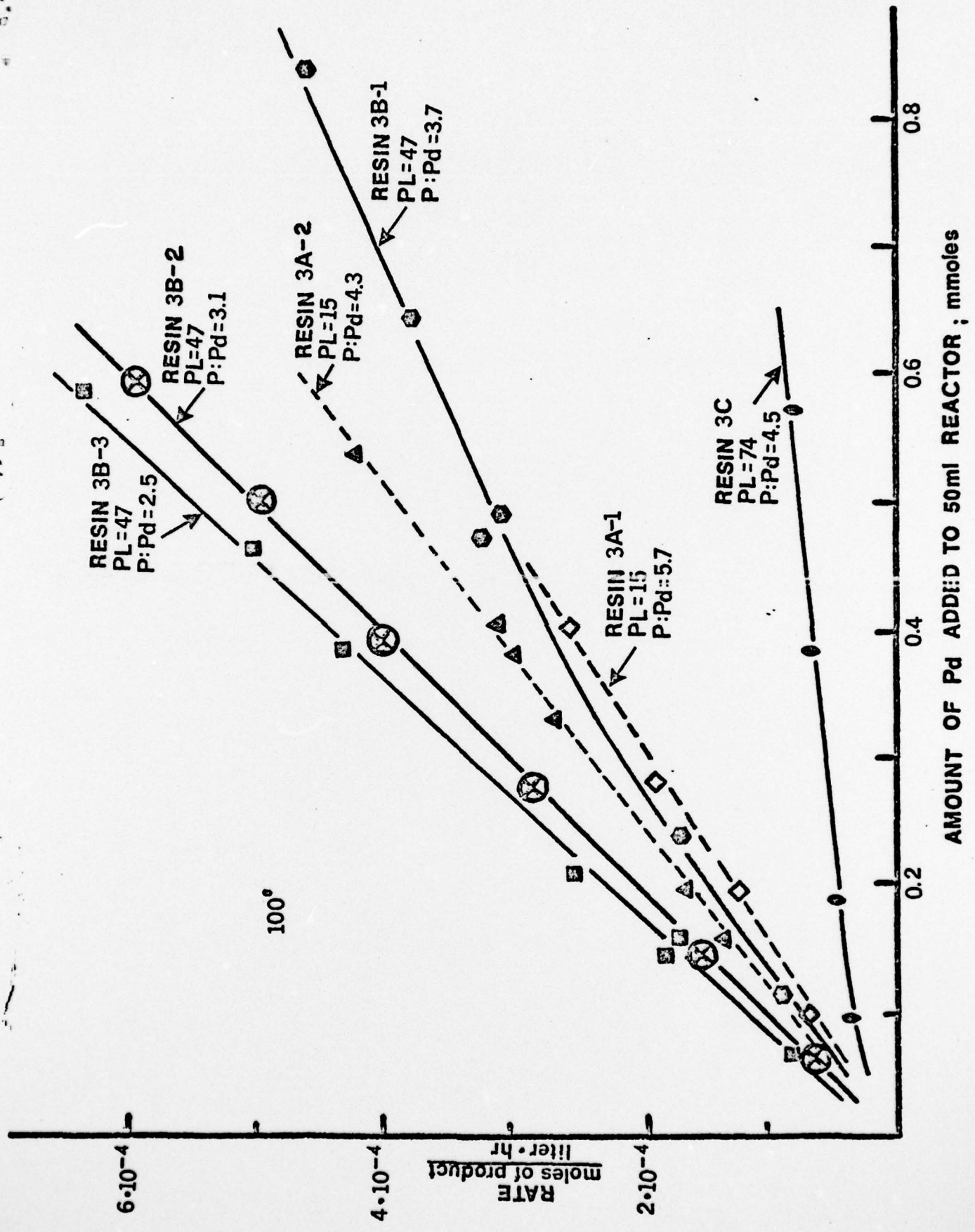
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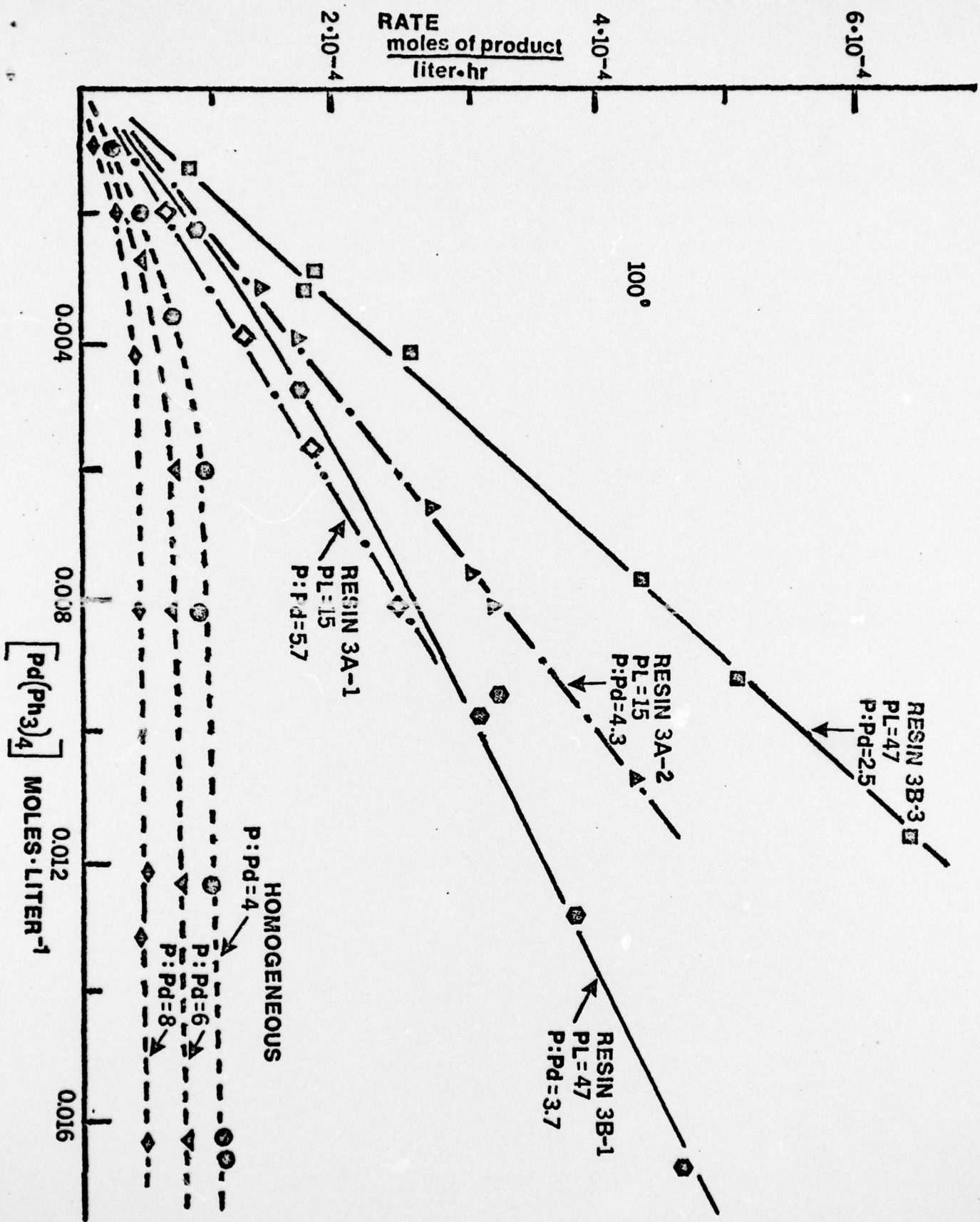


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