CHAPTER I

Introduction

1.1 General

1.1.1 Catalysis

Catalysis is the phenomenon in which one or more substances isothermally and non-radioactively increase the rate of a chemical reaction without appearing in the stoichiometric equation of the reaction. The material concerning is termed as a catalyst [1]. Since the presence of a catalyst can speed up a reaction without being consumed, the equilibrium constant will not be altered. A catalyst provides a new reaction pathway that has a lower activation energy and the catalysed reaction proceeds through a new and energetically more favorable pathway [2].

In 1836, a catalyst was first used in the scientific era by Berzelius [2]. To describe a variety of diverse observations concerning the effect of trace substances on reaction rates. The effectiveness of a catalyst is determined by the difference in the ease with catalysed and uncatalysed pathway. Each pathway usually has a particular step which controls the overall rate, i.e. the rate determining step. The

rate of this step is determined by its free energy of activation which corresponds to the highest free energy barrier along the route from reactants to products. A catalyst sets out to make this free energy of activation as small as possible or at least less than that found in the uncatalysed mechanism. Pictorially the situation can be represented as shown in Figure 1.1 [3].

- Uncatalysed reaction path

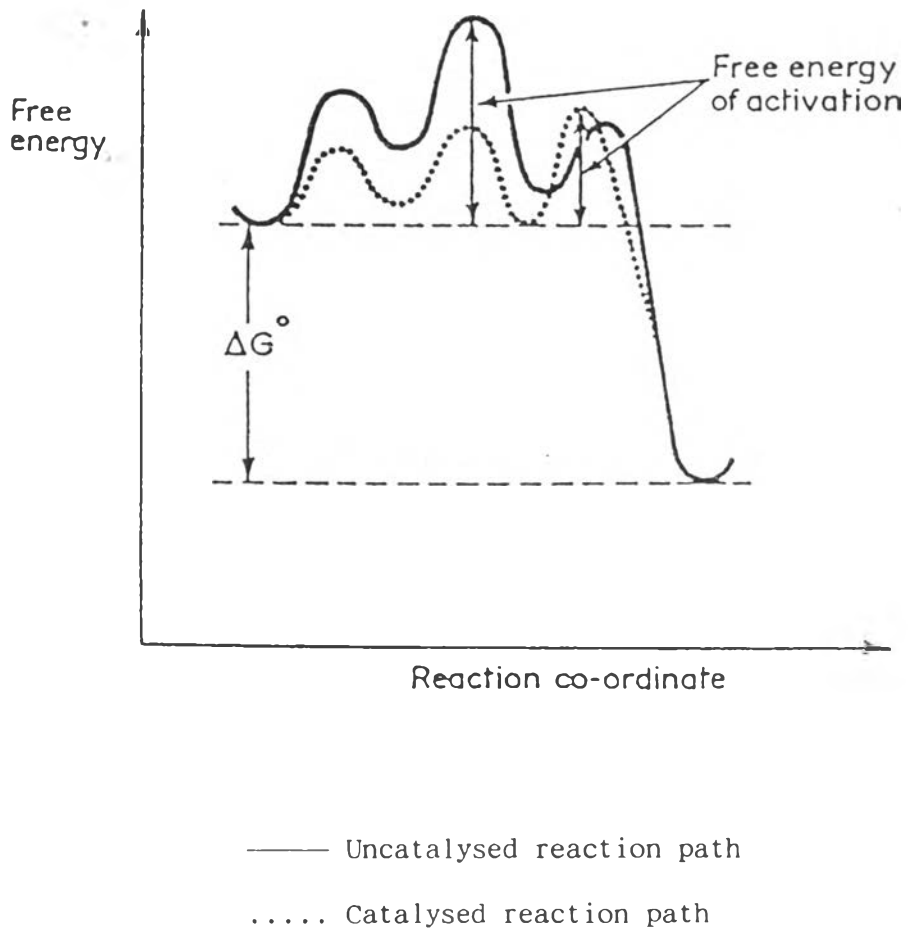..... Catalysed reaction path

Figure 1.1 Free energy plot for a hypothetical uncatalysed and catalysed reaction.

To be useful, a catalyst must have three predominant characteristics: activity, stability, and selectivity. Low activity is undesirable and impracticable, as it necessitates either excessively long contacts times or high temperatures to achieve the required conversion. Catalyst stability, i.e., a long life or an easy in situ regenerability, is the next important property. Since a catalyst only operate by forming chemical bonds with at least one of the reactants or its fragments, the danger is always imminent that even stronger bonds will be formed with one of the by-products of the reaction. One important reason to strive for high selectivity is, therefore, to avoid the formation of such by-products, which poison the catalyst surface. The problem of catalyst stability, therefore, often reduces to a problem of catalyst selectivity

More generally, the selectivity of a catalyst is of interest when it is required only one out of several thermodynamically permitted reactions. Sometimes different catalysts have been developed, each of which selectivity catalyzes one particular reaction from a given set of possible routes [4].

1.1.2 Homogeneous and heterogeneous catalysts

In general, transition-metal catalysts can be either homogeneous or heterogeneous. Homogeneous catalysts, comprised of discrete, soluble metal complexes, are in most cases more

active and operate at lower temperatures and pressures than their heterogeneous counterparts. The metal center activity is controlled by supporting ligands. In heterogeneous systems the metal centers are either a part of the support surface, or part of a surface metal crystallite , and may have no soluble analogs [5].

Heterogeneous catalysts have several advantages, including acceptable thermal and mechanical stability, high activity for a wide range of reactions, and capacity for used in packed and fluidized beds as well as ready separation from reaction products. Disadvantages may include design and improvement limits due to frequently ill defined actives sites, limited accessibility and effectiveness of the catalytic components, and severe and costly reaction conditions, i.e., high temperatures and pressures.

In contrast, homogeneous systems are characterized by well studied and interpreted catalytic activity, reported activity under mild reaction conditions, efficient and reproducible use of metal atoms, and electronic and steric properties that can be varied and frequently controlled. A major disadvantage lies with the separation problem. Additional advantages stemming from the attachment process per se include the introduction of preferred orientations, an altered stereochemistry about the metal atom, a changed equilibrium between the metal atoms and their ligands, and

advantageous stabilization of catalytically active but normally unstable structures. The hope is that the immobilization of transition metal complexes on solid supports eventually will give superior hybrid catalysts possessing the advantages of both traditional catalyst systems with few disadvantages [6].

1.1.3 Polymer-bound catalysts

When a soluble catalyst is attached to an insoluble support through a covalently binding ligand, the complex becomes heterogeneous when considered at the bulk level but is essentially identical to a soluble analog or a molecular level. Consequently, the catalyst will show properties somewhere between the two major catalysts classes. Therefore a hybrid catalyst that combines the best properties of both systems while minimizing their inherent deficiencies [5]. For example, increased substrate size selectivity, increased activity, easier catalyst recovery and recycle, and protection of catalyst sites from water [7].

Some of the practical limitations of homogeneous catalysis in the liquid phase are corrosion and the difficulties of separating products from catalysts. In attempts to overcome these difficulties, soluble molecular catalysts have been attached to a variety of insoluble supports, including crosslinked polymers. As a result, it was intended that the catalysts would acquire the property of insolubility while

maintaining the activity exhibited in solution [8].

Anchoring ligands to insoluble polymeric supports, followed by complexation with transition metals, results in polymers having catalytic potential. These metal complexes, hydrids of homogeneous and heterogeneous approaches, are attractive because they often permit the activity of soluble catalysts and the ease of product separation inherent in heterogeneous catalysts. In referring to this class of catalysts the names "polymer-anchored", "polymer-bound", hybrid phase", or "polymer-supported" are common [9].

Polymer bound catalysts not only offer the potential to conserve energy inputs into the formation of chemical products, but also promise judicious use of metals [10]. Expensive or precious species, such as optically active molecules or platinum group metal complexes, will be retained more efficiently when immobilised on a polymer support, which in term might offer the prospect of efficient reuse or recycling.

Corrosive, noxious or toxic species are generally rendered safe when bound to a macromolecule. Corrosive reagents are essentially encapsulated and do not make contact with apparatus or plant. Volatile hazardous species have their vapour pressures reduced almost at zero, and toxic low molecular weight compounds become extremely difficult to absorb through the lungs, skin or digestive systems, when thus immobilised. Supported

systems have much to offer in the drive to develop more environmentally acceptable processes, and could make a significant contribution towards clean chemistry.

Some entirely chemical advantages might also arise. When a reactive species is attached to a polymer backbone, providing the number of groups attached (the *loading*) is kept low, the species will behave as though present in infinite dilution. Likewise one or more reactive species might be loaded in high concentration on the polymer, so that they are forced to be in constant proximity to each other.

These tricks may be used to reduce side reactions in the subsequent application or alternatively to enhance rates or selectivity. Indeed, reactive species with only a transient existence in homogeneous solution can be stabilised for useful exploitation when attached to a polymer support [11].

It seemed that all homogeneous catalysts could be bound, that decreases in activity were minimal and that the catalysts could be filtered off and recycled indefinitely with little or no loss in activity. There appeared to be no reason why commercialization would not be just around the corner [12]. Polymer-bound catalysts have shown as Table 1.1.

Table 1.1 Some examples of polymer-bound metal complexes

| Cross-Linked Polystyrene as the Polymer |
|---|

Silica or Alumina as the Polymer
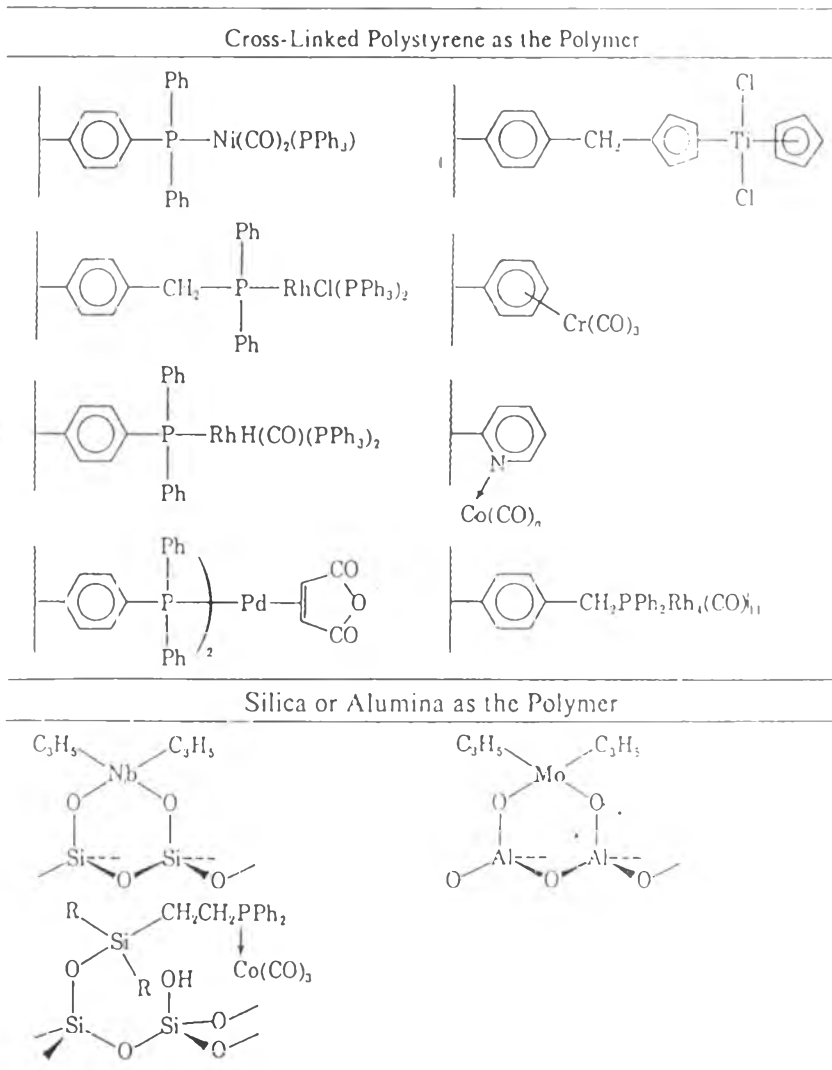
## 1.2 A literature review of polymer-bound catalysts

Historically, it is interesting that this area blossomed during a time when the efforts of many organometallic chemists were turned to synthesis gas (CO + H_2) chemistry and hydrogenation, oligomerization and carbonylation reactions [12]. Some important research works could be reviewed as follow.

J. Manassen [12] studied about polymer-supported homogeneous catalysts of some metal, for examples, Rh, Co and the other. Similarly, K. Tamaru[13] worked on the complexation of sodium and phthalonitriles or graphite, which were used as catalysts in olefin and acetylene hydrogenation. The research on active coordination compound binding with polymer supports was done by Mobil [14]. Carbonylation and hydroformylation were tested.

R.H.Grubbs and his coworker [15] reported that polystyrene beads (200-400 mesh) with 1.8 % cross-linking of divinylbenzene were chloromethylated and the chloromethylated polymer was treated with a tetrahydrofuran solution of lithiodiphenyl-phosphine. These beads were then equilibrated with tris (tri-phenylphosphine) chlororhodium (I). The catalysts were used in alkene hydrogenation (Scheme 1.1).
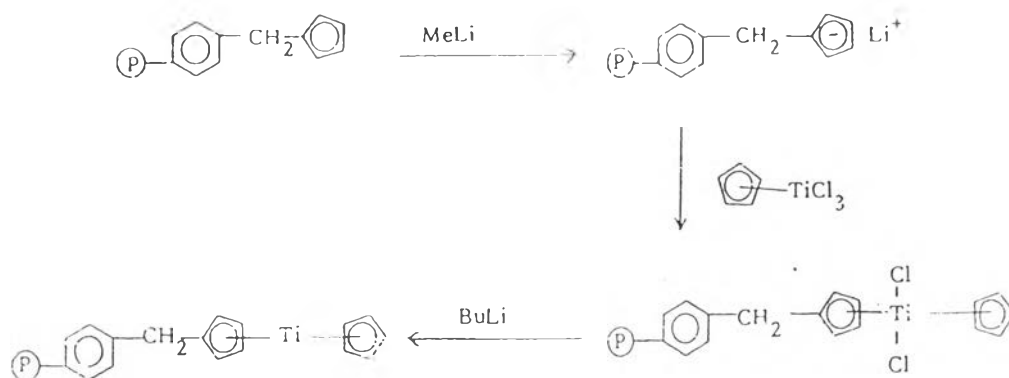
Scheme 1.1
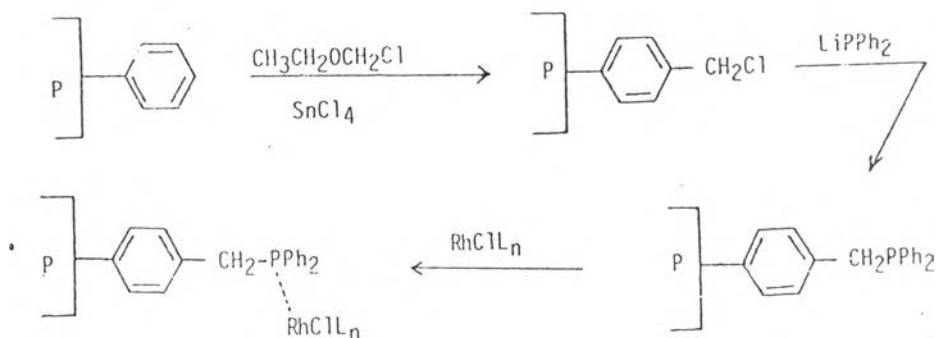
J.P.Collman et.al [16] presented that network polystyrene with p-di-phenylphosphine were reacted with rhodium and eridium coordination compounds. Rhodium and eridium catalysts were tested in hydrogenation. W.Dumont and his coworker [17] had studied an insoluble chiral polymer-supported rhodium complex, which was closely related to the soluble Rh(I)-diop complex (diop = 2,3-o-isopropylidine-2,3-dihydroxy-1,4-bis(biphenylphosphino) butane). This insoluble system (suspended in benzene) catalysts the asymmetric hydrogenation of -ethylstyrene and methyl atropate (Scheme 1.2).

Scheme 1.2

[Rh, Cl, 7, C_6H_6]
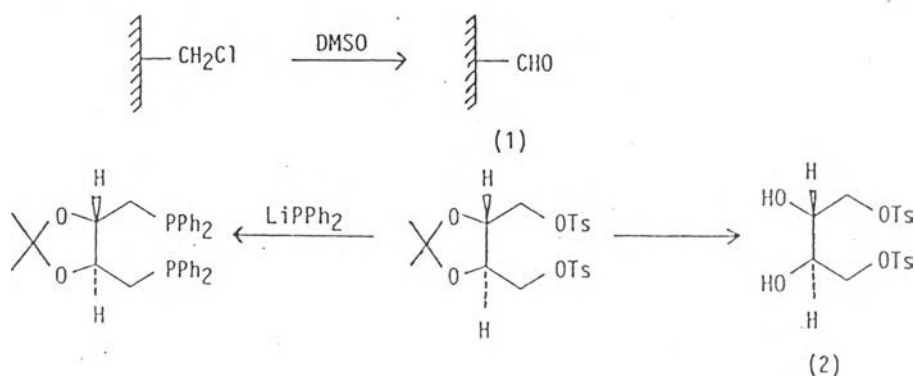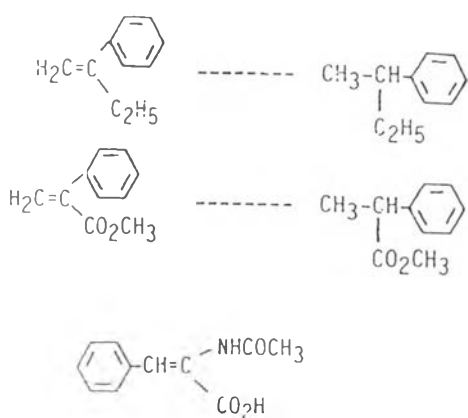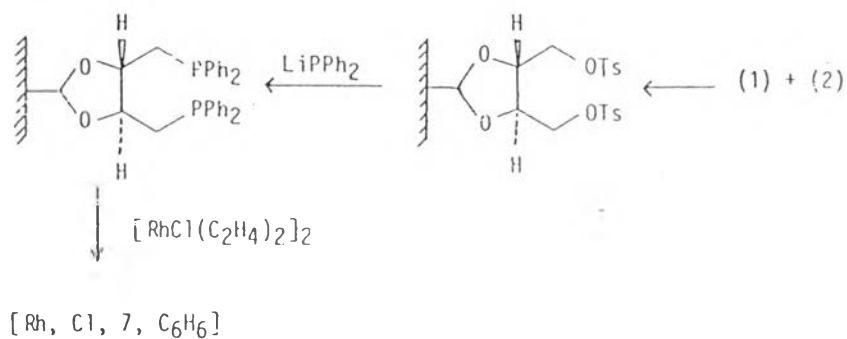
Scheme 1.2 (continued)

W.D.Bonds and his coworker [18] reported that cyclopenta-
dienyl compounds of titanium were prepared and attached to
polymers by firstly binding cyclopentadienes to a styrene-
divinylbenzene (20%) copolymer and then converting it to the
cyclopentadienyl anion. The resin-bound anion was treated with
cyclopentadienyl titanium trichloride and polymer-attached
$(C_5H_5)_2TiCl_2$ was formed. The effectiveness of the
material as a catalyst for hydrogenation of olefins was enhanced
by a factor of 25-120 compared to the correspondingly reduced
nonattached titanocene dichloride or benzyltitanocene dichloride
(Scheme 1.3).

Scheme 1.3

W.H.Lang and his coworker [19] measured the concentration of rhodium in solution over polymer-bonded hydroformylation catalysts and identified the factors influencing that concentration.

R.J.Card and D.C.Neckers [20] found that poly(styryl) bi-pyridine could be prepared by the reaction of lithiated polystyrene with bipyridine in tetrahydrofuran. The reaction of poly(styryl) bipyridine with a variety of transition metal salts were carried out in sereval swelling solvents which resulted in the formation of polymer-bound bipyridine transition-metal complexes. Zero valent metal complexes such as P-Ph-bipy-M(CO), (M = Cr, Mo, W) were readily prepared from the reaction of poly (styryl) bipyridine with the metal hexacarbonyl complexes. Poly (styryl) palladium acetate was an active catalyst for the hydrogenation of olefins at ambient pressure and temperature.

F.Pinna and his coworkers [21] studied about the hydrogenation of propane and other substrates in flow and batch reactors using various rhodium catalysts. However, J.Reed and his coworkers [22] studied the influence of cross-linking of divinylbenzene (DVB) in styrene polymer-bound bromotris(triphenylphosphine)-rhodium (I) catalyst by extended X-ray absorption fine structure (EXAFS) spectroscopy. This study suggests that there is probably some degree of cross-linking between 2 and 20 % which is optimum in catalytic activity, and that not all the phosphorus atoms are polymer bound.

N.Takaishi, and his coworkers [23] presented that the reaction of (-)-1,4-ditosyltheritol with 4-vinylbenzaldehyde afforded 2-p-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane, which was radical copolymerized with hydroxy ethyl methacrylate to incorporate 8 mol% in the crosslinked copolymer. Treatment of crosslinked copolymer with enough sodium diphenylphosphine to react with all the hydroxyl function plus the tosylate groups gave a hydrophilic polymer after neutralization which borethe optically active 4,5-bis(diphenylphosphino-methyl)-1,3-dioxolane ligand. Exchange of rhodium (I) onto $(C_2H_4)_2RhCl_2$ gave the polymer-attached catalyst. Hydrogenation of N-acylaminoacrylic acid in ethanol with this catalyst gave the amino acid derivatives having the same optical yields and absolute configuration as the ones obtained from the homogeneous analogue (Scheme 1.4).
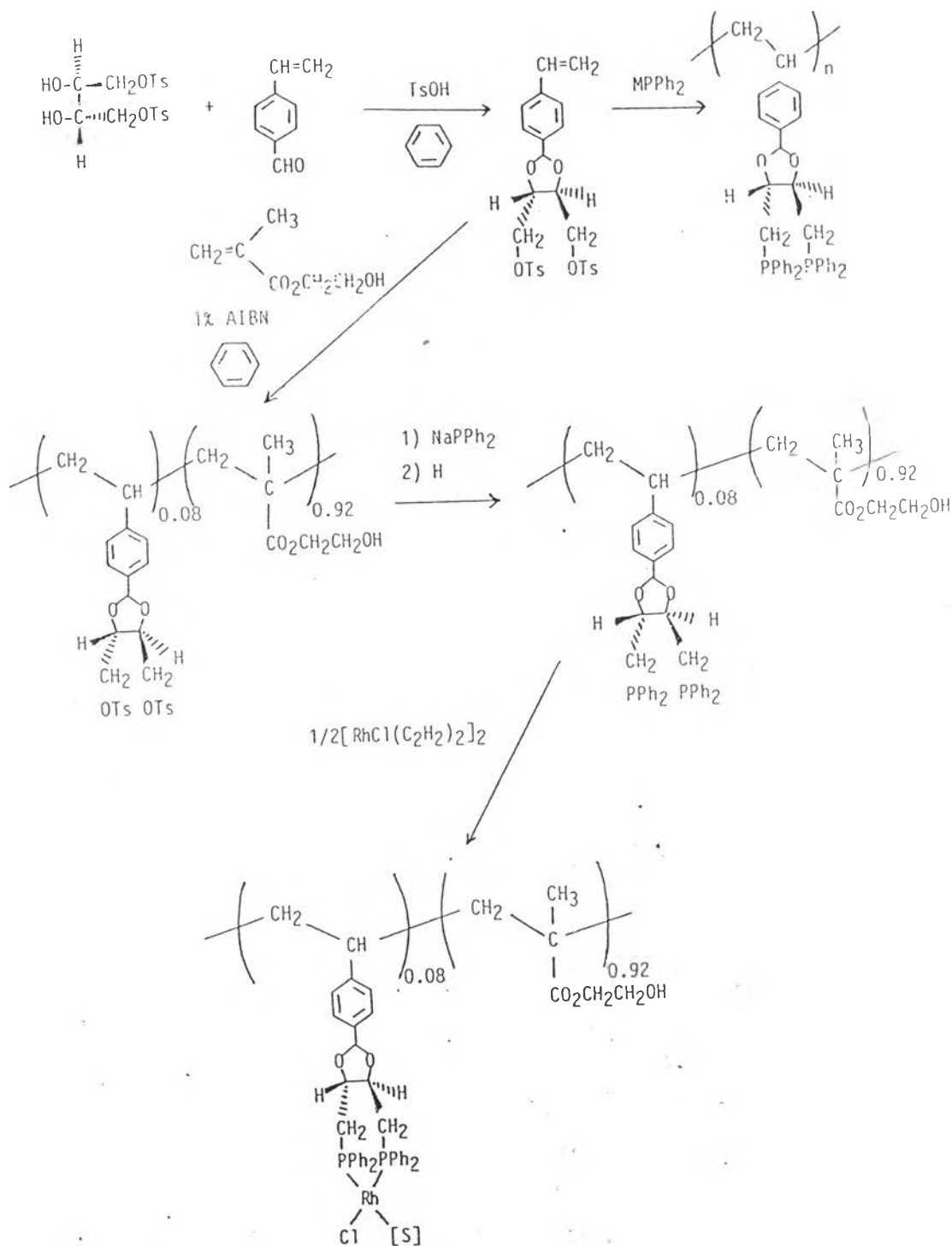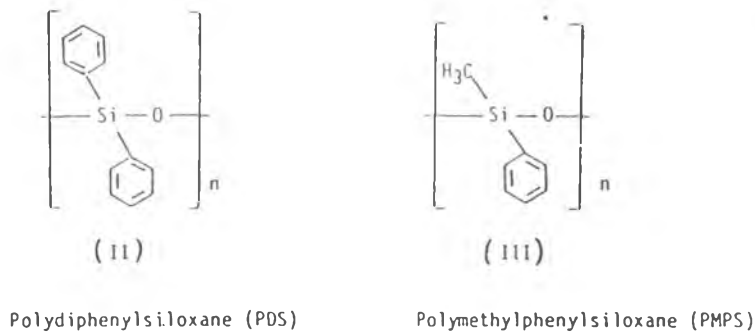
Scheme 1.4

B.H.Chang and his coworkers [24] prepared polymer-supported n^5-cyclopentadienylrhodium dicarbonyl and n^5-cyclopentadienyl-

cobalt dicarbonyl with 20 % divinylbenzene-poly-styrene copolymer. The macroporous beads have been tested for a variety of types of catalytic activity.

N.L.Holy [9] studied about the synthesizing rhodium (I) polymer-bound catalyst by using of the bidentate ligand, anthranilic acid , anchored to insoluble polystyrene beads (20-50 mesh). The activity of this catalyst was tested by the catalytic hydrogenation of aromatic hydrocarbon.

K.Ohkubo et.al. [25] documented asymmetric hydrogenation of prochiral olefins by insoluble crosslinked copolymer (styrene-divinylbenzene or styrene-methyl methacrylate)-supported Rh (I)-diop (2,3-o-isopropyridine-2,3-di-hydroxy-1,4-bis(diphenylphosphino)butane) complexes has been received considerable attention in terms of practical and technical asymmetric synthesis of chiral compounds.

R.A.Awl and his coworkers [26] studied the soluble tri-carbonylchromium complexes made by reacting $Cr(CO)_6$ with a ladder poly-phenylsilsesquioxane and a linear polydiphenylsiloxane. These silicone polymer complexes catalyzed stereoselective hydrogenation of methyl sorbate to cis-3-hexenoate in cyclohexane and tetrahydrofuran (Scheme 1.5).

(II)   (III)

Polydiphenylsiloxane (PDS)   Polymethylphenylsiloxane (PMPS)

Complexation of Phenyl Groups in Polymers (I-III):
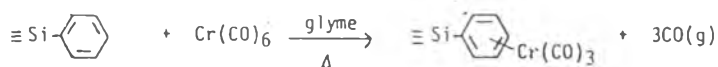
Scheme 1.5

B.Gordon and his coworkers [27] utilized polymers as binding sites for transition metal catalysts. However, general problems exist with the above system. The rate of reaction depends on the presence of solvents that adequately swell the polystyrene bead in order to allow access to the catalytic sites. Tris(triphenylphosphine)chlororhodium is bound to the surface of polyethylene single crystals. Hydrogenation studied have been conducted using the polyethylene supported catalyst system to show the potential effectiveness of the new system (Scheme 1.6).
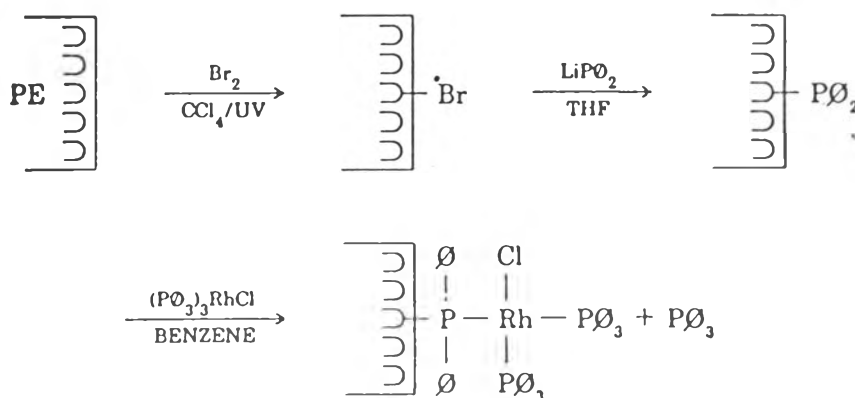
Scheme 1.6

S.Montelatici and his coworkers [28] worked on the effect of the nature of aryl or alkyl groups of the tert-phosphine in the complex tris(tertiary phosphine)chlororhodium(I) on the rate of cyclohexene hydrogenation. S.Yamaguchi et.al. [29] studied the oxidation of 2-methylnaphthalene to 2-methyl-1,4-naphthoquinone (vitamin K_3). The use of 0.24 % Pd(II)-sulfonated polystyrene type resins gave vitamin K_3.

D.E.Bergbreiter and R.Chandran [30] prepared homogeneous , recoverable hydrogenation catalysts with use of functionalized ethylene oligomers as ligands. ^{13}P-NMR spectroscopy and reactivity studied were used to characterize these catalytic.

D.L.Trumbo et.al. [31] studied a polymer-bound palladium catalyst synthesized from palladium diacetate and a single crystal polyethylene having 2,2'-bipyridyl moieties as pendant groups. The resulting material was used in place of a free palladium catalyst in the synthesis of acetylene-terminated resins. The use of diphenylphosphine-terminated ethylene oligomers as ligands for palladium(0) and palladium(II) was reported by D.E.Bergbreiter et.al. [32]. With these polymeric ligands, it was possible to carry out a homogeneous reaction which was a characteristic of $(Ph_3P)_4Pd$ and $(Ph_3P_2)Pd(OAc)_2$ with complete recovery of the Pd catalyst.

1.3 Objectives of this research

The aim of this research is concentrated to synthesize rhodium polymer-bound catalysts. Polymer synthesis is studied by varying types and amount of solvents in suspension polymerization and changing percentage of crosslinker.   Polymer beads are determined the surface area and chosen to bind with a bidentate anthranilic ligand. Polymeric ligand is anchored to rhodium salt. Finally, rhodium-anthranilic acid polymeric catalysts are tested.

The reaction is shown in the following steps.

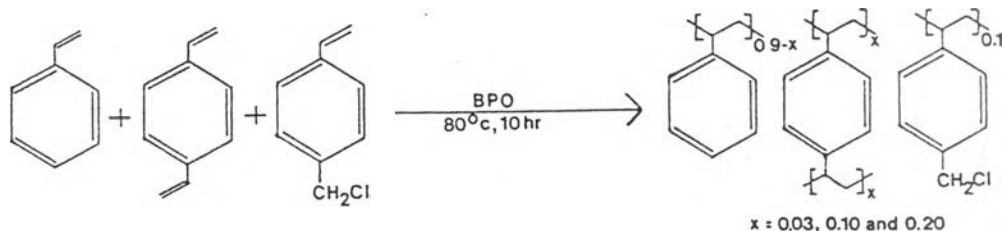1. Chloromethylation of 2-phenyl ethylbromide.
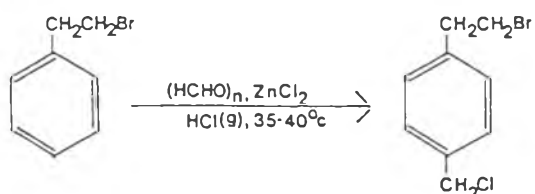
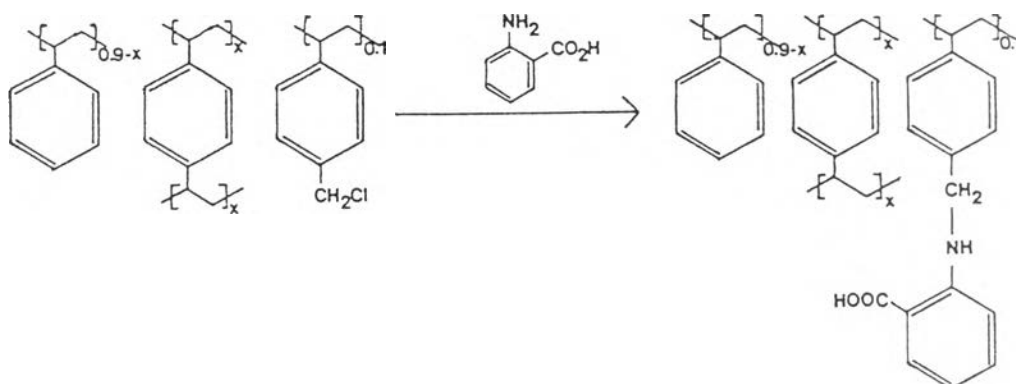2. Dehydrobromination of p-(2-bromoethyl) benzyl chloride.
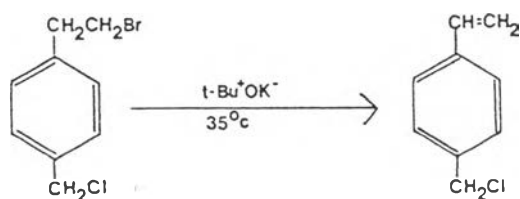
3. Suspension polymerization of styrene, divinyl benzene and vinylbenzyl chloride by varying of

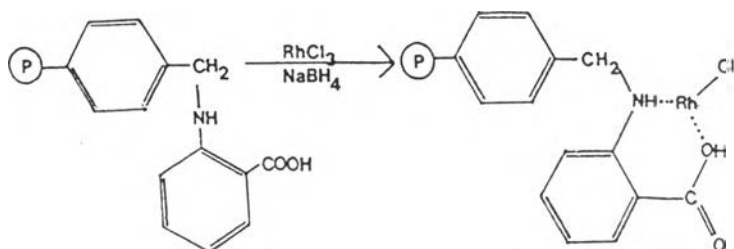   (a) Percentage of crosslinking

    (b) Types and amounts of swelling solvents

4. Anchoring anthranilic acid to chloromethylated polystyrene.

5. Complexation of anthranilic acid anchored chloromethylated polystyrene with rhodium(III) chloride and reduction reaction to rhodium(I) polymer-bound catalysts.

6. Test the reaction of catalysts by hydrogenation of cyclohexene.