Studies in Catalysis and Kinetics of Copolymerization Reactions Using Carbon Monoxide as a Comonomer

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By

Shrikant M. Kulkarni

Homogenous Catalysis Division
National Chemical Laboratory
Pune 411 008. India

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Form – A

Certified that the work incorporated in the thesis entitled, "**Studies in Catalysis and Kinetics of Copolymerization Reactions Using Carbon Monoxide as a Comonomer**" submitted by **Mr. Shrikant M. Kulkarni** was carried out by the candidate under my supervision. Such material as has been obtained from other sources has been duly acknowledged in the thesis.

January 2002 **(R. V. Chaudhari)**

Pune Research Guide

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Pune

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Abstract of the Thesis

The applications of synthetic polymers have permeated almost every aspect of our daily lives. This widespread use of polymers in diverse areas signifies the urgent need for continuous efforts in the development of newer polymeric materials with high functionality preferably by utilizing simple and cheaper feedstocks. Development of novel palladium catalyzed copolymerization of ethylene and carbon monoxide to perfectly alternating polyketones is an excellent example of such an advance. Polyketones are viewed as leading candidates in the conservation of conventional polyethylene. The low cost and easily available monomers (i.e. ethylene and carbon monoxide) required in the polyketone synthesis are difficult to beat in overall economics. Recent developments, derived from a better understanding of the basic chemistry and catalysis, have resulted in a perfectly alternating copolymer of ethylene and carbon monoxide having excellent mechanical properties and enhanced photo stability. Highly efficient palladium based homogeneous catalysts can produce polyketones with an average activity of 10^6 gm of copolymer per gm of palladium per hour. Second example is provided by a palladium catalyzed carboalkoxylation and amidation reactions, which can be used to convert aryl halides to a variety of high performance polymers like polyesters, polyamides, polyimides etc. in a single step. The recent literature has demonstrated the immense potential for CO based chemistry in the area of polymer synthesis. The literature also indicates that there exists considerable scope for studies on the fundamental aspects like catalysis and kinetics of these reactions. Apart from this, the extension of the existing knowledge on the carbonylation reactions to the synthesis of new polymers would be yet another area of interest. The particular objective of this thesis was to investigate the

polymerization processes utilizing carbon monoxide as one of the monomers. Following specific problems were selected for this study.

1. Kinetic modeling of copolymerization of ethylene and carbon monoxide to polyketone using homogeneous palladium catalyst
2. Synthesis of linear polyesteramides by palladium catalyzed carbonylation-polycondensation of aromatic dihalides and aminohydroxy compounds
3. Synthesis of polyesters by carbonylation-polycondensation of aromatic dihalides and diols using highly efficient palladium catalysts.

The thesis is presented in five chapters, the abstract of which is presented here. The first chapter presents a comprehensive literature review on the use of carbon monoxide as a building block for several important polymers. The literature reveals that there exists immense potential for newer polymers and polymerization methods using C_1 chemistry. The examples include polyketones, polyesters, polyamides, polyimides, polyesteramides, etc. Various aspects relevant to the chemistry and catalysis available in the literature have been discussed comprehensively and the scope for the present thesis is outlined.

The second chapter reports results on the kinetics of copolymerization of ethylene with carbon monoxide in a batch slurry reactor using a homogeneous Pd complex, $[(dppp)Pd(H_2O)(TsO)](TsO)$ as a catalyst precursor, in methanol. The copolymerization of ethylene and carbon monoxide is an excellent example of a multiphase catalytic reaction since it involves simultaneous absorption of two gases (ethylene and CO) followed by a reaction in the liquid medium (methanol) to produce a solid polymer product. The particular objective of this chapter was to investigate the detailed kinetics of this reaction and develop rate equations. Thus, the effect of catalyst loading, partial pressures of CO and ethylene on the rate of copolymerization has been studied over a temperature range of 353-373 K. The rate of copolymerization was found to increase with the increase in the catalyst loading and partial pressures of CO and ethylene. Several rate equations based on probable reaction mechanisms were evaluated for fitting the rate data. The rate data have been interpreted in terms of activities of the monomers in solution. The rate models were discriminated using statistical as well as thermodynamic criteria. A model derived by assuming insertion of ethylene into the tetra-coordinated Pd–acyl species as the rate-determining step has been found to represent the kinetics in good agreement with the experimental results. The apparent energy of activation for co-polymerization was found to be 49 kJ/mole.

The third chapter reports for the first time the preparation of polyesteramides using palladium catalyzed carbonylation-polycondensation of aromatic diioide and an amino alcohol. Effect of various reaction parameters like temperature, base, ligand, CO pressure, solvent used on the catalytic activity and inherent viscosity of the polymers has been investigated. It was observed that linear alternating polyesteramides could be prepared in excellent yields under optimized reaction conditions. A detailed characterization of these polymers was carried out.

The fourth chapter presents studies on the preparation of fully aromatic polyesters by carbonylation-polycondensation method. The key challenge in these reactions is improvement of extremely low catalytic activity (TON < 100). It was observed that use of diiodo derivatives in place of dibromo derivatives resulted in lowering of the reaction times. Further, it was also observed that under optimum reaction conditions very high TON could be obtained that are almost three orders of magnitude higher than reported earlier using diiodo substrates. Effect of various reaction parameters like temperature, solvent, CO pressure and base on the polymerization reaction using diiodo substrates was also investigated

The fifth chapter summarizes the conclusions and future scope of the CO based chemistry in polymer synthesis. It also addresses key issues, which are anticipated to decide the further scope of these reactions.

Thus, to summarize, this work reports investigations on the fundamental aspects related to catalysis and the reaction engineering of polymerization reactions using carbon monoxide as a comonomer. The results indicate carbonylation route as an alternative approach for polymer synthesis, which may prove to be advantageous over some of the conventional routes.

Key References

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Chapter One

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Introduction and Literature Survey

1.1 Introduction

Polymeric materials are an integral part of the modern day-to-day life. The wide range of areas where polymers are used with diverse applications have resulted in ever increasing demands for highly functional polymers [1]. In view of the growing demands, it has become necessary to provide materials with high functionality and performance at an economical price. This implies an urgent need for continuous efforts in the development of new polymers and also newer approaches for the synthesis of the existing ones. Since, almost all polymerization reactions e.g. via addition, polycondensation, polyaddition and ring opening polymerization etc., require a catalyst or an initiator, the preparation of polymers with the desired properties very often depends or at least may be controlled by proper choice of catalysts [2]. Thus, a sound understanding of the basic chemistry and catalysis involved during polymerization processes is necessary for the optimum design of functional materials. Therefore, the field of *catalysis in precision polymerization* has gained importance in academic as well as industrial research and development [2].

It is apparent that the advances in catalysis and organometallic chemistry will significantly contribute in the practice of modern polymer science. The particular area where it will have a large impact is probably the design of catalysts and catalytic processes, which will allow use of cheaper and non-conventional resources for the polymer synthesis. An example of such an advance that can make direct use of simple, inexpensive feedstock for the synthesis of novel polymers is the development of palladium-catalyzed copolymerization of ethylene and carbon monoxide to perfectly alternating polyketones [3]. As low cost monomers, ethylene and carbon monoxide are difficult to beat. Recent developments, derived from better understanding of the basic chemistry and catalysis, have resulted in a perfectly alternating copolymer of ethylene and carbon monoxide having excellent mechanical properties and enhanced photo stability. Highly efficient palladium based homogeneous catalysts can produce polyketones with an average activity of 6000 gm of copolymer per gm of palladium per hour [4]. The second example is provided by the palladium catalyzed carboalkoxylation and amidation reactions, which can be used to convert aryl halides and carbon monoxide to a variety of high performance polymers like polyesters, polyamides, polyimides etc. in a single step [5].

The cost and availability of highly efficient processes will be a crucial factor in deciding the commercial feasibility of these reactions. Also, the information on fundamental aspects e.g. catalysis, kinetics and reaction engineering, which is a key requirement for the process development, would be required. At present, the available information on these issues is very limited and there is a wide scope for further investigations. The key objectives for the present thesis were therefore to investigate the catalysis and reaction-engineering aspects related to the novel polymerization reactions using carbon monoxide as a comonomer.

1.2 Carbon Monoxide as a Comonomer

Carbonylation reactions have attracted considerable commercial as well as academic interest because of their wide utility in several industrial and laboratory scale synthesis. The initial work of Reppe concerning conversion of olefins and acetylenes into corresponding carboxylic acids or esters in the presence of metal carbonyls such as $Ni(CO)_4$ marked the beginning of C_1 chemistry [6]. The early carbonylation processes required very high pressures and temperatures. The subsequent advances in organometallic chemistry further complemented the developments in the carbonylation chemistry and made it possible to operate the same processes efficiently at comparatively milder conditions [7-9]. Today, carbon monoxide (CO) is used as a cheaper building block for the synthesis of several important classes of organic compounds like carboxylic acids, esters, anhydrides, alcohols, aldehydes, amides, carbamates, isocyanates, amino acids etc. [10]. The key features that make carbonylation reactions increasingly important are: (1) carbon monoxide is a cheaper and easily available feedstock, (2) higher activity, selectivity and complete atom utilization may be achieved using tailor made catalysts, (3) comparatively mild reaction conditions, (4) reduction in number of synthetic steps and, (5) provide cleaner and greener routes to many industrial chemicals like carboxylic acids, carbonates, isocyanates etc. for which the conventional preparation methods employ hazardous reagents like phosgene, HCN etc.

Because of these advantageous features, the carbonylation reactions have attracted considerable interest, particularly in the area of pharmaceuticals, fine and bulk chemicals where the conventional processes currently in operation are less selective and produce large quantities of undesirable byproducts and wastes. Table 1-1 lists some of the important industrial processes based on carbonylation chemistry. Efforts to develop catalytic processes based on carbonylation chemistry for few other important products e.g. phenylglycine [11], arylpropionic acids (ibuprofen, naproxen) [12] and diphenyl carbonate [13] etc. are at significantly advanced stage.

Table 1-1. Industrial Processes Based on Carbonylation Reactions

Sr.	*Process*	*Catalyst*	*Company*	*Ref.*
1.	*Methanol to acetic acid*	$Co_2(CO)_8$	*BASF*	*[14]*
		Rh/iodide	*Monsanto*	*[15]*
		Ir/iodide	*BP*	*[16]*
2.	*Acetylene to acrylic acid*	*Ni salts or carbonyls*	*BASF*	*[17]*
3.	*Ethylene to propionic acid*	$Ni\ (OCOC_2H_5)_2$	*BASF*	*[18]*
4.	*Methanol to dimethyl carbonate*	$PdCl_2/CuCl_2$	*Assoreni*	*[19]*
5.	*Methyl acetate to acetic anhydride*	*Rh/MeI*	*Eastman*	*[20]*
		Rh/MeI	*Halcon*	*[21]*
6.	*Benzyl chloride to phenyl acetic acid*	$Co_2(CO)_8$	*Montedison*	*[22]*
7.	*Butadiene to adipic acid*	$Co_2\ (CO)_8$*/pyridine*	*BASF*	*[23]*
8.	*p-isobutylphenethanol to ibuprofen*	$PdCl_2/PPh_3/HCl$	*Hoechst-Celanese*	*[24]*
9.	*Propyne to methylmethacrylate*	*Pd-pyridylphosphine*	*Shell*	*[25]*
10.	*Propene to butyraldehyde*	$HRhCO(PPh_3)_3$	*Union Carbide*	*[26]*
		Rh/TPPTS	*Ruhrchemie-Rhone-Poulenc*	*[27]*
11.	*Diacetoxybutene to 1-methyl-4-acetoxy-butanal (intermediate for vitamin A synthesis)*	$HRhCO(PPh_3)_3$	*Hoffmann-La-Rosche*	*[28]*
		Rh catalyst	*BASF*	*[29]*

Preparation of several high performance polymers using CO as a comonomer is one of the major achievements in the application of carbonylation chemistry in recent years [3,5]. These reactions are emerging as potential alternatives for conventional polymerization processes and especially for the preparation of polymers that are difficult to synthesize using conventional polymerization approaches.

These catalytic reactions have attracted considerable academic as well as industrial interests because they provide an opportunity to use cheaper and abundantly available carbon monoxide as a raw material and in some cases even produce polymers with novel properties e.g. polyketones. A list of processes with potential applications using CO as a comonomer for synthesis of a variety of polymers is given in Table 1-2.

Table 1-2. Synthesis of Polymers Using Carbon Monoxide (CO) as a Comonomer

Sr.	***Reactants***	***Polymer***	***Ref.***
1.	*Olefins + CO*	*Polyketones*	*[3]*
2.	*Dihalides + Diols + CO*	*Polyesters*	*[30]*
3.	*Dihalides + Diamines + CO*	*Polyamides*	*[5]*
4.	*Bis-iodoaromatics + Diamines + CO*	*Polyimides*	*[5]*
5.	*Diiodoaromatics + bis (o-aminophenols) + CO*	*Polybenzoxazoles*	*[5]*
6.	*Dihydrazides + Dibromoaromatics + CO*	*Polyacylhydrazides*	*[31]*
7.	*Diiodoaromatics + amino alcohols + CO*	*Polyesteramides*	*[32]*
8.	*Bisphenols +* O_2 *+ CO*	*Polycarbonates*	*[13]*
9.	*Polyamines +* O_2 *+ CO*	*Polyurethanes*	*[33]*
10.	*Aziridine + CO*	*Poly-* β *- peptides*	*[34]*
11.	*Imines + CO*	*Poly-*α*-peptides*	*[35]*

The data given in Table 1-2 indicates that the CO based processes will assume considerable importance in near future for the synthesis of several polymers. In view of this, the aim of the present thesis was to study some of the fundamental aspects related to the preparation of polymers using catalytic carbonylation reactions. A review of the relevant literature on copolymerization as well as carbonylation-polycondensation reactions is presented in the following sections.

1.3 Polyketones by Copolymerization of Olefins with CO

Polyketones are perfectly alternating copolymers of carbon monoxide with α-olefins. Although, a variety of olefins can be copolymerized with CO, the perfectly alternating copolymer of ethylene and CO only has found a commercial application so far. The polyketone resulting form ethylene and CO has excellent engineering thermoplastic and mechanical properties [36]. Polyketones contain 50 mol % of carbon monoxide in the form of a ketonic carbonyl function regularly placed in the polymer backbone which makes them photodegradable [37]. This property is advantageous over the conventional polyolefin thermoplastics that are largely non-degradable and are posing environmental threats because of disposal problems. Polyketones are therefore viewed as the potential alternative to polyethylene. Further, the reactive carbonyl function in the polyketones can be transformed into a variety of other functional groups like amines, alcohols, esters, ethers through simple organic reactions and thus, polyketones can serve as cheaper starting material for several functional polymers like polyamines, polyesters, polyethers, polyalcohols [38, 39].

Shell Chemical Company has become the global technology leader in polyketone polymers and has several patents in almost every aspect of polyketones including catalyst and processes development, polymeric blends and end use applications. The first commercial grades of polyketones by Shell Chemicals (*Carilon*®) are based on carbon monoxide, ethylene and a minor amount of propylene. The typical melting point for pure alternating ethylene-CO copolymer is 250°C. Such a high melting point makes their processing difficult. Introduction of minor amount of propylene lowers the melting point of polyketones without affecting the basic engineering properties and this makes the melt processing of polyketones possible. The key properties of polyketone polymers (*Carilon*®) are:

- Unique balance of stiffness / toughness
- Good retention of modulus over a wide temperature range
- Superior chemical resistance with high permeation resistance
- Very good barrier performance
- Superior abrasion / wear resistance
- Superior mechanical resilience
- High rupture and creep resistance
- Easy processing

Presently Shell has announced disinvestments in the polyketones because of domestic reasons, but many other companies are developing their own processes for polyketones. A notable example is of BP Chemicals, which is planning to commercialize similar polymers under the trade name of *Ketonex*®.

The development of palladium-catalyzed copolymerization of ethylene and CO to polyketones provides an excellent example of an advance in the transition metal catalytic chemistry that makes direct use of simple and inexpensive carbon monoxide as a feedstock in the preparation of novel polymers [40]. The commercial catalyst produces 30 kg (3×10^4 gm) of polymer per gram of palladium per hour [1]. Such a highly efficient process makes the polyketones potential competitor to polyethylene in terms of process economics also. The following sections briefly but comprehensively present the account of developments in the area of polyketone chemistry.

1.3.1 Historic Developments

Brubaker first obtained non-alternating, random copolymers of ethylene and carbon monoxide by radical initiated copolymerization as early as in 1940 [41]. The reaction conditions were relatively harsh (230°C and 2000 atm). In the subsequent paper [42], Brubaker noted that the reaction variable such as feed composition, combined gas pressure, polymerization temperature and solvent significantly influenced the composition, yield, molecular weight and physical properties of the copolymer. The amount of carbon monoxide incorporated in the product polymer increased proportionally with the total pressure and close to 50 mol% incorporation of CO could be achieved by employing CO rich feed (> 70 mol % of CO in the feed mixture). Higher polymerization temperatures resulted in lowering the amount of CO incorporated. The highest molecular weight obtained was 8000 at a combined gas pressure of 1000 atm.

Since then, a variety of radical initiators have been employed for the copolymerization of olefins with CO. These include azobisisobutylnitrile (ABBN) [41], peroxides and hydroperoxides [43], dicyclohexylperoxydicarbonate [44], oxygen [41], alkali metal hydrides [45], ammonium persulfate [46], copper salts [47] etc. Gamma rays have sufficient energy to initiate radical formation. Therefore, the possibility of their use as initiators instead of conventional radical initiators was also explored [48]. Gamma ray induced copolymerization reactions were carried out at surprisingly lower temperatures but the copolymers obtained had almost similar properties to those obtained using conventional radical initiators. A wide variety of olefins were copolymerized with CO using radical initiators. These included α-olefins (propylene, butene etc.) [41, 49], cyclic olefins [50], vinylic monomers [51] and acrylates [52]. A variety of terpolymers incorporating CO, ethylene and a second olefin such as propylene, isobutylene, butadiene, vinyl acetate, tetrafluoroethylene and diethylmaleate were also prepared using radical initiated copolymerization reactions [41, 53]. Despite extremely high pressures and temperatures, the radical promoted copolymerization reactions produced only low molecular weight copolymers with random distribution of individual monomers and olefin to CO ratio always greater than one. These structurally irregular polymers had poor physical properties. Although the percentage of the CO incorporated was proportional to the CO partial pressure only 48 mol percent of CO could be incorporated at the maximum. This had driven research towards finding newer methods for copolymerization that could furnish perfectly alternating copolymers with olefin/CO ratio of unity.

In 1963 researchers at Union Carbide reported that the Zeigler type catalysts system ($TiCl_4$ and $Al(^{i}Bu)_3$) catalyzed the copolymerization of ethylene and CO [54]. But the polymer obtained had low molecular weight and random structure. Reppe and Margin [55] reported that nickel containing compounds like aqueous $K_2Ni(CN)_4$ catalyzed the co-oligomerization of ethylene and CO and produced low melting oligomers of CO–ethylene and diethyl ketone and methyl propionate as the by-products. Addition of strong acids like TfOH or TsOH in some solvents like *hexafluoroisopropanol* (HFIPA) further improved the molecular weights but the catalyst activity was very low [56]. Other nickel catalysts used included nickel modified by bidentate phosphorous-oxygen ligands, similar to those used in Shell process for ethylene oligomerization (SHOP)[57]. A variety of other transition metals have been reported to catalyze the copolymerization of CO and olefins. These include rhodium [58], copper [59], cobalt [60] and titanium [48]. In 1967, Gough [61] claimed *bis(tertiaryphosphine)palladiumdichloride* complex catalysts for the alternating copolymerization of olefins and CO. These catalysts had activities around 300 g polymer per g of Pd per hour, but the reaction conditions were severe (250°C and 2000 bar). Following this initial report, Fenton [62] and Nozaki [63] reported that variety of other palladium compounds could be used as catalysts for the copolymerization reaction. Sen and Lai [64] reported that palladium catalyst having general formula $[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$ (n = 1, 2, 3) efficiently catalyzed the dimerization of ethylene and also the alternating copolymerization of CO and ethylene in non-coordinating solvents such as $CHCl_3$ at 25°C and combined pressures as low as 2 MPa. But, the polymer yields and molecular weights were still low. Several other palladium catalysts were also reported [65]. These catalysts could produce perfectly alternating copolymers with moderate molecular weights but the activity and yields were too low for any industrial application. The catalyst reported by Drent [4] made a technological breakthrough in the synthesis of polyketone polymers. The active form of this catalyst contained palladium complexes with bidentate P- or N-ligands. These catalysts often required presence of protonic acid as promoters. Today, it is demonstrated that highly efficient catalyst systems for the copolymerization of ethylene and CO essentially require a cationic palladium complexes in which the palladium metal is modified by a suitable bidentate ligand and a weakly or non-coordinating anion. Unlike the radical or radiation initiated copolymerization, the transition metal catalyzed copolymerization could give perfectly alternating (1:1) olefin-CO copolymers. This was achieved probably because of the typical sequential chain growth mechanism followed during the copolymerization reaction as discussed in the later text. Table 1-3 presents a brief account of the various catalysts used in copolymerization reactions.

Table 1-3. Catalytic Copolymerization of CO with Olefins

Catalyst system	***Olefin***	***Polymerization conditions***	***Activity***[a]	***Ref.***
$K_2Ni(CN)_4$	*Ethylene*	*T =150°C, P = 150 atm, t = 14 h*	*0.8*	*[55]*
$Pd(CN)_2$	*Ethylene*	*T =100°C,* $P_{CO} = P_{C2}$ *= 27 atm,*	*6.7*	*[62a]*
$Pd(CN)_2/Hg(OAc)_2$	*Ethylene*	*T =125°C,* $P_{CO} = P_{C2}$ *= 27 atm,*	*6.5*	*[62a]*
$Pd(PPh_3)_4$	*Ethylene*	*T =120°C,* P_{CO} *=10 atm,* P_{C2} *= 58 atm,*	*14.7*	*[63a]*
$PdCl_2/PPh_3$ *or* $(PPh_3)_2PdCl_2$	*Ethylene*	*T =95°C,* P_{CO} *= 10 atm,* P_{C2} *= 58 atm,*	*35*	*[63b]*
$HPd(CN)_3/PPh_3$	*Ethylene*	*T =115°C,* P_{CO} *=10 atm,* P_{C2} *= 58 atm,*	*4.7*	*[63c]*
$Pd(CN)_2$*/acid*	*Ethylene*	*T = 50-200°C, P =200 atm,*	-	*[62b]*
$Ni(Bu_4N)_2(CN)_4[Ni(CN)_4]^{2-}$*/acid*	*Ethylene*	*T = 115°C, P =70 atm, t = 66 h*	*19.7*	*[43]*
$[Pd(PPh_3)_n(CH_3CN)_{4-n}](BF_4)_2$	*Ethylene*	*T = 25°C, P =48 atm*	*3*	*[64]*
$Pd(OAc)_2$*/dppp/acid*	*Ethylene*	*T = 135°C, P =60 atm,*	*6000*	*[4a]*
[Pd(dppp)(bipy)] $[PF_6]_2$	*Ethylene*	*T = 80°C, P =56 atm,*	*8500*	*[66]*
$[Pd(dppp)(CH_3CN)_2](BF_4)_2$*/MeOH*	*Ethylene*	*T = 50°C, P =40.8 atm,*	*775*	*[65]*
$Pd(OAc)_2$*/dppp/TsOH*	*Ethylene*	*T = 65°C, P = 55 atm,*	*3000*	*[67]*
$Pd(OAc)_2$*/dppp/TsOH/quinone*	*Ethylene*	*T = 65°C, P = 55 atm,*	*6000*	*[67]*
$Pd(OAc)_2$*/dppp/TsOH*	*Ethylene + propylene*	*T = 65°C, P = 55 atm,*	*2000*	*[67]*
$Pd(OAc)_2$*/dppp/TsOH/quinone*	*Ethylene + propylene*	*T = 65°C, P = 55 atm,*	*3300*	*[67]*
$Pd(OAc)_2$*/dmpp/TFA*	*Ethylene*	*T = 100°C, P = 55 atm,*	*3900*	*[67]*

[a] *Activity expressed as g polymer/ g metal / h*

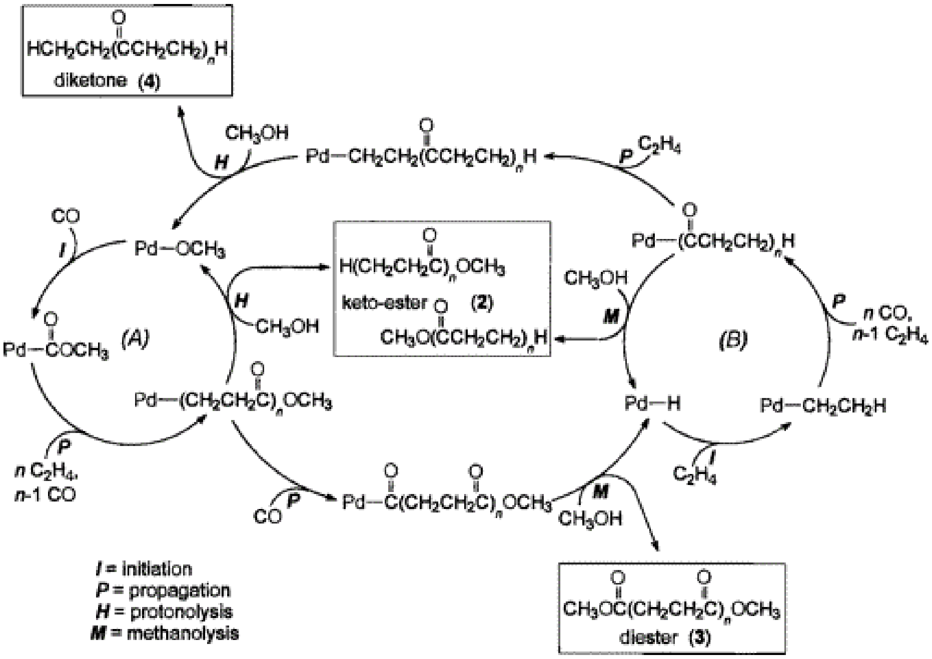
Catalyst system	**Olefin**	**Polymerization conditions**	**Activity** [a]	**Ref.**
$Pd(OAc)_2$/dmpp/TsOH/quinone	Ethylene	T = 96°C, P = 55 atm,	9200	[67]
$Pd(OAc)_2$/phen/TsOH	Ethylene	T = 90°C, P = 60 atm,	13.7	[68]
$Pd(OAc)_2$/bipy/TsOH	Ethylene	T = 100°C, P = 60 atm,	27.5	[68]
$Pd(OAc)_2$/bipy/TsOH/quinone	Ethylene	T = 100°C, P = 60 atm,	321	[68]
$Pd(OAc)_2$/dppp/CF_3SO_3H	Ethylene	T = 90°C, P = 40 atm,	6900	[69]
$Pd(OAc)_2$/dppp/HBF_4	Ethylene	T = 90°C, P = 40 atm,	5000	[69]
$Pd(OAc)_2$/dppp/CCl_3COOH	Ethylene	T = 90°C, P = 40 atm,	300	[69]
$Pd(OAc)_2$/dppp/CF_3COOH	Ethylene	T = 90°C, P = 40 atm,	6000	[69, 70]
$Pd(OAc)_2$/dppp/HCl	Ethylene	T = 115°C, P = 45 atm,	30	[69]
$Pd(OAc)_2$/dppp/CF_3SO_3H	Ethylene	T = 90°C, P = 40 atm,	6900	[69]
$Pd(OAc)_2$/dmppo/CF_3COOH	Ethylene	T = 90°C, P = 55 atm,	9500	[70]
$Pd(OAc)_2$/dmppo/CF_3COOH	Ethylene + propylene	T = 80°C, P = 55 atm,	11000	[70]
$Pd(OAc)_2$/dppp/CF_3COOH	Ethylene + propylene	T = 87.7°C, P = 56 atm,	5300	[70]
$[Pd(dppp)(dmbipy)][PF_6]_2$/quinone	Ethylene	T = 80°C, P = 56 atm,	3640	[71]
$[Pd(dppp)(tmphen)][PF_6]_2$/quinone	Ethylene	T = 80°C, P = 56 atm,	780	[71]
$[Pd((R,R)\text{-}Me\text{-}DuPHOS)(MeCN)_2](BF_4)_2$	ω-Undecylenyl alcohol	T = 40°C, P_{CO} = 68 atm	44.5	[72]
$[Pd((R,R)\text{-}Me\text{-}DuPHOS)(MeCN)_2](BF_4)_2$	5-Hexen-1-ol	T = 50°C, P_{CO} = 68 atm	39.3	[72]
$[Pd((R,R)\text{-}Me\text{-}DuPHOS)(MeCN)_2](BF_4)_2$	ω-Undecylenic acid	T = 40°C, P_{CO} = 68 atm	23.88	[72]

Catalyst system	Olefin	Polymerization conditions	Activity	Ref.
$[Pd((R,R)\text{-}Me\text{-}DuPHOS)(MeCN)_2](BF_4)_2$	3,5-difluoroallylbenzene	$T = 60°C$, $P_{CO} = 34$ atm	19.4	[73]
$Rh_6(CO)_{16}$	7-tert-butoxynorborna-2,5-diene	$T = 55°C$, $P_{CO} = 100$ atm		[74]
$[Ni(o\text{-}tolyl)(PPh_3)]$	Ethylene	$T = 60°C$, $P_{CO} = 10$ atm, $P_{C2} = 10$ atm	687.5	[75]
$Pd(CF_3COO)_2/Na_2DPPPDS/TsOH/BQ$	Ethylene	$T = 85°C$, $P = 900$ atm, MeOH + water	7200	[76]
$Pd(CF_3COO)_2/Na_2DPPPDS/TsOH/BQ$	Ethylene + propylene	$T = 85°C$, $P(C_1+C_2) = 40$ atm, MeOH+water	7400	[76]
$Pd(OTs)_2(AcCN)_2/NaDPPPS/TsOH/BQ$	Ethylene	$T = 90°C$, $P(C_1+C_2) = 40$ atm, MeOH+water	4000	[77]
$Pd(AcCN)_2(BF_4)_2/bipy$	Phenacetylene	$T = 90°C$, $P_{CO} = 33$ atm	49.8	[78]
$Pd(BF_4)_2/CH_2[CH_2P(CH_2CH_2OCy)_2]_2$	Ethylene	$T = 60°C$, $P_{CO} = P_{C2} = 30$ atm,	3007	[79]
$Pd(BF_4)_2/CH_2[CH_2P(CH_2CH_2OCy)_2]_2$	Propylene	$T = 25°C$, $P_{CO} = 30$ atm,	24	[79]
$Pd(OAc)_2/JOSIPHOS/BF_3.Et_2O$	Propylene	$T = 50°C$, $P_{CO} = 75$ atm,	369	[80]
$Pd(OAc)_2/dppp/NiCl_4/MOM$	Propylene	$T = 50°C$, $P_{CO} = 80$ atm,	34.7	[81]
$Pd(OAc)_2/dppp/NiCl_4/MOM/NQ$	Propylene	$T = 50°C$, $P_{CO} = 80$ atm,	125	[81]

1.3.2 Mechanistic Aspects of Ethylene /CO Copolymerization

The mechanism of radical as well as γ-ray initiated copolymerization of ethylene and CO has been investigated in elaborate details [82]. In general, the radical initiated copolymerization is started by the formation of ethylene radical, which initiates the copolymerization reaction.

The palladium-catalyzed copolymerization of olefins and carbon monoxide (CO) is a typical example of living polymerization and involves steps like initiation, propagation and termination. Drent [3] has proposed a catalytic cycle for the palladium catalyzed copolymerization of ethylene and CO, which involves the sequential alternate addition of monomers resulting in the growth of polymer chain. (Scheme 1-1)



Scheme 1-1. Proposed Catalytic Cycle for Palladium Catalyzed Copolymerization of Ethylene and CO [3].

Two types of initiation mechanisms are proposed to operate. In the first mechanism, the copolymerization is initiated by palladium carbomethoxy species [69, 83] which can be formed either by insertion of CO into the *Pd-OMe* or by attack of methanol on the *Pd-CO* intermediate. Alternatively, the copolymerization may also be initiated by the insertion of ethylene into the *Pd-H* species [69, 40 (a-c)]. Subsequent addition of CO results in the formation of *Pd-acyl* species, which starts the polymerization. Depending on the reaction conditions, both mechanisms are known to operate.

The necessary *Pd-H* can be generated in the reaction system through five different pathways as shown below.

(a) β - Hydrogen elimination from a palladium methoxide

$$L_2Pd_2^+ + CH_3OH \rightleftharpoons L_2PdH^+ + CH_2O + H^+ \qquad (1.1)$$

(b) Water-gas shift reaction generating carbon dioxide from CO and water

$$L_2Pd^{2+} + CO + H_2O \rightleftharpoons L_2PdH^+ + CO_2 + H^+ \qquad (1.2)$$

(c) Wacker-type oxidation of ethylene

$$L_2Pd^{2+} + C_2H_4 + CH_3OH \rightleftharpoons L_2PdH^+ + CH_2{=}CHOCH_3 + H^+ \qquad (1.3)$$

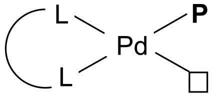
(d) Direct hydrogen activation (in presence of hydrogen)

$$L_2Pd^{2+} + H_2 \rightleftharpoons L_2PdH^+ + H^+ \qquad (1.4)$$

(e) Alcoholysis of the *Pd-acyl* bond at during the chain termination.

$$L_2PdCO\mathbf{P}^+ + CH_3OH \rightleftharpoons L_2PdH^+ + CH_3OCO\mathbf{P} \qquad (1.5)$$

The initiation by *Pd-hydride* specie gives an alkyl end group while that by carbomethoxy specie results in an ester group. Both the *Pd-acyl* and *Pd-alkyl* species are catalytically active and can initiate copolymerization reaction and subsequent alternate insertion of ethylene and CO leads to the chain propagation. The key catalytic intermediate involved during copolymerization is believed to be the d^8 square planer cationic palladium specie **1**.



1

In structure **1**, out of the four sites available for coordination, two sites are occupied by the *bis*-chelating ligand. The third site is occupied by the growing polymer chain and remains occupied until termination step. Thus, only one site (indicated by rectangle in **1**) is available for coordination by other species. This fourth coordination site is competitively occupied by the monomers i.e. CO and ethylene and the solvent methanol. While the coordination of monomers (CO and ethylene) leads to chain growth, the insertion of methanol results in the chain termination. Thus, competition for vacant site is one of the important factors affecting catalysis and explains the sensitivity of the reaction to the choice of solvent and counter ion in the copolymerization reactions. Model studies have revealed that strongly coordinating group effectively reduces the rate of insertion steps [84]. Thus, two types of propagation steps are operating. In one of the steps, CO occupies the fourth vacant coordination site in the *Pd-alkyl* species and it's subsequent insertion in the *Pd-alkyl* bond results in the formation of *Pd-acyl* species, which in the next step undergoes migratory insertion of ethylene, and the chain formation continues.

$$\mathrm{L_2PdCH_2CH_2}\mathbf{P}^+ \xrightarrow{\mathrm{CO}} \mathrm{L_2PdCOCH_2CH_2}\mathbf{P}^+ \qquad (1.6)$$

$$\mathrm{L_2PdCO}\mathbf{P}^+ \xrightarrow{\mathrm{C_2H_4}} \mathrm{L_2PdCH_2CH_2CO}\mathbf{P}^+ \qquad (1.7)$$

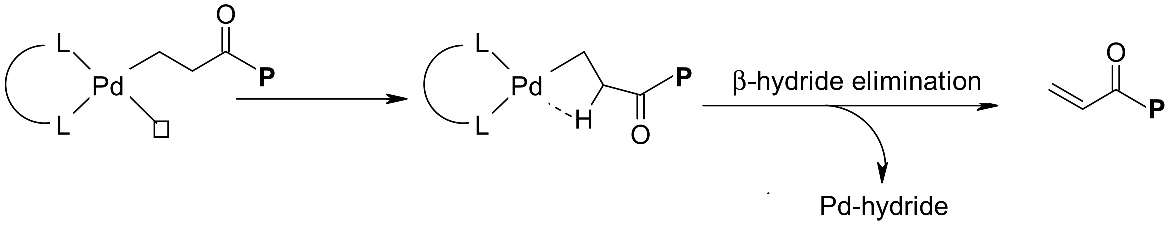
During copolymerization reaction, the chain termination is achieved by the intermediacy of solvent (methanol) or by β-hydride elimination. The protolysis of the *Pd-alkyl* intermediate terminates the chain and liberates the copolymer with saturated ketone end group.

$$\mathrm{L_2PdCO}\mathbf{P}^+ + \mathrm{CH_3OH} \rightleftharpoons \mathrm{L_2PdH^+} + \mathrm{CH_3OCO}\mathbf{P} \qquad (1.8)$$

The second termination mode involves the alcoholysis of the *Pd-acyl* intermediate resulting in the formation of copolymer with ester end group.

$$\mathrm{L_2PdCH_2CH_2CO}\mathbf{P}^+ \xrightarrow{\mathrm{CH_3OH}} \mathrm{L_2PdOCH_3}^+ + \mathrm{CH_3CH_2CO}\mathbf{P} \qquad (1.9)$$

In β-hydride elimination, β-hydrogen of the growing polymer chain (Pd-alkyl stage) is eliminated as shown below.



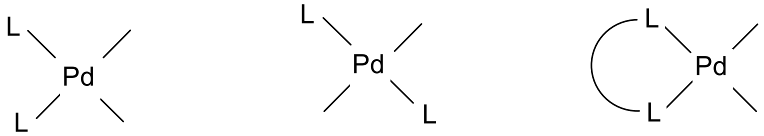
(1.10)

The existence of above initiation and termination mechanisms has been experimentally confirmed by end group analysis [69]. Further, it has also been observed that the distribution of end groups depends on reaction temperature, catalyst used etc. [69]. Recently, Rix et al. have presented a detailed mechanistic account of the key steps involved in the copolymerization reaction with catalyst containing a *bipyridine* ligand using *insitu* NMR technique [85]. This study confirmed that the co-polymerization reaction proceeds through palladium mediated alternate insertion of olefins and CO resulting in the sequential chain growth of the copolymer. It was also observed that the insertion of ethylene into the palladium-carbonyl bond is the slow step i.e. the rate-determining step.

1.3.3 Role of Ligand

Under the reaction conditions (employed for polyketone preparation), cationic Pd(II) catalysts modified by excess monodentate phosphine ligands and weakly coordinating anions selectively give methyl propionate with high reaction rates, suggesting that the catalysis involved during the formation of methyl propionate is similar to that operating during polyketone formation [69]. Formation of methyl propionate is a special case in the polyketone catalysis wherein there is no propagation step but only the initiation and termination steps.

This interesting ligand effect on the product distribution is explained on the basis of the difference in the coordination modes of mono and bidentate ligands. As mentioned earlier, the active catalytic species during coordination is a cationic 16-electron Pd complex **1** for which, a d^8 square planar geometry would be expected. In case of monodentate ligands, the ligands can assume either *cis* or *trans* configuration. It is obvious that the monomer insertion can occur only if monomer and polymer are bound in *cis*-configuration to the Pd center, and the remaining ligands are also in *cis*-configuration. However, in case of monodentate ligands, both *Pd-alkyl* and *Pd-acyl* species would prefer a *trans* orientation of ligands because of the steric reasons.



cis trans always trans

Monodentate ligand **Bidentate ligand**

One more probable reason for preferential *trans* orientation of the ligands could be to avoid the unfavorable position wherein the *Pd-P* and *Pd-C* bonds are *trans* to each other. Also, in these complexes the *cis-trans* isomerism would be quite rapid [86]. In the absence of excess ligands, one would expect formation of at least oligomeric polyketones using monodentate ligands. Indeed, it has been observed that at low temperature in a methanol solvent, $[Pd(PPh_3)_2(CH_3CN)_2]^{2+}$ converts CO and ethylene into methyl propionate and a significant amount of keto ester oligomers [64]. In contrast to this, the use of *bis* chelating ligands ensure that the ligand coordination is always *cis*, probably because of the steric constraints. This also ensures *cis*-configuration of the monomer and the polymer chain, which is essential for the chain propagation.

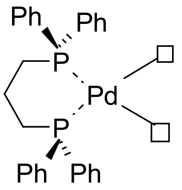
The presence of particular geometry in the active catalytic intermediate is required for highly efficient catalysts. Thus, in a series of diphosphine ligands $Ph_2P(CH_2)_mPPh_2$, the average degree of polymerization depends on the length of the alkylene bridge [69] (Table 1-4).

Table 1-4. Effect of Ligand on Ethylene/CO Copolymerization.[a] [69]

Sr.	*Bisphosphine ligand*	*m*	*Activity*[b]	*(n)*[c]
1.	*1,1-bis(diphenylphosphino)methane*	*1*	*1*	*2*
2.	*1,2-bis(diphenylphosphino)ethane*	*2*	*1000*	*100*
3.	*1,3-bis(diphenylphosphino)propane*	*3*	*6000*	*180*
4.	*1,4-bis(diphenylphosphino)butane*	*4*	*2300*	*45*
5.	*1,5-bis(diphenylphosphino)pentane*	*5*	*1800*	*6*
6.	*1,6-bis(diphenylphosphino)hexane*	*6*	*5*	*2*

[a] ***Reaction conditions***. *Catalyst precursor* $Pd(MeCN)_2(OTs)_2$*: 0.1 mmol;* $C_2H_4/CO=1$*; temperature: 84°C; pressure: 45 atm; methanol: 150ml.* [b] *Activity defined as g polymer/g Pd/h.* [c] *The average degree of polymerization n (defined as* $H(CH_2CH_2CO)_nOCH_3$*) determined by end group analysis from* ^{13}*CNMR spectra.*

These results indicated that the catalyst activity and molecular weight was strongly dependent on the chain length of the alkyl bridge in the bisphosphine ligand. Thus, highest activity and molecular weight was obtained at *m*=3 and decreased on lower or higher values of *m*. One of the reasons why 1,3-bis(diphenylphosphino)propane (with *m*=3) gave highest activity could be that it provided a sterically favoured six member configuration to the active catalyst with minimum hindrance around the palladium centre (structure **2**).



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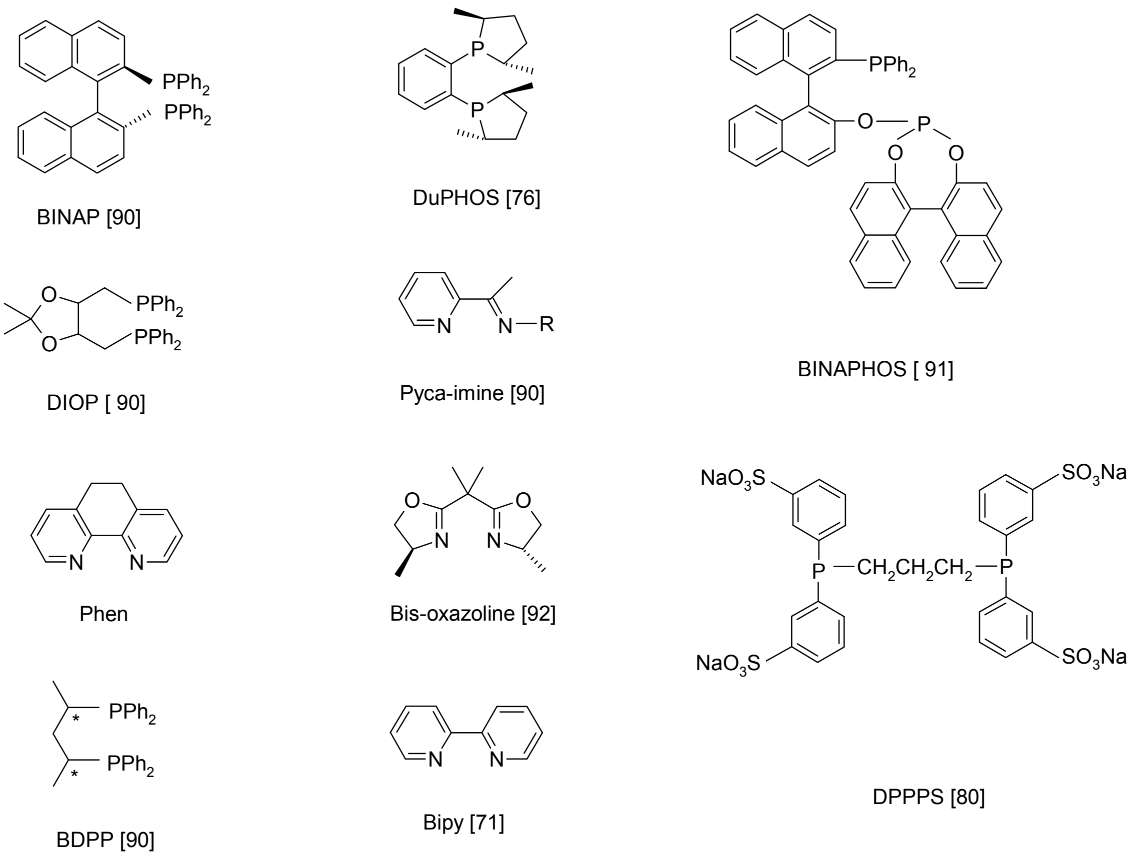
Several other types of chelating ligands have been reported for the copolymerization reactions. Few representative examples are given in Figure 1-1.


BINAP [90]

DuPHOS [76]

BINAPHOS [91]

DIOP [90]

Pyca-imine [90]

Phen

Bis-oxazoline [92]

DPPPS [80]

BDPP [90]

Bipy [71]

Figure 1-1. Examples of Ligands Used in Copolymerization Reactions.

1.3.4. Role of Anion

As a general requirement, the highly active catalyst for copolymerization reaction need a source of palladium, a *bis* chelating ligand and a weakly or non-coordinating anion [69]. It is believed that the anions are actively involved in the catalytic cycle. Their presence in the proximity of the cationic Pd center forms cation-anion pair that can easily undergo dissociation generating a more electrophilic center. The lower electron density on the Pd center may cause lower binding energy for the monomers because of the less back bonding of metal to ligand. Such intermediates are less stable and therefore result in lower activation energies during monomer coordination and insertions. Protic solvents such as methanol provide extra stabilization by solvation of these ion pairs than aprotic solvents [90] and therefore are most suitable solvents for copolymerization reaction. A wide variety of anions can be used for this purpose and a comparison between their activities is given in Table 1-5 [69].

Table 1-5. Effect of Anion (Acid) on the Ethylene/CO Copolymerization[a] [69].

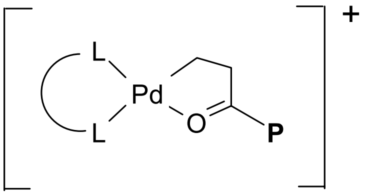
Acid	*Temp., °C*	*Pressure, atm*	*Activity* [b]	*DP* [c]
CF_3SO_3H	90	40	6900	150
TsOH	90	40	6200	150
HBF_4	90	40	5000	115
CCl_3COOH	90	40	300	> 100
CF_3COOH	90	40	6000	200
HCl	115	45	30	50

[a] *Reaction carried out using Shell catalyst (Ligand : 1,3-bis(diphenylphosphino)propane, Pd source: Pd* $(OAc)_2$*); pressure maintained by 1:1 mixture of ethylene and CO; solvent: methanol.* [b] *Activity defined as g polymer/g Pd/hr.* [c] *Average degree of polymerization (DP) determined from the end group analysis by* ^{13}C *NMR.*

1.3.5 Perfect Alternation During Ethylene/CO Copolymerization

The palladium-catalysed copolymerization of ethylene (and other olefins) with CO produces perfectly alternating polyketone without double insertion of any monomer. Insertion of CO in Pd-C bond is a fairly common reaction [91]. There are no reports on the insertion of CO in *Pd-acyl* bond. The double insertion of CO seems to be thermodynamically unfavourable [92]. On the other hand, olefin insertion in the *Pd-acyl* bond appears to be particularly facile [84c, 93]. The insertion of olefin into the Pd-C bond is not thermodynamically ruled out. In fact the catalysts used for copolymerisation reaction efficiently catalyze the dimerization of ethylene to butene [94]. The perfect alternation is maintained even in the low concentration of carbon monoxide [69]. Thus, during the batch polymerization experiments at high ethylene/CO ratio, error-free copolymer was produced until all CO is consumed and then the system started producing butene, the product of double olefin insertion (dimerization of ethylene). Two factors that prevent double insertion of olefin are the greater binding ability of CO over the olefin and the nature of the rate-determining step during copolymerization reaction. Because of the stronger coordination of CO, the local concentration of CO would be higher than the olefin. Once a *Pd-alkyl* specie is formed, the stronger CO coordination ensures that the next monomer inserted is CO to give *Pd-acyl* specie. Although, CO also coordinates strongly to *Pd-acyl*, but since the double insertion of CO is not thermodynamically favoured, the system has to wait for an ethylene molecule to displace CO, to coordinate and insert. Since the olefin insertion is the slow step, insertion of another olefin monomer into *Pd-alkyl* bond would be still slower. Therefore, although the double olefin insertion is not altogether ruled out thermodynamically it is the kinetic control that comes into the picture. Thus, in presence of CO, which can compete leadingly with olefin, double insertion of the olefin monomer doesn't take place across the *Pd-alkyl* bond, thereby forcing the alternation.

Drent [3] has suggested that apart from the difference in coordination affinity discussed above, internal coordination effects of the growing polymer chain may also be playing a significant role in forcing the alternate insertion of individual monomers. According to this explanation, each time after the ethylene insertion, the growing polymer chain acts as a chelating ligand. This is achieved through the coordination of oxygen of the β-carbonyl group (structure **3**). Such stable species have been recently observed spectroscopically in studies related to the olefin insertion in the *Pd-acyl* bonds [93]. During such chelate formation, the only vacant site is occupied by the coordinating oxygen and that next incoming monomer has to break this coordination before it can coordinate to palladium centre and insert itself in the growing polymer chain. The olefins coordinate weakly to the Pd(II) centre and therefore can not displace the coordinated carbonyl group in the five member stable ring (structure **3)**.



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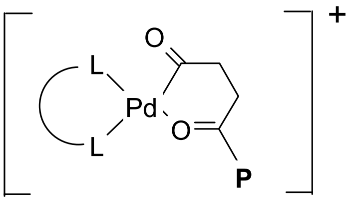

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On the other hand, because of the high binding ability and less steric bulk, CO easily displaces the coordinated carbonyl group and it's subsequent insertion results in the formation of structure **4** in which the carbonyl group is α and γ with respect to the palladium. The γ-carbonyl may still remain coordinated to the palladium centre but in this case forming a less stable six-member ring. This weakly coordinated carbonyl group can be easily displaced by ethylene. Since, the double CO insertion is not thermodynamically favoured, the only possibility is coordination and subsequent insertion of the ethylene. Continuation of this sequence ends up in producing perfectly alternating polyketones. One more advantage of such chelate formation due to the internal coordination is that it prevents the chain termination due to the β-hydride elimination. Inhibition of β-hydride elimination in metallacycles is well known [95].

To summarize, the chain propagation involves alternating reversible carbon monoxide insertion in *Pd-alkyl* species and irreversible olefin insertion in the *Pd-acyl* species. While double insertion of CO is not thermodynamically favoured, the internal coordination of the growing polymer chain and stronger coordination ability of CO over the olefin prevents the double olefin insertion.

1.3.6 Catalyst Deactivation and Role of Promoters

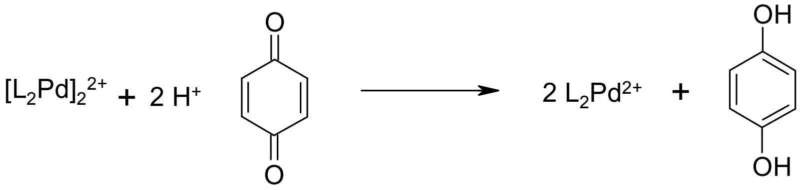
As mentioned earlier, there is almost equal possibility that the copolymerization is initiated by the palladium hydride and palladium methoxy species. The Pd-hydride species can decompose to catalytically inactive Pd(0) complex as shown below:

$$L_2PdH^+ \rightleftharpoons L_2Pd^{(o)} + H^+ \qquad (1.11)$$

The resulting Pd(0) species still retains the stabilizing ligands. In case of phosphine ligands and in particular the biphosphine ligands, the resulting Pd(0) has reasonable stability, while in case of the nitrogen ligands, the Pd(0) immediately looses it's ligand and precipitates as catalytically inactive metallic Pd(0). This is one of the major modes of deactivation. In the other mode, the Pd(0) species formed initially, combines with another molecule of catalytically active Pd (II) species to form a catalytically inactive palladium dimmer. This mode of deactivation removes two palladium atoms from the active reaction sphere. Such palladium dimmers have been detected and structurally characterized in literature [84 (a, b), 96].

$$L_2Pd^{(o)} + L_2Pd^{2+} \rightleftharpoons [L_2Pd]_2^{2+} \qquad (1.12)$$

The effect of these deactivation processes can be minimized by the addition of a variety of oxidizing agents like quinones which, probably reoxidize the deactivated Pd(0) species to catalytically active Pd(II) intermediates as shown below.



(1.13)

The use of oxidant promoters in low concentrations results only in rate enhancement without affecting the chain lengths. This indicates that the rate enhancement is probably not because of the promotion of the propagation rate and therefore because of increase in the number of active catalytic species. One interesting observation is that use of oxidants like quinones in small concentrations results in more ester end groups [3]. This suggests that more chains are initiated by the carbomethoxy species. If both hydride and carbomethoxy precursors remained intact until they started a new chain and both initiation step would be rapid compared to the propagation steps then they could affect the end groups and not the copolymerization rates. This also indicates that the use of oxidants converts the deactivated catalyst into the active catalyst. As mentioned earlier, in case of the nitrogen ligands, there is high rate of catalyst deactivation. Thus it becomes mandatory to add oxidizing agents in copolymerization of styrene with CO where only nitrogen ligands are known to yield polyketones [3].

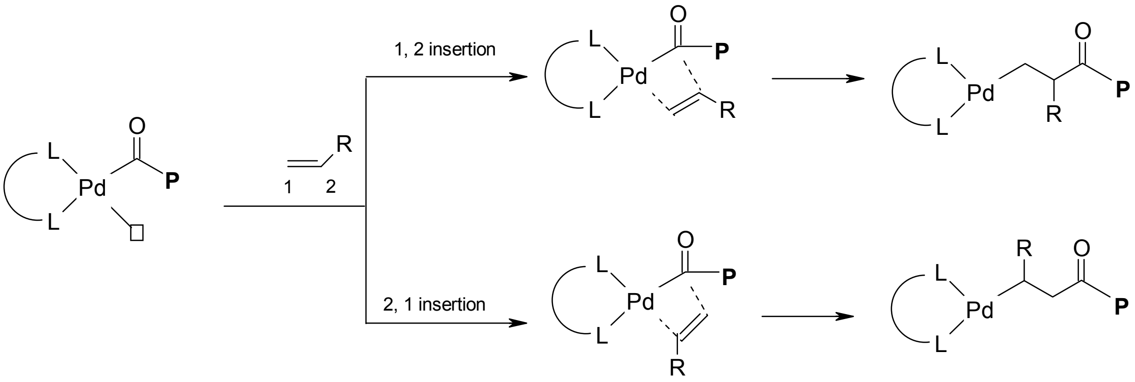
It has been reported that the addition of small amounts of water or hydrogen promotes the copolymerization and produces copolymers with predominantly ketone end groups [97]. The added hydrogen or water helps in generation of the *Pd-hydride* specie which acts as initiators for copolymerization reactions.

1.3.7 Copolymerization of Other Olefins with CO

Although the ethylene–CO copolymerization has been investigated in details and has received a commercial attention too, many other olefins can also be copolymerized with carbon monoxide to the corresponding polyketones. Interestingly, the nature of olefins has a significant effect on the rate of copolymerization, structural features and physical properties of the resulting polyketone.

Ethylene being the simplest and least hindered olefin, it is most reactive and the copolymerization proceeds at very rapid rates. Other olefins can be considered as substituted ethylene. Thus, these are more hindered than ethylene and the rate of copolymerization decreases with the increase in the bulk of the substituent. The typical order of the reactivity *is ethylene>propylene>styrene* [3]. This decrease in reactivity is probably because the rate determining steps in copolymerization is the insertion of the olefin into the *Pd-acyl* intermediate. The increased steric bulk retards the olefin insertion step even more and results in lower rates and molecular weights since the slower insertion steps is dominated by the chain terminations through β-hydride elimination. This phenomenon is even more evident in case of styrene. Thus, whereas *1,3-bis(diphenylphosphino)propane* is the most active ligand for copolymerization of ethylene and CO, it is almost ineffective for the styrene/CO copolymerization and only nitrogen containing ligands are known to be active in the later case.

Several olefins have been copolymerized with CO. Drent first reported the alternating copolymerization of propylene and carbon monoxide using bischelating phosphine ligand modified Pd catalysts [98a]. The average catalytic activity was 100-1000 moles of propylene reacting (per mol of Pd) per hour. Molecular weight as high as 30000 could be obtained. Several other groups have studied the copolymerization of propylene and CO [83, 98, 99]. The control of regioselctivity is one of the major issues in the copolymerization of higher olefins including the propylene. The higher olefins can react with the palladium metal center in either *1,2* or *2,1* fashion (Scheme 1-2).

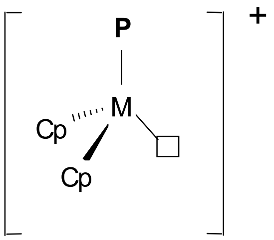
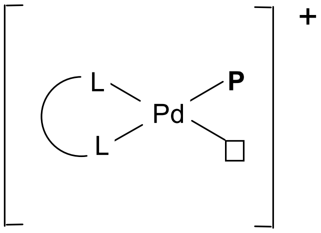


Scheme 1-2. Insertion Modes During Copolymerization of Higher Olefins with CO

By suitable choice of the ligands and anions, it seems possible to control the regioselectivity of the olefin insertion into the *Pd-acyl* intermediate to produce highly regioregular polyketone polymers [99a]. The stereoregularity of olefin insertion can also be controlled to give atactic, isotactic, or syndiotactic olefin/CO polymers and highly steroregular polyketones have been prepared using chiral ligands [99(a-e)]. Several other olefins including styrene [98(c-e), 99(b), 100-104] and functional olefins [105] have been copolymerized with carbon monoxide. The copolymerization reactions of olefins other than ethylene with CO have been recently reviewed [3,40(c)].

Finally it can be seen that the there are striking mechanistic similarities in the palladium-catalyzed homogeneous olefin/CO copolymerization and modern homogeneous olefin polymerization by early transition metal complex catalysts as given in Table 1-6 [3].

Table 1-6. A Comparison Between Pd-catalyzed CO/Olefin Copolymerization and Early-Transition Metal-catalyzed Olefin Polymerization. [3]

Feature	*Polyolefins*	*Polyketones*
Metal ion	Ti^{IV}, Zr^{IV}, Hf^{IV}	Pd^{II}
Ligands	$2Cp^{-}$, $2X^{-}$	$2L$, $2X^{-}$
Anions	*Non-coordinating*	*Weakly or non-coordinating*
Coordination geometry	*Tetrahedral*	*Square planer*
Active centers		

Cp = cyclopentadienyl; X = anions; L = ligand

1.4 Carbonylation – Polycondensation Reactions

The carbonylation of C-X (X=halides) derivatives represents an important class of reactions with versatile applications in organic synthesis [106]. Prof. R. F. Heck in his classical work demonstrated that a wide variety of amides and esters could be efficiently prepared in high yields by palladium catalyzed carbonylation and coupling reactions of aromatic halides and amines [107] or alcohols [108] respectively. Further investigations and refinements resulted in application of these reactions in the preparation of several other functions e.g. aryl oxazoles and imidazoles [109], thiazoles [110], carboxylic acids [22], anhydrides [111], imides [112] etc. But, it was nearly 15 years before this chemistry was applied to polymer synthesis. In the past several years, a variety of polymers have been prepared by catalytic carbonylation of hydrolytically stable aromatic halides under relatively mild reaction conditions. This method complements conventional approach to the synthesis of polymers and attempts some of the important shortcomings of the conventional reactions as outlined below:

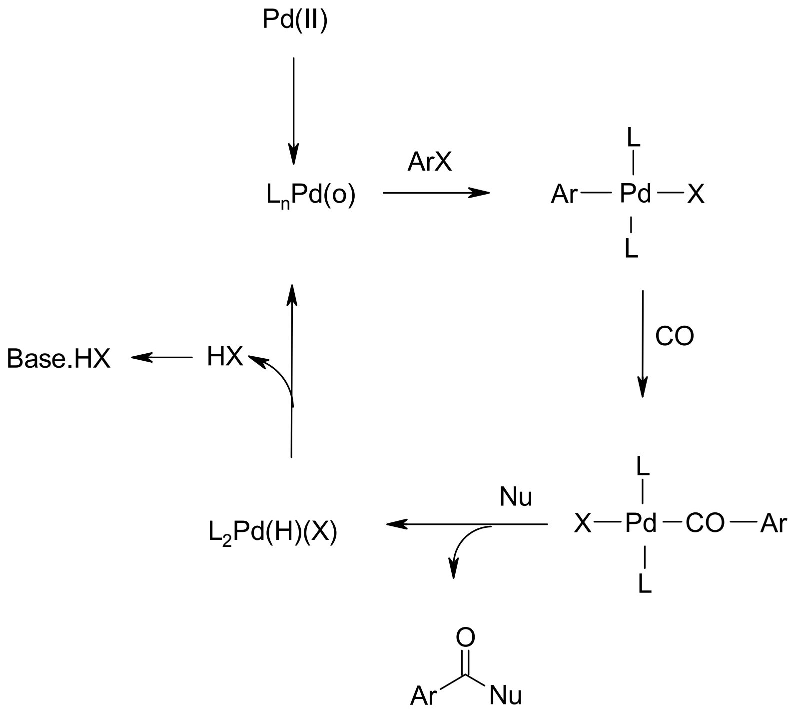
1. The conventional route to many carbonyl-containing polymers involves the condensation reaction of diacid derivatives and therefore the presence of carboxylic acid function on the reacting monomer is must. Although this is not a problem with some of the commercially available diacids (e.g. terephthalic acid), difficulty arises when diacids with less common substitution patterns are required.
2. The conventional polycondensation reactions require handling of sensitive compounds like acid chlorides.
3. The reaction conditions employed conventionally require high temperatures (normally above 200°C)

The transition metal catalyzed carbonylation-polycondensation reactions have emerged as promising alternative for the conventional synthetic routes to several high performance polymers. Unlike the sequential chain growth (living) polymerization during the copolymerization reactions, the carbonylation-polycondensation reactions are examples of step growth polymerization processes and involve carbonylation of halide as the key step.

1.4.1 Mechanistic Aspects

The carbonylation-polycondensation are emerging reactions and there is no information on the systematic investigation of their mechanism. Intrinsically, the carbonylation-polycondensation polymerization is an extension of classical Heck carbonylation reaction and are believed to follow a similar mechanism as given in Scheme 1-3 [107,113].

The carbonylation-polycondensation reactions like many other transition-metal catalyzed reactions are made feasible through a change in the valence of the involved metal. This change in the valance is predominantly a two-electron process. The reaction (in palladium-catalyzed reactions) proceeds through the initial formation of coordinatively unsaturated Pd (0) species, which oxidatively adds the aromatic halide, producing a Pd (II) complex. Carbon monoxide then inserts in the aryl-palladium bond, giving aroyl complex. This is followed by attack of the amine (or alcohol), leading to the regeneration of the active Pd (0) catalyst and liberation of the free amide (or ester). A particular case can be seen in case of Pd(II) copolymerization of ethylene with CO when perfectly alternating polyketones are produced. This is possible because in presence of CO, which has greater coordination ability, the CO insertion is faster than the β-hydride elimination. Thus the same metal can yield different behaviors depending on the reaction conditions.



Scheme 1-3. Proposed Mechanism for Carbonylation-Polycondensation Reaction.

The formation of various catalytic intermediates is discussed in the next sections.

1.4.1.1 Formation of Pd (0)

The catalytic cycle is started by Pd(0) species. Under the given reaction conditions, Pd(0) can be formed by two different routes. In one of the routes, the Pd(0) configuration is achieved by the intermediacy of the excess ligand L, typically a tertiary phosphine.

$$PdX_2 + \text{excess ligand (L)} \longrightarrow PdL_4 \qquad (1.14)$$

Alternatively, Pd(0) complex can be formed in presence of amine [107] or alcohol [113] and CO as follows .

$$L_2PdX_2 + 2\,CO + 2\,ROH \longrightarrow (CO)PdL_2 + (RO)_2CO + 2\,HX \qquad (1.15)$$

$$L_2PdX_2 + 2\,CO + RNH_2 \longrightarrow (CO)PdL_2 + RNH(CO)NHR + 2\,HX \qquad (1.16)$$

1.4.1.2 Oxidative addition of halide to Pd(0)

Once the Pd(0) specie is formed, the next step is the oxidative addition of the aryl halide. This results in the formation of the Pd(II) complex and a displacement of a coordinated ligand or CO molecule.

$$(X)(Ar)PdL_2 + CO \longrightarrow (X)(ArCO)PdL_2 \qquad (1.17\}$$

The reactivity of the particular halide during the carbonylation reaction is decided in this step only. Thus the typical order of reactivity towards oxidative addition is *Iodo* > *Bromo* > *Chloro* substrates [114].

1.4.1.3 Insertion of CO

In the next step, the CO coordinates to the Pd(II) complex and it's subsequent insertion in the *Pd-Ar* bond results in the formation of *Pd-acyl* intermediate, which through a nucleophillic attack by the nucleophile (alcohol or amine) liberates the amide or ester respectively.

$$(X)(ArCO)PdL_2 + ROH \longrightarrow ArCOOR + (H)(X)PdL_2 \qquad (1.18)$$

1.4.1.4 Elimination of HX

The active catalyst (Pd (0)) is regenerated by the reductive elimination of HX from the hydridopalladium complex obtained in the earlier step. The released HX is trapped by the organic base, often a tertiary amine.

$$(H)(X)PdL_2 + CO \longrightarrow (CO)PdL_2 + HX \tag{1.19}$$

1.4.1.5 Catalyst deactivation

The major deactivation mechanism for the Pd(0) is by formation of Pd metal and cluster compounds [115].

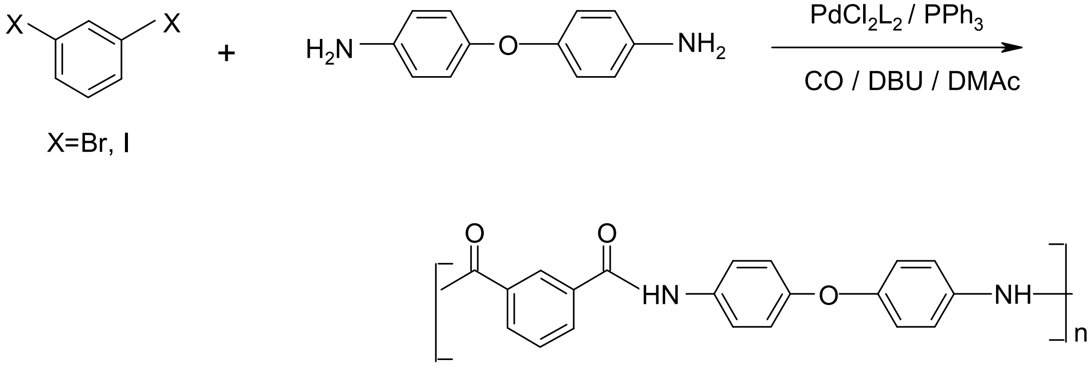
1.4.2 Applications to Polymer Synthesis

The Heck carbonylation chemistry when applied to bifunctional substrates becomes a convenient and efficient method for the synthesis of a wide variety of polymers. The relevant literature on these reactions is presented in the following sections.

1.4.2.1 Polyamides

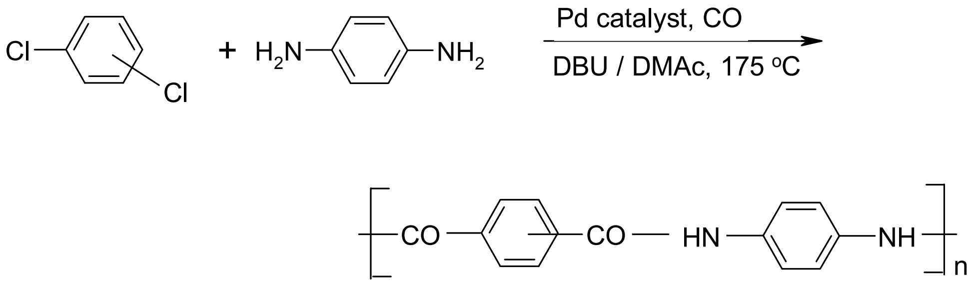
Aromatic polyamides (aramides) were the first polymers synthesized using palladium-catalyzed carbonylation and condensation reactions. Yoneyama et al. [116] prepared several aliphatic-aromatic polyamides by the palladium-catalyzed carbonylation of aliphatic diamines and aromatic dibromides in presence of a base. They investigated effect of reaction variables such as nature and amount of base, reaction temperature and different palladium catalysts on the yield and inherent viscosity of the polyamide obtained. Polyamides having inherent viscosities in the range of 0.13 to 1.21 dL/g could be obtained. Shortly thereafter, Perry et al. [117]

reported that the use of aromatic diiodides and elevated CO pressures gave aramides of much higher molecular weight in shorter reaction times (Scheme 1-4).



Scheme 1-4. Synthesis of Polyamides by Catalytic Carbonylation Route

The increase in the molecular weight and reduction in the reaction times by increasing the CO pressure was explained on the basis of existence of different rate determining steps [117]. In case of aryl bromides the oxidative addition of aryl bromide to Pd(0) species is the slowest and hence the rate determining step. Because of the higher coordination ability of the CO, increasing CO pressure makes the oxidative addition even difficult thereby requiring more reaction time. The longer reaction time results in lower molecular weights. In contrast, due to higher reactivity of the aryl iodide, the oxidative addition step is fast and the CO insertion becomes the rate determining. A wide variety of aramides with moderate molecular weights (M_w in the range of 23,000 – 86,000) were prepared using this approach. It was further reported that the optimum stoichiometry for achieving maximum molecular weight was to use a slight excess of the diamine. Model studies [118] indicated that the use of excess diamine decreased the likelihood of reduction of aryl-halide, which would effectively terminate the polymer chain. Recently, Kim et al. [119] prepared polyamides using dichlroaromatics (Scheme 1-5).



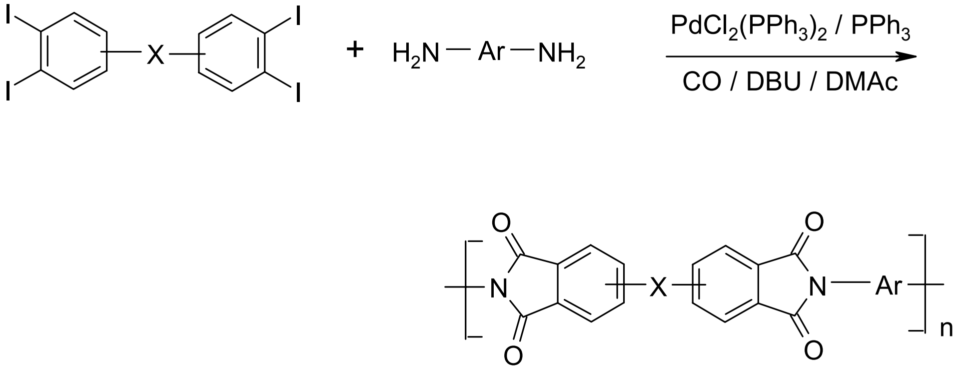
Scheme 1-5. Synthesis of Polyamides by Carbonylation of Aromatic Dichlorides

This procedure was partly based on the earlier observation [120] that palladium catalysts modified with bulky trialkyl phosphines effectively catalyzed the carbonylation of aryl chlorides. The reaction using dichlorides required very high temperatures (around 175°C) to obtain even moderate viscosities e.g. 0.40 dL/g. Despite the moderate molecular weights, high temperature and longer times, the use of dichloro derivatives was significant because of their low cost and immediate availability.

1.4.2.2 Polyimides

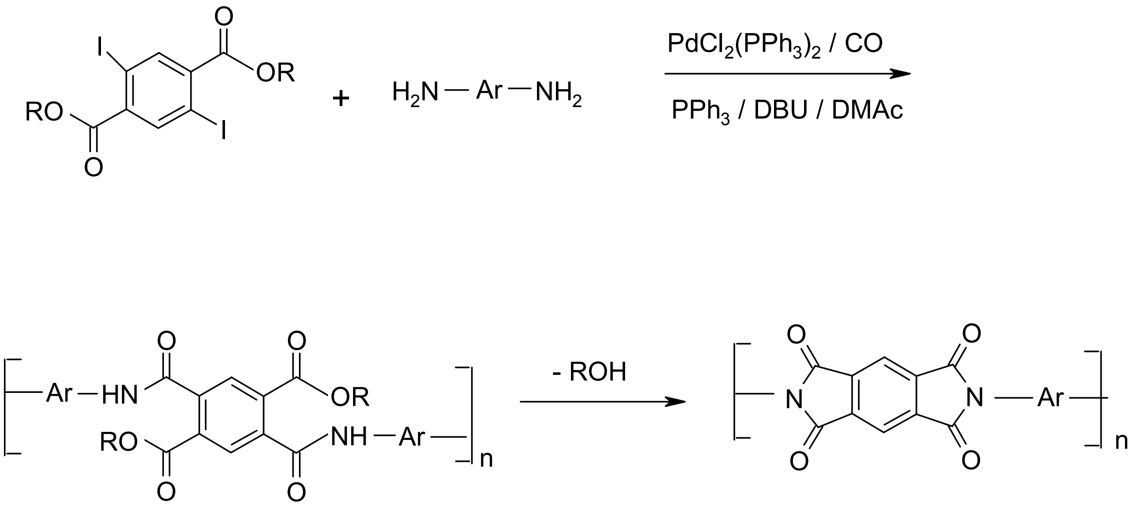
Polyimides contain the imide group (–CO-N-CO-) in the polymer backbone and find applications as insulating films, coating and laminates, molded parts, structural adhesives, high modulus fibers, selective membranes, high temperature composites etc. The typical methods for the synthesis of polyimides involve polycondensation of dianhydrides and diamines, polycondensation of dianhydrides and diisocyanates, aminolysis of diimides by diamines etc. [121]. In view of the commercial importance of the polyimides several approaches have been taken to extend carbonylation chemistry to the formation of polyimides.

Although, the synthesis of phthalimides by carbonylation could be accomplished efficiently [112], preparation of high molecular weight linear polyimides was not easy. Perry and Turner [122] reported that the reaction of bis(*o*-diiodoaromatics) with diamines and CO (Scheme 1-6) gave polyimides with broad polydispersities, branching and residual iodide and amide groups.



Scheme 1-6. Synthesis of Polyimides by Catalytic Carbonylation of Bis(*o*-diiodoaromatics) and Diamines.

In order to overcome these problems less reactive monomers e.g. mixed dihalides were used but there was no improvement. In an attempt to get the higher molecular weight polyimides a different approach which combined the advantageous features of both the conventional polycondensation and catalytic carbonylation was employed. Thus, the bis(*o*-iodoesters) were reacted with diamines in presence of CO and a palladium catalyst to get the corresponding polyamide esters (Scheme 1-7).

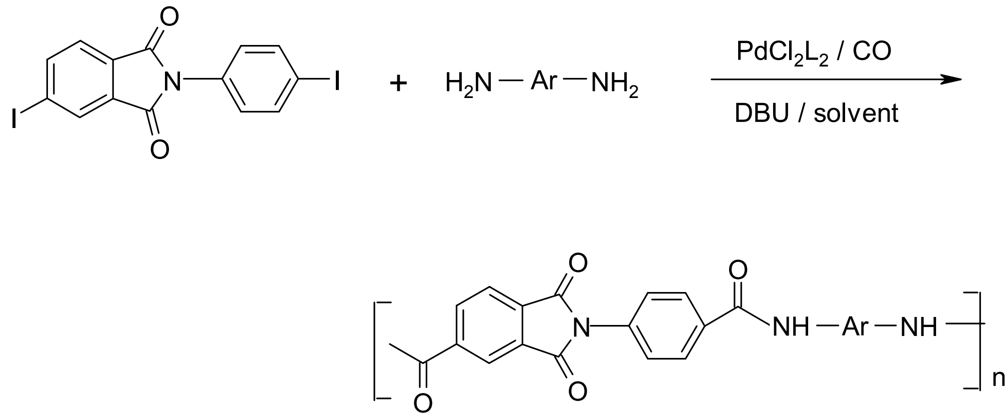


Scheme 1-7. Synthesis of Polyimides by Catalytic Carbonylation of Bis(*o*-iodoesters) with Diamines

The polyamide-ester thus obtained spontaneously cyclized to the corresponding polyimides in the presence of a base. Further studies indicated that *tert*-butylesters were particularly useful in this approach [123a]. Polyimides were also obtained by the palladium catalyzed carbonylation and coupling of bis(o-iodo amides) and diamines [123b]

1.4.2.3 Poly(imide-amides) (PIA)

Palladium catalyzed carbonylation and condensation of aryldiiodides containing one or two preformed imide moieties, diamines and CO gives high molecular weight poly(imide-amides) (Scheme 1-8) [124].

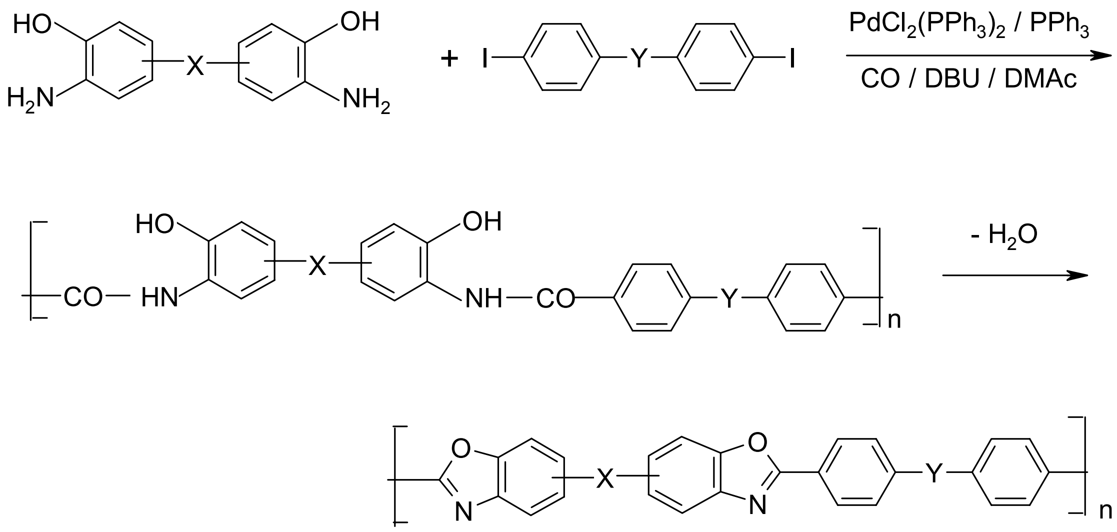


Scheme 1-8. Synthesis of Poly(imde-amide)s by Catalytic Carbonylation Route

This methodology was successful for the synthesis of homopolymers as well as copolymers. The imide moiety even activated chlorosubstituted phthalimides to react similar to the diiodo substrates [125].

1.4.2.4 Poly(benzoxazole)s (PBO)

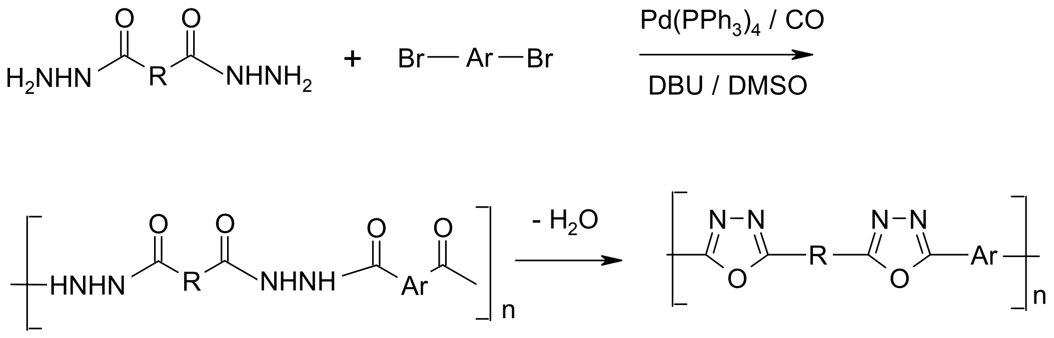
Another class of fused-ring heterocyclic polymers produced by carbonylation chemistry was the polybenzoxazoles (PBOs) [126]. The palladium catalyzed carbonylation-polycondensation of diiodoaromatics with bis(*o*-aminophenols) gave polybenzoxazoles (Scheme 1-9). The phenol groups were sufficiently unreactive under the reaction conditions and the intermediate poly(amide-ol) could be easily isolated. It was soluble in dipolar aprotic solvents and could be precipitated, purified and subsequently cyclized by simple thermal or chemical cyclization to produce the thermally stable PBO.



Scheme 1-9. Preparation of Poly(benzoxazole)s by Catalytic Carbonylation Route

1.4.2.5 Polyacylhydrazides

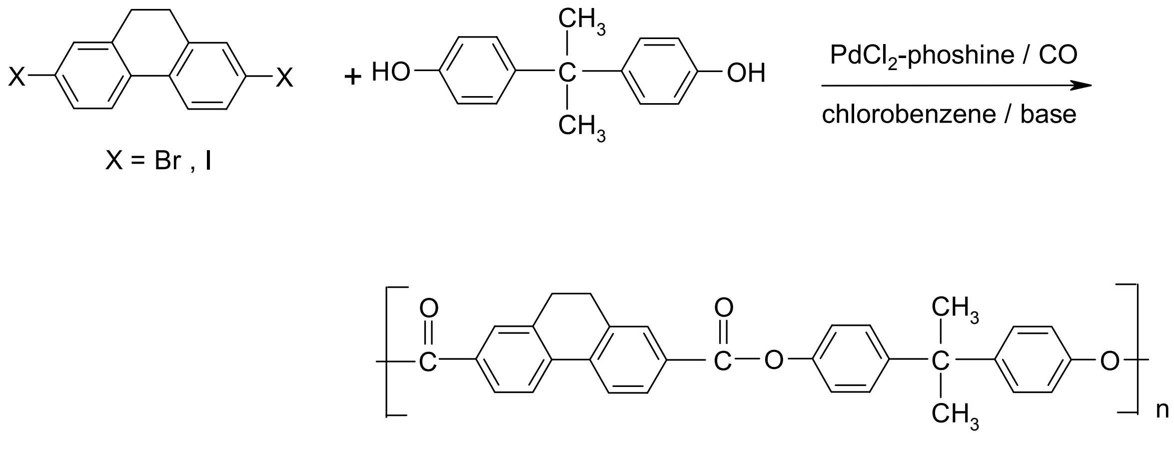
Poly(acylhydrazides) serve as intermediates for the preparation of poly(1,2,3-oxadiazole)s which are employed as high temperature plastics [127]. Conventionally, poly(acylhydrazides) are prepared by condensation of hydrazides and acid chlorides [128]. The alternate catalytic approach involves palladium-catalyzed carbonylation-polycondensation of aromatic dibromides and dihydrazides in presence of an organic base (Scheme 1-10)[31]. Polymers with inherent viscosities from 0.13-0.65 were obtained. These prepolymers could be subsequently cyclized.



Scheme 1-10. Synthesis of Poly(acylhydrazides) by Catalytic Carbonylation Route

1.4.2.6 Polyesters

Variety of polyesters could be synthesized by palladium-catalyzed carbonylation of aromatic dihalides and suitable diols. Both dibromides [30] and diiodides[129] were found to efficiently give polyesters (Scheme 1-11).



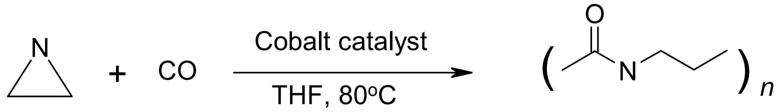
Scheme 1-11. Synthesis of Polyesters by Catalytic Carbonylation Route

It was observed that in case of partially aromatic dihalides higher molecular weight polyesters could be obtained using dibromo substrates whereas in case of fully aromatic dihalides the diiodo substrates were required to get higher molecular weight polyesters.

The carbonylation-polycondensation reactions can be applied to substrates other than dihalides also. Thus, aromatic bis(trifluoromethanesulfonates) and triflates can also be used instead of aromatic dihalides in these reactions [130].

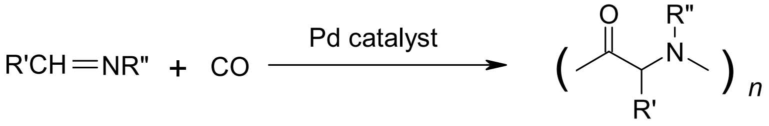
1.4.2.7 Polypeptides

Recently Jia at al. [34] proposed a catalytic route for the preparation of poly-β-peptides by cobalt-catalyzed copolymerization of aziridine and CO (Scheme 1-12).



Scheme 1-12. Synthesis of Poly-β-peptides by Cobalt Catalyzed Copolymerization of Aziridine and CO

Poly-β-peptides with very high molecular weights (Mw~ 63,300) could be obtained be obtained at high CO pressures (~ 68 atm) and longer reaction times (60hours). Similarly, poly-α-peptides were prepared by catalytic copolymerization of imines and CO (Scheme 1-13) [35].



Scheme 1-13. Synthesis of Poly-α-peptides by Palladium Catalyzed Copolymerization of Imines and CO.

Dghaym et al. [35b] have proposed that the insertion of imine into the Pd-acyl bond occurs in a manner directly analogous to that of the olefins.

1.5 Objectives for the Present Thesis

The literature survey presented in this chapter reveals that the use of carbon monoxide as a cheap monomer for the synthesis of polymers has gained a considerable importance. The availability of highly efficient catalytic processes will be a key factor in deciding the economical viability of these CO based polymerization processes. Therefore, studies relating to fundamental aspects like catalysis of these reactions assume significant importance. Further, the application of the catalytic carbonylation reactions in the preparation of new polymers would also be desirable. The objective for the present thesis was to study some of the key issues especially related to the catalysis and reaction engineering of polymerization processes using carbonylation reactions.

The following polymerization reactions were selected as model reactions:

1. Copolymerization of ethylene and carbon monoxide to polyketones.
2. Synthesis of polyesteramides by catalytic carbonylation-polycondensation reaction of aromatic diiodides and amino alcohols.
3. Synthesis of polyesters by catalytic carbonylation-polycondensation of aromatic dihalides and diols.

The copolymerization of ethylene and carbon monoxide to perfectly alternating polyketones is an excellent example of metal complex catalyzed living polymerization reaction (sequential chain growth) whereas the carbonylation-polycondensation of dihalides is an example of non-living (step growth) polymerization reaction. The specific objectives for this work were as follows.

1. To study the kinetic modeling of perfectly alternating copolymerization of ethylene and carbon monoxide to polyketones.
2. To investigate the possibility of preparing polyesteramides by catalytic carbonylation-polycondensation route.
3. To investigate the preparation of fully aromatic polyesters by catalytic carbonylation-polycondensation route.

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Chapter Two

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Kinetics of Copolymerization of Ethylene and Carbon Monoxide Using Homogeneous Palladium Catalyst

2.1 Introduction

The copolymerization of ethylene and carbon monoxide (CO) to perfectly alternating aliphatic polyketones is an interesting example of a multiphase catalytic reaction system. The copolymerization reaction involves simultaneous absorption of two gases (ethylene and CO) followed by a catalytic reaction in liquid phase (methanol) in the presence of a homogeneous catalyst. As the reaction proceeds, the product copolymer precipitates out being insoluble in methanol and forms slurry of solid polymer particles. The overall performance of such a multiphase catalytic reaction may depend on various reaction engineering factors like gas to liquid mass transfer, intrinsic reaction kinetics and the effect of suspended solid product on the mass transfer efficiency. To analyze such a multiphase catalytic reaction from the reaction-engineering point of view, it is important to understand the rate behavior and intrinsic kinetics of the reaction. Further, such a detailed kinetic study may provide some new insights into the mechanism of this catalytic reaction.

From the literature review presented in Chapter 1, it is evident that the previous work on this subject is related mainly to the investigation of the catalysis, reaction mechanism and polymer properties and there are only few reports on the kinetics of this industrially important reaction [1-5]. Zhao et al. [1] investigated the kinetics of copolymerization of ethylene and CO using a homogeneous cationic palladium complex $[(dppp)Pd(CH_3CN)_2](BF_4)_2$ and observed that the catalytic activity increased linearly with CO partial pressure at a constant ethylene partial pressure whereas the reaction was zero order with respect to ethylene at a constant CO pressure. The calculated energy of activation energy was 75 kJ/mole. Koide and Barron [2] investigated the kinetics of copolymerization of ethylene and CO using $(dppp)Pd(OAc)_2$ and (dppp)Pd[(CO)*t*Bu]Cl catalysts in the presence of *tert*-Bualumoxane as a cocatalyst in dichloromethane (CH_2Cl_2) solvent. A key observation made for this system was that the catalytic activity increased linearly with temperature till 348 K and decreased beyond that. The copolymerization rate was linearly proportional to the individual monomer pressures and also to the total pressure. Belov et al. [3] investigated the kinetics of ethylene-CO copolymerization using $Pd(C_5H_7O_2)$-PPh_3-TsOH catalyst in acetic acid and $Pd(OAc)_2$-dppb-CF_3COOH catalyst in methanol solvent. The rate of copolymerization increased proportionally with individual monomer partial pressures as well as the total gas pressure. None of the above studies have proposed any rate equations and a detailed kinetic analysis at process conditions relevant to the industrial operation. There are few reports on the mechanistic studies and in particular on the kinetics of the migratory insertion reactions relevant to copolymerization reactions [4], but these studies have been often carried out at lower pressure and temperatures than those typically employed in the industrial process. In the only significant report on this subject, Fatutto et al. [5] investigated the kinetics of copolymerization of ethylene and carbon monoxide using a homogeneous palladium complex $[(dppp)Pd(H_2O)(TsO)](TsO)$ as a catalyst at higher pressure and temperature (363K). These authors had also derived several rate equations assuming different reaction mechanisms. But a conclusive discrimination between individual rate equations was not possible because the data were collected only at one temperature (363K). Importantly, this study also did not present the detailed analysis of mass transfer effects during the copolymerization reaction.

Since no comprehensive information was available on the kinetics of this industrially important reaction, the aim of this work was to investigate the kinetics of the copolymerization reaction with detailed analysis of interparticle and intraparticle mass transfer effects at different temperatures of industrial relevance and further develop rate equations that could be used for design applications.

The first objective for this work was to investigate the solubility of CO and ethylene in methanol over a temperature range of interest. The knowledge of solubility data would be most essential in ascertaining the importance of mass transfer effects and also in the interpretation of the reaction kinetics. Since such data was not available in the literature, it was decided to measure it experimentally. The second objective of this study was to evaluate various rate equations derived on the basis of mechanistic considerations using the experimental rate data to find a suitable rate equation for predicting the intrinsic kinetic parameters for the copolymerization of ethylene and CO.

Thus, the kinetics of the copolymerization of ethylene and CO was studied in a stirred pressure reactor using a homogeneous palladium complex catalyst $[(dppp)Pd(H_2O)(TsO)](TsO)$. The rate data was obtained at different catalyst loading and partial pressures of ethylene and CO in a temperature range of 353 to 373 K. The rate data was interpreted in terms of activities of the monomers in solution instead of their partial pressures and the liquid phase concentrations. This aspect was in particular important since the copolymerization reaction involved two gaseous reactants with significant difference in their solubilities and more importantly, in their ideal behavior. Under the prevailing conditions, ethylene was expected to display a non-ideal behavior, which had to be considered while correlating the experimental data. The details of these studies are given in the following text.

2.2 Experimental

2.2.1 Materials

Palladium acetate [Pd (OAc) $_2$]; 1,3 Bis-(diphenylphosphino)propane [dppp]; *p*-Toluenesulphonic acid [TsOH] were purchased from Aldrich Chemicals (Milwaukee, WI, USA). Methanol (HPLC grade, water content 800 ppm) was purchased from SD Fine Chemicals (Mumbai, India). Carbon monoxide (99% stated purity) was supplied by Matheson Gas Company (Montgomery Ville, PA, USA) and ethylene was obtained from Specialty Gas (Mumbai, India). All chemicals were used as obtained without any further purification.

2.2.2 Analytical Measurements

The gas chromatographic analysis was performed on HP 5890 series gas chromatograph equipped with a thermal conductivity detector. The infrared spectrum was recorded on Bio-Rad FTS 175C instrument using KBr pellets. All NMR characterizations were carried out on Brucker 200 MHz instrument. Thermal analysis was performed on Metler Toledo–5 STAR thermal analyzer. Differential Scanning Calorimetric (DSC) analysis was performed on a Perkin-Elmer D100 DSC instrument.

2.2.3 Catalyst Preparation

The catalyst precursor [(dppp)Pd(H_2O)(TsO)](TsO), was prepared using a literature procedure [6]. Thus, 1,3-bis(diphenylphosphino)propane (dppp) (0.184 gm; 0.446 mmol) and Pd(OAc)$_2$ (0.100 gm; 0.446 mmol) were dissolved in 20 ml of methanol and the contents were stirred vigorously for 10 minutes. A yellow colored solution thus obtained was taken to dryness on rotavap at room temperature. The yellow solid obtained was washed with diethyl ether and dissolved in 25 ml of methanol and two equivalents of *p*-toluenesulphonic acid monohydrate (0.170 gm; 0.892 mmol) were added to this solution under vigorous stirring. The solution immediately turned deep yellow and after around 10 minutes to faint yellow. The contents were again taken to dryness at room temperature and the residue thus obtained was treated with *n*-hexane to give yellow microcrystalline particles of the catalyst in almost pure form. The overall yield of the complex was 0.2 gm (50%). The elemental analysis was in agreement with the calculated composition (calculated for $C_{41}H_{44}O_8P_2S_2Pd$). The catalyst was also characterized with ^1H NMR (Figure 2-1).

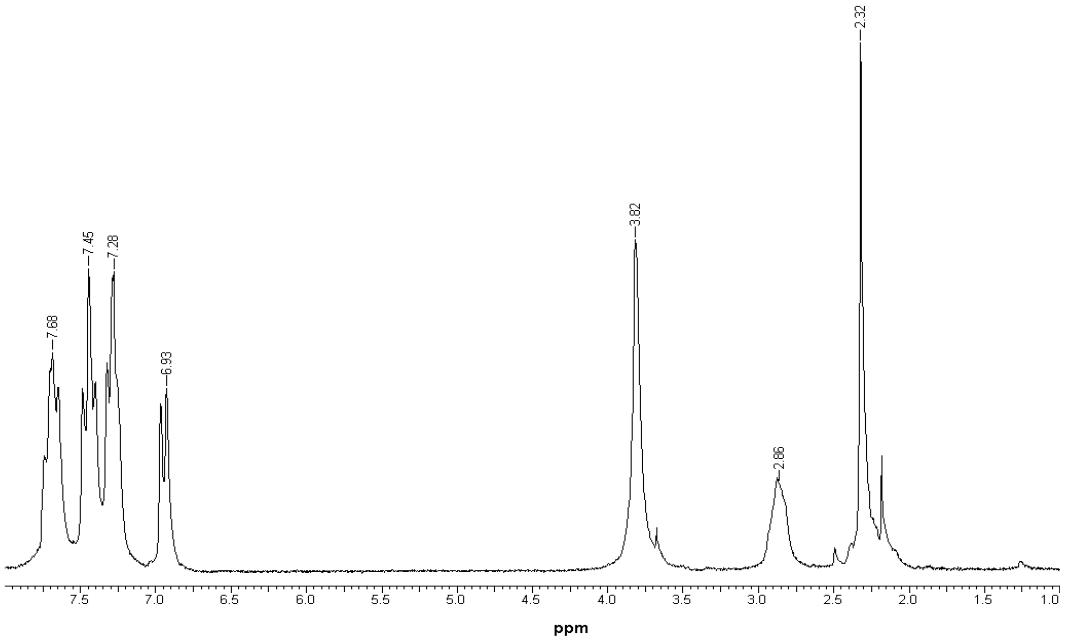


Figure 2-1. ^1H NMR Spectrum of the Catalyst [(dppp)Pd(H_2O)(TsO)](TsO) in $CDCl_3$

The ^{1}H NMR spectrum of the catalyst complex [(dppp)Pd(H_2O)(TsO)](TsO) in $CDCl_3$ (Figure 2-1) showed a singlet at δ 2.32 due to the CH_3 protons of the tosylate ligand. The signals at δ 2.86 and 3.82 were due to the PCH_2 and $–CH_2–$ protons in the dppp ligand respectively.

2.2.4 Solubility Measurement

The solubility of carbon monoxide and ethylene in methanol was measured using an absorption technique in a high-pressure stainless steel reactor of 300 cm^3 capacity (supplied by Parr Instruments Company, USA). The reactor was fitted with internal cooling coil and magnetically driven impeller with four-blade stirrer capable of operations up to 1500 rpm. Temperature of the liquid in the reactor was maintained at a desired level (with the precision of $\pm$ 1K) with the help of a PID controller, which provided alternate heating and cooling arrangement. The reactor was also equipped with internal thermocouple and digital pressure transducer (with a precision of ± 1 psig) for temperature and pressure monitoring respectively. The relevant safety equipment like rupture disc and high temperature-pressure cut off was installed as a part of the reactor setup.

In a typical experiment for solubility measurement, a known volume of methanol (100 cm^3) was charged into the reactor and the contents were heated to a desired temperature. After the thermal equilibrium was attained, the void space above the liquid was pressurized with the solute gas to a required level ($P_{initial}$). The contents were then vigorously stirred for 10 minutes to establish the gas-liquid equilibrium. As a precaution the stirring was continued further for another 30 minutes to ensure that the gas absorption had practically stopped. The final pressure in the reactor was recorded as P_{final}. From the initial and final pressure readings, the solubility of the gas was calculated as;

$$S = \frac{\left(P_{initial} - P_{final}\right)V_g}{RTV_L} \tag{2.1}$$

where,

S = Solubility of solute gas, $kmol/m^3$
P_{intial} = Initial pressure of solute gas, MPa
P_{final} = Final pressure of solute gas, MPa
V_g = Volume of gas, m^3
V_L = Volume of liquid, m^3
R = Gas constant
T = Absolute temperature, K

While calculating the solubility, it was assumed that under the equilibrium conditions the amount of dissolved gas in the liquid phase was negligible compared to the amount of solvent and therefore, there was practically no change in the liquid volume due to absorption. Following this procedure, the solubility of CO and ethylene in methanol was measured at different partial pressures and temperatures. The Henry's law constant, H, was calculated as,

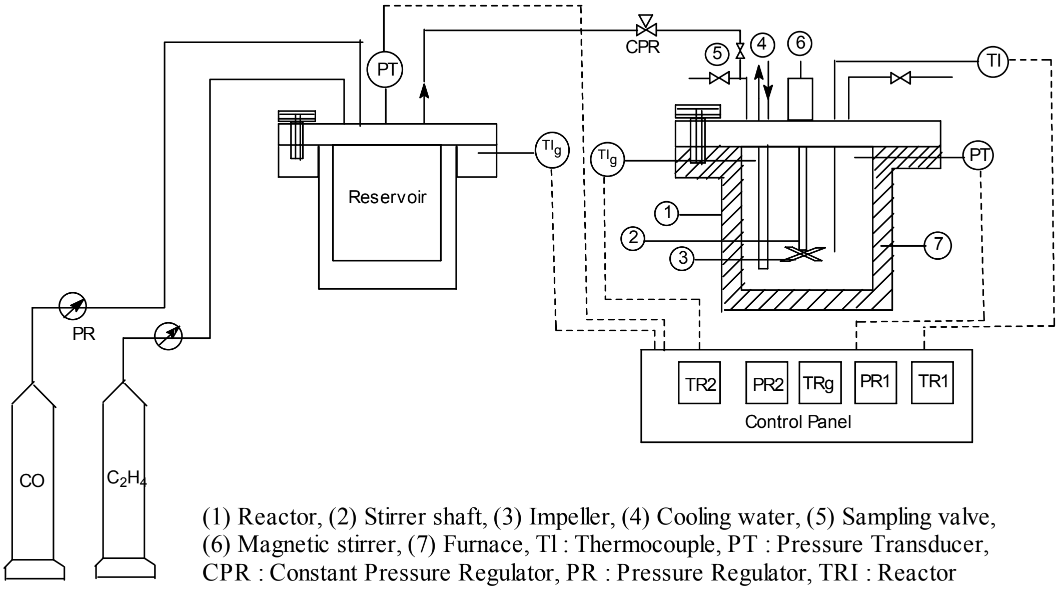
$$H = \frac{P_{final}}{S} \tag{2-2}$$

where, P_{final} represents the final equilibrium partial pressure of the solute gas. In order to ensure the accuracy of the experimental setup and the procedure, few initial results were compared with the literature data, which indicated an agreement within 5% error.

In order to measure the solubility of carbon monoxide and ethylene when present in mixtures, the above method was slightly modified. In a typical experiment, the individual gases were introduced into the reactor through separate inlet valves. The gas phase composition was then analyzed using HP 5890 series gas chromatograph. The solute gas mixture was then equilibrated with liquid as in the earlier case and final gas composition after equilibrium was also analyzed. From the initial and final gas compositions, the amount of individual gas absorbed in the solution was calculated. Using this method, the solubility of carbon monoxide and ethylene in presence of each other was measured at 363 K.

2.2.5 Kinetic Studies

The copolymerization reactions were carried out in a 300 cm^3 capacity stirred pressure autoclave. The details of the reactor set up are already discussed in the experimental section on solubility studies (Section 2.2.4). In order to monitor the progress of the reaction, the reaction was carried out at a constant pressure by a supply of the mixture of ethylene and CO in 1:1 ratio (stoichiometric) from a reservoir vessel through a constant pressure regulator valve. The schematic of the rector set-up used for the solubility and kinetic studies is given in Figure 2-2. In a typical experiment for kinetic study, 2.5 mg (3.5×10^{-5} kmol/m^3) of catalyst precursor was charged into the autoclave along with 80 ml of methanol.



(1) Reactor, (2) Stirrer shaft, (3) Impeller, (4) Cooling water, (5) Sampling valve, (6) Magnetic stirrer, (7) Furnace, Tl : Thermocouple, PT : Pressure Transducer, CPR : Constant Pressure Regulator, PR : Pressure Regulator, TRI : Reactor Temperature Indicator, TRG : Gas Temperature Indicator, PRI : Reactor Pressure Indicator, PR2 : Reservior Pressure Indicator, TR2 : Reservior Temperature Indicator.

Figure 2-2. Schematic of the Experimental Setup Used for Copolymerization Reactions

The reactor was then closed and degassed with nitrogen twice to ensure removal of any dissolved air and oxygen. The contents were then heated to the desired temperature under slow stirring. After the temperature was attained, ethylene was introduced in the reactor first and allowed to equilibrate at the desired pressure. This was then followed by introduction of carbon monoxide to the desired pressure level. The gas phase was then analyzed using a HP 5890 gas chromatograph equipped with thermal conductivity detector. The operating conditions for gas analysis were; column: Poropak-Q (10’×1/8”); carrier gas: hydrogen (30 ml/min); oven temperature: 313 K; injector temperature: 373 K; TCD temperature: 483 K.

The copolymerization reaction was continued at a constant pressure by supplying a mixture of ethylene and CO (1:1) from the reservoir using a constant pressure regulator. The pressure drop in the reservoir containing ethylene and CO mixture was measured as a function of time using a digital pressure transducer. The partial pressure of ethylene and CO in the reactor was maintained at the initial values by continuously supplying a mixture of ethylene and CO (1:1) through the reservoir vessel. The copolymerization was continued for one hour in each experiment. A final gas sample was taken for analysis after the reaction. After the reaction, the reactor was cooled to room temperature and unreacted gases were vent off. The polymer being insoluble in methanol was removed by simple filtration and dried under vacuum. Several experiments were carried out using this procedure at different initial conditions. The polymer (polyketone) was obtained as a white powder melting at 252°C. The polyketone polymer obtained was characterized using several spectral techniques as described below.

2.2.6 Polyketone Characterization

The typical infrared spectrum of the polyketone polymer produced during copolymerization is shown in Figure 2-3. It showed major absorption bands at 3000 and 1692 cm^{-1} corresponding to carbon-hydrogen stretch and carbonyl group. A strong absorption at 1692 cm^{-1} and a weaker harmonic at 3300 cm^{-1} in polyketone spectrum indicated the presence of carbonyl function. This abnormally low value for $\nu_{C=O}$, in comparison with the normal aliphatic ketones ($\approx$ 1715 cm^{-1}) has been attributed to the presence of intra and intermolecular dipole interactions between the carbonyl groups. The peaks corresponding to 1408 and 1335 cm^{-1} were characteristics of α–hydrogen structures and therefore were assigned to methylene structures adjacent to the carbonyl groups. The perfectly alternating nature of the prepared polyketone sample was further confirmed by the absence of the strongly absorbing doublet at 732 and 720 cm^{-1} (attributable to the presence of units consisting of more than four carbon atoms). This IR spectral data was consistent with the earlier literature report [7].

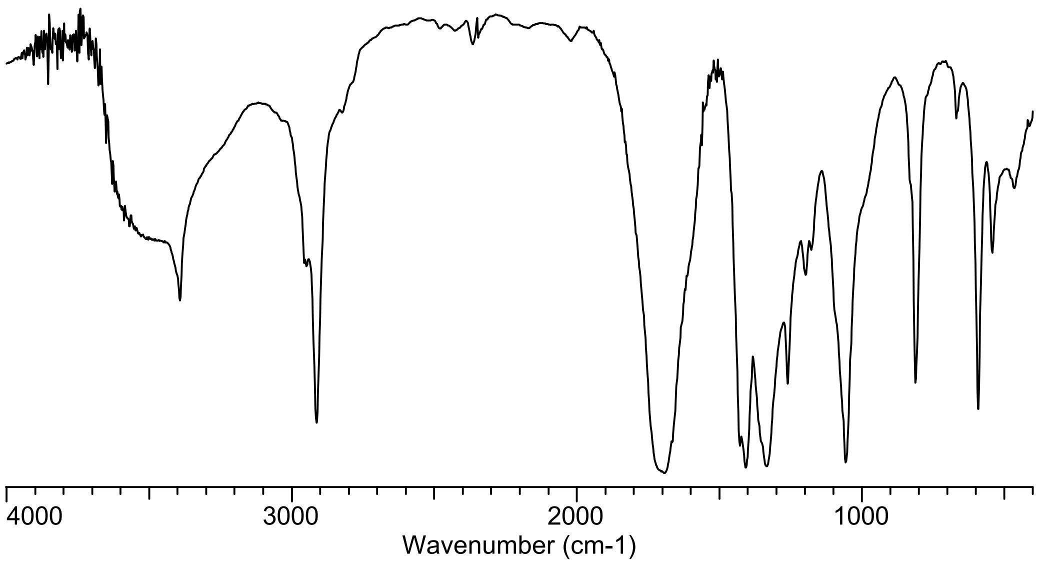


Figure 2-3. Infrared Spectrum of the Polyketone (KBr pellet)

The typical proton NMR spectrum of the polyketone in a mixture of hexafluorophenol and $CDCl_3$ (90:10 % v/v) is given in Figure 2-4. The methylene protons in the polyketone appear at δ 2.8. The peaks at δ 4-5 are due to solvent. The ^{13}C NMR of the polyketone (Figure 2-5) showed signals at δ 212.02 (carbonyl group) and δ 35.03 (methylene carbons). The observed NMR data was consistent with the literature reports [8].

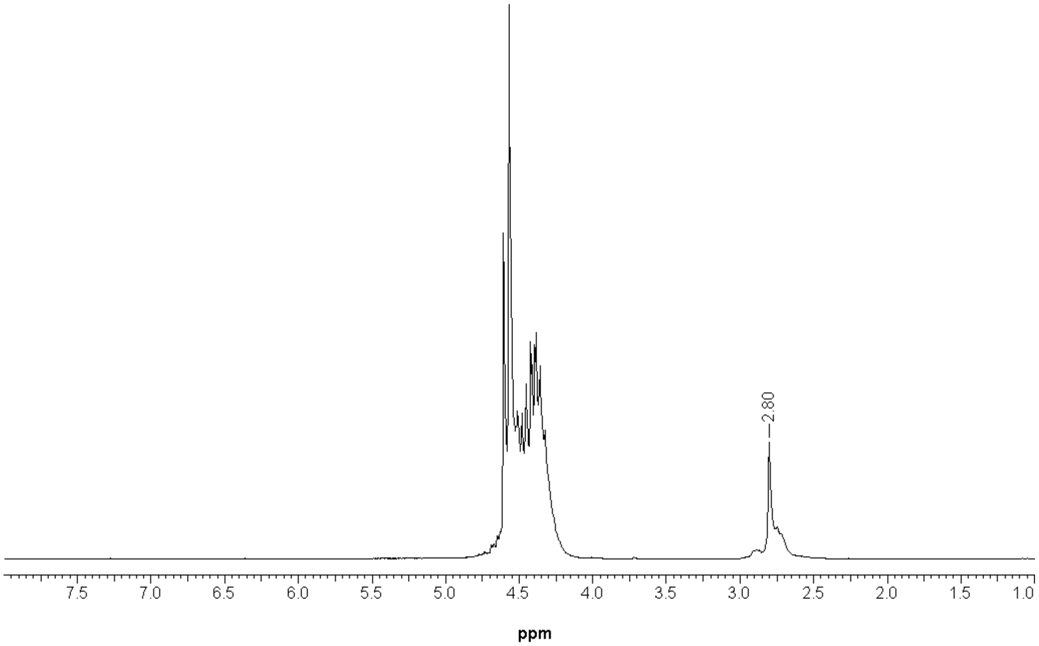


Figure 2.4. ^{1}H NMR of Polyketone (in a mixture of hexafluoroisopropanol and $CDCl_3$ (90:10 %v/v))

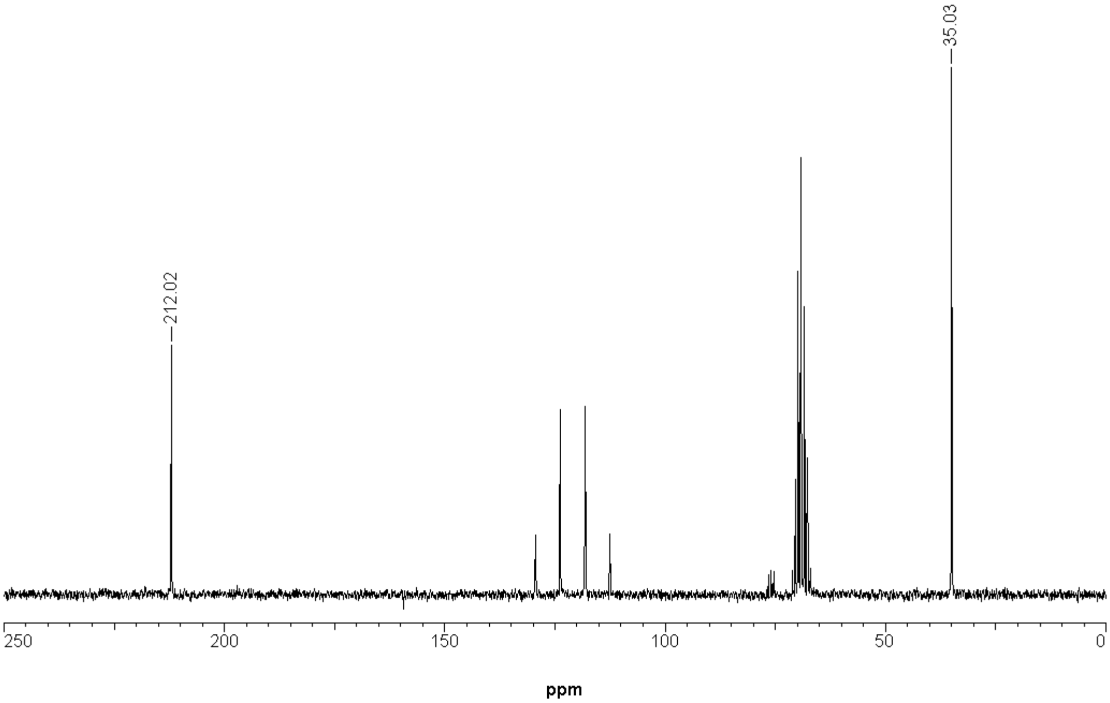


Figure 2.5. ^{13}C NMR of Polyketone (in a mixture of hexafluoroisopropanol and $CDCl_3$ (90:10 %v/v))

The typical DSC plot of the polyketone is given in Figure 2-6. The primary thermal transition in the polyketone polymer was the crystalline melting occurring at 253°C, with the heat of fusion of 129.4 J/g. The sample crystallizes at a crystallization temperature of 193^{o}C with heat of crystallization of 77.8 J/g.

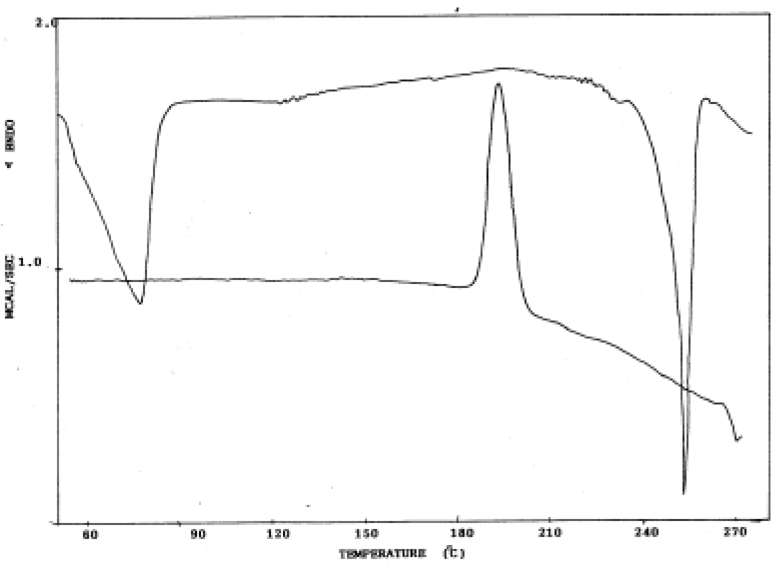


Figure 2-6. DSC Curve of Polyketone (heating rate 10 °C/min)

The thermo gravimetric analysis (TGA) of the prepared polyketone sample (Figure 2-7) indicated that the degradation started at about 290°C and was almost complete at 600°C.

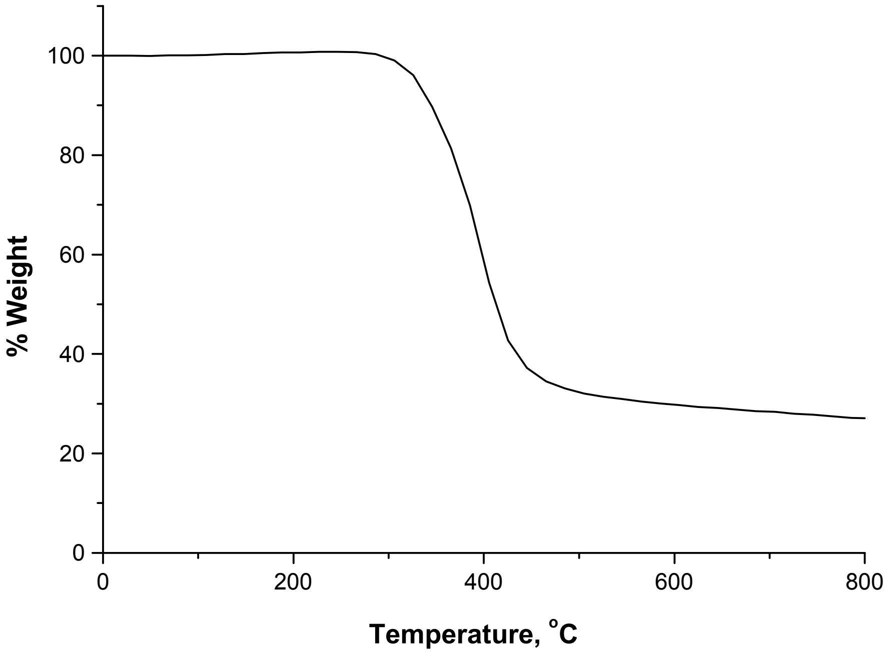


Figure 2-7. Thermo Gravimetric Analysis of Polyketone (in air, heating rate 10 °C/min).

2.3 Results and Discussion

2.3.1 Solubility Studies

The solubility data for CO and ethylene in methanol was determined in a temperature range of 353-373K and the results are presented in Tables 2-1 and 2-2 respectively. The solubility of both the gases were found to increase with increase in the partial pressure at all temperatures. The linear dependence of solubility on the partial pressure was in accordance with the Henry's law. It was further observed that the solubility of carbon monoxide increased with the temperature while that of ethylene decreased. Also, the solubility of ethylene in methanol was almost 10 times higher than that of carbon monoxide.

Table 2-1. Solubility of Carbon Monoxide in Methanol

353 K		***363 K***		***373 K***	
P, MPa	***S, kmol/m³***	***P, MPa***	***S, kmol/m³***	***P, MPa***	***S, kmol/m³***
0.660	*0.0069*	*0.867*	*0.0074*	*0.625*	*0.0045*
1.422	*0.0145*	*1.422*	*0.0157*	*1.252*	*0.0119*
1.914	*0.0185*	*2.014*	*0.0185*	*1.799*	*0.0189*
2.502	*0.0214*	*2.502*	*0.0209*	*2.057*	*0.0172*
2.800	*0.0250*	*2.773*	*0.0278*	*2.496*	*0.0267*
3.150	*0.0310*	*2.999*	*0.0293*	*2.770*	*0.0275*

Table 2-2. Solubility of Ethylene in Methanol

353 K		***363 K***		***373 K***	
P, Mpa	***S, kmol/m³***	***P, MPa***	***S, kmol/m³***	***P, MPa***	***S, kmol/m³***
0.465	*0.0275*	*0.488*	*0.0250*	*0.502*	*0.0265*
1.010	*0.0469*	*0.857*	*0.0392*	*0.607*	*0.0263*
1.554	*0.0718*	*1.424*	*0.0666*	*1.325*	*0.0572*
1.810	*0.0908*	*1.918*	*0.0871*	*1.813*	*0.0781*
2.565	*0.1281*	*2.450*	*0.1031*	*2.445*	*0.0956*
2.937	*0.1449*	*2.537*	*0.1039*	*2.612*	*0.1058*

The values of Henry's constant calculated from the above data using equation 2-2 are given in Table 2-3.

Table 2-3. Experimental Henry's Constants

Temperature, K	***H, MPa/(kmol/m³)***	
	Carbon Monoxide	*Ethylene*
353	*10.70*	*2.03*
363	*10.51*	*2.32*
373	*10.13*	*2.46*

The enthalpy (ΔH_s) and entropy (ΔS_s) of the solution for the dissolution of these gases were determined using the following equations [9].

$$\left[\frac{\partial \ln x}{\partial (1/T)}\right]_P = \left(-\frac{\Delta H_S}{R}\right) \tag{2-3}$$

Equation 2-3 on rearrangement gives,

$$\ln x = -\frac{\Delta\ H_S}{RT} + \frac{\Delta S_S}{R} \tag{2-4}$$

where, x is the mole fraction of the solute gas in the liquid phase. In equation (2-4), the solubility (as a mole fraction) of the solute gas is expressed as a function of temperature using a two-constant equation. Thus, a plot of *ln x* versus $1/T$ gives a straight line with slope equal to ($-\Delta H_s/R$) and intercept equal to ($\Delta S_s/R$). The results of these thermodynamic quantities (ΔH_s and ΔS_s) as obtained by the linear regression are given in Table 2-4. The dissolution of ethylene was found to be an exothermic process, consistent with the observation that the solubility of ethylene decreases with increase in the temperature.

Table 2-4. Enthalpy and Entropy for Dissolution of CO and Ethylene in Methanol

Gas	***ΔH_S, kJ/mol***	***$\Delta S_S \times 10^2$, kJ/mol***
Carbon Monoxide	*0.736*	*- 6.30*
Ethylene	*- 21.34*	*- 11.00*

Since, ethylene is almost 10 times more soluble than carbon monoxide, the nature of the solvent is expected to change, which can influence the solubility of other gaseous components. The highly soluble gas (ethylene in the present case) acts as a second solvent (in addition to methanol in the present case) for the less soluble gas (CO). In view of this, it was essential to study the effect of presence of the ethylene on the solubility of carbon monoxide. Indeed the solubility of carbon monoxide was found to be enhanced, although marginally, in the presence of ethylene gas. The results presented in Figure 2-8 indicate that the solubility of CO increases with increase in the ethylene mole fraction.

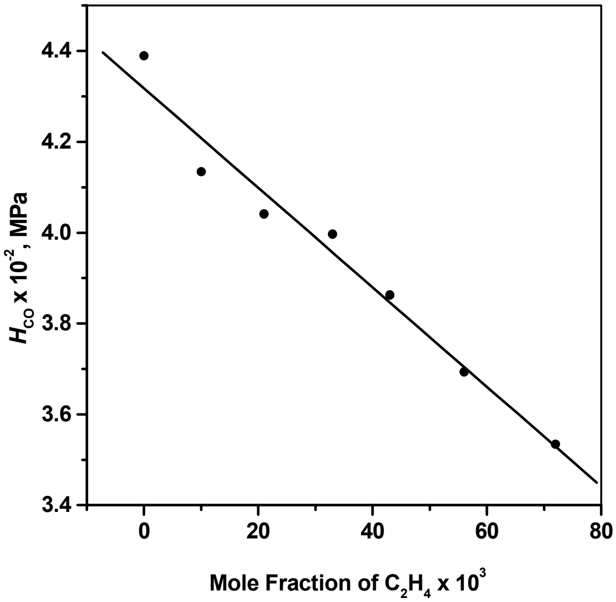


Figure 2-8. Enhancement in the Solubility of CO in Presence of Ethylene

2.3.2 Kinetic Studies

As mentioned earlier, the kinetics of the copolymerization of ethylene with CO was investigated using a preformed palladium catalyst precursor, [(dppp)Pd(H_2O)(TsO)](TsO). This catalyst was similar to those previously reported for this reaction and had comparable activity (~ 6000 gm polymer/gm Pd/h) especially to those reported by Shell [10]. We preferred to use this well-defined, preformed catalyst precursor in order to obtain consistent and reproducible rate data in kinetic studies. Further, this catalyst was stable at the reaction conditions, as observed during preliminary runs which indicated that the copolymerization rate was constant over the reaction time (Figure 2-9) and also from the absence of any palladium black in the after reaction products.

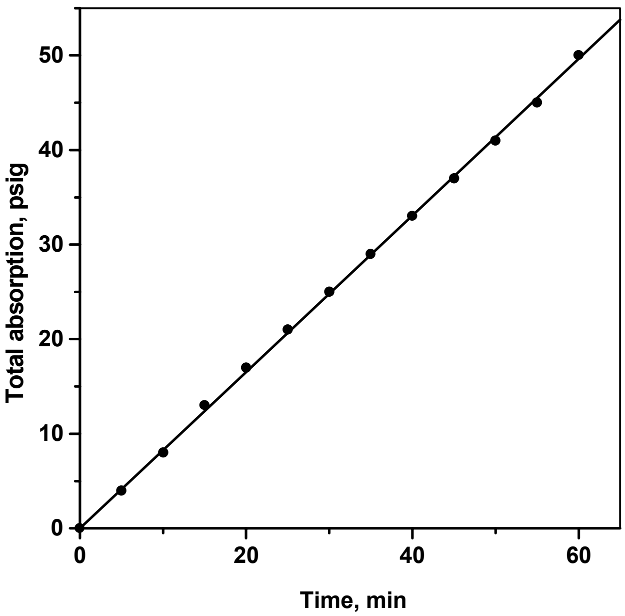


Figure 2-9. Typical Absorption Profile During the Copolymerization Reaction
Reaction conditions. *catalyst: 3.5×10^{-5} kmol/m³; P_{CO}: 1 MPa; P_{C2H4}: 1 MPa; methanol: 80 $\times 10^{-6}$ m³; agitation speed: 900 rpm; temperature: 353 K.*

In a few preliminary experiments, the amount of polyketone formed was compared with the consumed ethylene and CO, which indicated almost stoichiometric material balance. Liquid phase analysis by gas chromatography showed absence of any other carbonylation products in appreciable amounts. This confirmed that the copolymerization reaction was highly selective. Therefore, initial rate data were calculated from the observed ethylene or CO consumption *vs* time profiles. The range of conditions employed in the present study is given in Table 2-5.

Table 2-5. Range of Conditions Used for Kinetic Studies

Temperature, K	*353 – 373*
Catalyst loading, kmol/m^3	3.5×10^{-5} - 1.4×10^{-4}
CO partial pressure, MPa	*1 – 3*
C_2H_4 *partial pressure, MPa*	*1 – 3*
Total reaction pressure, MPa	*1– 6*
Agitation, rpm	*600 – 900*

2.3.2.1 Analysis of Mass Transfer Effects

For the evaluation of rate equations and determination of intrinsic kinetic parameters, it was necessary to ensure that mass transfer did not limit the reaction. For the reaction under consideration, it should be pointed out that, as the reaction proceeds, the polymer precipitates, since it is insoluble in methanol. The growing chain remains bound to the catalytic metal centre till the termination step. However, it is not certain whether the catalyst can be considered as a solid catalyst (heterogeneous catalyst), or as a homogeneous catalyst system in soluble form with product precipitating. Between these two extreme cases, palladium may be bound to a colloidal-type growing chain. In case the catalyst acts as a heterogeneous system, we have to consider also the liquid-solid and intraparticle diffusion effects. At the present stage, it is not well understood whether the reaction occurs entirely in homogeneous or heterogeneous mode and hence some observed trends discussed to assess the mass transfer effects.

The gas-liquid mass transfer step is common to both homogeneous and heterogeneous gas-liquid reactions, and to determine the significance of this step, the effect of agitation frequency on the rate of co-polymerization was studied. The results presented in Figure 2-10 for different temperatures, clearly indicated that the copolymerization rate was independent of agitation frequency above 700 rpm and hence, the reaction could be considered to operate under kinetic control.

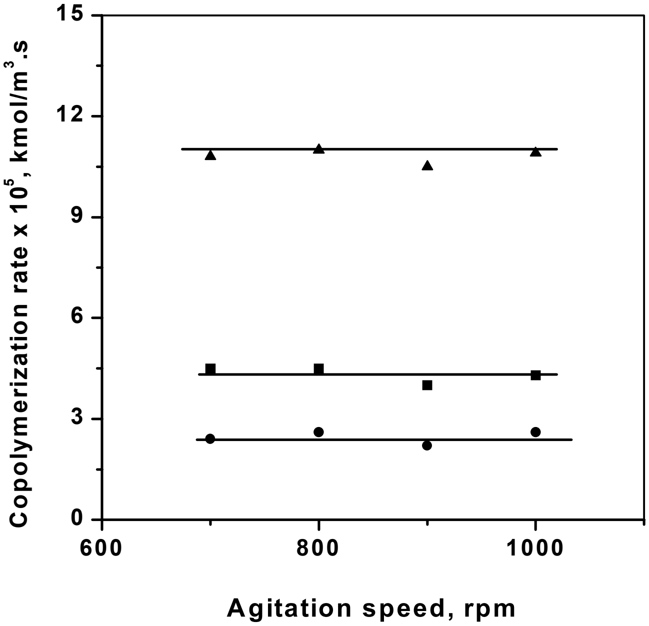


Figure 2-10. Effect of Agitation Frequency on the Copolymerization Rate. ***Reaction conditions***. *catalyst: 3.5 × 10^{-5}, kmol/m^3; P_{CO}: 1 MPa; $P_{C_2H_4}$: 1 MPa; methanol: 80 × 10^{-6} m^3; agitation speed: 900 rpm. Temperature: (●) 353 K; (■) 363 K; (▲) 373 K.*

These observations also indicated the absence of external mass transfer limitations such as liquid to solid mass transfer applicable for a heterogeneous reaction. In order to further confirm the kinetic control, a quantitative criterion described by Chaudhari and Doraiswamy [11] was used according to which, the maximum reaction rates were compared with the maximum rates of gas to liquid mass transfer under the prevailing conditions. Thus, the factors α_A and α_B defined as;

$$\alpha_A = \frac{R_A}{k_L a_B A^*} \quad \text{and} \quad \alpha_B = \frac{R_A}{k_L a_B B^*}$$

respectively were evaluated for all the rate data at different temperatures. This required knowledge of solubility and gas-liquid mass transfer coefficient. The solubility data for ethylene and CO taken from the earlier results (Section 2.3.1), while k_La_B values were evaluated from a correlation proposed by Chaudhari et al. for equipment similar to that used in the present work [12]. These values are given in Table 2-6.

Table 2-6. Experimental Values of α_A and α_B

Temperature, *K*	α_A	α_B
353	2.75×10^{-3}	5.52×10^{-4}
363	3.72×10^{-3}	1.71×10^{-3}
373	1.04×10^{-2}	2.39×10^{-3}

The values of α_A and α_B were found to be in ranges 2.75×10^{-3} to 1.04×10^{-2} and 5.52×10^{-4} to 2.39×10^{-3} respectively, which clearly indicated that the gas to liquid mass transfer did not limit the reaction.

The copolymerization reaction also involved precipitation of solid product as the reaction progressed, and therefore, it was important to understand whether the reaction occurred in the liquid phase or shifted to the solid particle. In one possibility, the growing polymer chain could remain bound to the catalytic metal center until termination, and hence, the reaction could be considered heterogeneous. On the other hand, if the polymer remained soluble while growing and precipitated only after the termination step, the catalytic reaction could be considered as homogeneous. Because the particle size of the polymer as observed by SEM analysis was is in the range of 5 to 30 μm, the complexities of liquid-solid and intra-particle mass transfer would be expected to be negligible. Also, the observation of a constant rate of copolymerization over an hour or so indicated that precipitation of the polymer has no significant influence on the controlling regime in the initial period of reaction that was used for initial rate calculations.

Finally, it was also important to note that the precipitated polymer formed slurry as the reaction proceeded and the concentration of solid particles in the slurry increased. But reaction conditions were so chosen that the total solid content in the reactor was never more than 10% by weight of the slurry. Under these conditions the effect of suspended particles on the mass transfer may be safely neglected.

2.3.2.2 Effect of Catalyst Loading

The effect of catalyst loading on the copolymerization rate was studied at different temperatures in the range of 2.5 to 10 mg (3.5×10^{-5} - 1.4×10^{-4} kmol/m^3). In these experiments partial pressure of ethylene and carbon monoxide was kept constant (1 MPa). The copolymerization rate was found to increase linearly with increase in catalyst loading (Figure 2-11), which also supported the conclusion that the reaction was operating under the kinetic regime. The increase in the copolymerization rate could be because of the increase in the catalyst concentration and in turn in the concentration of active catalytic species. Further, a linear dependence of copolymerization rate with respect to the catalyst loading indicates that the external gas-liquid mass transfer might not be significant.

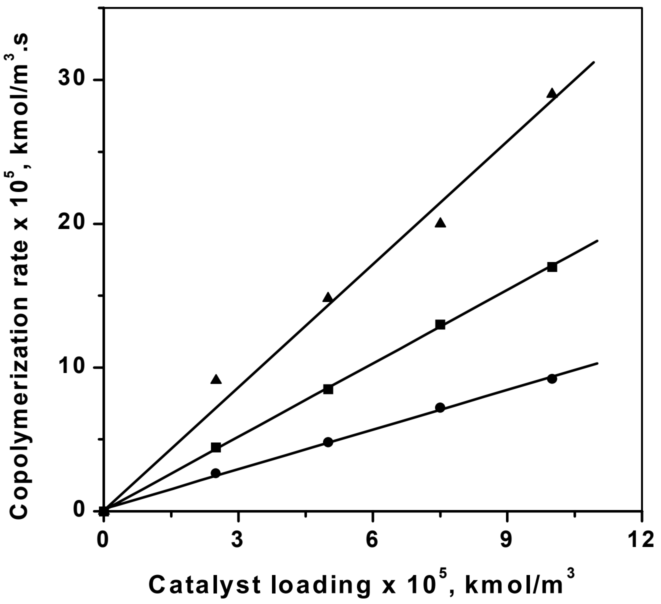


Figure 2-11. Effect of Catalyst Loading on the Copolymerization Rate
Reaction conditions. *P_{CO}: 1 MPa; P_{C2H4}: 1 MPa; methanol: 80 × 10^{-6} m^3; agitation speed: 900 rpm. Temperature: (●) 353 K; (■) 363 K; (▲) 373 K*

2.3.2.3 Effect of Ethylene Partial Pressure

The effect of ethylene partial pressure on the co-polymerization was investigated at 353-373 K and total pressure of 1-6 MPa (Figure 2-12). The rate of co-polymerization increased almost linearly with the ethylene partial pressure with an approximate order of 0.72. The observed rate dependency could be probably because of the increase in the local concentration of ethylene in the bulk liquid and consequently around the palladium center at higher ethylene pressures.

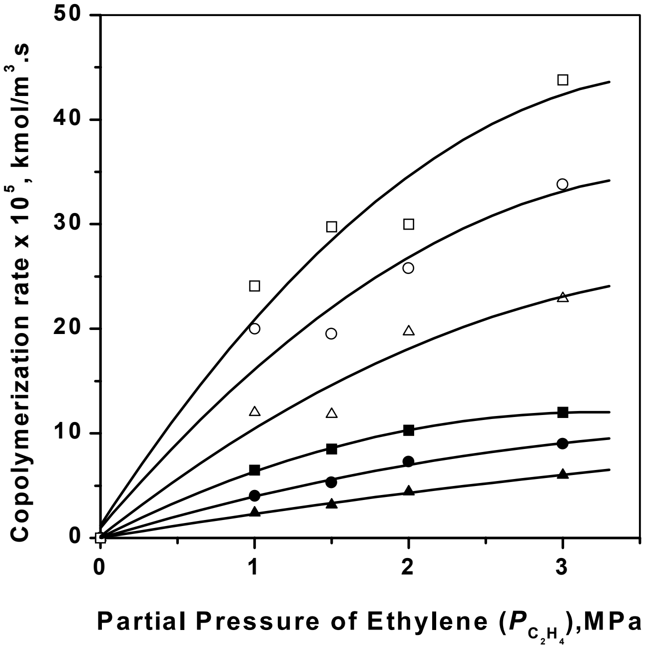


Figure 2-12. Effect of Ethylene Pressure on the Copolymerization Rate.

***Reaction conditions**. catalyst: 3.5 × 10^{-5} kmol/m^3; methanol: 80 × 10^{-6} m^3; agitation speed: 900 rpm; temperature: 353 K. (▲) P_{CO}: 1 MPa; (●) P_{CO} : 2 MPa ; (■)P_{CO} : 3 MPa . Open symbols represent the corresponding data at 373 K*

2.3.2.4 Effect of CO partial pressure

The effect of CO partial pressure on co-polymerization rate was studied at 353 – 373 K in a CO partial pressure range of 1 - 3 MPa (Figure 2-13). In these experiments ethylene pressure and catalyst concentration were kept constant. The rate of copolymerization increases almost linearly with the increasing CO partial pressure with an approximate order of 0.63.

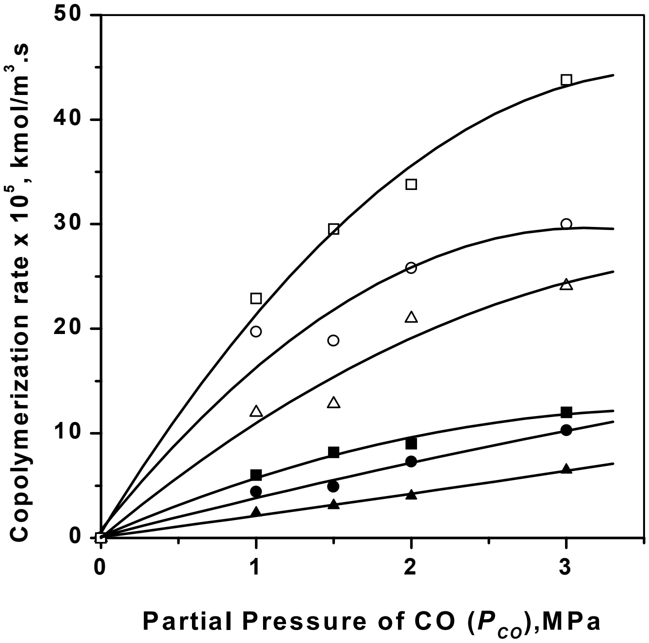


Figure 2-13. Effect of CO Pressure on the Copolymerization Rate

***Reaction conditions**. catalyst: 3.5 × 10^{-5} kmol/m^3; methanol: 80 × 10^{-6} m^3; agitation speed: 900 rpm; temperature: 353K. (▲) P_{C2H4}: 1 MPa; (●) P_{C2H4}: 2 MPa; (■)P_{C2H4}: 3 MPa . Open symbols represent the corresponding data at 373 K.*

2.3.2.5 Effect of Total Reaction Pressure

The effect of total pressure on the copolymerization rate was investigated at 353K and 373K. In all these experiments, the gas phase composition was maintained at 1:1 ratio of ethylene and CO. As in earlier experiments, the copolymerization reactor was fed with 1:1 mixture of CO and ethylene from the reservoir. The copolymerization rate was found to increase with increase in the total pressure at all temperatures under investigations as shown in Figure 2-14.

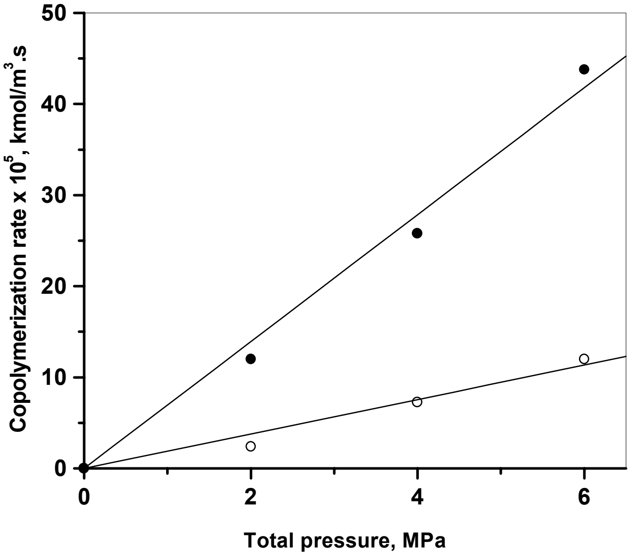


Figure 2-14. Effect of Total Reaction pressure on the Copolymerization Rate ***Reaction conditions***. *catalyst: 3.5 × 10^{-5} kmol/m^3; methanol: 80 × 10^{-6} m^3; agitation speed: 900 rpm. Temperature: (○) 353 K (●) 373 K.*

2.4 Kinetic Modeling

2.4.1 Mechanism and Rate Equations

It is now established that the palladium catalyzed co-polymerization of ethylene with carbon monoxide proceeds without double insertion of any monomer leading to a perfectly alternating copolymer [13]. The double insertion of carbon monoxide is not observed because of thermodynamics reasons. While double ethylene insertion is thermodynamically possible, it does not occur because of difference in the binding affinity of CO and ethylene with palladium center (kinetic control). Carbon monoxide has higher binding affinity for the palladium center and therefore binds rapidly compared to ethylene. The local concentration of CO is thus always in excess around the palladium center and the vacant sites around the palladium are completely but reversibly occupied by CO. Since the double insertion of CO into Pd-acyl species is not thermodynamically favored it has to be the ethylene that will be inserted in the Pd-acyl bond to give a Pd-alkyl species. The vacant site thus created is competitively occupied by carbon monoxide because of high affinity. It is also documented that CO inserts faster than olefin. This prevents the double ethylene insertion. Two different mechanisms can be proposed after careful study of the geometry around the palladium center coupled with the above evidences [5]. In one site model, the palladium atom is in more common four-coordinate state (Figure 2-15).

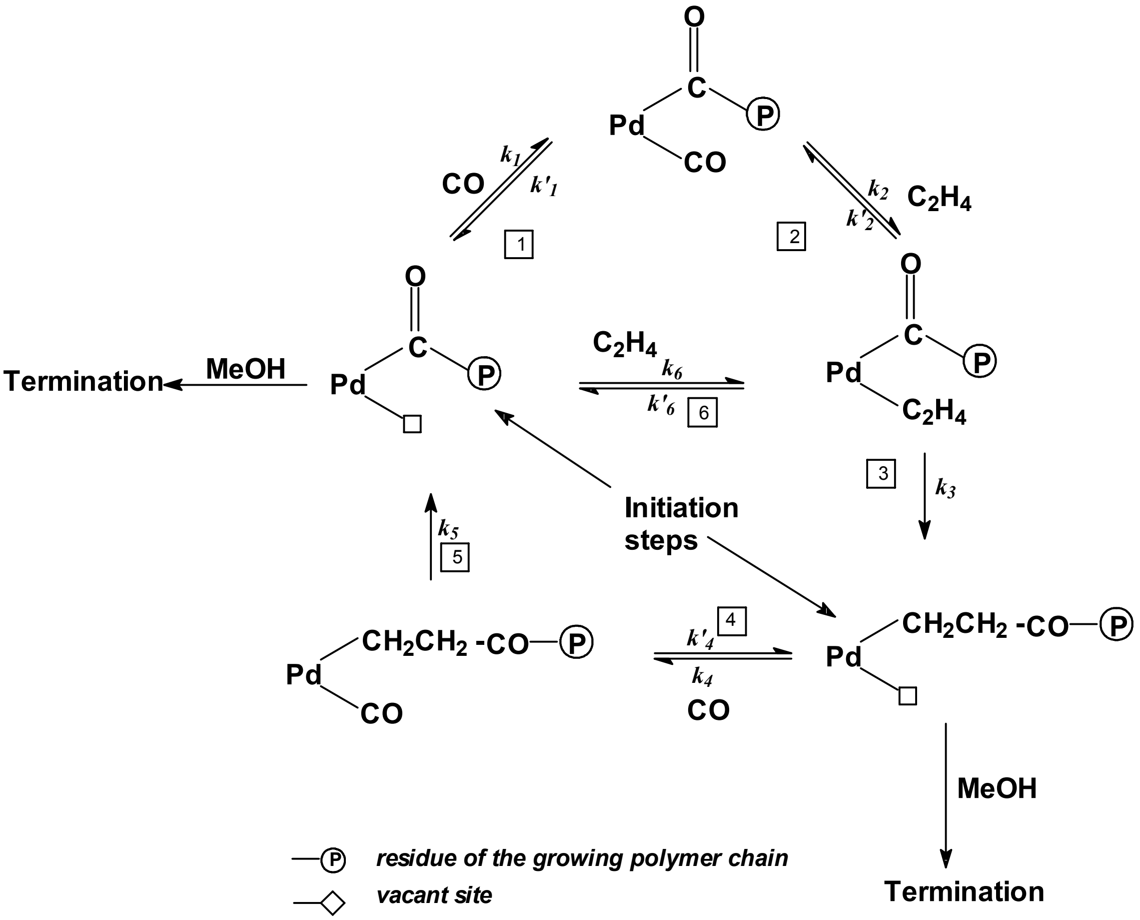
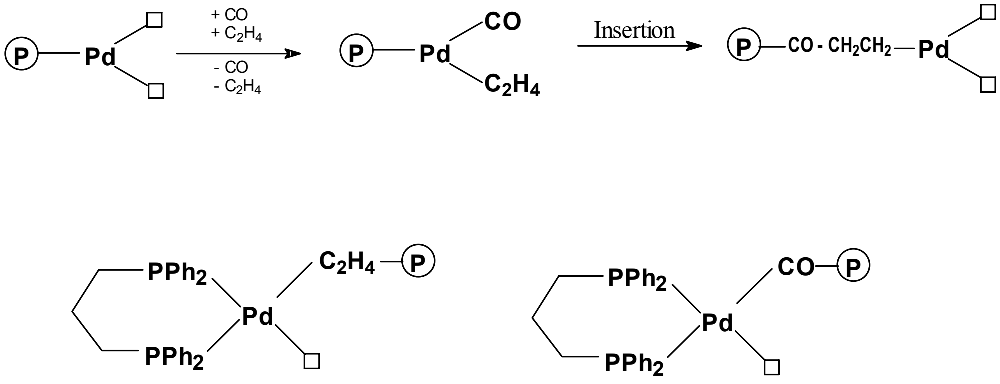


Figure 2-15. Proposed Mechanism for One-Site Models

Of the four available sites, two sites are occupied by the chelating diphosphine and one by the growing polymer chain. The remaining fourth site can be occupied by any of the weakly coordinating anion, methanol, ethylene or CO. In a typical chain growth sequence this fourth site is occupied by any of the monomers i.e. ethylene or CO. The insertion of this co-ordinated monomer into the growing polymer chain vacates this site again, which is again occupied by the monomer resulting in chain growth. In the two-site mechanism (Figure 2-16), the palladium center is in less common five coordinated state. Of these five sites, two sites are occupied by chelating diphosphine, one by the growing polymer chain and the remaining two sites are available for the coordination by the monomers. A particular case, applicable for both the models, in which the vacant site is occupied by the solvent molecule i.e. methanol, leads to the termination of the chain growth.



Intermediate - I

Intermediate - II

Figure 2-16. Proposed Mechanism for Two Site Models

Both the mechanisms were considered in this study. The kinetic equations were derived by assuming different rate-determining steps. The set of rate equations obtained thus is given in Table 2-7 [5].

Table 2-7. Rate Equations and Proposed Mechanisms [5]

Model	***Rate equation***	***Proposed mechanism***
	Two Site Models	
I	$r_{pol} = \dfrac{k_r K_{CO} K_{et} AB}{(1 + K_{CO}A)(1 + K_{et}B)}$	The two sites on Pd atom are non-equivalent and one can coordinate to only CO and the other to only ethylene. The rate determining step is the insertion of one monomer from an intermediate I
II	$r_{pol} = \dfrac{k_r K_{CO} K_{et} AB}{(1 + K_{CO}A + K_{et}B)^2}$	The two sites in Pd atoms are equivalent and can be occupied by any of the monomers. The rate-limiting step is the insertion of one monomer from an intermediate in which both the sites are occupied.
III	$r_{pol} = \dfrac{k_r K_{CO} K'_{et}\, AB}{(1 + K_{CO}A + K_{et}B)(1 + K'_{CO}\, A + K'_{et}\, B)}$	The two sites on the Pd atom are non-equivalent but can be occupied by any of the monomers. The rate-limiting step is the insertion of one monomer from an intermediate in which both the sites are occupied by the monomers.

	One Site Models	
IV	$r_{pol} = \dfrac{k_2 k_4 K_1 AB[Pd]}{k_4 + k_4 K_1 A + k_2 K_1 B}$	CO rapidly occupies the free sites on the Pd atom and the rate-limiting step is reaction 2 in the Figure 10. Reactions 3 and 5 are very fast making steps 2 and 4 practically irreversible.
V	$r_{pol} = \dfrac{k_3 k_4 K_6 AB[Pd]}{k_4 A + k_4 K_6 AB + k_3 K_6 B}$	On the intermediates I and II, the sites are non-equivalent and therefore one site can coordinate to only CO and the other to ethylene. The rate-determining step is reaction 3.
VI	$r_{pol} = \dfrac{k_5 k_6 K_4 AB[Pd]}{k_6 B + k_6 K_4 AB + k_5 K_4 A}$	As in equation V, but the only difference here is that the rate-determining step is reaction 5.
VII	$r_{pol} = \dfrac{k_3 k_4 K_6 AB[Pd]}{k_4 A + k_4 K_6 AB + k_3 K_6 B + k_4 K_1 A^2}$	As in equation V but here the CO can occupy both the sites.
VIII	$r_{pol} = k_r A^l B^m$	Empirical power law equation used to calculate the order of the copolymerization reaction.

Equations I-III are based on "two-site mechanism " while the remaining (IV-VII) are based on “one-site” mechanism. Equation VIII is an empirical power law equation used to note the dependence of copolymerization rate on the monomer concentrations. The derived rate equations along with the proposed mechanistic details are given in Table 2-7. In each case, A represents the activity of the ethylene and B represents the activity of the carbon monoxide in methanol.

2.4.2 Kinetic Parameters and Model Discrimination

Each kinetic model given in Table 2-7 contains a set of kinetic constants, which were to be estimated using the observed experimental data on copolymerization rate (r_{pol}) as a function of monomer concentration, temperature etc. The liquid phase concentration of carbon monoxide and ethylene was calculated by means of Henry's law. In order to account for any non-ideal behavior because of the presence of the activity was corrected using Krichevsky-Kasarnovsky [14] correlation as the ratio of partial pressure and the Henry's constant as

$$f_i = a_i H_{i,j} = \gamma_i c_i H_{i,j}^{0} e^{\left(\frac{V_i^{\infty} (P_{Total} - P_j^{0}}{RT} \right)} \tag{2-5}$$

where, f_i and a_i represent the fugacity and activity of the solute gas respectively. $H^0_{i,j}$ is the value of Henry's constant at P^0_j = 1 atm. V_i is the molar volume of the gas, P_{Total} is the pressure of the system, and P^0_j is the vapor pressure of the solvent. As the value of (P_{Total} - P^0_j) tends to zero, the system becomes ideal and the activity coefficient tends to unity. Equation (2-5) can be rearranged as:

$$\ln\left(\frac{f_i}{a_i}\right) = \ln H^0{}_{i,j} + \frac{Vi\left(P_{Total} - P^0{}_j\right)}{RT} \tag{2-6}$$

Thus, the value of $H^0{}_{i,j}$ can be calculated from the intercept of the graph of $ln\ (f_j/a_j)$ versus $(P_{\mathrm{Total}} - P^0{}_j)$. The fugacity and activity values for the pure gases were calculated using the Redlich-Kwong equation of state [15]. Since no mass transfer limitations were found, the species concentration in the bulk liquid phase was assumed to be uniform. The calculated fugacity values are compared with observed pressures in Table 2-8.

Table 2-8. Fugacity Values for CO and Ethylene at Various Temperatures

P, atm	*353 K*		*373 K*	
	f_{CO}, *atm*	f_{C2H4}, *atm*	f_{CO}, *atm*	f_{C2H4}, *atm*
9.869	*9.863*	*10.244*	*9.875*	*10.08*
14.804	*14.787*	*14.971*	*14.812*	*14.817*
19.738	*19.706*	*19.457*	*19.746*	*19.366*
24.673	*24.623*	*23.719*	*24.682*	*23.789*
29.606	*29.536*	*27.773*	*29.619*	*27.945*

In order to estimate the kinetic constants, the individual rate equation was subjected to a non-linear regression analysis using an optimization routine based on Marquard's method [16]. The objective function was chosen as follows:

$$\Phi = \sum_{i=1}^{n} (r_{exp} - r_{mod})_i^{2} \qquad (2.7)$$

The value of ϕ is because of *"lack of fit"* of the kinetic model used. The non-linear regression analysis was performed to estimate the kinetic constants such that the objective function ϕ has the minimum value. The values of the kinetic constants obtained using optimization program for two-site and one-site models are given in Tables 2-9 and 2-10 respectively.

Table 2.9 Kinetic Parameters for Two Site Models

Rate model	***Temp.*** (K)	k_r (kmol/m³.s)	K_{co} (m³ / kmol)	K_{et} (m³ / kmol)	K'_{co} (m³ / kmol)	K'_{et} (m³ / kmol)	ϕ_{min}
I	353	1.473×10^{-3}	1.494	0.337			1.038×10^{-8}
	363	1.590×10^{-3}	2.874	0.526			3.385×10^{-10}
	373	2.159×10^{-3}	3.101	0.651			6.419×10^{-10}
II	353	6.149×10^{-3}	0.731	0.164			6.657×10^{-10}
	363	6.510×10^{-3}	1.301	0.281			3.340×10^{-10}
	373	9.348×10^{-3}	1.482	0.304			1.140×10^{-8}
III	353	7.028×10^{-4}	-2.544	0.375	7.560	-0.413	4.041×10^{-10}
	363	2.415×10^{-3}	1.81×10^{-3}	0.0493	2.935	2.88×10^{-2}	3.385×10^{-10}
	373	8.859×10^{-3}	-1.882	6.986	1.595	-0.545	6.026×10^{-9}

Table 2.10 Kinetic Parameters for One Site Models

Rate model	Temp. (K)	K_1 ($m^3/kmol$)	K_2 ($m^3kmol.s$)	k_3 (s^{-1})	k_4 ($m^3kmol.s$)	K_4 (m^3kmol)	k_5 (s^{-1})	k_6 (m^3kmol)	K_6 ($m^3/kmol$)	ϕ_{min}
IV	353	1.974	11.334		51.203					6.837 x 10^{-10}
	363	5.049	18.184		94.689					3.301 x 10^{-10}
	373	6.240	26.546		128.139					1.444 x 10^{-8}
V	353			-5.666	16.116				-0.612	1.231 x 10^{-9}
	363			3040.6	45.448				4.81 x 10^{-3}	5.793 x 10^{-10}
	373			-41.843	73.964				-0.371	1.462 x 10^{-8}
VI	353					-0.613	- 5.665	16.658		1.231 x 10^{-9}
	363					0.00477	9526.2	14.607		5.787 x 10^{-10}
	373					-0.373	-41.843	73.960		1.462 x 10^{-8}
VII	353	-1.269		15.465	0.101			0.093		5.836 x 10^{-10}
	363	2.6 x 10^{-6}		5.410	2.000			4.788		1.602 x 10^{-8}
	373	-0.042		40.950	262.295			0.183		9.689 x 10^{-9}

Since magnitude of Φ value for all the models was more or less the same, model discrimination was necessary. The models were therefore tested by two other methods.

(a) Thermo-dynamical constraints

(b) Residual analysis

(a) Thermo-dynamical Analysis

Since the analysis of the experimental data is performed purely on the mathematical basis it does not account for the thermodynamic significance of the kinetic constants. Thus according to these criteria, the values for the kinetic constants have to satisfy few conditions, which are derived from the thermodynamic considerations [16] as summarized below.

Rule 1: $k > 0$ (k should be a positive value)

Rule 2: $E_a > 0$ (energy of activation should be positive)

Since models III, V, VI and VII have negative values for some of the k, these were rejected following the first rule. The models I, II and IV had all positive constants and therefore these had to be discriminated further. The activation energy for individual models was calculated using the Arrhenius plots (Figure 2-17) and the results are presented in Table 2-11.

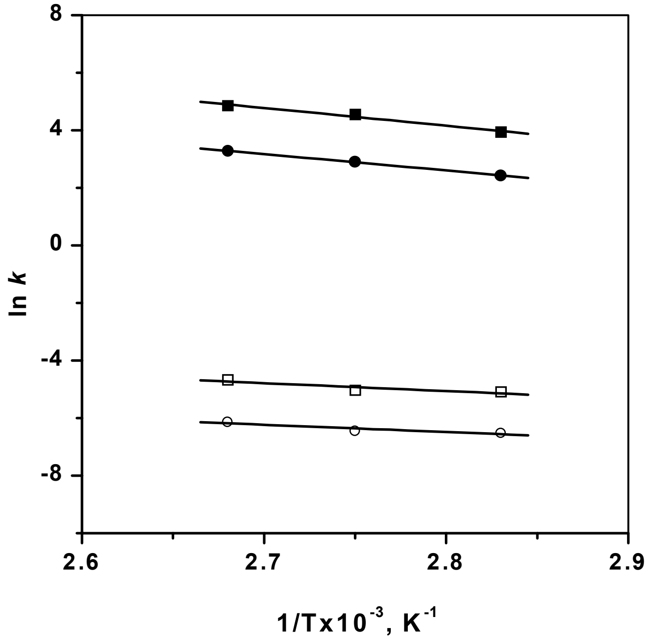


Figure 2-17. Arrhenius Plots: *(○) k_r in model II, (●) k_2 in model IV, (□) k_r in model I, and (■) k_4 in model IV.*

Table 2-11. Activation Energies Calculated for Different Rate Models

Model	*k used*	*E_{act} (kJ/mol)*
I	k_r	*20.82*
II	k_r	*22.78*
IV	K_2	*47.04*
IV	K_4	*50.99*

The energy of activation for a kinetic reaction, for the one like under present discussion, is in the region 40-80 kJ/mole. This criterion was therefore used in the further discrimination of the models I, II and IV. Since the value of the calculated apparent energy of activation using model I and II is much lesser than that observed for a typical kinetic reaction which is not mass transfer limited, these models can be rejected. The energy of activation calculated using Model- IV is in better agreement with those earlier reported of 46.88 kJ/mole.

(b) Residual Analysis

In order to assess the adequacy of the rate model IV and accuracy of the kinetic constants, the results of the fittings were analyzed using the statistical criteria suggested by Kittrel [17] and Froment and Bischoff [18]. This model was further subjected for the residual analysis in which a relative residual (RR) defined as [19];

$$RR = \frac{r_{\exp} - r_{\mathrm{mod}}}{r_{\exp}} \tag{2.8}$$

was plotted as a function of ethylene and CO pressures. The relative residuals are normally distributed with almost zero means and exhibit no trend effect as a function of any independent variable (Figure 2-18)

Therefore, it could be concluded that model IV based on one site mechanism in which the insertion of ethylene into a tetra-cordinated Pd-acyl intermediate is assumed to be a rate determining step can represent the co-polymerization kinetics in excellent agreement. The results obtained using this model satisfy the thermodynamic and statistical constraints.

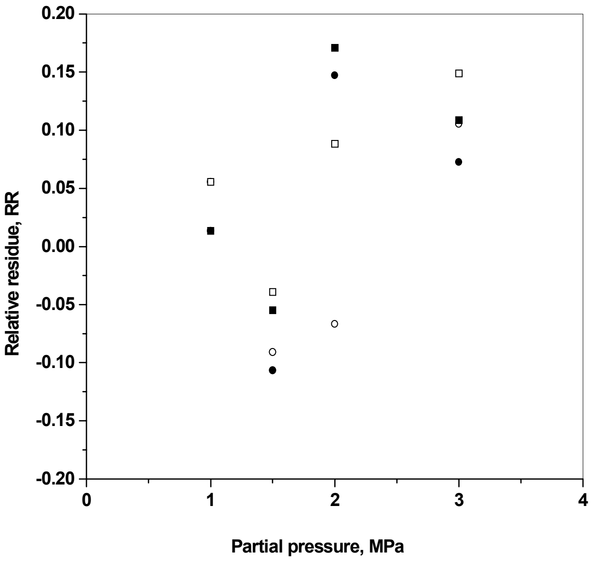


Figure 2-18. Residual Plots. *(○) CO, 353 K, (●) CO, 373K, (□) C_2H_4, 353K, (■) C_2H_4, 373K.*

A further comparison of experimental and predicted data using model IV is shown in Figure 2-19.

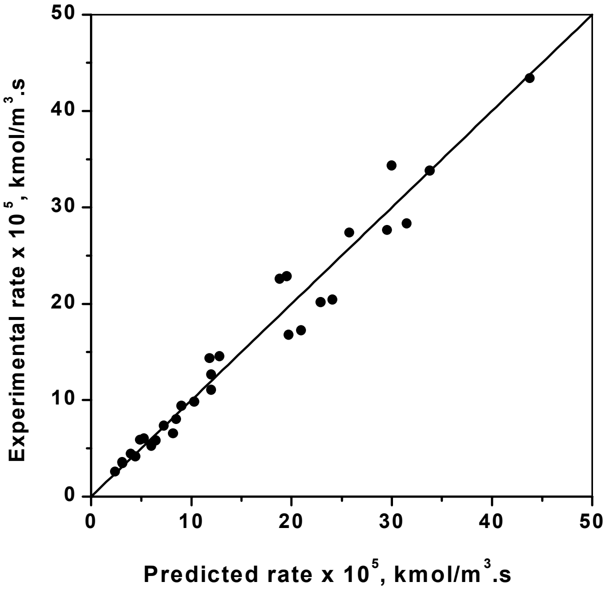


Figure 2.19. Comparison of Experimental and Predicted Results.
((●) Experimental, (--) Predicted)

2.5 Conclusions

To summarize, the solubility of CO and ethylene in methanol was determined at high-pressure and high temperatures (up to 30 MPa and 353-373K). The solubility of CO was enhanced due to the presence of ethylene while there was no effect on the solubility of ethylene due to CO. Ethylene was almost ten times more soluble than CO. Kinetics of the perfectly alternating copolymerization of ethylene with carbon monoxide was also investigated using homogeneous palladium catalysts precursor, [(dppp)Pd(H_2O)(TsO)](TsO) in methanol in a pressure range of 1-6 MPa and temperatures of 353-373 K. The rate of copolymerization was found to increase with the increase in the catalyst concentration, partial pressures of CO as well as ethylene. The model derived assuming the insertion of ethylene into a tetra co-ordinated Pd-acyl species (model IV) was found to represent the copolymerization kinetics in good agreement with respect to the observed rate data and the thermodynamic considerations. The apparent energy of activation using this model was estimated to 49 kJ/mole.

Notations

A	liquid phase activity of CO, kmol/m^3
A^*	concentration of CO, kmol/m^3
a_B	interfacial area for the gas – liquid interface, m^2/m^3
B	liquid phase activity of ethylene, kmol/m^3
B^*	concentration of ethylene, kmol/m^3
D_L	diffusion coefficient of gas in liquid phase, m^2/s.
E_{act}	energy of activation, kJ/mol.
f_i	fugacity of i^{th} gas
H	Henry's law constant, MPa / (kmol/m^3)
k_i	pseudo rate constant for the i^{th} reaction.
k_L	mass transfer coefficient at gas – liquid interface, m/s.
k_r	reaction rate constants used in kinetic equations, kmol/m^3.s
k_{obs}	reaction rate constant used in kinetic equation VIII, kmol/m^3.s
K_{CO}	equilibrium constant for CO coordination on Pd atom, m^3/kmol.
K_{et}	equilibrium constant for ethylene coordination on Pd atom, m^3/kmol.
K_i	equilibrium constant for i^{th} reaction
l	order of reaction with respect to dissolved CO, adimensional.
m	order of reaction with respect to dissolved ethylene, adimensional.
[Pd]	catalyst concentration, kmol/m^3
q	number of experiments.
r_{pol}	experimentally observed rate of copolymerization, kmol/m^3.s
r_{mod}	rate of co-polymerization obtained by model fitting, kmol/m^3.s
R_A	maximum rate of reaction, kmol/m^3·s
T	absolute temperature, K

Greek letters:

α_A, α_B parameters defined in ref. 16 for CO and ethylene respectively. (dimensionless)

ψ objective function used in non–linear regression defined as the sum of squares of the difference between experimental and predicted co-polymerization rates.

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Chapter Three

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Synthesis of Polyesteramides by Palladium Catalyzed Carbonylation of Aromatic Diiodides and Amino Alcohols

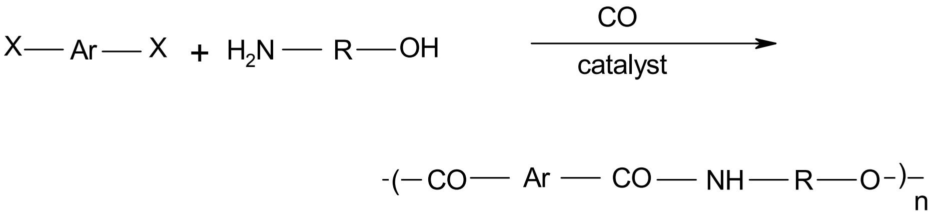
3.1 Introduction

Polyesteramides belong to an important class of polymers with wide applications mainly because of their excellent heat resistant and gas barrier properties. Polyesteramides are hybrid structures of polyesters and polyamides since these contain ester as well as amide functions. Polyesters and polyamides are condensation products of carboxylic acids (or their suitable derivatives) with diols and diamines respectively and have established applications essentially as engineering polymers. Despite their wide applicability, both, polyesters and polyamides have certain advantages and disadvantages [1]. Thus, although polyamides have excellent tenacity, durability and dye-ability, the fibers drawn from them have some defects due to low initial modulus and poor stiffness. On the other hand, polyesters have exceptionally high strength and initial modulus but are high melting and have less dye-ability. In an effort to combine the advantageous properties of the polyesters and polyamides in a single material, it was proposed to melt spin the blend of these two polymers [1]. One of the serious problems associated with melt spinning of such blends was that the individual polymers reacted differently to the drawing process resulting in defects in the fibers. Yet another way to obtain such materials was to introduce the ester and amide units in the same polymer backbone, which lead to the development of polyesteramide copolymers. Because of the structural similarity, the properties of polyesteramides are often intermediate to those of polyesters and polyamides. Moreover, these properties can be controlled in part by adjusting the amount of ester and amide units. Currently, the main interest in this area is the preparation of the ordered polyesteramides having regular enrichment of ester and amide functionality [2].

Polyesteramides are known since 1940 when Brubaker et al. [3] reported the preparation of polyesteramides by condensation reaction of dicarboxylic acid containing amide linkages with diols. Laakso and Williams [4] also provided a similar route for polyesteramides. Since then several synthetic approaches have been reported for polyesteramides. In principal, these methods were based on classical condensation reactions of carboxylic acids or their derivatives with suitable functional molecules capable of providing the amide and ester functions. A few such synthetic approaches to polyesteramides are summarized below.

Frosch et al. [5] prepared alternating polyesteramides by condensing mono-alcohol amine with dibasic or dicarboxylic acid preferably at a temperature of 200 – 250° C. In this case, one of the reaction products i.e. water had to be removed continuously to obtain sufficiently high molecular weight polymers. Okazaki et al. [1] prepared polyesteramides by heating a mixture of polyester and polyamide to a temperature intermediate to the glass transition temperature and melting temperature of the individual polymers. Goodman et al. [6] described the preparation of random polyesteramide copolymers by reacting diamine and diacid in the presence of a lactone. Other synthetic approaches to the polyesteramides include condensation of bisesteramide and diol [7], diamidediol and dicarboxylic acid [8], ω-aminoalcohol or aminophenol with diacid [9], bis-oxamidodiols and dicarboxylic acids or dicarboxylic esters [10]. Fully aliphatic polyesteramides have also been prepared using aliphatic substrates [9, 11]. Gaymans et al. [12] reported a two-stage preparation of polyesteramide. In the first step, the alkylterephthalate (e.g. dimethylterephthate) was condensed with diamine to form a diesteramide, which in the second step was condensed with a diol and diamine at 150-200° C. Lohmeijer et al. [13] reported a similar procedure for the preparation of polyesteramides with lower gas permeability by reacting an amino alcohol and a dicarboxylic acid. Ishimaru et al. [14] reported a two-step synthesis of the polyesteramides in which the first step was condensation of an aromatic monoalkyl dicarboxylates with an aromatic diisocynate to produce aromatic dialkyl diamidedicarboxylate, which in the second step was condensed with a polyhydroxy compound. Casagrande et al. [15] disclosed a method for polyesteramide preparation by condensation of aminophenol and hydroquinone derivative with aromatic dicarboxylic acids. The polyesteramides were also prepared by condensing dicarboxylate-capped polyamide with a diol [16].

From the literature survey presented above, it can be seen that the conventional methods for the synthesis of polyesteramides employ carboxylic acids or their suitable derivatives. Such methods would be suitable for a few easily available diacid derivatives. But, a difficulty may arise when diacid derivatives with less common substitution patterns are required. Thus, there exists a need for simple and efficient alternative synthetic route to polyesteramides, which does not require presence of a carboxyl group on the reacting monomers. The use of catalytic carbonylation-polycondensation route (as proposed in scheme 3-1) would be one such attractive alternative.



Scheme 3-1. Proposed Catalytic Route for the Synthesis of Polyesteramides

As summarized in Chapter 1, the catalytic reactions involving CO as a comonomer have emerged as an attractive alternative to conventional polycondensation reactions employing carboxylic acids or their derivatives. The feasibility of these reactions has been demonstrated for the synthesis of several carbonyl containing high performance polymers like polyesters, polyamides, polyimides, polyacylhydrazides etc. (see review presented in Chapter 1). One of the advantageous features of these novel catalytic reactions is that these employ cheaply available carbon monoxide as one of the reactants. Since, there was no report on the synthesis of polyesteramides by catalytic carbonylation route, the aim of this work was to explore the possibility of synthesis of polyesteramides by catalytic carbonylation-polycondensation reaction as suggested in Scheme 3-1. Accordingly, this work describes the successful extension of the catalytic carbonylation-polycondensation chemistry for the synthesis of alternating polyesteramides, which involves the carbonylation-polycondensation of aromatic diiodides and amino alcohols in presence of an organic base and a catalyst. The effect of various reaction parameters like solvent, base, ligand concentration, CO pressure and temperature on the yield and intrinsic viscosity of the polyesteramide obtained was also investigated.

3.2 Experimental Section

3.2.1 Materials.

4,4'-Diiodobiphenyl (DIBP); 4,4'-dibromobiphenyl (DBBP); 1,4-diiodobenzene (DIB); palladium chloride ($PdCl_2$), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); 1,4-diazabicyclo[2.2.2]octane (DABCO); 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 4-aminophenol were received either from Fluka or Aldrich Chemicals and used without any further purification. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), triethylamine (TEA), 3-aminopropan-1-ol; 3-aminobenzyl alcohol and ethanolamine were received from Merck Chemicals, India. *N,N*-dimethylacetamide (DMAc); *N,N*-dimethylformamide (DMF); *N*-mehtylpyrrolidone (NMP), chlorobenzene, methanol, toluene and triphenylphosphine (PPh_3) were purchased from SD Fine Chemicals, India. Carbon Monoxide (CO) gas was purchased from Matheson Gas Company and had a stated purity of 99%. All solvents were freshly distilled before use.

3.2.2 Experimental Setup

All polymerization experiments were carried out in a 50 ml capacity Haste alloy autoclave supplied by Parr Instruments Company (Moline, IL). The reactor was provided with magnetic stirrer capable of operating upto 1500 rpm. The reactor could be maintained at a constant temperature with the help of PID controller which provided alternating heating and cooling. Temperature (± 1° C) and pressure (± 1 psig) in the reactor was recorded from a digital display. The reactor was also equipped with relevant safety features like high temperature-pressure auto cut-off and safety rupture disc. The schematic of the experimental setup was similar to that used during polyketone reactions except for the provision for ethylene (Chapter 2, section 2.2.5, pp 61).

3.2.3 Analytical Measurements

Intrinsic viscosity where possible was measured in NMP at a concentration of 0.5 g/dL at 30°C. IR spectra were recorded on a Bio-Rad Model FTS 175C series machine using KBr pellets. Thermo gravimetric analysis was performed on Metler-Toledo instrument in air environment. NMR was recorded on a Brucker-300 or 500

MHz instruments using a mixture of trifluoroacetic acid and chlorofofrm-*d*$_1$. Gas chromatographic analysis was performed on HP 5890 series gas chromatograph equipped with HP-1 column and a thermal conductivity detector using helium as a carrier gas. GPC analysis was performed on Waters GPC system. The catalytic activity expressed as Turnover Frequency (TOF) was defined as

$$\text{TOF, } h^{-1} = \frac{\text{Moles of dihalide reacted}}{\text{Moles of Pd} \times \text{Reaction time (hour)}}$$

3.2.4 Model Polymerization Reaction (preparation of polymer **2c***)*

In a typical experiment, a stirred pressure reactor was charged with 4,4'-diiodobiphenyl (2.08 g, 5 mmol); 3-aminopropan-1-ol (0.380 ml, 5 mmol); 1,8 diazabicyclo[5.4.0]undecene-7-ene (1.4 ml, 10 mmol); $PdCl_2$ (2 mg, 0.011 mmol), triphenylphosphine (12 mg, 0.044 mmol) and chlorobenzene (25 ml). The reactor was flushed with high purity nitrogen twice to ensure exclusion of any dissolved air or oxygen from the reaction medium. The reactor was then heated to 120°C under low stirring (100 rpm) and the temperature was allowed to stabilize at the desired set point (120°C). Then CO was introduced to the desired level (3 atm) and the contents were stirred at an agitation speed of 900 rpm. The reactor was operated at a constant pressure conditions throughout the reaction by supplying CO from a reservoir vessel using a constant pressure regulator. The pressure drop in the reservoir vessel was measured using a digital pressure transducer as a function of time. After the reaction, the reactor was cooled and the excess gas was vented. The reaction mixture was poured in 100 ml of methanol to obtain solid product. The solid obtained was dissolved in NMP and re-precipitated using methanol. The product was washed with methanol twice and dried *in vacuo*. The yield was 1.20 gm (85% based on the diiodide used in the reaction). The relevant characterization data is discussed in the next section. All further experiments were performed essentially in the similar fashion. Depending on the nature of monomers, polyesteramides were obtained as viscous oils or solids. In every experiment, the contents after the reaction were dissolved in NMP and re-precipitated using methanol.

3.3 Results and Discussion

3.3.1 Preliminary Experiments

The catalytic carbonylation-polycondensation reactions have emerged as an attractive alternative for the synthesis of several carbonyl-containing polymers, which are otherwise prepared by the condensation reactions involving carboxylic acids or their suitable derivatives. From the literature survey presented in Chapter 1 on the catalytic carbonylation-polycondensation reactions, a few general observations can be made. Thus, both bromo as well as iodo aromatics served as substrates during the carbonylation reactions depending on the reaction conditions whereas the chloro substrates were almost unreactive. The catalyst normally used for these reactions was $PdCl_2$ modified with phosphine ligands (mostly triphenylphsophine). These reactions were conducted at a temperatures between 90-130°C and CO pressures upto 20 atm. All these reactions employed hindered organic bases like DBU as acceptor for the hydrogen halide released during the reaction course. In all these reactions either amine or hydroxyl groups acted as a nucleophiles which attacked the intermediate Pd-CO species resulting in the formation of amide or ester respectively. We therefore thought that using an amino alcohol as a bifunctional nucleophile should in principle result in the formation of esteramide unit and this chemistry when applied to carbonylation of dihalides should provide polyesteramides.

In order to develop a catalytic carbonylation route for direct single step synthesis of polyesteramides, a few preliminary reactions were carried out using dihaloaromatic compounds and aliphatic amino alcohols in presence of CO and a catalyst. Since there was no prior literature on the preparation of polyesteramides by carbonylation route we used the combination of $PdCl_2$ and PPh_3 as catalyst for the initial exploratory reactions, since this combination was successfully used for the synthesis of several other polymers (e.g. polyesters, polyamide, polyaimides etc.) by carbonylation-polycondensation reaction. The first experiment was conducted using 4,4'-diiodobiphenyl and 3-aminopropan-1-ol as substrates. The catalyst used was $PdCl_2$ in combination with 4 equivalents of triphenylphosphine (TPP) and the reaction was conducted at 3 atm of CO pressure and 120°C in presence of chlorobenzene solvent (Details are given in experimental section). The CO absorption profile indicated that the CO absorption was completed within first 18 minutes. The reaction was continued for 1 hour. After the reaction, the autoclave was cooled to room temperature, the excess CO was vented and the reaction mixture was poured into 100 ml of methanol. The solid obtained was collected by filtration, dissolved in NMP and re-precipitated using methanol. The white solid thus obtained was washed with methanol and dried overnight under vacuum. The yield was 1.2 gm.

Before proceeding to further investigations it was important to confirm that the product obtained was polyesteramide. This was accomplished by several characterizations. The elemental analysis was consistent with the proposed polyesteramide structure (Found: C, 71.85; H, 5.26; N, 4.65 %. Calculated (*for* $C_{17}H_{15}O_3N$; 281): C, 72.59; H, 5.34; N, 4.98). The infrared spectrum of this solid (KBr pellets) shown in Figure 3-1 showed several characteristic absorption peaks clearly indicating the presence of an ester and amide functions e.g. 3350 (amide), 1712 (ester), 1638 (amide I), 1542 (amide II).

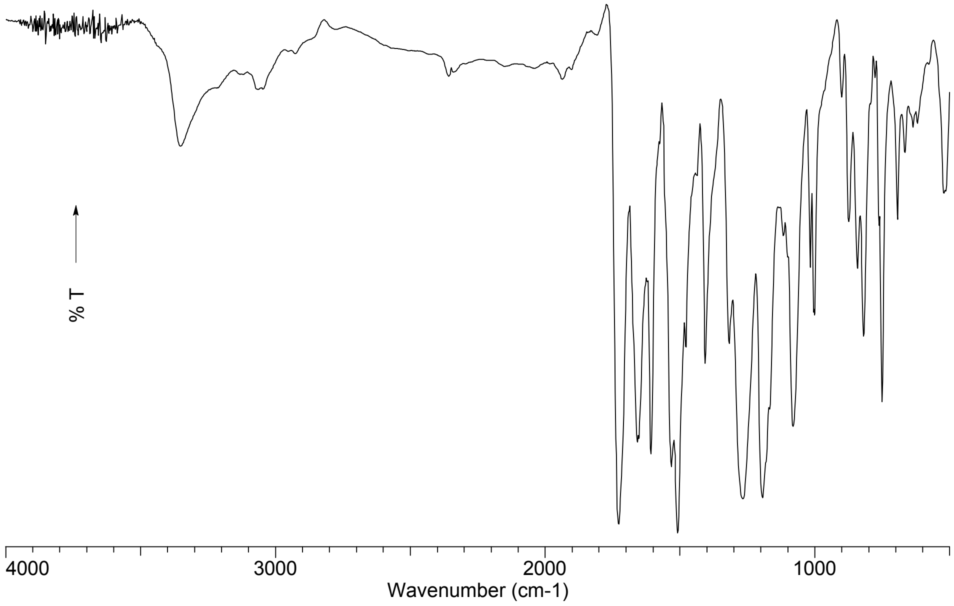


Figure 3-1. FTIR Spectrum of Polyesteramide **2c** (KBr pellets)

The proposed structure for this polyesteramide (Figure 3-2) was further confirmed by the NMR analysis.

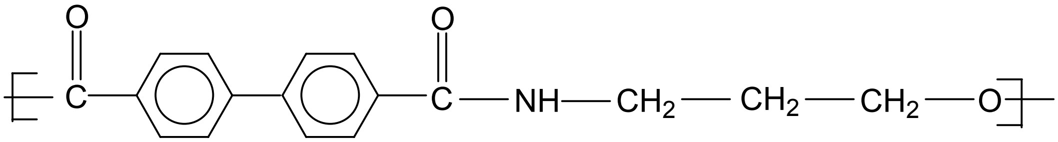


Figure 3-2. Proposed Structure for Polyesteramide **2c**.

The proton NMR spectrum of the solid obtained i.e. polyesteramide **2c** (recorded in a mixture of trifluoroacetic acid and chlroroform-*d*$_1$ (20:80 v/v)) is given in Figure 3-3. The aliphatic protons appeared at δ 2.25 (-CH$_2$-$\underline{CH_2}$-CH$_2$); 3.76 (-NH-$\underline{CH_2}$-), 4.61 (-O-$\underline{CH_2}$)-. The aromatic protons appeared at δ 7.65, 7.81 and 8.09. The signal at δ 11.54 was due to the amide proton (-N$\underline{H}$-CO).

The ^{1}HNMR spectrum clearly indicated the absence of any amine linkages, which would have resulted in a signal around δ 5-6. The partial ^{13}C{^{1}H}NMR spectrum (Figure 3-4) of the solid in a mixture of trifluoroacetic acid and chloroform-*d*$_1$ (20:80% v/v) showed signals at δ 177.62 (ester carbonyl) and 174.16 (amide carbonyl). These evidences further confirmed the proposed structure for polyesteramide **2c** as shown in Figure 3-2.

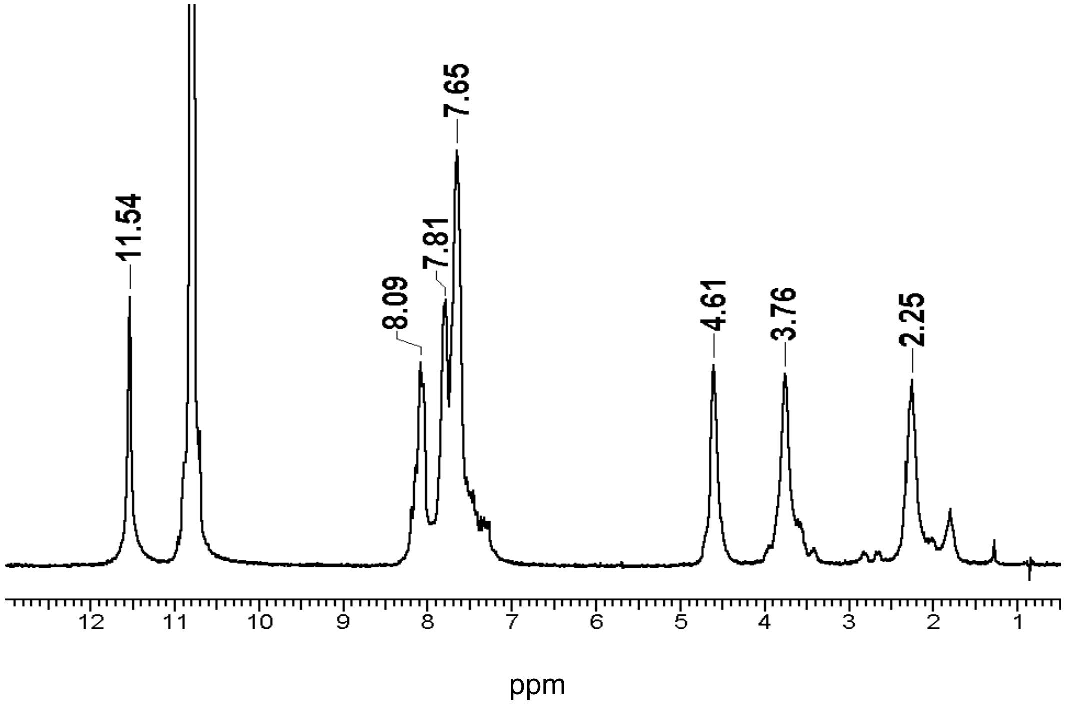


Figure 3-3. ^{1}HNMR Spectrum of the Polyesteramide **2c** (*in a mixture of trifluoroacetic acid and chlroroform-d*$_1$ *(20:80 % v/v)*

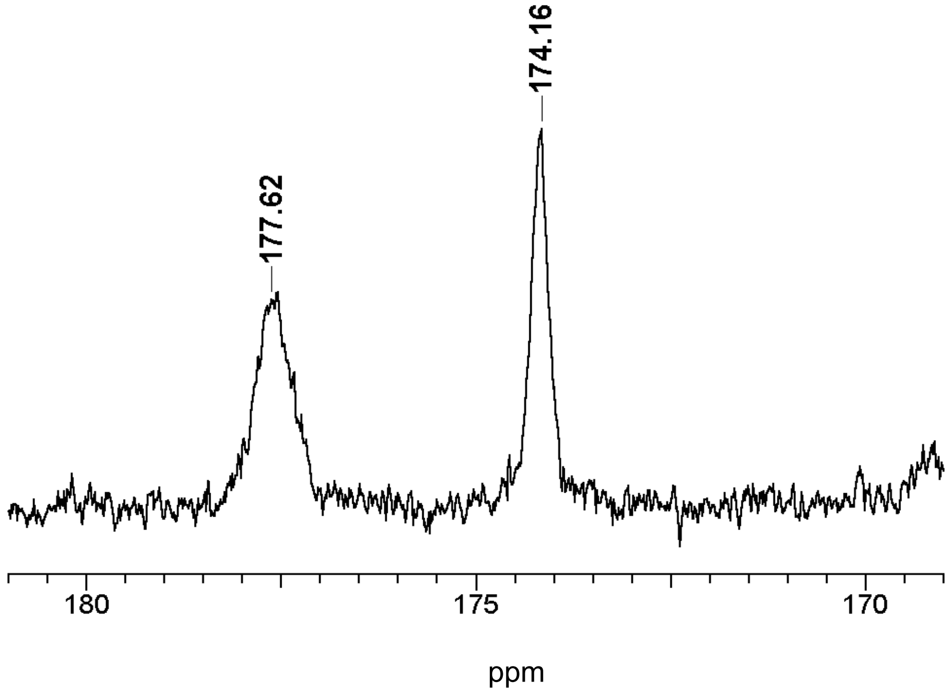


Figure 3-4. $^{13}C\{^{1}H\}$ NMR Resonance of the Carbonyl Groups in Polyesteramide **2c**. *The peak at 177.62 δ is due to ester carbonyl and at 174.16 is due to amide carbonyl. The spectrum was recorded in a mixture of trifluoroacetic acid and chloroform-d_1 (20:80 % v/v).*

Once it was established that the polymer obtained was polyesteramide, we repeated the above experiment except for the change that 4,4'-diiodobiphenyl was replaced by 4,4'-dibromobiphenyl. In this case also 0.240 gm of polyesteramide was obtained (with consistent characterization data) but here the yield based on the dihalide consumed was very low (17%). Furthermore, the inherent viscosity was just 0.086 dL/g, which was considerably lower than for the polymer obtained using 4,4-diiodobiphenyl. On the other hand when dichloroderivative was used as substrate, no polymer was obtained. These preliminary experiments indicted that the diiodo substrates efficiently underwent the carbonylation-polycondensation reaction with 3-aminopropan-1-ol to give polyesteramides in excellent yields and moderate viscosity. Therefore, the diiodoaromatics were used as substrates in further studies. Following this procedure, we prepared several polyesteramide derivatives using different combinations of diiodosubstrates and amino alcohols (see Table 3-1 for the polymer identification codes) and results are presented in Table 3-2.

Table 3-1. Identification Codes for Polyesteramides

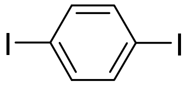
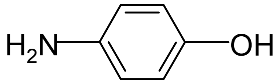
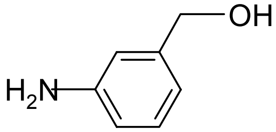
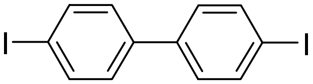
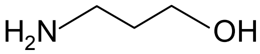
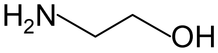
I—Ar—I	H_2N— R—OH
1. 	a. 
	b. 
2. 	
	c. 
	d. 

Table 3-2. Synthesis of Polyesteramides by Catalytic Carbonylation Polycondensation Reaction [a]

Polymer code [b]	***Molecular formula***	***Yield*** *(%)* [c]	***[η]*** *(dL/g)* [d]	***Elemental analysis*** *(%)*				***Thermal properties*** *(°C)* [e]		***IR spectra (ν)*** *(cm^{-1})*
					C	*H*	*N*	T_5	T_{10}	
1a	$C_{14}H_9O_3N$	*90*	[f]	*Calc.*	*70.29*	*3.76*	*5.86*	*380*	*430*	*3351, 1729, 1653, 1509,*
				Found	*69.50*	*3.52*	*5.30*			*1268, 1196, 1078, 720.*
1b	$C_{15}H_{11}O_3N$	*25*	*0.17*	*Calc.*	*71.15*	*4.35*	*5.53*	*342*	*392*	*3436, 1716, 1645, 1542,*
				Found	*70.80*	*4.22*	*5.43*			*1370, 1107, 783.*
2a	$C_{20}H_{13}O_3N$	*95*	[f]	*Calc.*	*76.19*	*4.13*	*4.44*	*375*	*410*	*3354, 1727, 1653, 1531,*
				Found	*75.48*	*4.06*	*4.12*			*1266, 1194, 1082, 750.*
2b	$C_{21}H_{15}O_3N$	*40*	*0.20*	*Calc.*	*76.60*	*4.56*	*4.25*	*360*	*385*	*3371, 1714, 1648, 1541,*
				Found	*75.90*	*4.48*	*4.21*			*1489, 1274, 1111, 753.*
2c	$C_{17}H_{15}O_3N$	*85*	*0.25*	*Calc.*	*72.59*	*5.34*	*4.98*	*300*	*320*	*3350, 1712, 1638, 1542,*
				Found	*71.85*	*5.26*	*4.65*			*1278, 1111.*
2d	$C_{16}H_{13}O_3N$	*35*	*0.18*	*Calc.*	*72.91*	*4.87*	*5.24*	*316*	*331*	*3321, 1718, 1639, 1541,*
				Found	*71.89*	*4.42*	*5.12*			*1273, 1108, 843.*

[a] ***Reaction conditions***. *diiodide: 5 mmol; aminohydroxy compound: 5 mmol; $PdCl_2$: 0.011 mmol; triphenylphosphine: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml, CO pressure: 3 atm;; temperature: 120°C; agitation: 900 rpm; reaction time: 1 hour.* [b] *Table 3-1.* [c] *Isolated yields.* [d] *[η] (intrinsic viscosity) measured at a concentration of 0.5 g/dL in NMP at 30°C.* [e] *5 % (T_5) and 10% weight-loss temperature (T_{10}) in air determined by TGA.* [f] *Insoluble in NMP.*

We further investigated the effect of various reaction parameters on the efficiency of the carbonylation-polycondensation reaction. For this purpose, the carbonylation-polycondensation of 3-aminopropan-1-ol and 4,4'-diiodobiphenyl in presence of a catalytic amount of $PdCl_2/4PPh_3$ was investigated at 120°C as a model polymerization reaction. In these reactions the amount of CO consumed was compared with the final amounts of 4,4 diiodobiphenyl and 3-aminopropan-1-ol consumed, which indicated almost stoichiometric material balance as shown in Scheme 3-1. This also indicated that the carbonylation-polycondensation reaction was highly selective. The gas chromatographic analysis of the liquid phase after completion of reaction did not indicate formation of any side products arising because of potential side reactions. Therefore, the absorption of CO was taken as a direct measure of polymerization progress to compare the different reactions. Unless otherwise mentioned, all reactions were completed (100% conversion) in the specified reaction time as indicated by the CO absorption profiles and further confirmed by the final liquid phase analysis. Following this procedure several polymerization experiments were carried out at different reaction conditions and the results are discussed below.

3.3.2 Effect of Solvent

The effect of solvent on the carbonylation-polycondensation reaction was investigated and the results are summarized in Table 3-3. Considering the reaction time, yield and intrinsic viscosity, chlorobenzene appeared to be the most suitable solvent. It was interesting to note that despite better solubility of the resulting polyesteramide in NMP, comparatively lower yield and viscosity was obtained when NMP was employed as a solvent. No polymer was obtained in dichloromethane solvent. Further reactions were therefore carried out in chlorobenzene solvent. The resulting polyesteramides were often insoluble in chlorobenzene and considerable amount of the polymer could be collected as a solid product after the reaction.

Table 3-3. Effect of Solvent on Synthesis of Polyesteramides by Carbonylation.

Sr.	*Solvent*	*Reaction time (min)*	*Yield (%)*	*[η] (dL/g)*	*TOF (h^{-1})*
1.	*Chlorobenzene*	*17*	*85*	*0.25*	*1604*
2.	*N,N-Dimethylformamide*	*20*	*60*	*0.17*	*1363*
3.	*N,N-Dimethylacetamide*	*30*	*62*	*0.16*	*909*
4.	*N-Methylpyrrolidone*	*24*	*20*	*0.11*	*1136*
5.	*Toluene*	*50*	*43*	*0.15*	*545*
6.	*Dichloromethane*	*-*	*0*	*0*	*0*

Reaction conditions. *4,4' diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; solvent: 25 ml; CO pressure: 3 atm; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour.*

3.3.3 Effect of Ligand

It is well known that the aryl iodide can be oxidatively added to Pd (0) complexes even in the absence of the added phosphine ligand because of their high reactivity [17]. In order to investigate the role of ligand in the present case, a standard carbonylation-condensation reaction was conducted using $PdCl_2$ as catalyst without any ligand. It was observed that the polyesteramide **2c** was still obtained but in very low yield (14%) and inherent viscosity (0.06 dL/g). The typical CO absorption profiles for these reactions (Figure 3-5) indicated that the reaction without any phosphine ligand required considerably higher reaction times compared with those using phosphine ligands. There was practically no effect of increasing the ligand concentration beyond four equivalents on the CO absorption rates and, yield and viscosity of the polyesteramide.

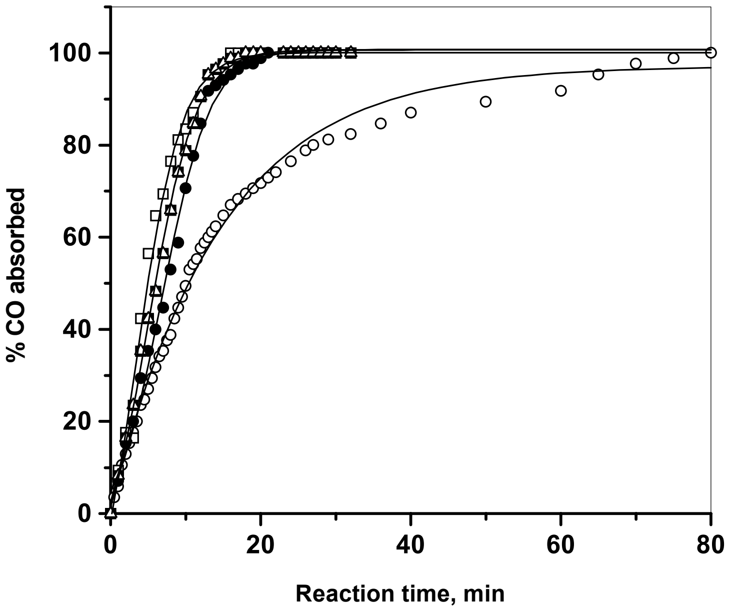


Figure 3-5. Effect of Ligand/Pd Ratio on CO Absorption Profile.
***Reaction conditions**. 4,4' diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol;* $PdCl_2$*: 0.011 mmol; DBU: 10 mmol; CO pressure: 3 atm; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour. Ligand:* PPh_3*. Ligand/Pd ratio: (○) 0; (●) 2; (□) 4; (■) 7 and (△) 10.*

The reaction without any phosphine ligand was accompanied by separation of palladium black. This type of deactivation has been often observed previously during similar carbonylation-polycondensation reactions and has been addressed in details in several papers [18]. The use of 4 equivalents of phosphine ligand efficiently suppressed the deactivation of catalyst and also facilitated the catalyst separation and subsequent recycles. As mentioned earlier, the product polyesteramides often separated as viscous materials or solids because of their low solubility in chlorobenzene. In the absence of any stabilizing ligand, the (Pd(0)) may adhere to the polymer particles making the separation difficult. We found that use of 4 equivalents of phosphine ligand completely suppressed the formation of catalytically inactive palladium black. Secondly, it allowed easy separation and recycling of the catalyst as in this case the product was a solid. The polyesteramides obtained (e.g. using 4,4'-diiodobiphenyl and 3-aminopropan-1-ol) were insoluble in chlorobenzene and therefore could be separated by simple filtration or decantation. The filtrate containing the soluble Pd-phosphine complex was then recycled with fresh charge of reactants. We found that even after four recycles, there was no appreciable loss in the catalytic activity, yield and the intrinsic viscosity of the resulting polyesteramide (Figure 3-6). The successful recycle of the catalyst gave a total cumulative TON of 2275 (455 × 5), which was highest, reported typically for polycondensation reactions. This also demonstrated for the first time that a careful manipulation of reaction conditions could significantly improve the catalyst efficiency during carbonylation-polycondensation reactions.

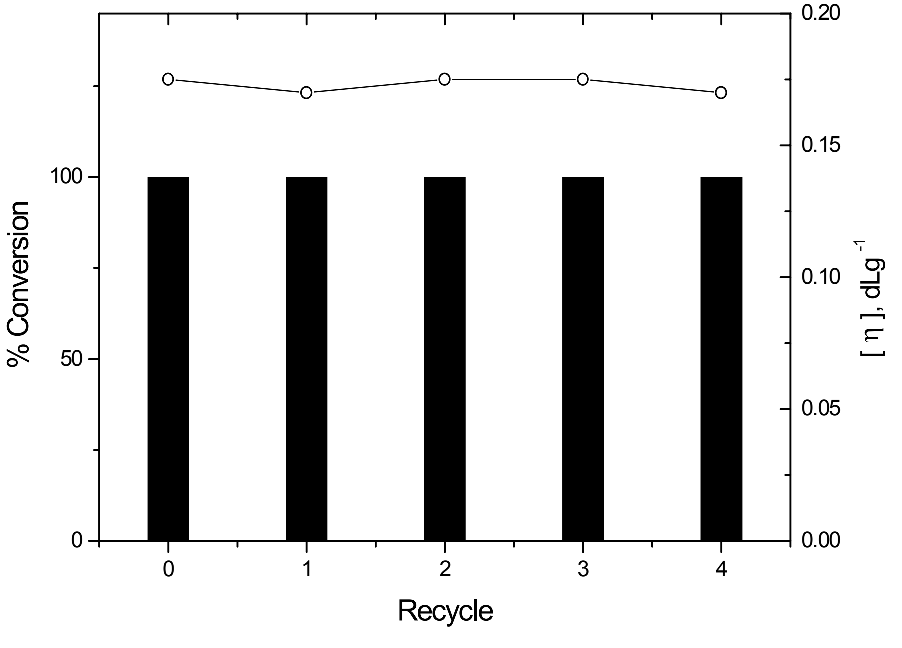


Figure 3-6. Catalyst Recycle Experiments.
Reaction conditions. *4,4' diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol;* $PdCl_2$*: 0.011 mmol;* PPh_3*: 0.044 mmol; DBU: 10 mmol; CO pressure: 45 psig; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour. Bar graph corresponds to conversion and line graph corresponds to the intrinsic viscosity of the obtained polyesteramide. Conversion based on dihalide.*

3.3.4 Effect of Base

The base plays a key role during the carbonylation-polycondensation reaction. The base acts as a scavenger for the hydrogen iodide (HI) produced during the reaction. The efficiency of various bases during the carbonylation-polycondensation reactions was studied and the results are summarized in Table 3-4. It can be seen that use of strong and hindered organic bases like DBU was particularly effective for better yields and higher intrinsic viscosities whereas the inorganic bases were almost ineffective in these reactions. The amine ($-NH_2$) function in the amino alcohol could also efficiently trap the HI released in the reaction. Indeed, in a reaction when no external base was used, only 25% of the total theoretical carbon monoxide was consumed. This indicated that the carbonylation continued until sufficient free amine was available for trapping the released HI.

Table 3-4. Influence of Base on the Carbonylation-Polycondensation Reaction.

Sr.	*Base*	*pKa*	*Reaction time (min)*	*Yield (%)*	*[η] (dL/g)*	*TOF (h^{-1})*
1	DBU	11.9	17	85	0.25	1604
2	DBN	11.0	17	80	0.20	1604
3	DABCO	9.15	55	65	0.14	496
4	Et_3N	10.75	50	20	0.09	545
5	TMEDA	9.15	56	15	0.08	487
6.	NaOH	-	45	20	0.09	606
7.	NaOAc	-	50	18	0.07	545

Reaction conditions. *4,4 diiodobiphenyl: 5 mmol; 3-amino-1-propanol: 5 mmol;* $PdCl_2$*: 0.011 mmol;* PPh_3*: 0.044 mmol; base: 10 mmol; CO pressure: 3 atm; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour; pKa values for aqueous solutions of the corresponding conjugate acids [Reference 19]*

We further investigated the effect of DBU amount on the polymerization. The typical results presented in Figure 3-7 indicate that a little more than two equivalents (2.4 equivalents) of DBU were required for optimum results. Use of even higher amount of base did not further affect the yield or intrinsic viscosity of the resulting polyesteramide.

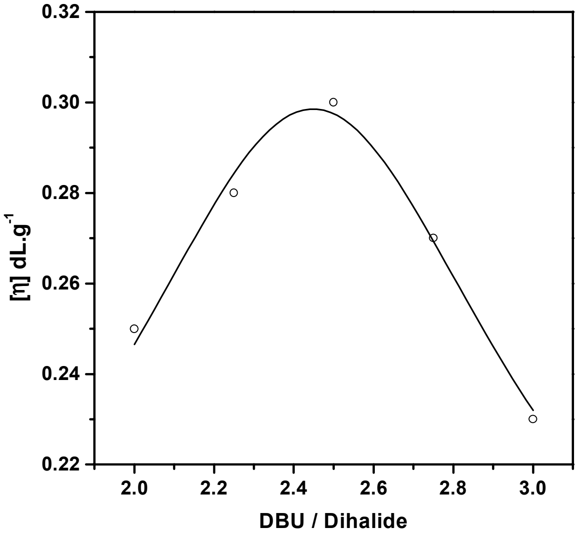


Figure 3-7. Effect of Amount of DBU on the Polycondensation Reaction.
Reaction conditions. *4,4'-diiodobiphenyl: 5 mmol; 3-aminopropan-1-ol: 5 mmol;* $PdCl_2$*: 0.011 mmol;* PPh_3*: 0.044 mmol; CO pressure: 3 atm; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour.*

3.3.5 Effect of CO Pressure

The effect of CO pressure on the polymerization reaction was also investigated and results are presented in Table 3-5. Interestingly, the yield of the polyesteramide was found to be nearly independent of CO pressure but there was a marginal increase in the intrinsic viscosity of the polyesteramide.

Table 3-5. Effect of CO Pressure on the Synthesis of Polyesteramides by Carbonylation-Polycondensation Reaction.

Sr.	*CO pressure* (*atm*)	*Reaction time* (*min*)	*Yield* (*%*)	*[η]* (*dL/g*)	*TOF* (*h^{-1}*)
1.	*1*	*50*	*87*	*0.23*	*545*
2.	*3*	*17*	*85*	*0.25*	*1604*
3.	*5*	*15*	*86*	*0.27*	*1818*
4.	*7*	*12*	*85*	*0.26*	*2272*
5.	*11*	*10*	*89*	*0.27*	*2727*

Reaction conditions. *4,4 diiodobiphenyl: 5 mmol; 3-amino-1-propanol: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour.*

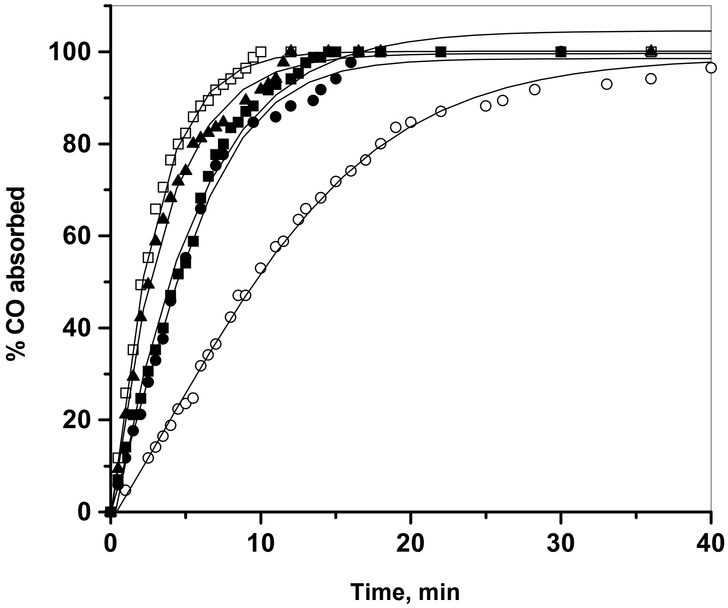


Figure 3-8. Effect of CO Pressure on the CO Absorption Profile
Reaction conditions. *4,4 diiodobiphenyl: 5 mmol; 3-amino-1-propanol: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour. CO pressure: (○) 1 atm; (●) 3 atm; (□) 5 atm; (■) 7 atm, and (△) 11 atm.*

The CO absorption profiles at different CO pressures are compared in Figure 3-8. It can be seen that the rate of carbonylation increases with increase in the CO pressure. These observations are consistent with the earlier reports on the palladium carbonylation of aryl halides and in particular the aryl iodides [20]. It has been demonstrated earlier that in case of carbonylation of aryl iodides, the oxidative addition of aromatic iodide is a fast step and the insertion of carbon monoxide into the tetra-coordinated palladium (II) complex is the rate-determining step [21]. Thus, increasing the CO pressure would result in increased rate of carbonylation.

3.3.6 Effect of Temperature

The effect of temperature on the carbonylation-polycondensation reaction was investigated in a temperature range of 90 – 130°C. The results presented in Table 3-6 indicate that there was no substantial change in the yield of the polyesteramide produced at the end of 1 hour, but the intrinsic viscosity was strongly influenced by the temperature. The intrinsic viscosity was highest at a temperature of 120°C and decreased on either side. The CO absorption profiles at different temperatures are given in Figure 3-9. It can be seen that in each case the reaction was completed well before the reaction time (1 hour) and therefore did not affect the yield of the reaction. From the CO absorption profiles it can also be concluded that the initial rate of carbonylation increased with temperature. The apparent energy of activation calculated using Arrhenius plots was 18 kJ/mole.

Table 3-6. Effect of Temperature on the Carbonylation-Polycondensation Reaction

Sr.	*Temperature* (*° C*)	*Reaction time* (*min*)	*Yield* (*%*)	*[η]* (*dL/g*)	*TOF* (*h^{-1}*)
1.	*90*	*44*	*87*	*0.25*	*619*
2.	*100*	*36*	*85*	*0.265*	*757*
3.	*110*	*26*	*86*	*0.25*	*1049*
4.	*120*	*17*	*85*	*0.25*	*1604*
5.	*130*	*13*	*89*	*0.27*	*2098*

Reaction conditions. *4,4 diiodobiphenyl: 5 mmol; 3-amino-1-propanol: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; CO pressure: 3 atm; chlorobenzene: 25 ml; agitation 900 rpm; reaction time: 1 hour.*

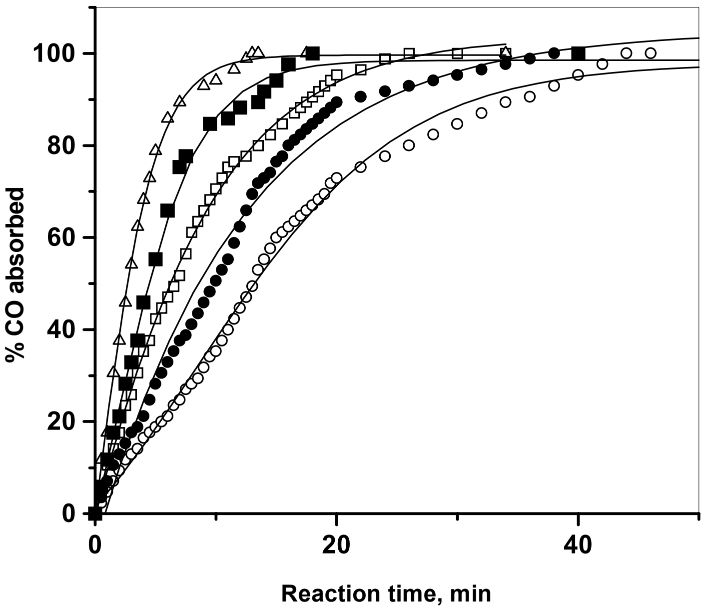


Figure 3-9. Effect of Temperature on the CO Absorption Profile
Reaction conditions*. 4,4 diiodobiphenyl: 5 mmol; 3-amino-1-propanol: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; CO pressure: 3 atm; chlorobenzene: 25 ml; agitation 900 rpm; reaction time: 1 hour. Reaction temperatures: (○) 90 °C, (●) 100° C, (□) 110° C, (■) 120° C, and (△) 130° C.*

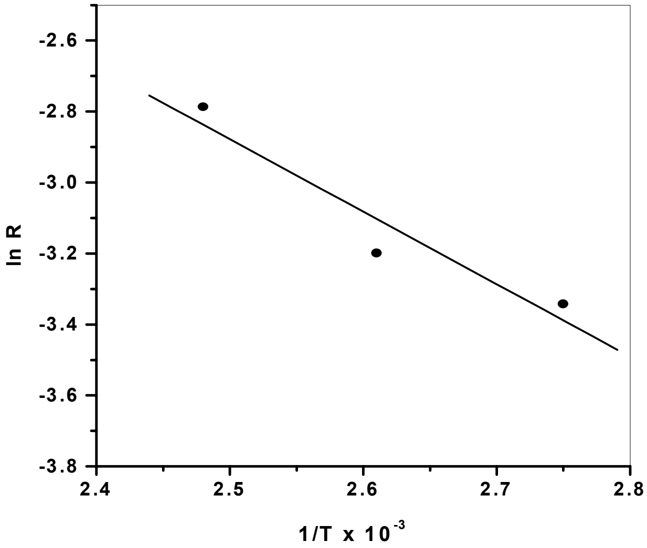


Figure 3-10. Arrhenius plot

3.3.7 Proposed Mechanism for the Polymerization Reaction

The mechanism of carbonylation-polycondensation reactions is not very clear at present but it may be similar to the classical Heck type carbonylation of aryl halides. The mechanism of Heck type carbonylation reaction has been investigated in elaborate details previously [17, 22-25] and based on these investigations, a probable mechanism may be proposed for the present carbonylation-polycondensation polymerization reaction (Figure 3-11). The catalytically active species during the catalytic cycle is believed to be a Pd (0) complex **1**, which can be formed during the reaction in presence of CO and phosphine ligand e.g. $Pd(PPh_3)_4$ or $(PPh_3)_2Pd(CO)$ [22]. The oxidative addition of aromatic iodide to this zero-valent palladium complex forms the arylpalladium (II) halide complex **2**. Subsequent coordination and insertion of carbon monoxide into arylpalladium (II) halide species leads to the Pd-acyl intermediate **3** which on a nucleophilic attack by either OH or NH_2 moiety results in the formation of corresponding ester or amide. The Pd (II)-HI complex **4** then reductively eliminates HI and regenerates Pd (0) complex marking the completion of the catalytic cycle. The observed effect of CO pressure on the carbonylation provides support for this proposed mechanism. The oxidative addition of aryl iodide is a comparatively fast step [20] and therefore the insertion of CO into the Pd-aryl complex becomes the rate-limiting step [21]. Increase in the CO pressure therefore, results in the increase in the rate of carbonylation.

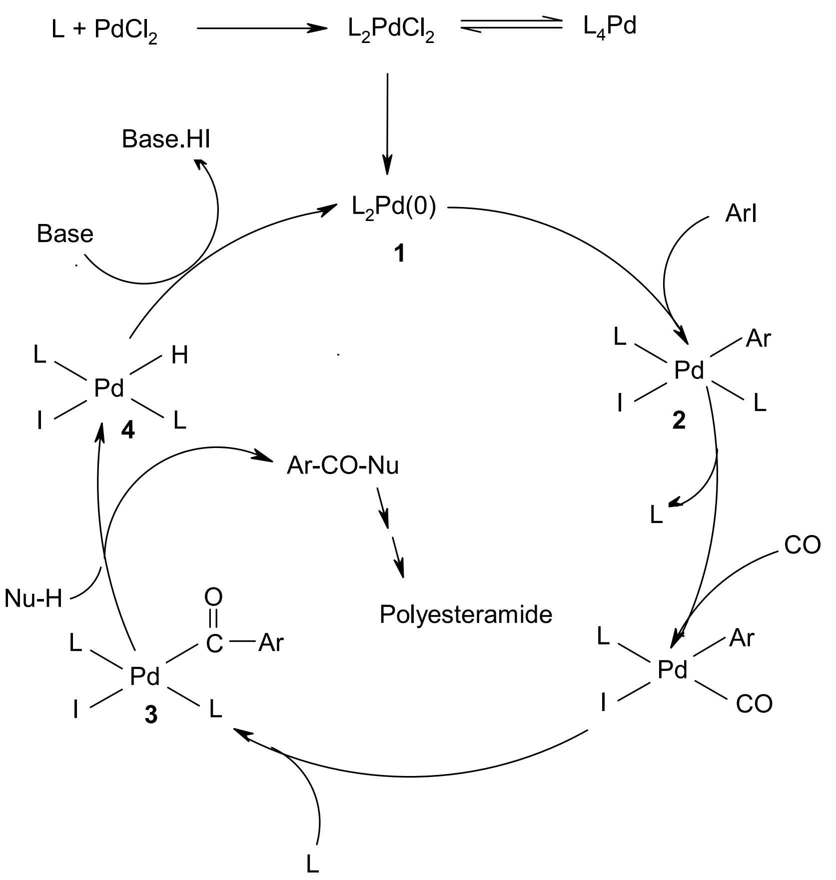


Figure 3-11. Proposed Reaction Mechanism for the Synthesis of Polyesteramides by Catalytic Carbonylation-Polycondensation Reaction (Nu = HN- or –O and L = PPh_3)

While the other carbonylation-polycondensation reactions e.g. those used in the polyamide or polyester synthesis involve only one type of nucleophile i.e. either amine or alcohol, the polyesteramide synthesis involves both. Certainly the difference in reactivity between individual amine and hydroxyl group would influence the placement of individual amide and ester units in almost the same way as during the conventional condensation reaction using diacid and needs detailed investigation.

3.3.8 Properties of the Polyesteramides

Several alternating polyesteramides were prepared using the catalytic carbonylation of different diiodoaromatics and amino alcohols (Table 3-2). The polyesteramides were obtained in high yields when both the reacting monomers were aromatic in nature. The wholly aromatic polyesteramides (Table 3-2, entries 1 and 5) were insoluble in common solvents while those containing flexible alkyl units were soluble NMP. The infrared spectrum of all the polyesteramides showed a strong absorption around 1720 and 1650 cm^{-1} indicating the presence of the ester and amide carbonyl groups. The molecular weight of a THF soluble fraction of polymer **2c** determined using GPC against polystyrene standards was 5000. A thermo gravimetric analysis indicated that all polymers were heat stable in air till the temperature of 315°C. TGA curves for all the prepared polyesteramides are given in 3-12.

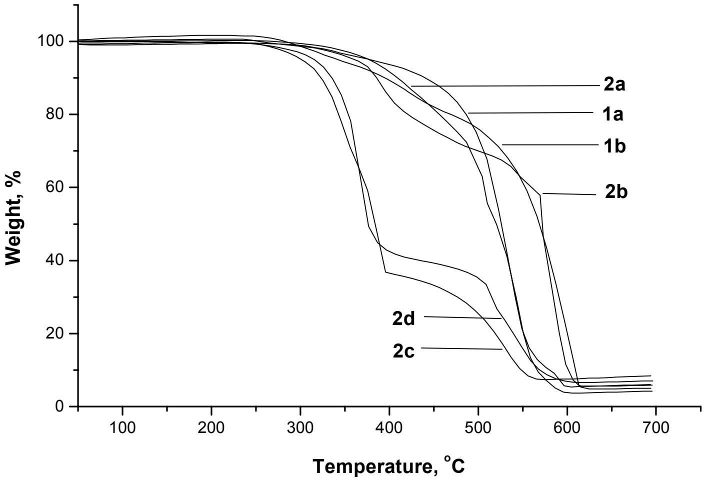


Figure 3-12. Thermogravimetric Behavior of Different Polyesteramides

3.4 Conclusions

We have successfully demonstrated that linear alternating polyesteramides can be efficiently prepared by the carbonylation-polycondensation reactions of aromatic diiodides and suitable amino alcohols in high yields. The polyesteramides obtained are free of defects arising because of the competing side reactions and especially the amine formation reactions. The proposed catalytic route does not require the presence of acid function on the monomers and has three major advantages. Firstly, the catalyst employed can be efficiently recycled easily. Secondly, a wide variety diiodoaromatics can be obtained regioselectively in high yields using the available procedure [26]. Thirdly, the iodide released during the reaction can be oxidized back to iodine and recycled in the preparation of diiodoaromatics [27]. The major disadvantage of the current route is the lower degree of polymerization.

3.5 References

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Chapter Four

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Synthesis of Polyesters by Palladium Catalyzed Carbonylation of Aromatic Diiodides and Diols

4.1 Introduction

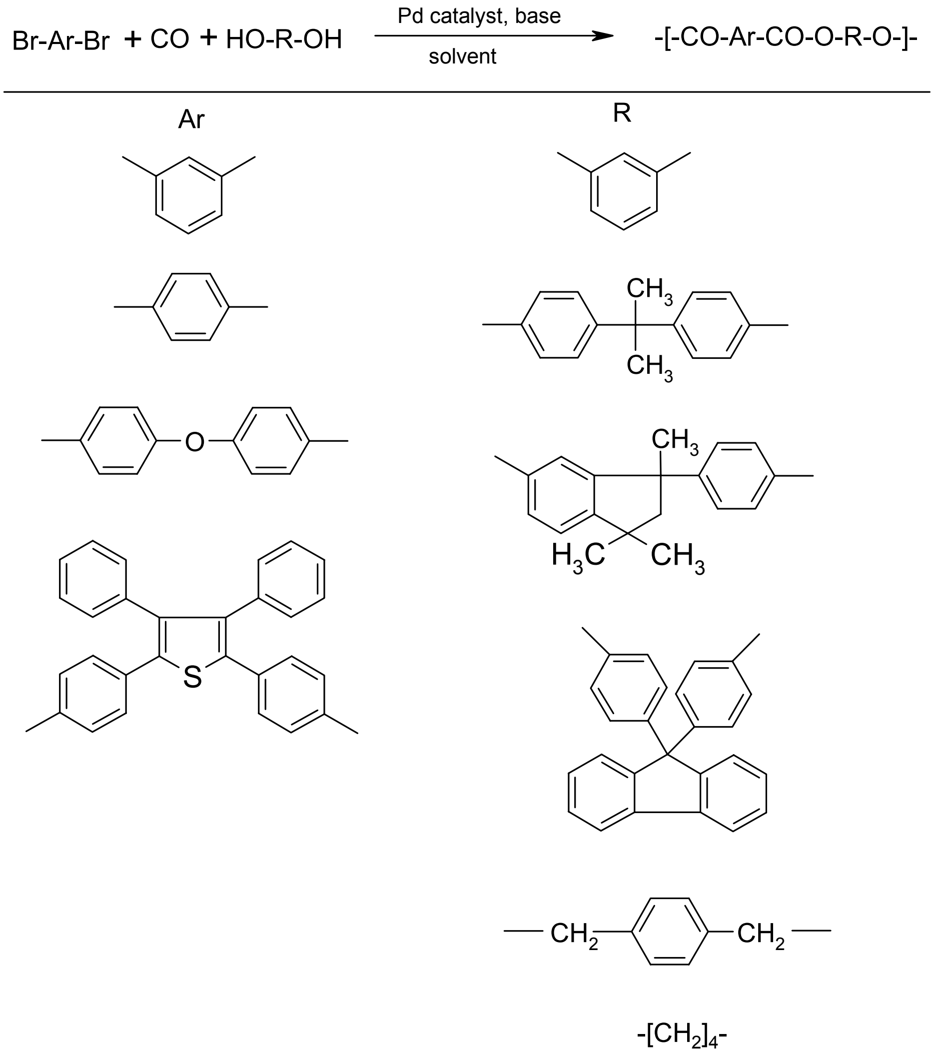
Aromatic polyesters belong to an important class of high performance polymers and find wide-ranging applications as thermoplastics and liquid crystalline materials [1]. A wide variety of methods may be used for the synthesis of aromatic polyesters but the most useful ones are summarized in Table 4-1 [2]. These conventional synthetic approaches for polyesters are often based on relatively high temperature condensation reactions of dicarboxylic acids or their suitable derivatives with the required diols. Further, such condensation reactions are suitable only if the appropriate diacid (or it's derivative) is easily available. Although, the availability may not be the problem for a few easily available dicarboxylic acids e.g. terephthalic acid, difficulties may arise when diacids with less common substitution patterns are required. In view of the growing interest in polyester polymers, it is useful to explore simple alternative methods for their synthesis, which would not require presence of diacid function in the reacting monomers.

In this context, the palladium catalyzed carbonylation-polycondensation route reported by Yoneyama et al. [3] seems to be promising. These catalytic polymerization reactions involving CO as a comonomer provide a versatile synthetic route for the preparation of several carbonyl containing high performance polymers including polyesters (See Chapter 1). These reactions use carbon monoxide as a source for the carbonyl function in these polymers and have emerged as an attractive alternative to the conventional condensation methods at least on laboratory scale.

Table 4-1. Synthetic Methods for the Preparation of Aromatic Polyesters [2]

Sr.	***Reactants***	***Typical reaction conditions***	***Reaction byproducts***
1.	***Direct Polyesterification*** *Dicarboxylic acid + diol* *or* *Hydroxycarboxylic acid*	*High temperature in the bulk or solvent* *Basic catalysts e.g. metal oxides (Titanium alkoxide, antimony fluoride etc.)*	*Water*
2.	***Ester exchange*** *Di-ester + diol*	*High temperature in the bulk or solvent and in presence of basic catalysts*	*Phenol or alcohol*
3.	***Transacylation*** *Diacid + diacetate of bis-phenol*	*High temperature in the bulk and in presence of basic catalysts*	*Alkanoic acid*
4.	***Acylation*** *Diacid chloride + bisphenol* *or* *Diacid chloride + bisphenoxide*	*High temperature in the bulk or inert solvent. Also low temperature with tertiary amine as a promoter.* *Low temperature under interfacial condensation conditions with acceptor for the HCl*	*HCl* *Chloride ions*
5.	***Others*** *(a) Diacid salt + alkylene dihalide*	*High temperature, heterogeneous conditions in presence of inert diluent and Cesium salts as catalysts*	*Halide ions*
	(b) Diacid chloride + trialkylsilylphenyl ether *(R_3Si-O-Ar)*	*High temperature in the melt or in presence of an inert sovent*	*Trialkylsilyl chloride* R_3SiCl

It is well known that palladium catalyzed carbonylation of aromatic halides in presence of hydroxy compounds gives the corresponding esters in excellent yields [4]. Based on this chemistry, Yoeneyama et al. were the first to synthesize polyesters by palladium-catalyzed reaction of aromatic dibromides, CO and bisphenols or aliphatic diols in presence of a base (Scheme 4-1) [3]. These authors also investigated the effect of various reaction variables such as the type of catalyst, solvent, base and reaction temperature on the polymerization reaction using the carbonylation-polycondensation of bis(4-bromophenyl) and bisphenol-A as a model reaction.



Scheme 4-1. Synthesis of Polyesters by Palladium Catalyzed Carbonylation of Aromatic Dibromides and Diols [3].

Several polyester derivatives (Scheme 4-1) were prepared with intrinsic viscosities in the range of 0.1 to 0.7 dL/g. One of the major advantage of this proposed catalytic method over the conventional route for polyester synthesis using aromatic diacids or their derivatives was that aromatic dibromides could be readily obtained by the direct bromination of aromatic compounds, whereas aromatic diacids or their derivatives had to be synthesized, often by multistep synthetic procedures [3]. Sugi et al. [5] further investigated the preparation of polyesters by palladium catalyzed carbonylation-polycondensation using partially aromatic substrates (e.g. 2,7-dibromo-9,10-dihydrophenanthrene) with the objective of obtaining polyesters with higher solubility in organic solvents. These authors also observed that comparatively low molecular weight polyesters were obtained when fully aromatic dihalides e.g dihalobiphenyls were used as substrates (Table 4-2, entries 3 and 4). It was also concluded that in case of partially aromatic dihalides, higher molecular weight polyester could be obtained with dibromo substrates whereas in case of fully aromatic dihalides, the diiodo substrates furnished higher molecular weight compared to the dibromo substrates.

Table 4-2. Preparation of Polyesters by Catalytic Carbonylation Route [5]

Sr.	***Dihalide***	***Yield (%)***	M_w	M_w/M_n
1.	*2,7-Dibromo-9,10-dihydrophenanthrene*	*99*	*35, 000*	*3.6*
2.	*2,7-Diiodo-9,10-dihydrophenanthrene*	*98*	*24, 000*	*2.8*
3.	*4,4'-Dibromobipheyl*	*94*	*5, 600*	*6.3*
4.	*4,4'-Diiodobiphenyl*	*98*	*12, 000*	*2.5*

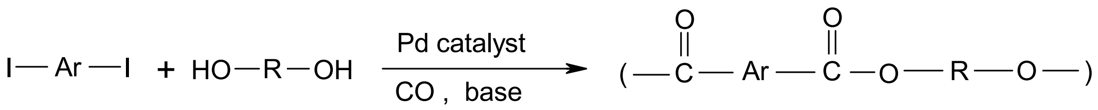
Reaction conditions*: dihalide: 2.5 mmol; bisphenol-A: 2.5 mmol; DBU: 5 mmol; chlorobenznene: 20 ml; temperature: 120° C; CO pressure 20 atm; reaction time: 3 hours.*

Perry et al. [6] prepared several fully aromatic polyesters in excellent yields and moderate intrinsic viscosities by palladium catalyzed carbonylation-polycondensation reaction of aromatic diiodides and diols. However, no details on the effects of reaction variable were provided.

The catalytic carbonylation-polycondensation reactions suffer from several limitations, which have so far not allowed any commercial applications. These limitations primarily include:

(a) Difficulties in availability of suitable dihalide substrates,
(b) Low catalytic activities, (TON<100 and TOF<30)) and
(c) Low degree of polymerization (intrinsic viscosities < 0.7 dL/g)

Although, the use of aromatic dichloride will be a major breakthrough in this subject, it appears difficult to achieve this using simple catalyst like $PdCl_2/PPh_3$ [7]. While dibromo derivatives are known to give better results, their availability on large scale may not be economically feasible. The use of diiodoaromatics would be an attractive option in this regard at least for two reasons. Firstly, because there exists possibility of preparing a wide variety of diiodoaromatics with high regioselectivity by direct iodination of aromatic compounds in presence of oxygen and a catalyst [8]. Secondly, the iodide released (as HI) during the carbonylation-polycondensation reaction can be reoxidized and recycled in the iodination process, which may partly compensate for the high cost of iodine [9]. The preliminary results by Sugi et al. (Table 4-2) and Perry et al. [6] also indicated that fully aromatic diiodo substrates give polyesters in excellent yields. Perry et al. had also demonstrated that in the preparation of polyamides by carbonylation-polycondensation reactions, the use of diiodo monomers instead of dibromo derivatives resulted in lowering of the reaction times and higher molecular weights [10]. Despite these attractive gains, the use of diiodoaromatics as substrates for the preparation of polyesters by carbonylation has received little attention and the information available on this subject is rather qualitative without any detailed investigation on the effects of reaction conditions on the polymerization process using diiodo substrates. The scope of this work was therefore to investigate the suitability of aromatic diiodides as substrates for the synthesis of fully aromatic polyesters using palladium catalyzed carbonylation-polycondensation reactions (Scheme 4-2).



$$\mathrm{I{-}Ar{-}I} + \mathrm{HO{-}R{-}OH} \xrightarrow[\text{CO , base}]{\text{Pd catalyst}} \left(-\overset{\overset{\displaystyle O}{\|}}{C}-\mathrm{Ar}-\overset{\overset{\displaystyle O}{\|}}{C}-O-R-O- \right)$$

Scheme 4-2. Synthesis of Polyesters by Palladium Catalyzed Carbonylation-Polycondensation of Aromatic Diiodides and Diols

Accordingly, the preparation of polyesters by palladium catalyzed carbonylation of aromatic diiodides and diols was investigated. The effect of various reaction variables e.g. ligand concentration, solvent, base, CO pressure and temperature on the polyester yield and intrinsic viscosity was studied and the results are presented in the following sections.

4.2 Experimental

4.2.1 Materials

Palladium chloride ($PdCl_2$); 1,4-diiodobenzene (DIB); 4,4'-dibromobenezene (DBB); 4,4'-diiodobiphenyl (DIBP); 4,4'-dibromobiphenyl (DBBP); 1,8-diaza [5.4.0] undec-7-ene (DBU); 1,4-diazabicyclo [2.2.2] octane (DABCO); 1,5-diazabicyclo [4.3.0] non-5-ene (DBN) were received from Aldrich Chemicals, USA and used without any further purification. *N,N,N',N'*-Tetramethylethylenediamine (TMEDA), triethylamine (TEA) were received from Merck Chemicals, India. *N,N*-dimethylacetamide (DMAc); *N,N*-dimethylformamide (DMF); *N*-mehtylpyrrolidone (NMP); triphenylphosphine (PPh_3), chlorobenzene, *o*-chlorophenol; toluene and methanol were purchased from SD Fine Chemicals, India and were analytical grade. All solvents were freshly distilled before use. 4,4'-dihydroxyphenylsulfone was received as gift sample. High Purity CO was obtained from Matheson Gas Company, USA. The reactor setup used for this study was similar to that described in Chapter 3 (section 3.2.2, pp. 102).

The homogeneous catalysts were prepared by adding appropriate amounts of $PdCl_2$ and PPh_3 in chlorobenzene to prepare a stock catalyst solution. The stock solutions were prepared and used freshly in all experiments. The heterogeneous palladium catalysts were prepared using literature procedures.

4.2.2 Analytical Measurements

Intrinsic viscosity where possible was measured in *o*-chlorophenol at a concentration of 0.5 g/dL at 303 K. FT-IR spectra were recorded on Bio-Rad FTS 175C model spectrometer in KBr. Thermo gravimetric analysis was performed on Metler-Toledo 5 Star system. The yields were reported as isolated yields.

4.2.3 Model Polymerization Experiment

In a typical experiment, the polyester (Table 4-3, entry 1) was prepared as follows. 4,4-Diiodobiphenyl (2.040g, 5 mmol), bisphenol-A (1.140g, 5 mmol), DBU (2.1 ml, 15 mmol), $PdCl_2$ (2 mg, 0.011 mmol), PPh_3 (12 mg, 0.044 mmol) and chlorobenzene (25 ml) were charged in the clean autoclave. The contents were flushed with nitrogen twice to replace any dissolved air or oxygen. The contents were then heated to 120°C under slow stirring. After the temperature was equilibrated at the set point, carbon monoxide was introduced to a desired pressure (3 atm) and stirring switched to 900 rpm. The reactor was operated at a constant pressure (3 atm) conditions throughout the reaction by supplying CO from a reservoir vessel using a constant pressure regulator. The pressure drop in the reservoir vessel was measured using a digital pressure transducer as a function of time. After completion of the reaction, the reactor was cooled to room temperature and the unreacted CO was vented off. The product polymer often separated as a solid material because of their low solubility in chlorobenzene. The reaction mixture was poured into 100 ml of methanol. The precipitated polymer was filtered, washed with additional 2 × 50 ml portions of methanol and dried under vacuum overnight. The viscosity of the polymer was measured in *o*-chlorophenol at a concentration of 0.5 g/dL at 30°C.

4.3 Results and Discussion

The carbonylation-polycondensation of 4,4'-diiodobiphenyl and bisphenol-A was investigated as a standard reaction. As in case of polyesteramides (Chapter 3), few initial experiments were carried out to establish the mass balance. It was found that the amount of CO consumed during the carbonylation-polycondensation reaction matched very well with the dihalide consumed at the end of the reaction. All experiments were therefore followed by the CO absorption data and the yield and intrinsic viscosity of the resulting polyester was measured. All polymers were also characterized by FTIR spectroscopy, which confirmed the presence of ester carbonyl frequency (around 1730 cm^{-1}). Several experiments were carried at different initial conditions to investigate the effect of various reaction parameters and the results are discussed below.

4.3.1 Effect of Substrate

The previous studies on preparation of polyesters by carbonylation route have been conducted comparatively at high catalyst loadings (around 4 mol%) [3,5]. We feel that the intrinsic catalytic behavior of bromo and iodo substrates may not be evident at such a high catalyst loadings. We therefore compared the activity of dibromo and diiododo substrates at lower catalyst loadings and the results are presented in Table 4-3. It can be seen that at low catalyst loadings (0.22 mol%), the reaction using diiodobiphenyl was practically completed within first 21 minutes whereas the reaction using dibromobiphenyl took almost 150 minutes (Table 4-3). The typical CO absorption profiles for these reactions are compared in Figure 4-1.

Table 4-3. Effect of Dihalide Substrate on the Carbonylation-Polycondensation Reaction

Sr.	*Dihalide*	*Reaction time (min)*	*Yield (%)*	*[η] (dL/g)*
1.	*4,4-Diiodobiphenyl*	*21*	*92*	*0.27*
2.	*4,4-Dibromobiphenyl*	*150*	*85*	*0.22*

***Reaction conditions**. dihalide: 5 mmol; bisphenol-A: 5 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; $PdCl_2$: 0.011 mmol; triphenylphosphine: 0.044 mmol; CO pressure: 3 atm; temperature: 120°C; agitation: 900 rpm.*

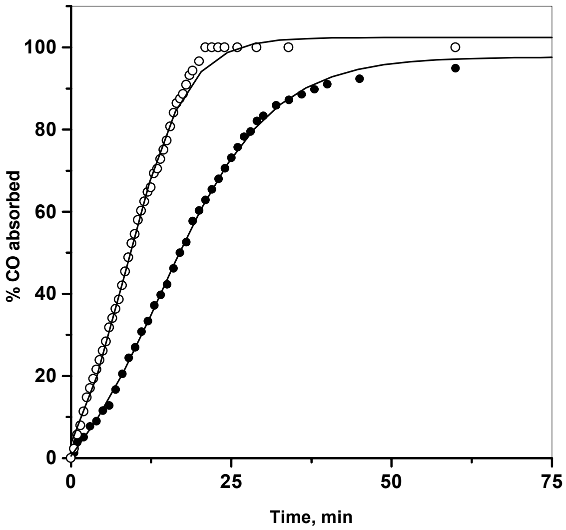


Figure 4-1. Effect of Dihalide on CO Absorption Profile During Carbonylation-Polycondensation Reaction.

Reaction conditions. *dihalide: 5 mmol; bisphenol-A: 5 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; PdCl$_2$: 0.011 mmol; triphenylphosphine: 0.044 mmol; CO pressure: 3 atm; temperature: 120°C; agitation: 900 rpm. Dihalides. (○) 4,4'-diiodobiphenyl (●) 4,4'-dibromobiphenyl.*

When the same reaction was carried out at higher CO pressure (7 atm) the reaction with DIBP was finished in 8 minutes and there was no reaction with DBBP even after 4 hours. The final reaction contents in case of reaction with DBBP contained large amount of palladium black whereas in case of DIBP a viscous yellow liquid was obtained without any palladium black. These results indicated that use of diiodosubstrates in carbonylation-polycondensation polymerization reactions resulted in decrease in the reaction time without significantly affecting yield and intrinsic viscosity compared to dibromoaromatics. Further, due to the higher reactivity of diiodo substrates, it was possible to use very low amount of catalyst (around 0.2 mol%) resulting in increase in the catalyst turn over number at least by a factor of 10. Once it was established that the polyesters could be obtained by carbonylation-polycondensation of diiodo substrates, we prepared several polyesters using different diiodosubstrates and the results are presented in Table 4-4.

Table 4-4. Synthesis of Polyesters by Palladium Catalyzed Carbonylation-Polycondensation Reaction.[a]

Sr.	***Dihalide***	***Diol***	***Catalyst*** [b] *(mmol of Pd)*	***Time*** *(min)*	***Yield*** [c] *(%)*	***[η]*** [d] *(dL/g)*	***TON*** [e]	***TOF*** [f] *(hr-1)*
1.	*4,4-diiodobiphenyl*	*bisphenol-A*	*0.011*	*20*	*92*	*0.27*	*454*	*1363*
2.	*4,4-diiodobiphenyl*	*Bispenol-A*	*0.0002*	*355*	*90*	*0.24*	*25,000*	*4230*
3.	*4,4-diiodobiphenyl*	*4,4-dihydroxydiphenylsulfone*	*0.011*	*22*	*95*	*0.32*	*454*	*1238*
4.	*4,4-diiodobiphenyl*	*1,4-dihydroxybenzene*	*0.011*	*19*	*87*	*0.27*	*454*	*1434*
5.	*4,4-diiodobiphenyl*	*2,7-dihydroxynaphthalene*	*0.011*	*21*	*85*	*0.24*	*454*	*1297*
6.	*1,4-diiodobenzene*	*4,4-dihydroxydiphenylsulfone*	*0.011*	*24*	*80*	*0.21*	*454*	*1135*
7.	*1,4-diiodobenzene*	*1,4-dihydroxybenzene*	*0.011*	*25*	*82*	*0.23*	*454*	*1089*
8.	*4,4-diiodobiphenyl*	*2,7-dihydroxynaphthalene*	*0.011*	*21*	*85*	*0.24*	*454*	*1297*
9.	*1,4-diiodobenzene*	*1,2-ethanediol*	*0.011*	*180*	*40*	*0.12*	*454*	*151*

[a] ***Reaction conditions***. *dihalide: 5 mmol; diol: 5 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; temperature:120°C; agitation: 900 rpm.* [b] *PPh3:Pd=4.* [c] *Isolated yield.* [d] *Intrinsic viscosity measured for the soluble fraction in o-chlorophenol at a concentration of 0.5 g/dL at 30°C.* [e] *TON expressed as moles of dihalide converted per mole of Pd.* [f] *TOF expressed as TON per hour.*

The results presented in Table 4-4 indicate that a wide variety of polyesters with moderate intrinsic viscosity can be prepared in excellent yields by catalytic carbonylation-polycondensation reaction using diiodo substrates. Very high turnover numbers (25,000), which are almost 500 times higher than reported earlier for this reaction can be obtained by using lower catalyst loadings. The reaction using aliphatic diol (Table 4-4, entry 9) required higher reaction times compared to the reactions employing phenols and the former resulted in lower yields and intrinsic viscosity polyester.

Once it was demonstrated that polyesters could be obtained in excellent yields, we next investigated the effect of various reaction variables on the polymerization reaction. The carbonylation-polycondensation of 4,4'-diiodobiphenyl and bisphenol-A was investigated as the model reaction and several experiments were carried out at different reaction conditions and the results are discussed in the following sections.

4.3.2 Effect of Solvent

The efficiency of several organic solvents in the carbonylation-polycondensation reaction was examined and the results are presented in the Table 4-5. These results are consistent with earlier reports [3, 5] and indicate that chlorobenzene is the most suitable solvent among the various solvents screened. The suitability of chlorobenzene over other solvents may be partly because of enhanced solubility of resulting polyesters in chlorobenzene compared to other solvents [4]. All further experiments were therefore carried out in chlorobenzene solvent. The CO absorption profiles for different reactions are given Figure 4-2.

Table 4-5. Effect of Solvent on Polyester Synthesis by Carbonylation.

Sr.	*Solvent*	*Reaction time* (min)	*Yield* (%)	*[η]* (dL/g)	*TOF* (h^{-1})
1.	*N,N'-Dimethylacetamide*	*23*	*60*	*0.12*	*1185*
2.	*N,N'-Dimethylformamide*	*28*	*62*	*0.13*	*974*
3.	*N-Methylpyrrolidone*	*27*	*60*	*0.18*	*1010*
4.	*Toluene*	*56*	*74*	*0.21*	*487*
5.	*Chlorobenzene*	*20*	*92*	*0.27*	*1363*

Reaction conditions. *4,4' diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; CO pressure: 3 atm; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour; solvent: 25 ml.*

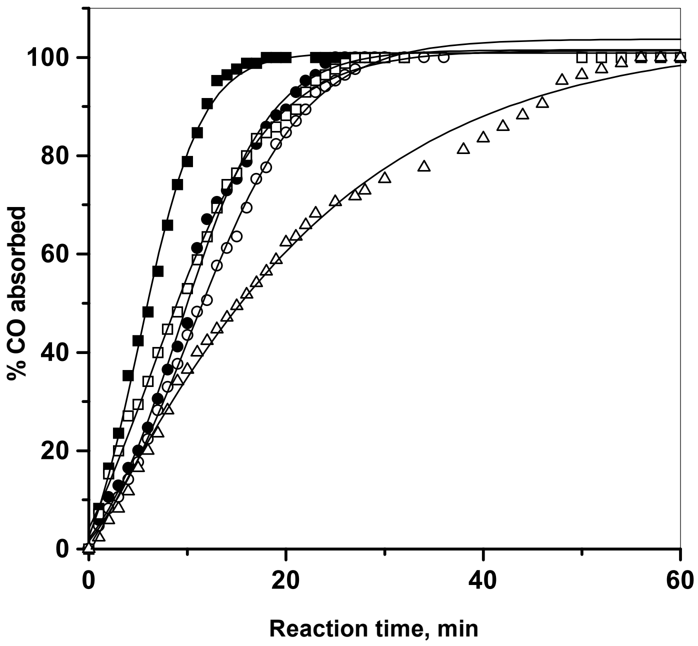


Figure 4-2. Effect of Solvent on CO Absorption Profile in the Synthesis of Polyesters by Carbonylation.

Reaction conditions. *4,4' diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 10 mmol; CO pressure: 3 atm; temperature:120°C; agitation 900 rpm; reaction time: 1 hour; solvent: 25 ml. (■) chlorobenzene, (□) N-methylpyrrolidone, (●) N, N'-dimethylformamide, (○) N,N'-dimethylacetamide, and (△) toluene.*

4.3.3. Effect of Ligand

As discussed during the polyesteramides (Chapter 3), the aryl iodides can be oxidatively to the Pd(0) even in the absence of any stabilizing ligands. This was true even in the present case and the carbonylation-polycondensation reaction of 4,4-diiodobiphenyl and bisphenol-A provided the corresponding polyester (yield - 35%, [η] – 0.11) using only $PdCl_2$ (without any ligand) as the catalyst. The results are presented in Table 4-6.

Table 4-6. Effect of Ligand/Pd Ratio on the Synthesis of Polyesters by carbonylation

Sr.	*Ligand/Pd*	*Reaction time* (*min*)	*Yield* (*%*)	*[η]* (*dL/g*)	*TOF* (*h^{-1}*)
1.	*0*	*70*	*35*	*0.11*	*389*
2.	*2*	*21*	*85*	*0.24*	*1298*
3.	*4*	*20*	*90*	*0.27*	*1363*
4.	*7*	*22*	*86*	*0.23*	*1240*
5.	*10*	*20*	*89*	*0.25*	*1363*

Reaction conditions. *4,4' diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour.*

4.3.4 Effect of Base

The earlier reports [3, 5] have investigated efficiency of various bases in the preparation of polyesters by catalytic carbonylation using dibromo substrates and found that higher activities could be obtained using sterically hindered organic bases e.g DBU. These results were also applicable for carbonylation-polycondensation reactions using diiodo substrates (Table 4-7)

Table 4-7. Effect of Base on the Synthesis of Polyesters by Carbonylation

Run	*Base*	*pKa*	*Reaction time (min)*	*Yield (%)*	*[η] (dL/g)*	*TOF (h^{-1})*
1.	DBU	11.9	20	92	0.27	1363
2.	DBN	11.0	21	86	0.23	1298
3.	DABCO	9.15	43	70	0.18	634
4.	Et_3N	10.75	30	42	0.10	909
5.	TMEDA	9.15	42	53	0.09	649
6.	NaOH	-	51	18	0.06	535
7.	NaOAc	-	48	23	0.07	568

***Reaction conditions**. 4,4 diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; base: 15 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour. pKa values for aqueous solutions of the corresponding conjugate acids [Reference 9]*

4.3.5 Effect of CO Pressure

The effect of CO partial pressure on the rate of carbonylation-polycondensation reaction was investigated in the range of 1-7 atm at 120°C and the results are presented in Table 4-8. These results indicate that the CO pressure has very little effect on the yield of the polymerization reaction. However, the intrinsic viscosity of the polyester increased marginally with increase in the CO partial pressure. Although, the increase in the carbonylation rate in case of iodo substrates could be explained on the basis of difference in the rate determining steps, the variation of intrinsic viscosity with CO pressure was not clear.

The typical CO absorption profiles at different CO partial pressures are compared in Figure 4-3. The rate of carbonylation increased with increase in CO pressure. The variation of initial rate of carbonylation (calculated from the CO consumption data) is given in Figure 4-4.

Table 4-8. Effect of CO Pressure on the Synthesis of Polyesters by Carbonylation.

Sr.	*CO pressure (atm)*	*Reaction time (min)*	*Yield (%)*	*[η] (dL/g)*	*TOF (h^{-1})*
1.	*1*	*25*	*95*	*0.27*	*1090*
2.	*3*	*20*	*92*	*0.29*	*1363*
3.	*5*	*11*	*90*	*0.30*	*2479*
4.	*7*	*8*	*85*	*0.33*	*3409*

Reaction conditions. *4,4 diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; temperature: 120°C; agitation 900 rpm; reaction time: 1 hour.*

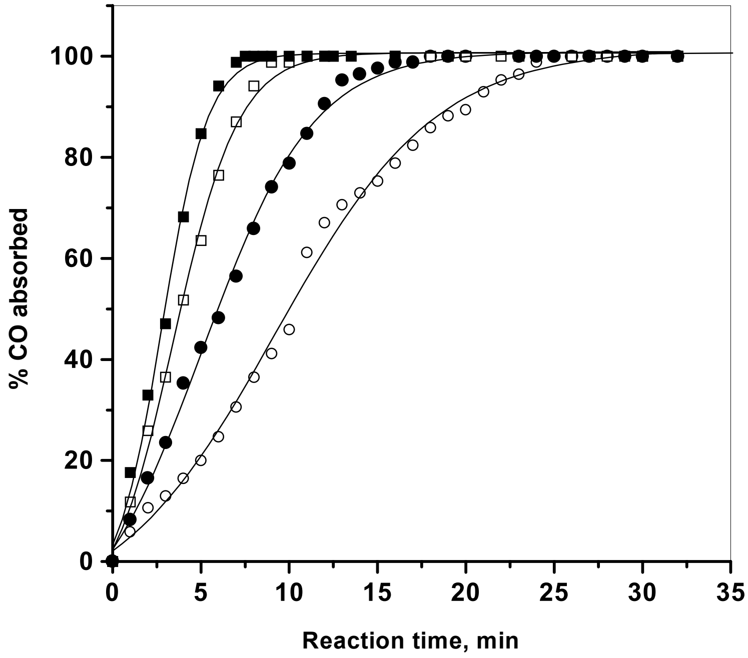


Figure 4-3. Effect of CO Pressure on the CO Absorption Profile in the Synthesis of Polyesters by Carbonylation.

Reaction Conditions. *4,4'-diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; $PdCl_2$: 0.011 mmol; triphenylphosphine: 0.044 mmol; temperature: 120°C; agitation: 900 rpm. CO pressures (○) 1 atm, (●) 3 atm, (□) 5 atm, and (■) 7 atm.*

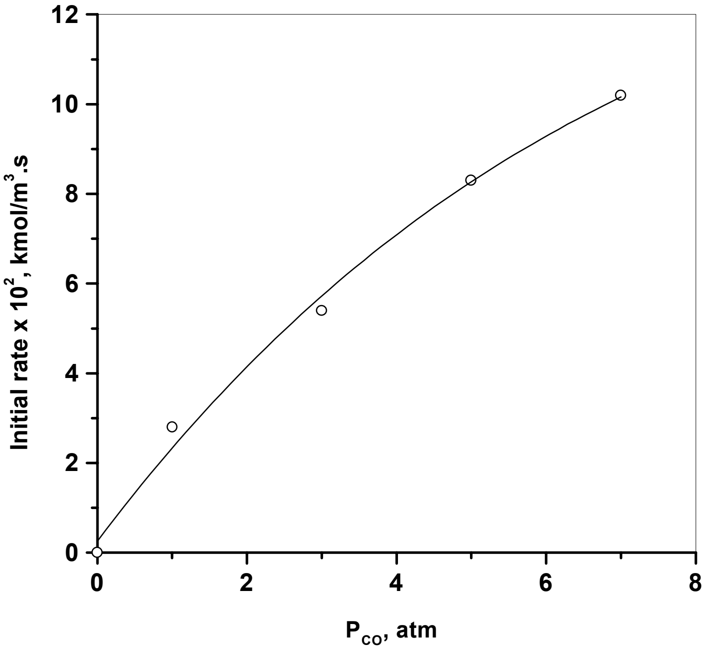


Figure 4-4. Effect of CO Pressure on the Initial Rate of Carbonylation

4.3.6 Effect of Temperature

The effect of temperature on the carbonylation-polycondensation of 4,4'-diiodobiphenyl and bisphenol-A was investigated in the temperature of 90-130°C. The CO partial pressure was kept constant (3 atm) during these experiments. The results are given in Table 4-9, which indicated that there was not much effect of temperature on the yield of the polyester but the intrinsic viscosity was strongly affected by the temperature. Thus, the intrinsic viscosity was highest at 120°C and decreased on either lowering or increasing the temperature. The almost constant yield of the polyester at different reaction temperatures was consistent with the CO absorption data (Figure 4-5). It may be seen that the increase in reaction temperature resulted in increase in the carbonylation rate but since all these reactions were completed within reaction time (1 hour), the yield remained almost same. The energy of activation calculated from the Arrhenius plot (Figure 4-6) for this reaction is 34kJ/mole.

Table 4-9. Effect of Temperature on the Synthesis of Polyesters by Carbonylation.

Sr.	***Temperature*** *(°C)*	***Reaction time*** *(min)*	***Yield*** *(%)*	***[η]*** *(dL/g)*	***TOF*** *(h^{-1})*
1.	*90*	*40*	*91*	*0.19*	*681*
2.	*100*	*28*	*86*	*0.21*	*974*
3.	*110*	*23*	*90*	*0.25*	*1186*
4.	*120*	*20*	*92*	*0.27*	*1363*
5.	*130*	*12*	*89*	*0.24*	*2272*

***Reaction conditions**. 4,4'-diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 15 mmol; chlorobenzene: 25 ml; CO pressure: 3 atm; agitation 900 rpm; reaction time: 1 hour.*

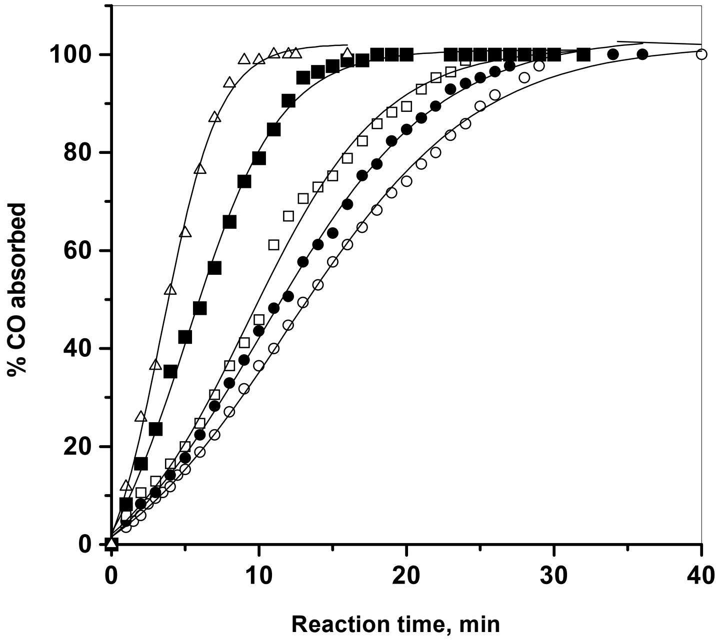


Figure 4-5. Effect of Temperature on CO Absorption Profile in the Synthesis of Polyesters by Carbonylation.

***Reaction conditions**. 4,4' diiodobiphenyl: 5 mmol; bisphenol-A: 5 mmol; $PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 15 mmol; chlorobenzene: 25ml; CO pressure: 3 atm; agitation 900 rpm; reaction time: 1 hour. Temperatures (○) 90°C, (●) 100°C, (□) 110°C, (■) 120°C, and (△) 130°C.*

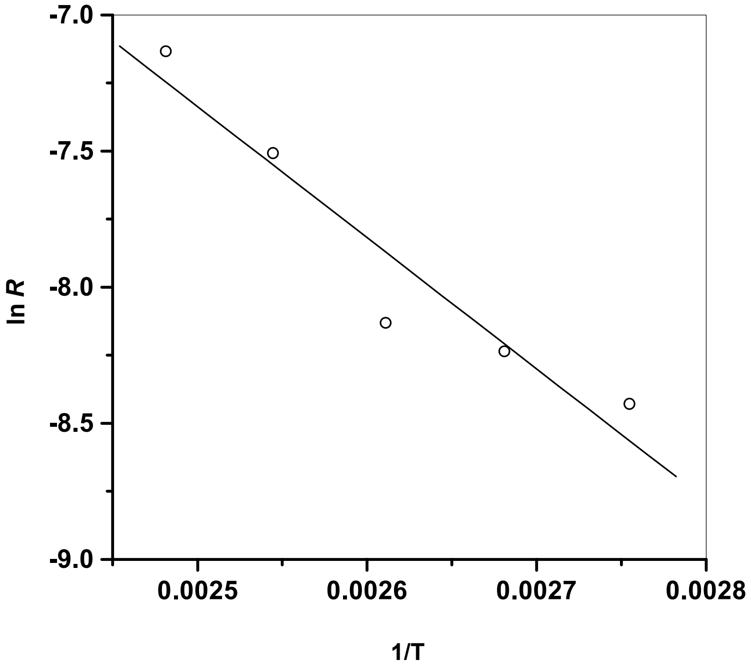


Figure 4-6. Arrhenius Plots

4.3.7 Effect of Diiodide/Diol Ratio

Finally, we investigated the effect of diiodide/diol ratio on the carbonylation-polycondensation reaction. In these reaction the concentration of diol (bisphenol-A) was kept constant (2.5 mmol) and the concentration of 4,4'-diiodobiphenyl was varied in the range of 1.25 to 5 mmol. The reaction using excess of bisphenol-A produced polyester in low yields (19%) and in all other cases quantitative formation of polyester was observed. The results are given in Table 4-10. The corresponding CO absorption profiles given in Figure 4-7 indicate that the in each the CO was consumed as long as both, the diiodides and the diol were present in the reaction system.

Table 4-10. Effect of Diiodide/Diol Ratio on the Synthesis of Polyester by Carbonylation

Sr.	*DIBP* (mmol)	*BPA* (mmol)	*Reaction time* (min)	*Yield*	*[η]* (dL/g)
1.	*1.25*	*2.5*	*3*	*19*	*0.08*
2.	*2.5*	*2.5*	*8*	*89*	*0.26*
3.	*5.0*	*2.5*	*3*	*64*	*0.17*

Reaction conditions. *$PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 15 mmol; chlorobenzene: 25ml; CO pressure: 3 atm; agitation 900 rpm; temperature: 120°C; reaction time: 1 hour.*

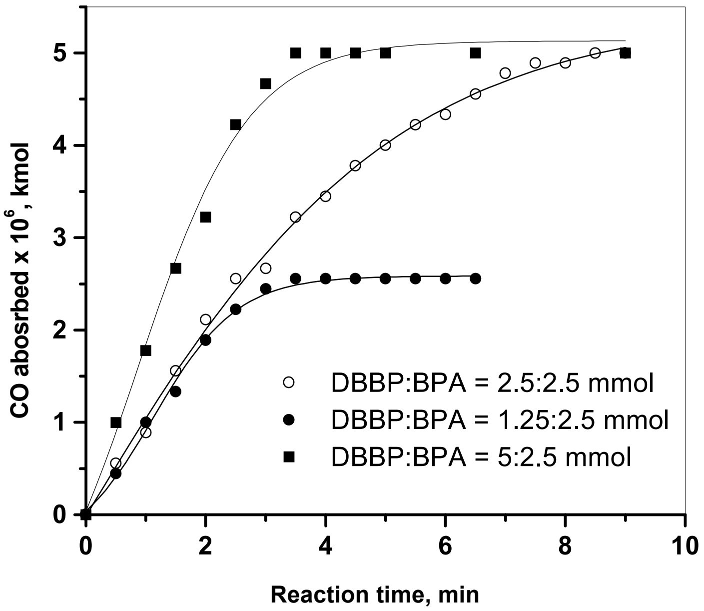


Figure 4-7. Effect of Diiodide/Diol Ratio on the CO Absorption Profile in the Synthesis of Polyesters by Carbonyaltion.
Reaction conditions. *$PdCl_2$: 0.011 mmol; PPh_3: 0.044 mmol; DBU: 15 mmol; chlorobenzene: 25ml; CO pressure: 3 atm; agitation 900 rpm; temperature: 120°C; reaction time: 1 hour. (●) DIBP: 1.25 mmol, BPA: 2.5 mmol, (○) DIBP: 2.5 mmol, BPA: 2.5 mmol, (■)DIBP: 5.0 mmol, BPA: 2.5 mmol.*

4.3.8 Use of Heterogeneous Catalysts

The prior art on the preparation of polyesters by carbonylation-polycondensation reaction has employed homogeneous palladium catalysts only. The particular disadvantage, which neglects the commercial use of the homogeneous catalysts in the carbonylation-polycondensation reactions, is the difficulty in the efficient separation and recycling of the catalyst. The loss of precious metal during frequent recovery cycles makes homogeneous catalytic processes uneconomical to operate and overshadows the technologically attractive homogeneous processes. One way to solve the problem of catalyst recovery and recycle would be to use the heterogeneous palladium catalysts. To investigate the applicability of this approach, several heterogeneous palladium catalysts were prepared and screened for their activity in carbonylation-polycondensation polymerization reaction. The results are presented in Table 4-11. It was observed that no polymer could be obtained with heterogeneous palladium catalyst in the absence of any added phosphine ligand (Table 4-11, entries 1 and 2). Same reactions when repeated using four equivalents of PPh_3, produced polyesters in moderate yields. Among the several heterogeneous catalysts used, $Pd/CaCO_3$ gave highest yields (72%) and inherent viscosity (0.21 $dL.g^{-1}$). In all experiments using heterogeneous catalysts, the analysis of the reaction mixture after reaction indicated that considerable amount of the palladium was leached in the reaction solvent. The leached palladium metal however, remained in the solution and no redeposition of the leached metal was observed in the present case as reported in the literature [11]. The leaching of catalyst resulted in decrease in the catalytic activity of the heterogeneous palladium catalysts. The results for the recycle experiments using $Pd/CaCO_3$ catalyst are given in Figure 4-8.

Table 4-11. Synthesis of Polyesters by Carbonylation-Polycondensation Reactions Using Heterogeneous Palladium Catalysts.

Sr.	*Catalyst*	*Yield* (%)	*[η]* (dL/g)
1.	5 % Pd/C	0^a	-
2.	5% $Pd/CaCO_3$	0^a	-
3.	5% Pd/C	45	0.12
2.	5 % $Pd/CaCO_3$	72	0.21
3.	5 % $Pd/\gamma\text{-}Al_2O_3$	64	0.18
4.	5 % $Pd/ZSM\text{-}5$	40	0.12
5.	5 % $Pd/MgCl_2$	52	0.14
6.	5 % Pd/C	0^b	-
7.	5 % $Pd/CaCO_3$	0^b	-

Reaction conditions: *4,4'-diodobiphenyl: 5 mmole; bisphenol-A: 5 mmo), catalyst: 200 mg (equivalent to 0.1 mmole of palladium);* PPh_3*: 0.4 mmol; chlorobenzene: 25 ml; CO pressure: 20 atm; temperature: 120°C, agitation: 900 rpm.* ^{a} *without any* PPh_3*.* ^{b} *4,4-dibromobiphenyl was used instead of 4,4-diiodobiphenyl.*

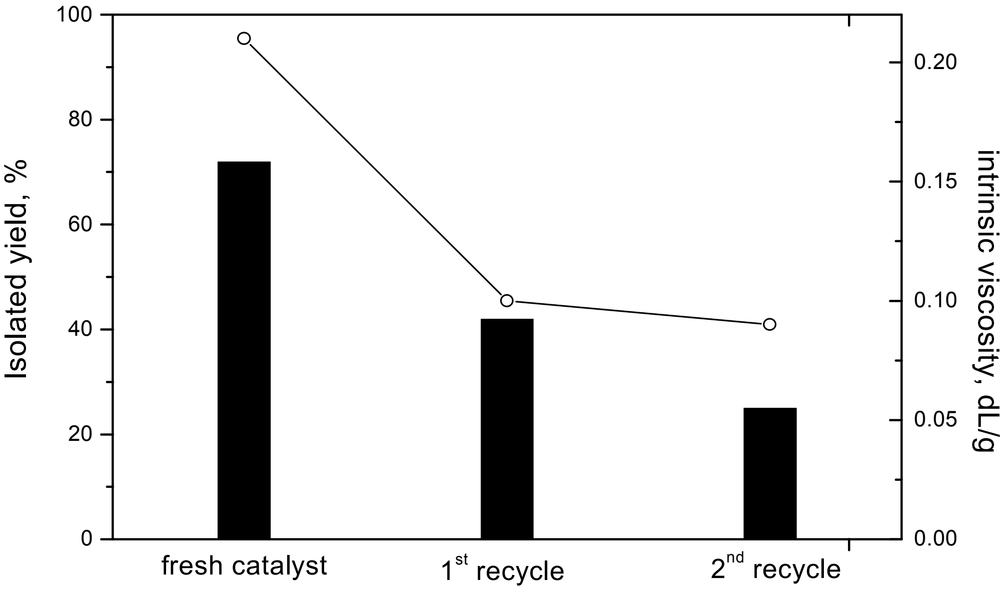


Figure 4-8. Recycle Experiments Using Heterogeneous Palladium Catalyst (*5%* $Pd/CaCO_3$*) Bar graph represents isolates yields and line graph the intrinsic viscosity*)

For the catalyst recycle experiments, the reaction mixture containing heterogeneous catalyst and product polyester was added to 20 ml of *o*-chlorophenol. All other reaction components except the heterogeneous catalyst were soluble in o-chlorophenol and were removed by filtration. The solid catalyst was washed with ether twice and dried in vacuum. This catalyst was then recycled for the next reaction with fresh charge. The recycle results indicate that the use of heterogeneous catalyst did not provide any attractive solution to efficient catalysis. The data presented in Table 4-11 also indicated that there was absolutely no reaction when the 4,4'-diiodobiphenyl was replaced by the 4,4'-dibromobiphenyl (Table 4.11, entries 6 and 7) in presence of heterogeneous palladium catalysts. Similar observations were noted when 1,4-dibromobenzene was used as substrate. This striking difference in the activity of bromo and iodo derivatives could probably be attributed to the reactivity of these substrates. It should be noted that due to the obvious problems of separation of heterogeneous catalysts and more importantly loss of activity due to leaching was undesired and thus use of heterogeneous catalysts did not provide any significant improvement in the state of the art.

4.4 Conclusions

In conclusion, the studies presented here demonstrate that polyesters can be efficiently prepared starting from aromatic dibromides as well as diiodides. However, the use of diiodo derivatives is attractive at least for two reasons.

(1) Availability of diiododerivatives,

(2) Lower reaction times and temperatures.

It can be seen that very high turnover numbers and turnover frequencies can be obtained using proper reaction conditions. The only serious problem at present seems to be the fairly low degree of polymerization. The premature precipitation of the polymer because of the poor solubility in the polymerization solvent could be the key factor in deciding molecular weight and needs detailed studies.

4.5 References

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Chapter Five

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Summary and Future Scope

The major focus of the future industrial processes will be on developing new catalytic reactions that will be energy saving, environment friendly and allow optimal use of raw materials. In this context, the recent developments in C_1 chemistry and particularly in the area of novel polymerization reactions using CO as a comonomer have assumed significant importance. These emerging catalytic polymerization reactions utilize a non-conventional and cheaper feedstock like CO in the preparation of several high performance polymers like polyamides, polyesters, polyketones, polypeptides, polyimides etc. This thesis has addressed a few specific problems related to the catalysis and kinetic modeling of novel polymerization reactions using CO as a building block. These aspects are important in not only understanding the fundamental chemistry but also in improving the efficiency of this synthetic route. The following specific problems were investigated:

1. Kinetic modeling of copolymerization of ethylene and carbon monoxide to polyketone using homogeneous palladium catalyst
2. Synthesis of linear polyesteramides by palladium catalyzed carbonylation-polycondensation of aromatic dihalides and aminohydroxy compounds.
3. Synthesis of polyesters by carbonylation-polycondensation of aromatic diiodides and diols using highly efficient palladium catalysts

In the preceding Chapters of this thesis, elaborate details of the results achieved have been presented. In this Chapter, some important conclusions and future scope of research in this area is highlighted.

Detailed kinetic modeling of copolymerization of ethylene and CO to perfectly alternating polyketones was one of the first comprehensive attempts to study the kinetics of this class of reactions. The kinetics was investigated over a wide range of reaction conditions in methanol solvent using a homogeneous palladium complex, [(dppp)Pd(H_2O)(TsO)](TsO) as a catalyst precursor. The copolymerization of ethylene and carbon monoxide was an excellent example of a multiphase catalytic reaction since it involved simultaneous absorption of two gases (ethylene and CO) followed by a reaction in the liquid medium (methanol) to produce a solid polymer product. The effect of catalyst loading, partial pressures of CO and ethylene on the rate of copolymerization was investigated over a temperature range of 353-373 K. The kinetic analysis indicated that a model derived by assuming insertion of ethylene into the tetra-coordinated Pd–acyl species as the rate-determining step represented the kinetics in good agreement with the experimental results. However, several important problems need further investigations. Some of these are:

(a) The effect of reaction conditions and conversion levels on the molecular weight distribution and properties of polyketone polymer.

(b) Investigation of the catalysis and kinetics of the copolymerization of CO with substituted olefins (e.g. propylene, styrene, vinyl acetate etc.) because these copolymers may have attractive properties.

(c) Since, the commercially important polyketone is a terpolymer of CO, ethylene and propylene, it would be a challenge to understand the detailed catalysis, kinetics and reaction engineering aspects during such terpolymerization reactions.

Synthesis of polyesteramides by carbonylation route has reported for the first time in this thesis. As discussed in Chapter 3, this aspect could open new opportunities for the synthesis of several polyesteramides eliminating the need for the diacrboxylic acid substrate. The third chapter reports for the first time the preparation of polyesteramides using palladium catalyzed carbonylation-polycondensation of aromatic diioide and an amino alcohol. Effect of various reaction parameters like temperature, base, ligand, CO pressure, solvent used on the catalytic activity and intrinsic viscosity of the polymers has been investigated. It was observed that linear alternating polyesteramides could be prepared in excellent yields under optimized reaction conditions. A detailed characterization of these polymers was also carried out. Obviously, several details about these reactions need further investigations, which include the understanding of the effect of several reaction parameters such as catalysts, promoters, solvents and reaction conditions. The present thesis has reported a study, which is only the beginning of the story for this important class of polymers. One of the major challenges in these reactions is the improvement of molecular weights. Other major challenges from practical point of view would be to economize the catalyst use by further improvement of the TON. At the same time, the basic chemistry and catalytic cycles also require deeper understanding.

Polyesters by catalytic carbonylation-polycondensation reactions has been investigated in this thesis to understand the role of reaction conditions and explore the possibility of using heterogeneous catalysts. Similar to polyesteramides, polyesters by carbonylation is also gaining attention as it eliminates the requirement of diacid substrate and utilize cheaper CO as a comonomer. Some important conclusion include the observation that use of diiodoaromatics substrate results in significant decrease in reaction times. Also, very high TON and TOF could be obtained using diiodo substrates compared to dibromo substrates. In this case too, there is need to improve the catalyst system such that it is economical to use in practice. Investigations of other alternative catalysts, fundamental catalytic chemistry and catalytic cycle as well as the reaction engineering aspects are the major challenges for the future. The improvement in molecular weights is also one of the major challenges. The possibility of using even cheaper dihalides like dichloroaromatics would be desirable in the carbonylation-polycondensation reactions in general.

In conclusion, a specific study reported here on the polymerization reactions using CO as a comonomer has lead to a better understanding of the effect of the reaction conditions and kinetics. However, a deeper understanding of this subject covering catalysis, reaction engineering as well as the characterization of the polymers would be necessary to evolve a competitive alternative to the conventional synthetic routes for polyketones, polyesteramides and polyesters.

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List of Publications

1. Synthesis of polyesteramides by a new palladium catalyzed carbonylation-polycondensation reaction
   Shrikant M. Kulkarni, Ashutosh A. Kelkar and Raghunath V. Chaudhari
   Chem. Comm. 1276, **2001**.

2. Kinetic modeling of copolymerization of ethylene with carbon monoxide using Pd complex catalyst.
   L. Toniolo, **Shrikant M. Kulkarni**, D. Fatutto and Raghunath V. Chaudhari
   Ind. Eng. Chem. Res. 40, 2037, **2001**.

3. Synthesis and characterization of polyesteramides by palladium-catalyzed carbonylation polycondensation of aromatic diiodides and amino alcohols.
   Shrikant M. Kulkarni, Mahesh R. Didgikar, Ashutosh A. Kelkar and Raghunath V. Chaudhari
   Communicated, **2001**.

4. Synthesis of polyesters by palladium mediated carbonylation polycondensation of aromatic dihalides and diols.
   Shrikant M. Kulkarni and Raghunath V. Chaudhari
   Communicated, **2001**.

5. Synthesis and properties of Polyketone-clay nanocomposites.
   Neelima N. Bulakh, **Shrikant M. Kulkarni**, Raghunath V. Chaudhari and Jyoti P. Jog
   Communicated, **2001**.

List of Patents

1. Process for the preparation of a polyester.
   Ashutosh A. Kelkar, **Shrikant M. Kulkarni**, and Raghunath V. Chaudhari
   US Pat. 6335415, **2002**.

2. A process for polyesteramides
   Ashutosh A. Kelkar, **Shrikant M. Kulkarni**, and Raghunath V. Chaudhari
   US patent Application No. 09/112345