

Transition Metal Catalyzed Polymerization in Aqueous Systems

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1 Introduction

As a reaction medium for transition metal catalyzed polymerizations, most likely one will not consider water as first choice. The extreme water sensitivity of Ziegler or Phillips catalysts is well known. However, carrying out polymerization reactions in aqueous systems offers unique advantages. Thus, traditional free-radical emulsion and suspension polymerization are carried out on a large scale industrially. A brief review of these established reactions demonstrates some specific properties of polymerizations in aqueous systems.

1.1 *Traditional free-radical polymerization in aqueous systems*

In *emulsion polymerization*, polymer latices are obtained as a product.^[1-4] A polymer latex is a stable dispersion of polymer particles in the size range of ca. 50 to 1000 nm in a liquid medium, usually water. Latices are also referred to as polymer dispersions, or polymer colloids. In such latices, coagulation and precipitation of the polymer particles must be prevented. Stabilization can occur by different mechanisms: by electrostatic repulsion between the diffuse counterion layers surrounding particles (electrostatic stabilization), or by means of a layer of polymer on the particle surface, which has a good miscibility with the dispersing medium and thus results in repulsion when the polymer layers of two approaching particles get in contact (steric stabilization). Electrostatic stabilization most often involves ionic low-molecular-weight surfactants adsorbed to the particle surface, whereas steric stabilization is usually brought about by water-soluble polymers adsorbed or covalently bound to the particle surface. The mechanism of free-radical emulsion polymerization is complex, nonetheless the following simplified considerations can illustrate underlying principles.

In a typical aqueous emulsion polymerization, a water-immiscible monomer is

polymerized in the presence of a surfactant employing a water-soluble initiator, such as potassium peroxydisulfate. A water-soluble radical, e.g. $\cdot\text{SO}_4^-$ formed by thermal decomposition of the initiator, grows by addition of monomer dissolved in the aqueous phase (also for 'water-immiscible' monomers a small equilibrium concentration is present in the aqueous phase). Repeated monomer addition results in the formation of an oligomeric radical, which is initially water-soluble due to the incorporated sulfate moiety (Scheme 1.1). Upon reaching a certain critical chain length the growing radical chain becomes insoluble and collapses upon itself, thus nucleating a particle ('homogeneous nucleation'). This primary particle is stabilized by adsorption of surfactant, and further polymerization within the particle results in particle growth. Alternately, a particle can be nucleated by the water-soluble oligomer entering a surfactant micelle prior to reaching its critical chain length ('heterogeneous micellar nucleation').

During emulsion polymerization the emulsified monomer droplets serve as a reservoir for monomer, however polymerization usually does not occur in these droplets but in the formed polymer particles to which the monomers diffuse through the aqueous phase (Scheme 1.2).

Particular features of emulsion polymerization and polymer latices are:

- After the polymerization, the polymer can be isolated by precipitation but for many applications latices are used as such. *Film formation* upon evaporation of the dispersing medium (Scheme 1.3) is a key step in many applications, and the fact that colloids are composed of submicron particles is advantageous for the capability to form continuous films.
- Water is *non-flammable and non-toxic*. This is advantageous not only in the polymerization process, but particularly in applications. By film formation from latices,

several million tons of water are evaporated into the atmosphere annually.

- *Particle sizes* can be controlled precisely in some cases (albeit usually involving trial and error). For example, monodisperse polystyrene latices suitable as calibration standards can be prepared conveniently by emulsion polymerization.
- Due to the *kinetics* of the polymerization in small particles, emulsion polymerization allows for high polymerization rates and also high polymer molecular weights at the same time. This differs from free-radical polymerization in bulk, where an increase in rate occurs at the expense of molecular weight and vice versa. However, this is obviously a feature of classical free-radical polymerization and must therefore not be considered further in the context of most transition metal catalyzed polymerizations.
- Polymer latices possess a *low viscosity* by comparison to a solution of the polymer in an organic solvent. During the polymerization process, this enables high yields per reactor volume. The latex products can be handled readily, e.g. they can be pumped. Also, many applications require a restricted viscosity. Polymer dispersions with up to 70% solids contents (that is the aqueous dispersion contains only 30 weight-% water) are prepared commercially.

Aqueous dispersions of poly(vinyl acetate) and vinyl acetate-ethylene copolymers, homo- and copolymers of acrylic monomers, and styrene-butadiene copolymers are the most important types of polymer latices today. Applications comprise paints, coatings, adhesives, paper manufacturing, leather manufacturing, textiles and other industries.

In addition to emulsion polymerization, other aqueous free-radical polymerizations are applied on a large scale. In *suspension polymerization* a water-immiscible olefinic monomer is

also polymerized. However, by contrast to emulsion polymerization a monomer-soluble initiator is employed, and usually no surfactant is added. Polymerization occurs in the monomer droplets, with kinetics similar to bulk polymerization. The particles obtained are much larger ($> 15 \mu\text{m}$) than in emulsion polymerization, and they do not form stable latices but precipitate during polymerization (Scheme 1.2).

Miniemulsion polymerization represents a special technique. Miniemulsions^[5-7] can be prepared by subjecting a mixture of water, a surfactant, an organic phase and a small portion of a so-called hydrophobe to high shear. High shear results in the formation of very small droplets. These are stabilized towards Ostwald-ripening^[8] to larger droplets by the hydrophobe. Typical droplet sizes are in the range of 50 to 200 nm. In miniemulsion polymerization a miniemulsified monomer is polymerized to a latex, polymerization occurring in the droplets by contrast to emulsion polymerization.

Ideally, the latex particles resemble replica of the monomer droplets (Scheme 1.2). As the monomer must not diffuse through the aqueous phase, by contrast to emulsion polymerization, also very hydrophobic water-insoluble monomers can be polymerized with good rates. Water-insoluble initiators, but also water-soluble initiators can be utilized. In the latter case, entry into monomer droplets, which usually does not occur in emulsion polymerization, is favored by the very high number of small droplets. The advantages of miniemulsion polymerization are contrasted by the requirement of introducing high shear for miniemulsification, which is not routine on a larger scale. For this reason, industrial applications are limited to date.^[9]

In *dispersion polymerization*, by contrast to emulsion or suspension polymerization a monomer which is soluble in the reaction medium is polymerized. In analogy to the aforementioned types of polymerization, an insoluble polymer is obtained. The reaction is

carried out in the presence of non-ionic surfactants or soluble polymers, which can stabilize the polymer particles generated to form a stable latex. With particle sizes of ca. 1 to 15 μm , dispersion polymerization can cover the particle size range between emulsion and suspension polymerization.

In aqueous *solution polymerization* a water-soluble monomer is polymerized to a water-soluble polymer. For example, polyacrylic acid is produced on a large scale by free radical techniques in this manner.^[10] Again, the non-flammability and high heat capacity of water are advantageous. Such polymerizations in homogeneous solution can offer better molecular weight control by comparison to polymerization in a multiphase system in some cases.

1.2 *General aspects of transition metal catalyzed polymerization in aqueous systems*

The previous section demonstrates the utility of polymerization reactions in aqueous systems. Carrying out transition metal catalyzed polymerizations in aqueous systems is of strong interest, as they can afford a variety of new materials not accessible by the aforementioned established free radical techniques. Thus, various monomers subject to catalytic polymerization can not be polymerized by free radical polymerization, and catalytic polymerization also offers access to other polymer microstructures. In addition, a control of free radical polymerization (e.g. with respect to molecular weight distributions) can be brought about by metal complexes.

Transition metal catalysis in aqueous media has developed into a broad field in the past two decades, and such reactions can by no means be regarded as exotic today.^[11] The Ruhrchemie-Rhone Poulenc process is applied commercially on a large-scale. In this process,

propene is hydroformylated using a rhodium catalyst in a biphasic aqueous system. Hereby, a simple separation of the water-soluble catalyst from the apolar products is enabled. To date, the majority of investigations have focused on the synthesis of low-molecular-weight compounds. However, as shown in the preceding section, polymerization reactions in aqueous systems are of particular interest.^[12] A major reason why aqueous catalytic polymerizations had received relatively little attention for a long time is the notorious water-sensitivity of the early transition metal based Ziegler or Phillips catalysts^[13-17] used for industrial olefin polymerization.

Albeit encapsulation techniques, e.g. in a hydrophobic polymer (*vide infra*), can restrict the access of water to the metal centers, a certain stability towards water of the different metal species involved in the polymerization reaction is desirable. Scheme 1.4 summarizes mechanisms of various metal catalyzed polymerizations. The majority of reactions involve organometallic species, most often metal-alkyl complexes. While such complexes are generally considered to be prone to hydrolysis [Eq. (1.1)], examples of quite stable alkyl complexes of late transition metals (that is, group 8 to 10 metals) also exist (section 2.2).

Also for species not involving metal-carbon bonds, such as in ATRP, possible hydrolysis of coordinating ligands (L) must be considered. Another reaction of general importance is the possibility of coordination of water as a ligand. Hereby, coordination sites can be blocked for the substrate reversibly [Eq. (1.2)].

Whereas early transition metal (that is metals of group 4 to 6) centers generally strongly bind water, coordination to relatively less oxophilic late transition metal complexes can be comparably weak and does not pose a severe problem in many cases. Other possible side reactions are attack of water on coordinated olefin monomer or other ligands.^[18]

In addition to the reactivity of the catalytically active metal centers, a sensitivity of added cocatalysts towards water obviously can also be detrimental. For instance, Ziegler-catalysts or metallocenes are most often employed with aluminum alkyls as cocatalysts. For polymerization in aqueous systems, catalysts which do not require water-sensitive cocatalysts are desirable.

This contribution reviews aqueous transition metal *catalyzed* polymerizations of olefinic monomers. For example, classical free-radical polymerizations employing metal-containing redox-systems as initiators are not considered.

To enable a comparison of polymerization of different monomers and of catalysts based on different metals, activities are usually given as turnovers per hour, TO h^{-1} ($\text{TO} \equiv \text{mol substrate converted per mol of metal}$). Comparing activities determined by different authors under strongly varying conditions, the values should be taken as an indication of the order of magnitude. The same holds true for polymer molecular weights.

2 Catalytic olefin and alkyne polymerization in aqueous systems

2.1 *Historical development*

The reaction of ethylene with carbon monoxide in the presence of potassium tetracyanonickelate(II) can be regarded as the first example of an aqueous polymerization. In a patent filed 1948, Reppe and Magin described the formation of oligomers ($n = 1, 2$) and higher ‘polyketones’ [Eq. (2.1)].^[19] Albeit based on the analytical data provided it is unlikely that a true higher-molecular weight polymer was formed, without doubt several repeat units were incorporated per product molecule, as a mechanistic feature which also applies to polymerization reactions.

In the 1960's a number of publications on aqueous polymerizations of different monomers appeared. Rinehart et al. and Canale and coworkers independently reported aqueous polymerization of butadiene catalyzed by rhodium salts. Utilizing $\text{Rh}^{\text{III}}\text{Cl}_3 \cdot 3 \text{H}_2\text{O}$ as a catalyst precursor, semicrystalline *trans*-1,4-polybutadiene was obtained stereoselectively [Eq. (2.2); > 99% *trans*].^[20, 21] By comparison, free-radical butadiene polymerization in aqueous emulsion typically yields polymers with 60 % *trans*-incorporated units under similar conditions.^[22] Polymer molecular weights of $2.6 \times 10^4 \text{ g mol}^{-1}$ were determined by light scattering.^[21]

A free-radical polymerization mechanism can be excluded on the basis of the polymer microstructure and experiments with radical inhibitors. Rhodium(I)-species, formed by reduction of Rh^{III} salts used as catalyst precursors by butadiene monomer, have been suggested as the active species. The catalyst is stable during the aqueous polymerization for over 30 h.^[23] Catalyst activities are moderate with up to ca. $2 \times 10^3 \text{ TO h}^{-1}$.^[24, 25] By contrast to industrially important free-radical copolymerization, styrene is not incorporated in the rhodium-catalyzed butadiene polymerization.^[26] Only scarce data is available regarding the stability and other properties of the polymer dispersions obtained. Precipitation of considerable portions of the polymer has been mentioned at high conversions in butadiene polymerization.^[23, 27]

Under similar conditions as those described by Rinehart for butadiene polymerization, Natta et al. investigated the polymerization of cyclobutene. With low conversions, they obtained a crystalline, highly stereoregular polymer (Scheme 2.1, **a**).^[28] An insertion-mechanism is evidenced by the intact ring structure of the polymer.

By contrast, in the presence of RuCl_3 as a catalyst precursor, ring opening polymerization of cyclobutene and 3-methyl-cyclobutene was observed exclusively (Scheme 2.1, **b**).^[29] With low efficiencies of ca. 15 TO, low-molecular-weight stereoirregular oils were formed. Rinehart et al. have also reported ring opening polymerization of norbornene and of 2-functionalized norborn-5-enes with polar ester moieties in aqueous emulsion with moderate activities. Iridium(III) or Iridium(IV) salts in combination with a reducing agent, or Ir^{I} olefin complexes were employed as catalyst precursors. Norbornadiene and dicyclopentadiene were also polymerized, reacting with only one double bond.^[24, 30]

In summary, this pioneering work clearly demonstrated the principal possibility of aqueous catalytic insertion-polymerization of acyclic and cyclic olefins, as well as aqueous ROMP. On the other hand, metal salts without any additional ligands to control the properties of the metal centers were utilized, and activation to the active species was probably also relatively ineffective in most cases. Consequently, catalyst efficiencies were moderate at the most. Most of the polymerizations also afforded low molecular weight materials, or employed rather special monomers. The possibility of polymer latex synthesis appears not to have received much attention, although free-radical emulsion polymerization of styrene and butadiene was already a large-scale process at the time.

2.2 *Recent progresses in catalytic insertion polymerization of olefins*

Since the aforementioned investigations, significant advances in aqueous catalytic insertion polymerization have only been made in the past decade. Alternating copolymerization of olefins with carbon monoxide, polymerization of ethylene and 1-olefins, and polymerizations of norbornenes and of butadiene have been studied.

2.2.1 Alternating olefin/carbon monoxide copolymerization

Since the aforementioned pioneering discovery of Reppe and Magin, catalytic olefin-CO copolymerization (in non-aqueous media) has found continuous, widespread interest. Carbon monoxide is an exceptionally cheap starting material, and the aliphatic alternating polyketones obtained possess attractive materials properties.^[31-33]

A major breakthrough has been the finding that catalysts based on cationic palladium(II) complexes with *bidentate* ligands, most often diphosphines, exhibit substantially increased activities in ethylene-carbon monoxide copolymerization by comparison to previously known nickel(II) and palladium(II) systems.^[34-38] Methanol is typically used as a reaction medium, demonstrating the stability of these catalysts towards protic media.

An alternating ethylene-CO copolymer melts at 257 °C. Incorporation of propylene decreases the melting point, enabling processing of the materials (e.g. 6 mol-% propene: T_m 220 °C).^[35] Semicrystalline ethylene/propylene/carbon monoxide terpolymers have been commercialized by Shell as a new engineering thermoplastic termed Carilon™ since 1995, and BP has developed similar materials termed Ketonex.^[39, 40] However, this business has recently been announced to be abandoned for undisclosed reasons.^[41] The polyketones have a good resistance to hydrocarbon solvents and good abrasion properties.^[42] As a drawback, the presence of a large number of carbonyl groups renders the polymers sensitive to UV light, furthermore undesired condensation-crosslinking can occur at the high temperatures required for processing.

In 1994, Sen and Jiang reported aqueous ethylene/CO copolymerization by cationic palladium(II) catalysts with water-soluble bidentate sulfonated nitrogen- or phosphine-based ligands, such as **1**. At 50 °C and 35 bar each ethylene and CO, moderate activities of up to ca.

10^2 TO h^{-1} were observed (with a catalyst prepared *in situ* from $[\text{Pd}^{\text{II}}(\text{NCCH}_3)_4](\text{BF}_4)_2$ /bidentate water-soluble ligand). An alternating propylene-CO copolymer with a molecular weight of 1.4×10^4 g mol^{-1} (vs. polystyrene standards) was also prepared, albeit at lower rates.^[43] A few years later, Sheldon et al. reported significantly higher activities of up to 1.5×10^4 TO h^{-1} in aqueous ethylene/CO copolymerization, using a very similar catalyst system comprising the same ligand **1**. These higher activities, comparable to those observed with 1,3-*bis*(diphenylphosphino)propane (dppp) as the non-sulfonated model for **1** in non-aqueous polymerization in methanol, were ascribed to a higher purity of the sulfonated phosphine ligand and the addition of a Bronstedt acid, increasing catalyst stability. Molecular weights of the copolymer were found to be similar to materials obtained in methanol as a non-aqueous reaction medium under otherwise comparable conditions with up to M_w 6×10^4 g mol^{-1} , M_w/M_n ca. 2. A high catalyst stability in the aqueous reaction is evidenced by a constant productivity over several hours.^[44, 45, 46] Specially designed water-soluble ligands with two sulfonated moieties attached to the C_3 -ligand backbone (**2**),^[47] or hydroxylated neutral ligands such as **3**^[48] were found to display higher activities by comparison to **1**.

Introduction of methoxy-substituents in *ortho* position of the aryl rings of diphosphine-modified cationic palladium catalyst results in markedly increased catalyst performance.^[49] With the fully *o*-OMe-substituted analogue of ligand **1**, ethylene-CO copolymers with molecular weights of up to M_w 1.2×10^5 g mol^{-1} and narrow polydispersities (M_w/M_n ca. 2) were obtained in polymerizations in aqueous suspension. Employing a well-defined complex **4** of this ligand, at rather moderate conditions (90 °C, 30 bar each of ethylene and CO) high activities of 6.1×10^4 TO h^{-1} have been reported.^[50]

As previously mentioned, the properties of olefin-CO copolymers depend strongly on the nature of the olefin employed. The glass transition temperature of 1-olefin/CO copolymers decreases from room temperature to nearly -60 °C upon increasing the chain length of the 1-olefin from propylene to 1-dodecene.^[33] By contrast to polar ethylene-CO copolymers, copolymers with higher 1-olefins display a hydrophobic character. For 1-olefin copolymerization, catalysts with entirely alkyl-substituted diphosphine ligands $R_2P-(CH_2)_n-PR_2$ (R = alkyl, by comparison to R = Ph in dppp) such as **3** are particularly well-suited.^[48] Ethylene-1-olefin-CO terpolymers and 1-olefin-CO copolymers can be prepared in aqueous polymerizations.^[43, 47, 48] In the aforementioned copolymerization reactions, the polyketone was reported to precipitate during the reaction as a solid.^[45, 50, 47, 48] However, in the presence of an emulsifier such as sodium dodecyl sulfate (SDS) and under otherwise suitable conditions, stable polymer latices can be obtained. Such polymerizations can be carried out with water-soluble catalysts based on e.g. ligands of type **3**.^[51] By using a miniemulsion technique (vide infra) non-water soluble catalysts can also be employed to prepare stable latices.^[52] Hereby, modification of the diphosphine ligands to attain water-solubility is not necessary which can reduce synthetic effort. *In situ* catalyst systems [$\{R_2P(CH_2)_3PR_2\}Pd(OAc)_2$] / strong acid (R = Ph or $(CH_2)_{13}CH_3$) or well-defined complexes [$\{Ph_2P(CH_2)_3PPh_2\}PdMe(NCCH_3)^+Y^-$] ($Y^- = [B\{3,5-(F_3C)_2C_6H_3\}_4]^-$ or SbF_6^-) were used in the form of a solution of the palladium(II) complex in miniemulsion droplets of a hydrocarbon dispersed in the continuous aqueous phase (cf. section 2.2.2 for the concept of catalyst miniemulsions). Catalyst activities of up to 5×10^3 TO h⁻¹ slightly exceed those of non-aqueous polymerizations in methanol with the same catalysts, evidencing effective activation also of the *in situ* system despite the multiphase nature of the aqueous systems. Stable latices of 1-olefin-carbon monoxide copolymers and of ethylene-undec-10-enoic acid-carbon

monoxide terpolymers ($M_w > 10^4 \text{ g mol}^{-1}$ vs. PMMA standards) have been prepared (Fig. 2.1). In the latter, the undecenoic acid termonomer, with a hydrophilic carboxylic acid moiety, can function as a copolymerizable stabilizer. By comparison to terpolymerization in non-aqueous polymerizations in methanol, the high local concentration of the liquid termonomer in droplets in the aqueous polymerization is beneficial for its incorporation. The 1-olefin copolymers exhibit glass transition temperatures of $T_g +10$ to $-55 \text{ }^\circ\text{C}$, and thus can form films upon drying of a latex at room temperature.

Regarding the mechanism of the aqueous polymerization, chain growth by alternating insertion of ethylene and CO in Pd-acyl or Pd-alkyl species, respectively, is identical to the well-investigated copolymerization in methanol. A significant difference is represented by hydrolysis as an important chain transfer step: in non-aqueous polymerization methanolysis of a Pd-alkyl species affords a Pd-OMe species which initiates chain growth, resulting in formation of a new $-\text{CH}_2\text{CH}_2\text{C}(=\text{O})\text{OMe}$ endgroup in the polymer. By contrast, hydrolysis affords a Pd-OH species, which reacts with CO to form a Pd-hydride prior to initiation of the next chain (Scheme 2.2). Therefore, polyketones with two keto-endgroups are obtained preferentially or exclusively in the aqueous reaction.^[44, 47] The aforementioned reaction can be regarded as a 'reactivation' pathway after hydrolysis of a metal-alkyl bond, which is specific to aqueous reactions involving CO.

2.2.2 Polymerization of ethylene and 1-olefins

The discoveries of several new types of catalysts for (non-aqueous) ethylene and 1-olefin polymerization based on late transition metals in the last decade have initiated a strong

interest in this field.^[16, 53-55] By comparison to early transition metal based Ziegler- or Phillips catalyst used for industrial polyolefin synthesis,^[13-17] complexes of late transition metals are less oxophilic, and they can be much more stable towards polar media.

It can be noted that latices of low-density-polyethylene (LDPE) are prepared via free-radical emulsion polymerization as a specialty product.^[56] However, the low variability with respect to the polymer microstructure is disadvantageous for tailoring latex properties (e.g film forming properties), resulting in a narrow property profile. In addition, working at pressures in excess of 1000 bar in the presence of water is challenging for the equipment used.

In 1993, Flood and coworkers reported ethylene polymerization in water using the rhodium complex $[(N^{\wedge}N^{\wedge}N)RhMe(OH_2)(OH)]^+$ as a catalyst precursor ($N^{\wedge}N^{\wedge}N = 1,4,7$ -trimethyl-1,4,7-triazacyclononane).^[57] After 90 days of reaction at 60 bar ethylene pressure and room temperature, some low-molecular-weight polyethylene was obtained ($M_w 5 \times 10^3 \text{ g mol}^{-1}$). The amount of polymer obtained corresponded to 1 TO per day.

In 1995 Brookhart and coworkers reported that cationic diimine-substituted palladium complexes of type **5** can polymerize ethylene to high-molecular-weight, highly branched material in organic solvents like methylene chloride. The unique structure of the ethylene homopolymers obtained results from a propensity of the metal centers to 'run' along the growing polymer chain between insertions (a similar behavior had been observed previously for 1-olefin polymerization by a neutral nickel catalyst by Fink et al.).^[58, 59] An extensive patent on these polymerizations was filed by Brookhart and DuPont, and McLain demonstrated in several examples that these can also be carried out in water.^[60] Detailed investigations by Mecking et al. revealed that in this suspension-type aqueous polymerization the catalyst is remarkably stable, ethylene being polymerized at a steady rate for days.^[61, 65] At slightly elevated ethylene pressures of 20 bar, with **5a** activities of 10^3 TO h^{-1} , similar to non-

aqueous polymerization in methylene chloride, are observed. However, this high stability is due to an 'encapsulation' of the water-insoluble catalyst in the growing hydrophobic polymer, which protects the catalyst from access of water. Aqueous *solutions* of water-soluble derivatives of **5** with sulfonate-substituted diimine ligands are inactive for ethylene polymerization.^[62] Mechanistic studies revealed that a complex of type **5** is stable in a water-containing solution, which means that neither the Pd-Me moiety nor the diimine ligand are hydrolyzed. However, decomposition occurred instantaneously upon addition of ethylene monomer.^[61]

Regarding a possible undesired binding of water as a ligand [cf. Eq. (1.2)], in this cationic palladium system water coordinates weakly relative to ethylene, and does not block coordination sites for the monomer.^[63, 65]

Whereas traditional polymerization in methylene chloride at similar reaction conditions (temperature, ethylene pressure) affords a highly viscous liquid polyethylene (M_w 3×10^4 g mol⁻¹, ca. 100 branches / 1000 carbon atoms, T_g -70 °C), polymerization by **5a** in aqueous suspension yields a rubbery amorphous solid of significantly higher molecular weight and lower branching [Eq. (2.3)]. Rather than a conceivable direct interaction of water with the catalyst, this effect appears to be related to the different phases encountered by the catalyst during polymerization (heterogeneous aqueous suspension of polymer encapsulating the catalyst vs. homogeneous solution).^[61] Polymerization of 1-olefins by catalysts of type **5** in aqueous emulsion has been claimed to afford stable latices.^[64]

In view of many potential applications, synthesis of a largely linear polyethylene with some degree of crystallinity in aqueous emulsion would be of interest. Very recently, Mecking et al. and Spitz et al. independently reported nickel(II)-catalyzed polymerization of ethylene to linear material in aqueous emulsion.^[65, 66] Neutral nickel(II) complexes **6** and **7** (Scheme 2.3)

based on known bidentate P[^]O-ligands^[67-70] were found to be suited as catalyst precursors. Using water-soluble catalyst precursors **6a**, stable latices of low-molecular-weight polyethylene could be obtained.^[65, 71, 72] E.g., a dispersion of polyethylene of M_w 3×10^3 g mol⁻¹, M_w/M_n 2 to 3, was obtained with 10^3 TO h⁻¹ at moderate reaction conditions (70 °C, 50 bar ethylene pressure). The catalysts are stable in the aqueous polymerization for hours. With **7** significantly higher activities of up to ca. 3×10^4 TO h⁻¹ were observed in aqueous emulsion, however the latices prepared with these lipophilic catalyst precursors were reported not to be colloidal stable.^[66, 73] By comparison to traditional polymerization in non-aqueous organic media such as toluene, catalyst activities and polymer molecular weights are reduced in the aqueous polymerizations. The lower activities and molecular weights can be related to a lower rate of chain growth in the aqueous polymerization, caused by an insufficient local ethylene concentration at the catalytically active centers.^[71] To improve catalyst performance, good catalyst activities at limited ethylene concentrations can be expected to be advantageous. In this context, a systematic understanding of the relationship between catalyst structure and the effect of ethylene concentration on the chain growth rate is of interest.* It must be noted that in some aqueous polymerizations local catalyst concentrations (e.g. in a droplet) can also be much higher than in traditional polymerization in organic media.

By introducing electron-withdrawing perfluorinated substituents to the bidentate P[^]O-ligand (**8**; cf. Scheme 2.3), Claverie et al. have obtained highly active catalysts.^[77, 78] At rates

*) To date, there is no concise picture: for several neutral nickel catalysts with bidentate ligands a strong dependence of chain growth rate on ethylene concentration has been reported (in organic solvents as a reaction medium).^[74] For very similar systems however, zero-order dependence on ethylene concentration has been found.^[78, 75] Similarly, the polymerization of ethylene by cationic Pd^{II} or Ni^{II} diimine complexes investigated by Brookhart et al. is zero-order in ethylene^[58], but very similar cationic catalysts with an osazone-moiety instead of the aryl-imine

of up to $1.7 \times 10^5 \text{ TO h}^{-1}$ low-molecular-weight linear material ($M_w 3 \times 10^3 \text{ g mol}^{-1}$) can be obtained in aqueous emulsion at ethylene pressures of 25 bar.[†]

High-molecular-weight polyethylene has been prepared in aqueous polymerizations with a different class of catalysts.^[71, 82] In traditional polymerization in toluene, suitable representatives of the aforementioned P[^]O-substituted catalysts and recently reported N[^]O-substituted salicylaldimine-based catalysts are known to afford polymers of similar maximum M_w .^[68, 69, 79, 80, 81] However, by contrast to the previously discussed aqueous polymerizations with P[^]O-substituted catalysts, the latter type of complexes was found to yield high-molecular-weight material also in aqueous polymerization. Semicrystalline polyethylenes of up to $M_n 10^5 \text{ g mol}^{-1}$ with narrow polydispersities (M_w/M_n 2 to 4) are accessible in a suspension-type polymerization with precursors **9**. Albeit these catalysts display a limited stability to water, activities of $3 \times 10^3 \text{ TO h}^{-1}$ at room temperature are observed. Like the polymers obtained in traditional polymerization in organic solvents, the materials obtained in water with salicylaldimine-based nickel(II) complexes possess a moderate number of methyl branches. Overall, as in the case of the linear polyethylenes obtained with **6** to **8**, the presence of water has no effect on the basic polymer microstructure. Polymer crystallinity can be influenced by employing norbornene as a comonomer. High molecular weight, amorphous ethylene-norbornene copolymers which form films at room temperature can be obtained in aqueous polymerizations.^[71]

function were reported to be first order in ethylene.^[76]

†) In contrast to the observations made with non-fluorinated ligands, these authors have found that molecular weights of polymers obtained in aqueous and non-aqueous polymerizations are not different. On the other hand, as for the non-fluorinated ligands, the activity is lowered in aqueous polymerization, hinting that, for these catalysts, chain growth and chain transfer have the same rate order dependence on ethylene concentration.

Synthesis of stable latices requires suitable nucleation of primary particles and subsequent stabilization. In classical free-radical emulsion polymerization water-soluble initiators are used. Chain growth initially affords water-soluble oligomeric radicals, which can nucleate particles by collapsing upon themselves or by entering a surfactant micelle (cf. section 1). Similar considerations appear reasonable for the aforementioned catalytic polymerization to stable latices by the water-soluble complex **6a**.^[65, 71] As a different strategy, a very fine initial dispersion of a *hydrophobic* catalyst precursor can be achieved as a solution in a large number of toluene/hexadecane miniemulsion droplets (\varnothing ca. 100 nm), dispersed in the continuous aqueous phase.^[77, 82]

As outlined in the introduction (section 1.1), miniemulsion are obtained by subjecting a mixture of water, a surfactant, an organic phase and a so-called hydrophobe to high shear. Miniemulsions can be stable over prolonged periods of time. Free-radical miniemulsion polymerization has been investigated extensively. It should be noted, that the catalytic polymerization reactions of ethylene discussed in the following paragraph differ from typical free-radical polymerization of a preformed *miniemulsion of a liquid monomer* (Scheme 2.4). Gaseous ethylene monomer is fed continuously to the reaction mixture subsequently *to miniemulsification of the catalyst solution*. Thus, polymerization of preformed miniemulsion droplets of monomer to particles of the same size as the typical feature of 'miniemulsion polymerization' does not apply.

The strategy of using a catalyst miniemulsion for latex synthesis offers two advantages: a) catalyst precursors do not have to be modified hydrophilically, often reducing synthetic effort;^[77] b) somewhat water-sensitive precursors can be applied.^[82]

Employing miniemulsions of the aforementioned catalysts of type **8**, Claverie et al. have prepared stable latices of low-molecular-weight linear polyethylene at high

polymerization rates.^[77] Latices of ethylene copolymers with other olefins, such as undecene, tetradeca-1,13-diene or even styrene have also been prepared.^[83] In addition to the various attractive aspects of polymerization in emulsion, in such copolymerizations another significant advantage is relevant: in conventional ethylene copolymerizations using late transition metal catalysts in organic media, incorporation of 1-olefins is usually low and requires addition of large amounts of the comonomer. In emulsion, the high local concentration of the liquid comonomer in droplets can enable high comonomer incorporations. Copolymerization of ethylene with comonomers bearing polar, hydrophilic moieties is of strong interest in the context of polymer latices. To date, ethylene copolymerization with undec-10-en-1-ol or ethyl undec-10-enoate has been reported.^[83] By comparison to ethylene copolymerization with non-functionalized 1-olefins, no significant differences in polymerization rate are observed, indicating that there are no disadvantageous interactions between the polar moieties and the catalyst. As for the apolar olefins, comonomer incorporation is high, due to the high local concentration of the liquid comonomer in droplets. A trade-off between the amount of incorporated comonomer and polymerization activity is observed, an increased ethylene concentration under otherwise identical conditions results in higher polymerization rates but also lower comonomer incorporation. In all cases, the resulting copolymers were found to be very heterogeneous in nature, due to significant comonomer concentration drifts during the polymerization. This translates into T_m , as measured by DSC, spanning over as much as 60°C.

In the aforementioned ethylene polymerizations yielding stable latices, low-molecular-weight polymer was obtained. To exploit the property profile of polymer latices, the synthesis of dispersions of polyolefins with higher molecular weights is necessary. Mecking et al. have employed miniemulsions of the somewhat water-sensitive catalyst precursor **9b** for ethylene

polymerization. Hereby, stable latices of high molecular weight semicrystalline polyethylene ($M_w 4 \times 10^5 \text{ g mol}^{-1}$, M_w/M_n 2 to 4) could be obtained.^[82]

The polyethylene latices obtained in the different emulsion polymerization procedures using the various aforementioned nickel(II) complexes display average particle sizes of 100 to 600 nm diameter. A number of anionic surfactants or neutral stabilizers are suited, i.e. compatible with the catalysts and capable of stabilizing the latex. Solids contents of up to 30 % have been reported to date. A typical TEM image is shown in Figure 2.2. By comparison to smooth, spherical latex particles of amorphous polystyrene as a well studied hydrocarbon polymer prepared by free-radical emulsion polymerization, the ruggedness of the particles shown can be rationalized by their high degree of crystallinity.

Very recently, an aqueous olefin polymerization using an early transition metal catalyst has also been reported.^[84] A toluene-solution of styrene is prepolymerized briefly by a catalyst prepared by combination of $[(C_5Me_5)Ti(OMe)_3]$ with a borate and an aluminium-alkyl as activators. The reaction mixture is then emulsified in water, where further polymerization occurs to form syndiotactic polystyrene stereoselectively. It is assumed, that the catalyst is contained in emulsified droplets and is hereby protected from the access of water, the formation of crystalline polymer enhancing this effect. Cationic or neutral surfactants were found to be suited, whereas anionic surfactants deactivated the catalyst. The crystalline polystyrene formed was reported to precipitate from the reaction mixture as relatively large particles of 500 μm .

2.2.3 Miscellaneous insertion polymerizations

In addition to the previously mentioned rhodium-catalyzed butadiene polymerizations (section 2.1), cobalt-catalyzed polymerization in aqueous emulsion was investigated by

workers at Goodyear and a Japanese industrial group since the 1980s.^{**} The *in situ* system $[\text{Co}^{\text{III}}(\text{acac})_3]/\text{AlEt}_3/\text{H}_2\text{O}/\text{CS}_2$ and other similar catalysts can yield highly crystalline syndiotactic 1,2-polybutadiene (T_m 205 °C).^[86] The high stereoselectivity of these catalysts has been ascribed to coordination of carbon disulfide to the metal center as a ligand.^[87]

Such stereospecific polymerizations can be carried out in aqueous emulsion,^[88, 89, 90] affording polymer latices [Eq. (2.4)].^[89] A 'prepolymerization' with a small portion of butadiene monomer in the presence of only trace amounts of water is required. A hydrocarbon solution of this 'prepolymerized' catalyst mixture is subsequently dispersed in water together with further butadiene and polymerization proceeds. It has been speculated, that the catalytically active species is shielded from the access of water by the polymer formed during the 'prepolymerization'.^[88]

Aqueous insertion-type polymerization of norbornene and substituted derivatives [Eq. (2.5)] have also been investigated. Tolerance of norbornene polymerization using $[\text{Pd}(\text{NCCH}_3)_4](\text{BF}_4)_2$ as an initiator towards added amounts of water was noted by Risse and Mehler in 1992.^[91]

In 1993, Perez et al. reported norbornene polymerization in aqueous emulsion at 70 °C using PdCl_2 as a catalyst precursor.^[92, 93] A stable latex consisting of low-molecular-weight oligomeric material (degree of polymerization DP_n ca. 10) was obtained with low catalyst activities (70 TO h^{-1}). Very small latex particles of 10 to 20 nm diameter were reported. In

^{**}): In diene polymerization by late transition metal complexes, the growing polymer chain is generally assumed to coordinate to the metal center in a η^3 -allyl fashion.^[85] It is debatable, whether chain growth by coupling of the polymer chain with coordinated monomer mechanistically actually represents an insertion step, or a concerted coupling reaction with formation of a new allyl moiety. Within the context of this section, it is reasonable however to discuss diene polymerization together with other insertion polymerizations.

free radical polymerization of olefinic monomers, such small particles are only obtained by microemulsion polymerization. At the same time, Novak and Safir briefly reported polymerization of polar substituted norbornadienes **10** in aqueous emulsion with PdCl₂.^[94]

Rico-Lattes and coworkers have polymerized water-soluble norbornenes substituted with a gluconamide or a lactobionamide moiety with water-soluble [PdCl₂(TPPTS)₂] in aqueous solution.^[95] Oligomers (DP = 17 respectively 12) were obtained with moderate efficiency (ca. 10² TO over 24 h reaction time). Like their ROMP-analogs, such glycopolymers have been suggested as therapeutic agents. Cell transfection by DNA complexes of a polyelectrolyte prepared by polymerization of an ionically-substituted norbornene has been investigated.^[96] Goodall and coworkers have described polymerization of butylnorbornene in aqueous suspension by the catalyst system [{allyl}Pd(μ-Cl)]₂/TPPTS/Li[B(C₆F₅)₄], containing one equivalent of the water-soluble phosphine ligand TPPTS. A high activity of 4.5×10⁴ TO h⁻¹ was reported in a patent, which considerably exceeds the moderate activities reported for the other palladium-catalyzed aqueous norbornene polymerizations.^[97] This may be taken as an indication, that significantly higher productivities can be achieved in vinylic polymerization of norbornenes in aqueous systems, compared to the moderate catalyst efficiencies reported to date.

2.3 *Recent progresses in ring opening metathesis polymerization*

Ring opening metathesis polymerization (ROMP; cf. Scheme 1.1) of cyclic olefins in non-aqueous media is applied commercially for the synthesis of a number of specialty polymers.^[98] Poly(norbornene) is used as a synthetic rubber (Norsorex, Zeon Corp.). Amorphous polymers prepared by polymerization of norbornene-derivatives (such as dicyclopentadiene) and subsequent hydrogenation of double bonds in the polymer are

marketed for optical applications (Zeonex, Zeon Corp.). Poly(cyclooctene) is applied as a blend component in rubbers (Vestenamer, Degussa AG). Catalysts based on molybdenum, tungsten and ruthenium are most often used for ROMP.^[99, 100]

After first investigations in the 1960s (section 2.1), a publication by Grubbs and Novak in 1988 attracted interest in aqueous ROMP.^[101]

Polymerization of functionalized 7-oxanorbornenes **11** and **12** in aqueous solution using RuCl_3 or $[\text{Ru}^{\text{II}}(\text{OH}_2)_6](\text{OTs})_2$ as catalyst precursors afforded high-molecular-weight polymer with narrow molecular weight distributions [$M_w = 1.3 \times 10^6 \text{ g mol}^{-1}$; M_w/M_n 1.2 for poly-**12**; Eq. (2.6)]. The aqueous solution of the catalyst can be recycled several times, which demonstrates a high stability towards water. The microstructure of poly-**12** prepared by aqueous ROMP with RuCl_3 or OsCl_3 was analyzed by Feast and Harrison. The polymers are atactic with a varying ratio of *cis*- vs. *trans*-double bonds in the backbone.^[102, 103] A number of other functionalized norbornenes (**13** to **15**) have been polymerized to high molecular weight polymer in aqueous media.^[104-107] As far as can be told from the published data, in all these cases the catalyst precursor and the monomer (**11** – **15**) initially formed a homogeneous solution, and the water-insoluble polymer precipitated during the polymerization reaction. Molecular weights can be regulated by adding acyclic olefins as chain-transfer agents.^[102, 104, 108]

In the 1980s, well-defined metal alkylidenes were introduced as catalyst precursors for olefin metathesis.^[99, 109-111] Especially for aqueous ROMP, ruthenium alkylidenes represent readily activated, well-defined, easy to handle catalyst precursors respectively initiators. Whereas in initial work vinyl-substituted carbenes (cf. **16a**) were employed,^[112] soon afterwards more straightforward routes to aryl-substituted carbenes (**16b**) were also developed.^[113] Today, vinyl substituted carbenes are also accessible in one-pot procedures^[114],

and **16a** and **16b** are both commercially available.

Due to the water-insolubility of these metal carbenes, aqueous polymerizations represent heterogeneous multiphase mixtures. Nonetheless, ROMP of the hydrophilic monomer **15** or of a hydrophobic norbornene in aqueous emulsion (catalyst precursor **16a** or **16b** added as methylene chloride-solution) or suspension can be living. E.g., at a monomer to catalyst ratio **15/16b** = 100 with 78% yield poly-**15** of M_w/M_n 1.07 vs. polystyrene standards was obtained.^[115] As a surfactant for polymerization in emulsion, the cationic dodecyltrimethylammonium bromide (DTAB) was used preferentially. Block copolymers of narrow molecular weight distribution were also prepared.

With water-soluble carbene complexes **17** and water-soluble monomers **18**, living polymerization can be carried out in aqueous solution, without the addition of surfactants or organic cosolvents.^[116] Addition of small amounts of acid (up to 1 equiv. DCl) is advantageous for catalyst performance. Remarkably the metal-alkylidene moiety is not attacked by the acid, but a monophosphine complex and the phosphonium salt of the ligand are formed instead. Monitoring of ruthenium-alkylidene species during the polymerization reaction by NMR confirms their high stability towards water.

ROMP of norbornene in aqueous emulsion employing ruthenium(IV) complexes^[117] with bis(allyl) ligands such as the water-soluble $[(\eta^3\text{-}\eta^3\text{-C}_{10}\text{H}_{16})\text{Ru}(\text{OH}_2)(\text{OAc})]\text{BF}_4$ as catalyst precursors has been reported by Wache et al.^[118] High molecular weight polymer with an unusually high *cis* content was obtained with rates of 100 TO h⁻¹.

Kiessling et al. have utilized ROMP for the synthesis of neoglycopolymers, that is synthetic, non-natural polymer bearing carbohydrate moieties.^[119] Carbohydrate-substituted monomers can be employed without protection of the hydroxo-groups, considerably reducing synthetic effort. As the monomers and also the desired polymers are water-soluble, aqueous

ROMP can offer the advantage of a homogeneous reaction, beneficial for molecular weight control and catalyst efficiency. ROMP of 7-oxanorbornenes substituted with glucose or mannose moieties bound via *C*- or *O*-glycosidic linkages afforded neoglycopolymers, such as **19**.^[120, 121]

The polymerization can be carried out with an aqueous solution of RuCl₃ as a catalyst precursor. Relative molecular weights of ca. 10⁶ by comparison to dextran standards were estimated. The polymers contain *cis*- as well as *trans*-double bonds in the backbone in roughly equal amounts, which can be reduced to yield a saturated polymer employing hydrazine reduction.^[121] Utilization of alkylidene complexes **16** requires working in emulsion, due to their water-insolubility (water/methylene chloride/surfactant).^[122, 123] In ROMP of a carboximide-functionalized norbornene (cf. **15**) N-substituted with a carbohydrate moiety, increasing average degrees of polymerization in the range of DP_n = 10 to 143 were observed with increasing monomer to catalyst ratio (**16b** as a catalyst precursor). This indicates a certain degree of molecular weight control, albeit molecular weight distributions were not reported.^[123] The erythrocyte agglutinating activity of the protein concanavalin A can be inhibited by binding of carbohydrates. Structure/activity relationship have been investigated using carbohydrate-substituted polymers prepared by ROMP as multivalent inhibitors.^[120, 121, 122, 124]

In the aforementioned ROMPs in emulsion formation of a polymer latex has been noted briefly without further details. Booth et al. reported ROMP of the functionalized monomer **12** by RuCl₃ to stable dispersions of high molecular weight polymer (10⁵ g mol⁻¹ vs. PS standards). A PEO-b-PPO-b-PEO copolymer was utilized as a steric stabilizer (PEO = polyethylenoxide, PPO = polypropylenoxide).^[125] Whereas the monomer is water-soluble, the polymeric product is not, and in this respect the reaction resembles a dispersion

polymerization. The stable latices obtained consist of remarkably small particles of e.g. 60 nm diameter. Emulsion polymerization of norbornene by various ruthenium catalysts has recently been investigated in detail by Claverie et al.^[126] Using the water-soluble carbene complex **17b** or an in situ system $[\text{RuCl}_2(\text{TPPTS})_2]$ /ethyl diazoacetate as water-soluble catalysts, average activities of up to 10^4 TO h^{-1} were observed at 80 °C in a 15 min polymerization experiment (for the structure of the water-soluble phosphine TPPTS cf. section 2.2.3). Polynorbornene latices consisting of relatively small particles of generally less than 150 nm diameter were obtained. The anionic surfactants SDS or Dowfax3B2 were used, and electrostatically stabilized latices with solids contents of up to 46% were obtained with the latter surfactant (Dowfax3B2 is the disodium salt of disulfonated decyl-substituted diphenyloxide). Unlike typical free radical emulsion polymerizations, the particle number increases continuously with conversion, indicating continuous nucleation. The observed dependence of particle numbers on reaction conditions indicates homogeneous nucleation to occur, even in the presence of surfactant micelles. To enable utilization of the commercially available hydrophobic carbene complex **16b** as a catalyst precursor for latex synthesis, the latter was employed as a solution in toluene/hexadecane miniemulsion droplets (cf. section 2.2.2). Hereby, in addition to norbornene, cyclooctene and cyclooctadiene, which are unreactive towards the water-soluble catalysts, can be polymerized to latices of high molecular weight polymers. Copolymerization of cyclopentene and cyclooctene by **16b** in miniemulsion has also been reported independently by Kühn et al.^[127] Copolymerization of norbornene with poly(ethylene oxide)-substituted norbornene macromonomers by **16b** to afford latex particles has been reported.^[128] Although this reaction was carried out in ethanol/methylene chloride mixtures and thus does not represent an aqueous polymerization, from the viewpoint of colloid chemistry it is interesting that the concept of polymerizable stabilizers ('surfmers')^[129], well known from free radical

polymerization, has been applied to a dispersion-type ROMP.

2.4 *Recent progresses in catalytic polymerization of alkynes*

2.4.1 *Introduction*

Twenty five years after the first report on catalytic polymerization of acetylene by Shirikawa, McDiarmid and Heeger,^[130] the Nobel prize has been awarded to these researchers for their contribution to the field of conducting polymers. Indeed, such polymers have promising applications such as low weight/high charge density batteries, polymer modified electrodes, or capacitors to name only a few. Driven by these applications, different classes of polyacetylenes have been synthesized starting from acetylene itself and from mono- or disubstituted acetylene derivatives.

Alkyne polymerization in organic media has been reviewed recently.^[131] A large variety of catalysts has been reported to polymerize alkynes in organic media. Similar to polymerization of olefins, early transition metal as well as late transition metal catalysts are effective for this polymerization. Depending on the nature of the metal, two different mechanisms of polymerization have been suggested: polymerization via a metal alkyl intermediate, or via a metal carbene (Scheme 2.5). With metal alkyl complexes, polymerization proceeds via migratory insertion of the alkyne into the metal carbon bond [path (a)] whereas with metal carbenes, the mechanism is equivalent to that of metathesis [path (b)].

Most early transition metal complexes are considered to catalyze the polymerization through metal alkyl type intermediates. A typical example of such a catalyst, affording a high molecular weight polyacetylene,^[132] is $\text{Ti}(\text{O}^i\text{Bu})_4/\text{Et}_3\text{Al}$.^[133] The alkyl aluminum is thought to

alkylate the titanium center, thus generating a titanium ethyl complex, in which migratory insertion occurs. As in 1-olefin polymerization, chain transfer proceeds via β -hydride elimination, generating a titanium hydride complex. Other catalytic systems include $[\text{V}(\text{mmh})_3]/\text{Et}_3\text{Al}$,^[134] $[\text{Co}(\text{NO}_3)_2]/\text{NaBH}_4$ ^[136] or $[\text{Fe}(\text{acac})_3]/\text{Et}_3\text{Al}$ (mmh = 2-methyl-butane-2,3-dionato; acac = acetylacetonate).^[137] The necessity of activating most of these complexes with aluminium alkyl cocatalysts is disadvantageous with regard to polymerizations in aqueous systems.

Although several rhodium carbenes (used in cyclopropanation of alkenes) are known, alkyne polymerization catalysts based on rhodium are thought to propagate in a similar fashion as early transition metal catalysts. To our knowledge, the first rhodium-based catalyst system was $\text{RhCl}_3/\text{LiBH}_4$.^[138] Subsequently, rhodium complexes **20**^[139], **21**^[139] and **22**^[140] bearing diene ligands were then used for the synthesis of stereoregular *cis-transoidal* polyphenylacetylene with high polymer yield. Usually, initiation of chain growth with rhodium catalysts does not require any alkylating agent. Kern has postulated formation of an active species via oxidative addition of the terminal alkyne to rhodium, so called hydroethynylation.^[138] This reaction has also been reported by Werner *et al.*^[141]: when contacting $[\text{RhCl}(\text{P}^i\text{Pr}_3)_2]$ with phenylacetylene in the presence of pyridine, the alkyne hydride complex **23** is generated (Scheme 2.6). In the presence of a base such as cyclopentadienyl sodium, a tetracoordinated Rh^{I} complex **24** was obtained and isolated.

Metals of groups 5 and 6 (Nb, Ta, Mo and W) are known to form carbene complexes and are widely used in olefin metathesis.^[99,100,111] Therefore, the polymerization of substituted alkynes with catalysts based on these metals is assumed to proceed via a metathesis-type mechanism. For catalysts prepared *in situ*, metal chlorides and metal carbonyls are the two most important classes of precursors. Alkyne polymerizations with metal chlorides (MoCl_5 ,

WCl₆, NbCl₅ and TaCl₅) have been investigated by Masuda *et al.*^[131] MoCl₅, without any additional cocatalyst, has first been used for the synthesis of polyphenylacetylene^[142] but catalyst efficiency is greatly increased upon addition of a cocatalyst (such as ⁿBu₄Sn, Et₃SiH, Ph₃Sb or Ph₃Bi).^[143] In addition to these ill defined catalyst systems, alkylidene complexes based on tungsten (**25-27**^[144] and **28**^[145]), molybdenum^[145] (**28**) and tantalum^[146] (**29**) have been synthesized and isolated prior to polymerization. These well-defined catalyst precursor do not require a cocatalyst for polymerization. Despite their advantages, these metals of groups 5 and 6 are highly electrophilic which is disadvantageous for their use in aqueous polymerizations.

2.4.2 Catalytic polymerization of alkynes in aqueous systems

As for other coordination polymerizations, the utilization of water as a reaction medium raises issues such as catalyst stability towards water, and miscibility of the monomers, polymers and the catalyst with water. Concerning the catalyst stability towards water, to date polymerizations of alkynes in aqueous systems have only been reported with rhodium and iridium catalysts. Unfortunately, the mechanism of polymerization with these complexes in non-aqueous, organic reaction media has not been completely elucidated (*vide supra*).

Blum, Schumann and coworkers reported the first study on alkyne polymerization with water-soluble rhodium complexes in homogeneous or biphasic aqueous systems.^[147] Several complexes were utilized: RhCl₃·3H₂O, [RhCl(tppms)₃]·4H₂O (tppms = 3-Ph₂PC₆H₄SO₃Na), [RhCl(cod)(tppms)]·H₂O (cod = 1,5-cyclooctadiene), [Rh(μ-3-Ph₂PC₆H₄SO₃)(cod)]₂, [Rh(μ-SPh)(3-Ph₂PC₆H₄CO₂H)(CO)]₂ and the cluster [Rh₃O(OAc)₆-(H₂O)₃]OAc. Trimerization of propynoic acid and oligomerization of phenylacetylene were investigated with these catalyst

precursors.

In the cyclotrimerization of propynoic acid, trimellitic (1,2,4- $C_6H_3(CO_2H)_3$) and trimesic acid (1,3,5- $C_6H_3(CO_2H)_3$) are obtained as a product of head to head or head to tail linkage, respectively. For the sake of comparison, reactions were conducted both in neat water and in neat THF. In all cases, the yield of the trimer was higher in the aqueous system, evidencing the high tolerance of the rhodium catalyst towards water.

Polymerization of the water-insoluble monomer phenylacetylene with the same catalysts was investigated in both homogeneous (THF) and biphasic systems (toluene/water 5:1). In the biphasic mixture, $[RhCl(cod)(tppms)] \cdot H_2O$ afforded a polymer with a low activity (ca. $TO\ 10\ h^{-1}$), whereas all other catalysts only dimerized or trimerized the monomer. By comparison, in refluxing THF solution, $[RhCl(cod)(tppms)] \cdot H_2O$ yielded only low oligomers with a very low activity ($TO = 1.5\ h^{-1}$). The reasons for this apparent enhancement in propagation rate in the presence of water are unclear.

Later, Tang *et al.* studied the polymerization of phenylacetylene and of *para*-substituted phenylacetylenes with lipophilic and water-soluble catalysts.^[148] With $[Rh(nbd)Cl]_2$ (**22**; nbd = norbornadiene), a strong influence of the nature of the solvent on the polyphenylacetylene yield was observed. Whereas almost no polymer is obtained in toluene, 58% conversion is observed in water within 30 min (corresponding to 264 turnovers). This effect is even enhanced with (*p*-methyl-phenyl)acetylene as a monomer. The polymer molecular weight is also increased going from toluene to water, the polyphenylacetylene obtained in the aqueous system being insoluble even in THF. These two effects are intriguing as neither the catalyst nor the monomer have been noted to be soluble in the reaction medium. Similar results in terms of polymer yield and of molecular weight were obtained with $[Rh(cod)Cl]_2$ (**21**) in water. The polymer microstructure is highly stereoregular with a *cis*

content of 94% as determined by the method of Simionescu and Percec.^[149] Unfortunately, polymerization in pure phenylacetylene monomer has not been reported and therefore it is not possible to conclude whether water is only a dispersion medium, or if it interacts with the catalyst.

Aqueous polymerizations of phenylacetylene have been carried out with several other rhodium complexes of the general formula $[\text{RhCl}(\text{cod})(\text{L})]$, L representing a nitrogen-based ligand, such as NH_3 , $t\text{BuNH}_2$, piperidine or N-methylimidazole.^[148] These catalysts also afford high polymer yields, with polymer molecular weights between 7×10^3 and $2.3 \times 10^4 \text{ g mol}^{-1}$ (M_w/M_n around 2) with a high *cis* content (around 85%).

Besides this work with rather lipophilic catalyst precursors, two water soluble analogues have been investigated: $[\text{Rh}(\text{tos})(\text{cod})(\text{H}_2\text{O})]$ (**30**; tos = tosylate) and the similar compound $[\text{Rh}(\text{tos})(\text{nbd})(\text{H}_2\text{O})]$ (**31**).^[148] The authors have verified that water is still the best reaction medium for polymerization of phenylacetylene compared to toluene, THF and neat monomer, thus indicating a possible involvement of water in the formation of the active catalyst (830 TO in water). With catalyst precursor **30**, low polydispersities and a *cis* content of 90% are found, whereas catalyst precursor **31** affords a larger polydispersity but a higher *cis* content (100%). Interestingly, these catalysts proved to be tolerant to air since similar polymerization results are obtained with tap water without exclusion of air.

Joo *et al.* utilized the highly water soluble rhodium complex $[\text{RhCl}(\text{CO})(\text{TPPTS})_2]$ for the polymerization of terminal alkynes (phenylacetylene and (4-methylphenyl)acetylene. For the structure of TPPTS cf. section 2.2.3).^[150] This catalyst selectively produces *cis-transoid* polymers at room temperature in homogeneous solution in water/methanol mixtures, as well as in biphasic mixtures of water and chloroform. The rate of polymerization is higher in the homogeneous medium ($\text{H}_2\text{O}/\text{MeOH}$) than in the biphasic one ($\text{H}_2\text{O}/\text{CHCl}_3$). The iridium

analog of this complex, $[\text{IrCl}(\text{CO})(\text{TPPTS})_2]$, shows catalytic activity for the polymerization of phenylacetylene only at elevated temperature to give *trans*-polymers. The polymerization rate increases significantly when trimethylamine N-oxide (Me_3NO) is added to the reaction medium. The function of this reagent is unclear but it is considered to be a weakly coordinating ligand and could act as a stabilizing agent in the reaction.

The few aforementioned examples of alkyne polymerization in aqueous systems are restricted to phenylacetylene and its *p*-methyl derivative. It has even been reported that polymerizations of aliphatic acetylenes such as $\text{HC}\equiv\text{CR}$ ($\text{R} = \text{C}_6\text{H}_{13}$, $(\text{CH}_2)_2\text{OH}$, $(\text{CH}_2)_3\text{CO}_2\text{H}$) and $\text{HO}_2\text{CC}\equiv\text{CCO}_2\text{H}$ failed with the water soluble precursor **30**.^[148] However, Yashima and coworkers have recently reported successful polymerization of the acid functionalized alkynes (4-carboxyphenyl)acetylene^[151] and propynoic acid^[152] in water. Poly(4-carboxyphenyl)acetylene had previously been prepared via a three step procedure: protection of the acid as the ethyl ester, polymerization in THF with $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (**22**), and subsequent polymer-analogous hydrolysis of the ester moieties.^[153] By contrast, aqueous polymerization in the presence of a base advantageously allows for the direct synthesis of poly(4-carboxyphenyl)acetylene.^[152] Deprotonation is necessary as acids can be detrimental for polymerization – acetic acid is used as a termination reagent to cleave the metal from the polymer.^[154] This polymerization was carried out with various different complexes ($[\text{Rh}(\text{cod})_2]\text{BF}_4$ **32**, $[\text{Rh}(\text{nbd})_2]\text{ClO}_4$ **33** and $[\text{Rh}(\text{tos})(\text{cod})(\text{H}_2\text{O})]$ **30**), which are reported to be water soluble. Polymers with molecular weight between 2.9×10^4 and $1.6 \times 10^5 \text{ g mol}^{-1}$ ($M_w/M_n > 2$) with a *cis-transoidal* highly stereoregular structure were obtained with good yields.

Polymerization of propynoic acid was investigated with the same catalyst precursors **30**, **32** and **33**, also in presence of a base to deprotonate the monomer.^[152] By comparison to polymerization of (4-carboxyphenyl)acetylene (66 TO h^{-1}), the reaction is slower (5 TO h^{-1}).

The polymer microstructure is highly *cis-transoidal* (but isomerization from *cis* to *trans* configuration is observed upon converting the sodium carboxylate form of the polymer to the carboxylic acid).

2.5 *Summary*

Investigations in the 1960s clearly demonstrated the principal possibility of catalytic olefin polymerization in aqueous systems. Albeit various types of monomers were polymerized via different polymerization types, in most cases rather special monomers were employed or products of low molecular weight were obtained. The utilization of ill-defined catalyst precursors often resulted in low catalyst efficiencies, also the possibility of polymer latex formation was given little attention. Since then, considerable advances were achieved only during the past decade. The scope of polymers prepared in aqueous catalytic polymerizations has grown substantially, catalyst activities have been increased by two orders of magnitude already, and the preparation of stable aqueous polymer latices has been studied:

Olefin-CO copolymerization in aqueous systems can afford high-molecular-weight aliphatic alternating polyketones at rates similar to the commercial process performed in methanol as a non-aqueous medium (up to 6×10^4 TO h⁻¹). Stable latices can be prepared. By proper choice of the olefin component(s), the glass transition temperature can be adjusted to values desirable for film formation under ambient conditions. The accessibility of latices may enable new applications, which also do not require processing of the polyketones at disadvantageously high temperatures. *Ethylene polymerization in aqueous systems* can be carried out with a variety of different catalysts, affording high-molecular-weight completely amorphous or semicrystalline polymer. Particularly, stable latices of largely linear polyethylenes have been prepared. Copolymerization with various olefinic monomers enables

a control of polymer crystallinity. High catalyst activities have already been achieved in the synthesis of latices of low-molecular-weight material (up to 2×10^5 TO h^{-1}). Such polymerizations can be of interest as a convenient direct route to wax-dispersions. The accessibility of latices of high-molecular-weight polyethylene has also been demonstrated (M_w 4×10^5 g mol^{-1} ; M_w/M_n 2 to 4). In olefin polymerization as well as CO copolymerization, a limited conversion of liquid 1-olefin (co)monomers must yet be overcome in many cases. As an example of properties interesting for potential applications, polyolefins contain a negligible portion of double bonds by comparison to styrene-butadiene copolymers, a hydrocarbon-polymer currently prepared by free-radical emulsion polymerization on a large scale. This can result in a considerably higher stability of polymer films formed from polyolefin latices towards UV-light and air. *ROMP in aqueous systems* has been investigated intensively. A broad scope of monomers, including many water-soluble norbornene derivatives can be polymerized to high-molecular-weight hydrophilic or lipophilic materials. Utilization of well-defined metal carbenes as catalysts respectively initiators enables molecular weight control and living polymerization, and water-soluble ruthenium carbenes have recently become available. Whereas typically monomer/metal ratios of 100:1 have been applied in reactions of polar-substituted norbornenes, activities of up to 10^4 TO h^{-1} have been observed to date in the synthesis of polynorbornene latices. Aqueous ROMP represents a versatile synthetic route to specialty materials, e.g. resulting water-soluble polymers have been used for biomedical investigations. Aqueous polymerization of *butadiene* and *norbornenes*, as well as *alkynes* has also been studied, and stable latices can also be obtained in various cases.

3 Controlled free-radical polymerization in aqueous systems with metal complexes

3.1 General features of atom transfer radical polymerization (ATRP)

Radical polymerizations can be controlled by addition of a suitable metal complex, which reversibly transforms the free radicals into a dormant species. Such is the case in atom transfer radical polymerization (ATRP).^[155,156] Contrary to the polymerizations discussed in the previous section, polymerization does not proceed via active species with a metal carbon bond (Scheme 3.1): in ATRP, the metal complex promotes atom transfer, and an alkyl halide is used as an initiator. At the very beginning of the polymerization, the reaction of the halogenated initiator and the metal species generates a metal halide complex and radicals in high concentration, yielding polymers with polydispersities and molecular weights characteristic of an uncontrolled polymerization. Because the radical concentration is high, termination via radical-radical coupling or disproportionation are frequent events. However, the metal halide complex is specifically designed to react with free radicals and to act as a spin trap. Kinetics of the metal promoted radical trapping reaction are known to be very fast, e.g. $k_t = 1.1 \times 10^7 \text{ L mol}^{-1} \text{ s}^{-1}$ at 110°C for styrene polymerization catalyzed by $[\text{CuBr}_2(\text{dNbpy})]$.^[157]

Soon, due to radical termination, an excess of metal halide is present and radicals are more likely to react back to the dormant form than to terminate (persistent radical effect).^[158,159] Under these conditions, a metal-catalyzed equilibrium between dormant and active chains establishes and the reaction is controlled: the number average molecular weight grows linearly with conversion and the polydispersity remains close to 1. The tradeoff in

return for achieving polymer molecular weight control is a slow polymerization rate, characteristic for ATRP.

Kinetics are dependent on the nature of the metal complex, but also on the relative amount of initiator. Usually, the organic halide used as an initiator and the metal compound are employed in a 1:1 molar ratio as control of molecular weight is optimum under these conditions, but higher ratios can also be used.^[155] The metal compound is thus effective in ‘catalytic amounts’. It should be noted that by contrast to for instance olefin polymerization, the metal complexes involved in ATRP are not directly part of the polymerization chain growth cycle. Nonetheless, they are usually designated as catalysts in the literature, and this designation is adapted throughout this section.

Although many different catalytic systems, based on Fe^{II},^[160-163] Ni^{II},^[164,165,-166] Re^V,^[167] Mo^V,^[168] Mo^{III},^[169] Pd⁰,^[170] Co^{II},^[171] and Rh^I,^[172,173] exist, the most extensively investigated systems are Cu^I based^[174-182] - first developed by Matyjaszewski^[183-193] - and Ru^{II} systems, developed by Sawamoto.^[194-197]

The ATRP mechanism does not involve any metal-carbon bond potentially sensitive towards water. Free radicals, representing the actual active species, are also well-known to be stable in water. However, ATRP in aqueous media often results in loss of polymer molecular weight control. This is due to the very high intrinsic reactivity of most water soluble monomers, and for ionic monomers the formation of highly viscous polyelectrolytes. Regarding the stability of the transition metal complexes involved, reversible dissociation into cations and halogen anions can occur in water, but this does not affect the control of polymerization. Hydrolysis of Schiff-base ligands^[178] or displacement from the metal center by water as a ligand^[156] can occur occasionally.

3.2 Polymerization of water soluble monomers by ATRP

Control of the polymerization of water soluble monomers by ATRP is of particular interest, as free-radical polymerization today is the only viable route for the synthesis of industrially relevant water soluble polymers.

Numerous water soluble monomers have been polymerized via ATRP (Figure 3.1). Polymerization of acrylic and methacrylic monomers can be problematic as these monomers often contain trace impurities of acrylic or methacrylic acid (MAA). The presence of these carboxylic containing monomers can be detrimental: for example, Matyjaszewski *et al* have observed that (non-aqueous) polymerization of acrylic acid cannot be controlled with $[(\text{bpy})_2\text{CuCl}]$ (bpy = 2,2'-bipyridine), as the monomer (and the polymer) is likely to coordinate to the metal center, to form a species that is unable to control the polymerization.^[198]

The very first example of aqueous controlled radical polymerization has been reported by Matyjaszewski *et al* with the polymerization of **34** (HEA), catalyzed by CuBr/bpy in water at 90°C.^[199] Contrary to polymerizations carried out in organic solvents with this catalyst system, the catalyst is homogeneously dissolved in the 50:50 mixture of water and HEA-monomer. High conversions (87%) are achieved after 12 hours, and the resulting polymer has $M_n = 1.47 \times 10^4 \text{ g mol}^{-1}$ and a $M_w/M_n = 1.34$.

Armes *et al.* have intensively studied aqueous ATRP of a variety of different monomers. Using CuBr/bpy as a catalyst, methacrylic acid polymerization has been shown to be possible in aqueous media at pH values between 6 and 9.^[200] The polymerization occurs very slowly (80 % conversion after 21 h at 90°C, [monomer]:[initiator]:[catalyst] = 28:1:1) yielding polymers with low molecular weight ($M_n = 2.9 \times 10^3 \text{ g mol}^{-1}$) and a polydispersity of

$M_w/M_n = 1.3$. This is probably due to a loss of catalytic species occurring from the competitive coordination of carboxylic acids to the copper centers, as mentioned for the case of acrylic acid. The choice of pH is important: at $\text{pH} < 6$, protonation of the bipyridyl ligand occurs, resulting in loss of control. The choice of initiator is equally important: the polymerization is only controlled when the methoxy capped macroinitiator **46** is used.

Contrary to methacrylic acid, which is only polymerized slowly at 90°C , **36** (OEGMA) undergoes quantitative ATRP in 30 minutes at room temperature, using the system CuCl/bpy .^[201,202] Very high ATRP rates seems to be a general observation for a range of water-soluble monomers: indeed, quantitative and controlled polymerizations are observed for **44** (NaVBA)^[203] ($\text{pH} = 11$), **42** (MPC)^[204] ($\text{pH} = 7$), **43** (MEMA)^[205] ($\text{pH} = 7$), **41** (CBMA) ($\text{pH} = 7$)^[206], **37** (SEM)^[207], **39** (AEMA)^[207], and **35** (MADAME).^[208,209] In all cases, CuBr/bpy or CuCl/bpy was used as a catalyst, in combination with a 1-ketobromo compound. The motivations underlying the choice of CuBr versus CuCl are not presented: a study by Matyjaszewski^[210] et al., supported by a recent study by others^[211], indicates that, as CuCl has a lower oxidation potential than CuBr , the rate of activation k_+ is higher.‡ Consequently, polymerization rates are expected to be faster with CuCl/bpy systems. Indeed, for methacrylic monomers, the CuCl/bpy system was used preferentially by Armes (with the exception of **42** (MPC)^[204] and **38** (HEMA)^[212]). Monomer **42** (MPC) spontaneously polymerizes at room temperature in aqueous solution and the choice of the slowest catalyst is therefore justified. Poly-**38**^[212] not being soluble in water, the polymerization is run in a 50:50 MeOH:water. Consequently, rates are lower than in water (95% conversion requires 3-4 hours reaction time at room temperature). A comparison of polymerization rates in aqueous and non-aqueous

media reveals strong solvent effects. Polar solvents have been found to increase the polymerization rate, possibly because of the combined effect of an increase of rate constant k_+ ^[213] and a competitive coordination of the solvent and the ligand in the copper species.^[214]

CuX/bpy (X = Cl, Br) is not the only catalyst efficient in aqueous ATRP. Pelton *et al* have extensively studied the polymerization of **35** (MADAME) in organic solvents^[209] and aqueous media^[215] at room temperature, and found that CuBr/HMTETA (HMTETA = 1,1,4,7,10,10,-hexamethyltriethylenetetraamine) is less effective in insuring molecular weight control than CuBr/bpy under similar conditions. Using methyl bromophenylacetate as an initiator, the conversion in aqueous polymerization is similar with both catalyst systems CuX/bpy and by CuBr/HMTETA (85% conversion at room temperature), affording however monodisperse polymers for the former ($M_n = 1.28 \times 10^4 \text{ g mol}^{-1}$, corresponding to the theoretically calculated M_{nth} ; $M_w/M_n = 1.2$) and polymers with broader molecular weight distribution for the latter ($M_n = 1.84 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.5$). Excellent control in the aqueous polymerization of **36** (OEGMA) can be achieved with a copper-based catalyst with ligand **47**.^[216] Unexpectedly, the Schiff base ligand is not hydrolyzed during the polymerization reaction, and at room temperature, a polymer of $M_n = 1.2 \times 10^4 \text{ g mol}^{-1}$ ($M_w/M_n = 1.18$) is obtained in 93% yield in only 4 hours of reaction time.

Despite the large numbers of water soluble monomers that can be polymerized by ATRP, several problems remain to be solved. For example, Brittain *et al*^[217] have shown that the aqueous polymerization of **45** (DMA), catalyzed by CuBr/L (L = HMTETA, *tris*[2-(dimethylamino)ethyl]amine (Me₆-TREN) and 1,4,8,11-tetramethyl-1,4,8,11-

‡) k_- , which together with k_+ determines the radical concentration, is usually close to diffusion limited.

tetraazacyclotetradecane (Me₄Cyclam)), is not controlled, because of the slow but irreversible decomposition of the bromo terminated end-group of the dormant chains. Aqueous polymerization of acrylic^[199] and styrenic monomers^[203] also appears to be difficult to control, as implied by the rarity of known examples.

Except in the case of polymerization of **38** (HEMA), water-soluble polymers are formed in all the polymerizations regarded, and in this sense the reactions can be designated as solution polymerizations.

3.3 Polymerization of water insoluble monomers by ATRP

The first example of ATRP of methyl methacrylate (MMA) in an aqueous system was reported in 1996 by Granel *et al.*^[164] Using $[\text{Ni}^{\text{II}}\text{Br}\{\kappa^3\text{-}N,C,N\text{-}1,3\text{-(CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3\}]$ as a catalyst precursor and 2-ethylbromoisobutyrate as an initiator, suspension polymerization of MMA was carried out in water at 80°C. The polymerization proceeded to high conversion, but the polymer molecular weight was twice as high as the predicted value ($M_n = 6 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.7$). It is possible to infer that the polymerization was somewhat controlled, but that very poor initiation occurred, possibly due to initiator hydrolysis. Lecomte *et al.*^[170] have shown that MMA polymerization can be carried out conveniently in aqueous suspension also with $\text{Pd}(\text{OAc})_2/\text{PPh}_3$ and CCl_4 as an initiator. In the absence of surfactants, bimodal distributions have been obtained due to diffusion limitations at high conversion. This problem has been solved by adding a nonionic surfactant (Tween 80) that facilitates the dispersion of the polymer particles, resulting in a relatively narrow molecular weight distribution ($M_n = 3.25 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.55$) at high conversion.

Sawamoto has described the controlled radical polymerization of MMA using $[\text{RuCl}_2(\text{PPh}_3)_3]$ as a catalyst.^[218] In organic solvents, this ruthenium catalyst^[197] necessitates

the use of an aluminum-containing cocatalyst, usually $\text{Al}(\text{O}^i\text{Pr})_3$, thus affording a very efficient control of the polymerization of methacrylic monomers. As the aluminum compound can not be used in neat water, polymerizations were initially carried out in a biphasic toluene:water 1:1 mixture. Polymerizations in this aqueous system were found to be somewhat faster than in neat toluene. In view of these results, the authors have demonstrated that aqueous polymerizations do not necessitate the use of any aluminum cocatalyst. Thus, in the absence of an aluminum salt, suspension polymerization of MMA in water at 80°C was found to be efficient and controlled (83% conversion; $M_n = 9.6 \times 10^3 \text{ g mol}^{-1}$; $M_w/M_n = 1.42$).

ATRP in aqueous emulsion or suspension with copper-based catalysts has been the object of extensive research. Makino *et al.*^[219] have first reported MMA emulsion polymerization using CuBr/bpy as a catalyst and SDS as a surfactant. No living characteristics were observed, but it has later been shown that SDS interacts with the copper complexes to form a characteristic blue copper sulfate complex.^[185] Early experiments by Matyjaszewski *et al.*^[185] have demonstrated that butyl methacrylate can be polymerized in emulsion using dNbpy and dAbpy ligands in combination with CuBr . The polymerization was found to be controlled, as evidenced by linear evolution of molecular weights with conversion, and by narrow molecular weight distributions. For example, 89 % conversion were achieved after 75 minutes, yielding a polymer of $M_n = 2.82 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.26$ ($M_{\text{nth}} = 2.52 \times 10^4 \text{ g mol}^{-1}$).

Utilization of other ligands, such as Me_6TREN , afforded ill defined polymers. Careful elucidation of the polymerization mechanism by Matyjaszewski *et al.*^[220] revealed that the partitioning of $\text{CuBr}_2/2\text{dNbpy}$ and $\text{CuBr}/2\text{dNbpy}$ between the apolar organic phase and the aqueous phase is crucial. Despite the hydrophobicity of the ligand dNbpy , the catalyst, both in its Cu^{I} and Cu^{II} form, is partially soluble in water under the polymerization conditions. In a

mixture of water/butyl methacrylate, up to 90% of $\text{Cu}^{\text{II}}/\text{dNbpy}$ is present in the aqueous phase – the $\text{Cu}^{\text{I}}/\text{dNbpy}$ species being much less water soluble. This indicates that catalyst diffusion through the aqueous phase is possible.

It must be noted, that even with an extremely hydrophobic catalyst, catalyst-free particles would be formed by radical exit and nucleation of new particles, and thus uncontrolled polymerization would occur. On the other hand, it is also proposed that with more hydrophilic ligands (such as $\text{Me}_6\text{-TREN}$, or pentamethyl diethylenetriamine (PMDETA)^[221]), all the catalyst is located in the aqueous phase, and uncontrolled polymerization occurs in the hydrophobic polymer particles. However, it must be noted that these ligands are also ineffective in controlling the aqueous polymerization of *water-soluble* monomers (see above), hinting that ligand dissociation might also occur in these systems.^[215]

In addition to a proper choice of ligand hydrophobicity, the surfactant used is also critical. In general, non-ionic surfactants were found to be efficient for colloidal stabilization of the polymer particles.^[221] This is to be expected, as, due to the ionic nature of the catalyst, and the corresponding ionic strength, electrostatic stabilization is likely to be poor. Adequate hydrophilic/lipophilic (HLB) balance^[222] is also a necessary criterion to insure latex stability in ATRP emulsion polymerization.^[223] For the controlled polymerization of MMA, catalyzed by CuBr/dNbpy , an HLB of 17 was found to be optimal, and for the polymerization of BMA, stabilization was optimal with surfactants Brij98[§] (HLB = 15.3) and Tween80[§] (HLB = 15.0).^[220] Nevertheless, colloidal stability of the formed latex is usually poor, even at low solid contents (15%) and in the presence of large amounts of surfactant (10%).

Similar results were reported by Chambard *et al*^[224] for MMA polymerization using

[§]) Brij98: $\text{H}_{35}\text{C}_{18}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$. Tween80: Polyoxyethylene sorbitan monolaurate.

CuBr/dNbpy. The polymerization is controlled, as shown by linear evolution of M_n versus conversion, but at 60% conversion, a low-molecular weight tail in the GPC trace appears that results from 'dead' polymer, formed by termination reactions. Most of these problems were alleviated through the use of a miniemulsion technique (see section 1.1), as shown in the ATRP of butyl methacrylate with CuBr/dNbpy.^[225] The miniemulsion recipe used employed hexadecane (10% in volume relative to monomer), as dNbpy is not hydrophobic enough to prevent Ostwald ripening, shearing the mixture by means of sonication. Sonication generates droplets with sizes of down to 300 nm, allowing for the preparation of stable latices. In addition, the molecular weight of the polymer increases linearly with conversion, but the initiation efficiency is moderate. The found molecular weight ($M_n = 3.0 \times 10^4 \text{ g mol}^{-1}$; at 90% conversion achieved after 2 h at 70 °C) is somewhat higher than the theoretical value ($M_{nth} = 2.4 \times 10^4 \text{ g mol}^{-1}$). The authors hint that escape of Cu^{II} species from the miniemulsion droplets occur, resulting in a slightly increased termination.

Copper based ATRP in emulsion has been achieved successfully under reverse ATRP conditions, where one starts with a conventional free radical initiator and CuBr₂/dNbpy as a catalyst.^[226] Typical commercial water-soluble free radical initiators such as potassium peroxydisulfate (in a phosphate buffer, pH = 7), 2,2'-azobis(2-amidinopropane) dihydrochloride (commonly designated as V50) or 2,2'-azobis[2-(imidazol-2-yl)propane] dihydrochloride (V44) can be used. The reaction requires an initial induction period of up to one hour, which corresponds to the time required for the initiator to decompose, forming deactivated radicals before reaching the atom transfer equilibrium (Scheme 3.1). Molecular weights increase linearly with conversion, and molecular weight distributions are as narrow as 1.2, but the initiation efficiencies are very low (typically between 0.1 and 0.4), resulting in a mismatch between experimental and theoretical molecular weights. This is attributed to

irreversible early radical termination in the aqueous phase, where not enough Cu^{II} spin trap is present.

Finally, it has recently been reported that aqueous ATRP can be carried out conveniently in water in the presence of cyclodextrins.^[227] Complexation by a randomly methylated β -cyclodextrin rendered the catalyst CuBr/dNbpy fully water soluble, and allowed for the controlled polymerization of MMA at 80°C in water. Due to the presence of the cyclodextrin, the monomer too is water soluble, but the PMMA polymer formed ($M_n = 3.8 \times 10^4 \text{ g mol}^{-1}$; $M_w/M_n = 1.3$) is insoluble. In this respect, this type of polymerization is akin to a precipitation polymerization. Chain extension of the PMMA block by styrene is possible, albeit the blocking efficiency was limited.

4 Polymerization by Suzuki-coupling in aqueous systems

Transition metal catalyzed coupling reactions of aromatic halides, such as Heck or Suzuki coupling, are used extensively for the synthesis of low-molecular-weight organic compounds. With bifunctional substrates, polymers can be obtained. By contrast to all other polymerization reactions considered in this chapter, such reactions represent step-growth-type polymerizations. C-C coupling of aromatic halides usually requires the addition of a base in stoichiometric amounts, and the most common Bronstedt-bases are water soluble and can be employed conveniently in biphasic aqueous/organic systems.

Suzuki coupling, the palladium catalyzed cross-coupling of aryl or vinyl halides with organoboronates, is employed widely in organic synthesis. The reaction is most often carried out in an organic solvent (benzene) in the presence of a base.^[228] Because of the reasonable stability of boronic acids and esters towards hydrolysis, Suzuki coupling can also be carried out in aqueous media. An extensive study of the reaction has shown that similar results are

obtained in aqueous and non-aqueous systems.^[229]

The use of Suzuki coupling for the synthesis of polyphenylene polymers was introduced by Rehahn, Schlüter and Wegner [Eq. (4.1)].^[230] Poly(*p*-2,5-di-*n*-hexylphenylene) was prepared in a biphasic mixture of benzene and water as a reaction medium, using sodium carbonate as a water-soluble base. This AB-type polymerization afforded polymers containing e.g. an average of about 28 phenylene units.

This method is applicable to a variety of alkyl substituted phenylene AB-type monomers [Eq. (4.1)].^[231] The procedure was also extended to the condensation of AA and BB monomers (Scheme 4.1).^[233] Hereby, poly-*p*-phenylene polymers containing ether and carbonyl linkages in the polymer backbone are accessible. By polymerization of the AB₂ monomer 3,5-dibromobenzene boronic acid in a biphasic aqueous/organic medium, Kim and Webster obtained hyperbranched polyphenylenes.^[234] Suzuki polycondensation in aqueous systems has proven to be a versatile method, which has been applied to the synthesis of a variety of different polymer types.^[235]

Polymerization in a single-phase homogeneous solution in THF/water mixtures (2:1) was also reported.^[236] Such reactions allowed for the preparation of a poly(*p*-phenylene) with sulfonate ester and dodecyl side groups [Eq. (4.2)]. By comparison to the aforementioned biphasic polymerizations, synthesis of polymers with higher degrees of polymerization was reported in the solution procedure.

Polymerization via Suzuki coupling in aqueous solution was reported by Novak *et al.* for the first time [Eq. (4.3)].^[237] A water soluble catalyst precursor, [Pd(tppms)₃] (tppms = 3-Ph₂PC₆H₄SO₃Na) was employed. The resulting polymer is water soluble, and has a weight average molecular weight on the order of 5×10^4 g mol⁻¹. In later reports, Novak *et al.* pointed out that, alike traditional Suzuki coupling in non-aqueous organic solvents, the aqueous

Suzuki coupling reaction is accompanied by side reactions that strongly affect the structure of the resulting polymer.

First, a strong inhibition of the oxidative addition of aryl halide to Pd^0 by the coordination of the phosphine has been reported to be the source of slow kinetics.^[238] Accordingly, using phosphine-free catalyst precursors such as $\text{Pd}(\text{OAc})_2$, $[(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}]_2$ or $[\text{Pd}_2(\text{dba})_3]\cdot\text{C}_6\text{H}_6$ (dba = dibenzylidene acetone) for Suzuki-coupling (to prepare low-molecular-weight compounds), activities are an order of magnitude higher by comparison to polymerization with $[\text{Pd}(\text{aryl})\text{I}(\text{PPh}_3)_2]$.^[238] However, their use in polymerization has not been reported to date, perhaps due to a low stability of the active species, prone to decomposition to Pd black. Another side reaction, that has been studied with non sulfonated triarylphosphines, is the aryl-aryl interchange reaction in $[\text{Pd}(\text{aryl})\text{IL}_2]$ complexes (Scheme 4.2).^[239] In a typical organic synthesis by means of Suzuki coupling of a monohalogenated compounds with monoalkyl boronic esters, this reaction results in the formation of small amounts of side products. In AA-BB step polymerization however, this reaction represents a chain termination step or even results in branching (Scheme 4.2).^[240] Accordingly, with $[\text{Pd}(\text{aryl})\text{I}(\text{PPh}_3)_2]$ as a catalyst precursor in a THF/water mixture, the reaction results in the production of medium molecular weight polymer ($M_n = 9.7 \times 10^4 \text{ g mol}^{-1}$) that is not a rigid rod. This polymer contains significant amount of phosphorus incorporated into the backbone, thus, chain termination through phosphine-aryl exchange must have occurred to a significant extent. Using a catalyst with more bulky phosphine ligands, $[\text{PdI}\{\text{P}(\text{o-tolyl})_3\}_2]$, for which the rate of aryl exchange is significantly lower, a higher molecular weight polymer is formed ($M_n = 2.0 \times 10^5 \text{ g mol}^{-1}$), and no phosphorous can be detected in the polymer. Conformational analysis of the polymer by light scattering and viscosimetry indicate that the resulting polymer is close to a

rigid rod.

5 Conclusions and Outlook

Albeit the principal possibility of carrying out catalytic polymerizations in the presence of water had been known since the 1960s, significant advances in catalytic polymerizations in aqueous systems have only been achieved over the past decade. Today, 1) various different types of transition metal catalyzed polymerizations can be carried out efficiently in aqueous systems. 2) a wide range of polymers ranging from hydrocarbons to water-soluble polymers, and a scope of polymer architectures are accessible. 3) polymerization can be carried out in a controlled fashion. 4) synthesis of polymer latices is possible in many cases.

One major thrust for these developments are certainly the recent discoveries of new late transition metal based polymerization catalysts and initiators. Well-defined organometallic complexes, which do not require water-sensitive cocatalysts, are now available as catalyst precursors or initiators for olefin polymerization. Radical polymerization with metal complexes (ATRP) allows for a precise control of molecular weight in aqueous polymerization. An increased general concern with environmental issues makes water an attractive reaction medium. With polymer latices, this advantage is not restricted to the polymerization process, but also applies to the product itself. The general surge of interest in micro- and nanoparticles currently continues, and catalytic polymerization in aqueous emulsion provides convenient access to dispersions of a range of novel polymer nanoparticles in the size range of ca. 80 nm to 1 μm .

A number of issues and challenges will be of particular interest in the future. Up to now, little data is available regarding latex properties, such as stability and film formation,

and on the properties of the resulting films (such as adhesion to substrates of varying polarity). In aqueous olefin polymerizations, these properties can be controlled by copolymerizations of common monomers, including polar-functionalized olefins. Increases in catalyst efficiency regarding comonomer incorporation in ethylene polymerization and stability towards polar monomers are desirable. For instance, polyolefin latices with film forming properties could be useful for UV-stable coatings. The possibility to prepare a variety of different polymer architectures in aqueous polymerizations by ATRP, such as highly branched polymers, amphiphilic copolymers or surface grafted inorganic or organic polymer particles will be of strong future interest. Molecular weight control in the preparation of water-soluble polymers, such as polyacrylamide, is particularly attractive. Albeit very high catalyst activities have already been reported in some cases, for all polymerizations discussed further improvements in catalyst activities are desirable. For instance, in a polymerization aimed at preparing a latex, it is desirable to leave the catalyst in the product in order to maintain the intriguing simplicity of this direct route to a polymer dispersion. To achieve negligible contents of more or less precious and potentially harmful metals and ligands, high efficiencies are necessary.^{***} The mechanisms of particle formation and polymerization kinetics are of fundamental interest in their own right, but an understanding is also desirable for a rational control of polymerization and to increase catalyst efficiencies in these multiphase systems in general. For instance, the location of the catalytically active metal centers during the different stages of the reaction (aqueous phase; inside monomer droplets respectively polymer particles; or on the interface)

^{***}) The issue of catalyst residues in the polymer product has been discussed intensely in the general context of late transition metal catalyzed polymerizations. This awareness is contrasted by little data published regarding e.g. toxic effects of such residues. In detail, the relevance of metal and ligand residues will depend on the application sought and the catalyst used.

is largely unclarified to date. The scope of particle morphologies accessible, e.g. core-shell particles with domains of different glass transition temperatures, remains to be explored.

In summary, recent advances in aqueous catalytic polymerizations have afforded a range of new materials, particularly polymer latices previously inaccessible and new water-soluble polymers. Various attractive topics for fundamental research have in turn emerged, and potential applications can be envisioned. The attractivity and versatility of this field result from the overlap and combination of polymer chemistry, organometallic chemistry, catalysis, and colloid science.

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Captions to Schemes and Figures

Scheme 1.1. Possible mechanisms of particle formation in free radical emulsion polymerization.

Scheme 1.2. Free radical suspension, emulsion and miniemulsion polymerization.

Scheme 1.3. Film formation from a polymer latex upon evaporation of the dispersing medium.

Scheme 1.4. Schematic representation of the chain growth mechanisms of various metal-mediated polymerizations (R respectively Ar/Ar' = growing polymer chain. X = halogen).

Scheme 2.1. Aqueous cyclobutene polymerization by an insertion-mechanism (a) and by ring opening polymerization (b; SDS = sodium dodecyl sulfate).

Scheme 2.2. Mechanism of aqueous ethylene-CO copolymerization.^[44,47]

Scheme 2.3. Neutral Nickel(II) complexes utilized for polymerization of ethylene in aqueous emulsion.

Scheme 2.4. Typical free radical miniemulsion polymerization of a liquid monomer (a) vs. catalytic ethylene polymerization with a miniemulsion of a solution of the catalyst precursor (b).

Scheme 2.5. Mechanisms of alkyne polymerization.

Scheme 2.6. Oxidative addition of phenylacetylene (py = pyridine).

Scheme 3.1. Mechanism of atom transfer radical polymerization (ATRP).

Scheme 4.1. Synthesis of functionalized poly(p-phenylene) via AA/BB Suzuki coupling in an aqueous biphasic system.

Scheme 4.2. Effect of aryl-aryl exchange in polymerization by Suzuki coupling and modes of incorporation of phosphorus in the polymer.

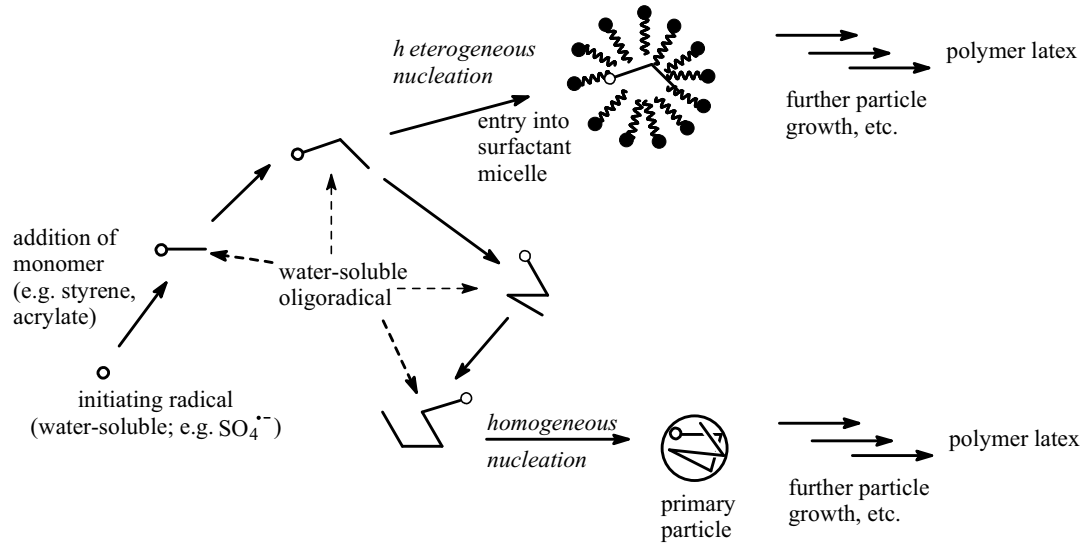
Figure 2.1. TEM images of a polyketone latex.^[52]

Figure 2.2. TEM micrograph of polyethylene latex particles prepared by catalytic polymerization (M_w 2.1×10^5 g mol⁻¹, M_w/M_n 2.2; crystallinity 54%; catalyst precursor **9b**).^[82]

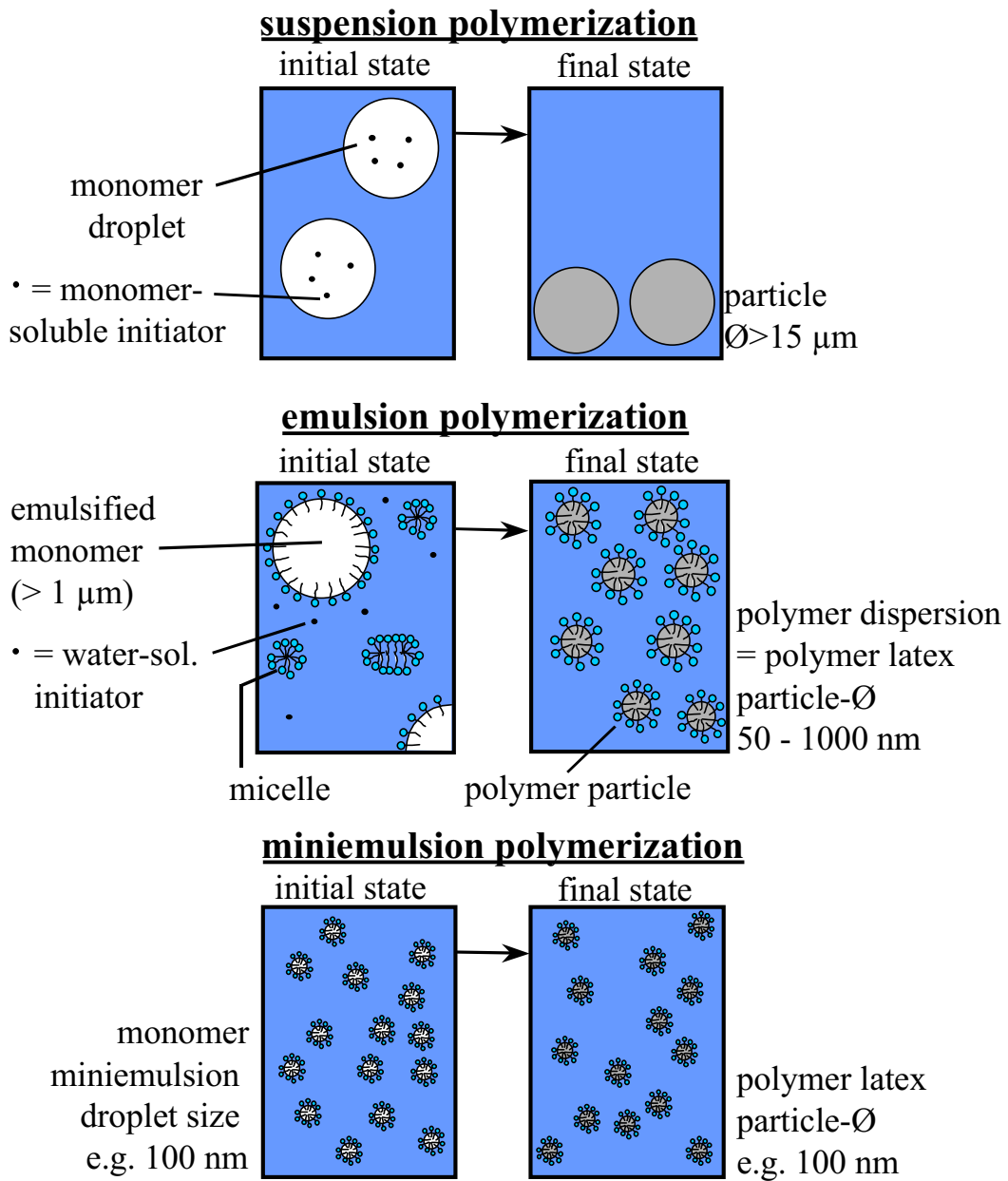
Figure 3.1: Water-soluble monomers polymerized by ATRP (common acronyms given in brackets).

Schemes

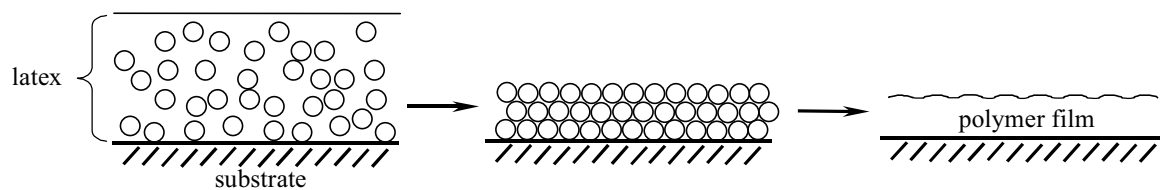
Scheme 1.1



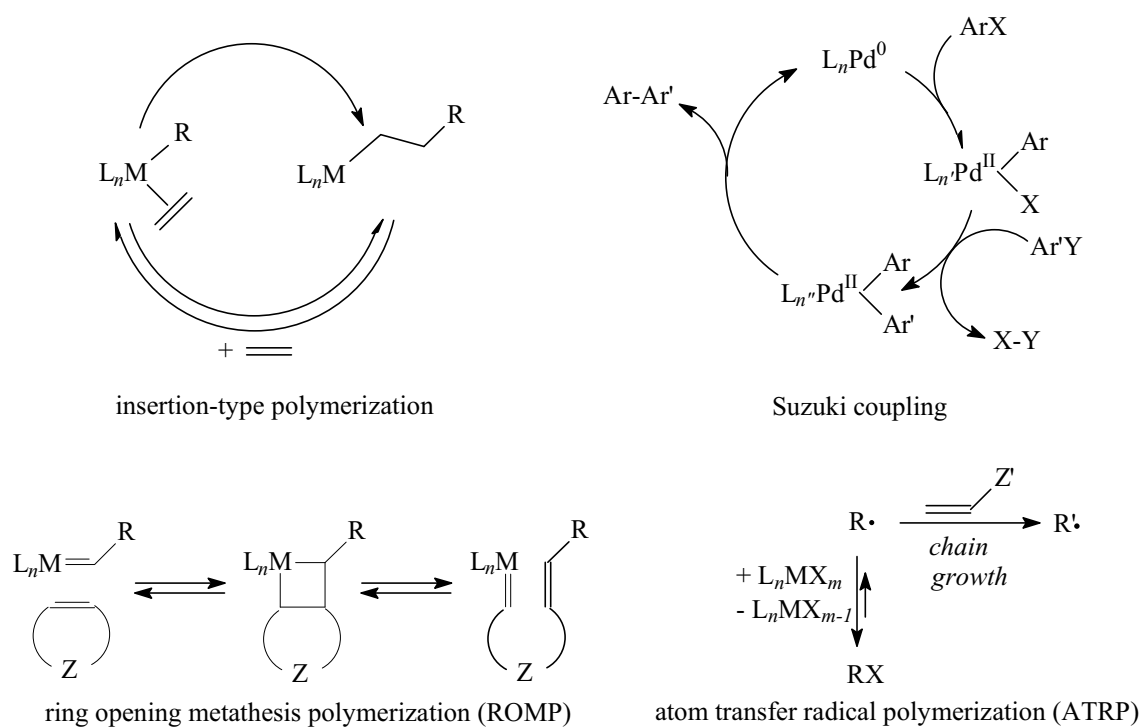
Scheme 1.2



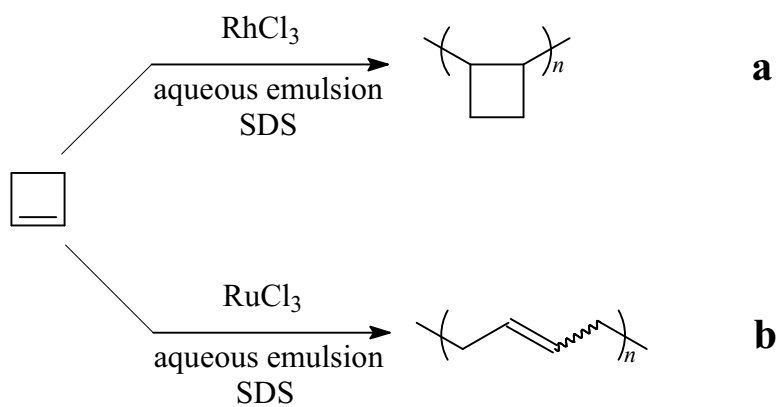
Scheme 1.3



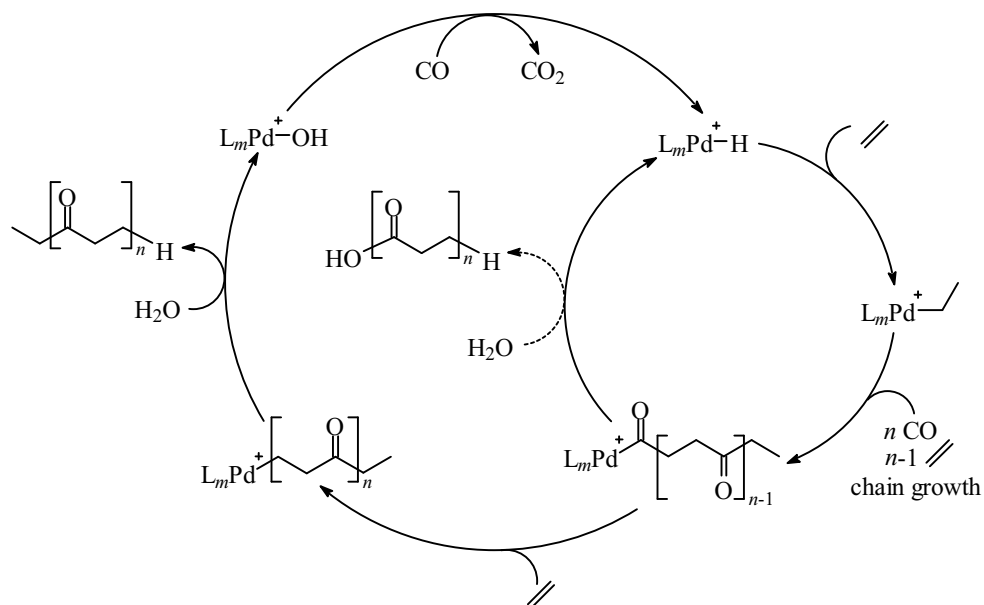
Scheme 1.4



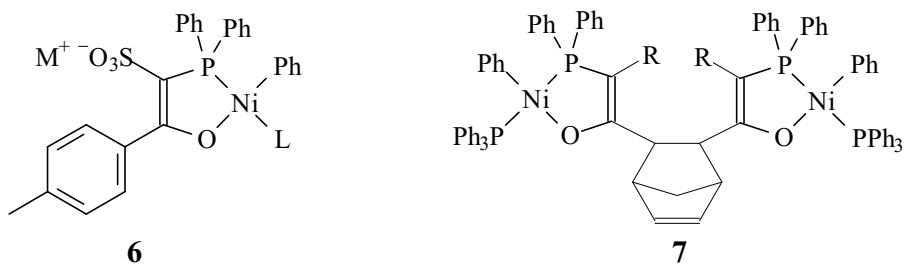
Scheme 2.1



Scheme 2.2



Scheme 2.3

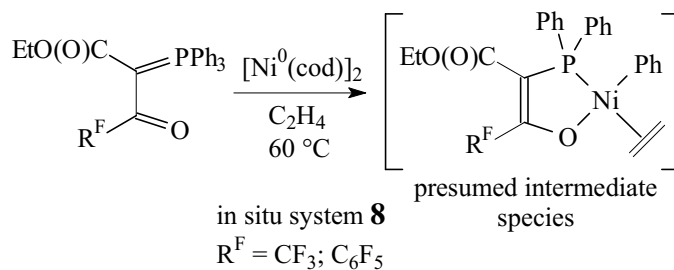


L = PPh₃ or pyridine

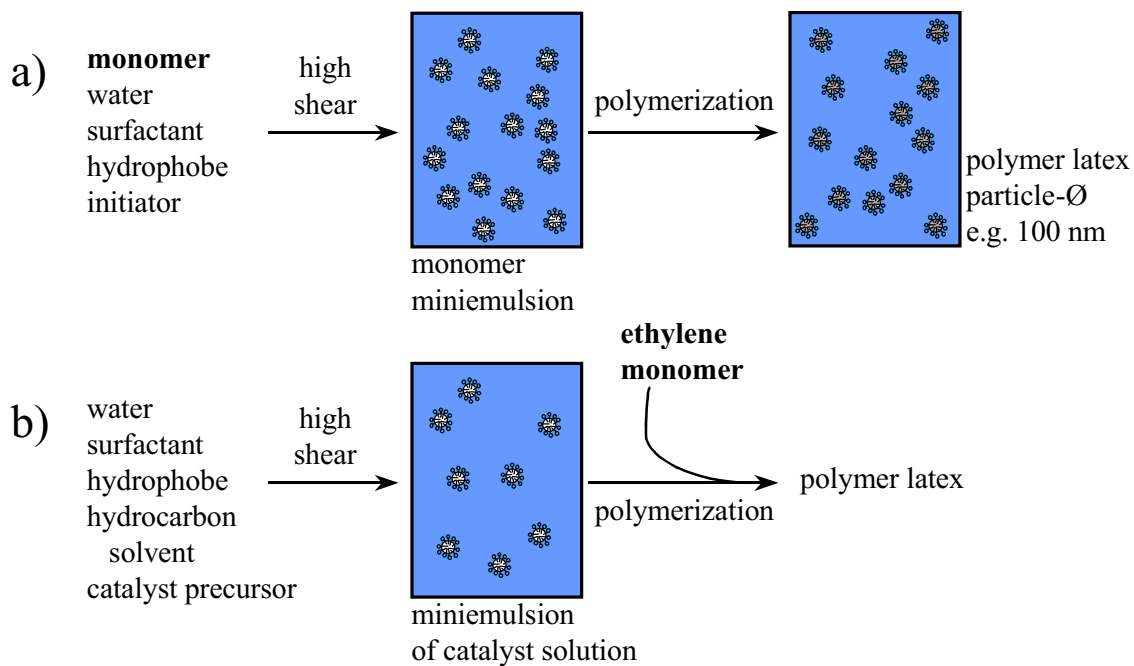
6a: M⁺ = Na⁺ (hydrophilic)

6b: M⁺ = H₃₃C₁₆NMe₃⁺ (lipophilic)

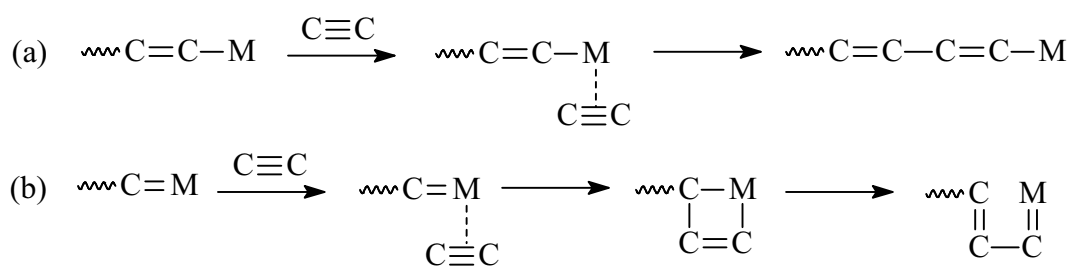
(activation of PPh₃ complexes of types **6** or **7** for polymerization by phosphine scavengers)



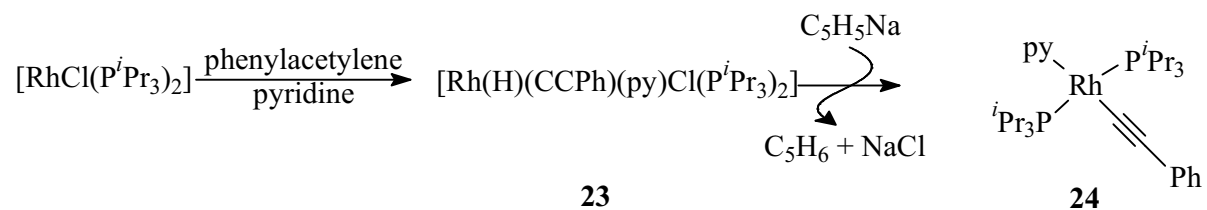
Scheme 2.4



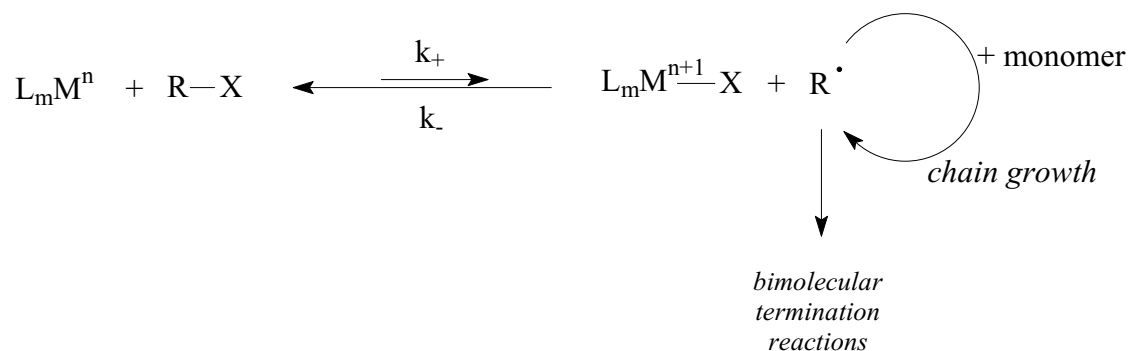
Scheme 2.5



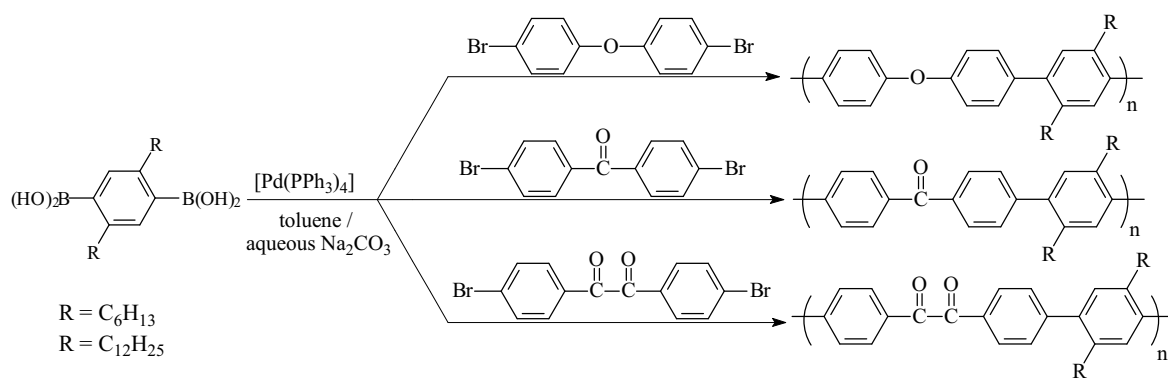
Scheme 2.6



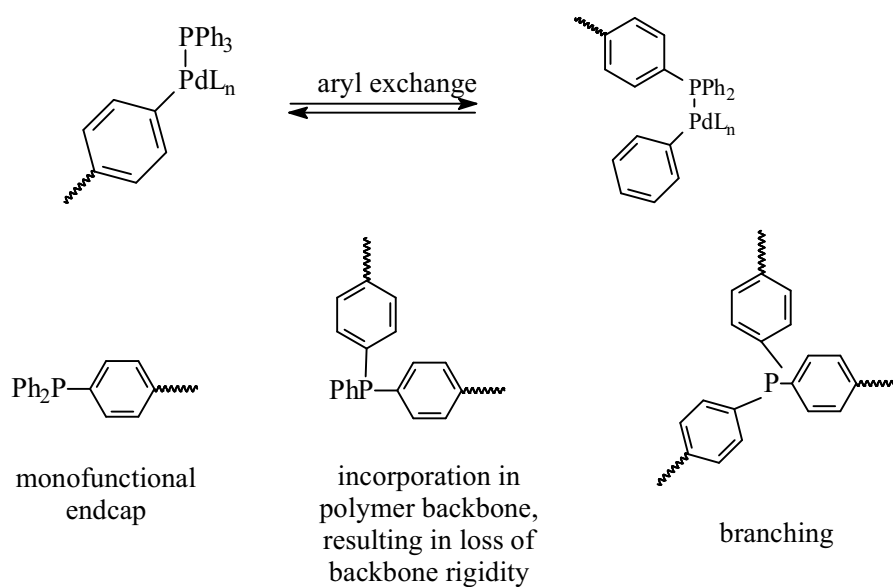
Scheme 3.1



Scheme 4.1



Scheme 4.2



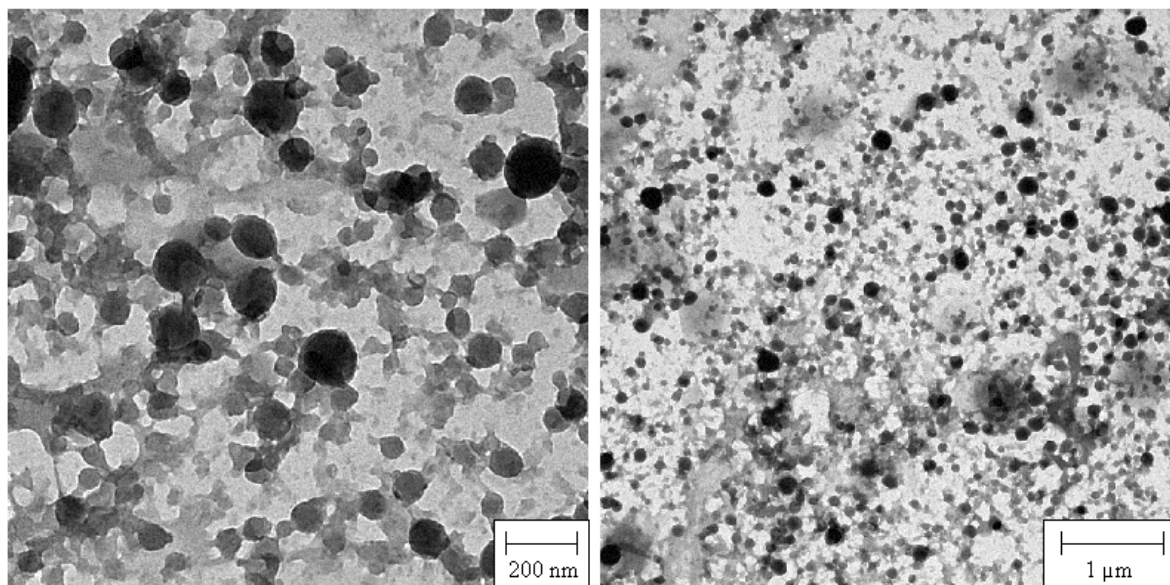
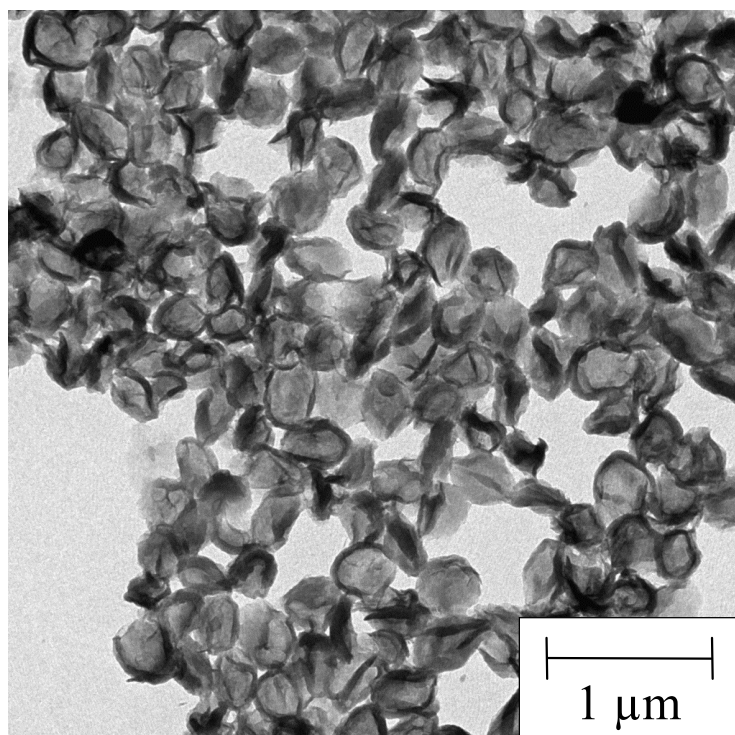
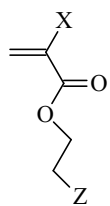
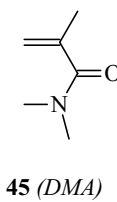
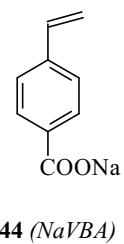
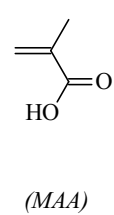
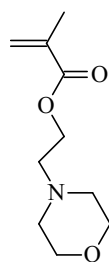
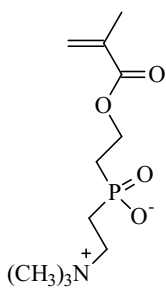
Figures*Figure 2.1**Figure 2.2*

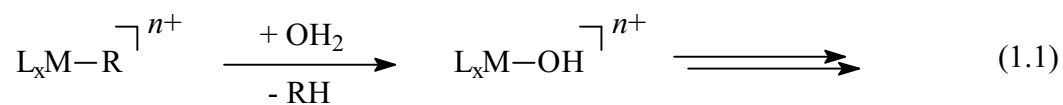
Figure 3.1



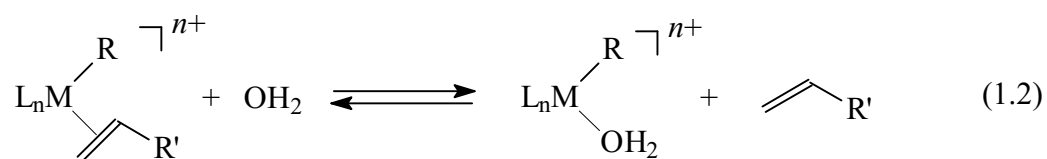
- 34: X = H, Z = OH (*HEA*)
 35: X = Me, Z = NEt₂ (*MADAME*)
 36: X = Me, Z = (OCH₂CH₂)_nOCH₃ (*OEGMA*)
 37: X = Me, Z = SO₄NH₄ (*SEM*)
 38: X = Me, Z = OH (*HEMA*)
 39: X = Me, Z = NH₂ (*AEMA*)
 40: X = Me, X = CH₂SO₃K (*KPSM*)
 41: X = Me, X = ⁺N(CH₂)₂(CH₂COO⁻) (*CBMA*)



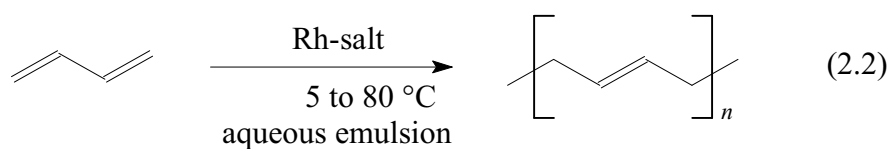
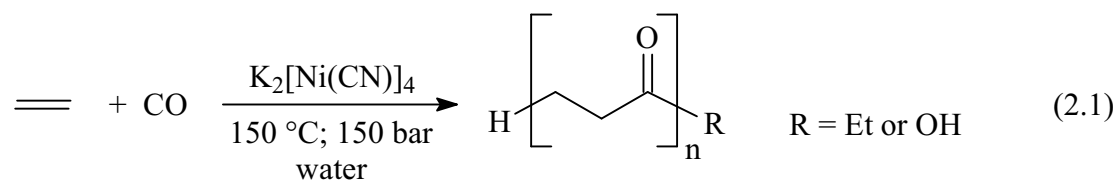
Equations

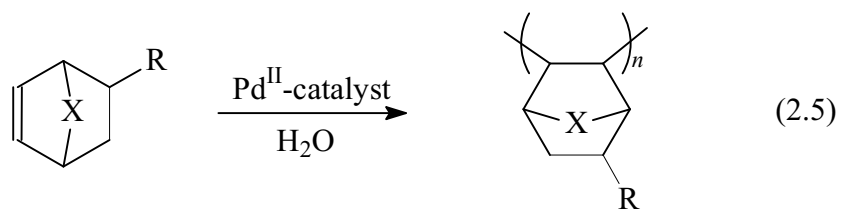
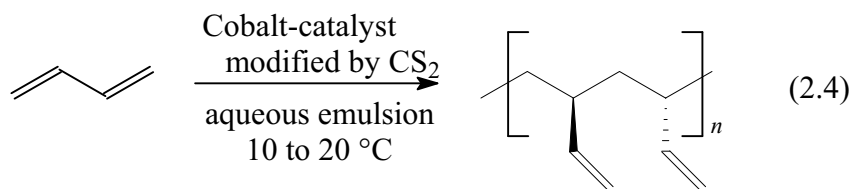
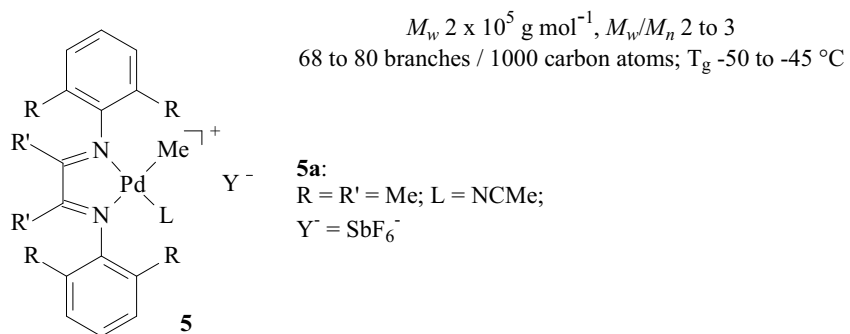
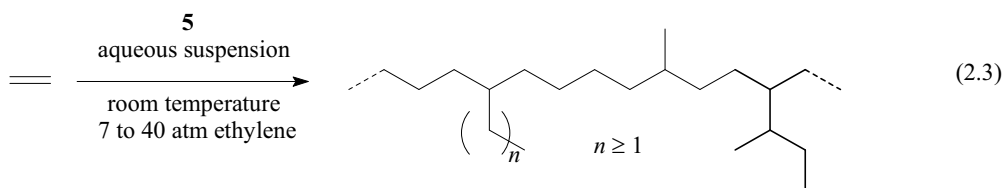


(n = 0 or 1, neutral or cationic)

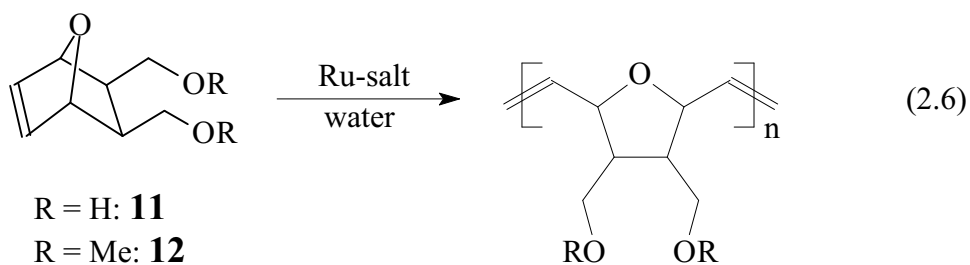


n = 0 or 1 (neutral or cationic)

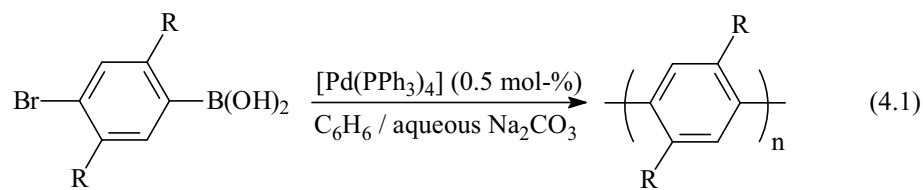




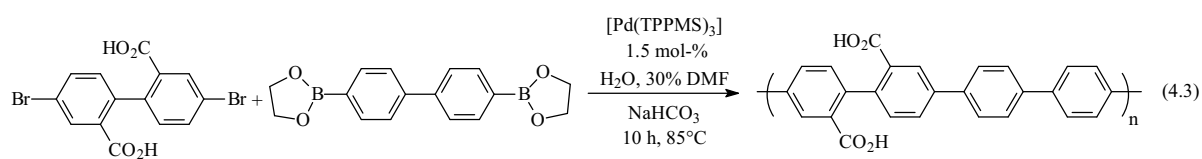
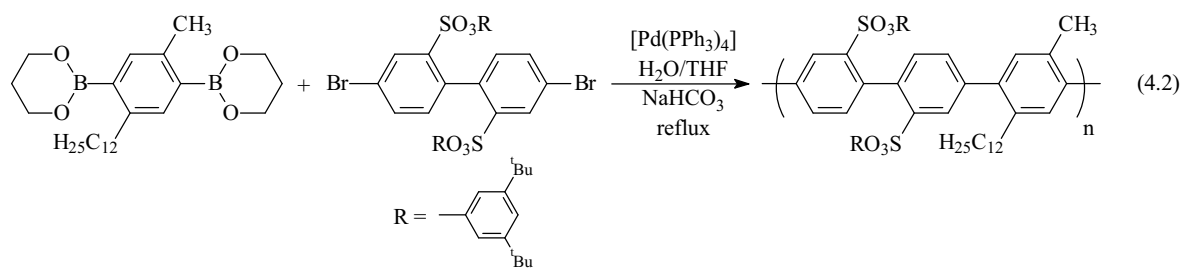
$X = \text{O}; \text{CH}_2$
 $R = \text{H}, \text{ polar-functionalized substituent}$



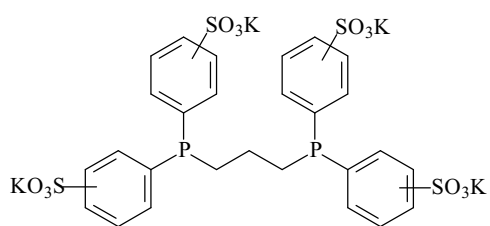
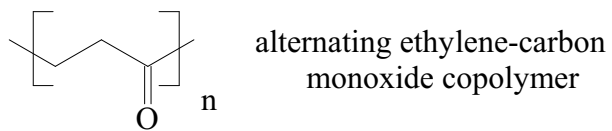
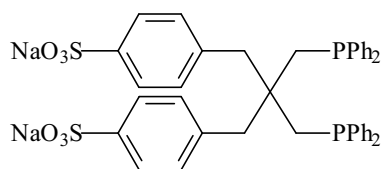
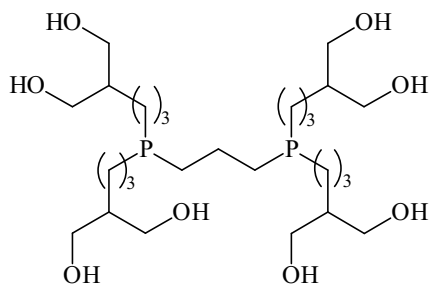
$R = \text{H}: \mathbf{11}$
 $R = \text{Me}: \mathbf{12}$

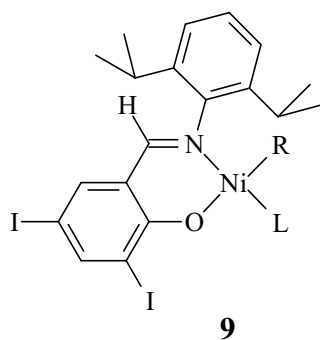
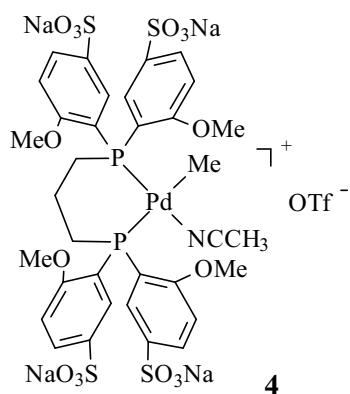


(e.g. R = H, CH₃, (CH₂)₃CH₃, (CH₂)₂C(CH₃)₃, ⁿC₈H₁₇, ⁿC₁₆H₃₃)



Figures added to text without numbering

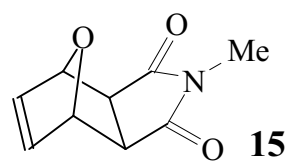
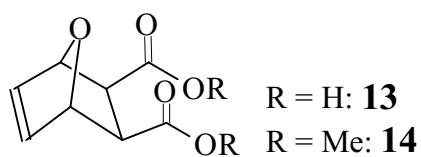
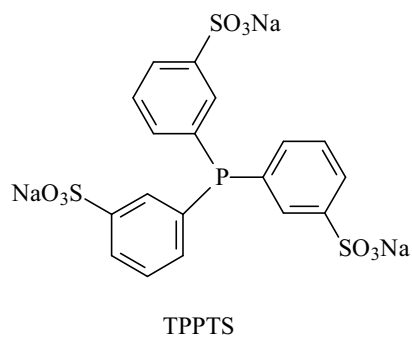
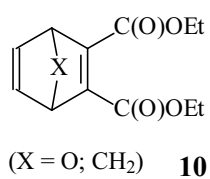
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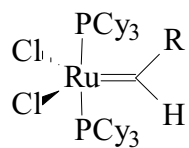


9a: R = Ph and L = PPh₃

9b: R = Me and L = pyridine

(activation of the PPh₃ complex for polymerization by [Rh(CH₂=CH₂)₂(acac)] as a phosphine scavenger)

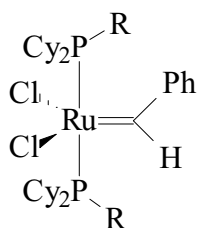




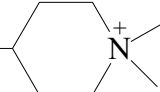
16a: R = -CH=CPh₂

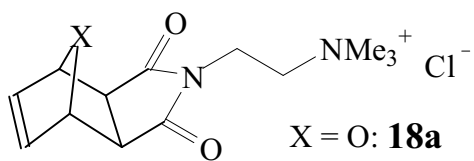
16b: R = Ph

(Cy = cyclohexyl)



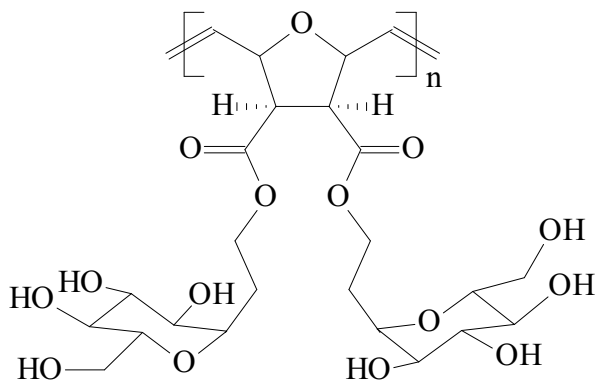
17a: R = -(CH₂)₂NMe₃⁺Cl⁻

17b: R =  Cl⁻

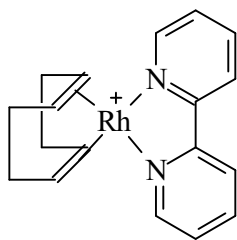


X = O: **18a**

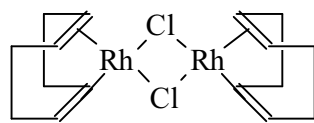
X = CH₂: **18b**



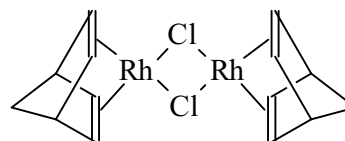
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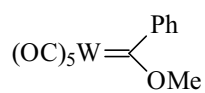
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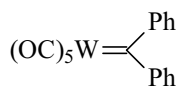
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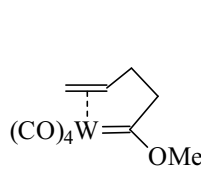
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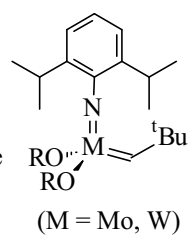
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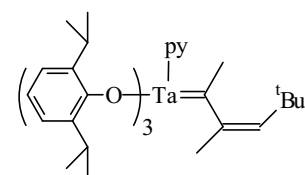
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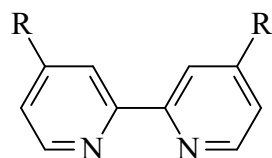
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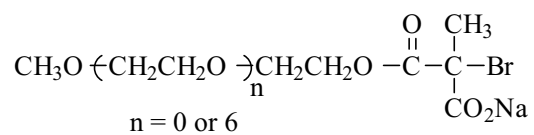
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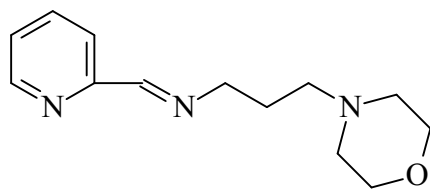


dNbpy: R = CH(C₄H₉)₂
 dAbpy: R = C₉H₁₉ (mixture of isomers)
 bpy: R = H



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