

## 7.1

### Introduction

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#### 7.1.1

##### General Background

The immobilization of metal complexes to be used in homogeneous catalysis was investigated at an early stage, in order to adapt their handling and separation from the products after a catalytic reaction to resemble those operations for the more widespread heterogeneous catalysts. Very soon after the discovery of Wilkinson's complex and its catalytic properties [1], the heterogenization of well-defined transition metal complexes on solid supports was already being investigated intensively [2]. Since then most approaches for immobilization of metal complexes have employed microporous organic or inorganic solids [3–5]. However, such heterogeneous catalyst systems are of limited practical utility to date. A limited diffusion of the substrates within the microporous support materials is disadvantageous. Also, the cross-linked copolymers used mostly as organic supports possess a heterogeneous structure consisting of domains of greatly differing composition, and their mechanical stability is limited in longer-term use [6]. As a possible alternative, binding of metal complexes to soluble polymers and other colloiddally dispersed systems has captured the interest of academic as well as industrial research groups.

The concept of binding catalytically active metal complexes to soluble metal complexes was brought forward by Manassen in the 1970s [7]. Results of hydroformylation and hydrogenation with rhodium complexes bound to phosphine-modified soluble polystyrenes were communicated by Bayer and Schurig soon afterward [8, 9]. It was not until ten years later that Bergbreiter initiated a broader investigation of the topic [10, 11], and since the mid-1990s the field has begun to attract a broader interest in academia as well as industry [12–14].

The separation of polymer-bound catalysts from a (single-phase, homogeneous) reaction solution after catalysis by means of properties specific to macromolecules is an alternative to homogeneous two- or multiphase catalysis as described in Chapters 2 to 6. Such specific properties, allowing for differentiation between the polymer-bound catalysts and low molecular weight compounds in the reaction mixture (products, substrates, and solvent), could be the dependence of polymer solubility on solvent composition or temperature. Another option is a separation based on the large difference in “size” of the dissolved species, by means of ultrafiltration. These approaches, which are the subject of this chapter, can be differentiated from the use of polymers as mere solubility-impeding groups in ligands for two- or multiphase catalysis. An example of the latter is the replacement of the sulfonate groups in the archetypical TPPTS by nonionic poly(ethylene glycol) chains. Such catalyst systems are treated in various other sections of this book and are beyond the scope of this chapter.

### 7.1.2

#### Structure and Synthesis of the Soluble Polymeric Supports

In linear polymers, catalyst binding can occur by coordination of the metal centers with two functional end-groups or with functional moieties (S) pendant on the polymer backbone chain (Figure 1). The latter approach obviously offers the advantage of higher possible loadings. A somewhat less common case is the coordination of the metal centers by heteroatoms which are directly part of the polymer backbone. The most prominent examples of the latter are (linear or branched) poly(ethylene imine)s with repeat units  $-\text{CH}_2\text{CH}_2\text{NH}-$ .

A variety of linear polymers have been employed as catalyst supports with functional groups serving as ligands covalently attached as end-groups or to the polymer backbone, e.g., polystyrene [8] and low molecular weight polyethylenes [15], and also polymers which can be water-soluble, such as poly(ethylene glycols) [16] or poly(*n*-alkylacrylamides) [17]. In addition to these organic polymers, polymers with an inorganic backbone have also been studied, most notably polysiloxanes [18, 19].

Concerning polymer synthesis in general, the functional groups which will represent the ligands for the metal center at a later stage in catalysis can be introduced by homo- or copolymerization of the corresponding substituted monomers, or by post-polymerization functionalization reactions of preformed polymers. An example of the former approach is the synthesis of polyvinylpyridine by polymerization of vinylpyridine. The choice of functional groups is somewhat restricted, as they must be compatible with the reaction conditions of polymerization, unless additional protection/deprotection steps are introduced. Depending on polymerization type, this translates to the presence of reactive radicals and temperatures around ca. 70 °C in free-radical polymerization, to reactive carbanions in anionic poly-

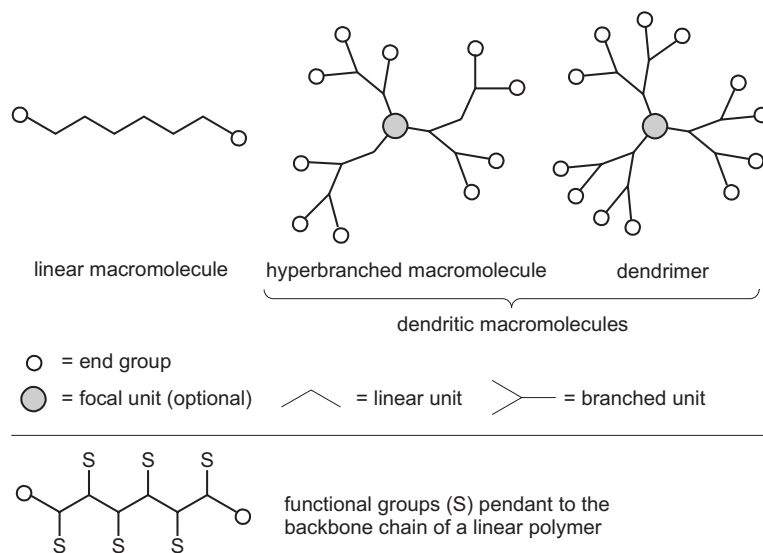
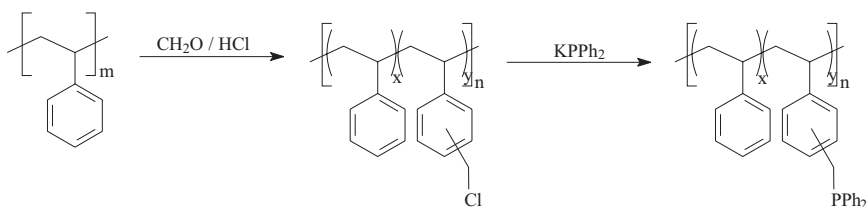


Figure 1 Schematic structure of linear and branched polymers.

merization, or to compatibility with transition metal catalysts in catalytic polymerization, to name the most common polymerization types employed.

More often, post-polymerization functionalization, also termed polymer-analogous reactions, is utilized. As the classical example [8], the synthesis of phosphine-substituted polystyrene by chloromethylation of styrene and subsequent reaction with potassium diphenylphosphide is depicted in Scheme 1. Polymer-analogous reactions are subject to some general restrictions. The high viscosity of polymer solutions at the concentrations of typical organic syntheses is problematic. Achieving full conversion is difficult in many polymer-analogous reactions. As a sideline of the properties of highly branched polymers in the context of catalyst supports, the high solubility, low viscosity, and good accessibility of functional end-groups can be of particular interest for catalyst synthesis by polymer-analogous reactions.



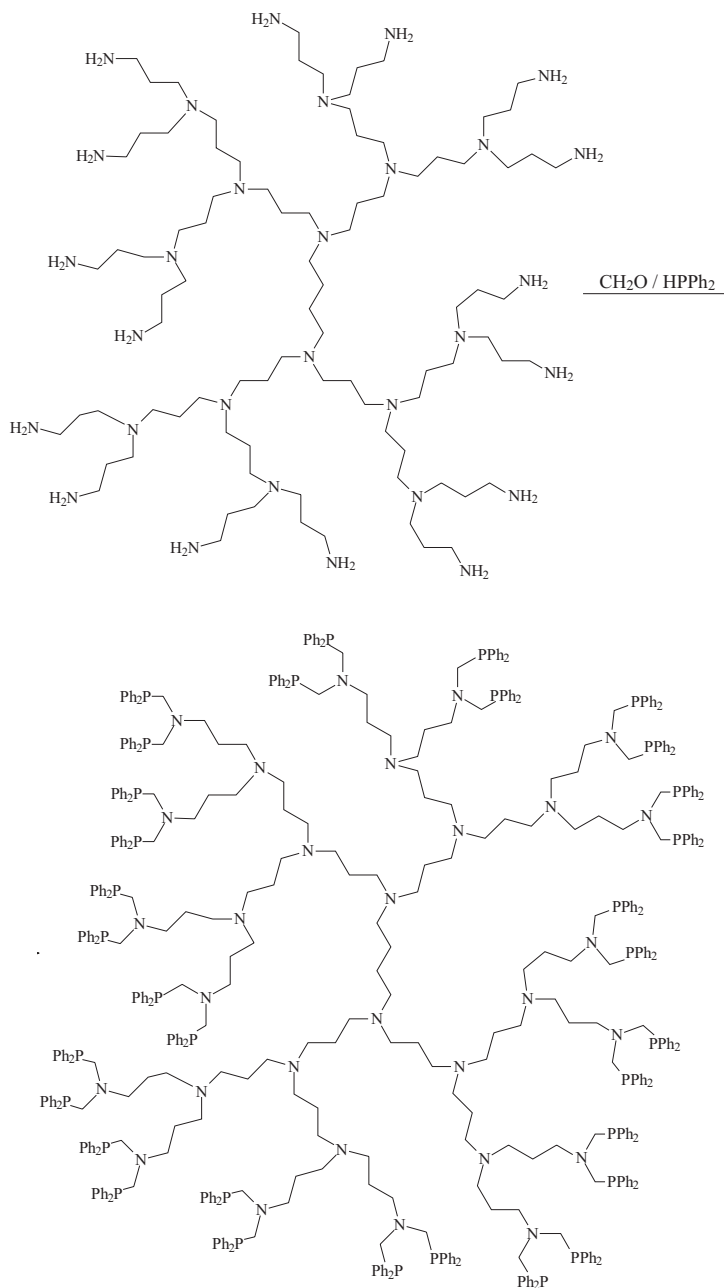
**Scheme 1** Synthesis of phosphine-substituted polystyrene by a polymer-analogous reaction.

It can be noted that the degree of functionalization of a polymer with ligand moieties is usually limited in order to control the solubility properties of the polymer.

Whereas linear polymers have been employed the most, highly branched dendrimers [20–22] [Figure 1 and Eq. (2)] have also found considerable interest recently as soluble supports for metal complex catalysts [12, 13]. In this context it should be noted that, not as frequently implied, dendrimers per se do not possess a spherical structure with a dense shell of end-groups on the outer surface of the molecules in solution. Rather, there is evidence that the solution structure varies with generation number, and that lower generations are very flexible molecules. For example, for a urea-functionalized G4 polypropyleneimine dendrimer (vide infra) the end-groups are mostly folded back into the interior of the molecule, in accordance with a dense-core picture of dendrimers [23, 24]. By contrast, for a G7 PAMAM dendrimer there is some experimental evidence that the end-groups are located at the periphery of the molecule [25]. Detailed experimental [24] and theoretical [26] investigations show that the earlier assumption [27] of a dense shell of dendrimers is not applicable. Rather, the density of dendrimers in solution usually decreases with increasing distance from the center of gravity of the molecule.

Clear advantages of highly branched macromolecules by comparison to linear polymers are their inability to crystallize and their corresponding high solubility, which is advantageous in catalyst synthesis as well as for the use of the resulting catalysts in solution. Also, the absence of chain entanglements results in low solution viscosities, which again are advantageous, particularly during polymer modification and catalyst synthesis [Eq. (1)]. Polypropyleneimine dendrimers [28–30] (abbreviated PPI, trade name Astramol<sup>®</sup> of DSM; cf. Figure 2) and polyamidoamine

dendrimers [31, 32] (abbreviated PAMAM, trade name Starburst<sup>®</sup> by Dendritech) are commercially available up to generation G4 (PPI) and G10 (PAMAM) respectively, corresponding to 64 and 4096 functional NH<sub>2</sub> or OH end-groups respectively. A G10 PAMAM dendrimer has a molecular weight of  $M = 934\,720\text{ g mol}^{-1}$ .



An ideal dendrimer structure without defects features only branched units and end-groups, in addition to the core (Figure 1). The molecules are monodisperse, i.e., they all possess the same molecular weight. While this perfect structure is not required for catalysis and recovery in principle, it enables the precise characterization of polymer-bound catalyst precursors. MALDI-TOF is a particularly useful technique. This well-defined nature of dendrimer-bound catalysts is advantageous also for systematic studies of their catalytic properties.

The synthesis of dendrimers, using either convergent [33] or divergent [31] routes, requires tedious multistep procedures. Therefore, so-called hyperbranched polymers [34] have found increasing attention recently [35–40].

In addition to the branching units and end-groups of dendrimers, hyperbranched polymers also contain linear units (Figure 1). The branching of a polymer molecule can be expressed illustratively by the degree of branching  $DB = 2D / (2D + L)$ ,  $D$  representing the number of dendritic, i.e., branching units and  $L$  being the number of linear units [40]. For a linear molecule the degree of branching is zero, whereas it is 100% for a perfect dendrimer. On this scale, typical hyperbranched polymers have a degree of branching of ca. 60–70%. Dendrimers and hyperbranched polymers are generally termed dendritic polymers.

By contrast to dendrimers, hyperbranched polymers can be obtained in one-step procedures. As a drawback, molecular weight distributions are often extremely broad. However, certain hyperbranched polymers can be prepared with reasonably narrow molecular distributions if suitable reaction conditions are employed. Hyperbranched polyethyleneimine, a polyamine with  $\text{NH}_2$  end-groups, is produced on a large scale industrially [41]. Hyperbranched polyesteramides with, e.g., terminal OH groups (trade name Hybrane<sup>®</sup> by DSM) and hyperbranched polyglycerol, a polyether-polyol with terminal OH groups, are currently available as specialty products on a kilogram scale [39, 42]. For molecular weights around  $M_n$  5000 g mol<sup>-1</sup>, polyethyleneimine and polyglycerol are available routinely with polydispersities of  $M_w/M_n \leq 1.3$  [41, 43]; higher molecular weight samples are more broadly distributed.

### 7.1.3

#### Binding of the Catalytically Active Complexes

The attachment of metal complexes to the polymer most often occurs via coordinating functional groups (ligands) bound to the polymer in a covalent fashion as outlined in Section 7.1.2, but various types of noncovalent attachment are also well documented (Figure 2). The latter can be achieved, for instance, by means of electrostatic interactions [45, 46], physisorption by amphiphilic polymer micelles (either as common association micelles or as unimolecular micelles) [47–49], by hydrogen bonding [50], or by specific interactions of proteins with a molecule [51]. Noncovalent attachment can offer the advantage of a lower synthetic effort in the catalyst preparation. On the other hand, it can be assumed that the resulting catalysts will often be restricted to a comparatively narrow range of organic solvents for reasons of solubility (electrostatic interactions) or leaching (physisorption and



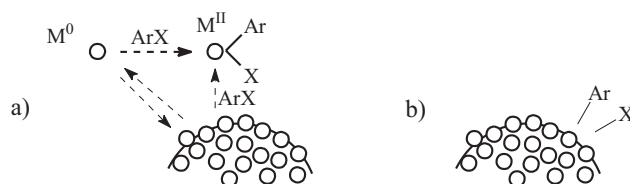
hydrogen bonding), and an enhanced sensitivity to temperature and changes in the solvent composition of the latter two types of binding versus covalent attachment or electrostatic interactions must be considered.

As for the synthetic protocol in general, the catalytically active metal center itself will be introduced only to the already prepared polymer, with very rare exceptions. A metal center which is sufficiently reactive to perform useful catalytic reactions will be susceptible to side reactions in most polymerization procedures.

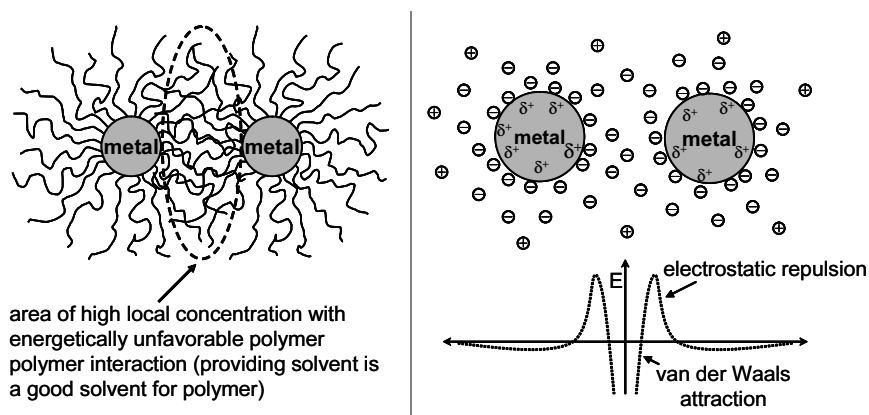
#### 7.1.4 Metal Colloids

Metal colloids, i.e., colloidally stable dispersions of metal particles in the size range of 1–10 nm, are often considered to be intermediate between classical homogeneous and heterogeneous catalysts. Like heterogeneous catalysts such colloids contain more than one phase: in them, the solid nanoparticles are dispersed in a liquid medium. In terms of practical handling they are more similar to homogeneous catalysts in resembling single-phase “solutions”. In terms of catalytic reactivity, metal colloids are known to catalyze a variety of reactions, such as hydrogenation, C–C coupling, and hydrosilylation, to name the most prominent. Most interest to date has certainly been devoted to catalytic hydrogenation with metal colloids. Generally speaking, the reactivities and activities observed are roughly similar to hydrogenations with standard heterogeneous catalysts, albeit in detail colloids can offer advantages in some cases [52, 53]. In terms of reaction mechanisms, hydrogenation by “soluble metal colloids” do not appear to differ from the well-known mechanism of hydrogenation on metal surfaces of heterogeneous catalysts. By contrast, the role of colloids in C–C coupling reactions, especially the Heck and Suzuki reaction, is currently the topic of debate [54–57]. Possible mechanistic pathways include the colloidal particles being in equilibrium with mononuclear complexes, which are the active species (Figure 3a), or reaction occurring directly on colloid particle surface atoms (Figure 3b). For hydrosilylation, the importance of platinum colloids has long been recognized [58].

The synthesis of metal particles and their properties have attracted considerable attention for more than a century [59, 60]. They are usually prepared by reduction of metal salts in the presence of suitable, low molecular weight or polymeric stabilizers [60], and electrochemical preparation [61–63] and decomposition of organometallic precursors [64, 65] have also been investigated intensively. Most often spherical particles with sizes in the range of 1–10 nm are obtained. However,



**Figure 3** Possible mechanisms of C–C coupling with soluble metal colloids.



**Figure 4** Steric stabilization of colloidal metal particles by a polymer layer (left) and electrostatic stabilization of colloidal particles (right).

it is interesting to note that geometrically regular particles can also be obtained under suitable conditions [66–70]. Electrostatic or steric stabilization is required to prevent coagulation to the thermodynamically preferred bulk metal (Figure 4). Steric stabilization by polymers has been widely applied to the stabilization of catalytically active metal colloids [71–73]. By comparison to electrostatic stabilization, steric stabilization is less sensitive to the nature of the solvent (as long as it is a good solvent for the polymer) and to charged substrates, which is advantageous in view of catalytic reactions.

By comparison to homogeneous catalysts based on metal complexes, the properties of which can be tuned via the ligands coordinating to the metal center, the scope of reactions and viable substrates is certainly less broad for metal colloids. The strong interest in metal colloids as catalysts which exists nonetheless (beyond the current surge of interest in nanoparticles for their own sake) can be traced to several, partially overlapping, aspects:

- Metal colloids can represent precursors for highly active catalysts for some reactions, which cannot be performed on heterogeneous catalysts (albeit the actual active species is not always clear).
- In many reactions catalyzed by metal complexes, colloids also are formed.
- In reactions catalyzed by metal complexes, irreversible formation of bulk metal is frequently a major catalyst deactivation route, e.g., in nearly any reaction involving palladium complexes. Stopping the aggregation at the stage of small particles in combination with a re-oxidation step can enhance catalyst activity.
- As a model for reactions on heterogeneous catalysts, colloids can be advantageous in some cases.



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