

# Hyperbranched Polymers Containing Transition Metals: Synthetic Pathways and Potential Applications

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## 1 Background

Incorporation of transition metals into organic monomers and polymers has been thoroughly examined over the past five decades in light of the promising electrical, magnetic, optical, sensing and catalytic properties that these organometallic materials possess [1–4]. Thanks to their intriguing properties, which are often inaccessible by their pure organic parents, these organometallic polymers have found applications in the coating, pharmaceutical, and aerospace industries.

Whereas many of these studies focused on the synthesis of linear polymers with either transition metals integrated into the main chain or attached as pendant groups at the side chains, the preparation and study of highly branched three dimensional (3-D) macromolecular architectures—such as dendrimers and hyperbranched polymers containing organometallic complexes—has only recently received greater attention. Depending on their position, metal centers have been shown to act as cores, simulating artificial models of biological systems such as metalloenzymes, as well as connectors, branching points, and terminal (surface) units distributed throughout the whole structure with potential applications in the field of sensors, catalysts, and as light-harvesting antennas [5,6]. Despite their structural beauty, dendrimer synthesis needs to be carried out in a thoughtful manner involving multi-step reaction and purification protocols in order to construct the various tree-like generations, which will in many cases restrict their potential applications to academic interests only [7]. Moreover, recent advances in mass spectrometric techniques have revealed depictions of dendrimers showing them to be highly idealized and that the real samples indeed exhibit imperfections and structural defects [8].

Compared with their “perfect” dendrimer congeners, “imperfect” hyperbranched polymers often exhibit similar, or even comparable, molecular properties despite their random and polydisperse structures. Nevertheless, they can be readily prepared by single-step polymerization procedures, allowing access to large-scale production and thus widening their potential uses and applications.

Our group is particularly interested in the synthesis of hyperbranched conjugated organic and organometallic polymers [9–14]. We have developed different synthetic routes toward high-metal loaded materials by either polymerizing metal containing monomers or by postfunctionalizing the hyperbranched scaffolding with organometallic complexes [15–20]. This chapter review our results along with the relevant work of expert groups on this young but promising research field.

## 2 Research and Discussion

### 2.1 Theoretical Background

Hyperbranched polymers exhibit tree-like molecular structures and have been the focus of active research since the groundbreaking work of Kim and Webster [21,22]. Throughout the structure three main units can be identified (Chart 1): Dendritic or branching units (D), linear units (L), and terminal units (T).

Different synthetic strategies have been employed for the preparation of the pure organic hyperbranched polymers [23–25]. The most commonly adopted approach is self-condensation of  $AB_n$ -type monomers with  $n \geq 2$  [26–29]. This type of polymerization can be carried out in a concurrent mode or by slow addition of the monomer or even in the presence of a core molecule of  $B_f$  ( $f \geq 3$ ), which allows various structural control over the growing polymer [30–32]. Another approach is copolymerizations of  $A_2$  monomers with  $B_n$  comonomers ( $n \geq 3$ ) [33–35]. However, the stoichiometric requirements between the pairs of the functional comonomers

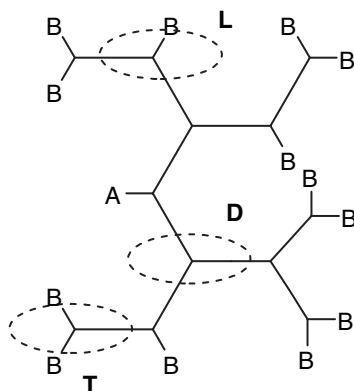


Chart 1

and the potential risk of gelation are severe drawbacks. As an alternative concept, Frechet has reported the synthesis of hyperbranched polymers by self-condensing vinyl polymerization (SCVP), which has recently been further applied to various other types of living/controlled polymerization, such as nitroxide-mediated radical polymerization, atom transfer radical polymerization, group transfer polymerization, and ring-opening polymerization [32,36–46].

Different from their dendrimer counterparts, hyperbranched polymers contain not only dendritic and terminal repeating units but also linear ones, which can be expressed in the degree of branching (DB). The DB is an important structural parameter of hyperbranched polymers and can be described in the following Eq. 2.1 [47].

$$DB = (D + T) / (D + L + T) \quad (2.1)$$

where  $D$  is the number of dendritic units,  $T$  is the number of terminal units, and  $L$  is the number of linear units. Frey has suggested a modified definition of DB that is based on the direction of growth, as shown in Eq. 2.1 [48]

$$DB = 2D / (2D + L) = (D + T - N) / (D + T + L - N) \quad (2.2)$$

where  $N$  is the number of molecules. For the hyperbranched polymers with high molecular weights  $N$  is negligible and Eqs. 2.1 and 2.2 are almost the same. Frey also pointed out that the DB statistically approaches 0.5 in the case of the polymerization of  $AB_2$  monomers, which is much lower than their dendrimer counterparts whose DB is unity.

## 2.2 Synthetic Pathways

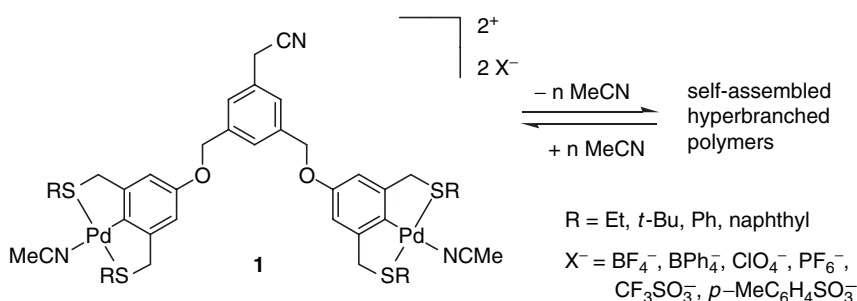
In order to directly synthesize organometallic hyperbranched polymers, all the above described established methods could be utilized to knit metal-containing monomers together, provided they are stable under the applied polymerization conditions and do not interfere with the reaction mechanism. As an alternative, suitable pure organic hyperbranched polymers can be functionalized with organometallic complexes. Both approaches have been utilized by other research groups and will be briefly reviewed at the beginning of Chapters 3 and 4.

### 2.2.1 Incorporation of Transition Metals through the Building Block

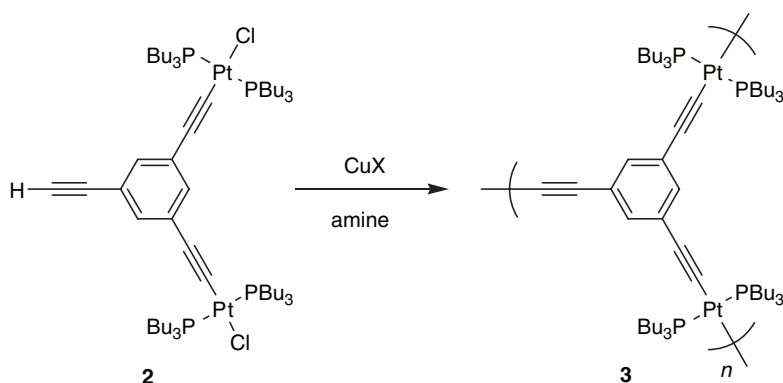
Although a wide range of methodologies exist for the preparation of hyperbranched polymers, examples of metal-containing materials—which are directly synthesized from organometallic monomers—are very limited. Reinhoudt and coworkers reported the preparation of hyperbranched polymers via self-assembly of an

AB<sub>2</sub>-type monomer (**1**) composed of organopalladium complexes, sandwiched in between SCS pincer ligands and attached labile acetonitrile molecules (Scheme 2.1) [49]. Ligand exchange through solvent removal leads reversibly to spherical assemblies, as confirmed by atomic force microscopy (AFM) and transmission electron microscopy (TEM). The size of the spheres is controllable through manipulation of the substituents on the pincer ligand as well as by exchanging the counter anions [50,51]. Interestingly, linear analogs did not show any globular structures, confirming the necessity of the branching units.

Lewis et al. attempted hyperbranched organometallic polymers via A<sub>2</sub> + B<sub>3</sub> protocol by reacting Pt(PBu<sub>3</sub>)Cl<sub>2</sub> with 1,3,5-triethynylbenzene in a molar ratio of 3:2. However, the resulting product was insoluble in common organic solvents and only the addition of excess amounts of *p*-1,4-diethynylbenzene (triyne:diyne = 1:50) could depress the involved cross-linking reactions [52]. In an alternative approach by Takahashi and coworkers, a formally similar hyperbranched polymer was constructed by self-polycondensation reaction from the AB<sub>2</sub>-type analog of Lewis' monomers (Scheme 2.2) [53]. The resultant organometallic polymer was soluble in



**Scheme 2.1** Self-assembly of hyperbranched Pd-containing polymers



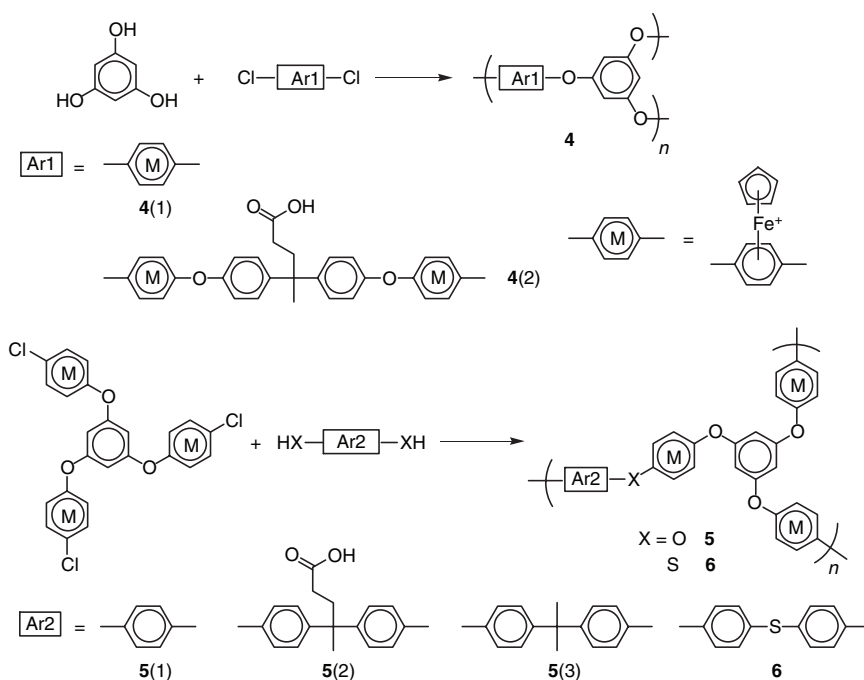
**Scheme 2.2** Synthesis of hyperbranched platinum-containing polyiyne from AB<sub>2</sub>-type monomers

common organic solvents and could be characterized by means of spectral analyses and gel permeation chromatography (GPC).

Recently, Abd-El-Aziz and colleagues reported different hyperbranched poly(arylethers) (**4,5**) and poly(arylthioethers) (**6**) containing cyclopentadienyliron moieties, which were successfully furnished by nucleophilic substitution of  $A_2 + B_3$  type monomers (Scheme 2.3) [54]. The polymers were thoroughly characterized by standard spectroscopic analysis techniques, they exhibited generally low viscosities, and the organometallic complexes were stable up to 230 °C, as evaluated by thermal gravimetric analysis (TGA).

Ferrocene is an attractive building block for the preparation of highly branched materials. Galloway and Rauchfuss reported the synthesis of high-molecular-weight poly(ferrocenylenepersulfides) by desulfurization-induced ring-opening polymerization (ROP) (Scheme 2.4) [55]. Whereas polymer **9** was insoluble, the attached bulky *t*-butyl group of **10** kept the polymer network soluble.

Similarly, our group has utilized ferrocene as a metal-containing building block and prepared hyperbranched poly(ferrocenylsilanes) through salt-eliminative poly-coupling of 1,1-dilithioferrocene with alkyltrichlorosilanes (Scheme 2.5) [56,57]. The solubility as well as the molecular weight increased with increasing spacer length from methyl to *n*-dodecyl-substituted polymers. Spectroscopic analyses revealed that the polymers possess rigid skeleton structures with extended conjugations, with their absorption spectra tailing into the infrared region (> 700 nm). This



**Scheme 2.3** Synthesis of cyclopentadienyliron-containing polymers via  $A_2 + B_3$  method