

Hyperbranched Polymers

Macromolecules in-between of Deterministic Linear Chains and Dendrimer Structures

Albena Lederer and Walther Burchard



Hyperbranched Polymers Macromolecules in between Deterministic Linear Chains and Dendrimer Structures

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Preface

Hyperbranched macromolecules are an integral part of nature. Since Flory's first successful effort to calculate such structures it took several decades before they could be synthesized. In the 1980s the first success in preparing polymers with AB_2 monomers was reported.

Some 40 years ago uncontrolled branching was classified as an undesired side-effect of polymerization, causing a delay in network formation. At present the variety of defined branched architectures and their application potentials seem to be endless. Countless numbers of functional groups fascinated chemists, permitting modifications which are used for different applications, such as processing or coatings. They also possess significant potential in sensorics, diagnostics, catalysis and therapeutics. In addition, the compact structure causes a decrease of the viscosity when applied as additives to melts.

Challenging requirements for suitable tailoring of material properties generates the need to understand the molecular characteristics of hyperbranched macromolecules. The discovery potential in this area is huge, taking into account the statistical character and manifold modification possibilities. Academic interest in hyperbranched molecules has continuously increased during the past 20 years since the discovery by Kim and Webster. More than 700 research articles per year regarding hyperbranched polymers are reported, with a continuously growing tendency.

Since Flory's fundamental work major efforts have been undertaken to synthesize dendritic structures. With the appearance of hyperbranched molecules many new routes for applications have opened. Yet, only a few research groups attempt to understand their properties by suitable theories.

Preparative physical chemists commonly possess a widespread experimental experience but lack knowledge in modern theory. *Vice versa*,

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theoreticians tend to have insufficient insight into the feasibility of polymer sythesis for special structures. When the present two authors came together they recognized that their experience overlapped. Collaboration over several years led to the idea to assemble this knowledge in a book.

In this book we are attempt to present the knowledge of physical chemistry characterization in a suitable mathematical scheme. The main problem of hyperbranched structures arises from statistical processes combined with the formation of large structures. As far as we know, this book is the first attempt to bridge the experimental and theoretical views in a consistent way.

We hope that our book will support a new trend in future studies of hyperbranched polymers.

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Abbreviations

$[\eta]$	intrinsic viscosity
2D-LC	two-dimensional liquid chromatography
A	functional group of type A
A_2, A_3	second, third virial coefficient
$a_{A2}; a_{\eta}$	scaling exponents
AF4	asymmetric flow field flow fractionation
AFM	atomic force miscroscopy
arbPS	arborescent polystyrene
b	bond length
В	functional group of type B
С	concentration
C*	overlap concentration
D	diffusion coefficient
D	dendritic units
Ð	molar mass distribution, polydispersity index
d_{app}	apparent density
DB	degree of branching
$d_{ m f}$	fractal dimension
DLS	dynamic light scattering
DMF	dimethylformamide
DMSO-d ₆	dimethylsulfoxide
dn/dc	refractive index increment
DP	degree of polymerization
DP_n	number average polymerization degree
DP_w	weight average polymerization degree
DSC	differential scanning calorimetry
ELS	electrophoretic light scattering

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f	functionality
J FB	branching fraction
FTIR	Fourier-transform infrared spectrometry
G	generation
ď	contraction factor, branching parameter, radius
Š	contraction factor
al	viscosity contraction factor
g a(r)	radial distribution function
g(r)	humerbranched
	Kuha Mark Haunink Calurada
KMH5	Kunn-Mark-Houwink-Sakurada
	linear units
LAC	inquid adsorption chromatography
LCB	long-chain branched
LCCC	liquid chromatography under critical conditions
LCST	lower critical solution temperature
LDPE	low density polyethylene
lin	linear
LLDPE	linear low density polyethylene
$l_{\rm p}$	persistence length
LS	light scattering
Μ	molar mass
M_0	molar mass of the monomer unit
MALDI-TOF-MS	matrix assisted laser desorption/ionization-time of
	flight-mass spectrometry
MALLS	multi-angle laser light scattering
MALS	multi-angle light scattering
$M_{\rm app}$	apparent molar mass
M _c	molar mass of the core
MD	molecular dynamic
M_n	number average molar mass
M _t	molar mass of the terminal units
M _w	weight average molar mass
	z-average molar mass
$\tilde{n_0}$	refractive index of the solvent
Nh	functionality of the branching site
Nc	functionality of the core
n	number of end-groups in a dendrimer
NMR	nuclear magnetic resonance
n.	probability of reaction/conversion of functionality A
n n	pressure
P(a)	particle scattering factor
ngf	probability generating function
PIST	polyamidoamine
DDI	polydispersity index
	nolvetheramide
r LA DC	polyculcialliuc
ro	polystyrelle

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Abbreviations

q	scattering vector
RAFT	reversible addition-fragmentation chain transfer
R_{g}	radius of gyration
RG theory	renormalization group theory
R _h	hydrodynamic radius
RI	refractive index detection
r _{ik}	distance vector
$r_{\rm m}$	monomer ratio AB/AB ₂ in the feed
R_N	end-to-end distance of the chain
r _p	monomer ratio AB/AB ₂ in the product
$\dot{R_{ heta}}$	Rayleigh ratio
SANS	small-angle neutron scattering
SAW	self-avoiding walk
SAXS	small-angle X-ray scattering
SCVP	self-condensing vinyl polymerization
SEC	size exclusion chromatography
SLS	static light scattering
SY	TBDMS capped end group
t	time
Т	terminal units
TBDMS	<i>tert</i> -butyldimethylsilyl group/ether
TCF	time correlation fucntion
TEM	transmission electron microscopy
$T_{\rm g}$	glass transition temperature
THF	tetrahydrofuran
V	volume
X_{ABB^*}	molar fraction of one monomer type
Z	numer of end-groups
α, β	extent of reaction, transition probability
α_{η}, a_{η}	Kuhn–Mark–Houwink exponent
γ	damping factor
3	draining exponent
ζ	frictional coefficient
η	viscosity
θ	scattering intensity
λ	number of branches per 1000 monomer units
λ	wavelength
μ	chemical potential
ν	scaling exponent
π	osmotic pressure
ho	ratio of radius of gyration, and hydrodynamic radius
τ	relaxation time
φ	draining parameter
Ψ	interpenetration parameter
ω	frequency

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CHAPTER 1 Introduction

1.1 Overview

Macromolecular branching belongs to nature and is of significant importance for the life functions of organisms. Branching in polymer science has been known since almost the time when first synthesis of linear chains was carried out. No doubt when Staudinger and Schulz carried out the synthesis of styrene they also tried to add divinyl benzene as a second monomer for a co-monomer.¹ The effect was dramatic and rather unexpected. In those days besides the monomer conversion the reaction was also followed by a change in viscosity because the increase of viscosity was a qualitative mean for the increase in molar mass. In the corresponding co-polymerization the increase in the viscosity was significantly lower but after certain time a sudden increase occurred and an non-measurable high value was attained. A highly elastic, gel-like material was obtained whose behaviour greatly resembled that of natural rubber.

The sudden change from a low solution viscosity to an elastic gel remained unclear for some time until, in 1941, Paul J. Flory² put forward the mathematically simple expression for the condition of the gelation point:

$$\alpha_{\rm c} = \frac{1}{f - 1} \tag{1.1}$$

He described the extent of reaction by the probability α and found a critical conversion α_c when gelation takes place. *f* is the number of functional groups per monomer of the same reactivity, and solubility remains in the pre-gel state of $\alpha(f-1) < 1$. Branching takes place only if f > 2 and gelation will occur at a connversion beyond the critical point defined by eq. (1.1).

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Flory intensely tried to derive the molar mass distributions of such randomly branched polymers. It was Walter H. Stockmayer who, in 1943– 1944,^{3,4} found the solution and with this distribution he could derive the weight average molar mass expressed in term of the probability of reaction:

$$M_{w}/M_{0} = 1 + \frac{\alpha f}{1 - \alpha (f - 1)} = \frac{1 + \alpha}{1 - \alpha (f - 1)}, \quad \beta = \alpha/2$$
(1.2)

with M_0 the molar mass of the monomer. Flory, as well as other researchers, was excited because this equation now gave a mathematical proof for his derivation of the prediction for the critical point of gelation. A lifelong friendship between the two pioneers, Flory and Stockmayer, began here.

The derivation of the so-simple looking equation was a hard challenge for Stockmayer. He was frustrated that he could not find a solution. It was Maria Goeppert Mayer (the later Nobel Prize winner in 1963 and wife and co-author with Joseph E. Mayer) who gave Stockmayer the decisive hint. She observed Stockmayer's attempt and after a while she said, 'Stocky, why don't you try to use our cluster description when we treated the interparticle interactions between colloidal spheres?'⁵

Flory confirmed the Stockmayer' distribution by applying combinatoral mathematics which will be given in Chapter 7 of this book. In the course of the time Flory also derived a molar mass distribution for the polymerization of AB_2 monomers⁶ and the corresponding weight average degree of polymerization. No critical conversion for gelation was obtained.

This result surprised even Flory, because he realized that a divergence can be obtained only at full conversion, *i.e.* $\alpha = 1$ or in other words, the branching of *such* AB₂ *samples can never lead to a gel or network*. This discovery was the birth date for hyperbranching.

Flory's interest in this type of structure arose from a book by K. H. Meyer in 1950⁷ and from Staudinger.⁸ The structure of natural polymers was one of the reasons why Staudinger, with co-workers, turned to chemical synthesis of model polymers in the hope of gaining a deeper understanding of these structures. Amylopectin, the branched component of starch, was one of them.^{9,10}

It took more than 20 years before the subject of AB_2 polymers was taken up^{11,12} but the decisive change was made by Kim and Webster¹³ by coining the name '*hyperbranching*'. These two authors were trying to find a less laborious synthesis for dendrimers, which were known to possess advantageous properties as nano-objects. Although Kim and Webster could not achieve the high accuracy of a perfect structure, so they stated, at least the samples are *hyperbranched*. This now generally used notation is rather unfortunate because also co-polymers of the $A_3 + B_2$ type are often included in this class of polymers although this type of co-polymerization was, for Flory and Stockmayer, the model system for random branching. Indeed gelation can be avoided by external constraints by choosing the appropriate composition of the two monomers.

Introduction

One may wonder why the research with hyperbranched macromolecules was so much delayed compared to the research on network formation with the remarkable property of rubber elasticity. The answer to the question appears obvious, because in the preparation of an AB₂ monomer the various functional groups should not react when it is synthesized. In order to obtain a polymer, the functional groups has to be activated, by an enzyme, an ionic initiator or other activators, for instance for ester formation. When these activating techniques were elaborated, the method of chemical synthesis for hyperbranched polymers was open. The almost boundless chemical possibilities for modifications made hyperbranched polymers preferred candidates for large-scale applications as the cheap analogue of dendrimers, e.g. as reactive components in coatings and resins, and as additives in linear systems for improved rheology and processing. Thermal stability and modulus can be easily modified just by modifying the huge number of functional groups in a single macromolecule.¹⁴ The synthetic procedures for these structures have taken unconventional routes over the years and have led to increasing control over the design of hyperbranched macromolecules, giving rise to new applications, particularly in areas of nanotechnology such as sensorics, diagnostics, catalysis and therapeutics.^{15–20}

With the challenging requirements for precise design of materials properties, the need to understand the molecular characteristics of hyperbranched macromolecules becomes urgent. The potential for discovery in this area is enormous taking into account the statistical character and versatile modification possibilities of the dendritic architectures. Thus, academic interest in hyperbranched structures has increased continuously in the last 20 years since their innovation by Kim and Webster.¹³ At present more than 700 articles per year report on research activities in hyperbranched polymers and the tendency is continuously growing.²¹

In fact, the theoretical treatment is lagging behind synthetic development, and it is a serious challenge. The difficulties with a suitable theory are not based on the complexity of branching alone, but also the polydispersity, excluded volume interaction and segment over-crowding have to be taken into account. We will show that several of these problems are on the way to being solved. However, the cases of special long range ionic or hydrophobic interactions have not been touched yet. Chemists are presently drawing conclusions more or less intuitively. It is our belief that a sensible theory on the new phenomena caused by the hyperbranching will be indispensable to obtaining a reasonable understanding for future applications of hyperbranched polymers.

1.2 Branched Polymers

In 1935 Staudinger and Schulz observed that the changes in the viscosity of polystyrene solutions depended on the reaction conditions during synthesis.¹ Later, Staudinger and Husemann found a higher number of end groups than expected during their studies on the natural polymers

amylopectin and glycogen, which was explained by the existence of branching.²² Both low viscosity and high number of end groups are typical characteristics of branched polymers. In addition, impeded crystallinity and poor mechanical strength are very common in branched polymers. These properties become more pronounced with branching density and depend on branching topology.

The type of branching can strongly influence polymer properties. Examples include natural polysaccharides, which occur after enzymatic polymerization of glucose, forming different types of branching. Glycogen is formed of glucose monomers and possesses high number of branching points (Figure 1.1). There are up to 50 000 monomer units of glucose on glycogen coupled together. The glucose units are arranged in a tree-like branched structure with a branching point every 8–12 glucose units. Glycogen is an energy supplier for animal cells and is the product of an enzymatic decomposition of starch. Starch is composed of amylose and amylopectin, which are also formed of glucose units, but while amylose possesses linear or very slightly branched chains, in amylopectin branching occurs every 25 units. Starch is the product of photosynthesis in plants. Despite the similar chemical character of the monomer units, the properties of starch and glycogen are different; starch is not soluble in cold water and is semi-crystalline, while glycogen is soluble in water and is not crystalline.

Today the variety of branching in synthetic polymers is manifold and 'branching' becomes a generic term for a huge class of polymer structures. The systematic development in branched polymers started with the discovery of long-chain branched polymers in the 1940s, the synthesis of the first star and graft polymers in the 1960s and the invention of dendrimers in the 1980s and of hyperbranched polymers in the 1990s. Nowadays, the combination of different branched topologies in one macromolecule becomes a common approach to control material properties. Some of these hybrid structures are overviewed in part 1.2.3 of this chapter. Roughly, the



Figure 1.1 Glycogen, amylopectin and amylose are chemically identical polysaccharides but with different branching architecture essential for their physiological functions.

structure of branched polymers could be classified depending on different characteristics and could be illustrated as a multidimensional property.

The *regularity* of branching is significant for calculating global and local properties as well as for further calculation of structural parameters. Branching can be regular or random with regard to either the length of the branches or the frequency of branching points. Figure 1.2 elucidates the differences in stars, comb polymers and dendritic polymers.

The quantification of branching is of immense importance for estimation of structure-property relationships, although, its definition is substantially influenced by the type of branching. Stars can be classified by the functionality of the core possessing only one branching point; comb-like and classical long-chain branched polymers are classified by the *number of*



regular star



comb like polymers



dendrimer

long or short chain branching

irregular star



hyperbranched polymer



branches per molecule or per 1000 C-atoms; dendritic branching is characterized by the relative number of branched units, *e.g. degree of branching*, due to the significantly higher density compared to the above branching types. The calculation and determination of branching degree is described in detail in Chapter 2.

Other characteristics of branched polymers are the *length of branches* and the *functionality of the branching point*. Both are variables which have to be taken into account calculating scaling characteristics of the polymers. The length of the branches also defines their properties in solution and in bulk. Long-chain branched polymers can possess properties typical for entangled macromolecules influencing flow and crystallinity properties. Short-chain branched polymers and dendritic structures are typically non-entangled and non-crystalline objects.

In the next section of this introductory chapter a short historical and structural background of dendritic polymers and their hybrids is given. The correlation to other types of branching is part of this book as far as a systematic comparison of properties is needed for better understanding the particularities of hyperbranched polymers. Additionally, the theoretical considerations developed for long-chain branched or star polymers are critically validated for the case of dendritic polymers.

1.2.1 Dendrimers

The term 'dendritic' comes from the Greek word for tree, $\delta\epsilon\nu\tau\rho\sigma$, and is related to the branching character of polymers. The ideal examples for dendritic polymers are dendrimers (Figure 1.3), which are built step-wise and have a branching point at every monomer unit.²³ Due to their perfectly branched nature, aesthetic 'look', complete dimensional control and variety of functional possibilities, dendrimers have fascinated the scientific community for several decades, especially in their role as nano-objects for high-end applications. Organic chemists were attracted by the challenging synthesis,²³ and highly interesting potential applications in the fields of biomaterials and nanotechnology have been found. A drawback of these perfect polymers is their limited industrial relevance because of high manufacturing costs.

The history of dendrimers started in 1978 with the cascade polymers of Buhleier *et al.*,²⁴ while iterative synthetic concepts were reported in the early 1970s by Lehn²⁵ and Cram *et al.*²⁶ In 1982, Aharoni *et al.*²⁷ studied lysine trees for peptide synthesis. In 1985 the first concepts of dendrimers,²⁸ or arborols,²³ were reported, giving birth to a new polymer topology class which expanded quickly to a huge variety of chemical structures, modifications and applications.

The special properties of dendritic polymers could easily be explained on the basis of the very well defined structure of dendrimers reflecting complete branching and regularity, which could be achieved in a three-dimensional sense. The formation of dendrimers starts with a core with functionality N_c . The functionality of the branching site N_b depends on the monomer



Figure 1.3 Dendrimer in the third generation from AB_2 monomer. Dendrimers possess terminal (*T*) and dendritic units (*D*), and a core.

functionality. Based on these values the development of the dendrimer structure can be simply calculated for every generation G. The number of end groups z increases according to

$$z = N_{\rm c} N_{\rm b}^G \tag{1.3}$$

which means that for the simplest case of a three-functional core and two-functional branching site ($N_c = 3$, $N_b = 2$) the number of end groups increases from 2 in the core to 48 in the fourth generation.

The number of repeating units N_r increases greatly with the generation number even for the simplest case:

$$N_{\rm r} = N_{\rm c} \frac{N_{\rm b}^{G+1} - 1}{N_{\rm b} - 1} \tag{1.4}$$

and the molar mass M accordingly increases exponentially with every generation:

$$M = M_{\rm c} + N_{\rm c} \left(N_{\rm r} \frac{N_{\rm b}^{G+1} - 1}{N_{\rm b} - 1} + M_{\rm t} N_{\rm b}^{G+1} \right)$$
(1.5)

with M_c the mass of the core and M_t , the mass of the terminal units.

The synthesis of dendrimers is well controlled and could proceed according to a divergent or convergent approach, described in Chapter 3.

Dendrimers show very interesting materials properties because of their globular, very compact structure and very high functionality, especially due to their fully defined structure. However, their synthesis is elaborate and very time consuming, which makes their implementation in largescale applications very complicated and expensive. This fact stimulated scientists and polymer manufacturers to search for alternative routes to produce polymers with similar properties as dendrimers but with easier synthesis.

1.2.2 Hyperbranched Polymers

For applications in which easy and efficient synthesis is more important than a perfectly branched architecture, hyperbranched polymers prepared by only one synthesis step are considered. This was the reason why Kim and Webster, researchers at Du Pont, developed new dendritic polymers that can be synthesized rapidly, in large quantities, for application as rheology modifiers and multifunctional initiators.^{13,29} In 1990 they reported on the first *hyperbranched* polymers, the polyphenylenes, which possess irregular structures with linear segments within the dendritic structure and a high polydispersity.

In fact the existence of synthetically produced, highly branched architectures started much earlier, in the 19th century. The first works are not directly available, but they were the basis of later developments on the polymerization of multifunctional monomers $(A_2 + B_3)$ based on phthalic anhydride or phthalic acid and glycerol.^{30,31} In 1909, Baekeland used the $A_2 + B_3$ reaction between formaldehyde and phenol to produce the first commercialized polymer, a cross-linked material, which exists as an irregularly branched structure just before the network formation.

The theory of polycondensation between multifunctional monomers was extensively treated in the works of Flory in the 1940s and 1950s.^{6,32,33} Flory was interested in the statistics of molar mass distribution before gel formation in polymers with trifunctional and tetrafunctional branching points. Before reaching the so-called gel point, *e.g.* the critical conditions for cross-linking, highly branched structures with a certain branching degree are formed. Flory found that, theoretically, the combination of both reaction functionalities in one monomer of type AB_x ($x \ge 2$) should prevent gelation if A reacts only with B (condition 1). The one-pot synthetic route yields dendritic structures that possess highly dense branching with the potential of a branching point at each repeat unit. Simplification of the calculation, which corresponds also to conditions leading to ideal statistics, requires the assumptions that no cyclization or side reactions occur (condition 2) and that the reactivity of B is independent of the degree of polymerization (condition 3).

In the simplest case of an AB_2 monomer this type of reaction leads to the formation of three types of unit (Figure 1.4). If only one of the two



Figure 1.4 Hyperbranched polymer with AB_2 units. Hyperbranched polymers possess terminal (*T*), dendritic units (*D*), linear units (*L*). The point indicated by the arrow belongs to the focal unit, which corresponds to the unreacted A-function.

B-groups in an AB₂ monomer has reacted, a *linear* unit (L) is formed, carrying the non-reacted B-group available for further reactions. If both B-groups have reacted a dendritic unit is obtained (D); and, finally, if both B-groups no longer have reacted a terminal unit (T) is obtained. If the above conditions (1 to 3) for ideal statistics are fulfilled, the frequencies of the three types of polymer units at high conversion are

$$\frac{L}{L+D+T} \approx 0.5, \quad \frac{D}{L+D+T} \approx 0.25, \quad \frac{T}{L+D+T} \approx 0.25$$
$$L+D+T \approx DP_n \tag{1.6}$$

75% of the polymer units carry B-groups, which corresponds to free B-functionalities approximately equal to the degree of polymerization, $z = DP_n - 1$.

On the basis of these assumptions Flory calculated the molar mass distribution in a polycondensation reaction leading to statistical branching. A monomer with functionality f would possess in this case one A- and (f - 1)B-groups. The probability that a B-group has reacted is p_b and the probability for an A-group to react is p_a . The variable p_b corresponds to the fraction of reacted B-groups while the fraction of reacted A-groups would be $p_a(f - 1)$ due to the remaining focal group (cyclization reactions are excluded). In this case the conversion of the reaction could be expressed with $p_{\rm a}$ and the fraction of branching should correspond to

$$\alpha = \frac{p_{\rm a}}{f - 1} \tag{1.7}$$

where α is the extent of reaction, and with this notation the number averaged and weight averaged degrees of polymerization are using α and p_{a} , then

$$DP_n = \frac{1}{1 - p_a} = \frac{1}{1 - \alpha(f - 1)}$$
(1.8)

$$DP_{w} = \frac{1 - \alpha^{2}(f - 1)}{\left[1 - \alpha(f - 1)\right]^{2}}$$
(1.9)

the distribution of the polymerization degree can be expressed as

$$\frac{DP_{w}}{DP_{n}} = \frac{1 - \alpha^{2}(f-1)}{1 - \alpha(f-1)} = \frac{1 - \alpha p_{a}}{1 - p_{a}}$$
(1.10)

This equation shows that if the conversion of A-groups approximates unity, the molar mass distribution should increase infinitely. This means that at full conversion the molar masses could achieve extremely high values but without network formation. In practice, such molar masses are seldom due to non-ideal statistics which the polycondensation reactions follow.

In the next four decades research activities following from Flory's calculations are not reported. The expected macromolecular characteristics which can be hardly controlled, as irregular branching, very broad polydispersities and amorphous materials with poor mechanical properties were found unprofitable. The understanding of these very complex structures with multidimensionally distributed parameters was limited at that time.

With exception of the activities of Kricheldorf *et al.*, on copolycondensation of AB_2 and AB monomers in 1982,³⁴ the first intentional development of hyperbranched polymers was started in 1988 by Kim and Webster, who also invented the term *hyperbranched*.

Kim and Webster synthesized hyperbranched polyphenylenes by a catalyzed reaction of multifunctional monomers (Figure 1.5) and observed very good solubility of the polymers in organic solvents even at high molar masses, which was affected by the high number of end groups.

By modification of these end groups to carboxylate end functions the polymers became soluble in water. The glass transition temperature of these polymers was less influenced by the molar mass but was controlled by endgroup modification. The hyperbranched polyphenylenes were brittle with rather poor mechanical characteristics but with excellent thermal stability. Their application as materials was put aside but their potential as additives for modification of materials properties was rapidly recognized and invented.

Since this time hyperbranched architectures have attracted increasing attention in the scientific community based on the unique properties in



Figure 1.5 Hyperbranched polyphenylene first synthesized by Kim and Webster.¹³

combination with straightforward preparation. The classical synthesis for hyperbranched polymers remains polycondensation, but in the last 20 years great effort has been made to obtain new chemical structures using unconventional synthetic routes, driven by the occurrence of new fields of application.^{15,16,35,36} In addition to their well-known use in resins and coating formulations, hyperbranched polymers appeared as additives in linear polymers for rheology modification, or for the improvement of processing, thermal stability, mechanical and surface properties. This huge range of application fields has to be ascribed to the highly branched nature which leads to excellent solubility, low melt and solution viscosities, combined with a high number of reactive end functionalities, which can arbitrarily be greatly modified.^{37–40} Furthermore, interesting areas of application have been found in thin films for sensor devices and diagnostics by tuning the confinement of the hyperbranched structures, as pore-forming agents in nanofoams by using their globular shape, in drugs and as catalytic carriers using molecular cavities and functional group geometry.^{14–18} Nowadays, there is a number of suppliers who specialize in the development of applicationoriented hyperbranched structures and commercial products. Some wellknown examples of hyperbranched polymers on the market are the aliphatic polyester Boltorn[™],³⁷ the poly(esteramide) Hybrane[™],³⁸ and the poly(ethylene imine) Lupasol^M, as well as a number of hyperbranched polyesters⁴¹ and polyurethanes⁴²⁻⁴⁴ for applications in coatings and resins, and hyperbranched polyglycerols and polyesters for nanotechnology and bioapplications.^{45–47}

1.2.3 Dendritic Hybrids

The high functionality and special geometry of branching conceals great potential not only in the classical dendritic structures, dendrimers and

hyperbranched polymers. The combination of dendritic and linear chains opens many more variations of polymer architectures and new molecular properties. Such types of combination can be found in dendritic-linear hybrids, which could exist in a different structure but two prominent examples are *dendronized polymers* and hypergraft polymers (Figure 1.6). The concept of dendronized polymers was motivated by the challenging aspects to realize giant macromolecules (DenPols) with high functionality. Along with the perfectly branched dendrimers and hyperbranched polymers, DenPols⁴⁸ also belong to the structural family of dendritic macromolecules. They can be described as hybrid macromolecules possessing a linear backbone decorated with dendrons. The dendronization of a linear polymer results in a high concentration of functional groups along the linear backbone and a very dense packing leading to a cylindrical shape.⁴⁸⁻⁵⁰ In contrast to dendrimers, where the dendrons are coupled to a core and the size and functionality of the molecules are limited, the fabrication of dendronized linear structures enables the realization of diverse nano-objects which vary in their length, branch point frequency, and dendron generation.

The dendronization could be performed instead of perfectly branched dendrons in different generation, also with imperfect, hyperbranched



Figure 1.6 Dendritic hybrids.