Hyperbranched polymers: from synthesis to applications

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Abstract

Over the past 15 years, hyperbranched polymers have received much attention due to their unique chemical and physical properties as well as their potential applications in coatings, additives, drug and gene delivery, macromolecular building blocks, nanotechnology, and supramolecular science. Hyperbranched polymers can be prepared by means of single-monomer methodology (SMM) and double-monomer methodology (DMM). In SMM, the polymerization of an AB\_n monomer leads to hyperbranched macromolecules. SMM consists of at least four components: (1) polycondensation of AB\_n monomers; (2) self-condensing vinyl polymerization; (3) self-condensing ring-opening polymerization; (4) proton-transfer polymerization. In DMM, direct polymerization of two suitable monomers or a monomer pair gives rise to hyperbranched polymers. A classical example of DMM, the polymerization of A\_2 and B\_n (n > 2) monomers, is well known. Recently, a novel DMM based on the in situ formation of AB\_n intermediates from specific monomer pairs has been developed. This form of DMM is designated as ‘couple-monomer methodology’ (CMM) to clearly represent the method of polymerization. Many commercially available chemicals can be used as the monomers in these systems, which should extend the availability and accessibility of hyperbranched polymers with various new end groups, architectures and properties. Because a number of comprehensive reviews have been published on SMM, research involving DMM is emphasized here. In addition, recent developments in the modification, functionalization and application of hyperbranched polymers are described.

Keywords: Hyperbranched polymer; Dendritic polymer; Polymer brush; Modification; Functionalization; Application; Surface

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Hyperbranched polymers are highly branched macromolecules with three-dimensional dendritic architecture. Due to their unique physical and chemical properties and potential applications in various fields from drug-delivery to coatings, interest in hyperbranched polymers is growing rapidly, as confirmed by the increasing number of publications (Fig. 1). As the fourth major class of polymer architecture, coming after traditional types which include linear, cross-linked and branched architectures, dendritic...
**Nomenclature**

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
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<tbody>
<tr>
<td>ACPA</td>
<td>4,4'-azobis(4-cyanopentanoic acid)</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>ATRP</td>
<td>atom transfer radical polymerization</td>
</tr>
<tr>
<td>BIEM</td>
<td>2-(2-bromoisobutyryloxy)ethyl methacrylate</td>
</tr>
<tr>
<td>bis-MPA</td>
<td>2,2-bis-hydroxymethyl propionic acid</td>
</tr>
<tr>
<td>BPEA</td>
<td>2,2-(bromopropionyloxy)ethyl acrylate</td>
</tr>
<tr>
<td>Bu4N</td>
<td>tetra-n-butylammonium</td>
</tr>
<tr>
<td>CAC</td>
<td>critical association concentration</td>
</tr>
<tr>
<td>CAH</td>
<td>2-chloroethylamine hydrochloride</td>
</tr>
<tr>
<td>CMM</td>
<td>couple-monomer methodology</td>
</tr>
<tr>
<td>CP</td>
<td>chitosan powder</td>
</tr>
<tr>
<td>CPS</td>
<td>chloromethylstyrene</td>
</tr>
<tr>
<td>DB</td>
<td>degree of branching</td>
</tr>
<tr>
<td>DBOP</td>
<td>diphenyl(2,3-dihydro-2-thioxo-3-benzoxazolyl)phosphonate</td>
</tr>
<tr>
<td>DCC</td>
<td>N,N-dicyclohexylcarbodiimide</td>
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<tr>
<td>DIPC</td>
<td>diisopropylcarbodiimide</td>
</tr>
<tr>
<td>DMA</td>
<td>dynamic mechanical analysis</td>
</tr>
<tr>
<td>DMAC</td>
<td>N,N-dimethylacetamide</td>
</tr>
<tr>
<td>DMAP</td>
<td>4-(dimethylamino)pyridine</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-dimethylformamide</td>
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<td>DMM</td>
<td>double-monomer methodology</td>
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<tr>
<td>DPMP</td>
<td>diphenylmethy1potassium</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EG</td>
<td>ethylene glycol</td>
</tr>
<tr>
<td>EHBp</td>
<td>epoxy-functionalized hyperbranched polyesters</td>
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<tr>
<td>EL</td>
<td>electroluminescence</td>
</tr>
<tr>
<td>EO</td>
<td>ethylene oxide</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>GTP</td>
<td>group transfer polymerization</td>
</tr>
<tr>
<td>L</td>
<td>linear unit</td>
</tr>
<tr>
<td>LALLS</td>
<td>low-angle laser light scattering</td>
</tr>
<tr>
<td>LCST</td>
<td>lowermost critical solution temperature</td>
</tr>
<tr>
<td>LDA</td>
<td>lithium dioctylsulfonate</td>
</tr>
<tr>
<td>MA</td>
<td>methyl acrylate</td>
</tr>
<tr>
<td>MAH</td>
<td>maleic anhydride</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>matrix-assisted laser desorption/ionization time-of-flight</td>
</tr>
<tr>
<td>M6c-TREN</td>
<td>tri(2-(dimethylamino)ethyl)amine</td>
</tr>
<tr>
<td>MHO</td>
<td>3-methyl-3-(hydroxymethyl)oxetane</td>
</tr>
<tr>
<td>MMA</td>
<td>methyl methacrylate</td>
</tr>
<tr>
<td>$M_n$</td>
<td>number average molecular weight</td>
</tr>
<tr>
<td>MOI</td>
<td>2-methacryloyloxyethyl isocyanate</td>
</tr>
<tr>
<td>MUA</td>
<td>mercaptopendecanoic acid</td>
</tr>
<tr>
<td>$M_w$</td>
<td>weight average molecular weight</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>NMP</td>
<td>N-methyl-2-pyrrolidone</td>
</tr>
<tr>
<td>NMR</td>
<td>nuclear magnetic resonance</td>
</tr>
<tr>
<td>PA</td>
<td>polyaniline</td>
</tr>
<tr>
<td>PAA</td>
<td>poly(acrylic acid)</td>
</tr>
<tr>
<td>PAAM</td>
<td>poly(allylamine)</td>
</tr>
<tr>
<td>PCL</td>
<td>poly(ε-caprolactone)</td>
</tr>
<tr>
<td>PCS</td>
<td>photon correlation spectroscopy</td>
</tr>
<tr>
<td>PDI</td>
<td>polydispersity index ($M_w/M_n$)</td>
</tr>
<tr>
<td>PDMA</td>
<td>poly(2-dimethy laminoethyl methacrylate)</td>
</tr>
<tr>
<td>PE</td>
<td>polyethylene</td>
</tr>
<tr>
<td>PEHO</td>
<td>poly[3-ethyl-3-(hydroxymethyl)oxetane]</td>
</tr>
<tr>
<td>PEI</td>
<td>poly(ethyleneimine)</td>
</tr>
<tr>
<td>PEO</td>
<td>poly(ethylene oxide)</td>
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<tr>
<td>PG</td>
<td>hyperbranched polyglycerol</td>
</tr>
<tr>
<td>PL</td>
<td>photoluminescence</td>
</tr>
<tr>
<td>PMDETA</td>
<td>pentamethyldiethylenetriamine</td>
</tr>
<tr>
<td>PMHO</td>
<td>poly[3-methyl-3-(hydroxymethyl)oxetane]</td>
</tr>
<tr>
<td>PP</td>
<td>polypropylene</td>
</tr>
<tr>
<td>PPMA</td>
<td>phosphorus pentoxide/methanesulfonic acid</td>
</tr>
<tr>
<td>PPO</td>
<td>poly(propylene oxide)</td>
</tr>
<tr>
<td>PPV</td>
<td>poly(phenylenevinylene)</td>
</tr>
<tr>
<td>PS</td>
<td>polystyrene</td>
</tr>
<tr>
<td>PTBA</td>
<td>poly(tert-butyl acrylate)</td>
</tr>
<tr>
<td>PTHF</td>
<td>polytetrahydrofuran</td>
</tr>
<tr>
<td>PTP</td>
<td>proton-transfer polymerization</td>
</tr>
<tr>
<td>PVK</td>
<td>poly(9-vinylcarbazole)</td>
</tr>
<tr>
<td>ROMBP</td>
<td>ring-opening multibranching polymerization</td>
</tr>
<tr>
<td>SCROP</td>
<td>self-condensing ring-opening polymerization</td>
</tr>
<tr>
<td>SCVP</td>
<td>self-condensing vinyl polymerization</td>
</tr>
<tr>
<td>SDS</td>
<td>sodium dodecyl sulfate</td>
</tr>
<tr>
<td>SEC</td>
<td>size exclusion chromatography</td>
</tr>
<tr>
<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>SMM</td>
<td>single-monomer methodology</td>
</tr>
<tr>
<td>T</td>
<td>terminal unit</td>
</tr>
<tr>
<td>$T_d$</td>
<td>decomposition temperature</td>
</tr>
<tr>
<td>TEM</td>
<td>transmission electron microscopy</td>
</tr>
<tr>
<td>$T_g$</td>
<td>glass transition temperature</td>
</tr>
<tr>
<td>TGA</td>
<td>thermogravimetric analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
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</table>
architecture consists of six subclasses: (a) dendrons and dendrimers; (b) linear-dendritic hybrids; (c) dendri-grafts or dendronized polymers; (d) hyperbranched polymers; (e) multi-arm star polymers; (f) hypergrafts or hypergrafted polymers (Fig. 2) [1]. The first three subclasses exhibit perfect structures with a degree of branching (DB) of 1.0, while the latter three exhibit a random branched structure. Dendrons and dendrimers with high regularity and controlled molecular weight are prepared step by step via convergent and divergent approaches. A linear polymer linked with side dendrons is called as dendronized polymer. Dendronized polymers can be obtained by direct polymerization of dendritic macromonomers, or by attaching dendrons to a linear polymeric core.

A number of excellent reviews have been published on dendrimers, linear-dendritic hybrids, and dendronized polymers, covering synthesis, functionalization, supramolecular self-assembly and applications [1–34]. This article reviews the synthesis, modifications, and applications of random hyperbranched and hypergrafted polymers, focusing on the recently developed novel synthetic strategy for hyperbranched polymers.

1.1. History of hyperbranched polymers

As shown in Table 1, showing the development of hyperbranched polymers, highly branched artificial molecules have a long and complex history. The history of hyperbranched macromolecules can be dated to the end of 19th century, when Berzelius reported the formation of a resin from tartaric acid (A₂B₂ monomer) and glycerol (B₃ monomer) [35]. Following the Watson Smith report of the reaction between phthalic anhydride (latent A₂ monomer) or phthalic acid (A₂ monomer) and glycerol (B₃ monomer) in 1901 [35], Callahan, Arsem, Dawson, Howell, and Kienle, et al. [35–37] studied that reaction further, obtaining results and conclusions still used today. For example, Kienle [36] showed that the specific viscosity of samples made from phthalic anhydride and glycerol was low when compared to numerous specific viscosity values given by Standinger for other synthetic linear polymers, such as polystyrene. In 1909, Baekeland [38] introduced the first commercial synthetic plastics, phenolic polymers, commercialized through his Bakelite Company. The cross-linked phenolic polymers are obtained by the polymerization of soluble resole precursors made from formaldehyde (latent A₂ monomer) and phenol (latent B₃ monomer). Just prior to gelation, these polymers have a so-called random hyperbranched structure.

In the 1940s, Flory et al. [39–43] used statistical mechanics to calculate the molecular weight distribution of three-dimensional polymers with trifunctional and tetrafunctional branching units in the state of gelation, and developed the ‘degree of branching’ and ‘highly branched species’ concepts. However, both the experiments and calculations mentioned above are based on polycondensation of bifunctional A₂ monomer with trifunctional B₃ monomers, so gelation occurs when the degree of polymerization approaches the critical condition. In 1952, Flory [44] developed the theory that highly branched polymers can be synthesized without the gelation by polycondensation of a monomer containing one A functional group and two or more B functional ones capable of reacting with A (A₂Bᵅ monomer, n ≥ 2). Finally, in 1982, Kricheldorf [45] obtained highly
branched polyesters by copolymerization of AB and AB$_2$ type monomers.

‘Hyperbranched polymer’ was first coined by Kim and Webster [46,47] in 1988 when the authors intentionally synthesized soluble hyperbranched polyphenylene. Since then, hyperbranched polymers have attracted increasing attention owing to their unique properties and greater availability as compared with dendrimers.

1.2. Synthesis methodology

Up to now, the synthetic techniques used to prepare hyperbranched polymers could be divided into two major categories. The first category contains techniques of the single-monomer methodology (SMM), in which hyperbranched macromolecules are synthesized by polymerization of an AB$_n$ or a latent AB$_n$ monomer. According to the reaction mechanism, the SMM category includes at least four specific approaches: (1) polycondensation of AB$_n$ monomers; (2) self-condensing vinyl polymerization (SCVP); (3) self-condensing ring-opening polymerization (SCROP); (4) proton-transfer polymerization (PTP).

The other category contains methods of the double-monomer methodology (DMM) in which direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers. Table 2 shows the synthetic methodologies and approaches to hyperbranched polymers.

<table>
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<th>Year</th>
<th>Case</th>
<th>Lead authors</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before 1900</td>
<td>Tartaric acid + glycerol</td>
<td>Berzelius</td>
<td>[35]</td>
</tr>
<tr>
<td>1901</td>
<td>Glycerol + phthalic anhydride</td>
<td>Smith</td>
<td>[35]</td>
</tr>
<tr>
<td>1909</td>
<td>Phenolic + formaldehyde</td>
<td>Baekeland</td>
<td>[38]</td>
</tr>
<tr>
<td>1929–1939</td>
<td>Glycerol + phthalic anhydride</td>
<td>Kienle</td>
<td>[35–37]</td>
</tr>
<tr>
<td>1939</td>
<td>Molecular size distribution in theory</td>
<td>Flory</td>
<td>[39–41]</td>
</tr>
<tr>
<td>1941</td>
<td>AB$_n$ polymerization in theory</td>
<td>Flory</td>
<td>[44]</td>
</tr>
<tr>
<td>1952</td>
<td>AB$_2$ + AB copolymerisation</td>
<td>Kricheldorf</td>
<td>[45]</td>
</tr>
<tr>
<td>1982</td>
<td>AB$_2$ homopolymerization</td>
<td>Kim/Webster</td>
<td>[46,47]</td>
</tr>
</tbody>
</table>
1.2.1. SMM—polycondensation of AB$_2$ monomers

A broad range of hyperbranched polymers, including hyperbranched polyphenylenes [46–49], polyethers [50–53], polyesters [54–76], polyamides [77–82], polycarbonates [83], and poly(ether ketones) [84–87], are prepared via one-step polycondensation of AB$_2$ monomers. If one group of AB$_2$ monomers contains double or triple bonds, small molecules may not be formed in the polymerization. Through polyaddition of the AB$_3$ monomers, hyperbranched polyurethanes [88–91], polycarbosilanes [92–95], polyamides [96,97], and poly(acetophenone)s [98,99] have been successfully obtained. AB$_3$, AB$_4$, AB$_5$, and even AB$_6$ monomers are also used to synthesize hyperbranched polymers while controlling the branching pattern [94,100].

1.2.2. SMM—self-condensing vinyl polymerization

SCVP was invented by Fréchet and coworkers in 1995 [101]. This polymerization method is quite versatile, as hyperbranched polymers can be approached via polymerization of AB vinyl monomers. In the reaction, the B groups of the AB monomers are activated to generate the initiating B’ sites. B’ initiates the propagation of the vinyl group A in the monomer, forming a dimer with a vinyl group, a growth site, and an initiating site. The dimer can function as an AB$_2$ monomer, and undergo further polymerization to yield the hyperbranched polymer. In SCVP, the activities of chain propagation of the growth sites and the initiating sites differ, resulting in a lower DB when compared to the DB of the hyperbranched polymer prepared via polycondensation of AB$_2$ monomers. The theoretical maximum DB of SCVP is 46.5% [127]. On the other hand, SCVP does exhibit some disadvantages. For example, side reactions may lead to gelation, the molecular weight distribution is usually very broad, and it is difficult to determine DB directly via an NMR analysis. In order to avoid crosslinking, living/controlled polymerizations such as atom transfer radical polymerization (ATRP) and group transfer polymerization (GTP) are combined in SCVP [121–126]. Monomers used in SCVP and polymerization results such as number-average molecular weight ($M_n$) and polydispersity index (PDI, $M_w/M_n$) are summarized in Table 3 [101–126].

1.2.3. SMM—self-condensing ring-opening and proton-transfer polymerizations

Hyperbranched polyamines [128,129], polyethers [130–138] and polyesters [139,140] have been prepared through SCROP. Table 4 shows some of the monomers employed in SCROP and the polymerization results. Finally, hyperbranched polyesters with epoxy or hydroxyl end groups [141–143] and hyperbranched polysiloxanes [144] were synthesized through PTP. A number of reviews have been published on hyperbranched polymers prepared by SMM [145–158].

1.2.4. DMM—polymerization of two types of monomers

DMM can be divided into two main subclasses based on the selected monomer pairs and different reaction pathways. The classical one, the polymerization of A$_2$ and B$_3$ (or B$_n$, $n > 2$) monomers, taken up in Section 2, can be called the ‘A$_2$ + B$_3$’ methodology, and was first adopted intentionally to prepare soluble hyperbranched polymers by

<table>
<thead>
<tr>
<th>Methodology</th>
<th>Approach</th>
<th>Lead author</th>
<th>Year</th>
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<tr>
<td>SMM</td>
<td>Polycondensation of AB$_2$</td>
<td>Kim/</td>
<td>1988</td>
<td>[46,47]</td>
</tr>
<tr>
<td>SCVP</td>
<td>Fréchet</td>
<td>1995</td>
<td>[101]</td>
<td></td>
</tr>
<tr>
<td>SCROP</td>
<td>Suzuki/</td>
<td>1992/</td>
<td>[128,131]</td>
<td></td>
</tr>
<tr>
<td>PTP</td>
<td>Fréchet</td>
<td>1999</td>
<td>[141]</td>
<td></td>
</tr>
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<td>DMM A$_2$ + B$_3$</td>
<td>Polycondensation of A$_2$ and B$_3$ monomers</td>
<td>Jikei/</td>
<td>1999</td>
<td>[159]</td>
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<td>CMM A$_2$ + B$_3$</td>
<td>Yan/Gao</td>
<td>2000</td>
<td>[161,162]</td>
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<td>CMM A$_2$ + B$_3$ + B$_2$</td>
<td>Gao/Yan</td>
<td>2001</td>
<td>[163]</td>
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<td>CMM A$_2$ + CB$_n$</td>
<td>Gao/Yan</td>
<td>2001</td>
<td>[164]</td>
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<td>CMM AA$_p$ + CB$_2$</td>
<td>DSM research</td>
<td>2000</td>
<td>[165,166]</td>
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1.2.5. CMM—polymerization of two types of monomers

Table 3
The monomers used in SCVP and the polymerization results

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Condition</th>
<th>( M_n ) (GPC)</th>
<th>PDI</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Monomer 1" /></td>
<td>SnCl(_4) Bu4N(^+) Br(^-) — 20 to (-15) °C</td>
<td>660,000–17,000</td>
<td>9.8–2.9</td>
<td>[101]</td>
</tr>
<tr>
<td><img src="image2" alt="Monomer 2" /></td>
<td>ATRP</td>
<td>6280–1900</td>
<td>2.5–1.3</td>
<td>[102]</td>
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<tr>
<td><img src="image3" alt="Monomer 3" /></td>
<td>Bulk polymerization at 130 °C</td>
<td>4280</td>
<td>1.4</td>
<td>[103]</td>
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<td><img src="image4" alt="Monomer 4" /></td>
<td>80 °C in toluene for 40 h</td>
<td>4410</td>
<td>1.38</td>
<td>[104]</td>
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<tr>
<td><img src="image5" alt="Monomer 5" /></td>
<td>Photopolymerization (UV light at 20 °C)</td>
<td>38,900</td>
<td>2.03</td>
<td>[105]</td>
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<tr>
<td><img src="image6" alt="Monomer 6" /></td>
<td>ATRP (50 °C, conversion = 87%)</td>
<td>27,700</td>
<td>2.9</td>
<td>[115]</td>
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<tr>
<td><img src="image7" alt="Monomer 7" /></td>
<td>ATRP (24 °C for 0.5 h in bulk)</td>
<td>2270</td>
<td>14.2</td>
<td>[116]</td>
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<tr>
<td><img src="image8" alt="Monomer 8" /></td>
<td>100 °C for 18 h</td>
<td>18,100</td>
<td>1.91</td>
<td>[117,118]</td>
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<tr>
<td><img src="image9" alt="Monomer 9" /></td>
<td>ATRP in emulsion (90 °C for 44 h)</td>
<td>22,100</td>
<td>9.5</td>
<td>[119]</td>
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(continued on next page)
Table 3 (continued)

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<tr>
<th>Monomer</th>
<th>Condition</th>
<th>$M_n$ (GPC)</th>
<th>PDI</th>
<th>Reference</th>
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<tr>
<td></td>
<td>ATRP (24 °C for 26 h in benzene)</td>
<td>1990</td>
<td>6.6</td>
<td>[116]</td>
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<td></td>
<td>ATRP (24 °C for 24 h in benzene)</td>
<td>650</td>
<td>4.3</td>
<td>[116]</td>
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<td></td>
<td>GTP at −50 °C</td>
<td>1630</td>
<td>34</td>
<td>[121,122]</td>
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<tr>
<td></td>
<td>Copolymerisation at 50 °C for 24 h</td>
<td>5980</td>
<td>1.87</td>
<td>[124]</td>
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</table>

Table 4

The monomers used in SCROP and the polymerization results

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Condition</th>
<th>$M_n$ (GPC)</th>
<th>PDI</th>
<th>DB</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pd(0), 25 °C for 48 h in THF</td>
<td>1800</td>
<td>1.5</td>
<td>0.61</td>
<td>[128,129]</td>
</tr>
<tr>
<td></td>
<td>BF$_3$OT~2, −10 to 4 °C for 48 h</td>
<td>1780</td>
<td>1.28</td>
<td>0.33</td>
<td>[136]</td>
</tr>
<tr>
<td></td>
<td>CH$_3$OK, 95 °C for 12 h</td>
<td>6310</td>
<td>1.47</td>
<td>0.59</td>
<td>[137]</td>
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<tr>
<td></td>
<td>Sn(Oc)$_2$, 110 °C in bulk</td>
<td>20,300–26,500</td>
<td>3.2</td>
<td>0.5</td>
<td>[139]</td>
</tr>
<tr>
<td></td>
<td>Sn(Oc)$_2$, 110 °C in bulk</td>
<td>3000</td>
<td>2.8</td>
<td>0.5</td>
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</table>
Kakimoto [159] and Fréchet [160]. Combination of the basic SMM synthetic principle and the multi-monomer character of ‘A$_2$ + B$_3$’ methodology results in the other DMM, relevant to Section 3: couple-monomer methodology (CMM) based on in situ formation of AB$_n$ intermediates from specific monomer pairs due to the non-equal reactivity of different functional groups [161,162]. Many commercially available chemicals can be used as reactive monomers for CMM, which should extend the availability and accessibility of hyperbranched polymers with various new end groups, architectures and properties, without the danger of crosslinking [161–167]. One aim of this review is to introduce in detail the double-monomer methodologies, since both ‘A$_2$ + B$_3$’ and CMM have been incompletely covered or even omitted in prior reviews.

2. ‘A$_2$ + B$_3$’ methodology

The first intentional preparation of hyperbranched polymers via the ‘A$_2$ + B$_3$’ approach was reported by Kakimoto [159] and Fréchet [160], although the method had been explored to prepare cross-linked polymeric materials more than a century before [38]. It is well known that direct polycondensation of A$_2$ and B$_3$ monomers generally results in gelation [39–43]. Thus, the crucial problem of this approach is how to avoid gelation, and obtain soluble three-dimensional macromolecules. Soluble hyperbranched polymers can be obtained by stopping the polymerization through precipitation or end-capping prior to the critical point of gelation, by the slow addition of monomer, or by using special catalysts and condensation agents. Table 5 lists the A$_2$ and B$_3$ type monomers reported in the literature recent years.

The reaction between aromatic diamines (A$_2$) and aromatic tricarboxylic acids (B$_3$) was first investigated by Aharoni [168–171]. However, only insoluble networks composed of aromatic rigid segments were obtained. Although the direct connection of aromatic rings by amide rings led to good heat and flame resistance, as well as high tensile strength and modulus, the cross-linked materials possessed poor processibility.

Kakimoto [159] further studied the reaction, and obtained soluble hyperbranched aromatic polyamide with monomers 22, 23 and 24 as raw materials in the presence of triphenyl phosphite and pyridine as condensation agents through consideration of the polymerization conditions (Scheme 1).

When p-phenylene diamine (monomer 22) reacted with trimesic acid (monomer 24) with a feed ratio of A$_2$ to B$_3$ of 1/1 at 80°C for 3 h with a total monomer concentration of 0.21 mol/l (3.3 wt%), no gelation was observed for the polymerization. When the total monomer concentration in N-methyl-2-pyrrolidone (NMP) was increased to 0.31 mol/l or 4.9 wt%, cross-linking occurred in 2 h at the same reaction conditions. Addition of LiCl can accelerate the polymerization. In the absence of LiCl, three equivalents of triphenyl phosphate to monomer 24 were required to gain a high inherent viscosity sample. In the presence of LiCl, only two equivalents of triphenyl phosphate were needed to obtain a polymer with a high viscosity. If monomer 23, instead of 22, was used to react with 24, soluble hyperbranched aromatic polyamide was successfully achieved with three equivalents of triphenyl phosphate. If the amount of triphenyl phosphate was decreased to two equivalents, gelation occurred when the reaction was performed with LiCl even if the total monomer concentration was decreased from 0.21 to 0.168 mol/l. So, gelation occurred more easily for the polymerization of 23 and 24 than that of 22 and 24, which may be attributed to the higher DB or the higher percentage of trisubstituted 24 units in the resulting polymer formed from 23 and 24. Gel formation was observed within 10–20 min, and soluble hyperbranched polyamide was not obtained when the feed ratio of A$_2$ to B$_3$ was set to 3/2.

A powdery polymer was obtained by pouring the reaction mixture into methanol containing 12N aqueous HCl. The hyperbranched polyamides HP1 and HP2 aggregated in N,N-dimethylforamide (DMF) even when LiBr was added to the solution system. The resultant hyperbranched polymer with carboxylic acid terminal groups was end-capped with p-anisidine in order to avoid the aggregation effect in the measurement of molecular weight.
The weight-average molecular weights $M_w$ of the end-capped samples HP3 and HP4 as determined by SEC measurements with a laser light-scattering detector for solutions in DMF containing LiBr (0.01 mol/l) were 285,000 and 86,700, respectively. The polydispersity indices for HP3 and HP4 were 5.26 and 4.93, respectively.

Fréchet and coworkers [160] independently applied the ‘$A_2 + B_3$’ approach to synthesize hyperbranched polyether employing 1,2,7,8-diepoxyoctane (25).

<table>
<thead>
<tr>
<th>$A_2$</th>
<th>B$_3$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="A2_monomer" /></td>
<td><img src="image2" alt="B3_monomer" /></td>
<td>[159]</td>
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<tr>
<td><img src="image3" alt="A2_monomer" /></td>
<td><img src="image4" alt="B3_monomer" /></td>
<td>[160]</td>
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<tr>
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<td>[173,174]</td>
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<td><img src="image10" alt="B3_monomer" /></td>
<td>[175]</td>
</tr>
<tr>
<td><img src="image11" alt="A2_monomer" /></td>
<td><img src="image12" alt="B3_monomer" /></td>
<td>[176]</td>
</tr>
<tr>
<td><img src="image13" alt="A2_monomer" /></td>
<td><img src="image14" alt="B3_monomer" /></td>
<td>[177]</td>
</tr>
</tbody>
</table>

(continued on next page)
as the A2 monomer and 1,1,1-tris(hydroxymethyl)ethane (26) as the B3 monomer. The initiation and propagation steps are schematically shown in Scheme 2. Tetra-n-butylammonium chloride (Bu₄NCl, 5 mol% based on 25) was adopted as the nucleophilic catalyst. Nucleophilic attack of the chloride ion on an epoxide of 25 at the less-hindered terminal carbon led to the formation of secondary alkoxide 25⁺. Equilibrium between primary and secondary alkoxides was established through rapid proton exchange, nucleophilic attack of primary alkoxides on the epoxide rings resulted in the propagation of the formed oligomers, and finally the formation of aliphatic hyperbranched polyether epoxy HP5. As the feed ratio of 25 to 26 varied from 1.5 to 3, the epoxy content of the isolated polymer product increased, and the percentage of trisubstituted B3 units in the resulting polymer also increased. However, the PDI of the polyether increased with the increase of molecular weight (~1.5–1.8 at Mₚ ~ 1000 and ~5.0 at Mₚ ~ 7000).

Aliphatic hyperbranched polyethers are viscous liquids with glass-transition temperatures (Tgs) below room temperature (about ~20 °C for the product with Mₚ ~ 8000) [172]. The decomposition temperature (Td) of a polymer with a Mₚ of about 10,000 is about 305 °C. Although HP5 is isolable by fractionation into water, it is still a hydrophilic material, as demonstrated by a contact-angle goniometry value of 42–44° for a drop of water on spin-coated films of HP5 on silicon wafers. After the hyperbranched polymer was modified with hydrophobic chains (Scheme 2), the obtained products HP6, HP7 and HP8 increased hydrophobicity over
the hydroxy-rich precursors, as demonstrated by water contact angles that were 20–30° greater than that for HP5.

The direct polymerization of 1,4-butanediol (27) and triepoxide (28) under a variety of reaction conditions using Bu₄NCl as the catalyst was also explored by Fréchet et al. [172]. Again, the reaction was very slow in THF solution. In bulk polymerization, the reaction was much faster, and gelation occurred after 30 h at 75°C. Analysis by SEC showed that the PDI of the soluble polymers isolated before the critical point was extremely broad ($M_w/M_n > 20$). Unfortunately, the product could not be separated from either the catalyst or the residual monomers by fractionation, so it was difficult to fully characterize the material.

Through the formation of a Schiff-base between dialdehyde (29) and triamine (30), Dai et al. prepared hyperbranched polyconjugated conducting polymers which showed relatively strong fluorescence emission and high conductivities (ca. $10^{-3}$ S/cm) after doping [173,174]. Hyperbranched conjugated poly(1,3,5-trisvinylic)benzene was synthesized via a Wittig reaction between 31 and 32 [175], discussed in detail in Section 5.

Tanaka and coworkers [176] prepared a new conjugated alternate copolymer (HP9) consisting of triphenylamine and phenylene units (Scheme 3) by palladium catalyzed Suzuki coupling of an A₂ monomer, benzene-1,4-diboronic acid (33), and a B₃ monomer, tris(p-bromophenyl)amine (34). The light-yellow powder polymer was isolated after evaporating the solvent and then pouring the crude product into acetone. The resulting conjugated hyperbranched polymer had an average molecular weight of 5400 and was soluble in organic solvents such as chloroform and THF. The conjugated polymer had an absorption band at 365 nm and an emission peak at 430 nm. The cyclic voltammogram of the polymer film deposited on a platinum plate displayed reversible $p$-type doping and undoping, with a color change between brown-yellow (undoped) and green (doped). By using the reference electrode of Ag wire and the supporting electrolyte of a 0.1 mol/l Bu₄NBF₄ solution in propylene carbonate, an anodic and cathodic peaks were found at 1.2 and 1.0 V, respectively. In the neutral state the polymer film was brown-yellow, while in the doped state it turned green; 0.47 electron per monomeric units was found during the redox cycle. This conjugated hyperbranched polymer could potentially be used as a charge storage material, such as an electrode for secondary batteries.

Fang et al. successfully fabricated wholly aromatic hyperbranched polyimides by direct polycondensation of commercially available dianhydrides 35 [2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride], 36 (3,3',4,4'-diphenylsulfonetetracarboxylic dianhydride) and 37 (pyromellitic anhydride) and triamine 38, employing a two-step
polymerization method [177]. First, the hyper-
branched polyamic acid precursors were prepared
by reaction of the dianhydrides and 38 in N,N-
dimethylacetamide (DMAc). Then, chemical or
thermal imidization of the precursors gave rise to
the final hyperbranched polyimides (Scheme 4).

Reaction conditions, such as the monomer feed
ratio, monomer addition manner, and concentration
strongly influenced the polymerization results. A
hyperbranched polyimide with amino terminal
groups was obtained when a dianhydride solution
was added to the solution of 38 with a 1/1 molar
feed ratio of A₂ to B₃ (manner 1). In comparison, the addition of 38 to a dianhydride solution with a 2/1 molar feed ratio of A₂ to B₃ (manner 2) yielded the anhydride-terminated hyperbranched polyimide. The concentration of the added dianhydride or triamine approached zero during addition to avoid a high local concentration of added monomer, which could cause immediate gelation. Higher concentration of the feed monomers also led to crosslinking. The total feed monomer content should be kept below 0.2 mol/l for method 1 and 0.075 mol/l for method 2. ¹H NMR spectra showed that the DB for the amine-terminated HP10, HP11, and HP12 were 0.64, 0.72 and 0.68, respectively. The anhydride-terminated HP13, HP14, HP15 were fully branched (DB = 1) due to the relatively high content and high reactivity of the anhydride groups. SEC determination revealed that the hyperbranched polyimides HP10 and HP13 had moderate number-averaged molecular weights (6400 for HP10 and 8400 for HP13) and broad molecular weight distributions (5.8 for HP10 and 18 for HP13). No T_g was observed for HP12 and HP15 using differential scanning calorimetry (DSC); the T_g ranged from 339 to 295 °C for other four hyperbranched polyimides. The amine-terminated polyimides showed a higher T_g than the corresponding anhydride-terminated ones, owing to their lower DBs and stronger macromolecular interaction resulting from the hydrogen bonds between amino groups. Thermo-gravimetric analysis (TGA) showed that the hyperbranched polyimides had a 5% weight loss at 450 °C in N₂.

HP10 and HP13 based on the monomer 35 showed good solubility in strong polar solvents such as DMAC, NMP, and dimethyl sulfoxide (DMSO), and poor solubility in tetrahydrofuran (THF), acetone and 1,4-dioxane. However, the hyperbranched polyimides
Scheme 4.
based on monomers 36 and 37 were insoluble in all of the aforementioned solvents.

To improve the solubility of aromatic hyperbranched polyimides, a new triamine [1,3,5-tris(4-aminophenoxy)benzene, 41] was introduced to react with conventional dianhydrides such as 35, 39 (4,4'-oxydiphthalic anhydride) and 40 (3,3',4,4'-benzophenonetetracarboxylic dianhydride) [178–180]. The resulting hyperbranched polyimides exhibited excellent solubility in strong polar solvents such as DMAc, DMF, DMSO, NMP and m-cresol. It was found that the polyimides made from 35 and 41 were soluble, even in common low-boiling-point solvents such as THF, acetone and chloroform. Photosensitive hyperbranched polyimide was prepared by reaction of cinnamoyl chloride with phenol-terminated hyperbranched polyimide generated from the end capping of the anhydride-terminated hyperbranched poly(amic acid) precursor of 35 and 41 with 4-aminophenol during the course of polymerization. Highly resolved patterns with a line width of 10 μm were obtained via photolithography of the photosensitive polyimide [179].

Two novel B₃ monomers [tri(phthalic anhydride), 42] and [tri(phthalic acid methyl ester), 43] were synthesized and used to polycondense with 1,4-phenylenediamine (22) in a feed mole ratio of 1/1, resulting in hyperbranched polyimides (Scheme 5) [181]. The polymerization of 42 and 22 was termed method A, and that of 43 and 22 termed method B. In method A, direct reaction of 42 and 22 in the solution of DMAc afforded the hyperbranched poly(amic acid) precursor. Further chemical imidization of the poly(amic acid) in the presence of pyridine and acetic anhydride (Ac₂O) gave the anhydride-terminated hyperbranched polyimide HP16. If the poly(amic acid) precursor was end-capped with p-toluidine, and then chemical imidization of the end-capped precursor occurred, toluidine end-capped hyperbranched polyimide HP17 was obtained. As shown in Scheme 5, HP16 and HP17 can also be prepared via method B through chemical imidization of poly(amic acid methyl ester) and toluidine end-capped poly(amic acid methyl ester) precursors, respectively. Polymerization by method A often generated a gel due to high reactivity between anhydride and amino groups, so the reaction temperature was set at 0°C. In method B gelation was effectively avoided by using diphenyl(2,3-dihydro-2-thioxo-3-benzoaza-zolyl)phosphonate (DBOP) as a condensation agent under room temperature (RT) at a concentration lower than 0.1 g/l.

It is interesting that the polymers made by methods A and B exhibit different properties from each other, even though they have the same structure. The precursor and hyperbranched polyimides made by method A are hardly soluble in organic solvent at room temperature, but are soluble upon heating in strong polar solvents, and the solution remains homogeneous when cooled to room temperature. By comparison, the precursor and the hyperbranched polyimides made by method B are soluble in DMAc, DMF, DMSO and NMP at room temperature. Furthermore, the HP17 made by method A has a high $M_w$ (3.02 × 10⁵), a broad PDI (23) and a low inherent viscosity ($\eta_{inh} = 0.28$ dL/g in DMAc at 30°C). The HP17 with a $M_w$ of 1.25 × 10⁵ and a PDI of 2.63 made by method B has a much higher inherent viscosity ($\eta_{inh} = 0.97$ dL/g). The authors [181] explained this phenomena, saying that the high molecular weight component of HP17 made by method A was actually a slightly cross-linked microgel formed at the precursor formation stage.

The resulting hyperbranched polyimides have DBs of 0.52–0.56 determined by ¹H NMR, and $T_{g,sp}$ of 212–236 °C as measured by DSC. Self-supporting films were successfully fabricated by casting the DMAc solutions of toluidine end-capped hyperbranched poly(amic acid) and poly(amic acid methyl ester) precursors onto glass plates upon heating. Dynamic mechanical analysis (DMA) showed that the storage modulus of HP17 films by method B ranged from 3.1 to 4.0 GPa, similar to that of their linear analogs. A TGA analysis revealed that the 5% weight loss temperature of the films approached 500 °C.

### 3. Couple-monomer methodology

Although the A₂ + B₃ approach to hyperbranched polymers holds some merit over the conventional AB₂ polycondensation approach, such
Scheme 5.


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as facile preparation and commercial availability of monomers, it still exhibits the major problem of uncontrollable gelation, especially under conditions of relatively high monomer concentration and high reaction temperature. To avoid cross-linking, the reaction must be performed under low monomer concentration or slow monomer addition, or the polymerization must be stopped prior to the critical point of gelation. This strongly limits the wide application of the \( A_2 + B_3 \) approach in large-scale manufacture of hyperbranched polymers. A new strategy with the advantages of commercial availability of monomers and lack of incidence of gelation is eagerly anticipated.

### 3.1. General description of CMM

Flory’s gelation theory for the ideal polymerization of \( A_2 \) and \( B_3 \) monomers is based on three assumptions: (1) equal reactivity of all A or B groups at any given stage of the reaction; (2) no side reactions, and the reaction restricted to the condensation of A and B groups; (3) no intramolecular cyclization and chain termination in the process [182]. If the first assumption is invalid gelation should be avoided, leading to soluble hyperbranched polymers with high molar mass. The new strategy based on the non-equal reactivity of functional groups in specific monomer pairs was invented independently by Yan and Gao [161,162], and DSM Research [165,166], and further developed and extended by Gao and Yan. Because the two sorts of raw monomers would preferentially generate one type of \( AB_n \) intermediate in situ in the initial stage of polymerization, to produce hyperbranched macromolecules without gelation, we call the new strategy for preparation of hyperbranched polymers CMM or couple-monomer strategy.

Choosing a suitable monomer pair is the most important step for the molecular design of a hyperbranched polymer using CMM. The basic principle of CMM is shown in Fig. 3. In monomer \( AA’ \), if \( A \) is identical to \( A_0 \), and \( B \) is equal to \( B_0 \), CMM degenerates into the \( ‘A_2 + B_3’ \) polymerization. It is anticipated that cross-linking will not occur if an asymmetric monomer \( AA’ \) or \( B’B_2 \) is used. If \( A’ \) has a higher reactivity than \( A \), CMM affords \( ‘AA’ + B_3’ \) polymerization; and if \( B’ \) is more active than \( B \), CMM presents \( ‘A_2 + B’B_2’ \) and \( ‘A_2 + CB_2’ \) polymerization systems. When both \( A \) and \( B \) groups are different from \( A_0 \) and \( B_0 \) groups, CMM gives an \( ‘AC + DB_2’ \)

![Fig. 3. ‘AA’ + B’B2’ approach to hyperbranched polymers as a typical example for the basic principle description of CMM.](image-url)
polymerization. In all of the designed polymerization systems, AB₂ intermediates will be generated in situ, and further reaction of the AB₂ species will result in hyperbranched macromolecules. For example, if the reactivity of the B' group in the B'B₂ monomer is greater than that of the two B groups, AB₂ intermediates can be formed in situ during the initial reaction. Further self-polycondensation of the formed AB₂ species will give rise to hyperbranched polymers without gelation. This reaction process is shown in route 1 of Fig. 3. On the other hand, the molecule containing four B groups should be generated if the molar feed ratio of AA is adjusted by the feed ratio of the two monomers. Higher molecular weight products can be obtained if the reactivities of B and B' groups are different from each other. The difference in reactivities may be attributed to the differences in the chemical environment or chemical structures of the two functional groups. If the reaction between B and A is much faster than that between B' and A, an Aa-bB₂ intermediate will be predominantly formed at the initial stage of the polymerization. This intermediate can be regarded as a new kind of AB₂ monomer. Subsequently, a core molecule with four B groups will be formed, with further reaction leading to hyperbranched macromolecules. Through this approach, a series of hyperbranched poly(sulfone amine)s and poly(ester amine)s were successfully prepared without any catalysts. Scheme 6 shows the reaction mechanism and the selected monomers.

In the 'A₂ + B+B₂' approach, vinyl group is the A group, and the active hydrogen of the secondary amino group and the hydrogen of the primary amino group are the B and B' functions, respectively. Because of the influence of the electron-donating group attached to the secondary-amino group, B is more active than B' in the nucleophilic addition, which has been demonstrated by monitoring the reaction process with in situ Fourier transform infrared (FTIR) spectroscopy.

Polymerizations of 44 (divinyl sulfone) and 51 [1-(2-aminoethyl)piperazine] were carried out in either

\[ \text{AB}_n \text{+ B}_m \text{ approach} \]

Finally, CMM can be used to design and develop novel hyperbranched polymers with new architectures and structures. Through the new strategy, series of hyperbranched polymers with alternating different units, for example ab' and ab units, can be easily fabricated. On the contrary, it is very difficult to acquire hyperbranched polymers with the same structure through the conventional 'AB₂ + Bₘ' approach or polycondensation of AB₂ monomers.

3.2. 'A₂ + B+B₂' approach to hyperbranched poly(sulfone amine)s and poly(ester amine)s

The polymerization of an A₂ type of difunctional monomer and BB₂ type of trifunctional monomer to synthesize hyperbranched polymers is termed the 'A₂ + BB₂' approach \([161,162,183]\). The BB₂ monomer contains one B functional group and two B' functional groups. Both the B and B' groups can react with the A group, but the reactivities of B and B' groups are different from each other. The difference in reactivities may be attributed to the differences in the chemical environment or chemical structures of the two functional groups. If the reaction between B and A is much faster than that between B' and A, an Aa-bB₂ intermediate will be predominantly formed at the initial stage of the polymerization. This intermediate can be regarded as a new kind of AB₂ monomer. Subsequently, a core molecules with four B' groups will be formed, with further reaction leading to hyperbranched macromolecules. Through this approach, a series of hyperbranched poly(sulfone-amine)s and poly(ester amine)s were successfully prepared without any catalysts. Scheme 6 shows the reaction mechanism and the selected monomers.

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Polymerizations of 44 (divinyl sulfone) and 51 [1-(2-aminoethyl)piperazine] were carried out in either
water or organic solvents such as chloroform and DMF under mild temperature (20–60 °C) [161]. When the feed ratio of 44 to 51 was 1/1, no gelation was observed for a total monomer concentration below 7.0 mol/l, and in situ FTIR measurements showed that the reaction was completed after approximately 5 h. A higher concentration results in extremely fast reaction times, and a very high local temperature, resulting in loss of control of the polymerization. Solid state product rapidly appeared. The solids were generally soluble in aqueous HCl solution, although sometimes they were found to be gel particles, insoluble in any solvents tested. When the feed ratio of 44 to 51 was set at 3/2, gelation was not found when the reaction mixture was kept in solution. The resulting hyperbranched poly(sulfone-amine)s contain large amounts of amino and vinyl groups (Scheme 7), which further reacted and finally led to cross-linking after the solvent was removed from the system. If the terminal amino groups were protected with hydrochloride acid or the vinyl groups were end-capped with added amines in the solution, no gelation was observed even though the product was separated from the solution. The resultant solution, including the hyperbranched polymers, can be preserved for a long time (at least one year), and used as material for other functional macromolecular building blocks.

Hyperbranched poly(sulfone amine)s were also successfully prepared from 44 and 52. Monomer 53 (N-ethylethylenediamine) and 44 reacted in either water or organic solvents such as chloroform, DMAc, DMF, and NMP to yield hyperbranched polymers [183–185]. Similar to the reaction between 44 and 51, no gelation was observed when the feed ratio of 44 to 53 was 1/1. The resulting hyperbranched polyamines were characterized with 1H NMR and FTIR. Amino groups were clearly detected, while no signals of the carbon–carbon double bonds could be measured, which suggested that the vinyl groups had completely reacted with the amino groups, so that the resulting polymers had terminal amino groups.

For reaction with a 3/2 feed ratio, the polymerization medium dramatically influenced the results. If the reaction was performed in organic solvents, no gelation occurred, even after 30 days. The hydrochloride of

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**Scheme 6.**

![Scheme 6](image-url)
the product was highly soluble in water, and the sample end-capped with benzoyl chloride was soluble in organic solvents such as chloroform, DMF and NMP. If water was used as the reaction medium, the reaction solution turned into a turbid heterogeneous mixture at around 15–20 min, and cross-linking was observed at 12–15 h. The turbid mixture turned transparent in the aqueous HCl, indicating that no networks formed in the initial stage. This phenomenon, termed ‘pseudo-gelation’, may be caused by the interactions between water and the oligomers formed from 44 and 53.

The reaction between 44 and 54 (N-methyl-1,3-propanediamine) is very similar to that between 44 and 53 [186]. No cross-linking was found in organic solvent for monomer feed ratios of 1/1 or 3/2. The ‘pseudo-gelation’ phenomenon appeared at 12–18 min, for polymerizations carried out in water, and gelation occurred at 15–20 h for a reaction with a feed ratio of 3/2.

For the reaction systems described above (44 + 51, 44 + 53, and 44 + 54), product can be obtained by two means: (1) pouring the reaction solution into the mixture of concentrated aqueous HCl and a precipitation agent such as acetone, methanol or ethyl ether to obtain protonated hyperbranched polycations; and (2) pouring the reaction solution into ethyl ether and drying the precipitate under vacuum at room temperature to afford hyperbranched polymers with copious active amino groups. SEC measurements with water as the solvent and PEO as standards showed that the resulting hyperbranched poly(sulfone amine)s had moderate apparent $M_n$.
(20,000–40,000) and very narrow PDIs (1.2–2.5), which was in agreement with the in situ formation of the core molecules in the reaction system. A peak in the mass spectrum of the sample taken from the reaction system at initial reaction moment corresponded to the core molecules.

The dendritic units (D), linear units (L), and terminal units (T) of the hyperbranched poly(sulfone amine)s in a 1/1 feed ratio are the tertiary amino, secondary amino and primary amino groups, respectively (Scheme 7). The terminal units of the polymers in a 3/2 feed ratio contain primary amino and vinyl groups. The DBs of the resulting hyperbranched polymers can be determined from the corresponding $^1$H NMR spectrum. Theoretically, a hyperbranched polymer prepared by polycondensation of an AB$_2$ monomer has a maximum DB of 0.5 if the reactivity of the two B groups is the same [127, 187, 188]. Because of the higher reactivity of the secondary amino group over the primary amino
group, the DB of the prepared hyperbranched poly(sulfone amine)s ranged from 0.51 to 0.75. The DB of the product generated from a 3/2 feed ratio is higher than that with 1/1 feed ratio. By comparison, the DBs of the hyperbranched polyamidoamines made from AB₂ monomers containing vinyl and primary amino groups are also much higher than 0.5 [96,97]. The commercially available cross-linking agent, ethylene diacrylate (monomer 45), can be used as a raw material to synthesize water-soluble hyperbranched poly(ester amine)s via a Michael addition (Scheme 8) [189]. In situ FTIR measurements showed that the secondary amino groups disappeared at approximately 3 h, and that the reaction was completed after 72 h in a dilute solution. In the mass spectrum of the reaction mixture taken from the polymerization system of 45 and 51 at 3 h, the AB₂ intermediate (m = 299.4) and its dimer (598.7) and trimer (898.1) can be found as peaks at m/z = 300.4, 599.8 and 899.2, respectively. Propagation occurred as soon as the formation of AB₂ occurred although the reactivity between A and B' is not as high as that between A and B, so it was hard to separate the pure AB₂ species from the reaction mixture.

The initial molar ratio of 45 to 51, 52, 53 or 54 was set at 1/1 and 3/2. Relatively high molecular weight products were prepared in organic solvents. Chloroform was a good solvent for the reaction in which the highest molecular weight poly(ester amine) was obtained. When the monomers were added to water for the reaction, a heterogeneous mixture appeared at first due to the poor solubility of 45 in water. After several minutes a homogeneous solution appeared. This phenomenon indicates that the Michael addition of amino groups to vinyl groups can occur smoothly in water. For example, only oligomers were obtained with the preparation of HP20, HP21, HP22 and HP23. The number average degree of polymerization (DPₙ) and the molecular weight of the resulting product depend on monomer purity.

All of the hyperbranched poly(sulfone amine)s and poly(ester amine)s mentioned above are highly soluble in water and certain organic solvents such as chloroform, DMF, DMAc, NMP, DMSO, and are poorly soluble in THF.

The steric and electron-accepting effects of the adjacent groups influence the reactivity of the vinyl groups. For example, only oligomers were obtained through the use of monomer 46, instead of 45, reaction with the BB₂ monomers. Monomer 50 (1,4-divinylbenzene) is also often used as a cross-linking agent. Using lithium amide catalyzed anionic polyaddition of 50 to the compounds with two secondary amino groups, Tsuruta and coworkers [190,191] prepared linear polyamines with Mₙs of 1000–5000. Monomer 50 cannot react with amino groups without a catalyst. In the presence of a strong base such as lithium alkylamide, only branched products with Mₙs below 8000 were obtained in our laboratory.

In summary, the control of the structures and units with suitable monomers, the simplicity of polymerization process, and the efficiency in avoiding gelation would make the ‘A₂ + BB₂’ approach, and the new
hyperbranched polycations with many terminal amino groups prepared via this method, very attractive in the large-scale manufacture and application of polymeric materials.

3.3. ‘A$_2$ + CB$_n$’ approach to hyperbranched poly(urea urethane)

Linear polyurethanes and polyureas are now widely used in rubber, plastics, fiber, and coatings. It is well known that polyurethanes or polyureas can be prepared by polycondensation of diisocyanates with dihydroxyl compounds or diamines. Because of the high reactivity of isocyanato groups (–N=C=O) against the nucleophile, it is hard to obtain an AB$_2$ monomer with an isocyanato group. Therefore, hyperbranched polyurethanes or polyureas cannot be directly synthesized from AB$_2$ monomers. Generally, an AB$_2$ monomer containing a functional group such as a carbonyl azide that can be transferred in situ into the isocyanato group is synthesized in advance, and then polymerization of the formed monomers leads to hyperbranched polyurethanes or polyureas [88–91]. However, it is very difficult to apply the prepared hyperbranched polyurethanes or polyureas owing to the complexity of the synthesis and the purification procedures.

Through the ‘A$_2$ + CB$_n$’ approach, hyperbranched poly(urea urethane)s can be easily prepared by direct polymerization of commercially available diisocyanates and multi-hydroxyl amines (Scheme 9). A$_2$ monomers containing two isocyanato groups are industrial chemicals that have been widely used in the manufacture of linear polyurethanes and polyureas. A CB$_n$ monomer has one amino group and $n$ hydroxyl groups. The fast reaction between the A group and the C group in CB$_n$ affords AB$_n$ and B$_n$–B$_n$ intermediates at mild temperature. Further reactions between isocyanato and hydroxyl groups at higher temperature give rise to hyperbranched polymers with alternating ureido and urethano units [192–194].

This reaction process has been monitored with in situ FTIR spectroscopy. The reaction between monomer 57 and 62 was selected as a typical example. It was found that the carbonyl groups (C=O) of the ureido units (−HCONH−) first rapidly appeared as a peak at 1632 cm$^{-1}$, with a significant decrease in the absorption band of the isocyanato group at 2261.6 cm$^{-1}$ during the initial minute. The peak at 1632 cm$^{-1}$ then stayed constant, and the carbonyl groups of the urethano units (−HCONO−) appeared as a new peak at 1705 cm$^{-1}$, and gradually increased with decrease of the absorption peak of the isocyanato groups. After approximately 200 h, the absorption band of the isocyanato groups disappeared from the spectrum, the hydroxyl group absorption still clearly observed. This data shows that the one isocyanato group of 57 quickly reacted with the amino group of 62, resulting in the formation of intermediate 67. Then self-condensation of intermediate 67 along with other formed species generated the hyperbranched macromolecules HP24 with ureido and urethano units (Scheme 10). Similar results were obtained for other reaction systems of ‘A$_2$ + CB$_n$’.

The peaks of the AB$_n$ and B$_n$–B$_n$ species formed during the initial reaction period were also detected with mass spectroscopy. For example, the molecular ion peaks 67 ($m=327.4$) and 72 ($m=432.6$) were found as two peaks at $m/z = 328.3$ and 433.4, respectively. Their corresponding $m + Na^+$ ion peaks were also observed at $m/z = 350.3$ and 455.4, respectively. The mass spectrum measurements for
other reaction systems indicated that the ABₙ and Bₙ⁻
Bₙ intermediates did form in the initial stage.

Reaction conditions such as temperature, concentra-
tion, and monomer feed ratio strongly influenced
the reaction. The temperature during the initial several
hours should be kept below 25 °C, otherwise,
insoluble product was generated. Gelation was barely
observed for the polymerization in a feed ratio of 1/1
(A₂/CBₙ) at given conditions. For the reaction with a
3/2 feed ratio (A₂/CBₙ), cross-linking mainly
depended on the temperature and concentration. Gelation occurred within several minutes in the conditions of high concentration (1.0 mol/l) and high temperature (60–80 °C), whereas at low concentration (0.15 mol/l) and low temperature (20 °C) gelation was not observed. SEC with 0.05 M LiCl in DMAC eluent at 70 °C showed that the resulting hyperbranched poly(urea urethane)s had a moderate $M_w$ ranged from 18,000 to 130,000, and relatively narrow PDIs with typical values of 1.7–3.5.

The DBs of the prepared hyperbranched polymers were determined with $^{13}$C NMR spectroscopy. For the polymers made from A$_2$ and CB$_2$, there are two hydroxyl groups in the terminal units, one hydroxyl group in the linear units, and no hydroxyl group in the dendritic units. Scheme 11 shows the three repeating units of the polymer derived from the reaction between A$_2$ and 64. The terminal ((CH$_2$OH)$_2$) and linear (CH$_2$OH) units can be assigned independently in the $^{13}$C NMR spectrum, so the DB can be calculated with Eq. (1)

$$DB = \frac{(D + T)/(T + L)}{(T - 1 + T)/(T - 1 + T + L)} = \frac{2T/(2T + L)}{1/(1 + L/2T)}$$

DBs calculated from Eq. (1) ranged from 0.42 to 0.56.

Scheme 12 shows the structure of the hyperbranched polymers made from A$_2$ and CB$_3$ (65). It was found that there are two sorts of branched units (Scheme 13), so the DBs were much higher than 0.5, approaching 0.7–0.74.

Although the reactivity of the primary hydroxyl group is greater than that of the secondary hydroxyl group, the poly(urea urethane)s made from A$_2$ and CB$_3$ (66) are also highly branched (Scheme 14). In their corresponding DEPT-135 $^{13}$C NMR spectra, the ratio of the residual primary hydroxyl group (CH$_2$OH) in the resulting polymer to the primary hydroxyl group (CH$_2$O–) is higher than 50%. Therefore, it can be deduced that the secondary hydroxyl groups of 66 also reacted with isocyanato groups, and highly branched polymers containing a high density of hydroxyl groups were formed. $T_g$s of the obtained hyperbranched poly(urea urethane)s measured by DSC were 25–50 °C. The hyperbranched poly(urea urethane)s are soluble in polar organic solvents, such as DMF, DMAc, DMSO and NMP.

3.4. ‘AB + CD$_n$/C$_n$’ approach to hyperbranched poly(amine ester)s and poly(amide amine) 3.4.1. ‘AB + CD$_n$ approach’ to hyperbranched poly(amine ester)

The monomer AB contains one A and one B functional group, which cannot react with each other. Monomer CD$_n$ has one C and n D functional groups, and C cannot react with D. The reaction between B and C is more easily conducted than that between A and D. At mild temperatures, the B group reacts with the C group to form an AD$_n$ intermediate. Hyperbranched macromolecules can be produced by self-condensation of AD$_n$ under stronger conditions (Scheme 15). If the methyloxy carbonyl (CH$_3$OC=O), the acrylate group (CH$_2$=CHCO), the secondary amino group (HN–), or the hydroxyl (–OH) moiety are selected as A, B, C and D groups, respectively, water-soluble hyperbranched polyesters with tertiary amino units in their backbones can be prepared [195,196].

Some side reactions may occur between AB and CD$_n$ reactions during the initial stage. For example, at least three intermediates 78, 79 and 80 may be generated in the reactions of 77 and 62 as shown in Scheme 16. The reactions between A and C or D can be suppressed by using methanol as solvent, since methanol would be generated accompanying with
formation of 79 or 80. Measurements of in situ $^1$H NMR with diethylamine and 1,4-butanediol as model compounds confirmed that the reaction between the methyloxy carbonyl and the amino or hydroxyl group was negligible under mild conditions.

The reaction temperature during the initial stage is very important in the preparation of a high molecular weight product. In the mass spectrum of the sample taken from the reaction system at room temperature, the molecular ion peak of 78 ($m = 191.2$) appeared at $m/z = 192.3$, and the peak of 78 coupled with a Na$^+$ appeared at $m/z = 214.2$. The molecular ion peaks of the dimer (M$_2$H$^+$), trimer (M$_3$H$^+$), and tetramer (M$_4$H$^+$) of 78 were found at $m/z = 351.5, 510.5$, and 691.7, respectively. No peaks attributed to 79 and 80 were detected. As a comparison, the peaks of 79 and 80...

Scheme 12.

\[ \text{Scheme 12.} \]
80 did appear in the mass spectrum on increase of the reaction temperature to 60 °C during the initial stage. The existence of 79 and 80 may lead to cross-linking in the next reaction stages, so it is better to keep the temperature in the initial period below 40 °C for the polymerization of AB and CDₙ monomers.

To improve the conversion ratio of 62 or 77 and shorten the reaction time of the initial stage, the feed ratio of AB to CDₙ is a little higher than 1/1 (typically 1.05–1.1/1). The residual 77 was removed from the reaction system by reduce-pressure distillation on a revolving-distillation apparatus. After the residual MA and the solvent (methanol) were removed, an amount of catalyst (0.5 g per mole of CDₙ) was added to the reaction system. Under vigorous revolving and vacuum distillation, the mixture was kept at 60 °C for 1 h, 100 °C for 2 h, 120 °C for 2 h, and 135–150 °C for 2 h. After reprecipitation of the raw product from DMSO into acetone, hyperbranched poly(amine ester) with a yield of 75–80% was obtained.

Compared with zinc acetate anhydrous [Zn(CH₃CO₂)₂], tetrabutyl titanate [Ti(C₄H₉O)₄] exhibited higher catalytic efficiency for the polymerization. For the same amount of catalyst, the molecular weight of the product catalyzed with Ti(C₄H₉O)₄ was higher than that catalyzed with Zn(CH₃CO₂)₂. Nevertheless, insoluble product was formed if the amount of Ti(C₄H₉O)₄ was too high (>2 g per mole of CDₙ).

The structures of the hyperbranched poly(amine ester)s made from 77 and 62 or 66 are shown in Schemes 17 and 18, respectively. Depending on the reaction temperature and the catalyst, $M_n$ of HP29 ranged from 10,000 to 260,000, and that of HP30 ranged from 38,000 to 66,000, with a narrow molecular weight distribution. The molecular weight of HP29 was generally greater than that of HP30 under the same reaction conditions. Inter- or intra-molecular cyclization might have caused the lower $D_P$ of HP30 because of the high density of hydroxyl groups in its repeating unit.

The terminal and linear units of HP29 can be independently detected in a quantitative ¹³C NMR spectrum. The DB of HP29 calculated with Eq. (1) was slightly higher than 0.5 (0.52–0.56). Characterization by a quantitative ¹³C NMR spectrum showed that HP30 was also a highly branched polymer, although its DB cannot be accurately calculated due to its complex structure.

There is one ester bond and one tertiary amino group in each repeating unit of HP29 or HP30. Such a structure is very attractive in the field of drug-delivery. The hyperbranched polymers are degradable in water because of their ester bonds. Owing to the introduction of amino groups, the resulting polymers are easily soluble in water. Furthermore, the acid groups formed in the hydrolysis neutralize the amino groups. So, the pH of the aqueous system of HP29 or HP30 can be self-adjusted to about 7, which is an important parameter for a good drug-delivery material [197].

TGA measurements showed that the 5% weight-loss temperature for HP29 and HP30 is above 200 °C, and the 10% weight-loss temperature is above 250 °C. In the DSC curves, $T_g$s of about 10–20 °C were found for HP29 and HP30, but the transition was not as strong as that of general linear polyesters.

A methoxycarbonyl-terminated hyperbranched polymers could be synthesized by the reaction of methyl acrylate (77) with a compound containing a hydroxyl and one primary amino or two secondary amino groups (Scheme 19). The feed ratio and the catalyst have a dramatic influence on the polymerization. Gelation occurred for a ratio of 62 to ethanolamine (82) lower than 2.1/1. Cross-linking was not observed for a ratio higher than 2.3/1. In the presence of Ti(C₄H₉O)₄, the polymerization occurred faster, and a higher molecular weight product was approached under the same conditions. SEC measurements with polystyrene as standards showed that the methoxycarbonyl-terminated hyperbranched poly(amine ester)s had apparent $M_n$s of 35,000–70,000. The onset decomposition temperature ($T_d$) of HP31 was 275–290 °C.
3.4.2. 'AB + C_n' approach to hyperbranched poly(amide amine)s

Polyamines (C_n monomers) react with the aforementioned AB monomer to yield aliphatic hyperbranched poly(amide amine)s (Scheme 20). The AC_n or AC_{n-1} intermediate should be formed in situ at room temperature for a feed ratio of AB to C_n of 1/1. Hyperbranched polyamines could then be

Scheme 14.

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prepared by self-condensation of the intermediates at higher temperatures and in vacuum. Interestingly, the feed ratio of AB to \(C_n\) can be adjusted over a relatively wide range from 1/1 to \(n/1\); resulting in hyperbranched polymers with various terminal groups. Due to their different functional groups, the hyperbranched polymers exhibit different properties. Therefore, the structure and property of the hyperbranched polymers can be controlled through the feed ratio of AB to \(C_n\) [198,199].

The reaction conditions between AB and \(C_n\) are very similar to those between AB and CD\(_n\). Methyl acrylate (77) was added dropwise to the amine/methanol solution. The reaction mixture was kept at room temperature for 24–48 h, and then the solvent was removed from the reaction system under reduced pressure at 60\(\degree\)C on a rotary evaporator. Under vigorous revolving and vacuum distillation, the mixture was kept at 60\(\degree\)C for 1 h, 100\(\degree\)C for 2 h, 120\(\degree\)C for 2–4 h, and finally 135–150\(\degree\)C for 2–4 h. Pale yellow viscous solid hyperbranched polymers were produced. Since no extra reagents such as catalyst and condensation agent were added to the reaction mixture, it was not necessary to separate the raw product by reprecipitation, so the yield was very high (>95%).

The Michael addition of 84 to 77 affords 91. Intermediate 91 can be regarded as an asymmetrical AC\(_2\) monomer that can further self-condense to give rise to hyperbranched polymer HP32 (Scheme 21). There are two kinds of linear repeating units in HP32. The reaction between 77 and 85 would result in a symmetrical AC\(_2\) intermediate (92) and an asymmetrical AC\(_3\) species so the hyperbranched polymer HP33 contains the hybrid structures of 92 and 93 (Scheme 22). The reaction of monomer 86, 87 or 88 with 77 yields more AC\(_n\) or AC\(_{n-1}\) species. Thus, the corresponding hyperbranched polymers have a more complex structure, and more types of repeating units can be found. Both 89 and 90 have three primary amino groups. Three asymmetrical AC\(_3\) intermediates (94, 95, 96) occurred when 89 was employed to react with 77 (Scheme 23), and then hyperbranched polymers with hybrid structures were generated. Because of the symmetrical structure of 90, only one AC\(_3\) species (97) was formed. The resulting hyperbranched polymers HP34 have amido and tertiary amino units in their backbones and many primary amino groups in their terminal chains (Scheme 24).

Variation of the AB to \(C_n\) feed ratio results in a change in the structure and properties of the products. For example, the solubility of the hyperbranched polymer made from 77 and 85 decreases with an increase in the feed ratio of 77 to 85.

All of the hyperbranched poly(amide amine)s with a feed ratio of 1/1 described above are highly soluble in water and polar solvents such as DMF, DMAc, DMSO and NMP. The water-soluble cationic hyperbranched polyelectrolytes may be useful in the pigments, coatings, and gene delivery or transport fields.

3.5. ‘A’ + \(CB_2B_n^+\) approach to hyperbranched poly(ester amide)s and polyesters

3.5.1. ‘A’ + \(CB_2^+\) approach to hyperbranched poly(ester amide)s

DSM research first reported the ‘A’ + \(CB_2^+\) approach [165,166]. In their presentation, A’ and
CB$_2$ were denoted as Aa and bB$_2$, respectively [166]. They used 1,2-cyclohexane dicarboxylic anhydride as the Aa monomer, and di-2-propanolamine as the bB$_2$ source. Recently, Gao and Yan [200,201] developed the ‘A$^+$ + CB$_2$’ approach, using dicarboxylic anhydride compounds as A$^+$. An A$^+$ monomer contains two latent functional groups; one A group will be formed after the reaction of A$^+$ with the CB$_2$ group, giving rise to an AB$_2$ intermediate. Self-polycondensation of the intermediate results in the hyperbranched macromolecule (Scheme 25).

The reaction between 98 and 63 has been investigated using electrospray ionization (ESI) and matrix-assisted laser desorption ionization/time-of-flight (MALDI-TOF) mass spectrometry, and size exclusion chromatography (SEC) in combination with on-line differential viscosimetry detection (SEC-DV) [166, 202,203]. The exothermal reaction of 98 and 63 normally leads to a species (102) having one carboxylic acid group and two (2-hydroxypropyl)amide groups. Ester bonds were formed through an intermediate oxazolinium-carboxylate ion pair, and hyperbranched macromolecules were generated under reduced pressure (5 mbar) at around 180 °C, without a catalyst (Scheme 26).

The hyperbranched poly(ester amide) HP35 was then modified in situ with 1-dodecanoic acid to obtain hyperbranched resins with terminal long aliphatic chains. Other hyperbranched poly(ester amide)s series can be prepared by direct polymerization of 99, 100, or 101 with 62 or 63 with similar reaction routes and conditions. The $M_n$s of the hyperbranched poly(ester amide)s detected with SEC-DV by using polystyrene as standards and dichloromethane as solvent and eluent were very low (680–6000) [166,202,203].

3.5.2. ‘A$^+$ + B$_n$’ approach to hyperbranched polyesters

Polyhydric alcohols (B$_n$) can directly polymerize with the aforementioned dicarboxylic anhydrides,
forming hyperbranched polyesters (Scheme 27). The reaction between 99 and 104 had been investigated by Kienle et al. as early as 1929 [35]. However, only low-molecular-weight product or insoluble materials were obtained at that time. To obtain soluble high-molecular-weight hyperbranched polymers, it was necessary to re-investigate the reactions between dicarboxylic anhydrides and polyhydric alcohols.

Because each hydroxyl group of Bₙ has almost the same reactivity, gelation easily occurred in the reaction. It is crucial to remove water from the reaction system during the initial stage to avoid network formation. The existence of water in the monomers or solvents leads to the ring opening of the anhydrides, giving difunctional A₂ molecules and leading to insoluble product within several hours.

Two routes were employed in the polymerization. Scheme 28 describes a typical example. Route A represents direct polymerization of the in situ formed AB₂ intermediate possessing a carboxylic
acid group and two hydroxyl groups (107). In route B, the AB₂ species was modified with methanol in advance to afford the new monomer 108, and then hyperbranched polyesters were prepared by polymerization of the modified AB₂. Only moderate molecular weight product was obtained ($M_n = 5000–20,000$) via route A, even through the reaction was performed under reduced pressure at 140–150 °C for 10–20 h. The color of the raw product was very deep, indicating that carbonization

Scheme 19.

Scheme 20.
Scheme 21.

Scheme 22.
or oxidization occurred in part of the polymers. As a comparison, the products made through route B had a high $M_n$ (30,000–120,000) and an almost white color [200,201].

The hyperbranched polyesters made from 103 and polyhydric alcohols have carbon–carbon double bonds in every repeating unit, so the cross-linked membrane can be prepared by UV light irradiation. The polymerization of 106 with anhydrides is relatively difficult because of its poor solubility in organic solvents; only low molecular weight product was acquired.

Scheme 25.

Scheme 26.
3.6. ‘AA’/A₂⁺ + B₂’ approach to hyperbranched polyesters

The AA⁺ monomer contains one A and one A⁺ group, and A₂⁺ contains two A⁺ groups. As claimed above, one A⁺ is a latent A₂. In the ‘AA’ + B₂’ approach, the reaction between A⁺ and B groups generates an A₂B intermediate which can be self-polycondensed to attain hyperbranched polymer [204,205]. Scheme 29 shows the reported AA⁺ and B₂ monomers. Benzene-1,2,4-tricarboxylic acid-1,2-anhydride (109) has a carboxylic...
acid group (A) and an anhydride group (A'). Because of the much higher reactivity of anhydride group over the carboxylic acid group in the condensation, a species with two carboxylic acid groups and one hydroxyl group can be presented. Then hyperbranched polyesters can be prepared smoothly according to the conventional polymerization conditions and process. Similar to the reaction of AA' and B_2, the reaction of one of the A' of A_2 with one of the B groups in B_2 affords the species AA'B containing a carboxylic acid group, one anhydride group and one hydroxyl group. Self-condensation of two AA'B gives the A_3B species. Hyperbranched macromolecules can also be prepared by further polycondensation of the A_3B molecules. The A_2 monomers used are also given in Scheme 29.

A typical example for the ‘AA’ + B_2’ approach is described in Scheme 30. The first step was conducted at room temperature in chloroform. Two intermediates (115 and 116) were formed. Hyperbranched polymers were prepared through two routes. In route A, direct polymerization of the species 115 and 116 led to the carboxylic acid-terminated hyperbranched polyester HP37. Polymer HP37 contains two types of linear units (L1 and L2) and two types of terminal units (T1 and T2). In route B, A_3B intermediates 115 and 116 reacted with methanol, generating species 117 and 118, respectively. Further polycondensation of 117 and 118 gave rise to ester-terminated hyperbranched macromolecules HP38. Again, the products synthesized using route B exhibited a higher molecular weight than those synthesized using route A. The former products have M_n s of 20,000–120,000, while the latter products have M_n s of 3000–15,000. The hyperbranched polyesters HP37 and HP38 were further end-capped with 1-butanol, resulting in HP39. It is well known that n-butyl phthalate is a good plasticizer for polyvinyl chloride (PVC). However, the low molar mass n-butyl phthalate often releases from the PVC, which strongly influences the quality of the plasticized product. HP39 has a similar structure of n-butyl phthalate and a much higher molecular weight. Furthermore, the melting viscosity of hyperbranched polymers is very low. It is expected that in the future HP39 will become a better plasticizer for PVC or other commercial plastics.

The reaction conditions and processes for the reaction between dianhydrides and dihydroxy alcohols are the same as those employed in the reaction of AA’ and B_2. Two routes were applied to prepare hyperbranched polyesters (Scheme 31). Route B was more efficient than route A for preparing higher
molecular weight hyperbranched products. Through route B, hyperbranched polyesters with $M_n$ ranging from 15,000 to 100,000 can easily be synthesized, according to the feed ratios. On the contrary, only relatively lower molecular weight products (3000–12,000) were made from route A. On the other hand, almost linear oligomers appeared during the beginning reaction period owing to the higher reactivity of anhydride groups over carboxylic acid groups. Then branched molecules were formed because the content of carboxylic acid group is very high. However, the DBs of the obtained products were lower than those made from route B.

If one hydroxyl group of B$_2$ is replaced by a secondary amino group, water-soluble hyperbranched poly(ester amide)s can be prepared (Scheme 32) [206,207]. Direct polymerization of benzene-1,2,4-tricarboxylic acid-1,2-anhydride (109) with N-(2-hydroxyethyl)piperazine (127) failed to produce macromolecular products although the reaction occurred at a high temperature (160 °C) in the presence of catalyst. When 127 was added to a solution of 109 in DMSO, a precipitate was rapidly observed, caused by the interaction between acid and amino groups. To dissociate the aggregation species, an organic base such as triethylamine was
introduced to the reaction system. However, a powdery precipitate appeared again during polymerization after heating under reduced pressure. Therefore, the carboxylic acid was modified with methanol to obtain the intermediate 130 or 131. Under mild conditions and in the presence of catalyst such as phosphoric acid and tetrabutyltitanate (Ti(C₄H₉O)₄), hyperbranched polymers were prepared, with moderate $M_n$ (25,000–50,000) and narrow PDI (1.4–2.5). Although the acid groups were end-capped with methyloxy moieties, the prepared hyperbranched poly(ester amide)s were highly soluble in water because of their tertiary amino and amido units.
3.7. ‘A₂ + B₂ + BB₀₂’ approach to highly branched copolymers

CMM can be extended to prepare highly branched copolymers with different DBs by copolymerization of suitable difunctional monomers with the monomer pairs described above. The DBs and some thermal and mechanical properties can be controlled by the feed ratio of the monomers. Here, we selected the ‘A₂ + B₂ + BB₀₂’ approach as an example to recount how to control the architecture and properties of the resulting polymers in copolymerization [163,189, 208–210].

In the ‘A₂ + B₂ + BB₀₂’ approach, the A₂ and BB₀₂ monomers are the same as those of ‘A₂ + BB₀₂’ approach, and B₂ is the molecule with two secondary amino groups. During polymerization, the rapid reaction between the A and B groups results in the formation of an AB₂-type intermediate. The linear units formed from the reaction of A and B₂ also are embedded in the AB₂ species, which indicated that the segment between two branching points and the number of linear units can be adjusted by the feed ratio of B₂ to BB₀₂. On the other hand, the BB₂ species will also be generated. Highly branched copolymers with various linear units will be obtained from the further self-condensation of the intermediates (Scheme 33).

The feed ratio of A₂ to the total B₂ and BB₀₂ was set as 1/1, and the ratio of B₂ to BB₀₂ (n) was varied. For the reaction of 44 with B₂ and BB₀₂, the reaction conditions such as temperature, time, concentration and solvent influence on the polymerization [163]. A homogeneous solution was observed throughout
the reactions carried out in strong polar organic solvents such as DMF, DMAc, DMSO and NMP. Nevertheless, a precipitate was found for B$_2$ to BB$_2$ ratios greater than 3/1 if water or chloroform was utilized as the solvent. The phenomenon was attributed to the crystallization of the formed macromolecules rather than the appearance of a gel. In fact, the precipitate was soluble in polar solvents such as DMF and DMSO, and the hydrochloride of the polymers was highly soluble in water. No gelation was observed even through at a very high concentration of the total monomers (1 g per 1 ml of solvent) and at a high temperature (80°C). The incidence of cross-linking can be easily avoided under general reaction conditions.

The polymerization procedure was investigated with in situ FTIR spectroscopy. The reaction between secondary amino groups and vinyl ones was surprisingly fast, and completed within 1 min. The whole polymerization only took 6–10 h even at room temperature in a diluted solution. So highly branched macromolecules can be approached within several hours. The propagation of the molecules during the initial short period can be detected clearly from the corresponding mass spectrum. The dominant reactions were well in agreement with the prediction. Scheme 34 displays the dominant reaction pathways at initial stage for the polymerization of 44 with 51 and 132 in a 1/1 ratio.

The structures of the highly branched copoly(sulfone amine)s made from A$_2$, B$_2$ and BB$_2$ monomers are shown in Schemes 35 and 36. Every polymer contains two sorts of linear units (L1 and L2), one sort of dendritic unit and one sort of terminal unit. The DB can be calculated by Eq. (2)

$$ DB = \frac{(D + T)}{(D + T + L1 + L2)} $$

For a copolymer made from A$_2$, B$_2$ and BB$_2$, D, T and L2 depend on the reaction between A and B'. Therefore, DB can be controlled through the value of L1. When L1 is zero (no B$_2$ monomer is added), DB is that for a polymer made from A$_2$ and BB$_2$. When L1 becomes a large value (large feed ratio of B$_2$ to BB$_2$), DB approaches zero. Thus, DB of the copolymer can be adjusted at least from 0.5 to 0 by the feed ratio of B$_2$ to BB$_2$. On the other hand, each repeating unit has a sulfone bond resulting from A$_2$ monomer. So the total units are equal to the number of sulfone units (S), and DB can be obtained by the following equation:

$$ DB = \frac{(D + T)}{S} \approx 2T/S $$

The dendritic units (D) and terminal units (T) are tertiary amino formed from the reaction between A and B and primary amino groups. The methylene attached to primary amino groups (CH$_2$NH$_2$) and the methylene linked to sulfone bonds (CH$_2$SO$_2$CH$_2$) can be easily detected independently from the corresponding 1H NMR spectrum. So DB of each branched copolymer is conveniently available. When the feed ratio of B$_2$ to BB$_2$ is changed from 1/5 to 5/1, the DB is varied from around 0.5 to 0.1.

The dependence of inherent viscosity on DB is also interesting for the branched copolymers with different DBs. Fig. 4 gives a typical relationship between DB and $\eta_{inh}$ for the branched copoly(sulfone amine)s
In order to clearly reflect the increased segment density on increased DB, $M_n$ can be used as a normalizing factor. With the same molecular weight, $\eta_{inh}$ decreases slightly with increasing DB at first, and then decreases dramatically after DB equals around 0.3. The results suggest that the segment density of a branched polymer increases slightly, and then increases significantly with the increase of DB after a critical point. The studies for other copoly(sulfone amine)s show similar behavior, and the critical DB is 0.3–0.35.

The DB also influences the crystallization of a branched polymer. For the branched copoly(sulfone amine)s containing piperazine units, one sort of linear unit is the same. When the feed ratio of B$_2$ to BB$_2$ is equal to 3/1 ($n = 3$), crystallization and melting peaks can be observed in the DSC curves of copolymers made from 44, 51 (or 53) and 132 [163,208]. By
comparison, crystallization and melting peaks were found for the copolymer made from 44, 54 and 132
with \( n = 2 \) \[209\]. The copolymer side groups can alter
their thermal properties. The side group for the copolymer made from 44, 54 and 132 is methyl
(\(-\text{CH}_3\)) while that for the copolymer made from 44, 53 and 132 is ethyl (\(-\text{CH}_2\text{CH}_3\)). The steric effect of ethyl is stronger than that of methyl in crystallization,
so the macromolecules with the units of 53 are more difficult to crystallize than those with the units of 54.
Although there are no side groups in the unit of 51, no crystallization was detected for the sample with \( n = 2 \)
because the ring of piperazine is more rigid than the carbon–carbon single bond.

The crystallization is influenced not only by the side groups of a branched copolymer, but also by
the stiffness of its main chain. Double-melting

endotherms were observed for the copolymers with units of 133 \[209,210\]. Compared with the copolymer made from 44, 132 and 53, the copolymers made from 44, 133 and 53 are difficult
to crystallize, and no crystallization appeared for the sample with \( n = 3 \). Copolymers including units of 133 are rather slow to crystallize, and no crystallization peak can be observed at a normal cooling rate (10–20 °C/min). Furthermore, \( T_g \) s were not clearly for the copolymers found in DSC measurements. The \( T_d \) s for the copolymers in nitrogen are about 285–320 °C, with the \( T_d \) for a crystalline sample higher 10–20 °C than that of an amorphous one.

Branched copoly(ester amine)s with various DBs could be synthesized using monomer 45 to react with
B2 and BB2 monomers \[189\]. Similar phenomenon for the relationship of DB and \( \eta_{ab} \) was observed for the copoly(ester amine)s. Because the copolymers were
obtained as the hydrochloride, all of the samples were amorphous.

As illustrated above, CMM exhibits generality, simplicity, controllability, versatility and availability in the preparation of hyperbranched polymers. Although many new hyperbranched polymers have been produced via the novel approaches aforementioned, CMM is still developing, and more hyperbranched polymers with fundamental application potentials will be found through this novel methodology.

4. Modification of hyperbranched polymers

The properties of hyperbranched polymers are often affected by the nature of the backbone and the chain end functional groups, degree of branching, chain length between branching points, and the molecular weight distribution. Hyperbranched polymers are often modified to tailor their properties for a specialized purpose. Based on the highly branched architecture and the large number of terminal functional groups of hyperbranched macromolecules, five modification manners have been developed: (1) end-capping with short chains or organic molecules; (2) terminal grafting via living polymerization; (3) growing hyperbranched polymers on the surface, or grafting from/onto the surface; (4) hypergrafting to obtain hyperbranched polymers with a linear macro-molecular core; (5) blending or crosslinking. The first four methods will be discussed in this section, and the fifth one will be discussed in Section 5.

4.1. End-capping

The large number of functional end groups attached to the linear and terminal units of hyperbranched polymers can be conveniently end-capped with small organic molecules. In the end-capping process three major purposes are emphasized: (1) to exclude the influence of some functional groups on the measurement of molecular weight; (2) to investigate the effect of terminal groups on the properties of hyperbranched polymers; (3) to fabricate novel functional polymeric materials.

Many experiments demonstrated that the nature of terminal functional groups strongly influenced $T_g$, solubility and even $T_d$ of a hyperbranched polymer. Kim et al. [48] investigated the influence of end groups on the $T_g$ of hyperbranched polyphenylene (Scheme 37), and found that the $T_g$ can be varied over a wide range, from 96 °C for the polymer with $\alpha$-vinyl phenyl end groups to 223 °C for the polymer with $p$-anisol end groups although the modified hyperbranched polymers have the same backbone.

Wooley et al. [56] reproducibly prepared hyperbranched aromatic polyester by self-polycondensation of 3,5-bis(trimethylsiloxy)benzoyl chloride (138) in the presence of catalytic amounts of DMF or triethylamine hydrochloride. Then a variety of different functional groups were introduced into the hyperbranched macromolecules by modification of their phenolic groups.
(Scheme 38). $T_g$ of the hyperbranched macromolecules modified with monobenzylester of adipic acid is only 6 °C, whereas it is as high as 197 °C with terminal hydroxyl groups. The flexible alkyl units distributed throughout the macromolecular structure may play the role of plasticizers for the aromatic polyesters, reducing $T_g$ in comparison with that for samples with relatively shorter end chains. Furthermore, the solubility was also affected dramatically by the functionality of the chain ends. The phenolic terminated polyesters are only soluble in polar solvents, such as DMSO, NMP, methanol and THF, while the end-capped products are also soluble in non-polar solvents such as chloroform, dichloromethane and toluene.

Surprisingly, the effect of phenolic groups on the $T_g$ for hyperbranched aromatic polyethers made from monomer 139 is not so great as that for the polyesters mentioned above [50], and $T_g$ of the hyperbranched polyether with hydroxyl terminated groups is only 38 °C (Scheme 39). It seems that several factors such as the rigidity, polarity, length, and steric hindrance of the terminal functional groups can influence $T_g$ of the resulting polymers.

For the hyperbranched poly(ether ketone)s made from monomer 140 or 141, $T_g$ increased by nearly 200 °C on going from an octyloxy terminal group to a p-(carboxy)phenoxy terminal group (Scheme 40) [84]. Another feature for the hyperbranched poly(ether ketone)s is that their thermal properties, for example $T_g$, can be essentially independent of their macromolecular architecture (DB), illustrated by a $T_g$ for a polymer with a DB of 0.49 that is almost equal to that for a similar polymer with a DB of 0.15. Similarly, the fluoro-terminated hyperbranched poly(ether ketone) made from AB$_2$, AB$_3$, and AB$_4$ monomers differ in DB (0.49, 0.39, 0.71, respectively), but have the same $T_g$ (162 °C).

Few linear polyetherketones are soluble, they crystallize easily. When compared to their linear analogs, it is found that the solubility of a hyperbranched polymer is dependent on both the nature of terminal functional groups and its highly branched architecture. The polymer with polar end groups is soluble in polar solvents, and the non-polar-terminated polymer is soluble in apolar solvents. The fluoro-terminated sample is only sparingly soluble in DMF and totally insoluble in DMSO and aqueous solutions, while the phenolic-terminated polymer is soluble in DMF, DMSO, and aqueous K$_2$CO$_3$ or KOH solutions. In addition, the former is highly soluble in relatively weaker polar or non-polar solvents, such as chloroform and 1,2-dichloroethane, whereas the latter is totally insoluble in these.

Shu and coworkers [87] prepared carboxylic acid-terminated hyperbranched poly(ether ketone) from 5-phenoxyisophthalic acid (142), using phosphorus pentoxide/methanesulfonic acid in a weight ratio of 1:12 (PPMA) as condensing agent and solvent. Chemical modification of the carboxylic chain ends led to hyperbranched poly(ether ketones) containing a variety of different functional groups. DSC measurements showed that $T_g$ of the hyperbranched poly(ether ketone)s were strongly related to the chain end groups, with $T_g$ increasing with increasing the polarity of the end groups (Scheme 41). Compared with the carboxylic acid-terminated polymer or its ammonium derivative ($T_g$ of 226 and 236 °C, respectively), $T_g$s of polymers linked less polar terminal groups such as ester

(Scheme 39).
and ketone groups are lower than by about 100 °C. The solubility of the modified hyperbranched poly(ether ketone) made from 142 is similar to that for polymers made from 140 or 141. The non-polar group-terminated hyperbranched polymers are soluble in non-polar solvents, such as chloroform and dichloromethane, and the polar group-terminated polymers are soluble in polar solvents such as DMF and NMP; the ammonium derivative is even soluble in water.

Shu and coworkers [211] synthesized an ABB’ monomer (143) containing a pair of phenolic groups and an aryl fluoride, activated toward displacement by the attached oxazole ring. Nucleophilic substitution of the fluoride with the phenolic groups resulted in the formation of ether linkage, and subsequently the hyperbranched poly(aryl ether oxazole). The end-capping approach was used to chemically modify the phenolic terminal groups (Scheme 42). As in the preceding, \( T_g \) determined by DSC was very dependent on the nature of the chain ends, increasing with increasing end group polarity, e.g. \( T_g \) of the phenolic-terminated sample is as high as 247 °C, whereas \( T_g \) of the sample modified with 1-hexanol is only 119 °C. In addition, the data summarized in Scheme 42 also showed that \( T_g \) decreases with increasing length of the end chain for samples with same sort of end groups, and \( T_g \) of a sample with ester end chains is higher than \( T_g \) of a polymer with ether end chains, for comparable end chains length. Similar results are also observed for hyperbranched aromatic poly(ether imide)s made from \( N\text{-}[4\text{-}[1,1\text{-di}(4\text{-hydroxyphenyl})\text{ethyl}]\text{phenyl}]\text{-}4\text{-fluorophthalimide} \) (Scheme 43) [212].

As indicated in the preceding, the thermal and mechanical characters of hyperbranched polymers can be conveniently manipulated via the end capping method on the basis of the relationship between terminal groups and properties. Generally, alkyl- and ether groups-terminated hyperbranched polymers will have relatively low \( T_g \) values, low melting viscosity and low mechanical strength, and carboxylic acid- and hydroxyl-terminated hyperbranched ones have relatively high \( T_g \) values, high melting viscosity and high mechanical strength. Kim and coworkers [213] synthesized hyperbranched poly(ether ketone) analogs with heterocyclic triazine moiety by polymerization of monomer 145, and then modified the polymer with flexible moieties (Scheme 44). The phenolic-terminated hyperbranched polymer has a \( T_g \) of 264 °C, and the \( T_g \) of the methoxy-terminated polymer is only slightly lower (260 °C). The incorporation of longer flexible moieties such as di- or tetraethyleneoxy and stearyl units at the chain ends.

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**Scheme 40.**

| End group of polymer: | \(-\text{O}-(\text{CH}_2)_7\text{CH}_3\) | \(-\text{O}^\text{CH}_3\) | \(-\text{O}^\text{CH}_3\) | \(-\text{OH}\) | \(-\text{O}-(\text{CH}_2)_7\text{CH}_3\) |
| \(T_g/\degree \text{C}\): | 97 | 118 | 117/119 | 127 | 139 |

| End group of polymer: | \(-\text{O}^\text{O}_{\text{C}_2\text{H}_5}\) | \(-\text{F}\) | \(-\text{O}^\text{OH}\) |
| \(T_g/\degree \text{C}\): | 147 | 154 | 162 | 290 |

---

**Scheme 41.**
greatly lowered the $T_g$ values (169, 149 and 108 °C, respectively). On the other hand, because the di- and tetraethyleneoxy-terminated hyperbranched polymers consist of a hydrophobic core and hydrophilic surface, they may exhibit amphiphilic characteristics in an aqueous phase. The investigation of self-aggregation of the amphiphilic core–shell hyperbranched polymers using a pyrene fluorescence probe showed that the critical aggregation concentration (CAC) of the tetraethyleneoxy-terminated hyperbranched polymer was 12.6 mg/l, much lower than that of low molecular weight surfactants, e.g. 2.3 g/l for sodium dodecyl sulfate (SDS) in water [213].

The nature of end groups has also significant effect on the thermal properties of the hyperbranched poly(siloxysilanes) with flexible backbones. Miravet et al. [100] synthesized hyperbranched poly(siloxysilanes) by polyhydrosilation of methylvinylbis(methylsiloxy)silane (146). End capping of the terminal silicon hydride groups by hydrosilation with a variety of reagents gave a diversity of terminal modified hyperbranched poly(siloxysilane) materials (Scheme 45). Because of the conformation freedom of the carbosiloxane skeleton, the SiH terminated polymer made from 146 exhibits a very low $T_g$ (−106 °C). After end capping a SiH-terminated sample with di-tert-butylphenol units, $T_g$ increased significantly, by about 74–104 °C. Phenyl ether- and chloromethylbenzene-terminated polymers have intermediate $T_g$ values that are also greatly higher than that of the starting SiH-terminated polymer. Conversely, the $T_g$ values of polymers having flexible triethylene glycol type end chains are only slightly higher than that of starting hyperbranched poly(siloxysilane) with SiH end groups.

The influence of terminal alkyl groups on the thermal and mechanical properties of aromatic hyperbranched polyesters was also studied by introducing alkyl chains with different length into the end groups of hyperbranched polyester based on 3,5-dihydroxybenzoi acyl [214]. The degree of modification was varied from 11 to 100%. The $T_g$ first decreased with increasing length of the alkyl chain, but then did not decrease with further increasing chain length, perhaps owing to the possibility of crystallization. Thus, increase of the degree of modification led to a pronounced decrease of $T_g$, and an increase of the side chain crystallization for long alkyl chain modification.
The measurements showed that modification with C12 chains caused a pronounced decrease in the complex viscosity and the moduli.

By contrast with the preceding, it must be recognized that there are limits on the extent to which the thermal properties for aliphatic hyperbranched polyether polyols may be tailored by end group modification. DSC measurements for the hyperbranched polyglycerols \( \text{DP}_n = 23–83 \), \( M_w/M_n = 1.2–1.5 \) as well as their propoxylated derivatives esterified to different extents (23–100%) with various carboxylic acids (C2 to C18, benzoic, biphenylcarboxylic, and benzoic acid) indicate that \( T_g \) of these hyperbranched polymers is mainly controlled by two factors: (1) the extent of hydrogen bonding, and (2) the formation of order structure (mesophases and crystallization). The \( T_g \) values of the esterified polyether polyols are in the range –58 to –22 °C. The difference (\( \Delta T_g \)) in \( T_g \) value between the original and derivatized samples is only –9 to 34 K [215]. Gedde and coworkers [216] end capped the hyperbranched aliphatic polyester originating from 2,2-dimethylolpropionic acid (147) with 1,1,1-tri(hydroxymethyl)propane (105) as core, affording three hyperbranched polyesters with the same backbone structures, but different terminal groups (acetate, benzoate or hydroxyl groups) (Scheme 46). The \( \Delta T_g \) (33 K measured with DSC) between the hydroxyl-terminated polymer and acetate-terminated samples was less than had been anticipated.

On the other hand, end capping the hyperbranched polymers with specific compounds is an efficient approach to fabricate novel functional polymer materials. Frey et al. [137,217] synthesized
hyperbranched polyether polyols by ring-opening multibranching polymerization (ROMBP) of glycidol (19), using 1,1,1-tri(hydroxymethyl)propane (105) as core initiator. Then the hyperbranched polyglycidols were end capped with acid 148 or 149 in the presence of diisopropylcarbodiimide (DIPC) as condensing agent, affording hyperbranched polymer with mesogenic end groups (Scheme 47) [218]. The degree of functionalization of the hyperbranched polyglycerols achieved 88% for the lower molecular weight sample (\(M_n = 1500 \text{ g/mol}\)) and 73–79% for the higher molecular weight samples (\(M_n = 3500 \text{ g/mol}\)). SEC measurements showed narrow molecular weight distributions for all the three samples (\(M_w/M_n < 1.2\)). DSC, polarizing microscopy, and wide-angle X-ray scattering (WAXS) were used to investigate the liquid crystalline properties of the three samples. A dramatic increase of \(T_g\) (40–50 °C) was observed for the three samples. Apparently, molecular weight did not strongly influence the formation of the mesophase. The longer alkyl-terminated sample exhibits a much higher transition enthalpy, indicating the presence of more highly ordered smectic clusters.

Salazar et al. [219] synthesized hyperbranched amino-terminated polyglycidols by end-modification of terminal hydroxyls with tolylsulfonyl chloride (TsCl), followed by nucleophilic substitution of the tolylsulfonyl groups with secondary aliphatic amines (Scheme 48). The hyperbranched amino-terminated polymers obtained can be used as macromolecular ligands in an oxidative coupling reaction of phenylacetylene. It is found that the amino-terminated polyglycidols–CuCl complexes are more effective catalysts for the oxidative coupling reaction than the reference monomeric tertiary amines–CuCl, while less effective than the most efficient \(N,N',N',N''\)-tetramethylethylenediamine–CuCl complexes. The performance improvement for the hyperbranched polymeric ligands may
be attributed to two factors: (1) the better complexation abilities, and (2) local increase of the reagent concentration.

Bergenudd et al. [220] end modified the commercially available hyperbranched polymer Boltorn™ with 3-(3,5-di-tert-butyl-4-hydroxy-phenyl)-propionic acid, resulting in hyperbranched polymeric antioxidants. Then the antioxidants were evaluated in squalane, and in polypropylene (PP) films, to determine their oxidation induction time. The hyperbranched antioxidants are more effective than the commercial antioxidant Irganox 1010 in the liquid compound squalane, but inferior in PP. Low mobility in combination with low solubility may cause the lower efficiency in PP. This result suggests that the macromolecular antioxidants would be suitable as low volatile stabilizers for liquid systems such as oils and lubricants.

Wooley et al. [221] prepared a hyperbranched polyfluorinated benzyl ether polymer (Scheme 49), by deprotonation of benzylic alcohol and nucleophilic substitution of p-fluorines of the two pentafluorophenyl groups attached to 3,5-bis[(pentafluorobenzyl)oxy]benzyl alcohol (150). Then fluoroalkyl groups were introduced into the polymer by chemical modification.
of its p-fluorines with lithium trifluoroethoxide and lithium 1H, 1H, 2H, 2H-perfluorodecanoxide. Additionally, an X-ray opaque derivative was obtained by end capping the pentafluorophenyl-terminated hyperbranched polymer with p-iodophenol. Contact angle measurements of water and hexadecane on the films of fluoroalkyl-modified polymers indicate a high degree of hydrophobicity and lipophobicity. Interestingly, essentially equivalent hydrophobicity was obtained with 36 or 100% 1H, 1H, 2H, 2H-perfluorodecanoxy-substitution, with only a 5° difference in the lipophobicity between the former and the latter. Atomic force microscopy (AFM) was applied to investigate the surface morphologies and properties of the polymer films. Tapping mode AFM images showed phase separation in the partially 1H, 1H, 2H, 2H-perfluorodecanoxy-substituted polymeric material. More than a two-fold decrease in the coefficient of friction and adhesive force for the 1H, 1H, 2H, 2H-perfluorodecanoxy-modified polymer was detected with lateral force AFM using a silicon nitride probe.

An increase in the content of heavy atoms such as halogens would decrease the absorption in the near infrared (NIR), suggesting that the halogenated hyperbranched polymers may be utilized as photonic compounds. A good optical waveguide material also requires the combination of low optical loss, controlled refractive index, good thermal and mechanical properties, and ease of processing. On the basis of the high fluorine content of the AB₂ monomer 3,5-dipentafluorophenyl-1-(hydroxy)benzene (151) [51, 222], fluorinated hyperbranched polymer and its end-modified products have been developed, potentially useful for optical waveguide applications (Scheme 50) [223, 224]. Very low losses in the NIR, 0.1 dB/cm at 1550 nm, were demonstrated for the hyperbranched polymer made from 151, because of its amorphous structure and low C–H bond content. Depending on the type and amount of the terminal functional groups of the resulting polymers, the refractive indices at 633 nm can be varied from 1.450 to 1.638, which matches the index of materials involved in optical devices, and thus minimizes backscattering at interconnections. The T_g of the fluorinated hyperbranched polymer and its derivatives ranged from 91 to 140 °C, and the temperatures of initial decomposition ranged from 335 to 430 °C. A highly crosslinked polymer was achieved by cationic photoinitiating the fluorinated p-hydroxystyrene-terminated hyperbranched polymer.

Radical addition reaction can be used to functionalize the terminal groups of hyperbranched polymers. Matyjaszewski and coworkers [113–116] prepared

![Scheme 50.](image-url)
a hyperbranched polyacrylate by ATRP of 2-(bromopropionyloxy)ethyl acrylate (BPEA), followed by addition of 1,2-epoxy-5-hexene to the polymer chain end, resulting in epoxy-terminated functional hyperbranched polymer (Scheme 51) [225].

In addition, a hyperbranched polymer with azo chromophores end groups was prepared by modification of a hydroxyl-terminated hyperbranched polyester with ethyl 4-[[4-[(N,N-di(hydroxyethyl)aminobutoxy)phenylazo]benzoate] [226]. Depending on the difference between interior (closer to the focal unit) and periphery (distant from the focal unit) hydroxyl groups in the hyperbranched polyglycerol, core–shell-type hyperbranched polyglycrols were fabricated by selective chemical differentiation [227]. Fluorescent chromophores were introduced into the periphery of hyperbranched polymers via end-capping, affording fluorescent hyperbranched polymeric materials [228–230].

4.2. Terminal grafting

Terminal grafting can also be called ‘grafting from’. Grafting polymers from macromolecular initiators prepared by modification of the functional groups of hyperbranched polymers affords core–shell multi-arm star polymers or hyperstars. Some properties, such as polarity, solubility and flexibility of the hyperbranched scaffolds, can be conveniently tailored through terminal grafting modification. Three polymerization methods (e.g. anionic, cationic and living-/controlled radical polymerizations) have been adopted to fabricate the hyperstars via reaction processes including macromolecular initiator-first and in situ grafting. To date, most of the hyperbranched cores used are polyols.

Through a two-step, one-pot approach, Frey et al. [138] obtained short poly(propylene oxide) (PPO) multi-arm star polymers by anionic ring-opening multibranching polymerization (ROMBP) of glycidol, followed by anionic polymerization of propylene oxide (Scheme 52). The resulting polyether polyols containing up to five propylene oxide units per end group showed apparent $M_n$ values in the range 5000–12,000 g/mol and narrow polydispersity (PDI < 1.7) by using DMF as eluent and poly(propylene glycol) s with $M_n$ in the range 1000–12,000 as samples for calibration. The polarity of the highly hydrophilic
polyglycerols (PG) can be varied through this approach. Depending on the length of the propylene oxide segments, $T_g$ of the grafted polymers varied from $-37$ to $-71^\circ$C.

Through a macromolecular initiator-first approach, Lutz et al. [231] synthesized poly(ethylene oxide) (PEO) multi-arm star polymers by employing hyperbranched PG and PG modified with short oligo(propylene oxide) segments (PG-$b$-PPO) as polyfunctional initiators for the living anionic ring opening polymerization of ethylene oxide (EO) in the presence of diphenylmethylpotassium (DPMP) (Scheme 52). In the case of PG without modification, aggregation would occur after metatation, leading to inefficient initiation and propagation. By comparison, hydroxyfunctional PEO multi-arm star polymers (PG-$b$-PPO) with short oligo(propylene oxide) segments (PG-$b$-PPO) as polyfunctional initiators for the living anionic ring opening polymerization of ethylene oxide (EO) in the presence of diphenylmethylpotassium (DPMP) (Scheme 52). The length of PMA arms can be controlled through monomer/initiator ratio and conversion. No micro-phase separation of PG core and PMA arms occurred as demonstrated with the DSC-measurements (only one $T_g$ for each hyperstar).

ATRP have also been utilized to prepare multi-arm star polymers with PG core via the terminal grafting strategy. Maier et al. [234] synthesized a hyperbranched macromolecular initiator for ATRP by modification of PG with 2-bromoisobutyl bromide, then polymerized methyl acrylate (MA) in the presence of the initiator and CuBr/pentamethyldiethylenetriamine (PMDETA) affording a multi-arm block copolymers with polyether core and PMA arms (Scheme 52). The length of PMA arms can be controlled through monomer/initiator ratio and conversion. No micro-phase separation of PG core and PMA arms occurred as demonstrated with the DSC-measurements (only one $T_g$ for each hyperstar).

Hyperbranched polyether polyls made from 3-alkyl-3-(hydroxymethyl)oxetane have also been widely applied as core molecules in the preparation of multi-arm star block copolymers. Similar to the route employed by Frey et al. [234], Carlmark et al. [235] synthesized a hyperbranched multifunctional initiator with approximately 25 initiating points for ATRP by reacting hyperbranched poly[3-ethyl-3-(hydroxymethyl)oxetane] (PEHO) with 2-bromo-isobutylbromide (Scheme 53). Then the hyperstars with PEHO core and PMA arms (PEHO-$b$-PMA) were prepared by ATRP of MA in the presence of the macromolecular initiator and CuBr/tri(2-(dimethylamino)ethyl)amine (Me6-TREN) in ethyl acetate at room temperature. Because of the inter- and intramolecular reactions, gel would be easily formed in the polymerization. In order to prevent crosslinking, the concentration of propagating radicals in the system must be kept low by dilution with solvents, stopping the reaction after low conversion of the monomer, or decreasing the amount of catalyst used. In the case described above, the initiating sites-to-catalyst could not exceed 1:0.1, otherwise, either gelation would occur or the polymerization went out of control. The most successful reactions were conducted with a ratio of 1:0.05. Different from the thermal properties of PG-$b$-PMA, two glass transitions were observed from the DSC curves of the PEHO-$b$-PMA hyperstars,
suggested that phase-separation existed in the latter block copolymers. The lower \( T_g \) at around \(-40^\circ C\) originated from PEHO cores is hardly affected by the length of PMA arms, while the higher one assigned to PMA arms increased with increasing PMA chain length.

Yan and coworkers [236] synthesized hyper-branched poly[3-ethyl-3-(hydroxymethyl)oxetane]-block-poly(2-dimethylaminoethyl methacrylate) (PEHO-b-PDMA) via oxyanionic polymerization. Potassium alcoholate macroinitiators with high initiating efficiency were obtained by reaction of the hydroxyl groups of PEHO with KH. It was found that lower critical solution temperature of PEHO-b-PDMA decreased with either increasing DMA chain length or increasing pH of the solution.

Hou et al. [237] obtained hyperstars with hyper-branched poly(3-methyl-3-(hydroxymethyl)oxetane) (PMHO) core and short polytetrahydrofuran (PTHF) arms via an in situ grafting approach (Scheme 53). The cationic ring-opening polymerization of 3-methyl-3-(hydroxymethyl)oxetane (MHO) was initiated with \( \text{BF}_3\cdot\text{O(CH}_2\text{CH}_3)_2 \). Because the rate constant for the addition reaction between terminal units and MHO is much lower than that of MHO homopolymerization, the first stage polymerization in THF solution produced PMHO, with copolymerization with THF after the MHO was almost completely reacted. The results were confirmed as compared with those obtained using a two-step copolymerization, i.e. homopolymerization of MHO and then addition of suitable amount of THF to the reaction system to effect the copolymerization. The \(^1\)H NMR measurements showed that the average degree of polymerization of THF arms increased from 0.41 to 3.86 on increasing the feed ratio of THF to MHO from 0.5:1 to 6:1.

Commercially available aliphatic hyperbranched polyester with 32 hydroxyl groups (Bolton™-H30) was used as the core by Hult et al. [238] to prepare PCL multi-arm star copolymers in the presence of Sn(Oct)\(_2\). Rheological measurements of zero shear rate viscosity, \( \eta_0 \), showed that the star polyesters had a significantly lower \( \eta_0 \) than linear PCL. Dynamic mechanical data indicated that the films made from the shorter-armed resins were amorphous after curing, while those from longer-armed resins were crystalline. Another multi-arm star copolymer with hyper-branched poly[2,2-bis(hydroxymethyl)propionic acid] core and PCL arms was obtained via a similar route [239]. As a reference material, PCL multi-arm star copolyesters initiated from a dendrimer were also prepared. Comparison of the results obtained for dendrimeric and hyperbranched initiators showed that the reactivity of the terminal hydroxyl groups in the dendrimer was considerably higher than in the hyperbranched polymer.

Amphiphilic multi-arm star polymers with a hydrophobic hyperbranched core and hydrophilic graft arms have been reported by Weberskirch et al. [240]. Modification of the hyperbranched polymer derived from 4,4-bis(4'-hydroxyphenyl)valeric acid with 3-(chloromethyl)benzoyl chloride gave rise to hyperbranched macroinitiator, followed by cationic ring-opening polymerization of 2-methyl-2-oxazoline.
affording the core–shell amphiphiles with up to 12 arms. Single star molecules ranging from 22 to 50 nm in diameter were detected with photon correlation spectroscopy measured in methanol and chloroform.

4.3. Surface growing

The method to modify the specific surface or interface with hyperbranched macromolecules or to graft hyperbranched polymers onto the surface is denoted as ‘surface growing’ in this paper. The grafted hyperbranched polymers can be regarded as so-called polymer brushes, which are typically anchored to a surface by one end of the polymer chain, such that the polymer can extend away from the surface [241]. Surface growing is an efficient strategy to fabricate inorganic/organic-hyperbranched polymer hybrid materials and functional devices or improve the properties of surface objects.

Four routes have been developed in these modifications and functionalizations, as shown in Fig. 5. Route 1 can be called the graft-on-graft approach. The reaction procedure is similar to the step-by-step synthesis methodology of a dendrimer. Functional groups (D) are firstly introduced onto the surface, followed by reaction of AB₂ monomers or multifunctional polymers with the D groups and then reaction of CD monomers with the B groups attached (in some examples, the addition order of AB₂ or CD is reversed). Repeating the reaction between AB₂ and CD grows hyperbranched polymers with numerous functional groups onto the surface. Route 2 is a ‘grafting from’ technique of surface initiating polymerization in which the initiating functional groups are incorporated onto the surface and then initiate the polymerization of AB₂ or latent AB₂ (ABB') monomers. In route 3, a ‘grafting to’ approach is used, whereby prepared hyperbranched polymers are covalently linked to a prepared surface. Route 4 called ‘surface adsorption’, hyperbranched macromolecules are directly assembled or adsorbed onto the surface. Notably, routes 1-3 are chemical methods, while route 4 is a physical method. Therefore, both chemical and physical approaches can be used to graft hyperbranched polymers onto the surface.

A series of solid matrixes such as gold (Au), silica (SiO₂), silicon wafer (Si), aluminum (Al), porous alumina (Al₂O₃), C₆₀, carbon black, polyethylene (PE), polypropylene (PP), and chitosan powder (CP) have been adopted as supporting substrates for the functionalization of hyperbranched polymers. Some hyperbranched polymers grown on the surface and their grafted approaches are listed in Table 6.

4.3.1. On the surface of Au

Carboxylic acid functional groups are introduced on a gold surface or the surface of gold-coated porous alumina via the attachment of mercaptoundecanoic acid (MUA) to the substrate, followed by the conversion of the carboxylates to mixed anhydrides. Then amino-terminated poly(tert-butyl acrylate)
(PTBA) is grafted on the surface through the attachment sites of the mixed anhydrides. Hydrolysis of the tert-butyl groups to carboxylic acid generates a poly(acrylic acid) (PAA) layer. Repeating the steps of the formation of mixed anhydrides, grafting of PTBA and hydrolysis of tert-butyl groups affords multi-grafting hyperbranched PAA layers [241–249]. A typical procedure is described in Fig. 6. In order to change the surface properties, the carboxylic acid groups in PAA are further modified with other molecules such as H₂N(CH₂)₆CF₃ [242,245,247], and molecules containing pyrene, ferrocene, poly(ethylene glycol), 15-crown-5,3,4,9,10-perylene-tetracarboxylic diimide, etc. [244].

### 4.3.2. On the surface of SiO₂

The silica surface is also widely grafted with hyperbranched polymers. Tsubokawa et al. [250] achieved surface-grafting polymers with azo pendant groups by reaction between 4,4’-azobis(4-cyanopentanoic acid) (ACPA) and isocyanate groups of grafted polymer on a silica surface. The azo groups can initiate the copolymerization of methyl methacrylate (MMA) with 2-methacryloyloxyethyl isocyanate (MOI). The isocyanato groups in PMOI can be modified with ACPA, which can initiate copolymerization of MMA and MOI. Thus, hyperbranched copolymers can grow on the silica surface via the graft-on-graft approach. Polymer chains possessing peroxycarbonate groups may be obtained by copolymerization of tert-butyl peroxy-2-methacryloyloxyethyl carbonate with other vinyl monomers. Similar to the azo groups, peroxycarbonate groups can initiate the polymerization of vinyl monomers to give hyperbranched polymers anchored to the silica surface [251].

Reaction of terminal diamine-type polyoxyethylene with epoxy groups previously introduced onto the silica surface through 3-glycidoxypropyltrimethoxysilane treatment leads to a modified surface having numerous amino groups. By repeating Michael addition of MA to amino groups followed by amidation of the ester moieties with diamines (which is similar to the synthesis of polyamidoamine dendrimer), hyperbranched polyamidoamines are grafted onto the silica surface [252,253]. Aminosilylated surface can also directly initiate the ring-opening polymerization of aziridine to form hyperbranched poly(ethyleneimine) (PEI) on a solid support [254].

#### Table 6

Growing hyperbranched building blocks on the surfaces

<table>
<thead>
<tr>
<th>Surface</th>
<th>Introduced surface group</th>
<th>Major building units or monomers</th>
<th>Approach</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>−COOH</td>
<td>CI₂CO₂H₂CH₃ + PAA</td>
<td>graft-on-graft</td>
<td>[241–249]</td>
</tr>
<tr>
<td>SiO₂</td>
<td>−N−N−−</td>
<td>MMA + MOI</td>
<td>graft-on-graft</td>
<td>[250]</td>
</tr>
<tr>
<td></td>
<td>−OCO₂O−−</td>
<td>CH₂=CH-R</td>
<td>graft-on-graft</td>
<td>[251]</td>
</tr>
<tr>
<td></td>
<td>−NH₂</td>
<td>MA + H₂N(CH₂)₃,NH₂</td>
<td>graft-on-graft</td>
<td>[252]</td>
</tr>
<tr>
<td></td>
<td>−NH₂</td>
<td>MA + H₂N(CH₂)₃,NH₂</td>
<td>graft-on-graft</td>
<td>[253]</td>
</tr>
<tr>
<td></td>
<td>−NH₂</td>
<td>Aziridine</td>
<td>Grafting from</td>
<td>[254]</td>
</tr>
<tr>
<td></td>
<td>−CO₂Br(CH₂)₃₂</td>
<td>BPEA</td>
<td>Grafting from</td>
<td>[255]</td>
</tr>
<tr>
<td></td>
<td>−</td>
<td>PEI</td>
<td>Adsorption</td>
<td>[256]</td>
</tr>
<tr>
<td>Si</td>
<td>−OH</td>
<td>Hyperbranched EHBP</td>
<td>Grafting to</td>
<td>[257,258]</td>
</tr>
<tr>
<td></td>
<td>−OH</td>
<td>HP3/HBP4</td>
<td>Adsorption</td>
<td>[259]</td>
</tr>
<tr>
<td></td>
<td>−NH₂</td>
<td>Aziridine</td>
<td>Grafting from</td>
<td>[254]</td>
</tr>
<tr>
<td></td>
<td>−CO₂Br(CH₂)₃₂</td>
<td>BPEA, BIEM</td>
<td>Grafting from</td>
<td>[260]</td>
</tr>
<tr>
<td>PE</td>
<td>−COOH</td>
<td>CI₂CO₂H₂CH₃ + PAA</td>
<td>graft-on-graft</td>
<td>[261–267]</td>
</tr>
<tr>
<td></td>
<td>−NH₂</td>
<td>MA + H₂N(CH₂)₃,NH₂</td>
<td>graft-on-graft</td>
<td>[268]</td>
</tr>
<tr>
<td>PP</td>
<td>−COOH</td>
<td>CI₂CO₂H₂CH₃ + PAA</td>
<td>graft-on-graft</td>
<td>[269]</td>
</tr>
<tr>
<td></td>
<td>−</td>
<td>HBP-Boltorn E2</td>
<td>Grafting to</td>
<td>[270]</td>
</tr>
<tr>
<td>CP</td>
<td>−NH₂</td>
<td>MA + H₂N(CH₂)₃,NH₂</td>
<td>graft-on-graft</td>
<td>[271]</td>
</tr>
</tbody>
</table>
Müller and coworkers [255] obtained hyperbranched polymer–silica hybrid nanoparticles by SCVP via ATRP of BPEA from silica surface linked α-bromoester initiator layer. Mészáros et al. [256] investigated the direct adsorption on silica wafers of hyperbranched PEI with reflectometry, and showed that significant charge reversal and shift in the isoelectric point of silica wafer occurred because of the adsorption of PEI.

4.3.3. On the surface of Si

A molecular surface coating with a thickness of 4.5 nm has been fabricated by reaction of epoxy-functionalized hyperbranched polyesters (EHBP) with the hydroxyl groups of silicon wafers via a grafting to approach [257,258]. Around 3–4 epoxy groups per molecule attached to the uppermost surface layer provided residual functionality sufficient to graft another polymer layer. It was found that the grafted hyperbranched polymeric layers are very robust and can sustain high compression and shear stresses, while possessing high elasticity [257]. The uniform polymer layers were homogeneous on a nanoscale, without signs of the microphase separation [258].

The commercially available Boltorn™ hyperbranched polyesters with third and fourth generations (HBP3 and HBP4) can be directly adsorbed on a bare silicon surface; the adsorption amount of lower generation HBP3 is higher than that of HBP4 [259]. In a HBP3 adsorbed layer, surface coverage is observed with thickness ranging from less than 1 nm to about 3 nm. For HBP4 located on the surface, a stable, close-to-spherical shape with a diameter of 2.5 nm is found throughout the whole coverage, including both dense monolayers and isolated molecules. This differing surface behavior might be caused by the different molecular flexibility and constrained mobility between HBP3 and HBP4.
Similar to the process for growth of hyperbranched PEI and hyperbranched poly(BPEA) on the silica surface [254,255], hyperbranched PEI [254] and hyperbranched polyesters [260] have been successfully anchored to the silicon surface by ring-opening polymerization of aziridine and self-condensing ATRP of BPEA and 2-(2-bromoisobutyryloxy)ethyl methacrylate (BIEM), respectively, via grafting from approach.

4.3.4. On the surface of PE

Bergbreiter and coworkers [261–267] have grafted hyperbranched PAA onto the PE surface and modified the pendant carboxylic acid groups of PAA with fluorescent chromophores and hydrophobic molecules by extending the chemistry employed in the hyperbranched grafting on Au-coated silicon wafers described above [241–249]. Oxidized PE films with carboxylic acid functional groups are obtained by oxidation with CrO3–H2SO4. Then amino-terminated poly(tert-butyl acrylate) is attached to the oxidized PE through amidation, so that subsequent hydrolysis of the tert-butyl esters affords a PE film with one layer of PAA grafts. Repetition of the process through 2–4 more cycles can produce heavily grafted PE films. The resulting hyperbranched grafts exhibit higher efficiency as platforms for further ionic modification of PE by comparison with the simple oxidized PE [261].

Amidation or esterification of ultrathin hyperbranched PAA grafts with thiophenes having amino or hydroxyl groups generated thiophene units-contained interfaces that could be applied as substrates for an oxidative polymerization method with FeCl3 as an oxidant [265]. A conjugated fluorescence 2,5-coupled oligothiophene has been fabricated within the hyperbranched grafts, as demonstrated with its yellow–green light emitted under UV irradiation. The hyperbranched PAA grafts can also be used as substrates for a mild hydrogen-bond-based grafting method [266].

Nakada et al. [268] introduced amino groups to the unsaturated pendant and bridge sites of a PE substrate, followed by application of poly(amideamine) dendrimer synthesis methodology (repeating the steps of 2-methoxycarbonyl ethylation and 2-aminomethylamination), resulting in ultrathin hyperbranched poly(amideamine) grafts. The amino amplified PE films showed anionic exchange capacity and could adsorb acid dye.

4.3.5. On the other surfaces

The techniques previously adopted with PE surface can be extended to modify PP by hyperbranched grafting with PAA grafts [269]. Hydrophilic and hydrophobic surfaces were obtained by treatment of the as-prepared PAA-grafted PP with alkali, and with ethyl chloroformate followed by pentadecylfluorooctylamine. The adhesion of the surface increases from 2 J/m² for unmodified PP to 29 J/m² for the PP with five stages of hyperbranched grafting. Epoxy-terminated hyperbranched polyesters (Boltorn™-E2) were grafted on the PP surface modified with maleic anhydride (MAH) by melt blending in a twin-screw extruder [270].

In addition, hyperbranched polyamidoamine was grafted onto the surface of CP by repeating two processes including Michael addition of MA to surface amino groups and amidation of the resulting esters with ethylenediamine [271]. C60-polystyrene hyperbranched macromolecular thin films were also reported [272].

4.4. Hypergrafting

Hypergrafting represents grafting hyperbranched macromolecules to a multifunctional polymeric core, and the resulting hybrid material is called a ‘hypergrafted polymer’ in this article. If the core used is a linear polymer, a new sort of comb-like polymer cylinder will be formed. As shown in Fig. 7, four routes may be applied to obtain the hypergrafted polymers: (1) graft-on-graft from a polymeric core with functional side groups; (2) polymerization of hyperbranched macromonomers; (3) polymerization of AB2 or latent AB2 monomers initiated from macromolecules; (4) direct grafting hyperbranched molecules onto a polymer.

Using the graft-on-graft approach, Fréchet et al. prepared hypergrafted polystyrene (PS) and its copolymers [107]. A linear backbone incorporating latent ATRP initiating sites was first synthesized by nitroxide mediated ‘living’ radical polymerization of PS and chloromethylstyrene (CPS), followed by initiating ATRP of CPS in the presence of Cu(1)Cl/2,2’-bipyridine complex, giving rise to PS cylinders.
The active side points of CPS units were used to further initiate the atom transfer polymerization of other vinyl monomers, affording hypergrafted polymers.

Poly(allylamine) (PAAM) grafted chain-pendant hyperbranched PEI has been prepared by an in situ reaction of PAAM with 2-chloroethylamine hydrochloride (CAH) in the presence of sodium hydroxide \[273\]. The as-prepared polymers with abundant amino groups can react with CAH to produce hypergrafted polymers with multi-layers of PEI side chains. Potentiometric titration and ultraviolet-visible (UV–Vis) spectroscopy showed that the hypergrafted polyamines can act as multidentate ligands for ions and form stable complexes with Cu\(^{2+}\), with about three EI dents per ion.

Frey et al. \[274\] reported polyethyleneimines with apolar hyperbranched carbosilane side chains, prepared by ring-opening polymerization of oxazoline-based hyperbranched macromonomers earlier synthesized. The hypergrafted polymers can form superstructures in solution and in bulk.

Knauss et al. \[275\] obtained branched PS macromonomers by slow addition of a coupling agent (4-(chlorodimethylsilyl)styrene or CPS) to living polystyrllithium. Then, hypergrafted copolymers were produced by copolymerization of the macromonomer with PS or MMA.

Although the literature published on hypergrafted polymers is limited, this new class of polymers is likely to receive more and more attention and be widely explored and used in a variety of potential application areas such as supramolecular chemistry, biomaterials, nanotechnology and molecule-devices in the near future.

5. Application of hyperbranched polymers

5.1. Conjugated functional materials: optical, electronic and magnetic properties

Because of their good solubility and excellent processibility, three-dimensional hyperbranched conjugated polymers are attracting more and more attention as novel optical, electronic and magnetic materials. Linear conducting polymers are usually all para linked, while the hyperbranched polymers are almost always meta connected and have a far more limited conjugation. Consequently, very different properties are found for the hyperbranched polymers than their linear counterparts.

5.1.1. Hyperbranched poly(phenylenevinylene)

Lin et al. \[175\] synthesized hyperbranched poly(3,5-bisvinilic benzene) (HP42 or HP43) with a relatively low yield and low molecular weight via Gilch or Wittig reactions (Scheme 54). The SEC measurement showed that \(M_n\) of the product made from route A was 1934 with a PDI of 1.13, and the \(M_n\) value of the sample produced from route B was even smaller. The resulting hyperbranched polymers are soluble in common organic solvents such as THF, chloroform, dichloromethane and ethyl acetate. The optical properties of HP42 are listed in Table 7. The absorption maxima (\(\lambda_{\text{abs}}\)) determined with UV–Vis spectroscopy are 290 and 310 nm with a molar absorption coefficient in the order of \(10^4\), and the fluorescence emission maximum (\(\lambda_{\text{em}}\)) in dichloride methane solution monitored occur for 359 and 369 nm.
with a fluorescence lifetime ($\tau$) of 0.6–8 ns and a quantum yield ($\Phi_f$) of 36% for the excitation maximum ($\lambda_{ex}$) at 305 and 325 nm. The incorporation of the $m$-phenylene group decrease the effective conjugation length and increase the bandgap, so both the absorption and emission bands are blue shifted in comparison with the widely studied linear poly(p-phenylenevinylene) (PPV). The solid film of HP42 fabricated by spin coating technique exhibits an emission maximum ($\lambda_{em,s}$) at 446 nm as excited at its solid absorption maximum ($\lambda_{ab,s}$), about 80 nm red-shifted with respect to the value in solution. Enhanced inter-chain interaction in the solid film may cause the dramatic difference.

Table 7
Photophysical results of some hyperbranched conjugated polymers

<table>
<thead>
<tr>
<th>No.</th>
<th>$M_n$</th>
<th>PDI</th>
<th>$\lambda_{ab}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\lambda_{ex}$ (nm)</th>
<th>$\lambda_{ab,s}$ (nm)</th>
<th>$\lambda_{em,s}$ (nm)</th>
<th>$\Phi_f$ (%)$^a$</th>
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<tbody>
<tr>
<td>HP42</td>
<td>1930</td>
<td>1.13</td>
<td>289, 310</td>
<td>359, 369</td>
<td>305, 325</td>
<td>446</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>HP44</td>
<td>2810</td>
<td>2.15</td>
<td>323, 405</td>
<td>457</td>
<td>305, 325</td>
<td>329, 402</td>
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</tr>
<tr>
<td>HP45</td>
<td>315</td>
<td>0.97</td>
<td>326, 406</td>
<td>453, 480</td>
<td>306, 390</td>
<td>319, 405</td>
<td>46</td>
<td></td>
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<tr>
<td>HP46</td>
<td>330</td>
<td>0.97</td>
<td>310, 396</td>
<td>453, 480</td>
<td>306, 390</td>
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<td>317, 402</td>
<td>453, 480</td>
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<td>HP48</td>
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<td>307, 389</td>
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<td>HP49</td>
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<td>307, 389</td>
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<td>HP50</td>
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<td>1.76</td>
<td>322, 405</td>
<td>461, 490</td>
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<td>307, 389</td>
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<tr>
<td>HP51</td>
<td>40,180</td>
<td>1.76</td>
<td>500</td>
<td>305</td>
<td>473</td>
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<td>HP55</td>
<td>9080</td>
<td>2.24</td>
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<td>343</td>
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<td>334</td>
<td>397</td>
<td></td>
</tr>
<tr>
<td>HP56</td>
<td>4940</td>
<td>5.78</td>
<td>309</td>
<td>343</td>
<td>398</td>
<td>334</td>
<td>397</td>
<td></td>
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<tr>
<td>HP57</td>
<td>4940</td>
<td>5.78</td>
<td>309</td>
<td>343</td>
<td>398</td>
<td>334</td>
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<tr>
<td>HP58</td>
<td>4940</td>
<td>5.78</td>
<td>309</td>
<td>343</td>
<td>398</td>
<td>334</td>
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<tr>
<td>HP59</td>
<td>4940</td>
<td>5.78</td>
<td>309</td>
<td>343</td>
<td>398</td>
<td>334</td>
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<tr>
<td>HP60</td>
<td>4940</td>
<td>5.78</td>
<td>309</td>
<td>343</td>
<td>398</td>
<td>334</td>
<td>397</td>
<td></td>
</tr>
<tr>
<td>HP61</td>
<td>4940</td>
<td>5.78</td>
<td>309</td>
<td>343</td>
<td>398</td>
<td>334</td>
<td>397</td>
<td></td>
</tr>
<tr>
<td>HP62</td>
<td>28,000</td>
<td>2.5</td>
<td>351</td>
<td>400</td>
<td>484</td>
<td>398</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>HP63</td>
<td>2500</td>
<td>1.7</td>
<td>264, 419</td>
<td>404</td>
<td>533</td>
<td>404</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The fluorescence quantum efficiency was recorded with different standards.
Hyperbranched PPV derivatives with various of 2,5-aromatic substituted alkyl groups and terminal groups were prepared by direct polycondensation of A\textsubscript{2} monomer 31 (2,5-diR\textsubscript{1}O-1,4-bis(bromotriphenylphosphinomethyl)benzene) or 154 (2,5-dimethoxy-1,4-bis(chlorotriphenylphosphinomethyl)benzene) with B\textsubscript{3} monomer 32 (1,3,5-benzenetricarbaldehyde) in the presence of strong base through a Wittig reaction, followed by end group modification of the hyperbranched polymers (Scheme 55). Their photophysical properties were investigated in detail in solution and solid films [276–280]. As shown in Table 7, all the alkyl-substituted products showed a red shift in both the absorption and emission peaks. No significant variations in absorption and emission maxima were detected on increasing the length of the side alkyl groups, while marked difference was observed in their fluorescence quantum efficiency, with the sample with C\textsubscript{5}-alkyl exhibiting the highest $F_f$. On the other hand, the terminal groups of the resulting hyperbranched polymers showed slight or moderate influence on their absorption and emission maxima, but greater influence on the photoluminescence efficiency.

HP49, HP50 and HP51 were used as the active layer in electroluminescent devices. The turn-on voltages of the single- and double-layer light emitting diodes (LEDs) made from HP51 are approximately 6 V, and that of light emitting electrochemical cell with HP50 as active polymers is 3 V [280]. Significant enhancement in the device photoluminescent performance was observed by dispersing HP49 in a linear poly(9-vinylcarbazole) (PVK) matrix, owing to energy transfer between PVK and HP49. For the LED with PVK : HP49 = 5 : 1 as the emitting layer, bright blue emission up to 810 cd/cm$^2$ was achieved at a bias of 24 V, and the maximum transfer efficiency of current density to brightness of the blend polymer devices is as high as 0.27 cd/A, an order of magnitude greater than that of HP49-based single layer devices (0.025 cd/A) [278].

5.1.2. Hyperbranched poly(β,β-dibromo-4-ethynylstyrene)

Fully conjugated hyperbranched polymers and oligomers of β,β-dibromo-4-ethynylstyrene were prepared via a Heck reaction (Schemes 56 and 57). In the presence of triphenylphosphine (TPP), CuI and bis(triphenylphosphine)palladium(II) dichloride, polycondensation of 155 yielded HP52 with a $M_w$ of 70,722 and a PDI of 1.76 [281]. HP52 showed an emission maximum at 500 nm and a shoulder at 460 nm upon excitation at 420 nm. Similarly, blue emission with a peak of 440–500 nm was found for the oligomers of 155 synthesized by stepwise growth when excited at 350 nm. Interestingly, all of the oligomers except 161 exhibited two peaks in their corresponding excitation spectrum [282]. The broader and lower peak close to the absorption peak can be attributed to emission from S\textsubscript{1} state, but the origin for the sharper and higher one located very close to the emission peak is not yet clear.

5.1.3. Hyperbranched poly(arylene/1,1-vinylene)

Dihydridocarbonyltris(triphenylphosphine)ruthenium [RuH\textsubscript{2}CO(PPh\textsubscript{3})\textsubscript{3}] catalyzed self-polycondensation of 4-((trimethylsilyl)ethynyl)acetophenone (162) resulted in a hyperbranched polymer with regularly alternating arylene and 1,1-vinylene units (HP53) by...
catalytic addition of the ortho C–H bonds of acetophenone group to the triple bond of the trimethylsiylethynyl group (Scheme 58). The $M_n$ measured with SEC and $^1$H NMR for HP53 is 1077 and 2400, respectively. HP53 exhibited an absorption peak at 284 nm and fluorescence emission maximum at 450 nm with a $\Phi_f$ of 0.1% [98].

5.1.4. Hyperbranched polyarylenes

Hyperbranched polyphenylenes were first reported as novel hyperbranched polymeric materials [46–49]. Suzuki polycondensation of AB$_2$ monomer 3,5-dibromophenylboronic acid or polymerization of 3,5-dihalophenyl Grignard reagents gave hyperbranched polyphenylenes (Scheme 59). The polymers obtained from the Suzuki Pd(0) catalyzed aryl–aryl coupling reaction had $M_n$ s of 5000–35,000 with PDIs less than 1.5. The resulting hyperbranched polyphenylenes are thermally stable to 550 °C and soluble in many organic solvents such as THF, tetrachloroethane and o-dichlorobenzene although their backbones consist only of rigid aromatic rings. Research on
the potential photophysical properties of the resulting polymers was not reported.

Hyperbranched polyphenylenes with a higher density of benzene rings in one unit can be prepared by Diels-Alder self-[2 + 4]cycloaddition of AB₂ monomers, ethynyl-, propynyl and phenylethynyl-substituted tetraphenylcyclopentadienones, in the presence of tetrabutylammonium fluoride (Bu₄NF) at 180 °C (Scheme 60). The $M_n$'s of the resulting hyperbranched polymers determined by SEC with PS as standards ranged from 3000 to 107,455 with PDI's of 1.66–6.85 [283]. It is notable that polymers with such a high, dense packing of benzene rings are soluble in toluene or benzene. Their potential application as the polycyclic aromatic hydrocarbons has been proposed [284].

Tang et al. [285] successfully prepared soluble hyperbranched polyarylenes containing various side groups as shown in Scheme 61 by copolycyclotrimerization of compounds with double triple bonds and monomers with a single triple bond. The polymerization can be carried out at lower temperature (65 °C) if UV irradiation is employed to activate the Co catalyst. The temperature for 5% weight loss of each polyarylene is higher than 400 °C. The results and photophysical data of the resulting hyperbranched polyarylenes are summarized in Table 7. It is found that the emission properties of the polymers can be tuned by changing the comonomer pairs [286]. The polymer made from 163a and 164b exhibits the highest fluorescence quantum yield (49%) with 9,10-diphenylnaphthacene as the standard. The emission from the polymer with long side chains (HP56) is very weak ($\Phi_f = 9\%$), possibly caused by self-quenching due to absorption in the same spectral region. Because of their excellent optical limiting properties, good thermal stability and processing advantages, these hyperbranched polyarylenes may be useful in the field of functional materials and devices.

5.1.5. Hyperbranched non-linear optical polymers

Compounds possessing donor and acceptor chromophores may exhibit non-linear optical (NLO) properties. The NLO chromophores can be
aligned as shoulder-to-shoulder, head-to-tail, head-to-head, and random. Hyperbranched polymer with 4-(2-cyano-2-methoxy-carbonylviny)aniline as a second-order NLO chromophore was synthesized by Zhang et al. [287] via a one-pot Knoevenagel polycondensation of 4-formyl-\(N,N\)-di(2-hydroxyethyl)aniline (165) and cyanoacetic acid with \(N,N\)-dicyclohexylcarbodiimide (DCC) as a water acceptor and 4-(dimethylamino)pyridine (DMAP) as a base (Scheme 62). The resulting hyperbranched polymer was soluble in polar solvents such as DMF and DMSO, with a \(T_g\) of 86°C, a \(T_d\) of 330°C in air and a \(\eta_{inh}\) of 0.27 dl/g in DMSO at 30°C. Each branched chain of HP60 looks like a head-to-tail main chain backbone, so NLO properties are reasonably anticipated for HP60. The second harmonic generation measurements indicated that the second harmonic coefficient \(d_{33}\) for HP60 was about 2.8 pm/V with a Y-cut quartz crystal plate as a reference \(d_{11} = 0.5\) pm/V.

Carbazole moieties were incorporated into the backbones of hyperbranched polymer starting from 3,6-diformyl-9-(11-hydroxyundecyl)carbazole (166) and cyanoacetic acid (Scheme 63) via a method similar to that employed in the synthesis of HP60. The \(d_{33}\) of the obtained hyperbranched polymer HP61 was found to be higher than that of HP60, reaching 7 pm/V. However, the \(d_{33}\) value is still not large in comparison with linear main-chain polymer containing the similar NLO moieties, attributed to the decreased alignment of the NLO moieties in the hyperbranched macromolecules [288]. Light emitting devices consisting of poly(9-tetradecanyl-3,6-dibutadiynyl-carbazole) as a hole transport layer and HP61 as an electron transport and emitting layer have been fabricated. Strong
emission with the maximum at 480 nm was observed for the double-layered devices.

5.1.6. Hyperbranched coumarin-containing polymers

Coumarines (2H-1-benzopyran-2-ones) are widely used as laser dyes and light emitters because of their good photostability and high quantum yield of photoluminescence (PL). Hyperbranched coumarin-containing polymer (HP62) and copolymers have been prepared by polycondensation of (6-(3-carboxy)coumarinyl)diacetylhydroquinone (167) and by copolymerization of 167 with m-acetoxybenzoic acid in different feed ratios. The polymerization was carried out at 200 °C for 1 h under nitrogen flow, followed by reaction at 330 °C for 1 h more under reduced pressure (0.1 mm Hg), as shown in Scheme 64 [289]. Significantly, the measurements of \(^1\)H NMR suggested that the resulting hyperbranched polymer and copolymers had DBs close to 100%, which might result from the high temperatures of the reaction. Under these extreme conditions, the high mobility of the macro-molecular chains can overcome steric hindrances, enhancing the reaction between acetoxyl and carboxylic acid groups. The coumarin-containing polymers showed \(M_n\)s ranging from 21,000 to 54,000 with PDIs of 2.3–2.7, and \(T_g\)s of 230–160 °C. The \(T_g\) values of the resulting polymers increased on increasing the feed ratio of monomer 167. Fluorescence observations showed that all polymers were blue emitters, in the range 484–497 nm. Measurements of current density–voltage relationships for the single layer electroluminescence (EL) devices with the coumarin-containing polymers as light-emitting material revealed that the higher the content of coumarin units in polymer, the lower turn on voltage.

5.1.7. Hyperbranched polythiophenes

As shown in Scheme 65, light-harvesting hyperbranched polythiophene was prepared by
polycondensation of a Grignard reagent $169$ with Ni(bis(diphenylphosphino)propane)Cl$_2$ as the catalyst. The unsymmetrical $\text{AB}_2$ monomer $169$ was synthesized by treatment of 2,3-dibromothiophene ($168$) with lithium diisopropylamide (LDA) followed by MgBr$_2$ [290]. Determination of SEC with PS as standard and THF as the eluent gave $M_n$ and PDI of the as-prepared hyperbranched polythiophene as 3400 and 1.3, respectively. It was found that the solubility of bromo-terminated product was low, and introduction of the alkyl groups onto the periphery of the polymer improved its solubility. In the structure of end-capped polymer HP63 ($M_n = 2500$, PDI = 1.7), only 2,3 or 2,5-linked thiophene units are conjugated. So a gradient of conjugation lengths exists in a single hyperbranched macromolecule, resulting in a light-harvesting effect, and thus enhanced light emission or intramolecular energy transfer from the less conjugated units to the longest conjugation fragment. Furthermore, the conjugation length increases on increasing the molecular weight of the resulting polymer. A broad absorption band in the range of 220–600 nm appears in the UV spectrum of HP63, consistent with the gradient conjugation structure of the polymer. The emission maximum of HP63 is 533 nm for excitation at 404 nm. Compared with their linear analogs, the hyperbranched polythiophenes have a much broader distribution of conjugation lengths, which makes them potentially better light-absorbing materials for efficient photovoltaic as well as light emitting devices.

In addition to the $p-\pi$ and $\pi-\pi$ conjugation systems described above, a new structural class of $\sigma-\pi$ conjugated hyperbranched poly(2,5-silylthiophenes) has been reported [291]. As outlined in Scheme 66, an $\text{AB}_3$ type monomer, 2-bromo-5-trimethoxysilylthiophene ($170$), was firstly synthesized, followed by addition of $170$ to magnesium turnings in THF, resulting in rapid formation of the Grignard reagent. In situ polymerization of the Grignard reagent gave hyperbranched poly(2,5-silylthiophenes) (HP64). Hyperbranched polythiophenes with different terminal groups were obtained by reaction of HP64 with the appropriate nucleophilic reagents. The resulting hyperbranched polymers have $M_n$s of 4460–6580 determined by SEC and DB of 0.46 calculated from $^1$H NMR spectrum. UV–Vis measurements indicated that a high degree of conjugation through the silicon atoms existed in the polymer backbones, demonstrated by dramatic red-shift of the $\pi-\pi^*$ transitions in the polymers (around 250 nm) in comparison to thiophene (230 nm). In addition, charge transfer from
thiophene to silicon was detected for the polymers, according to their broad absorptions in the 300–320 nm regions.

5.1.8. Hyperbranched polyanilines

Linear polyanilines (PAs) are well known and have been widely studied as a conductive and magnetic polymeric materials. However, the linear polymers and their crosslinked products are hardly soluble in solvent, leading to poor processibility. Soluble PAs can be approached by the introduction of dendritic units into the polymer backbones. To date, soluble hyperbranched polyanilines and their derivatives have been successfully prepared. The AB₂ monomers used to synthesize hyperbranched PAs are shown in Scheme 67. The polymerization of 3,5-dibromoaniline (171) was performed in THF at 90 °C in the presence of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) ligand and 1.1 equivalents of sodium tert-butoxide (tert-BuONa) per amine [292]. The \( M_w \) and PDI determined with SEC in THF for the hyperbranched PA were 7000 and 3.2, respectively. The hyperbranched PA showed magnetic properties similar or superior to that of its linear analogs.

Hyperbranched poly(triphenylamine) was synthesized through aryl–aryl coupling of the AB₂ type Grignard reagent 172 [293]. The resulting hyperbranched polymer was soluble in common organic solvents such as THF and chloroform, and exhibited a new \( \pi-\pi^* \) transition absorption band at 360 nm, possibly resulting from the conjugation between biphenylene units and nitrogen atoms.

Hyperbranched polymers with alternating phenylene sulfide and phenyleneamine units have been designed, but attempts to obtain them by self-condensation of monomer 173 or 174 failed, and polymerization of monomer 175 gave insoluble product [294].

5.2. Polymer electrolytes

A solid polymeric electrolyte should meet the requirements of (1) being amorphous, (2) having a high solvating power for appropriate ions, (3) good ion transport, and (4) electrochemical stability. It is well known that oligo(ethylene glycol) segments satisfy the last three requirements, and hyperbranched polymers are usually amorphous. Thus, hyperbranched macromolecules possessing ethylene glycol (EG) chains have been designed, prepared and used as novel polymeric electrolytes or ion-conducting elastomers. Table 8 lists the monomers used to synthesize hyperbranched polymeric electrolytes and the properties of the resulting materials.

Hawker and coworkers [295] first prepared hyperbranched poly(ether ester)s containing linear EG units of varying lengths in good yields with high molecular weights \( (M_w = 50,000–81,000) \) by polymerization of AB₂ monomers (176, 177, 178) with EG segments. The properties of the hyperbranched polymer derived from hexaethylene glycol \( (n = 5) \)-lithium perchlorate complexes were examined as polymeric electrolytes. It is found that the \( T_g \) values of the complexes obeyed the Di Mario equation for general polymeric electrolytes [295]:

\[
\frac{T_g - T_{g0}}{T_{g0}} = \frac{ac}{1 - ac}
\]

In Eq. (4), \( T_g \) is the glass transition temperature of the polymer–lithium perchlorate complex, \( T_{g0} \) is the glass transition temperature of the salt-free polymer, and \( c \) is the mole ratio of LiClO₄ to repeat unit of polymer, \( a \) is a constant for a specific polymeric electrolyte. DSC measurements showed that \( a \) was equal to 0.049 for the hyperbranched macromolecule-LiClO₄ complex. The ionic conductivity (IC) of the hyperbranched polymeric electrolytes increases with both increasing temperature and concentration of Li⁺, with a value of \( 7 \times 10^{-5} \) S cm⁻¹ being observed at 333 K for [Li⁺] = 0.62 mol per mole repeat EG unit.

Itoh et al. [296] synthesized the AB₂ monomers reported by Hawker via a different chemistry. Bulk
polymerization of 176 or 177 in the presence of a catalytic amount of dibutyltin diacetate at 165 °C under nitrogen gave the hyperbranched poly(ether ester) with Mn of 8800 (made from 176) or 21,000 (made from 177). Then the hydroxyl-terminated hyperbranched polymers were acetylated with acetyl chloride in the presence of triethylamine in dichloromethane at ambient temperature, providing terminal-acetylated hyperbranched poly(ethylene glycol) derivatives containing diethylene and triethylene glycols and 3,5-dioxybenzoate branching units with Tg values of 276 and 259 K, respectively. Again, no evidence of melting transitions was observed in the DSC traces of the acetylated hyperbranched polymers. The IC of the polymeric electrolytes is not only affected by the testing temperature, salt concentration and the chain length of EG, but it is also affected by the sort of salt. Under the same conditions, the polymer with LiN(CF3SO2)2 salt exhibits lower Tg and somewhat higher conductivity compared with that using LiCF3SO3, attributed to the greater mobility of the polymer chains with the LiN(CF3SO2)2 salt because the large and flexible (CF3SO2)2N− ion can act as a plasticizer for the polymer matrix. For the hyperbranched polymer with triethylene glycols-LiN(CF3SO2)2 system, the IC is 4.9 × 10−7 S cm−1 at 30 °C and increases to 4.17 × 10−5 S cm−1 at 80 °C with [Li+]/EG of 1.2.

The influences of the terminal groups, the length of the EG unit, the composites of the linear polymeric electrolytes blended, and the addition of filler on the properties of the hyperbranched polymeric electrolytes were systematically investigated by Itoh and coworkers [297–301]. By compared with hyperbranched poly[bis(diethylene glycol)benzoate] capped with acetyl groups (HP65 in Scheme 68), hyperbranched poly[bis(diethylene glycol)benzoate] capped with 3,5-bis[(3′,6′,9′-tri-oxodecyl)oxy]benzoyl groups (HP66) exhibited higher ionic conductivity (7 × 10−4 S cm−1 at 80 °C and 1 × 10−6 S cm−1 at 30 °C) in the salt of LiNi(CF3SO2)2 [297]. The hyperbranched HP66 electrolyte showed an electrochemical stability window of 4.2 V at 70 °C and was stable until 300 °C. Increasing the length of EG

Table 8
The monomers and salts used in the preparation of ion-conducting materials.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Salt</th>
<th>Tg (K)</th>
<th>IC × 10^5 (S cm−1)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>176: n = 1; 177: n = 2; 178: n = 5</td>
<td>LiClO4</td>
<td>255 (n = 1), 268 (n = 2), 234 (n = 5)</td>
<td>7.0 (333 K), 1.0 (303 K)</td>
<td>[295]</td>
</tr>
<tr>
<td>176: n = 1; 177: n = 2; 178: n = 5</td>
<td>LiCF3SO3</td>
<td>276 (n = 1), 259 (n = 2)</td>
<td>4.17 (353 K), 0.05 (303 K)</td>
<td>[296–301]</td>
</tr>
<tr>
<td>179: n = 0; 180: n = 1</td>
<td>LiClO4</td>
<td></td>
<td>63.0 (333 K), 0.66 (293 K)</td>
<td>[303]</td>
</tr>
</tbody>
</table>
segments in the terminal-acetylated macromolecular unit to 6 \( n = 5 \), resulted in a hyperbranched polymer electrolyte with \( \text{LiN(CF}_3\text{SO}_2)\text{)}_2 \) had a maximum conductivity of \( 9 \times 10^{-5} \text{ S cm}^{-1} \) at 80 °C with a \([\text{Li}^+] / [\text{repeat unit}] \) ratio of 0.6. Interestingly, addition of hyperbranched HP65 to the system of linear PEO and \( \text{LiN(CF}_3\text{SO}_2)\text{)}_2 \) salt can also improve the lithium ionic conductivity and lithium/electrolyte interfacial performance. The blend-based polymer electrolyte with a HP65/PEO ratio of 20/80 in wt% and \([\text{LiN(CF}_3\text{SO}_2)\text{)}_2]_0.125 \) showed a extremely high ionic conductivity (8.1 \( \times 10^{-4} \text{ S cm}^{-1} \) at 80 °C and 3.8 \( \times 10^{-5} \text{ S cm}^{-1} \) at 30 °C), with an electrochemical stability of about 4.9 V [298,299].

Composite polymer electrolytes based on PEO, HP65, BaTiO\(_3\) (as a ceramic filler), and \( \text{LiN(CF}_3\text{SO}_2)\text{)}_2 \) salt were fabricated, and investigated as the electrolyte for all solid-state lithium polymer batteries. The optimized composite polymer electrolyte, \([\text{PEO-20 wt% HP65}\text{)}_2]_0.125\) showed a extremely high ionic conductivity (8.1 \( \times 10^{-4} \text{ S cm}^{-1} \) at 80 °C and 3.8 \( \times 10^{-5} \text{ S cm}^{-1} \) at 30 °C), with an electrochemical stability of about 4.9 V [298,299].

Amphiphilic hyperbranched polyglycerols (PGs) with a hydrophilic core and a hydrophobic shell were prepared via solvent casting method. It was observed that both nanosized fillers improved the mechanical properties, ionic conductivities and lithium ion transference numbers of the hyperbranched polymer electrolytes. The \( \alpha\)-LiAlO\(_2\) filler was more effective for improving the electrochemical compatibility with a lithium metal electrode, while the \( \gamma\)-LiAlO\(_2\) filler was more efficient in enhancing the mechanical properties of the hyperbranched polymer-based electrolytes [301].

Hong et al. [302] synthesized hyperbranched polyurethanes with EG units by polycondensation of \( \text{AB}_2 \) monomers 3,5-bis(2'-hydroxy ethanoyl)benzoyl azide (179) and 3,5-bis(5'-hydroxy-3'-oxopentyl)oxy]benzoyl azide (180), and prepared composite polymer electrolytes using hyperbranched polyurethanes, linear polyurethanes and \( \text{LiClO}_4 \) as raw materials. The IC of the composite electrolytes could approach 1.35 \( \times 10^{-6} \text{ S cm}^{-1} \) at 25 °C and 1.74 \( \times 10^{-5} \text{ S cm}^{-1} \) at 60 °C for a ratio of \([\text{Li}^+] / [\text{EG}] \) \((c) \) equal to 1/4.

The hyperbranched poly(2,3-dihydroxypropyloxyl) (PG) made from monomer 19 was also applied as a substrate for the composite polymer electrolyte with \( \text{LiClO}_4 \) salt [303]. The IC of the composite reached 6.6 \( \times 10^{-6} \text{ S cm}^{-1} \) at 20 °C and 6.3 \( \times 10^{-4} \text{ S cm}^{-1} \) at 60 °C.

Nishimoto et al. [304] prepared ethylene oxide-based network polymer electrolytes with hyperbranched ether side chains. The highest IC of the electrolytes approached 1 \( \times 10^{-7} \text{ S cm}^{-1} \) at 30 °C and 1 \( \times 10^{-5} \text{ S cm}^{-1} \) at 80 °C with lithium bis(tri-fluoromethyl) imidazolium (LiTFSI) as the salt.

5.3. Nanomaterials and biomaterials

5.3.1. Nanomaterials

Hyperbranched polymers and their substitutes can be used as nanomaterials for host–guest encapsulation and the fabrication of organic–inorganic hybrids, and even directly used as nanoreactors for some reactions. Amphiphilic hyperbranched polyglycerols (PGs) with a hydrophilic core and a hydrophobic shell were prepared by partial esterification of the pre-synthesized hyperbranched PG with a fatty acid such as palmitoyl
chloride in the presence of pyridine, as shown in Scheme 69 [305]. Water-soluble dyes such as Congo red, bromophenol blue and rose Bengal can be encapsulated irreversibly into the amphiphilic core–shell nanocapsules via phase transfer from the water phase to the organic phase (CHCl₃). UV–Vis measurements for the encapsulated nanoobjects revealed that the dye was quantitatively extracted from the aqueous layer into CHCl₃ if the dye concentration was lower than the saturation concentration. The average encapsulation maximum depended mainly on two factors: the molecular weight of the hyperbranched core and the length of the alkyl chains attached to the polymer scaffold. Interestingly, the degree of substitution of terminal groups had only a small influence on the encapsulation maximum. By variation of the factors mentioned above, the encapsulation maximum can be adjusted in the range of 0.7–2.7 dye molecules per polymer molecule. Although the encapsulation is irreversible, some chemical reactions can still take place in the encapsulated core in the organic phase. Comparison of these results with those obtained from the linear analogs suggests that the hyperbranched topology plays a crucial role in the supramolecular encapsulation [306].

Encapsulation of sulfonated pincer-platinum(II) complexes into amphiphilic nanocapsules was also realized [307]. The incorporated Pt(II) complexes showed catalytic activity in a double Michael addition for homogeneous catalysis. Furthermore, PdCl₂ or Pd(OAc)₂ were successfully encapsulated into nanocapsules based on hyperbranched PG [308]. Stable solutions of Pd colloids were prepared through reduction of Pd(II) in organic solution. The metal particle size increased with increasing the molecular weight of the hyperbranched polymer. The metal colloids were catalytically active.

Compositions of hyperbranched PPVs containing different side alkoxy groups with nanosized cadmium sulfide (CdS) were prepared and investigated using static and dynamic fluorescence spectroscopies and AFM [309]. Electrostatic force plays a key role in the behavior of these compositions, with the interaction between PPV and CdS particles controlled by the chain length of side alkoxy groups. The presence of hyperbranched PPV can efficiently decrease the self-aggregation of nanosized CdS particles.

Hyperbranched polymer layered silicate nanocomposites were made using a hydroxy-terminated hyperbranched polyester (HP67 in Scheme 70), prepared by condensation of 2,2-bis-hydroxymethyl propionic acid (bis-MPA) with a tetrafunctional ethoxylated pentaerythritol core as the organic phase and sodium montmorillonite (Na⁺MMT) as inorganic silicate layers in deionized water [310]. WAXS measurements showed that the silicate layer basal spacing could be increased from 2.5–2.8 nm to 3.6–3.9 nm by increasing the molecular weight of the hyperbranched polyester (1.06 nm for the as-received Na⁺MMT). Significantly, the nanocomposites can be redispersed in organic solvent and that the functional groups in hyperbranched polymers remain active, as demonstrated by the reaction of the composites with methyl diphenyl diisocyanate to produce a polyurethane network. The initial exfoliated state of the silicate layers did not change on incorporation of the polyurethane.

Hedrick et al. [311] prepared inorganic–organic hybrid materials from NMP solutions of
a precondensed poly(silsesquioxane) (181 in Scheme 70) and the relevant hyperbranched polymers (HP68 and HP69 in Scheme 70) containing 4% water and 2% base. In the hybrids, the content of hyperbranched macromolecules was maintained at about 20 wt%. The thermal stabilities of the composites were comparable to that of the pure inorganic material 181. On the other hand, the nature of the terminal groups of the hyperbranched polymers had a strong effect on the phase separation and morphology of the hybrids. For example, the size scale of phase separated domains was less than 50 nm for trimethoxysilyl-terminated HP69, while that for phenol-terminated polymer was in the order of 1–1.5 μm.

Mesoporous magnetocericamic materials were successfully prepared using a hyperbranched organometallic poly[1,1'-ferrocenylene(n-alkyl)silylene] as precursors (such as HP70 in Scheme 70) [312,313]. It was found that (1) the ceramization yield increased with decreasing alkyl chain length of the hyperbranched polymer precursors; (2) the hyperbranched polysilylmes were superior to their linear analogs with respect to the pyrolytic conversion to inorganic networks and the retention of elemental iron in the ceramic materials; (3) a three-dimensional mesoporous network of nanoclusters can be fabricated with the simultaneous evaporation of volatile organics and agglomeration of inorganic elements in the pyrolysis of HP70; (4) the resulting iron silicide nanocrystals made from HP70 exhibit a high magnetizability and a negligibly small hysteresis loss.

Copolymerization of ε-caprolactone with bis(hydroxymethyl)-substituted ε-caprolactone monomer 21 in a feed ratio of 4/1 in the presence of Sn(Oct)2 gave a hyperbranched aliphatic copolyester with a DB of 0.15 and a molecular weight of 8000 g/mol (PDI = 2.81). The hyperbranched polymers were observed to be superior materials for templating nanostructures in organosilicates, and a porous organosilicate film derived from a hybrid containing 30 wt% polyester with an average pore size of 200 Å had been prepared [314]. As novel templating agents, hyperbranched polymers showed several merits, such as higher solids content solutions, higher polymer compositions in solution and better film quality than obtained with linear and star-shaped polyesters.

Sol–gel processing of both linear and hyperbranched alkoxy-substituted polycarbosilanes of the type ‘[Si(OR)2CH2]n (R = Me or Et)’ led to cross-linked polycarbosilane/siloxane hybrid polymers [315]. The molecular structure of these hybrid gels and their pyrolysis to silicon oxycarbide ceramics has been studied.

Hyperbranched polymers can also be utilized in nanoimprint lithography [316]. A fascinating application of the nanoimprint lithography technique is to
fabricate so-called quantum magnetic disks, comprising single magnetic domain bits surrounded by a non-magnetic material. Lebibet al. [316,317] employed the commercially available hyperbranched poly(amide ester) Hybrane, prepared by polycondensation of cyclic anhydrides with diisopropanolamine as the top imaging resist to control the critical dimension in trilayer nanoimprint lithography. Dot arrays of 100 nm with a critical dimension control accuracy better than 10 nm were fabricated. Magnetic Co dot arrays with different diameters and thickness were made with the same mold. Compared with the frequently used PMMA, the hyperbranched polymer showed higher etch resistance. Recently, the technique has been applied at room temperature and low-pressure, using Hybrane HS2550, a semi-crystalline hyperbranched resist polymer, and a high-density pattern replication with graftings of 75 nm line and spacing has been realized [317].

Hyperbranched polyesters derived from bis-MPA and 4,4-bis(hydroxyphenyl)valeric acid have been used as the matrix polymers for molecular imprinting to cope with the major drawbacks resulted from the conventional crosslinked imprinted polymers [318].

5.3.2. Biomaterials

Because low-cost and well-defined hyperbranched polymers with multifunctional terminal groups and narrow polydispersity are available by improving synthesis methodology and techniques, hyperbranched polymers are receiving increasing attention in biomaterials application [319]. In this field, hyperbranched polymers can play two main roles: biocarriers and biodegradable materials. As carriers, hyperbranched macromolecules can offer their interior or peripheral functional groups to covalently fix bioobjects, or depending on their core–shell architecture, to sequester guest molecules. Some monomers used to prepare hyperbranched polymeric biomaterials are summarized in Scheme 71.
Hyperbranched aromatic polyamides as potential supports for protein immobilization have been prepared by self-condensation of AB$_2$ monomers 182 and 183, or by polymerization of reactant pairs (A$_2$ + B$_3$, A$_2$ + B$_4$ or A$_3$ + B$_3$, with the corresponding monomers being 22, 24, 184, 185, 186, 187, respectively) [320]. A rigid structure of the resulting hyperbranched polyamides is required for their use as enzyme-supporting materials, particularly in biotechnological processes with high flow rates. Using 1-ethyl-3-(3'-dimethylaminopropyl)carbodiimide hydrochloride as a coupling agent, α-amylase was covalently attached to carboxylic acid-terminated hyperbranched polymers. Evaluation of enzyme activity revealed that the hyperbranched samples with larger ‘holes’ in the structure or higher distance between the trifunctional branching points (e.g. the polymers made from 22 + 186, or 184 + 187) had a greater affinity for the substrate and lower enzymatic activity, while the samples with more compact structure (e.g. the polymers made from 22 + 24, or 22 + 185) showed a weaker substrate affinity and higher catalytic efficiency. Significantly, high bioactivity retention was found for all the samples analyzed three and six months after the binding reaction. Although a decrease of the enzymatic activity was observed for both the immobilized and the free enzyme at pH 4.7 and 9.0, the residual activity of the latter was considerably higher than that of the former at pH 9.0. Therefore, hyperbranched polyamides are suitable potential supports for protein immobilization, and may open new perspectives for the development of enzyme-based bioobjects with tuned binding affinity, structural stability and catalytic capability.

Steroidal ketones have been covalently linked to the periphery hydroxyl groups on a hyperbranched PG polymer support [319].

Park et al. [321] synthesized a hyperbranched polymer having interior tertiary amino groups and biodegradable units by bulk polymerization of monomer 83 in the presence of core moiety 188. The resulting hyperbranched poly(amine ester)s showed $M_n$s of 9100–11,400 determined from SEC with PS standard and DBs of 0.58–0.62 calculated from $^{13}$C NMR spectra. Then the methyl ester-terminated product was modified with benzyl N-(2-hydroxyethyl)carbamate, followed by catalytic hydrogenolysis with H$_2$ over Pd/C, affording primary amino-terminated hyperbranched polymer. It was observed that the hyperbranched poly(amine ester) with terminal amino groups is minimally toxic and shows relatively high transfection efficiency for DNA.

Oligosaccharides with branched architecture are found at natural cell surfaces and in intercellular systems. Chemical synthesis of hyperbranched am nopolysaccharides has been achieved by acid-catalyzed polycondensation of AB$_2$ saccharide monomer 189, with 10-camphorsulfonic acid as a catalyst [322]. The as-prepared hyperbranched polysaccharide was soluble in highly polar organic solvents such as DMF, DMSO and pyridine, but insoluble in the organic solvents of low polarity or water. The $M_n$ of the polymer was 6300 detected with SEC with PS as standard and DMF as eluent. Interestingly, DB of the resulting polymer calculated from $^1$H NMR was found to approach 1. So almost perfect-branched hyperbranched polymer was obtained.

Biodegradable hyperbranched polyesters were prepared through one-pot copolymerization of l-lactide (190) with D,L-mevalonolactone (191), using tin 2-ethylhexanoate as a catalyst [323], or polycondensation of AB$_2$ macromonomer 193 as well as copolymerization of 193 with other macromonomers based on monomer 190, 192 or 194 [324]. Polymerization of 193 in the presence of core moiety 195 gave biodegradable hyperbranched elastomers with a dendrimer-like structure [324,325].

5.4. Supramolecular chemistry

Supramolecules represent compounds beyond molecules, with an order organized by non-covalent interactions. As novel building blocks, hyperbranched macromolecules might play important roles in the following supramolecular areas: (1) self-assembly films and layers; (2) core–shell amphiphiles; (3) self-association objects; (4) macroscopic molecular self-assembly; (5) liquid-crystalline materials; (6) host–guest encapsulation.

An aldehyde-terminated hyperbranched PPV made from monomers 31 and 32 was used as a self-assembling building material [326,327]. The structure of the hyperbranched PPV (HP71) is shown in Scheme 72. The dehydration between aldehyde
groups of HP71 and alcohol groups of a pretreated quartz slide in the presence of DCC resulted in covalently linked films on the substrate. Then ordered homogeneous self-assembled films were obtained in situ by immersing the modified substrate in a chloroform solution of HP71. The morphology and aggregated grain size of the self-assembled objects examined by AFM depended on the immersion time and the HP71 concentration. For a concentration of $3.3 \times 10^{-5} \text{M}$, the average grain size decreased from 143 to 50 nm when the immersion time was prolonged from 1 day to 3 days. Investigations using AFM and spectroscopy techniques showed that the self-assembly film linked through covalent bond was more homogenous and stable than the spin-coated film. Excimers of HP71 were observed for the self-assembled film, indicating strong interactions between the excited state of the hyperbranched macromolecules in the solid state.

Tang and coworkers [328–330] prepared hyperbranched polyester with carboxylic end groups by polycondensation of 5-hydroxyethoxyisophthalic acid (196) with Zn(OAc)$_2$ as a catalyst (Scheme 73). Self-assembled films were successfully formed via an electrostatic layer-by-layer adsorption approach [331], from both aqueous solution and water–THF mixture, using poly(diallyldimethylammonium chloride) as a polycation and HP72 as a polyanion with a freshly treated quartz slide as the substrate [328]. The self-assembly procedure was monitored by UV–Vis spectroscopy and contact angle measurements. A linear relationship was observed between the absorbance at 215 nm and the number of bilayers, suggesting the same thickness for each assembled bilayer. After four dipping cycles, the contact angle of the surface increased from around 10–20 to 55°, indicating a dramatic change of the surface hydrophilicity.

Pyrene-labeled hyperbranched amphiphiles with hydrophilic core and hydrophobic shell were prepared by reaction of hyperbranched poly(sulfone amine), HP18, with 4-(1-pyrene)butyryl chloride (197), and then with palmitoyl chloride in the presence of triethylamine, as shown in Scheme 74 [332]. Fluorescence characterization exhibited that the core–shell amphiphiles could self-associate to form micelles in aqueous solution, with the excimer-to-monomer intensity ratio ($I_E/I_M$) increasing with increasing attached palmitoyl units. The critical association concentration (CAC) for the hyperbranched amphiphiles is 2–5 g/l at pH < 7, or 2–3 g/l in a basic solution ($\text{pH} = 8.5$). Moreover, the hyperbranched poly(sulfone amine)s without the hydrophobic shell can associate in aqueous solution through hydrogen bonds, as monitored with both fluorescence label and probe techniques [333,334]. Significantly, the self-association ability of the hyperbranched polymers depends on their DBs, with the tendency for association in increasing with the DB [333]. This phenomenon may be partially attributed to the different architecture of hyperbranched poly(sulfone amine)s with various DBs, and partially to different inter- and intra-molecular hydrogen bonds in the hyperbranched macromolecules.
Pyrene-labeled hyperbranched poly(ethylene imine) (PEI) containing different amounts of pyrene per polymer was prepared by reaction of PEI with 1-pyrenecarboxaldehyde [335]. The interaction of the as-prepared pyrene-labeled PEI with the anionic surfactant SDS in aqueous solution was also studied by steady-state fluorescence [336]. The monomer emission of pyrene increased with increasing SDS concentration, indicating that the SDS molecules protect pyrene fluorescence from quenching by forming a polymer-bound micelles at the sites of the pyrene groups.

An example of a non-covalent hyperbranched polymer formed by self-assembly of AB$_2$ monomer via coordination interactions is given in Scheme 75, where the counter anion X$^-$ is BF$_4$$^-$, ClO$_4^-$$,$ CF$_3$SO$_3^-$$,$ p-MeC$_6$H$_4$SO$_3^-$$,$ or BPh$_4^-$. Removal of acetonitrile through repeated evaporation and redissolving the residue in nitromethane leads to intermolecular coordination between cyano groups and Pd, forming hyperbranched coordination polymer HP73 [337]. Quasi-elastic light-scattering, AFM and transmission electron microscopy revealed that the size of the assembled hyperbranched spheres changed from 100 to 400 nm with variation of the building block structure and/or the counter anions.

Both thermotropic liquid crystalline hyperbranched polyesters [338–341] or polyethers [52, 53] and lyotropic liquid crystalline hyperbranched polyamides [79–82,159,342] made from AB$_n$ monomers or specific monomer pairs have been achieved, and their supramolecular behaviors have been studied. Scheme 76 listed some AB$_2$ monomers used to synthesize thermotropic liquid crystalline hyperbranched polymers.

Because of the three-dimensional character of hyperbranched macromolecules, some guest molecules can be encapsulated into their interior cavities. Therefore, hyperbranched polymers can be applied in the supramolecular encapsulation

![Scheme 74](image1)

![Scheme 75](image2)
as host macromolecular boxes. The related contents have been mentioned in the ‘nanomaterials’ section of this article.

5.5. Patterning of hyperbranched polymer films

Patterning of polymer films at micron or even submicron resolution is of critical technological importance in the microelectronics industry [343]. Because hyperbranched polymers have many functional groups, moieties with interesting optical, electrochemical, biological, and mechanical properties can be incorporated into the hyperbranched polymer films. Thus, patterning of hyperbranched polymer films on the substrates is receiving more and more attention. Related techniques including template-based approach and photolithography have been developed by Crooks and coworkers [343–346]. The templates consist of self-assembled monolayers fabricated by micro-contact printing (μCP) [347,348], while photolithographic patterning relies on a photomask.

Two typical approaches to pattern hyperbranched polymer films on a substrate are outlined in Fig. 8. The μCP (approach A) consists of three key steps: (1) applying CH₃(CH₂)₁₅SH (C₁₆SH) to the poly(dimethylsiloxane) (PDMS) stamp, followed by patterning of the Au substrate by manual application of the stamp to the surface for a short time; (2) exposing the C₁₆SH-patterned substrate to a 1 mM ethanolic solution of HOOC(CH₂)₁₅SH (MUA) for 1 min; (3) activating the carboxylic acid groups of the MUA-patterned portions by a reaction with a mixed anhydride and then α,ω-diamino-terminated poly(tert-butyl acrylate) (H₂NR-PTBA-RNH₂), subsequent hydrolyzing of the grafted PTBA layer with MeSO₃H to afford the first layer of PAA (1-PAA), and yielding a hyperbranched PAA films after two more cycles of activation, grafting and hydrolysis. As a consequence, the resulting polymer pattern is a negative image of the stamp. On an inorganic substrate such as Au, polymer layers with a thickness of 25 nm and critical lateral dimensions in the order of 1 μm can be patterned through the μCP approach. The method has been extended to pattern hyperbranched polymer films on
organic substrate such as PE [345]. Significantly, the fidelity of the underlying hyperbranched PAA patterns is still maintained after grafting PEG on the PAA films [347,348]. As pointed out by Crooks [343], however, this approach has some disadvantages although it is a fast, and flexible method for patterning polymer surface. For example, the performance of multiple patterning steps on a single substrate is very difficult, and it is inconvenient to prepare a patterned surface having two sorts of polymers with the \( \mu \)CP.

A method based on photolithography was developed to resolve the problems arising from the template-based approach. For example, patterning of multiple fluorescent dyes on hyperbranched PAA thin films was achieved using photoacid-based lithography (approach B) via three steps [349]: (1) covalent grafting of hyperbranched PTBA thin films on a Au substrate and then overcoating the polymer films with a layer of photoacid, (2) utilization photolithography to generate acid in the exposed region and catalyzed hydrolysis of PTBA to form PAA, and (3) chemical modification of the PAA regions with dyes. The patterns fabricated can serve as templates to segregate viable mammalian and bacterial cells. Consequently, preparation of more complex structures by the patterning approaches is anticipated, such as ensembles of organized tissues, including nerves and blood vessels.

5.6. Coatings

Hyperbranched polymers have been used as the base for various coating resins, such as powder coatings [350,351], high solid coatings [352], flame retardant coatings [353] and barrier coatings for flexible packaging [354], depending on their high solubility, low viscosity and abundant functional groups.

The most widely studied hyperbranched polymers in the field of coatings are the two products commercially available at the time of this review: Boltorn™ (hyperbranched aliphatic polyesters) [350, 352,354–358] and Hybrane™ (hyperbranched polyether-amides) [351,359]. For the purpose of UV-curing, the hyperbranched polymers are generally end-capped with methacrylate or acrylic groups [352–358,360]. Resins based on hyperbranched polymers have lower viscosities and higher curing rates than those of linear unsaturated polymers.

5.7. Modifiers and additives

Based on their unique properties, hyperbranched polymers can be applied as tougheners for thermosets [361–369], curing, cross-linking or adhesive agents [370–372], dye-receptive additives for polyolefins [373,374], compatibilizers [375], dispersers [376], processing aids, and rheology modifiers or blend components [48,377–383]. Table 9 lists some hyperbranched polymers and their applications.

The Boltorn™ three-generation hyperbranched polyesters can act as outstanding tougheners in epoxy matrix composites, and they can induce more than a two-fold increase in the critical strain energy release rate \( G_{IC} \) for both low and highly cross-linked matrices, without affecting either the viscosity of the uncured resins or the thermomechanical properties of the cured material. Until now, no other modifiers could meet the challenges of property improvement without loss of the general performance of the resin system [361]. A quantitative thermodynamic theory model for the prediction of phase equilibrium behavior of thermoset-reactive modifier polymer blends has also been suggested [366,384]. However, the Boltorn™ hyperbranched polyesters cannot provide more efficient toughness for bismaleimide (BMI) thermosets than a linear low molar mass thermoplastic [363,364].

As early as 1992, Kim and Webster [48] had pointed out that hyperbranched polymers could be useful as polymer rheology control agents, and the melt viscosity of PS blend decreased dramatically after addition of a trace amount (about 5%) of bromo-terminated hyperbranched polyphenylene to the PS blending system, without affecting the thermal stability of PS. Mulkern et al. [379] reported that Boltorn™-G4 is an excellent processing additive for PS. The hyperbranched polyesters behave as lubricants during processing, and as self-compatibilizing toughening agents in the final formation of the blend. A considerable drop in the blend viscosity of PS or styrene maleic anhydride (SMA) copolymer was immediately observed in addition of the hyperbranched polymer modifier.
In the tubular film blowing process of linear low-density polyethylene (LLDPE), Boltorn™-H30 hyperbranched polyester successfully acted as a processing aid, and sharkskin was eliminated with no significant influence on other physical properties of the LLDPE films [378]. In processing, the hyperbranched polymer has a tendency to migrate to the surface, leading to a hyperbranched polymer-rich surface, which creates the opportunity to tailor the surface properties for various potential applications.

PP is a versatile and widely used polymeric material. However, PP does not accept dyes, owing to its non-polar structure as well as its high crystallinity, resulting from the high stereo-regularity of the PP. The dyeability of PP with CI. Disperse Blue 56 can be markedly enhanced through the incorporation of hyperbranched macromolecules such as the Hybrane PS2550 (hyperbranched polyester-amide) into PP prior to fiber spinning [373]. The amphiphilic hyperbranched aromatic polyester prepared by polycondensation of 3,5-dihydroxybenzoic acid followed by end group modification with dodecanoyl chloride can also be used as a dye carrier in blends of PP or high-density polyethylene (HDPE), with similar

<table>
<thead>
<tr>
<th>Hyperbranched polymer</th>
<th>Role</th>
<th>Blended compound</th>
<th>References</th>
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<tbody>
<tr>
<td>Boltorn™</td>
<td>Toughener</td>
<td>Epoxy resins</td>
<td>[361,367]</td>
</tr>
<tr>
<td></td>
<td>Toughener</td>
<td>Bismaleimide</td>
<td>[363,364]</td>
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<td></td>
<td>Toughener</td>
<td>Vinylyster–urethane hybrid</td>
<td>[368,369]</td>
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<tr>
<td>Modifier</td>
<td>PS/PS–SMA</td>
<td></td>
<td>[379]</td>
</tr>
<tr>
<td>Modifier</td>
<td>Diglycyl ether of bisphenol-A</td>
<td></td>
<td>[381]</td>
</tr>
<tr>
<td>Processing aid</td>
<td>LLDPE</td>
<td></td>
<td>[377,378]</td>
</tr>
<tr>
<td>Compatilizer</td>
<td>PP/PA-6 blends</td>
<td></td>
<td>[375]</td>
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<tr>
<td>Curing additive</td>
<td></td>
<td></td>
<td>[370]</td>
</tr>
<tr>
<td>Hybrane PS2550</td>
<td>Processing aid</td>
<td>PET</td>
<td>[380]</td>
</tr>
<tr>
<td></td>
<td>Dyeing additive</td>
<td>PP</td>
<td>[373]</td>
</tr>
<tr>
<td></td>
<td>Dye carrier</td>
<td>PP/PE</td>
<td>[374]</td>
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<tr>
<td>Disperser</td>
<td></td>
<td>Carbon nanotube</td>
<td>[376]</td>
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<td>Processing aid</td>
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<td>PC</td>
<td>[382]</td>
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<td></td>
<td></td>
<td>bis(maleimide)</td>
<td>[383]</td>
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dynamic–mechanical behavior of the blends compared to that of the pure polyolefins [374].

To understand the physical properties of hyperbranched macromolecular blends, the melt and solution rheological behaviors of polymer blends containing hyperbranched polymers with different molecular weights or generations were investigated [385–388]. Study of the rheological features of melt processed hyperbranched polyesters (Boltorn Hx series dendritic polymers) and their blends indicated that the lower generation samples showed shear-thinning behavior, while the higher generation ones exhibited Newtonian behavior. Blends consisting of two hyperbranched polyesters showed only Newtonian characteristics in both steady shear and oscillatory shear conditions if at least one of the components behaved as a Newtonian fluid [385].

5.8. Other applications

Applications of hyperbranched polymers for gas and solution separation as well as chemical sensors have been suggested.

Hyperbranched polyimides were used as gas separation materials [389]. The synthesis route and chemical structure of the hyperbranched polyimides used are shown in Scheme 4. By controlling the monomer feed ratio and manner of the monomer addition, both amine-terminated and dianhydride-terminated polyimides were obtained. Reaction of the terminal groups with a difunctional crosslinking agent afforded hyperbranched polyimide films. The gas permeability coefficients of the as-fabricated films were mainly affected by three factors: (1) the nature of terminal groups of hyperbranched polymer; (2) the crosslinking density of the film; (3) the ‘flexibility’ of crosslinking agent. The amino terminal groups, lower crosslinking density and ‘rigid’ crosslinking agent (e.g. terephthaldehyde, TPA) were favorable to improved gas permeability coefficients. A better separation performance was obtained for the TPA-crosslinked hyperbranched polyimide membranes than for their linear analogs or many other linear polymeric membranes. For example, one amine-terminated hyperbranched polyimide membrane crosslinked with TPA exhibited fairly high CO₂/N₂ separation performance and good selectivity, i.e. \( P_{\text{CO}_2} = 65 \) barrier and \( P_{\text{CO}_2}/P_{\text{N}_2} = 30 \) at 1 atm and 35 °C.

Hyperbranched PG, hyperbranched polyester Boltorn™-H20, hyperbranched poly(ester amide) Hybran H1500, made from 1,2-cyclohexanedicarboxylic anhydride and diisopropanolamine, and hyperbranched poly(ester amide) Hybrane S1200, made from succinic anhydride and diisopropanolamine, are potentially useful in extractive distillation and solvent extraction [390,391]. It was found that hyperbranched polyglycerol and Hybrane S1200 had remarkable separation efficiencies for the ethanol–water azeotropic mixture.

Melt polycondensation of AB₃ monomers 3,5-trimethylsiloxyl benzoyl chloride, 3,5-diacetoxy benzoic acid, and 5-acetoxyphthalic acid resulted in three hyperbranched polyesters with the same backbones and different end groups (e.g. OH, COOH, and OAc). The hyperbranched polyesters proved to be promising materials for chemical sensors, able to calibrate and discriminate a series of alcohols and different halogenated hydrocarbons [392]. In addition, Bergbreiter and Crooks [393] reported a polymeric ‘molecular filter’ for chemical sensors, consisting of hyperbranched PAA films and β-cyclodextrin receptors.

6. Concluding remarks

In spite of the fact that highly branched topologies and patterns have been widely observed in both abiotic system and the biological world for tens of billions years, intentionally synthesized hyperbranched polymers still represent a new kind of material with promising, attractive properties and potential applications. Until now, hyperbranched macromolecules could be approached through SMM and DMM. In SMM, one type of ABₙ or latent ABₙ molecules is adopted as the raw monomers. As a consequence, hyperbranched polymers are available via polycondensation of ABₙ monomers, SCVP, SCROP, or PTP. On the other hand, hyperbranched macromolecules also can be prepared by polycondensation of two types of A₂ and B₃ monomers, ‘A₂ + B₃’ methodology, or by polymerization of unsymmetrical monomer pairs based on in situ formation of ABₙ intermediates, CMM. Through
CMM, hyperbranched polymers with alternating specific bonds in the frameworks can be conveniently produced in a large scale, without gelation, opening an avenue for the functionalization and application of hyperbranched polymers.

A hyperbranched polymer can be modified and functionalized from its core to periphery by end capping, terminal grafting, surface growing, hyper-grafting and hybrid blending, achieving tailor-made properties and complex structures. Hyperbranched polymers and their derivatives are potentially useful in the areas of supramolecular chemistry, nanoscience and technology, biomaterials, polymer electrolytes, coatings, additives, optical and electronic materials, and so forth. Because the properties of hyperbranched polymers such as solubility, polarity, capacity, crystallinity, chain entanglement, melt and solution viscosity or rheology, thermal stability as well as rigidity (glass transition temperature) can be tailored, more and more fascinating materials and devices based on hyperbranched polymers will be successfully developed and fabricated in the future.

However, one should recognize that extensive research of hyperbranched polymers, particularly the aspect of functionalization and application, is still in its infancy, and the main object to apply hyperbranched polymers in industry fields is still a dream. Thus, the opportunities for development space are unlimited.

From our point of view, the following directions deserve attention in the near future: (1) development of new synthesis strategies and approaches based on low cost for the whole system and good control of the process and product; (2) preparation of novel highly branched polymeric materials with hybrid architectures via covalent linking or supramolecular self-assembling (e.g. to obtain linear-hyperbranched, hyperbranched–hyperbranched, hyperbranched–polymer brush, or hyperbranched–dendritic hybrid materials); (3) tailoring the properties of hyperbranched macromolecules by living polymerization, inorganic–organic blending, molecular encapsulation, and other methods and techniques; (4) the opening of new interdisciplinary application fields for hyperbranched polymers, especially fields combining hyperbranched polymers with nanotechnology, micro-device technology, biology, supramolecular chemistry, or single-molecule science.

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References


Hong CY, Pan CY. Synthesis and characterization of hyperbranched polyacrylates in the presence of a tetrafunctional initiator with higher reactivity than monomer by self-condensing vinyl polymerization. Polymer 2001;42:9385–91.


Yan D, Gao C. Hyperbranched polymers made from A
Emrick T, Chang HT, Fréchet JMJ. An A2
Jikei M, Chon SH, Kakimoto M, Kawauchi S, Imase T,
Malmström E, Hult A. Hyperbranched polymers: a review.
Hobson LJ, Harrison RM. Dendritic and hyperbranched
Gao C, Yan D. Polyaddition of B2 and BB2 type monomers to
Emrick T, Chang H-T, Fréchet JMJ. The preparation of
Aharoni SM. Gelled networks prepared from rigid fractal
Aharoni SM, Murthy NS, Zero K, Edwards SF. Fractal nature
van Benthem RATM, Meijerink N, Gelade E, de Koster CG,
Froehling P, Brackman J. Properties and applications of
Gao C, Yan D. Polyaddition of 1-(2-aminoethyl)perazine to
Gao C, Yan D. Hyperbranched polymers made from commercially
Gao C, Yan D. Polyaddition of B2 and BB2 type monomers to
A2 type monomer. 1. Synthesis of highly branched
Gao C. Molecular design, preparation, characterization and
Froehling P, Brackman J. Properties and applications of
poly(propylene imine) dendrimers and poly(ester amine)s
van Benthem RATM, Meijerink N, Gelade E, de Koster CG,
Muscat D, Froehling PE, Hendriks PHM, Vermeulen CIAA,
Zwartkruis TJG. Synthesis and characterization of bis(2-
Emrick T, Chang H-T, Fréchet JMJ. The preparation of
hyperbranched aromatic and aliphatic polyether epoxies by chloride-catalyzed proton transfer polymerization from ABn,
Fang J, Kita H, Okamoto K. Hyperbranched polyimides for
Chen H, Yin J. Preparation of fully imidized hyperbranched photosensitive polyimide with excellent organosolubility and thermal property based on 4,4-[(hexafluorosisopropylidene) diphthalic anhydride (A2) and 1,3,5-tris(4-aminophenoxy)-benzene (B3). Polym Bull 2003;49:313–20.
Nishimura T, Maeda M, Nitadori Y, Tsuruta T. Synthesis and copolymerization of a polyanime macromer: molecular


[251] Hayashi S, Fujiki K, Tsukobokawa N. Grafting of hyperbranched polymers onto ultrafine silica: postgraft


Soraru GD, Liu Q, Interrante LV, Apple T. Role of precursor molecular structure on the microstructure and high temperature stability of silicon oxycarbide glasses derived from...


[346] Ghosh P, Lackowski WM, Crooks RM. Two new approaches for patterning polymer films using templates


[381] Ratna D, Simon GP. Thermomechanical properties and morpho-logy of blends of a hydroxy-functionalized hyper-


