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A review of hyperbranched polymers: their history, synthesis methodology and general applications

Nabeel H. Al-Mutairi[1*] (*orcid id: 0000-0001-5923*)
Ali Al-Zubiedy[1] (*orcid id: 0000-0002-2041-2737*)
Ali J. Al-Zuhairi[1] (*orcid id: 0000-0003-0764-4899*)
Magdalena Mazur[2] (*orcid id: 0000-0003-3515-8302*)
[1] University of Babylon, Iraq
[2] Czestochowa University of Technology, Poland

Abstract: Over the past two decades, hyperbranched polymers (HBPs) have been an interesting material for many researchers due to their unique physical and chemical properties. The purpose of this article is to review hyperbranched polymers, their history, their synthesis methodologies and their main applications. It was found that the first hyperbranched polymer was synthesized in the 19th century by Berzelius and since then several researchers have prepared other hyper-branched polymers. In addition, there are many methods for the synthesis of hyperbranched polymers, both simple and complex. There are also several applications of these polymers, ranging from construction and building materials to biomaterials. The structure of polymers is responsible for a wide range of material properties. These properties allow the use of polymer materials in the design of building and industrial structures.

Keywords: hyperbranched polymers, polycondensation, SMM, DMM, sensors, construction polymers

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Introduction

Staudinger introduced the two main architectural classes in the field of polymer science, (I) linear topologies like those found in thermoplastics and (II) crosslinked architectures like those found in thermosets, about 50 years after the “macromolecular hypothesis” was first put forth (Frechet & Tomalia, 2001).

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[*] Corresponding author: mat.nabeel.msc@uobabylon.edu.iq

As indicated in Figure 1, four key domains can now be identified and classified based on their characteristics and architectural styles:

I. Thermoplastics with linear, random coils, like nylon or plexiglass.
II. Crosslinked thermosets, like epoxies or rubbers.
III. Long chain branching-based branched systems in polyolefins like poly(ethylene) low-density and other similar branched topologies.
IV. Dendritic polymers, which can be divided into three groups based on how much structural control they have, including (a) random hyperbranched polymers, (b) dendrigraft polymers, and (c) dendrimers.

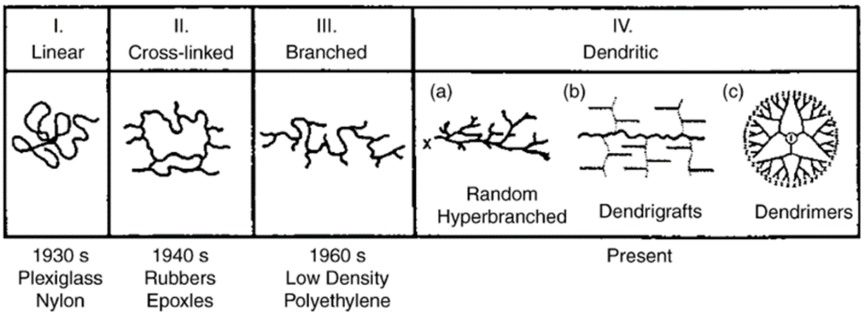


Fig. 1. The main macromolecular architectures of polymers (Frechet & Tomalia, 2001)

Highly branching macromolecules with a three-dimensional structure are referred to as dendritic polymers. The family of dendritic polymers is segmented as follows and is known as the fourth main type of polymers, following the more conventional linear, branched, and cross-linked macromolecules: Dendrons and dendrimers, linear--dendritic hybrids, dendrigrafts and dendrimer-like polymers, dendronized polymers, hyperbranched polymers brushes, hyperbranched polymer, linear macromolecules with hyperbranched polymer grafts and hyperbranched polymer-like macromolecules are just a few examples (Fig. 2) (Testud, 2015).

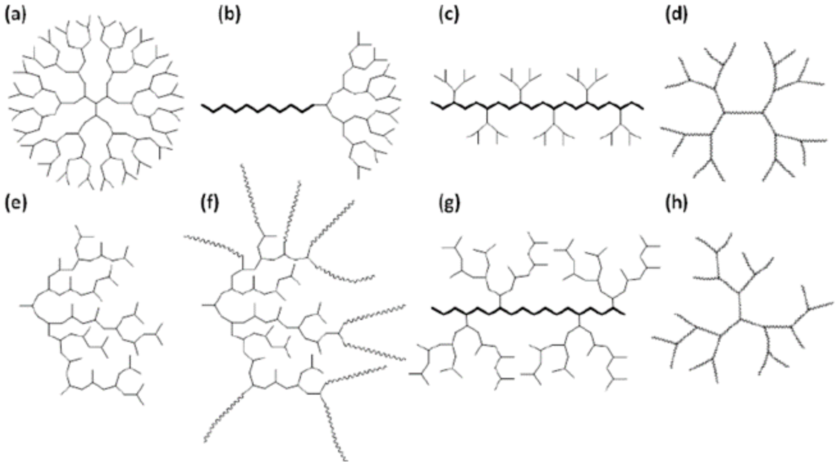


Fig. 2. The different structures of dendritic polymers (Testud, 2015)

A significant class of hyperbranched polymers are the hyperbranched polyesters (HBPEs) and the accessibility of low-cost raw materials has led numerous research teams to thoroughly examine HBPEs. Under the trade name Boltorn®, Perstorp has conducted considerable research on and marketed aliphatic HBPEs based on dimethylol propionic acid. Aromatic HBPEs have a higher melt point and glass transition temperature (Tg) than aliphatic HBPEs because of their significant aromaticity and stiffness (Voit, 2005). In general, aromatic HBPEs cannot be employed directly, but changing the end groups makes it simple to change their properties, which expands the variety of possible applications. Numerous sectors, including non-linear optics, mixtures, coatings and sensors, use aromatic HBPEs and their derivatives.

1. Hyperbranched polymers history

The development of a resin employing tartaric acid (A_2B_2 monomer) and glycerol (B3 monomer) by Berzelius at the end of the 19th century (Kienle & Hovey, 1929) is credited with the discovery of hyperbranched polymers. Following Smith's 1901 research, Kienle et al. (1939a) investigated the reaction between phthalic anhydride (latent A_2 monomer) or phthalic acid (A_2 monomer) and glycerol (B_3 monomer) in further detail. The findings and recommendations they came to are still in use today. According to Kienle et al. (1939b), samples made from phthalic anhydride and glycerol, for example, displayed lower specific viscosities than the various synthetic linear polymers provided by Standinger.

In order to determine the molecular-weight distribution of linear polymers, Flory (1941a; 1941b) created the words "degree of branching" and "highly branched species" in the 1940s. Flory proposed that multifunctional monomers, such as a monomer with one A functional group and two or more B functional groups capable of reacting with A (ABn monomer, n2) could be polycondensed to produce highly branched polymers without gelation in his renowned book: Principles of Polymer Chemistry, which was published in 1952. Since Flory believed that these polymers would result in materials with insufficient mechanical strength, he did not see the benefit of researching this area of study at the time (Flory, 1952).

2. Methodology for hyperbranched polymers synthesis

Now, in addition to the standard Flory method using ABn monomers, the synthetic strategy utilized to create hyperbranched polymers is widened to include versions of certain new synthetic processes. Depending on the type of monomers used, there are two types of synthetic processes. The single and the double monomer methodology (SMM, DMM). Figure 3 show a flow chart for this process and their branches (Chang & Fréchet, 1999; Frechet et al., 1995; Suzuki et al., 1992;).

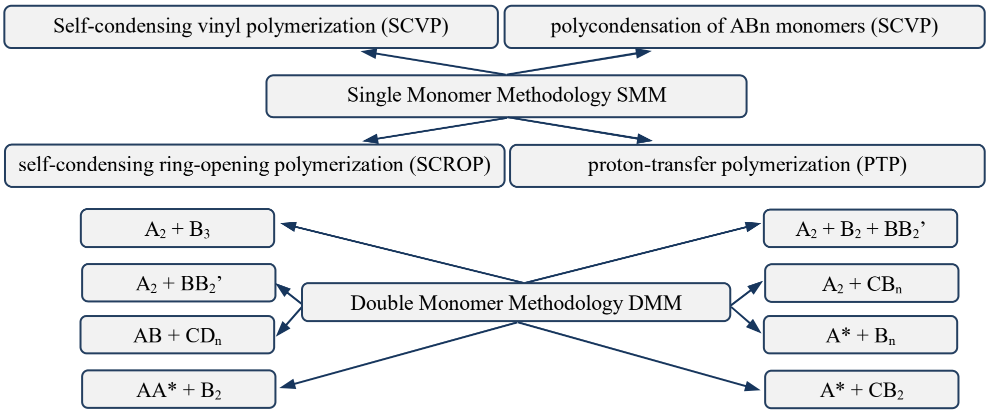


Fig. 3. Single and double monomer methodology and their types (Chang & Fréchet, 1999; Frechet et al., 1995; Suzuki et al., 1992;)

2.1. Single monomer methodology (SMM)

2.1.1. AB_2 monomers polycondensation

Based on Flory's research (1941b), the typical synthetic method for creating hyperbranched polymers involves polymerizing AB_2 (or ABn) monomers with complementary A and B functions (hydroxyl and carboxylic acid groups). Each polyfunctional oligomer present in the reaction mixture may pair with any other species in the absence of crosslinking, which is a characteristic of step growth reactions of this kind. The molecular weight and polydispersity are constrained by polycondensation of AB_2 monomers since no control over the polymerization reaction is possible. However, it is the most traditional and often used technique for creating a variety of hyper branching polymers. Additionally, hyperbranched polymers can be created while regulating the branching pattern using the monomers AB_3, AB_4, and AB_6 (Miravet & Fréchet, 1998). Even though one of the first AB_2 type polymers was created using a C-C coupling process, the most often used starting materials to create aromatic HBPs are 5-hydroxyisophthalic acid and 3,5-dihydroxybenzoic acid (Fig. 4).

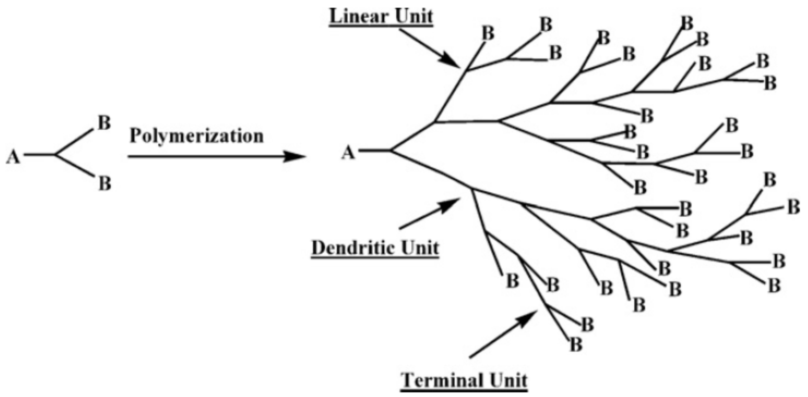


Fig. 4. Synthesis methodology of hyperbranched polymers using AB_2 monomers (Zhang, 2010)

2.1.2. Self-condensing vinyl polymerization (SCVP)

SCVP, which makes use of AB vinyl monomers, was developed instead of AB_2 polymerization. With vinyl monomers, there are two growth modes possible: (a) double bond polymerization (chain growth) and (b) double bond condensation of the starting group (step growth) (Chen & Kong, 2014). The key benefits of SCVP over polycondensation are faster reactions and shorter process times. The majority of the time, SCVP is paired with living/controlled polymerizations like GTP and ATRP (GTP), which are both types of group transfer polymerization (Hawker et al., 1995).

2.1.3. Ring-opening self-condensing polymerization (SCROP)

The SCVP method and SCROP method are identical. It is employed for cyclic monomers with an upcoming functionality on a heterocyclic ring that serves as an initiation site. The initial stage of a polymerization reaction is the opening of the ring, from which the method's name is derived (Gao & Yan, 2004; Gurunathan et al., 2016).

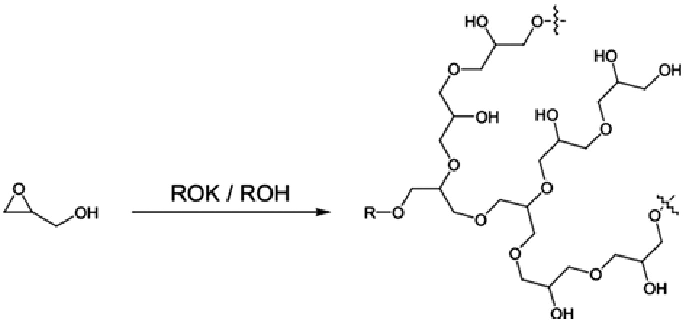


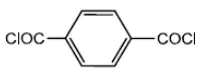
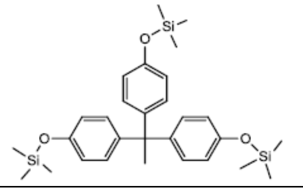
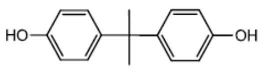
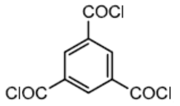
Fig. 5. Hyperbranched polyglycerol synthesis via SCROP (Sunder et al., 1999)

The polymerization of caprolactones uses this process. SCROP has been used to create hyperbranched polyamines, polyethers, and polyesters (Suzuki et al., 1992). Hyperbranched polyethers have been created with the use of SCROP. In their article from 1999, which was the first to employ this technology, Frey et al. employed glycidol as the latent AB_2 monomer. The hyperbranched polyglycerol was produced in this manner by anionic ring-opening polymerization, as shown in Figure 5 (Sunder et al., 1999).

2.2. Double monomer methodology (DMM) – $A_2 + B_3$ method

The $A_2 + B_3$ approach uses two monomers, one with two functional groups and the other with three, and it is based on three presumptions (Table 1). (1) The condensation of A and B groups is the only reaction that occurs; (2) there are no side reactions at any point in the reaction; (3) the procedure does not involve intramolecular cyclization or chain termination (Gao &Yan, 2003). These approaches have the benefits of simple synthesis and accessibility to a variety of reactants or monomers. The ratio of functionalities, the purity of the solvent and reagent, as well as the reaction time and temperature, all affect how well this method works. Polyamides, polycarbonates, and polyureas have been researched as the three main polymer architectures (Al-Mutairi et al., 2023; Jikei et al., 1999; Uhrich et al., 1992).

Table 1. Some of A_2, B_3 monomers (Gurunathan, et al., 2016)

A_2	B_3	Polymerization method
		Melt
		Solution

2.3. Couple-monomer methodology (CMM)

Couple monomer technology provides a way for creating hyperbranched polymers with the benefits of readily available commercial monomers and the absence of gelation. The Gao and Yan invention's method is based on the non-equal reactivity of the functional groups in certain monomer pairs. Couple monomer approach gets its name from the fact that two different types of monomers would preferentially make one specific type of ABn intermediate in-situ, which would then polymerize to create hyperbranched polymers (CMM). The most crucial stage in the molecular design of a hyperbranched polymer using CMM is selecting an appropriate pair of monomers. The fundamental idea behind CMM is displayed in Figure 6 (Al-Mutairi et al., 2023; Brenner et al., 1996; Malmström et al., 1996).

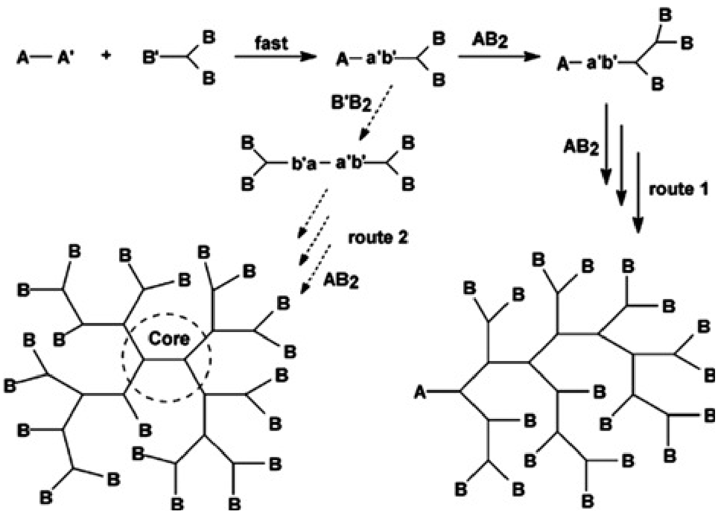


Fig. 6. An example for the principles of CMM (Gurunathan, et al., 2016)

2.4. Multicomponent methodology (MCM)

Multi-component approach is the name of the process used to synthesize HBPs when three or more monomers are involved (MCM). This is the most recently reported methodology. Although it still follows a step-growth method in a single pot, it uses a sequence-controlled pathway. For instance, the reaction between A and C in Figure 7 results in the development of the D function. The only intermediate group that can interact with B and produce HBPs with somewhat "controlled" architectures is this one (Testud, 2015). In this context, isocyanate-based multicomponent methods like the Passerini and Ugi reactions have been effectively used to prepare HBPs (Deng et al., 2014). This method has also been used to create HBPs that are biodegradable (He et al., 2020).

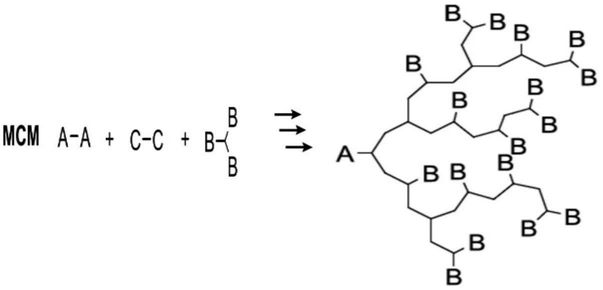


Fig. 7. A typical example of MCM polymerization (Testud, 2015)

3. Applications of hyperbranched polymers

These polymers are excellent candidates for usage in a variety of applications due to the new physical characteristics of hyperbranched macromolecules. Figure 8 (Yates & Hayes, 2004) depicts a schematic representation of the uses of hyperbranched polymers that are most frequently encountered.

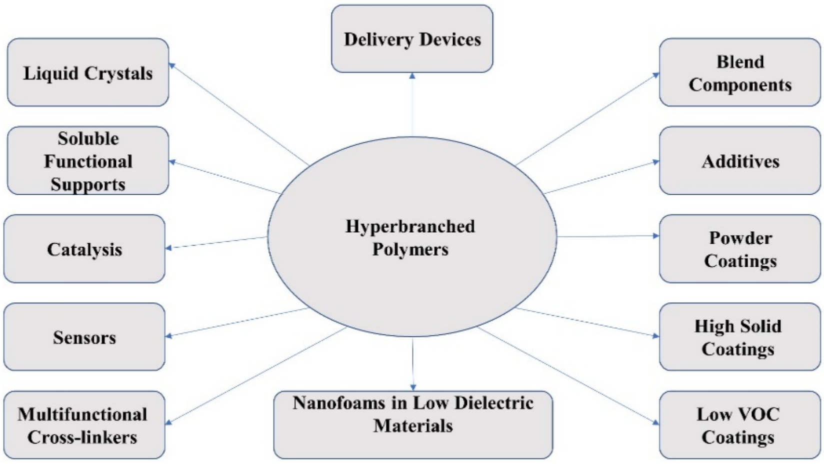


Fig. 8. Application of hyperbranched polymers (Yates & Hayes, 2004)

It may be advantageous to use aromatic HBPEs and their derivatives in the production of polymer blends, coatings, sensors, additives, optical and electronic materials and other products. It is anticipated that more and more intriguing materials and devices based on aromatic HBPEs will be effectively created and manufactured since the characteristics of aromatic HBPEs, such as good polarity, solubility, rheology, thermal properties and crystallinity may be regulated (Al-Mutairi et al., 2022; Elsayed, 2012; Sun et al., 2024).

3.1. Making blends

In the modern world, polymer blends are a crucial tool for creating and enhancing polymeric products. The physical and chemical characteristics of these polymers, such as their processability, toughness, modulus, chemical resistance and barrier properties, have almost all been improved by blending them with other polymers. High Tg values are given to HBPEs by their aromatic structures and high moduli are anticipated as a result. It may be possible to create innovative materials with enhanced moduli and heat-distortion temperatures by blending aromatic HBPEs with linear polymers. New polymeric materials have been created by combining hyperbranched polymers with linear polymers. Kim and Webster, for instance, combined both polystyrene and hyperbranched polyphenylenes. Due to thermal chain transfer, the addition of the hyperbranched polyphenylene to the polystyrene increased the material's melt viscosity and thermal stability (Al-Mutairi et al., 2022; Kim & Webster, 1992).

3.2. Coatings

HBPEs are most frequently used as reactive multifunctional polyols or other components in coating and resin compositions. The characteristics of HBPEs make them ideal for coating applications as well. The presence of many end groups offers a diverse range of crosslinking possibilities, while their almost spherical shape enables a remarkably low viscosity even when dealing with high molecular weights. Aromatic (HBPEs) are primarily employed in the formulation of coatings, particularly those that are UV-curable or hybrid in nature (Froehling, 2004; Gao & Yan, 2004; Johansson et al., 2000; Yates & Hayes, 2004).

3.3. Bio-application

Amphiphilic HMs can self-assemble into a variety of supramolecular structures in solution or via interfacial self-assembly, just like amphiphilic linear block copolymers. Supramolecular structures possess considerable promise for application in the biomedical domain due to their inherent biocompatibility and versatile molecular topologies. Potential candidates for biomedical applications in fields such as drug delivery, cytomimetic chemistry, bio-imaging, antimicrobial materials and gene transfection encompass hyperbranched polyethers, polyesters, polyphosphates and polysaccharides (Jin et al., 2012; Wang et al., 2013). The usage of HMs as antibacterial and antifouling compounds has also been very common. The chemical stability and exceptional biocompatibility of HPGs render them highly promising as antifouling materials capable of preventing protein adhesion (Liu et al., 2024; Siegers et al., 2004).

3.4. Shape memory materials

Shape memory polymers (SMPs) are substances that, when exposed to certain environmental stimuli, can temporarily preserve deformation while also regaining their original morphologies. The reversible storage and release of entropy energy is analogous to this deformation and recovery process. Advanced thermos-responsive SMPs include HPU-MWCNTs, HPU-GO and PCL-based HPUs (Zheng et al., 2015).

3.5. Adhesives

Adhesives are crucial for connecting two or more items together. An adhesive must have good wettability, robust interfacial contact and high mechanical capabilities. Due to their many rigid aromatics and triazole rings, hyperbranched poly(triazole)s have been employed as adhesives and have demonstrated strong adhesive strength at room temperature (such as 16.491.21 MPa) and at 200 °C (7 times epoxy glue 4006# and GY-1#). Additionally, the HP-based glue and metal substrates require a lot of binding energy because of their powerful polar triazole groups (Abdollahi & Khalili, 2024; Tang et al., 2010).

3.6. Elastomers

Elastomers typically have low Tg, extremely high molecular weights and an appropriate level of cross-linking. The elastomer has a high degree of deformability due to its low Tg and its slight degree of cross-linking allows for repairable deformation. PUs have been used as elastomers extensively. PU elastomers with hydroxyl functional HPs have products with superior mechanical qualities to those of their linear equivalents (Mahapatra et al., 2012).

4. Application of polymers in construction

The polymer production process is relatively cheap and easy to implement. These elements allow them to be used in virtually any shape, which also facilitates the implementation of individual projects. Polymer materials are widely used in construction, both as thermal and hydrophobic insulation materials, as well as resistance to chemicals. The advantages of this group of materials in terms of their use also include a wide range of colors, relatively low weight and simple connection methods. The most important aspect of using these materials in construction is mechanical resistance (designs of supporting structures) and fire resistance (flammability).

A great advantage of polymeric materials is the homogeneity of the material structure, which is a basic element in the selection of construction materials.

One of the most popular materials used in construction is polyvinyl chloride, i.e. the so-called PVC. This material is characterized by excellent resistance to chemicals. Additionally, by modifying its chemical composition, it is possible to obtain a material that will have optimal properties for a specific application. PVC is used to produce, among others: window frame profiles, gutters and external window sills. An interesting use of this material is to create waterproof coatings, which are perfect, for example, in the bathroom. In some cases, the advantage of plastics is that they do not conduct electricity. This allows them to be used in the production of fastening elements for electrical cables.

Interior design is the main area of application of polymers in construction. Where the primary use of these materials is:

- floor materials, e.g.: PVC or rubber floor coverings, carpet flooring, jointless floors, antistatic floors,
- wall materials, e.g.: sandwich panels, decorative boards, wall boards, plasters, vinyl wallpapers;
- roofing materials, e.g.: sandwich panels, single-layer boards, light-transmitting boards, gutters and downpipes;
- adhesives, e.g.: solvent adhesives, dispersion adhesives, liquid resin adhesives;
- putties, e.g.: chemically resistant putties, permanently plastic or elastic putties, sealing and putty compounds;
- thermal insulation materials, e.g.: expanded polystyrene – polystyrene, foamed polyvinyl chloride, foamed polyurethane;
- materials for hydrophobic insulation, e.g.: impregnation agents, foils;
- installation materials, e.g.: PVC or PP pipes and fittings, ventilation devices, bathroom equipment elements;
- construction joinery, e.g. windows and doors.

Plastics are excellent materials for reprocessing in recycling technologies. These issues require the organization of appropriate waste logistics, but they are technologically possible to use and apply in the aspect of efficient use of resources.

Conclusion

This review paper focuses on hyperbranched polymers since they are a new kind of polymeric material and represent the fourth kind of material. It was found that these polymers were discovered in the early 19th century by Berzelius when he mixed tartaric acid and glycerol. Following this discovery, a lot of researchers also prepared other types of hyperbranched polymer using different monomers. In addition, it is shown in this paper that there are several different synthesis methodologies, such as SMM, in which the same monomer is used to prepare hyperbranched polymer by using a certain catalyst and DMM, in which two monomers are reacted together to give hyperbranched polyester. In addition, it has been found that the

SMM has several approaches depending on the nature of the monomers being used. Both SMM and DMM are considered the most common methods for the preparation of hyperbranched polymers. Also, there are other methods for the synthesis of hyperbranched polymers like CMM and MCM, which use more than two monomers. Each method used has advantages and disadvantages. Also, from this review, it was found that hyperbranched polymers could be used in several applications, such as blends, to improve processability, coatings to improve viscosity and resist environmental factors and biological applications. The functionality of these applications relies on the existence of specific functional groups inside the hyperbranched polymer.

Bibliography

Abdollahi, M., & Khalili, B. (2024) Development of a novel hyperbranched unsaturated polyester resin: Synthesis, characterization, and potential applications in car body putty. *Current Chemistry Letters*, 13(2), 325-334.

Al-Mutairi, N.H., Al-Zubiedy, A., & Al-Zuhairi, A.J. (2023) Preparation and characterization of a novel hyperbranched polyester polymers using A2+B3 monomers. *Production Engineering Archives*, 29(1), 28-36.

Al-Mutairi, N.H., Al-Zubiedy, A., Al-Zuhairi, A.J., & Idzikowski, A. (2023) The biodegradation and the rheological properties of polypropylene/hyperbranched polyester blends for industrial applications. *Materials Research Proceedings*, 34, 109-119.

Al-Mutairi, N.H., Al-Zubiedy, A., & Al-Zuhairi, A.J. (2022) Hyperbranched polyester polymer preparation and study its effect on some properties of polypropylene. *Egyptian Journal of Chemistry*, 65(8), 35-43.

Brenner, B.I., Voit A.R., Massa, S.R., & Turner, D.J. (1996) Hyperbranched polyesters: End group modification and properties. *Macromolecular Symposia*, Wiley Online Library, 47-54.

Chang, J.M.J., & Fréchet H.T. (1999) Proton-transfer polymerization: A new approach to hyperbranched polymers. *Journal of the American Chemical Society*, 121, 10, 2313-2314.

Chen, J., & Kong, H. (2014) Terminal index: a new way for precise description of topologic structure of highly branched polymers derived from A2+B3 stepwise polymerization. *Journal of Physical Chemistry B*, 118, 12, 3441-3450.

Deng, Z.C., Cui, X., Du, Y., & Li, F-S. (2014) Functional highly branched polymers from multicomponent polymerization (MCP) based on the ABC type Passerini reaction. *Polymer Chemistry*, 5, 10, 3316-3320.

Elsayed, M.S.H. (2012) *Hyperbranched Polymers in Nanocomposites and Nanohybrides*. Dresden, PhD Thesis – Leibniz Institute of Polymer Research. Dresden.

Flory, P.J. (1941a) Molecular size distribution in three dimensional polymers. I. Gelation 1. *Journal of the American Chemical Society*, 63, 11, 3083-3090.

Flory, P.J. (1941b) Molecular size distribution in three dimensional polymers. II. Trifunctional branching units. *Journal of the American Chemical Society*, 63, 11, 3091-3096.

Flory, P.J. (1952) Molecular size distribution in three dimensional polymers. VI. Branched polymers containing A-R-Bf-1 type units. *Journal of the American Chemical Society*, 74, 11, 2718-2723.

Frechet, D.A., & Tomalia, J.M. (2001) Dendrimers and other dendritic polymers. *Fluid Phase Equilibria*, 241, 155-174.

Frechet, R.B., Henmi, J.M., Gitsov, M., Aoshima, I., Leduc, S., & Grubbs, M.R. (1995) Self-condensing vinyl polymerization: an approach to dendritic materials. *Science* 80, 269, 5227, 1080-1083.

Froehling, P. (2004) Development of DSM's Hybrane® hyperbranched polyesteramides. *Journal of Polymer Science Part A: Polymer Chemistry*, 42, 13, 3110-3115.

Gao G., & Yan, D. (2003) A2 + CB n' approach to hyperbranched polymers with alternating ureido and urethano units. *Macromolecules*, 36, 3, 613-620.

Gao, D., & Yan, C. (2004) Hyperbranched polymers: From synthesis to applications. *Progress in Polymer Science*, 29, 3, 183-275.

Gurunathan, S., Mohanty, T., & Nayak, S.K. (2016) Hyperbranched polymers for coating applications: a review. *Polymer-Plastics Technology and Engineering*, 55, 1, 92-117.

Hawker, J., Frechet, C.J., Grubbs, J., & Dao, R.B. (1995) Preparation of hyperbranched and star polymers by a "living", self-condensing free radical polymerization. *Journal of the American Chemical Society*, 117, 43, 10763-10764.

He, W., Zheng, J., Xie, N. Zheng, D., & Song, Y. (2020) Multicomponent polymerization toward biodegradable polymers with diverse responsiveness in tumor microenvironments. *Polymer Chemistry*, 11, 6, 1198-1210.

Jikei, T., Chon, M., Kakimoto, S.H., Kawauchi, M., & Imase, S. (1999) Synthesis of hyperbranched aromatic polyamide from aromatic diamines and trimesic acid. *Macromolecules*, 32, 6, 2061-2064.

Jin, W., Huang, H., Zhu, D., Zhou, X., & Yan, Y. (2012) Biocompatible or biodegradable hyperbranched polymers: from self-assembly to cytomimetic applications. *Chemical Society Reviews*, 41, 18, 5986-5997.

Johansson, T., Glauser, M., Rospo, A., & Hult, G. (2000) Radiation curing of hyperbranched polyester resins. *Journal of Applied Polymer Science*, 75, 5, 612-618.

Kienle, A.G., & Hovey, R.H. (1929) The polyhydric alcohol-polybasic acid reaction. I. Glycerol-phthalic anhydride. *Journal of the American Chemical Society*, 51, 2, 509-519.

Kienle, P.A., Meulen, R.M., & Petke, F.E. (1939a) The polyhydric alcohol-polybasic acid reaction. III. Further studies of the glycerol-phthalic anhydride reaction. *Journal of the American Chemical Society*, 61, 9, 2258-2268.

Kienle, P.A., Meulen, R.H., & Petke, F.E. (1939b) The polyhydric alcohol-polybasic acid reaction. IV. Glyceryl phthalate from phthalic acid. *Journal of the American Chemical Society*, 61, 9, 2268-2271.

Kim, O.W., & Webster, Y.H., (1992) Hyperbranched polyphenylenes. *Macromolecules*, 25, 21, 5561-5572.

Liu, R., Sun, Y., Sun, Y., Li, H., Chen, M., Long, L., Gong, J., Lv, B., & Ni, Y. (2024) Biomimetic design of micro- and nano-wrinkle wood surface via coating reinforced with hyperbranched polymer grafted cellulose nanofibers for skin-tactile performance. *Carbohydrate Polymers*, 334, 122035.

Mahapatra, J.W., Yadav, S.S., & Cho, S.K. (2012) Nanostructured hyperbranched polyurethane elastomer hybrids that incorporate polyhedral oligosilsesquioxane. *Reactive & Functional Polymers*, 72, 4, 227-232.

Malmström, A., Johansson, E., & Hult, M. (1996) The effect of terminal alkyl chains on hyperbranched polyesters based on 2, 2-bis (hydroxymethyl) propionic acid. *Macromolecular Chemistry and Physics*, 197, 10, 3199-3207.

Miravet, J.M.J., & Fréchet, J.F. (1998) New hyperbranched poly(siloxysilanes): variation of the branching pattern and end-functionalization. *Macromolecules*, 31, 11, 3461-3468.

Siegers, R., Biesalski, C., & Haag, M. (2004) Self-assembled monolayers of dendritic polyglycerol derivatives on gold that resist the adsorption of proteins. *Chemistry: A European Journal*, 10, 11, 2831-2838.

Sunder, R., Hanselmann, A., Frey, A., & Mülhaupt, H. (1999) Controlled synthesis of hyperbranched polyglycerols by ring-opening multibranching polymerization. *Macromolecules*, 32, 13, 4240-4246.

Suzuki, T., Ii, M., & Saegusa, A., (1992) Multibranching polymerization: palladium-catalyzed ring-opening polymerization of cyclic carbamate to produce hyperbranched dendritic polyamine. *Macromolecules*, 25, 25, 7071-7072.

Sun, J., Du, J., Yang, X., Fan, Z., Miao, Y., Dong, H., Liao, X., Wang, H., & Xu, B. (2024) Red hyperbranched conjugated polymers with thermally activated delayed fluorescence for solution-processed organic light-emitting diodes. *European Polymer Journal*, 213, 113119.

Tang, B.Z., Jim, Y., Liu, C., Ye, Y., Qin, L., Lam, A., Zhao, J., & Tang, Ch. (2010) Synthesis and curing of hyperbranched poly (triazole) s with click polymerization for improved adhesion strength. *ACS Applied Materials and Interfaces*, 2, 2, 566-574.

Testud, B. (2015) *Vegetable Oils as a Platform for the Design of Novel Hyperbranched Polyesters*. Bordeaux: Université de Bordeaux.

Uhrich, C.J., Hawker K.E., Frechet, S.R., & Turner, J.M.T. (1992) One-pot synthesis of hyperbranched polyethers. *Macromolecules*, 25, 18, 4583-4587.

Voit, B. (2005) Hyperbranched polymers – all problems solved after 15 years of research? *Journal of Polymer Science Part A: Polymer Chemistry*, 43, 13, 2679-2699.

Wang, H., Chen, D., Su, X., Qiu, Y., Zhu, F., Huan, L., Zhu, X., Yan, B., Guo, D., & Zhu, F. (2013) Supramolecular amphiphilic multiarm hyperbranched copolymer: synthesis, self-assembly and drug delivery applications. *Polymer Chemistry*, 4, 1, 85-94.

Yates, W., & Hayes, C.R. (2004) Synthesis and applications of hyperbranched polymers. *European Polymer Journal*, 40, 7, 1257-1281.

Zhang, X. (2010) Hyperbranched aromatic polyesters: From synthesis to applications. *Progress in Organic Coatings*, 69, 4, 295-309.

Zheng, C., Li, Y., Weng, S., & Gao, Z. (2015) Hyperbranched polymers: advances from synthesis to applications. *Chemical Society Reviews*, 44, 22, 4091-4130.