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Research progress on synthesis and applications of hyperbranched polymers

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Abstract. Hyperbranched polymers (HBPs) are a kind of highly branched three-dimensional macromolecule. Over the past decade, they have received much attention from interdisciplinary research. They have many branched points and their molecular chain is not easy to tangle. Additionally, as the molecular weight of the substance increases, its viscosity does not vary. Rich end functional groups are simple to alter and conducive to the synthesis of a variety of functional materials. Their simple synthesis and special properties have attracted a lot of attention from researchers in polymer science. Therefore, this review intends to introduce some methods to synthesize HBPs, including living polymerization, polycondensation, ring-opening polymerization and some other methods. Then, the properties of from the aspects of thermal, mechanical, rheological and solution properties are introduced. At last, the applications in materials and medicine of HBPs are reviewed in this paper followed by a discussion of the development prospects and potential challenges. HBPs have drawn great attention from researchers due to their special properties and unique application prospects. As the research on 3-dimensional HBPs is becoming more and more mature, 2-dimensional HBPs which are less focused on may be one of the focuses of future research.

Keywords: Hyperbranched Polymer, Synthesis Methods, Functional Materials, Drug Delivery.

1. Introduction

In the 50 years after Staudinger proposed Macromolecular Hypothesis, researchers have carried out a series of researches on polymers, especially hyperbranched polymers (HBPs), which has become a hot spot in this field. Dendritic polymers are usually classified into dendrimers and hyperbranched polymers on the basis of their topology. Compared with traditional linear polymers, dendritic polymers have unique physicochemical properties, such as low viscosity, good rheological properties and solubility and a great deal of modified end functional groups. Therefore, HBPs have been widely concerned and applied in biomedicine, drug delivery, functionalized molecular materials and so on.

The concept of hyperbranched polymer was first proposed by Flory in 1950. As long as the monomer is AB_x ($x \geq 2$) type, where both A and B are reactive functional groups, hyperbranched structure can be generated. Early studies were based on dendrimer synthesis, which had strict geometric characteristics. At a certain stage of the reaction, a spherical structure may be formed. The procedure must be strictly and carefully controlled, and the purity requirement is high, which is not conducive to large-scale production.

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In the following decades, hyperbranched polymers gradually emerged. Simpler to be synthesized, they have a wider range of applications and the process does not need to be too tightly controlled. In the beginning, the researchers used a one-step synthesis process, in which only the nuclear components, raw materials, and catalysts were added to the reactor. However, the yield of the products is not high, and the characteristics of branched chain randomization appear. Later, the synthesis method was improved, evolving into the 'pseudu-one-step', by which the yield can reach almost 100%. In particular, the molecular mass distribution is very well controlled.

For HBPs, a branched degree of structure is described because of the obvious difference between hyperbranched polymer and linear polymer. Fréchet put forward the concept of branching degree (DB), which refers to the mole fraction of fully branched units and terminal units. DB of HBPs is within 0–l. For the HBPs formed by the same chemical composition, a larger DB means higher solubility and lower melting viscosity. The characterization of hyperbranched structure is one of the difficulties in the research of HBPs. Previously used characterization techniques are linear molecules, but HBPs and linear polymers have very different rheological properties, so the Gel Permeation Chromatography (GPC) characterization of HBPs can only be qualitative but not quantitative.

In this paper, three polymerization types (1) Living polymerization; (2) Ring-opening polymerization; (3) Polycondensation and their research progress will also be introduced.

2. Synthesis

2.1. Living polymerization

Szwarc introduced the concept of active polymerization in 1956 as a polymerization without termination or transfer, with an initiation rate much greater than the growth rate. Without chain transfer, the number of polymer chains remains constant during polymerization. However, there is no chain termination, until the monomer in the system is exhausted and the polymerization reaction stops, the polymer chain remains the active group. In comparison with the polycondensation method, the molecular weight distribution is relatively narrow, which is mainly used to prepare linear polymers with narrow distribution. In the region of HBPs, living polymerization methods such as ATRP, RATP are available. Kim et al. used ATRP method to prepare vinyl-functionalized haloalkanes [1].

2.2. Ring-opening polymerization

The molecular weight of HBPs obtained by ring-opening polymerization is very large, which can reach hundreds of thousands or even millions. The reaction rate is fast, because few small molecules are generated. Moreover, the molecular weight distribution is narrow, so the products obtained are purer. In addition, it has the advantage that the reaction is easy to control. However, the disadvantages of this method are complex procedure, complex crafting, high technical requirement and high cost.

Parzuchowski et al. synthesized hyperbranched polyglycine through the principle of ring-opening copolymerization, which can absorb surrounding CO_2 [2]. Zhunxuan Li et al. carried out chemical modification of hyperbranched polyethylenimines by using ring opening polymerization of N-sulfonyl [3]. Toshifumi synthesized novel hyperbranched carbohydrate polymers from the ring-opening multibranching polymerizations [4].

2.3. Polycondensation

Polycondensation is a common method to prepare HBPs by reacting reactive hydrogen monomers with active organic intermediates. After a relatively long period of research, a mature synthesis system of polycondensation has already formed. Morikawa et al. synthesized a novel hyperbranched polymer through the self-condensation reaction of vinylbenzene, which can be used as flocculant for sewage disposal [5]. Fei demonstrated that through one-pot reaction (polycondensation), hyperbranched conjugated polyporphyrin arrays with high molecular weight could be synthesized [6].

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2.4. Other methods

Other synthesis techniques include click chemistry, coupling monomer method, irradiation polymerization, and host-guest interaction, in addition to the aforementioned hyperbranched polymer synthesis methods. [7].

Among them, three science laureates were just awarded the Nobel Prize in Chemistry in 2022 for the development of click chemistry. Complex chemical reactions become simple by the splicing of tiny components, which can quickly and consistently finish the synthesis of a wide range of compounds.

The most well-known click chemical reaction is the Cu-catalyzed azide-alkynyl cycloaddition [8]. Qin synthesized a new bis(aroylacetylene) by click chemistry which contained triazole and fluorene moieties. It has shown good property of being able to dissolve in various solvents, such as THF and DMF [9].

3. Properties

3.1. Thermal properties

HBPs are almost entirely amorphous materials because of their highly branched structure. Hence, the glass transition temperature Tg is of great importance, among thermal properties [10]. It directly affects the service performance and process performance of the material. When branched polymers are compared with linear polymers of the same molecular weight, the increased chain ends decrease Tg in branched molecules, while the limitation of mobility by junction points increases Tg. The properties of the chain end have a significant effect on the Tg of dendrimers, which increases with the increase of the polarity of the chain end [11]. The flexibility of molecular chain, intermolecular force, copolymerization, blending, plasticizing and so on are the important internal factors affecting polymer Tg. Furthermore, external conditions such as force, force rate and temperature velocity are noteworthy factors as well.

3.2. Mechanical and rheological properties

The special structure of hyperbranched polymer determines that it has special properties different from ordinary linear polymer. Due to the highly branched, globular structure, hyperbranched polymer and dendrimer configurations are created by the lack of chain entanglement [10].

The rheological properties of HBPs are mainly characterized by the rheological behavior in molten state. This type of polymer has no entanglement of chains, which leads to their poor mechanical properties. They are brittle polymers that cannot be used as an engineering thermoplastic alone. But its large number of end groups has reactivity which means that they can be used as an additive to improve the properties of thermoplastic resins.

3.3. Solution properties

HBPs show much reduced characteristic viscosity, Mark-Houwink index, hydrodynamic volume, and ratio of radius of gyration to hydrodynamic radius in comparison with linear equivalents with the same molar mass [10]. Furthermore, by combining a high density of suspended chains or groups in the presence of chief chains in HBPs, it is feasible to achieve tunable features of the solution [12].

4. Applications

Applications in functional materials

HBPs have been widely used in optical, electronic and magnetic materials due to their unique structure, good solubility and excellent processability. Optical imaging is a method of imaging using photon fluorescence or bioluminescent probes. Optical imaging is rapid, cheap, easy to reuse, compared with other methods, but also has the characteristics of safety, sensitivity and specific selection function.

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In contrast to the comparable linear polymers, Tadatomi created hyperbranched versions of epoxy-(meth)acrylate, oxetane-methacrylate, and poly(urethane)-methacrylate that had stronger photochemical reactivities and superior resolution qualities. Additionally, it was discovered that hyperbranched oxetane-(meth)acrylate has superior thermal stability than hyperbranched epoxy-(meth)acrylate with pendant carboxyl groups. These findings imply that innovative UV-curing materials can benefit from photo-functional HBPs that contain several radical polymerizable groups [13].

Radowski et al. created innovative multishell structures using polyethylene glycol as the arm and hyperbranched polymeric cores encased in double-layered shells [14]. Such HBPs HCP-star-PEG can form single-molecule micelles and self-assemble to form multi-molecule micelles in water, providing conditions for micellar imaging.

Magnetic resonance imaging (MRI) is a new examination technology based on the principle that the nuclei with magnetic distance can cause transitions between energy levels when subjected to a magnetic field. Due to the extremely low sensitivity of MRI, in order to solve this problem, scientists have developed various biological imaging detectors. The three primary contrast agents are organic contrast agents, super-paramagnetic iron oxide nanoparticles, and paramagnetic molecules. Kristofer et al. were able to successfully design and synthesize hyperbranched molecules that could be observed in vivo using F-19 MRI in under 10 min. After chain extension with PEGMA, these polymers are compatible with cells. Additionally, these macromolecules are easily functionalized, and the ligand presentation is accurate and available. It is anticipated that this hyperbranched polymer will usher in a new era of monitoring and focused MRI contrast agents [15].

4.1. Biomedical applications

The use of bioactive and biocompatible materials in the design and development of new systems for the localisation of anomalies and the diagnosis of various types of biological disorders is evolving quickly. As a result, macromolecular diagnostic system design has drawn a lot of attention. HBPs are regarded as one of the several forms of polymer compounds because of their highly branching structure and flexible end groups [16].

A biosensor is an analytical tool that measures chemical or biological processes by producing signals proportional to the concentration of an analyte in the reaction. HBPs can be used in this capacity. Antibodies, cells, enzymes, tissues, etc. can be used as recognition elements.

A novel conjugated polymer (CP) with several carboxylic groups has been created by Mo et al., and it can be used to create photoelectrochemical biosensors based on hyperbranched titanium dioxide that are CP sensitized for the detection of AFP in serum. The developed biosensor demonstrated great sensitivity, good selectivity, and stability for detecting AFP in serum. This method is anticipated to be applied to find AFP in clinical serum [17].

4.2. Applications in drug delivery

Compounds with particular characteristics are needed to transport therapeutic medicines since their accumulation in cancer cells improves the efficacy of medications. Applied in drug delivery system, the different structure of polymer drug-load according to their respective advantages to a variety of ways, including drug encapsulation in the polymer coating of the repository (reservoir), embedding drug in the polymer matrix (monolithic), through the way of conjugated polymers—drugs carry medication, and introduce targeted drugs targeted to a specific disease factor load area.

In the reservoir polymer nanodelivery system, the drug is stored and delivered in the form of a polymer-encapsulated (the drug reservoir is enclosed within the polymer coating), and the drug is carried to the target location by physical and chemical properties, such as active or passive targeting of the polymer, and the release of the drug is controlled.

Unlike the reservoir type, in the monolithic polymer drug delivery system, the drug is dissolved or dispersed in the polymer matrix, integrated with the delivery vehicle.

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Chen et al. synthesized amphiphilic hyperbranched core-shell polymers with folate moieties as the targeting groups. The nanoparticles contained 5-fluorouracil and paclitaxel, two anti-cancer medications. Via non-covalent interactions, the polymer complex contained the drugs. The findings demonstrated that medications loaded in micelles had good biocompatibility and restrict the uncontrolled proliferation of cancer cells since folate targeting boosted the cytotoxicity of drug-laden nanoparticles against folate receptor expressing tumor cells [18].

5. Challenges and future prospects

HBPs differ from polymers in that they have a three-dimensional structure, a lot of end groups that can be changed, good solubility, low viscosity, and significant chemical reactivity. They are extensively utilized in magnetic, electrical, and optical materials. Hyperbranched polymer manufacturing can contribute to relatively cutting-edge fields such as nanoscience, biomedicine, and optoelectronic materials. Rich functional groups, a highly branched chain structure, and special features demonstrate significant potential as luminescent materials, biomaterials, nanoscience and technology, composites and adhesives, etc [19].

However, as a new research field, it is still in the exploration stage in many aspects, and there are problems that the theoretical and experimental results proposed by different researchers are inconsistent. Replicating and verifying other researchers' experiments is time-consuming, and the complex process is prone to errors.

Scientists can work toward the HBPs with a higher level of branching and better control over branch production. So far, the main research is based on 3-dimensional HBPs (3D HBPs), and there is still little research on two-dimensional HBPs (2D HBPs). They differ a lot from 3D HBPs and the question remains what properties they might have, and how humans might use them. Some 2D HBPs synthesized have shown the properties of lightness, high strength, strong tightness and other properties, and have broad application prospects. Therefore, 2D HBPs may be one of the research hotspots in the future.

6. Conclusion

The synthesis methods, unique properties and applications of HBPs are reviewed above. Although many studies are only in the theoretical research stage, and there is an inconsistency between the theoretical and experimental results, the properties and functions of HBPs can be improved through the optimization of raw materials, catalysts and reaction conditions until they meet the requirements of industrial production. It is believed that with the further understanding and development of HBPs, they will be more widely used. The future of this field will be rosy and it is worthy of efforts of researchers.

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