# Synthesis and Application of Hyperbranched Polymers

Yiling Liu

University of Illinois Urbana-Champaign, Champaign 61820, United States

*lcr@gesanghua.org

**Abstract.** Hyperbranched polymers have the special structure caused by different types of synthetic procedures such as single monomer methodology and double monomer methodology. Under the process of single monomer methodology, polycondensation, self-condensation, and ring-opening polymerization will be introduced in this paper, from the traditional to recent methods. From different synthetic methodologies, hyperbranched polymers have specialized properties to fulfill applications in various fields. They can be used in oil recovery for petroleum engineering and drug delivery for biomedicine field. As the synthesis methods become more developed, the properties of hyperbranched polymers can match the application requirements in more refined way, which gives the prospect of enhancing the efficiency and accuracy use in different engineering fields. It is meaningful to keep the research on hyperbranched polymers to let them have more usage in many fields of engineering, which can benefit human beings' life from many aspects that causes influence of people's daily life.

**Keywords:** Hyperbranched polymers, polycondensation, self-condensation, ring-opening polymerization, synthesis methods.

## 1. Introduction

Hyperbranched polymers are a class of topological 3-dimensional polymers with highly branched structures. The interest and curiosity from the fields in hyperbranched polymers are expanding quickly as seen by the rise in science magazines. This is because of their distinctive physical and chemical features and prospective uses in many different industries, such as coatings and drug delivery. Dendrons or dendrimers, dendrigrafts or dendronized polymers, linear-dendritic hybrids, hyperbranched polymers, hypergrafted polymers and multi-arm star polymers are the six sub-genre that make up dendritic architecture, which comes after conventional forms like linear, cross-linked, and branching designs which is the 4th major type among polymer structures (Fig. 1) [1]. The upcoming three sub-genres display well-made structures which has a degree of branching (DB), presents the data of 1.0, whereas the following 3 subclasses display unsystematically branching structures. High regularity dendrons or dendrimers with regulated molecular weight are manufactured gradually using convergent or divergent techniques. Dendronized polymers are linear polymers connected within dendrons. They can be created by connecting dendrons to the linear polymeric center or by directly polymerizing dendritic macromonomers [2]. The functionalization, synthesis, supra-molecular self-assembly, and uses of linear-dendritic hybrids, dendrimers, and dendronized polymers have all been covered in several outstanding reviews.

Hyperbranched polymers have a lengthy and intricate history with artificial molecules. It all began at the turn of the 20th century when Berzelius discovered resin forming from glycerol (B3 monomer) and tartaric acid (A2B2 monomer); phthalic anhydride (possible A2 monomer) or phthalic acid (A2 monomer), and glycerol (B3 monomer) was described in Watson Smith's 1901 report [3]. Further research on the reaction was conducted by Callahan, Arsem, Dawson, Howell, and Kienle, who produced findings and recommendations that are still in use today [1]. Through his Bakelite firm, he created the first synthetic plastic to be used commercially, phenolic polymer, in 1909 [4]. In the 1940s, Flory developed the terms "degree of branching" and "hyperbranched substances" after using statistical methods to evaluate the molecular weight that distributed for 3D polymers with the structure of trifunctional and tetrafunctional branch units in the gel state [3]. Flory put forth the hypothesis that extremely branched polymers exist in 1952 [3]. In 1982, Kricheldorf finally succeeded in copolymerizing type AB and type AB2 monomers to produce highly branched polyesters [5]. When

Kim and Webster purposefully created soluble hyperbranched polyphenylenes in 1988, they coined the term "hyperbranched polymers" [6]. Since then, because of their distinctive features and greater availability compared to dendrimers, hyperbranched polymers have drawn increased attention.

The major focus of this article's overview of synthesis, adaptations, and use of unsystematically hyperbranched polymers is a recent invention of a novel synthetic approach for hyperbranched polymers.

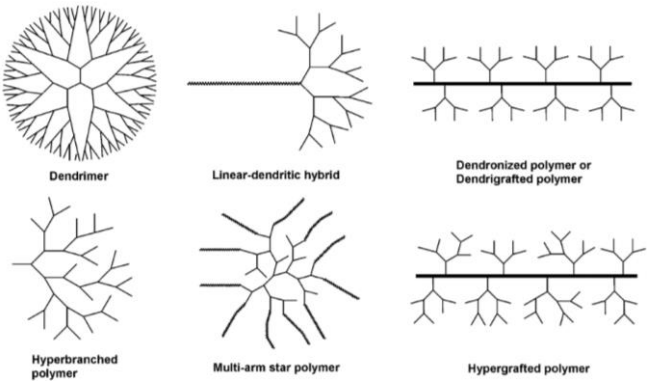



**Figure 1.** Structures of hyperbranched polymers

## 2. Synthesis

Hyperbranched polymers are able to be synthesized from 2 big methodologies as in use. The first one is acknowledged as the single monomer approach, while the second one is acknowledged as the double-monomer methodology. In SMM, there are three main different types of polymerizations, which are the polycondensation for ABn monomers, the self-condensing vinyl polymerization (SCVP), and the ring-opening polymerization. In DMM, it has direct way of polymerization of 2 genres of monomers and an indirect way of monomer pair generating hyperbranched polymers.

### 2.1. Single monomer methodology

#### 2.1.1. Polycondensation of ABn monomers

One-step polycondensation of ABn-type monomers yields a variety of hyperbranched polymers, which includes hyperbranched polyphenylenes, polyesters, polyethers, polyamides, and polycarbonates. It is possible that tiny molecules will not be produced during polymerization when a group of ABn monomers with double or triple bonds have been produced [2]. Through addition polymerization of ABn monomers, hyperbranched polyurethanes, poly-carbosilanes, polyamides, and poly-acetophenones can be successfully produced. Hyperbranched polymers can also be created while regulating the branching pattern using AB3 to AB5, and also AB6 monomers [3].

#### 2.1.2. Self-condensing vinyl polymerization

*S*CVP was established in 1995 by Fréchet and associates [7]. Because AB vinyl monomers can be polymerized to create hyperbranched polymers, this polymerization technique is incredibly flexible. The AB monomer's B group is activated during the process, creating an initial Bp site. Bp builds the base for the development of vinyl group A during the procedure, which is for the monomer, resulting in a dimer containing the vinyl group, also producing a growth spot, and an initiation spot. Dimers are AB2 monomers that can be used to create hyperbranched polymers through further polymerization [2]. The SCVP has a lower DB than the hyperbranched polymer made by polycondensation of AB2 monomer because the chain growth activities at the growth site and the initiation site are different. There are some issues with SCVP. For instance, because of the typically broad molecular weight dispersion, it is difficult to accurately measure DB using NMR analysis. Side reactions may also cause gelation. Living/controlled polymerizations like group transfer polymerization (GTP) and atom transfer radical polymerization (ATRP) are coupled in SCVP to prevent cross-linking [1].

### 2.1.3. Ring-opening polymerization

Ring-opening addition transforms a cyclic compound monomer into a linear polymer in a procedure known as ring-opening polymerization. Heterocyclic substances like ethylene oxide, caprolactone, tetrahydrofuran, and cyclic carbamate are utilized as monomers in the hyperbranched polymer produced via ring-opening polymerization. Hyperbranched polyamides, polyethers, and polyesters have all been created using the process of ring-opening polymerization. With the use of a phase transfer catalyst called tetrabutylammonium bromide (TBAB), the hyperbranched polymer Xing14 based on the ring-opening polymerization process was effectively created, and trimethylolpropane triglycidyl ether, butanediol and orthodiphenol with hydroxyls as monomers (Fig. 2) [8]. Another evidence is the creation of the multi-carboxyl hyperbranched polymer TOHBP using the basic ingredients methyl eleostearate (ME), maleic anhydride (MA), and diglycidyl ether of bisphenol A (DGEBA) (Fig. 3) [8]. The examination of the 2 hyperbranched polymers' synthetic methods reveals that this reaction provides a lot of benefits. Firstly, the synthesis of hyperbranched polymers from epoxy monomers simply calls for a single, straightforward reaction. Secondly, the process is easier to carry out under benign conditions than polycondensation, makes fewer number of byproducts, and let it possible to construct high molecular weighted polymers. The evidence that this reaction's raw substances must conclude epoxy-based monomers means that the supply of reactive monomers is constrained, which is not an insignificant disadvantage.

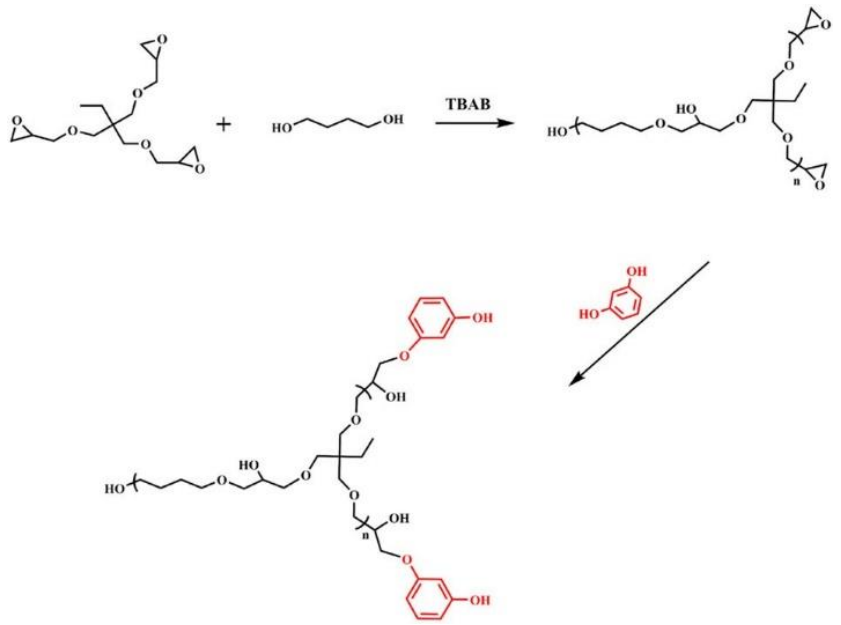



**Figure 2.** Synthetic route of Xing14

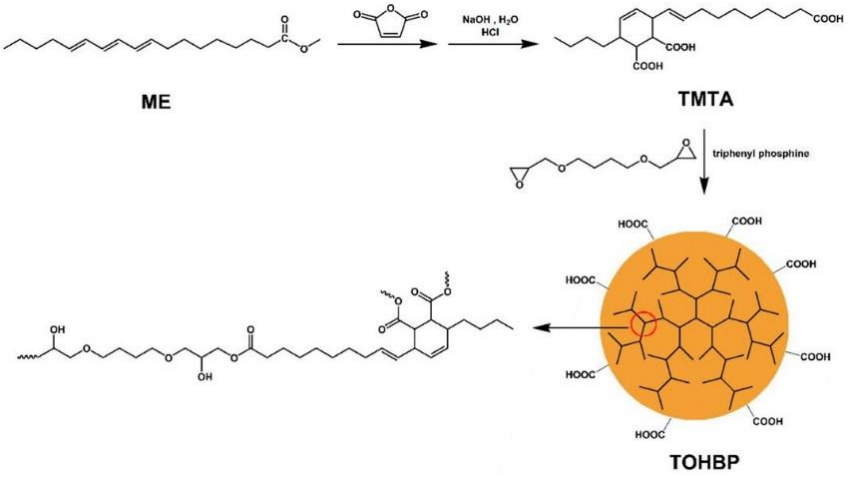



**Figure 3.** Synthetic route of TOHBP

### 2.2. Double-monomer methodology

DMMs can be separated into 2 main sub-genres based on the aggregation pairs that are used and the different reaction pathways. The classic method, the "A2+B3" procedure, is discussed in Introduction and involves polymerizing A2 and B3 purifications after generating hyperbranched polymers which are soluble on the Kakimoto [8] and also Fréchet [7] trays. When fundamental SMM synthetic principles and also the multi-modular features of the "A2+B3" approach is combined, coupled reaction methods (CMMs) based on the production of ABn intermediates via situ from particular chemical processes generate an alternative DMM. In order to increase accessibility and availability of the basis, architecture, and the properties that hyperbranched polymers have with a variety of unique terminals, without one of the dangers of crosslinking, a wide range of commercially available chemicals are now available for the reaction chemistry of CMMs [9]. Due to the fact that neither "A2+B3" nor CMM has been fully covered in prior works or even just briefly stated, the double branching technique is the subject of this review.

## 3. Properties

### 3.1. Solution and rheological properties

One of the key characteristics that distinguish hyperbranched polymers from their linear cognation is their high solubility. Hyperbranched polymers are induced by a branched backbone. According to Kim and also Webster [10], comparing with linear polyphenylenes, hyperbranched polyphenylenes with good solubilities are in a variety of solvents. In addition to being more soluble, hyperbranched polymers behave differently in solutions than linear polymers. It is commonly known that dendritic macromolecules have lower solution viscosities than traditional linear polymers. Given their spherical shape and low viscosity, dendritic macromolecules are thought to be less entangled. Fig. 4 depicts the connection between inherent viscosity and molecular weight (MW) [11]. Dendrimers' regular globular structures cause them to have a bell-shaped connection. On the other way, even if the plot slope number is smaller than the one for linear polymers, the intrinsic viscosity for hyperbranched polymers arises with their rising MW. For unsystematically coiled linear polymers, the valuable data used as Mark-Houwink-Sakurada equation typically fall between 0.5 and 1.0. Due to the other case, several different genres of hyperbranched polymers have values below 0.5, which indicates that the molecules in a solution are sphere-shaped [11]. In addition, hyperbranched polymers often have larger volumes of retention than linear polymers with the exact number of MWs in size exclusion chromatography (SEC) tests. Additionally, this shows that compared to linear polymers, hyperbranched polymers form more compactly in a solution.

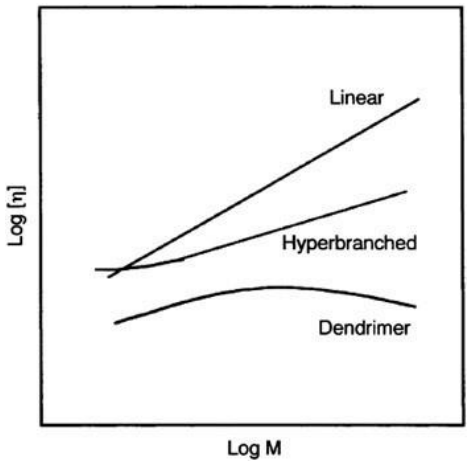



**Figure 4.** Relation between inherent viscosity and MW

### 3.2. Thermal properties

Although few rare cases have been documented in that the polymers can be changed to induce liquid crystallinity, hyperbranched polymers are nearly exclusively amorphous materials [12]. One of the most crucial characteristics is that hyperbranched polymers have a smaller number of glass transition temperature than that of their linear counterparts. Above the certain number of MW of the linear polymer, the function of the end groups can be abandoned due to the behaviors of glass transition being relatable to the substantial separated motions inside the chains of polymers. Their ranching points and the abundance of end groups, however, have a significant impact on the separated motions for hyperbranched polymers [11]. As a result, rather than a segmental movement, the translational movement of the complete molecule has a significant impact on the glass transition for hyperbranched polymers. The Tg values are also influenced by the chemical makeup of the materials; for instance, an aliphatic polyester typically has a significantly lower value of Tg than that of a fragrant polyester [13].

### 3.3. Mechanical properties

The Newtonian nature of hyperbranched polymers' rheological properties in the state of melting, which means that neither shear thinning and thickening can be seen, suggests that these polymers do not form entanglements [14]. Because of the rather weak mechanical qualities imposed by the non-entangled state, polymers can occasionally become brittle. Due to these characteristics, hyperbranched polymers have a limited application in thermoplastics where mechanical strength is crucial.

## 4. Application

### 4.1. Oil recovery

According to Zhang and Yu, polymers are regularly utilized as oil displacement agents, which improve oil recovery from the way to increase the injection fluid’s viscosity, oil-to-water ratio, and the displacement fluid's swept volume [15]. Due to their excellent solubility and viscosity-increasing qualities, polyacrylamides are frequently utilized as oil displacing agents [15]. However, the molecular chains of polyacrylamide are disrupted by cutting degradation during the mixing and pumping operation, severely weakening the polymer's network structure. Its fundamental effect will undoubtedly be significantly diminished. Conditions with a lot of heat and salt will speed up the breakdown of amino groups. Hyperbranched polymers' network structures can lessen the impact of shearing molecular chains on the polymers. Under conditions of high salinity and temperature, the copolymer can keep its useful viscosity due to temperature resistance and salt resistance. As a result, hyperbranched polymers have a number of advantages when it comes to polymer actuation in harsh environments [16].

Most of the crude oil that has been produced now exists in oil-in-water emulsions due to the fast-speed evolution of water flooding, flooding of polymers, and tertiary oil recovery technical methods.

Hyperbranched polymers have the potential to be effective demulsifiers due to their distinctive topology and changed terminal functional groups of their structures [17]. Zhang developed a "one-pot multi-step" technique to create by utilizing the methyl acrylate and ethylenediamine as synthetic raw substances, hyperbranched polyamidoamine H-PAMAM with high demulsification properties [18]. Because of its hyperbranched structure and a lot of amino groups, H-PAMAM reacts quickly. 91% of the oil has been removed, and the demulsification equilibrium can be reached in 30 minutes. The method's ability to produce a product without the need for purification lowers the cost of synthesis.

When in contact with external low-salinity inlet fluids as clay minerals in the deposit may enlarge, exfoliate, and move during oilfield development. This can decrease well productivity and restrict oil flow pore channels, particularly in low-permeability reservoirs [19]. According to Assemi and Marco-

Brown, clay minerals are the primary reason for water sensitivity [15]. Inorganic salts, cationic surfactants, and cationic polymers are the three most often employed clay stabilizers. The most common clay stabilizers are cationic polymer clay stabilizers, which prevent clay swelling by causing long-term adsorption on the surfaces of the clay particles. High molecular weight linear polymers make up the bulk of cationic polymers with easily entangled chains that can adsorb and become entangled in pores [16]. The result is a blockage of the pore channels and a decreased permeability of the reservoir. Hyperbranched polymer molecules have a lot of molecular structure designs that aided by active groups at the ends.

### 4.2. Drug delivery in biomedicine

For therapeutic medications to be more effective, it is vital for cancer cells to accumulate them. Polymer particles offer a specific advantage in this regard because of their enhanced permeability and retention (EPR) properties, which allow them to retain diseased tissue more effectively than healthy tissue [20]. To maximize the effectiveness of bioactive chemicals and avoid unwanted interactions and harmful side effects in patients undergoing therapy, numerous identification and targeting techniques have been studied. Taking branched glycerol-glycidyl methacrylate copolymer, as an illustration, by conjugating with surface hydroxyl functional groups, its previously described degradability was exploited to deliver the anti-cancer medication hydroxycamptothecin [21]. Due to the increased particle size and lack of additional targeting ligands, the medication successfully reduced the growth of cystic carcinoma cells that resembled the salivary gland in a mouse model.

Through triggered delivery made possible by a controlled release mechanism, non-specific interactions in the excretion activity payload from the carrier device are further diminished. Due to their degradability, simplicity of incorporation into sides, and similarities with thiols and thiolates found in biological systems naturally, disulfide linkages are frequently utilized in chemical compounds. Recently, RAFT polymerization with Transmer 5 was used to create hyperbranched PEGMA, which was then post-functionalized by ammonolysis to load thiol compounds [22]. The drug's tolerable cytotoxicity was discovered when it was released in vitro. New techniques for depolymerization have also been developed in addition to well-known polymer degradation technologies. For instance, the polycondensation of hydroxyaryl cyanate monomers is triggered by adjustable hydroxyl "trigger groups," which enable the depolymerization of hyperbranched structures to produce self-destructive hyperbranched polymers. When exposed to adjustable stimuli, it is also possible to use the target environment as a trigger [23]. Sometimes the given information can be changed to reply appropriately. In the manufacture of hyperbranched polymers, the reducing environment of tumor cells is utilized as a trigger for the aimed release of therapeutic components. Prodrug moieties that are cleaved in cancer cells are present in RAFT aggregates of Transmer 6 [24]. The therapeutic potential of loading massive biomacromolecules like RNA or DNA in hyperbranched polymers is immense. For an example, the cationic polymerization of aziridine was initiated using chitosan and amines as a macroinitiator, resulting in chitosan polymers that were grafted with several low molecular weight branches [20]. When used later to complex DNA, this polymer demonstrated improved DNA condensation and decreased in vitro cytotoxicity when compared to branching polyethyleneimines. Hyperbranched nanocarriers have generated interest in the delivery of these biomacromolecules into cells for RNA-based medicinal studies. The ATRP-built hyperbranched core-shell structure of Inimer 4 has been used to create hydrophobic (Fig. 5) and cationic charged core single molecule carriers for small interfering siRNA delivery [25]. It is important to carry ATRP uses a quaternary ammonium moiety as a linker following by chain extension with PEGMA to generate hyperbranched polymers with a positively charged core [20]. The loading of siRNA to this polymeric transporter indicates the effectiveness of gene silencing on the expression of Runt-associated transcription factor 2, which is essential for long-term decrease of the formation of mineralized nodules in osteoblast cells.

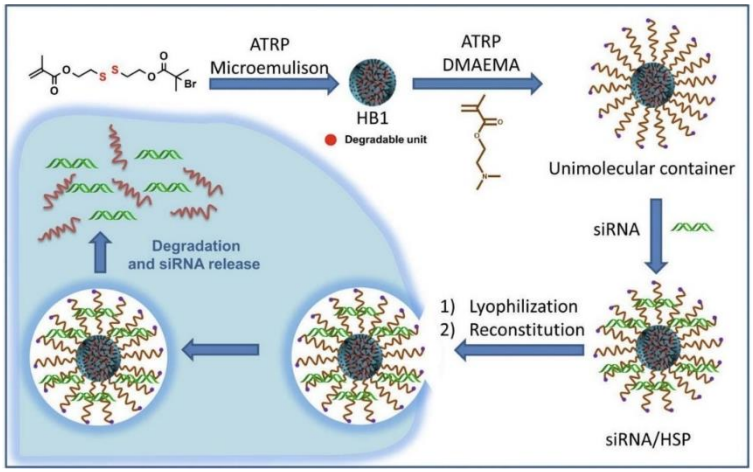



**Figure 5.** ATRP-built hyperbranched core-shell structure of Inimer 4

## 5. Conclusion

Purposefully synthesized hyperbranched polymers yet appear for a newly developed class of materials with expectable, alluring properties and prospective uses, despite the evidence that hyperbranched motifs have been extensively found in biomedicine systems and also the biochemical field for many years. Up till nowadays, SMM and DMM might be used to approach hyperbranched macromolecules. Hypergrafting, surface growth, end capping, terminal grafting, and hybrid blending are techniques for modifying and functionalizing hyperbranched polymers, giving them custom-made properties and intricate architectures. The fields of nanoscience, biochemicals, polymer electrolytes, glue-coatings, and electrical materials, as well as supramolecular chemistry, and others may benefit from the use of hyperbranched polymers and their derivatives. The ability to tailor, polarity, capacity, crystallinity, solubility, thermal stability, and crystallinity of hyperbranched polymers allows for the successful development and fabrication of an increasing number of fascinating materials and devices in the future. However, it is important to understand that thorough research on hyperbranched polymers, that the primary objective of employing hyperbranched polymers in industrial domains is still a pipe dream and that research, in the fields of and use, is also for its infancy. As a result, there are countless possibilities for development space. The following directions need to receive attention soon: the development of materials of newly hyperbranched polymerization with various structures for the covalent bonding or self-assembly; the alteration of hyperbranched macro-molecules' properties via living polymerization, inorganic-organic blending, molecular encapsulation, and some other strategies for the start of the new research directions.

## References

[1] Fréchet J and Tomalia A 2001 West Sussex: Wiley.

[2] Gao C and Yan D 2004 Prog. Polym. Sci. 29 183–275.

[3] Tobias K, Holger F 2020 Hyperbranched polymer architectures: From Flory's AB(f-1) polycondensates to controlled structures Polymer. Volume 211. (Preprint gr-qc/123113).

[4] Odian G. 1991 Principles for polymerization, 3rd ed. (New York: Wiley) p 125–32.

[5] Kricheldorf R, Zang Z, Schwarx G. 1982 New polymer syntheses. 6. Linear and branched poly (3-hydroxy-benzoates). 23: 1821–1829.

[6] Kim H, Webster W 1988 Hyperbranched polyphenylenes. 29 (2): 310–1.

[7] Fréchet J, Henmi M, Gitsov I, Aoshima S, Leduc M and Grubbs RB 1995 SCVP: an approach to dendritic materials. 269: 1080–1083.

[8] Zhang Y and Yu W 2022 Front. Energy Res. 10: 894096.

[9] Gao C, Yan D 2001 Polyaddition of B2 and BB2 type monomers to A2 type monomer. 1. Synthesis of highly branched copoly (sulfone-amine) s. Macromolecules 34: 156–161.

[10] Wanbin Z, Yanmeng W, Shaowu W, Zehua G, Ce Z, Xiuzhong Z and Guanghua Z 2022 Journal of Molecular Liquids. 355 118937.

[11] Higashihara T, Segawa, Y and Sinananwanich, W 2012 Polym J. 44 14–29.

[12] Mu B, Liu T and Tian W 2019 Macromol. Rapid Commun. 40 1800471.

[13] Voit I 1995 Acta Polym. 46 87–99.

[14] Malmstrom E, Johansson M and Hult A 1995 Hyperbranched aliphatic polyesters Macromolecules. 28 1698–1703.

[15] Zhang Y and Yu W 2022 Front. Energy Res. 10: 894096.

[16] Li X, Shi L, Li H and Yuan Z 2018 J. Petroleum Sci. Eng. 166, 25–32.

[17] Sun Y, Lu F, Yang H and Lu C 2019 Nanoscale 11 27 12889–12897.

[18] Sun H, Lei X, Shen B, Zhang H, Liu J and Li G 2018 J. Energy Chem. 27 (4), 1198–1207.

[19] Zheng C, Fu H and Duan W 2021 J. Petroleum Sci. Eng. 196.

[20] Cuneo T and Gao H 2020 WIREs Nanomed nanobiotechnol. e1640.

[21] Wang W, Ma J, Jin F and Liao J 2017 Experimental and Therapeutic Medicine. 14 3105–3111.

[22] Zhuang Y, Su Y, Peng Y, Wang D, Deng H, Xi X and Lu Y 2014 Biomacromolecules. 15 1408–1418.

[23] Liu G, Zhang G, Hu J, Wang X, Zhu M and Liu S 2015 Journ. of the Americ. Chem. Soc. 137 11645–11655.

[24] Hu X, Liu G, Li Y, Wang X and Liu S 2015 Journ. of the Americ. Chem. Soc. 137 362–368.

[25] Zhao L, Wu X, Wang X, Duan C, Wang H, Punjabi A and Han G 2017 ACS Mac. Letters. 6 700–704.