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AMPHIPHILIC HYPERBRANCHED POLYMERS

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ABSTRACT

Hyperbranched polymers are a class of synthetic tree-like macromolecules called as dendritic polymers[1]. They are polymers with densely branched structure and consist of a large number of end groups. Dendritic polymers include dendrimers which have completely branched star-like topologies and hyperbranched polymers have an imperfectly branched or irregular structures. Both dendrimer and hyperbranched polymer molecules are composed of repeating units emerging from a central core.

INTRODUCTION

Hyperbranched polymers are a class of synthetic tree-like macromolecules called as dendritic polymers[1]. They are polymers with densely branched structure and consist of a large number of end groups. Dendritic polymers include dendrimers which have completely branched star-like topologies and hyperbranched polymers have an imperfectly branched or irregular structures. Both dendrimer and hyperbranched polymer molecules are composed of repeating units emerging from a central core.

Amphiphilic polymers are the polymers, which contain hydrophilic and lipophilic part in their structure. [2,3]

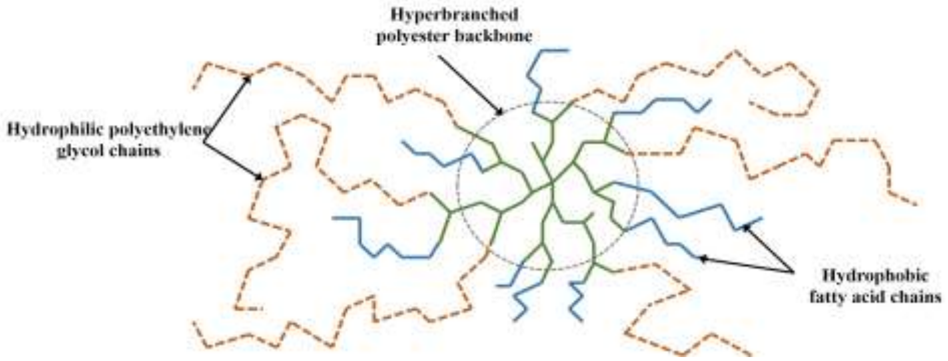

Fig 1: Schematic representation of the amphiphilic HBP Boltorn W3000 molecular structure.

HISTORY

The history of hyperbranched polymers commenced in the 19th century with the report of formation of a resin from tartaric acid (A2B2 monomer) and glycerol (B3 monomer), followed by the report of the reaction between phthalic anhydride (latent A2 monomer) or phthalic acid (A2 monomer) and glycerol (B3 monomer) in 1901 [4]. Kienle et al.[5] then studied this reaction further and found out that the specific viscosity of samples of phthalic anhydride and glycerol was low in comparison with that of other synthetic linear polymers. In 1909, the first commercial synthetic polymers, namely phenolic resins were introduced [6].

Just prior to gelation, these polymers are so called random hyperbranched materials.

In 1952, Flory[7] reported a theory concluding that highly branched polymers can be synthesized without gelation by polycondensation of an ABn monomer (n ^{3} 2) in which A and B functional groups can react with each other. It was not until 1978 that the first synthesis of branched systems was reported by Vögtle and coworkers[8]. In 1988, the first hyperbranched polymer was finally synthesized in the form of soluble polyphenylene by Kim and Webster [9]. Since then, hyperbranched polymers have gained considerable attention from both academia and industry due to their unique properties and ease of preparation, hence greater availability compared with dendrimers.

Amphiphilic branched copolymers with hydrophilic and hydrophobic segments have been the subject of numerous studies.[10,11] The amphiphilic nature of these copolymers containing dissimilar segments gives rise to special properties in selective solvents, at surfaces, as well as in the bulk.[12]

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) [13]. 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 [13,] Callahan, Arsem, Dawson, Howell, and Kienle, et al. [13–15]studied that reaction further, obtaining results and conclusions still used today. For example, Kienle [14] 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.

'Hyperbranched polymer' was first coined by Kim and Webster [16, 17] 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.

PREPARATION

The synthetic techniques for hyperbranched polymers can 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 ABx, AB* or a latent ABx monomer. The second category contains examples of the double-monomer methodology (DMM) in which direct polymerization of two types of monomers or a monomer pair generates hyperbranched polymers[18].

According to the reaction mechanism, the SMM category includes at least four specific approaches [19]: Step-growth polycondensation of ABn monomers method is used to prepare a broad range of hyperbranched polymers such as polyphenylenes, polyesters, polyamides and polycarbonates.

- Self-condensing vinyl polymerization (SCVP) of AB* monomers technique is applied to synthesize polystyrenes, poly(methacrylate) or poly(acrylate)s.
- Multibranching ring-opening polymerization (self condensing ring opening polymerization: SCROP) of latent ABn monomers approach can be used to obtain polyamines, polyethers and polyesters.
- Proton-transfer polymerization (PTP) forms hyperbranched polysiloxanes or polyesters with epoxy or hydroxyl end groups.
- DMM can be classified into two main subclasses based on the selected monomer pairs and different reaction pathways [20].
- 'A2 + B3' methodology has been applied to synthesize three main polymer architectures including polyamides, polycarbonates and polyureas [21]
- Couple-monomer methodology (CMM), which is the combination of the basic SMM and 'A2 + B3', is used to prepare many types of hyperbranched polymers such as poly(sulfone amine)s, poly(ester amine)s, poly(urea urethane)s[22] .

In addition, Gauthier et al. described the successful preparation of amphiphilic arborescent graft copolymers with a poly(ethylene oxide) (PEO) shell via the ''grafting from'' method.[23]

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 ABn or latent ABn monomer leads to hyperbranched macromolecules. SMM consists of at least four components: (1) polycondensation of ABn 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 A2 and Bn ðn . 2Þ monomers, is well known. Recently, a novel DMM based on the in situ formation of ABn 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.[24]

There is a growing interest in the properties of these nanostructured materials and the copolymerization of a vinyl and divinyl monomer in the presence of a chain transfer agent, provides a simple, versatile and scalable synthesis route. Catalytic chain transfer (CCT) is a very efficient and versatile chemistry for molecular weight control and the synthesis of vinyl ω-end functionalized polymers (e.g. macromonomers) in free radical polymerization. This makes CCT an interesting option for the synthesis of hyperbranched polymers as the use of cobaloxime complexes allows for control over the polymer architecture as well as ω-endgroup functionality. An overview of the synthesis of hyperbranched polymers via the copolymerization of a vinyl and divinyl monomer was presented, followed with a number of examples of amphiphilic hyperbranched polymers and their applications.[25]

The synthesis of novel hyperbranched amphiphilic poly(ethylene oxide)−polystyrene (PEO−PS)n copolymers obtained by controlled radical polymerizations: nitroxide mediated polymerization (NMP) and reversible addition−fragmentation chain transfer (RAFT) was reported. The macroinimers used to synthesize copolymers have the general structure AB*, where A stands for PEO with a terminal double bond and B* stands for a PS block with a terminal initiating group (TEMPO or RAFT CTA). Bulk NMP yielded copolymers with higher molecular weight and higher polydispersity. RAFT polymerization in solution gave hyperbranched copolymers with higher molecular weight but lower polydispersity. Langmuir monolayers displayed reversible amphiphilic behavior at the air−water interface. The random, mixed character of short hydrophilic and hydrophobic fragments results in peculiar surface behavior: unlike regular linear and star block copolymers, the amphiphilic hyperbranched macromolecules with higher PEO content are spread at the air−water interface and short PEO fragments are not submerged into the water subphase even at high compression.[26]

Janus structures have attracted a great deal of interest because of their fascinating properties and potential for applications. Hyperbranched polymers, bearing randomly placed docosyl (C22 alkyl segment) and PEG segments on their periphery, can readily reconfigure so as to segregate the alkyl and PEG segments, thereby generating Janus-type structures that were termed as Janus hybramers. DSC studies clearly revealed an endothermic transition that corresponds to the melting of the docosyl domains, while Langmuir isotherms demonstrated that these polymers form stable monolayers that appear to undergo a slight densification beyond a critical surface pressure; this suggested possible crystallization of the docosyl segments at the air–water interface. AFM studies of the transferred monolayers revealed various interesting aggregate morphologies at different surface pressures suggestive of island formation at the air–water interface; at the same time they also provided an estimate of the monolayer thickness. These Janus HBPs also form vesicles as evident from TEM and AFM studies; the AFM height of the deposited vesicles, as expected, was roughly 4 times that of the monolayer. SAXS studies revealed the formation of lamellar structures; the interlamellar spacing was largest when the relative mole fractions of docosyl and PEG segments were similar, but the spacing decreased when the mole fraction of either of these peripheral segments is substantially smaller; this suggested the possible presence of interdigitation within the domains of the minor component.[27]

PROPERTIES

Highly branched polymers that are comprised of dendrimers and hyperbranched polymers represent an intriguing class of macromolecules with compact structure, high density of branching linkers, three-dimensional globular shape and multiple chain-end groups. [28,29]

Hyperbranched polymers have special properties which are the key to their industrial applications.

One of the most interesting physical properties of hyperbranched polymers is their considerably different viscosity characteristics in comparison with their linear analogues[30], which is a consequence of the architecture of the molecules. Hyperbranched macromolecules in solution reach a maximum of intrinsic viscosity as a function of molecular weight as their shape changes from an extended to a more compact globular structure, especially at high molecular weights. The conditions for the existence of this maximum intrinsic viscosity as a function of molecular weight are however still not clear [31]. In addition, for linear polymers, the melt viscosity increases linearly up to a critical molar mass where the viscosity drastically increases as a consequence of the entanglement of polymer chains. However, this phenomenon is not observed for dendrimers or hyperbranched polymers which indicates that minimal entanglement of the branched chains occurs [32].

Other interesting characteristics of hyperbranched polymers are their conformation and degree of branching. X-ray and small-angle neutron scattering experiments show that dendrimers have spherical conformations, whilst hyperbranched polymers have globular structures [33].The degree of branching is reflected in the flexibility of the branching components contained within the architecture as well as the intrinsic viscosity of the polymer. Polymers with a higher degree of branching have lower viscosity. This affects the polymer's relative solubility in various media [34]

Besides, hyperbranched polymers have high chemical reactivity and enhanced solubility when compared to their linear analogues. They also exhibited enhanced compatibility with other polymers as has been demonstrated by blending studies[35].

Hyperbranched materials also have outstanding mechanical properties such as initial modulus, tensile strength and compressive moduli which reflect the compact highly branched structures [36]. The research of Massa et al.[37]showed that a blend of linear Bisphenol A polycarbonate with an all-aromatic hyperbranched polyester resulted in increased tensile and compressive moduli and decreased strain-to-break and toughness compared to those of polycarbonate. Hybrids of silver particles of 1 to 2 nm in size with highly branched amphiphilically modified polyethyleneimines adhere effectively to polar substrates providing environmentally friendly antimicrobial coatings.[38]

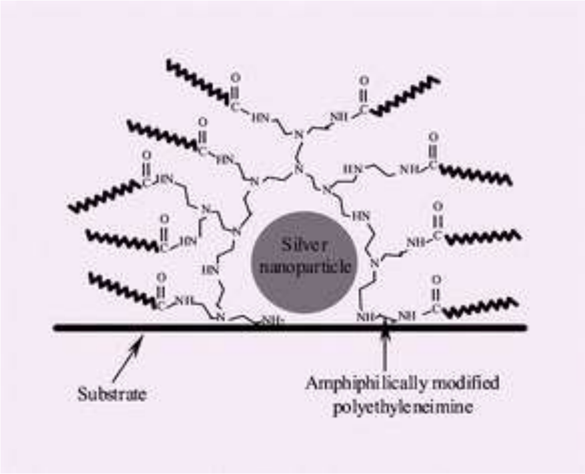

Fig. 2:

The amphiphilic hyperbranched poly(dimethylsiloxane) (HPDMS) bearing dimethylamine groups on the terminal position was synthesized and characterized. The obtained polymer exhibited low viscosity, and good solubility in ether, THF, and acidic aqueous solution. In the acidic aqueous polymer solution, UV-vis absorption and photo luminescence of water-insoluble chromic compounds such as diphenylhexatriene were measured in order to investigate solvating power of hyperbranched poly(dimethylsiloxane)s. It has turned out from the UV absorbance data that a HPDMS solubilized about five molecules of 1,6-diphenylhexatriene.[39]

APPLICATIONS

Due to their unique properties and easy synthesis, hyperbranched polymers have a wide range of potential applications.

Hyperbranched polymers and their substitutes can be used as nanomaterials for host-guest encapsulation [40], fabrication of organic-inorganic hybrids [41] and nanoreactors [42] Because of the low cost and well-defined architecture with multifunctional terminal groups and narrow polydispersity, hyperbranched polymers have increasingly attracted attention in biomaterials application, as biocarriers and biodegradable materials[43]. Based on their special properties, hyperbranched polymers have been used as rheology modifiers or blend components[44], tougheners for thermosets [45], cross-linking or adhesive agents[46] and dye-receptive additives for polyolefins [47]. In the early 1990s, it was found that adding a small amount of hyperbranched polyphenylenes to a polystyrene melt greatly reduced the melt viscosity[48] .Due to a large number of functional groups and interesting optical, electrochemical, biological and mechanical properties of hyperbranched molecules, patterning of hyperbranched polymer films is receiving increased attention [49].

Depending on the high solubility, low viscosity and abundant functional groups, hyperbranched polymers have been used as the base for various coating resins[50] including powder coatings [51], flame retardant coatings[52] and barrier coatings for flexible packaging[53] . Hyperbranched polymers such as poly(phenylenevinylene) and polythiophenes have been used as conjugated functional materials (optical, electronic and magnetic) because of their good solubility and excellent processibility [54.]

Hyperbranched macromolecules possessing ethylene glycol chains have been designed, prepared and used as novel polymeric electrolytes or ion-conducting elastomers as they meet the requirements of having a high solvating power for appropriate ions, good ion transport and electrochemical stability[55]

A condensed overview discusses the existing grafting approaches and the surface behavior of various hyperbranched polymers. Applications of hyperbranched polymers in biomedical fields, for resistive coatings, tough blends, and reinforced nanocomposites were summarized.[56]

Hybrids of silver particles of 1 to 2 nm in size with highly branched amphiphilically modified polyethyleneimines adhere effectively to polar substrates providing environmentally friendly antimicrobial coatings.[57]

Amphiphilically modified hyperbranched polymers can effectively stabilize solutions of metal nanoparticles in apolar organic solvents, as evidenced *e.g.* by the possibility of repeated recycling of catalytically active palladium particles stabilized by modified polyglycerol by means of ultrafiltration.[58]

The development of hyperbranched polymers is a rapidly expanding field in the area of macromolecular science. The synthesis of hyperbranched polymers and some of the key advances that have been made in the application of these hyperbranched materials in the areas of material property modifications and in high value technologies were highlightened.[59]

An amphiphilic hyperbranched polymer containing large amounts of pH sensitive bonds was synthesized. The hydrophobic chains are hyperbranched polyacetals (HBPAs) and the hydrophilic chains are polyethylene glycols. Polyethylene glycols are attached to the hyperbranched polyacetals by the hydrazone bonds. The amphiphilic hyperbranched polymer could be assembled into micelles easily by the dialysis method. The micelles containing large amounts of pH sensitive bonds were quite fragile in pH 5.0 buffer solution but very stable in pH 7.4 buffer solution. DOX-loaded micelles were also prepared by the dialysis method. The sizes of the blanked micelle and DOX-loaded micelle were 30 nm and 35 nm, respectively. The increase of the diameter confirmed that DOX was successfully loaded into the micelle. Drug loading content and drug loading efficiencies were 2.34% and 23.4%, respectively, which was detected by the UV-VIS at the wavelength of 482 nm. The drug release behavior demonstrated that DOX was released faster in pH 5.0 buffer solution than in pH 7.4 buffer solution.[60]

A novel kind of amphiphilic hyperbranched poly(propargyl quaternary ammomium methacrylate)-*co*-polymethyl methacrylate (HPPrAM-*co*-PMMA) is facilely synthesized via a combination of self-condensing vinyl polymerization (SCVP), reversible addition-fragmentation chain transfer (RAFT) polymerization, and a highly efficient Menschutkin reaction. With water soluble quaternary ammonium salt moieties and hydrophobic PMMA segments, the amphiphilic HPPrAM-*co*-PMMA is further employed as the host molecule for anionic dye supermolecular encapsulation. Due to the strong electrostatic interaction and large polar difference between the HPPrAM and PMMA moieties, the AHP exhibits a high loading capability of water soluble dyes (C_{dyes}) (such as rose bengal, methyl orange, and fluorescein sodium). Furthermore, the AHP-dye complex is used as a coloring additive for common polymers, such as styrene-*block*-butadiene-*block*-styrene copolymer (SBS) and poly(methyl methacrylate) (PMMA). A sample colored with the AHP-dye complex shows good dye dispersion, uniformity, and coloring stability. A novel amphiphilic hyperbranched poly(propargyl quaternary ammonium methacrylate)-*co*-polymethyl methacrylate is facilely synthesized via SCVP-RAFT polymerization and a sequential Menschutkin reaction. With a loose structure, tunable hydrophilic/hydrophobic segments, and strong interaction between binding site and guest molecule, it is used as an efficient dye-encapsulation additive and for common polymer coloring. The dyed polymer exhibits good uniformity, high transparency, and low dye release.[61]

Folate-conjugated amphiphilic hyperbranched block copolymer (H40–PLA-*b*-MPEG/PEG–FA) with a dendritic Boltorn® H40 core, a hydrophobic poly(L-lactide) (PLA) inner shell and a hydrophilic methoxy poly(ethylene glycol) (MPEG) and folate-conjugated poly(ethylene glycol) (PEG–FA) outer shell was synthesized as a carrier for tumor-targeted drug delivery. The block copolymer was characterized using ^{1}H NMR and gel permeation chromatography (GPC) analysis. Due to its core–shell structure, this block polymer forms unimolecular micelles in aqueous solutions. The micellar properties of H40–PLA-*b*-MPEG/PEG–FA block copolymer were extensively studied by dynamic light scattering (DLS), fluorescence spectroscopy, and transmission electron microscopy (TEM). An anticancer drug, doxorubicin in the free base form (DOX) was encapsulated into H40–PLA-*b*-MPEG/PEG–FA micelles. The DOX-loaded micelles provided an initial burst release (up to 4 h) followed by a sustained release of the entrapped DOX over a period of about 40 h. Cellular uptake of the DOX-loaded H40–PLA-*b*-MPEG/PEG–FA micelles was found to be higher than that of the DOX-loaded H40–PLA-*b*-MPEG micelles because of the folate-receptor-mediated endocytosis, thereby providing higher cytotoxicity against the 4T1 mouse mammary carcinoma cell line. *In vitro* degradation studies revealed that the H40–PLA-*b*-MPEG/PEG–FA block copolymer hydrolytically degraded into polymer fragments within six weeks. These results indicated that the micelles prepared from the H40–PLA-*b*-MPEG/PEG–FA block copolymer have great potential as tumor-targeted drug delivery nanocarriers.[62]

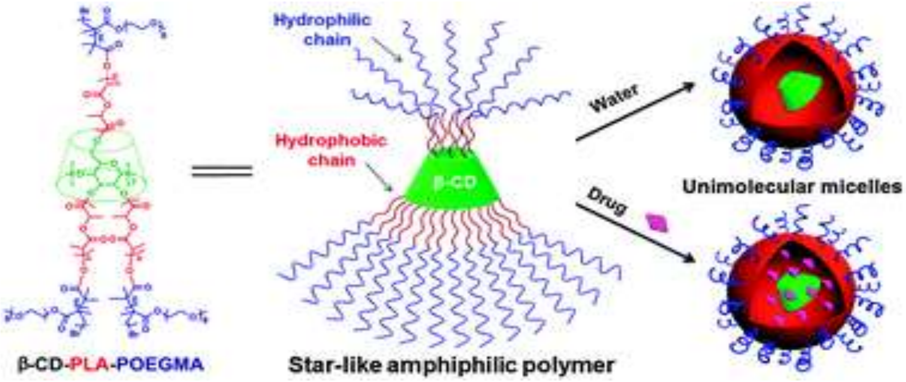

Fig. 3: Star-like amphiphilic polymers are efficient in the delivery of anticancer drugs.

Dendronized multifunctional amphiphilic polymers are excellent nanotransporters for biomedical applications.[63]

MISCELLANEOUS

The research progress in amphiphilic hyperbranched polymers is overviewed here. Synthetic methods of amphiphilic hyperbranched polymers are introduced, which covers the modification of end groups of the hyperbranched polymers with long chain alkyl and polyethylene glycol,and the polymerization of vinyl derivatives through free radical polymerization or ring-opening polymerization, using hyperbranched polymers as macroinitiator. Different structures of amphiphilic hyperbranched polymers have their unique properties in solution, such as core-shell unimolecule micelles and different micellar conformation aggregates. Moreover, the application of amphiphilic hyperbranched polymers,such as drug delivery carrier, material modification, and the encapsulation of dye molecules is also introduced. Then, the development trend of amphiphilic hyperbranched polymers is proposed. The preparation of special properties of amphiphilic hyperbranched polymers and the application of amphiphilic hyperbranched polymers in biological medicine was the main focus in the development of amphiphilic hyperbranched polymers.[64]

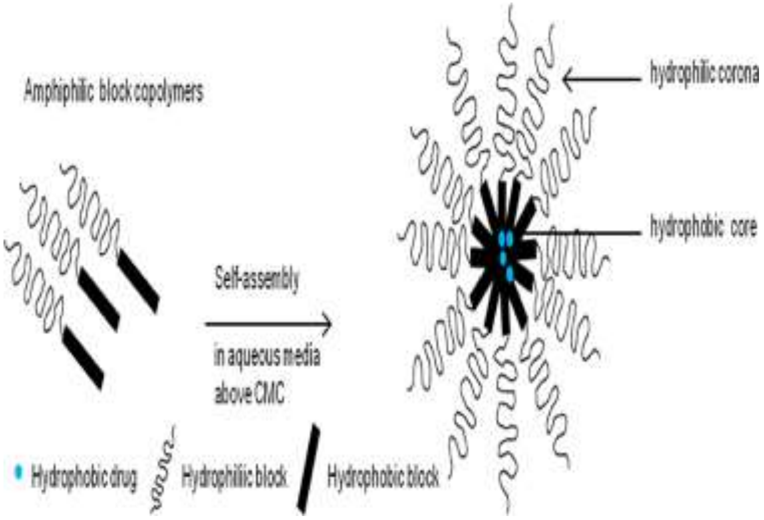

Fig.4: Micelle formation. Drug-loaded polymeric micelle formed from self -assembly of amphiphilic block copolymers in aqueous media.

A hyperbranched polyester based on 3,5-dihydroxybenzoic acid was completely modified with dodecanoyl chloride to result in an amphiphilic, globular polymer, which has a polar core and a nonpolar outer sphere with the ability both to incorporate an organic dye and to interact with a nonpolar matrix. A series of blends were prepared using either polypropylene or polyethylene (HDPE) as the matrix. The content of the polyester as disperse phase was varied between 0.05 and 20 wt %. The blends with polyester contents up to 5% were prepared for colorization of polyolefins using the polyester as a dye carrier. The blends with higher polyester contents were prepared in order to investigate the influence of the hyperbranched material on the material properties. The blends exhibited a heterogeneous morphology with very small particle sizes even at high polyester concentrations. The melt rheology measurements resulted in a reduced complex viscosity for both polyolefins when the hyperbranched polyester was added. The observed melt viscosity of the i-PP blends deviated from the linear mixing rule, whereas the HDPE blends followed it. The use of amphiphilic hyperbranched polyesters as dye carriers allowed a homogeneous distribution of an organic dye in a polyolefin matrix with similar dynamic-mechanical behavior of the blends compared to the case of pure polyolefins. The dyed samples exhibited good stability in extraction experiments.[65]

Amphiphilic hyperbranched core−shell polymers with folate moieties as the targeting groups were synthesized and characterized. The core of the amphiphilic polymers was hyperbranched aliphatic polyester Boltorn H40. The inner part and the outer shell of the amphiphilic polymers were composed of hydrophobic poly(ϵ-caprolactone) segments and hydrophilic poly(ethylene glycol) (PEG) segments, respectively. To achieve tumor cell targeting property, folic acid was further incorporated to the surface of the amphiphilic polymers via a coupling reaction between the hydroxyl group of the PEG segment and the carboxyl group of folic acid. The polymers were characterized by 1H NMR, 13C NMR, and combined size-exclusion chromatography and multiangle laser light scattering analysis. The nanoparticles of the amphiphilic polymers prepared by dialysis method were characterized by transmission electron microscopy and particle size analysis. Two antineoplastic drugs, 5-fluorouracil and paclitaxel, were encapsulated into the nanoparticles. The drug release property and the targeting of the drug-loaded nanoparticles to different cells were evaluated in vitro. The results showed the drug-loaded nanoparticles exhibited enhanced cell inhibition because folate targeting increased the cytotoxicity of drug-loaded nanoparticles against folate receptor expressing tumor cells.[66]

Gao Chao group have reported that the high polarity difference between the core and shell of an amphiphilic hyperbranched polymer could selectively load organic dyes into the core domain. [67]

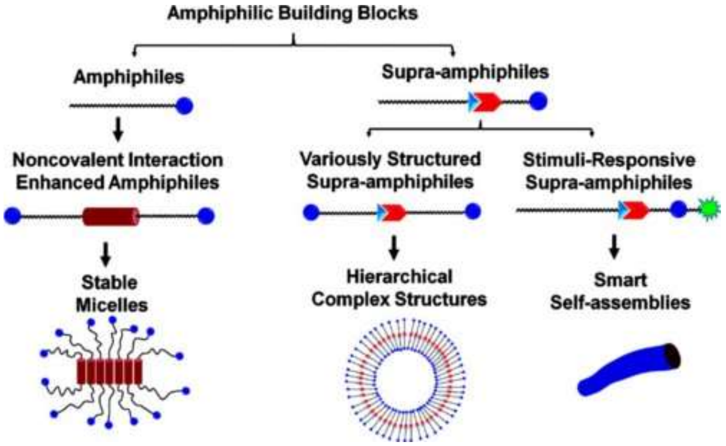

Fig. 5: Amphiphilic building blocks for self-assembly: From amphiphiles to supra-amphiphiles

CONCLUSION

Amphiphilic hyperbranched polymers have both hydrophilic and lipophilic parts in their structure so they are widely used in drug and gene delivery, nanotechnology and supramolecular science. They can be prepared by single-monomer methodology (SMM) and double-monomer methodology (DMM). They possess unique properties, such as solubility, polarity, capacity, crystallinity, solution viscosity, thermal stability as well as rigidity .They are also used as environmentally friendly antimicrobial coatings, as an efficient dye- encapsulation additive and as a carrier for tumour targeted drug delivery.

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