Influence of Branching Architecture on Polymer Properties

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ABSTRACT: Hyperbranched polymers (HBPs), invented at the end of 1980s, are one important subclass of the fourth generation macromolecular architectures following the linear, branched, and crosslinking polymers. Due to their unique topological structure and interesting physical/chemical properties, HBPs have attracted wide attention from both academia and industry. HBPs are composed of linear units, dendritic units, and terminal units. The degree of branching (DB), a term to describe the composition of these three structure units and thus the branching architecture of polymers, is one of the most important intrinsic parameters for HBPs. This review has summarized the effect of the DB on the physical and chemical properties of HBPs, including the rheological property, crystallization and melting behaviors, glass transition, thermal and hydrolytic degradations, phase characteristics, lower critical solution temperature phase transition, optoelectronic properties, encapsulation capability, self-assembly behavior, biomedical applications, and so on. Such a structure and property relationship will build a bridge between the syntheses and applications of HBPs, especially in the application areas of functional materials, biomedical materials, and nanotechnology. © 2011 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 49: 1277–1286, 2011

KEYWORDS: applications; branching architecture; degree of branching; hyperbranched; linear polymers; polymer properties; self-assembly; structure-property relations

INTRODUCTION Hyperbranched polymers (HBPs) are highly branched macromolecules with a three-dimensional dendritic architecture. Benefiting from their highly branching structure, HBPs have the advantages of non-entanglement, low viscosity, good solubility, and a large number of terminal function groups.[1–12] HBPs are composed of linear units, dendritic units, and terminal units. Thus, the term degree of branching (DB) was introduced to describe the composition of these three structure units and thus the branching architecture of polymers.[13–16] DB is one of the most important intrinsic parameters for HBPs, which greatly influences the physical and chemical properties of the polymers. Correspondingly, the control of DB and properties is one of the most significant tasks in the study of HBPs. In recent years, various approaches have been developed to control the branching architecture of HBPs, which has been well described in the literature.[1–8] With the help of these synthesis strategies, a series of polymers with different branching architectures from highly branched polymers to linear polymers have been successfully prepared. Therefore, the systematic researches on the relation between DB and polymer properties become feasible.

INFLUENCE OF BRANCHING ARCHITECTURE ON POLYMER PROPERTIES

The clarification of relation between structure and property is one of the basic goals in polymer science. Up to now, it has been well understood that the properties of polymer materials can be well adjusted by changing the polymeric structure. Because of their highly branching and functionalized architecture, the HBPs show many intriguing physical and chemical properties, which is distinct from their linear analogs. In the following sections, the influence of branching architecture on polymer properties is discussed.

Rheological Property

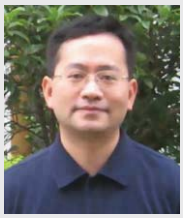
The intrinsic viscosity of polymers depends greatly on the molecular architecture. Generally, the intrinsic viscosity of linear polymer increases steadily with increasing molecular weight, whereas a maximum appears for a dendrimer system.[17] For an HBP, the intrinsic viscosity also increases with increasing molecular weight but much lower than that of linear counterpart.[18,19] The relationship of intrinsic viscosity with molecular architecture has been summarized by Fréchet.[20]

The conformational behavior of both uncharged and charged HBPs in dilute solutions was studied by Mulder et al.[21] They calculated the radius of gyration (R_g) of the polymers with different DBs, and then discussed the effect of DB on R_g. For uncharged HBPs, the R_g was insensitive to DB variation. However, when the polymers were charged, the R_g showed a decreasing function of DB, suggesting the considerablely compact shape of charged HBPs. Sendijarevic and McHugh[22]

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Xinyuan Zhu received his B.Sc. and M.Sc. degrees at Donghua University and obtained his Ph.D. degree at Shanghai Jiao Tong University under the supervision of Prof. Deyue Yan. Following academic appointments at the School of Chemistry and Chemical Engineering in Shanghai Jiao Tong University (1997–2003), he joined the BASF research laboratory at the ISIS in Strasbourg as a post-doctoral researcher. He became a full professor for Polymer Science and Engineering at Shanghai Jiao Tong University in 2005. His scientific interests focus on the controlled preparation and biomedical applications of functional polymers.



Yongfeng Zhou completed B.Sc. and M.Sc. degrees in Chemistry of Harbin Institute of Technology. In 2005, he obtained his Ph.D. in Polymer Chemistry and Physics at Shanghai Jiao Tong University under the supervision of Prof. Deyue Yan. Then, he worked in the same university as a lecturer and associate professor. In 2010, he was promoted as a full professor. His current research interests include the controllable synthesis, self-assembly and applications of block copolymers, especially the hyperbranched multiarm copolymers.



Deyue Yan received his B.Sc. degree in Chemistry at Nankai University and M.Sc. degree in Polymer Chemistry at Jilin University. In 2002, he got the Ph.D. degree in Polymer Chemistry at Catholic University of Leuven, Belgium. He began his work at East China University of Science and Technology as a lecturer in 1966, and then moved to Tongji University in 1980 as an associate professor. From 1987 to now, he was a full professor at Shanghai Jiao Tong University. Prof. Yan was elected Member of the Chinese Academy of Sciences in 2005. His main research interests concern the polymerization kinetics theory, the synthesis and application of hyperbranched polymers, the modification of carbon nanotubes, supramolecular self-assembly, etc.



studied the rheological behavior of hyperbranched poly(ether-imide) with DBs ranging from 0.42 to 0.68 in concentrated solutions. These hyperbranched poly(ether-imide)s showed characteristic Newtonian behavior, and a transition from Newtonian at the lowest molecular weight to shear thinning at higher molecular weights was observed. The magnitude of the shear viscosity, the onset of the shear thinning, and the rise of normal stress effects directly correlated with the DB. Kharchenko and Kannan[23,24] studied the role of architecture on the conformation, rheology and orientation behavior of linear, star, and hyperbranched polystyrenes. The intrinsic viscosity ($[\eta]$), radius of gyration (R_g), viscometric radius (R_η), and zero-shear rate viscosity (η_0) were measured. Compared with a linear polystyrene of the same molecular weight, the hyperbranched polystyrene had a significantly lower intrinsic viscosity, Mark-Houwink exponent, and hydrodynamic radius. Interestingly, a new parameter, shrinking factor h, was used to distinguish the effect of branching on the reduced hydrodynamic volume from the effect of molecular perturbation of chain conformation. The experimental data suggested that hyperbranched polystyrene with short branches underwent strong preferential stretches near the center of the molecule, which might be the reason of the partial molecular expansion. When the DB was high and the branch was short, steric hindrance prevented the formation of entanglements, resulting in a linear dependence of η_0 versus molecular weight.

With the aid of computer simulation, Adolf and coworkers[25] studied the rheology of HBPs with different DBs under shear. They found that the HBPs with a low DB revealed sparse structure, while those with high DB possessed very compact structure. Therefore, the conformation change of HBPs under the shear flow was quite different. When the DB was small, HBP was elongated in the direction of shear and were squeezed in the perpendicular direction. However, for a HBP with DB = 0.8, the elongation in the shear direction was small. This result suggested that with the increase of DB, higher shear rate was needed to initiate shear thinning for practical application. Subsequently, these authors further discussed the influence of the Wiener index on the $[\eta]$ and R_g of HBPs through the Brownian dynamics simulations.[26] A series of degree of polymerization (N) and DB were adopted, and molecules with different Wiener indices (W) were simulated for each DB and N. Both $[\eta]$ and R_g of HBPs were observed to scale with W at a constant N via a power law relationship.

Besides the solution behavior, the melt properties of HBPs were investigated, and a strong relation between the DB and melt rheological properties had been observed. Johansson and coworkers[27] synthesized a series of hyperbranched aliphatic polyethers originated from 3-ethyl-3-(hydromethyl)oxetane. Figure 1 gives the rheological curves of complex dynamic viscosity versus temperature for polyethers with different DBs. It can be found that the sample with the highest DB (DB = 0.41) exhibits a completely amorphous behavior, and its viscosity

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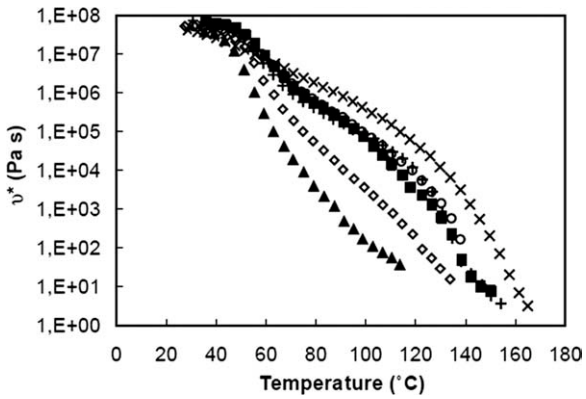


FIGURE 1 Complex dynamic viscosity versus temperature for polyethers with different DBs: 0.41 (▲); 0.32 (◇); 0.30 (■); 0.30 (+); 0.24 (○); 0.11 (×). Reprinted with permission from ref. 27, Copyright 2002, Elsevier.

decreases rapidly above the glass transition temperature (T_g) without any trace of a rubbery plateau, suggesting the absence of chain entanglement in the melts. On the other hand, those samples with a low DB behave more like a semi-crystalline polymer with only a small drop in viscosity at the T_g, together with the presence of a rubbery plateau before the viscosity drop at the crystalline melting temperature. The low viscosity of HBPs makes them excellent modifiers and additives.[28–33] For example, Kim and Webster[28] found that the addition of a small amount of hyperbranched polyphenylene into polystyrene reduced the melt viscosity greatly.

Crystallization and Melting Behaviors

The crystallization and melting behaviors of polymers are closely related to their chain architecture. For example, linear high-density polyethylene has a high crystalline melting temperature (135 °C), indicating a strong crystallization ability; by introduction of slight branching architecture into polyethylene, the obtained low-density polyethylene shows a low melting temperature (115 °C); for the highly branched polyethylene, it is amorphous and the melting peak in the differential scanning calorimetry (DSC) pattern disappears completely.[34] Apparently, the branching architecture has an important influence on the crystallization and melting behaviors of polyethylene.

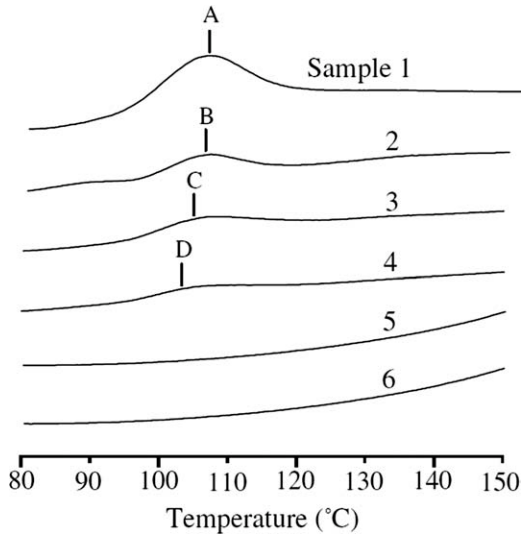


FIGURE 2 DSC melting curves of PEHO samples with different DBs: 1 (0.06); 2 (0.07); 3 (0.13); 4 (0.25); 5 (0.40); 6 (0.45). The temperature of peak A, B, C, D is near 108, 107, 105, and 102 °C respectively. Reprinted with permission from ref. 37, Copyright 2005, IOP.

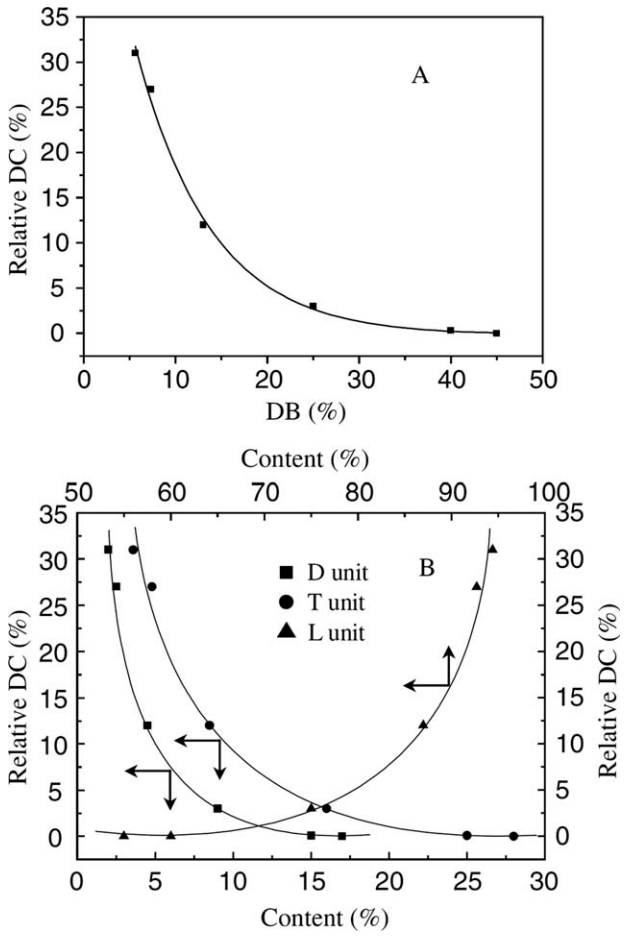


FIGURE 3 Effect of DB on crystallization behavior of PEHO. (A) Plot of relative DC versus DB; (B) curves of relative DC versus D unit content (■), T unit content (●) and L unit content (▲). Reprinted with permission from ref. 37, Copyright 2005, IOP.

By changing the ratio of catalyst to monomer or the reaction temperature, Yan and coworkers[35,36] prepared a series of polyethers with different DBs from the cationic polymerization of 3-ethyl(methyl)-3-(hydroxymethyl)oxetane. The DSC melting curves of poly[3-ethyl-3-(hydroxymethyl)oxetane] (PEHO) samples are given in Figure 2.[37] It can be found that the hyperbranched PEHO is amorphous and essentially linear sample is partially crystalline. With the decrease of DB, the crystallinity of polyethers increases. Figure 3(A) gives the plot of the relative degree of crystallization (DC) versus DB of PEHO.[37] It can be seen that the relative DC decreases from 0.31 to 0 with increasing DB from 0.06 to 0.40.

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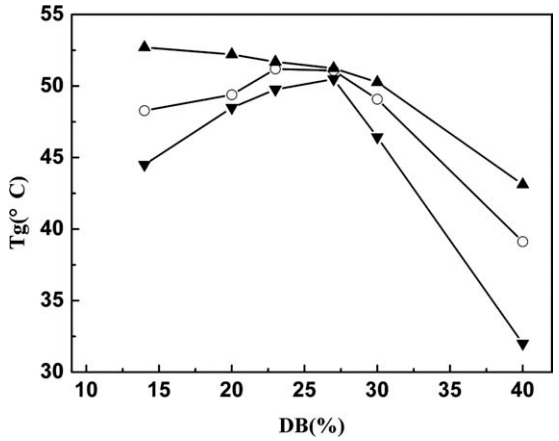


FIGURE 4 The relation between Tg and DB of PEHOs with different thermal treatments (▼: amorphous samples; ○: isothermally crystallized at 90 °C for 24 h; ▲: isothermally crystallized at 90 °C for 72 h). Reprinted with permission from ref. 42, Copyright 2009, American Chemical Society.

Apparently, the crystallization ability of PEHO is weakened dramatically with the introduction of branching structure into the molecular chain. To further clarify the effect of branching architecture on the crystallization behavior, the plots of relative DC versus the content of dendritic (D), terminal (T), and linear (L) units are presented in Figure 3(B).[37] It can be observed clearly that the crystallinity of PEHO decreases with increasing D and T unit content but goes up with increasing L unit content. Therefore, the crystallization and melting behaviors of polymers can be adjusted by polymer branching architecture.

The effect of DB on crystallization and melting behaviors of hyperbranched polyethers was also studied by Johansson and coworkers.[27] It was observed that the crystallinity decreased with increasing DB because of the presence of branched structure in the polymer. In the meantime, the melting temperature of polyether was slightly increased for the samples with high crystallinity.

Glass Transition

Glass transition is one of the typical characteristics of polymers. Because of the existence of highly branching architecture and plenty of end-groups, the glass transition of HBP is quite different from that of linear counterpart. For a traditional linear polymer, the glass transition originates from the long-range segmental motions. However, for an HBP, the glass transition is associated with many co-operative interactions.

Comparing the glass transition temperatures (T_gs) of hyperbranched polyphenylenes with some related small molecules, Kim and Beckerbauer[38] suggested that the HBPs had a similar relaxation mechanism with the small molecules. Their research also confirmed the large effect of chain end-groups on the thermal relaxation. Subsequently, Hawker and Chu[39] synthesized a series of hyperbranched poly(ether-ketones)s with a variety of functional end-groups and controllable DBs. The glass transition evaluation of these HBPs showed that thermal stability of polymers was independent of macromolecular architecture, but depended heavily on the nature of functional end-groups. Based on the comparison of T_gs of hyperbranched polyglycerols and their esterified derivatives, Frey and coworkers[40] proposed that T_g of a highly polar HBP with a large number of hydroxyl end-groups was controlled mainly by two factors: the hydrogen bonding of the end-groups and the tendencies of the substituents to form higher ordered phase.

With a copolymerization strategy of linear and branched comonomers, Jayakannan and Ramakrishnan[41] synthesized a series of poly(4-ethyleneoxyl benzoate)s with different DBs. They found that the introduction of branching units into linear polymers dramatically affected the glass transition. The variation of T_g with branching exhibited a minimum at a branching content of 10 mmol %, which might be related to the changes of free volume and interacting end-groups simultaneously.

Zhu and coworkers[42] prepared a series of PEHO with variable DBs. In these samples, the molecular weight, molecular weight distribution and the end-group content were quite similar. Therefore, the direct relationship of the molecular branching architecture and T_g could be disclosed. Figure 4 gives the relation between T_g and DB. For amorphous samples, T_g first increases with DB, then passes through a maximum, and finally decreases sharply. With increasing DB, the large amount of junction points in the PEHO backbone makes the molecule very compact. Therefore, the rigidity of PEHO increases and T_g of PEHO is enhanced. On the other hand, the free volume contributed from the terminal units also increases with DB, which strengthens the molecular mobility. The competition between the junction density and the free volume of terminal units results in a maximum T_g at an intermediate DB. After thermal treatments, the hyperbranched polyethers with various DBs perform quite different crystallization behaviors, which makes the relationship of branching architecture and T_g more complicated. When the samples are crystallized for a long time, the T_g of PEHOs decreases monotonically with DB.[42,43] The positron annihilation lifetime measurements in Figure 5 show that the enhancement of T_g can be attributed to the low concentration of free-volume hole.[44]

As stated above, the glass transition of HBP is different from linear polymer, which can be affected by many factors, such as the content and chemical property of end-groups, branching junctions, compactness of hyperbranched structure, and crystallization ability.

Thermal and Hydrolytic Degradations

Degradation property has become an important performance of temporary materials applied in biomedicine, agriculture, or structural components for reduction of the impact of synthetic functional materials upon the environment.[45–49] By using a phosphazene superbase catalyzed proton transfer polymerization and acid catalyzed ring opening polymerization, Paulasaari and Weber[50] prepared the isomeric hyperbranched

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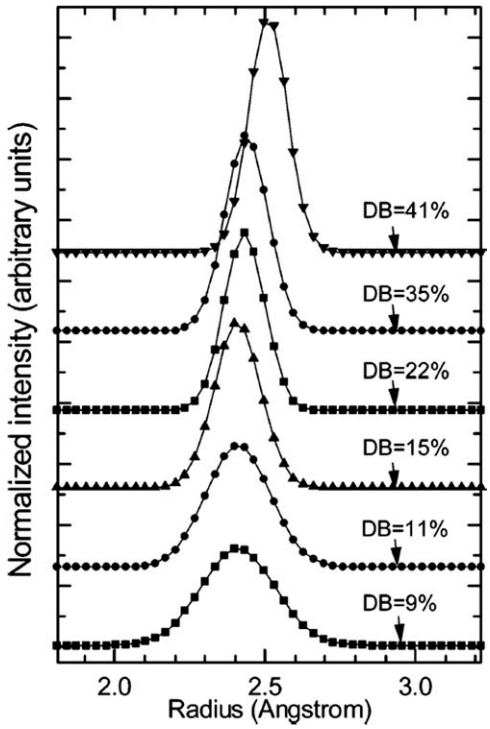


FIGURE 5 Effect of the DB on free-volume size distribution for the hyperbranched PEHO at room temperature. Reprinted with permission from ref. 44, Copyright 2005, American Chemical Society.

polysiloxanes and highly regular linear polysiloxanes, respectively. The thermogravimetric analysis of hyperbranched polysiloxane was similar to the linear one, but the former gave a higher final residue about 10% compared with almost zero of the latter. The high thermogravimetric residue might be related to the suppression of volatile cyclics formation by branching.

Wooley and coworkers[51] compared the hydrolytic degradation processes of linear and hyperbranched poly(silyl-ester)s (DB = 0.51). They found that the degradation behavior of HBP was very different from that of linear one. The hyperbranched poly(silyl-ester) exhibited a slow initial molecular weight loss, followed by rapid hydrolytic cleavage. But for linear polymer, a rapid initial degradation rate appeared and then followed by ever-decreasing decomposition rate. The hydrolysis difference of hyperbranched and linear poly(silyl-ester)s might be related to the existence of many silyl ether linkages at chain ends and the formation of macrocycles. Liu and coworkers[52,53] used the ^{1}H NMR to monitor the hydrolysis of hyperbranched and linear poly(amino-ester)s. Compared with the linear poly(amino-ester), the hydrolysis of hyperbranched samples was retarded due to the compact hyperbranched spatial structure preventing the accessibility of water.

Phase Characteristics

In 2002, Iedema and coworkers[54] studied the dynamics of polymer-solvent liquid-liquid phase separation by using the mesoscopic dissipative particle dynamics simulation method. They found that the branching structure had a pronounced effect on the radius of gyration (R_g) and the centre of mass diffusion of the polymer. For an HBP, because of a smaller difference in chemical potential between the collapsed state of the HBP solution and the melt state, the increase in the centre of mass diffusion with DB became less pronounced.

Arlt and coworkers[55] systematically investigated the phase behavior of HBP-solvent and HBP-solvent-supercritical gas system. After comparing phase behavior of polymers with different DBs in a same solvent, only a small influence on the vapor-liquid equilibria was found. However, because of a comparatively low ethanol activity in the hyperbranched polyglycerol solution, the ethanol adsorption by polyglycerol tended to increase with increasing DB.

Lower Critical Solution Temperature Phase Transition

Water-soluble thermoresponsive polymers are one of the most appealing stimuli-responsive species, which undergo fast and reversible phase transition from a soluble to an insoluble state at the lower critical solution temperature (LCST).[56,57] Very recently, Zhou and coworkers[58] have synthesized two series of thermoresponsive HBPs [series A: PEHO-*g*-PEOs, series B: PEHO-*g*-PDMAEMAs, PDMAEAM denotes poly(2-(dimethylamino)ethyl methacrylate)], and find that the LCST phase transition is highly dependent on the DBs of the polymers. In each series, the polymers have a similar PEO or PDMAEMA arm length but DB-variable PEHO cores. Series A belongs to the thermoresponsive polymer system with the LCST transition based on hydrophilic-hydrophobic balance, while series B belongs to the polymer system with the LCST transition based on coil-to-globule conformation transition.

For series A, all polymer samples demonstrate a clear phase transition on heating at a critical LCST according to the variable temperature ultraviolet-visible spectrometry (Fig. 6). Comparing the transmittance curves with one another, it is evident that the copolymer having a higher DB of PEHO core possesses a higher LCST (the LCST is determined from the first decline point on the curve) in water. The increase of DB from 0.05 to 0.44 causes a notable LCST enhancement from 18 to 38 °C (the inset of Fig. 6).

For series B, several polymer samples of PEHO-*g*-PDMAEMAs with variable PEHO DBs and PDMAEMA arm lengths have been synthesized. An abbreviation of D*m*-*n* is used (*m* means the DB of PEHO cores, and *n* means the number-average degree of polymerization of PDMAEMA arms). As PDMAEMA is a weak polybase, the solution pH changes with heating in pure water, which exerts a pronounced effect on the LCST behavior.[59,60] Thus, the LCST behaviors of series B in PBS (0.2 M) are investigated, in which the buffer pH values are set at 7.5, 8.0, and 8.5, respectively. Figure 7 has summarized the LCST values of the copolymers with linear (DB = 0.07) or highly branched (DB = 0.48) PEHO cores and different PDMAEMA arm lengths (4, 7, and 12) at different solution pH. Two conclusions can be drawn: one is that the LCST of PEHO-*g*-PDMAEMA is highly dependent on the solution pH, and the higher the pH, the lower the LCST; the other is that

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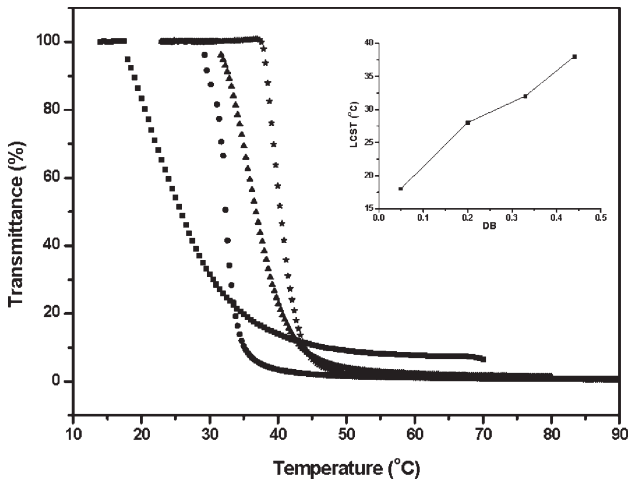


FIGURE 6 Temperature dependence of optical transmittance at 500 nm for aqueous solution of series A. The inset shows the dependence of the LCST on the DB of the PEHO core for copolymers in series A. Reprinted with permission from ref. 58, Copyright 2010, American Chemical Society.

the effect of the PEHO DB and PDMAEMA arm length on the LCST is small (most of the alternations are within 2 or 3 °C, and the highest alternation is 6 °C between the samples of D0.48-4 and D0.48-7).

To sum up, the LCST transition of the thermoresponsive polymers based on hydrophilic-hydrophobic balance is highly dependent on the DBs, while the dependence is weak for the thermoresponsive polymers based on coil-to-globule conformation transition.

Optoelectronic Properties

Conjugated polymers have attracted a great deal of attention due to their unique optoelectronic properties, good film-forming property and facile fabrication.[61–64] By changing the molecular architecture, the optoelectronic properties of conjugated polymers, such as emission efficiency, charge transfer, conductivity, energy transfer, and exciton migration, can be readily controlled. Due to the existence of strong π-π interaction, the solubility of traditional linear conjugated polymer is usually poor and the aggregation-induced emission quench happens frequently. To weaken such a strong π-π interaction, highly branched architecture has been introduced into the conjugated polymer systems to avoid the regularly molecular stacking.[65–67] Based on Suzuki crossing coupling, Wittig coupling, polycyclotrimerizations and alkine coupling, various hyperbranched conjugated polymers with different branching structures have been successfully synthesized.

Hyperbranched conjugated polymers show several greater advantages than their linear counterparts in high solubility, good processability, less unfavorable interaction, and absent/low crystallization ability. By introducing the branching units into the conjugated polymers, the strong π-π interaction between conjugated chains is weakened, which improves polymer solubility greatly. In the meantime, due to the decrease of conjugated length, the hypochromatic shift of maximum absorption peaks can be observed.[68,69] Compared with linear conjugated polymer in solid state, the maximum emission peak of hyperbranched conjugated polymer shows less red-shift in the photoluminescence spectra with higher fluorescence quantum efficiency.[70] This can be explained by the depression of molecular aggregation and excimer formation. After annealing at high temperature, the hyperbranched conjugated polymer shows stable photoluminescence spectrum.[66] Furthermore, benefiting from the existence of many terminal groups in the hyperbranched conjugated polymers, the optoelectronic properties can be easily adjusted by modifying the functional end-groups or changing the intra- and inter-molecular interactions of conjugated polymers.[71–73]

Nevertheless, because of the severe overlap of individual aromatic NMR signals in a very narrow range, the DBs of hyperbranched conjugated polymers are usually difficult to be determined. Therefore, the effect of DB on the optoelectronic properties of conjugated polymers is rarely reported.

Encapsulation Capability

The polymeric micelles of linear amphiphilic block copolymers are generally the multimolecular micelles, which will dissociate at high dilutions. In comparison, amphiphilic HBPs have been widely used as unimolecular micelles and exhibit high stability. Therefore, HBPs are used as the unimolecular carriers to encapsulate the hydrophobic and hydrophilic guests, such as dyes, metallic ions, and nanocrystals.[74–76] Frey and coworkers[77,78] prepared the esterified hyperbranched and linear polyglycerols. They found that the esterified hyperbranched polyglycerol could encapsulate Congo Red dye very well while the linear analog lost the encapsulation capability. Kumar and Brooks[79] compared the encapsulation capacity of hyperbranched and linear polyglycidol unimolecular reverse micelles, and also found that the HBP had a higher encapsulation capacity than the linear one. Stiriba and coworkers[80] reported the guest encapsulation

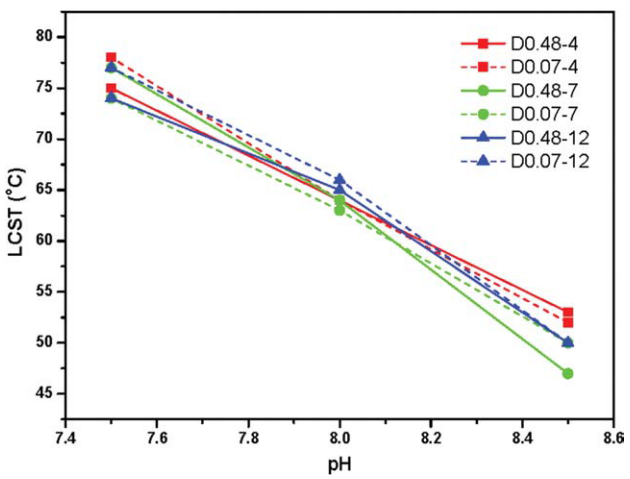


FIGURE 7 Dependence of LCST on solution pH for copolymers in series B with linear or highly branched PEHO cores and different PDMAEMA arm lengths. Reprinted with permission from ref. 58, Copyright 2010, American Chemical Society.

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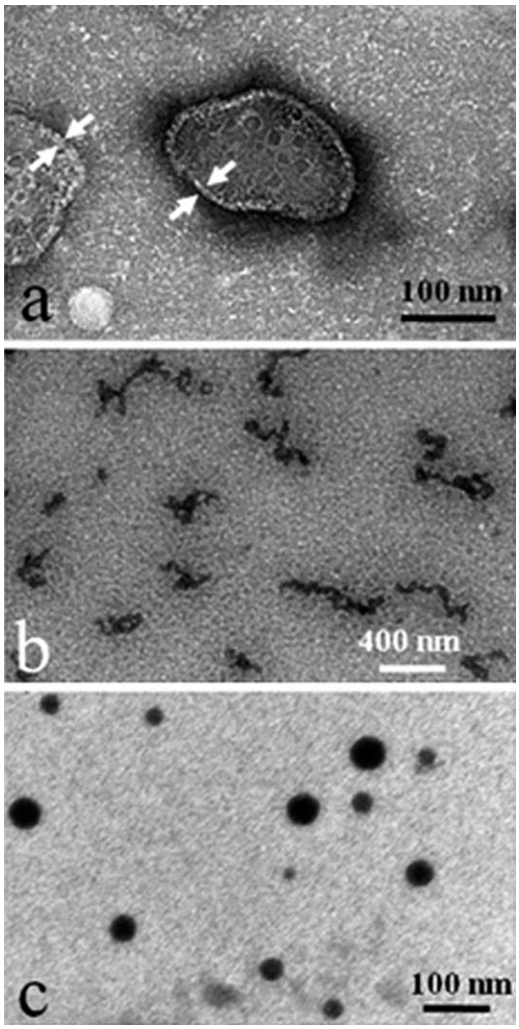


FIGURE 8 TEM photographs of PEHO-*g*-PEO assemblies. With the decrease of DB in PEHO cores, PEHO-*g*-PEOs self-assemble into vesicles (a), wormlike micelles (b), and spherical micelles (c). Reprinted with permission from ref. 81, Copyright 2010, American Chemical Society.

capacities of partially amidated hyperbranched and linear poly(ethylenimine)s in solution. The compact core-shell structure in the amidated hyperbranched poly(ethylenimine) provided a high encapsulation amount of dye in the polar interior. In contrast, the weak interaction between dyes and the secondary amines in linear poly(ethylenimine) resulted in the low loading of dyes. All of these aforementioned results demonstrated unambiguously the crucial role of the hyperbranched topology on the encapsulation capacity.

Self-Assembly Behavior

The self-assembly behavior of amphiphilic HBPs is highly dependent on the DB. Zhou and coworkers[36] synthesized a series of hydrophobic PEHO with variable DB but similar molecular weight. After that, many hydrophilic poly(ethylene oxide) (PEO) arms were grafted onto the surface of hydrophobic PEHO core, forming the amphiphilic multiarm copolymer of PEHO-*g*-PEO. The obtained PEHO-*g*-PEOs had different branching topologies depending on the DB of PEHO cores. For the hyperbranched core, a core-shell star copolymer was obtained. On the contrary, only a comb-like copolymer was formed for linear PEHO core. If the PEHO had an intermediate DB, the topology of the PEHO-*g*-PEO was between the star and comb type. Thus, these amphiphilic block copolymers showed different self-assembly behaviors. With the decrease of PEHOs DB, self-assembly morphology of PEHO-*g*-PEOs was changed from vesicles, wormlike micelles to spherical micelles.[81] Figure 8 gives the correspondent self-assembly morphologies.

The self-assembly behavior of plasmid DNA and cationic HBPs can also be affected by the DB.[82] Figure 9 gives the AFM images of DNA condensed by various poly(amidoamine)s (PAMAMs) with DBs from 0.44 to 0.04. Figure 9(A) shows typical plectonemic conformations of supercoiled plasmids deposited onto freshly cleaved mica in the absence of polycation. Keeping the *N/P* ratio as 2, various morphologies can be observed by only changing the topological structure of cationic polymers. Highly branched PAMAM forms tightly condensed nanoparticles with DNA, as shown in Figure 9(B). With reducing DB, the particles become looser and looser, and some dendritic or large gorgon-like DNA aggregates appear [Fig. 9(C–E)]. For the linear PAMAM, only loose circular plasmid DNA exists in the AFM image [Fig. 9(F)]. Therefore, by only changing the DB of cationic vectors, the self-assembly behavior of plasmid DNA and cationic polymer can be readily controlled.

Biomedical Applications

Benefiting from their unique topological structure and interesting physical/chemical properties, HBPs exhibit great potentials in biomedical applications.[83] By adjusting the branching architecture of polymers, biocompatibility and other related properties will be changed. Zhu and coworkers[82] synthesized a series of cationic PAMAMs with different branching architecture (DBs from 0.44 to 0.04) but similar compositions and molecule weights. The cytotoxicity of these PAMAMs with variable DBs was evaluated using the MTT assay in COS-7 cell line. It was found that the cytotoxicity of PAMAMs increased with decreasing branching architecture. The low toxicity of highly branched PAMAM might be related to its small molecular size and compact spatial structure.

Kannan and coworkers[84] conjugated the model drug methyl prednisolone onto hyperbranched polyol and PAMAM dendrimer respectively. Comparing the dendrimer, the drug payload of hyperbranched polyol was higher. More importantly, at short treatment time, the anti-inflammatory activity of hyperbranched polyol conjugates was much higher than that of dendrimer conjugates. It was believed that the imperfect branching polyol was easily uptaken into the lysosome to release the drugs, which improved the anti-inflammatory activity.

The branching architecture has a remarkable influence on the gene transfer. Through partial degradation of PAMAM dendrimer into the hyperbranched one, Szoka and

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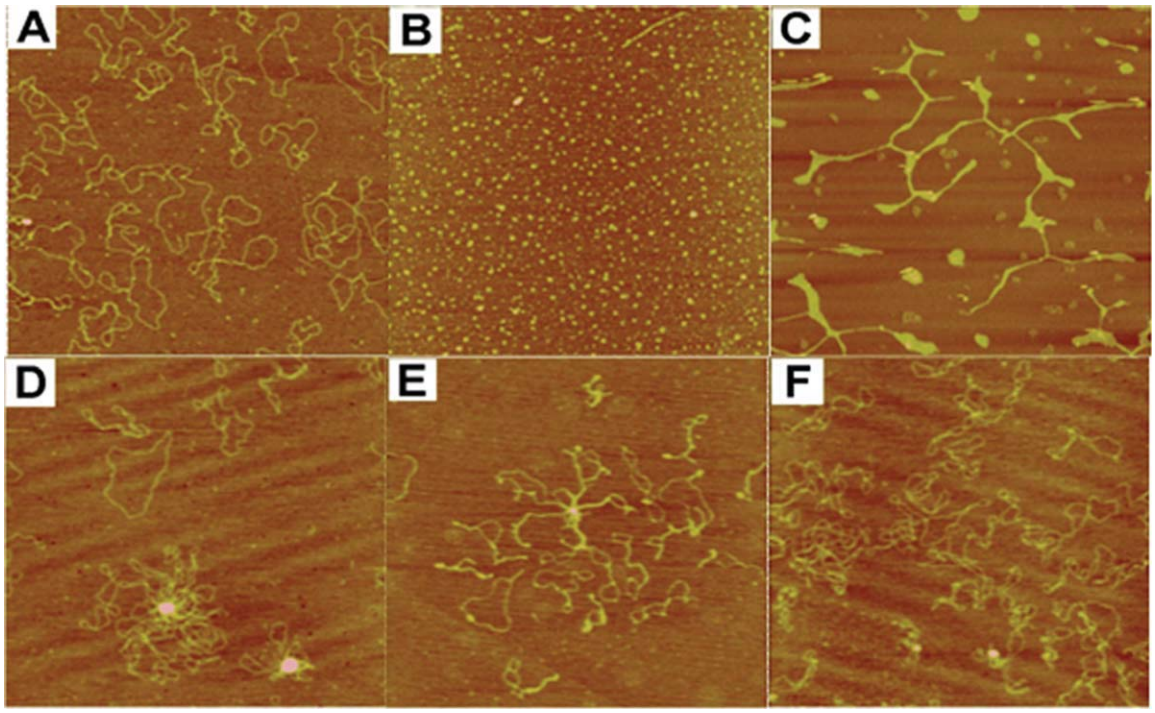


FIGURE 9 AFM images of DNA condensation by various PAMAMs. DNA was binding by polymers at N/P=2. All images were obtained with complexes deposited onto fresh mica surface. Each image represents a 2 × 2 μm scan. (a) Pure plasmid DNA in Hepes buffer. (b)–(f) DNA is binding by various PAMAMs with different branching architecture (DB = 0.44, 0.31, 0.21, 0.11, and 0.04, respectively). Reprinted with permission from ref. 82, Copyright 2010, American Chemical Society.

coworkers[85] increased the transfection efficiency of PAMAM dendrimer. They suggested that the high transfection efficiency resulted from the enhanced molecular flexibility of imperfect branching structure. Zhu and coworkers[82] prepared a series of cationic PAMAMs with DBs from 0.04 to 0.44. *In vitro* transfection studies in Figure 10 show that the

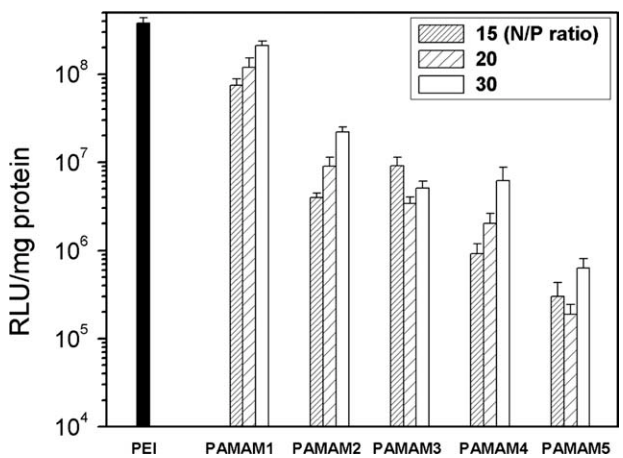


FIGURE 10 Transfection efficiency of PAMAMs (PAMAM1-PAMAM5) with different branching architecture (DB = 0.44, 0.31, 0.21, 0.11, and 0.04, respectively) in COS-7 cells at various *N/P* ratios. Luciferase expression levels were measured 48 h later. Data are expressed as mean ± standard deviation values of three determinations. Reprinted with permission from ref. 82, Copyright 2010, American Chemical Society.

transfection efficiency is improved for more than three orders of magnitude by increasing the DB of these cationic PAMAMs. By adopting a simple surface modification of polyethylenimine (PEI), Haag and coworkers[86] found that the DB of maximum transfection efficiency was around 0.6. On the other hand, both Kissel and coworkers[87] and Wightman et al.[88] reported that the transfection efficiency of linear PEI *in vitro* was greater than that of hyperbranched one. Therefore, the systematic studies on the relationship of DB and transfection efficiency are still to be explored.

Eichhorn and coworkers[89] studied the influence of the DB on the protein adsorption potential of hyperbranched polyester films. They found that with increasing DB and hydroxyl end-groups, the protein adsorption increased. To differentiate the influence of branching structure from the functional end-groups, the hydroxyl end-groups were modified. After modification, the protein adsorption behaviors of polyesters with variable DBs were quite similar. It appears to suggest that the DB itself has only a small influence onto the protein adsorption. However, the highly branching architecture produces a larger amount of polar end-groups, which dominates the protein adsorption.

CONCLUSIONS

As the newly emerging polymer architecture following the linear, branched, and crosslinking polymers, HBPs have attracted more and more attention in recent year. Herein, we have summarized the structure-property relationship of

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HBPs. As shown, many properties of HBPs, including the rheological property, crystallization and melting behaviors, glass transition, thermal and hydrolytic degradations, phase characteristics, LCST phase transition, optoelectronic property, encapsulation capability, self-assembly behavior, and biomedical applications, are highly related with the branching structures of the polymers. Nevertheless, due to the difficulty in controlling the DB of polymers, the studies on structure-property relationship of HBPs are still limited. Some relationships have been widely accepted, while some of them are still in controversial and need more experimental and theoretical works to support themselves. Out of question, more understandings on the field will build a bridge between the syntheses and applications of HBPs, which will lead to an enhanced controllability of the structures, properties and applications of such promising polymers.

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