

Review

Hyperbranched polymers: Phase behavior and new applications in the field of chemical engineering

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Abstract

During the last decade, hyperbranched polymers have become the focus of intense interdisciplinary research. The endeavor to demonstrate the full potential of hyperbranched polymers continuously results in more and more complex hyperbranched structures with new synthetic methodologies. A remarkable variety of applications for hyperbranched polymers has been investigated. Some of them have been already commercially realized. A new promising area of potential applications for hyperbranched polymers is the field of chemical engineering. The use of hyperbranched polymers in separation processes involving extractive distillation, solvent extraction, absorption, membranes or preparative chromatography might offer considerable potentials for cost savings. Therefore, this review intends to introduce these new potential applications of hyperbranched polymers. Based on a brief description of the synthetic methodologies and properties of hyperbranched polymers, a detailed overview of the investigated phase behavior of branched polymer systems is given, followed by a discussion of new potential applications of hyperbranched polymers in the field of chemical engineering.

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Abbreviations: VLE, vapor–liquid equilibrium; LLE, liquid–liquid equilibrium; DB, degree of branching; UCST, upper critical solution temperature; LCST, lower critical solution temperature; UST, upper solution temperature; LST, lower solution temperature; NMR, nuclear magnetic resonance; VPO, vapor pressure osmometry; EOS, equation of state; HX, heat exchanger; THF, tetrahydrofuran; PG, hyperbranched polyglycerol; ED, 1,2-ethanediol; wt.%, weight percent, mass percent; D, dendritic unit; L, linear unit; T, terminal unit; a.m.u., atomic mass unit

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1. Introduction

About 50 years after the introduction of the ‘macromolecular hypothesis’ by Staudinger, the entire field of polymer science could be described as consisting of only two major architectural classes: (I) linear topologies as found in thermoplastics and (II) crosslinked architectures as found in thermosets [1]. Now, at the beginning of the 21st century, four major domains can be defined and distinguished in accordance with their properties and architecture (see Fig. 1):

- (I) linear, random coil thermoplastics such as plexiglass or nylon;
- (II) crosslinked thermosets such as rubbers or epoxies;
- (III) branched systems based on long chain branching in polyolefins such as low density poly(ethylene) and other related branched topologies;
- (IV) dendritic polymers consisting of three subsets that are based on the degree of structural control, namely (a) random hyperbranched polymers; (b) dendrigraft polymers; and (c) dendrimers.

Due to the unique repertoire of new properties, dendritic polymers are recognized as a fourth major new architectural class [1], a class with a young but well established body of interdisciplinary research exploring a remarkable variety of potential applications.

Apart from the dendritic polymers, other important branched topologies in polymer science such as comb and star polymers, networks, and microgels are shown in Fig. 2.

The tedious and complex multistep-synthesis of dendrimers results in expensive products with limited use for large-scale industrial applications. For many applications, which do not require structural perfection, using hyperbranched polymers can circumvent this major drawback of dendrimers. Unlike dendrimers, randomly branched hyperbranched polymers with similar properties can be easily synthesized via one-step reactions and therefore represent economically promising products also for large-scale industrial applications. Companies such as the Perstorp Group (Perstorp, Sweden), DSM Fine Chemicals (Geleen, Netherlands), BASF AG (Ludwigshafen, Germany), and Hyperpolymers GmbH (Freiburg, Germany) already produce commercially available hyperbranched polymers on a large-scale¹ (Fig. 3).

Most of the applications of hyperbranched polymers are based on the absence of chain entanglements, the globular shape, and the nature and the large number of functional groups within a molecule. Modification of the number and type of functional groups on hyperbranched polymers is essential to control their solubility, compatibility, reactivity, adhesion to various surfaces, self-assembly, chemical recognition, and electrochemical and luminescence properties. In other words, the large number of functional groups allows for the tailoring of their thermal, rheological, and solution properties and thus provides a powerful tool to design hyperbranched polymers for a wide variety of applications. Fig. 4 gives an overview of the investigated applications for hyperbranched polymers (for further details see [2–41, 68,138]).

An area of application that, until now, has remained almost unconsidered in scientific discussions is the field of chemical engineering.

Unlike conventional linear polymers, hyperbranched polymers do not only show a remarkable selectivity and capacity [7,111], but, because of a lack of chain entanglements, also a comparatively low solution and melt viscosity [4,12,44–46] as well as an enormous thermal stability [4,47]. Since the polarity of hyperbranched macromolecules can be adjusted by controlled functionalization of the end groups, selective compounds (consisting of either pure hyperbranched polymers or fractions of hyperbranched additives) can be tailored. The remarkable selectivities and capacities of hyperbranched polymers in combination with their low melt viscosity, high solubility and thermal stability can be used for the optimization of a number of separation processes.

Therefore, this review focuses on new developments of hyperbranched polymers in the field of chemical engineering. Based on a brief description of the synthesis and properties of hyperbranched polymers, a detailed overview of the research regarding the phase behavior of hyperbranched polymers is given, followed by a discussion of new potential chemical engineering applications of hyperbranched polymers.

2. Definitions, synthesis and properties

2.1. Definitions

Dendritic polymers are recognized as a fourth major class of macromolecular architecture as illustrated in Fig. 1 [1]. They represent highly branched globular macromolecules, which can be subdivided according to their degree of structural control into three different categories, namely (a) random hyperbranched

¹ Currently Perstorp Specialty Chemicals AB (Sweden) produces hyperbranched polymers, known as Boltorn® products, on a ton-scale for ≥ 4 EUR/kg.

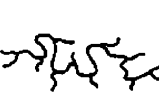
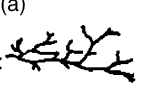
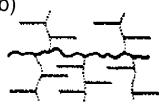
I. Linear	II. Cross-linked	III. Branched	IV. Dendritic		
			(a) 	(b) 	(c) 
1930 s Plexiglass Nylon	1940 s Rubbers Epoxies	1960 s Low Density Polyethylene	Random Hyperbranched	Dendrigrrafts	Dendrimers
			Present		

Fig. 1. Representation of the four major classes of macromolecular architectures [1].

polymers, (b) dendrigraft polymers, and (c) dendrimers (see Fig. 5).

The term *dendrimer* is derived from the Greek words dendron (tree) and meros (part). Dendrimers are highly uniform, three-dimensional, monodisperse polymers with a tree-like, globular structure and a large number of functional groups. Dendrimers were introduced at the end of the 1970s by Vögtle and co-workers [41], followed by the fundamental pioneering synthetic methodologies of Tomalia et al. and Fréchet et al. [1,41–43,115]. As shown in Fig. 5, a dendrimer is a symmetrical, layered macromolecule which consists of three distinct areas: the poly-functional central core (dendrimer) or focal point (dendron), which represents the center of symmetry, various well-defined, radial-symmetrical layers of repeating units (also called gen-

erations), and the end-standing groups, which are also termed peripheral or terminal groups.

Dendrigrrafts were introduced in 1991 as Comb-burst[®] polymers by Tomalia et al. [48] and as arborescent polymers by Gauthier and Möller [49]. Dendrigrraft polymers may be regarded as semi-controlled branched polymer architectures intermediate in terms of structure control between dendrimers and hyperbranched polymers [50]. As described by Teertstra and Gauthier dendrigrraft syntheses follow a generation-based growth methodology similar to dendrimers, but use polymeric chains as building blocks leading to a rapid increase in molecular weight per generation and therefore, in a few steps, to macromolecules with a high molecular weight (typically one to two orders of magnitude larger than for their dendritic counterparts). In comparison

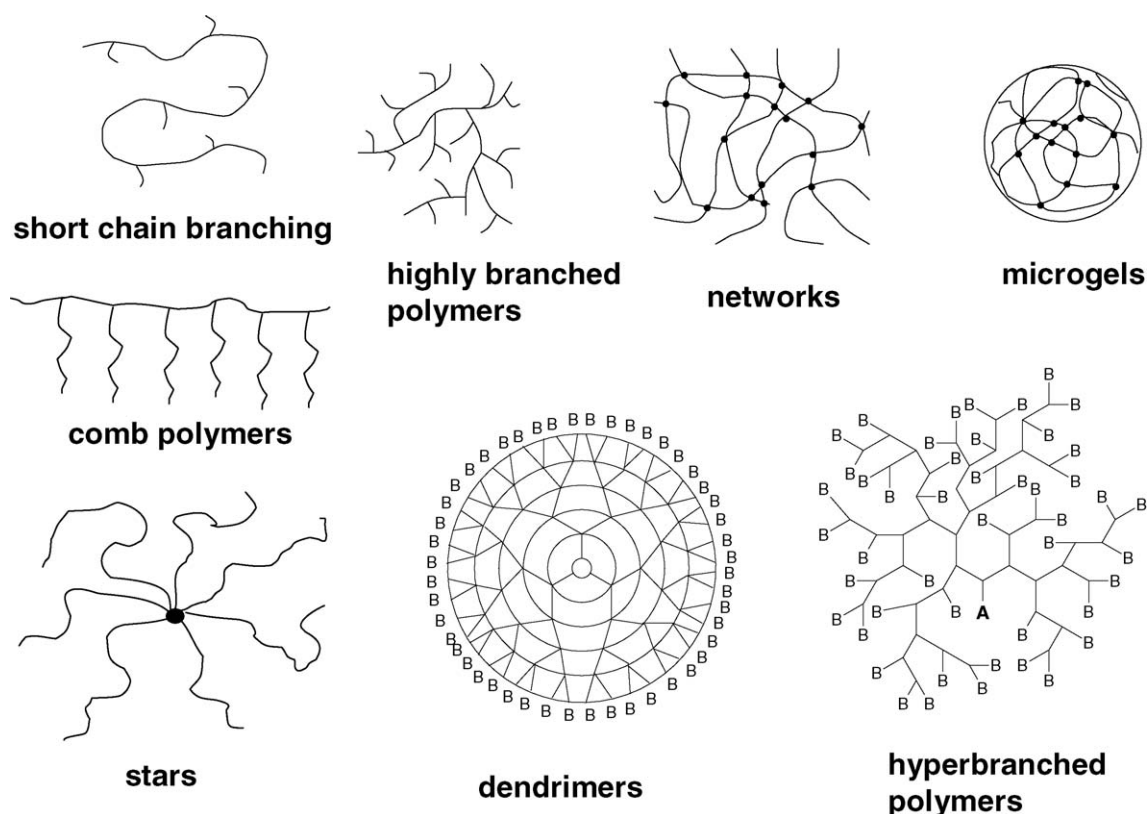


Fig. 2. Branched topologies in polymer science.

The figure has been supplied very kindly by Prof. B. Voit, Leibniz-Institut für Polymerforschung Dresden e.V., Germany.

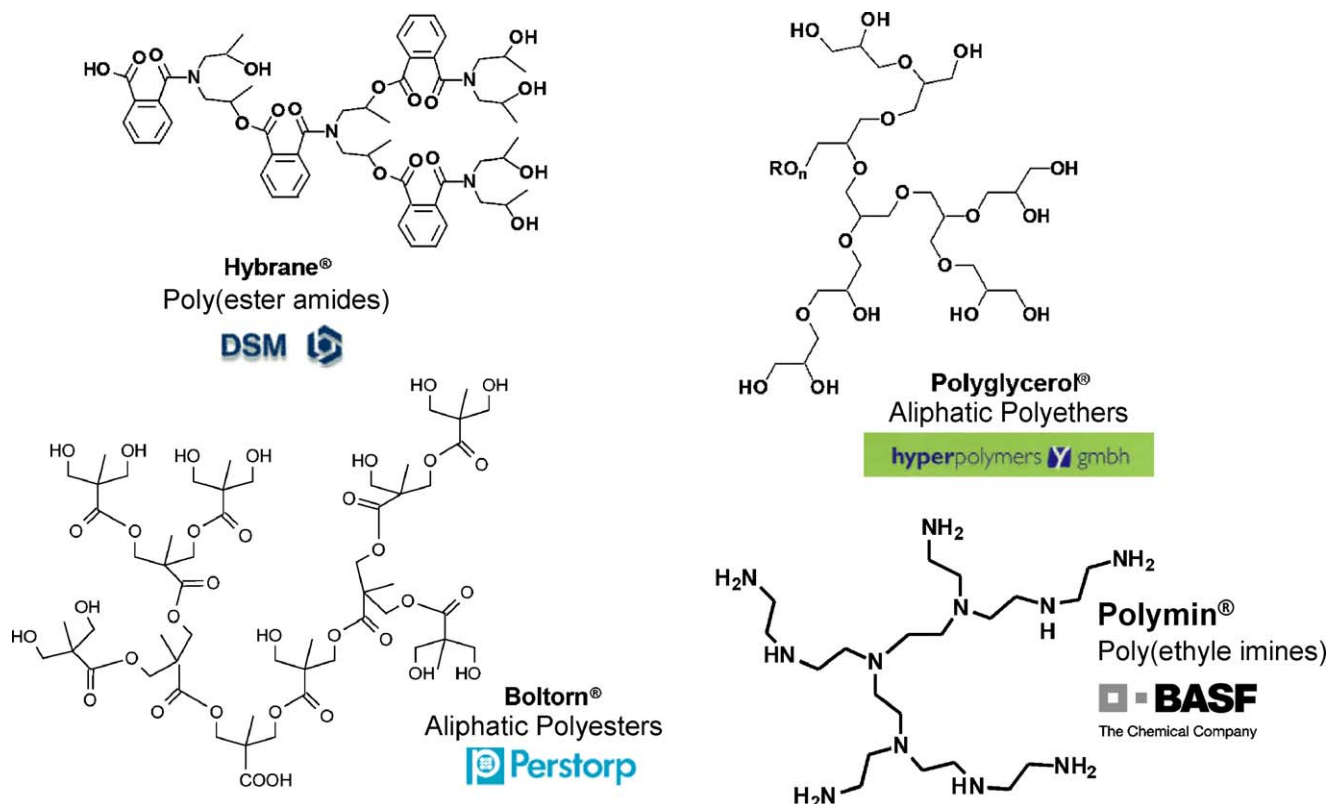


Fig. 3. Commercially available hyperbranched polymers.

to dendrimers, dendrigraft polymers are less controlled since grafting may occur along the entire length of each generational branch and the exact branching densities are arbitrary and difficult to control [1].

Hyperbranched polymers (see Fig. 5) represent another class of globular, highly branched macromolecules with a large number of functional groups. However, unlike dendrimers, hyperbranched polymers exhibit polydispersity and irregularity in terms of branching and structure. These kinds of polymer struc-

tures are known from polysaccharides such as glycogen, dextran, and amylopectin since the 1930s [51].

2.2. Synthesis and structural characterization of hyperbranched polymers

Hyperbranched polymers and dendrimers share a few common features such as their preparation from AB_x monomers leading to highly branched macromolecules with a large number

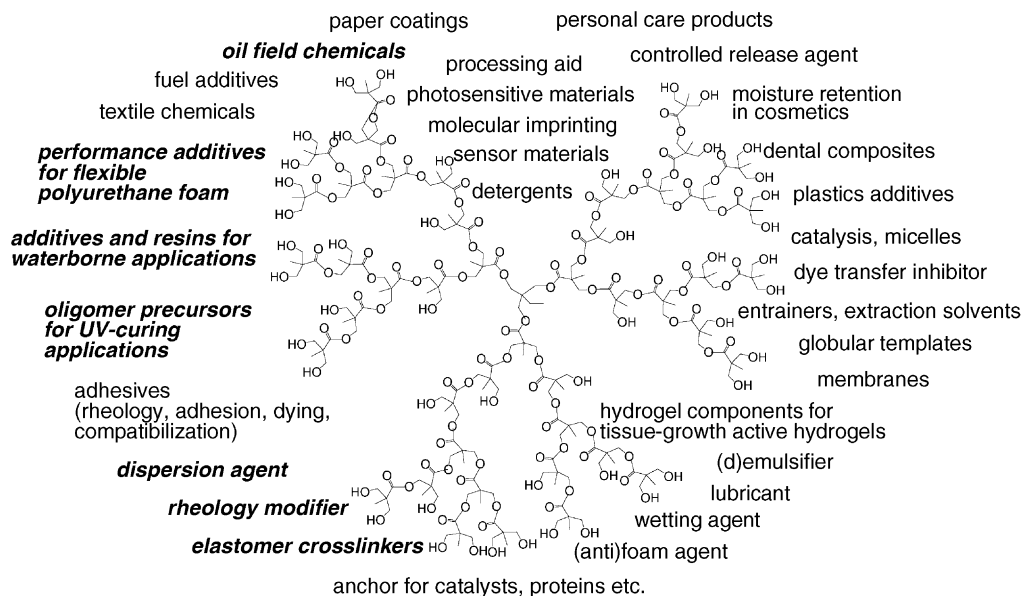


Fig. 4. Applications of hyperbranched polymers discussed in literature. Bold italic: commercial applications of hyperbranched polymers.

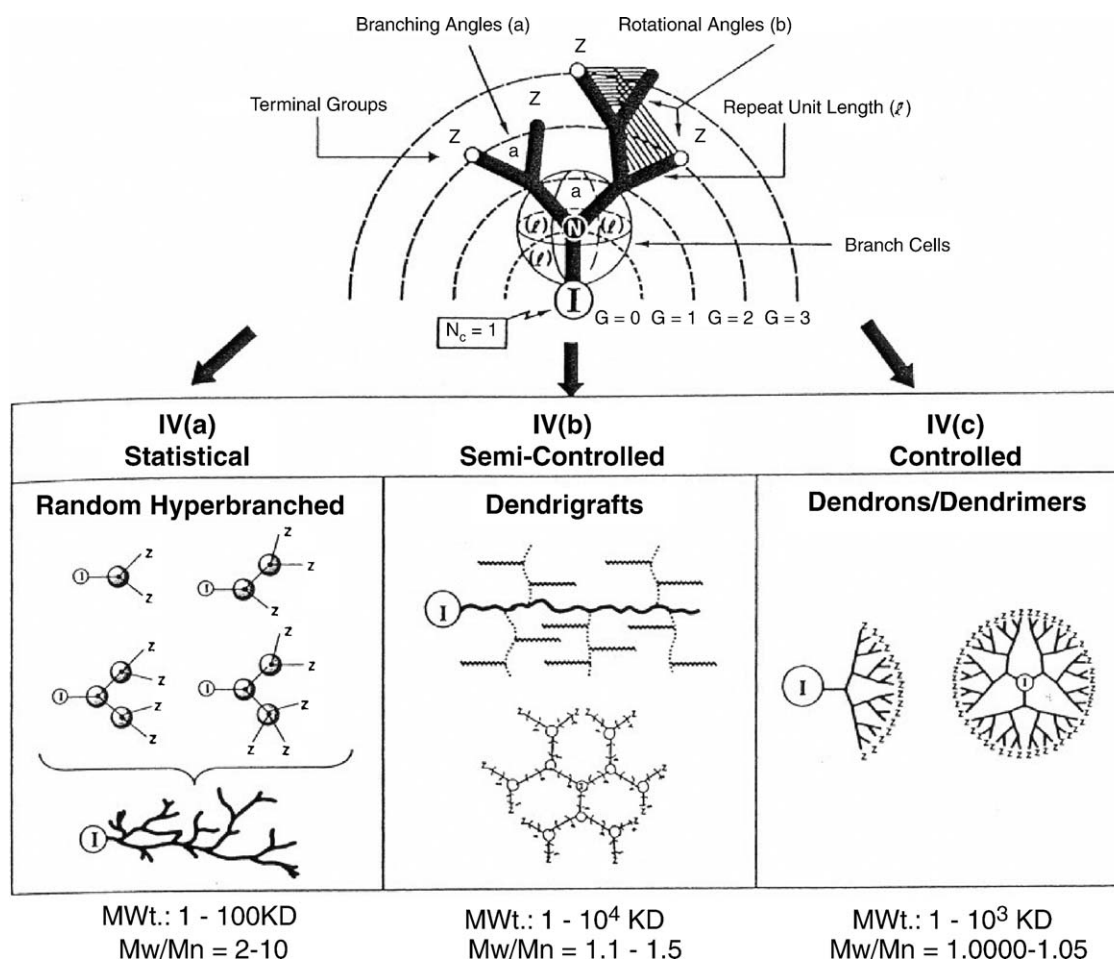


Fig. 5. Dendritic polymers divided into the subclasses hyperbranched polymers, dendrigrrafts, and dendrons/dendrimers. Branch cell structural parameters: (a) branching angles; (b) rotation angles; (ℓ) repeat unit lengths; (Z) terminal groups [1].

of functional end groups. However, the synthetic approaches for hyperbranched polymers and dendrimers differ substantially; hence differences in molecular shape and architectures and sometimes also in properties are observed.

The tedious step-wise procedure for dendrimers often results in expensive products with limited availability and therefore restricted use for large-scale industrial applications. Unlike dendrimers, hyperbranched polymers are often easy to synthesize on a large-scale and therefore are considered to be alternatives for dendrimers.

Hyperbranched polymers are prepared in one-step procedures, most common by polycondensation of AB_x monomers, as reported by Stockmayer [52,53], Flory [54] and Kim and Webster [55]. If $x \geq 2$ and the functionality A reacts only with functionalities B of another molecule, the polymerization of AB_x monomers results in highly branched polymers [54]. Apart from *polycondensation*, *addition polymerization* of monomers that contain an initiating function and a propagating function in the same molecule [44], *ring-opening polymerization* [56], and *self-condensing vinyl polymerization* (SCVP) [57] can be applied for the synthesis of hyperbranched macromolecules. By now, a number of excellent reviews on the synthetic approaches for hyperbranched polymers has been published (see for instance

[2–4,58,59,68,138]) giving a detailed insight in the underlying methodologies and reaction mechanisms.

The one-step procedures used for the preparation of hyperbranched polymers lead to uncontrolled statistical growth. Consequently, the resulting structures are imperfect and polydisperse. Furthermore, unlike dendrimers, the control over layers or generations as well as over the molar mass deteriorates. Due to the statistical nature of the coupling steps, steric hindrance of growing chains, and reactivity of functional groups, the propagation occurs at only two sites among branching units, which gives different polymer segments [60]. The different segment types within a hyperbranched macromolecule are depicted in Fig. 6.

Based on AB_2 monomers, linear segments, known as defects, show one functional B-group unreacted, whereas the terminal segments have two unreacted B-functionalities. Similar to dendrimers, the dendritic segments in hyperbranched macromolecules represent fully incorporated monomers which have no unreacted functionalities. The most prominent feature of hyperbranched polymers is their “degree of branching” DB or “branching factor”, which defines the ratio of branched, terminal, and linear units in the macromolecular structure [2].

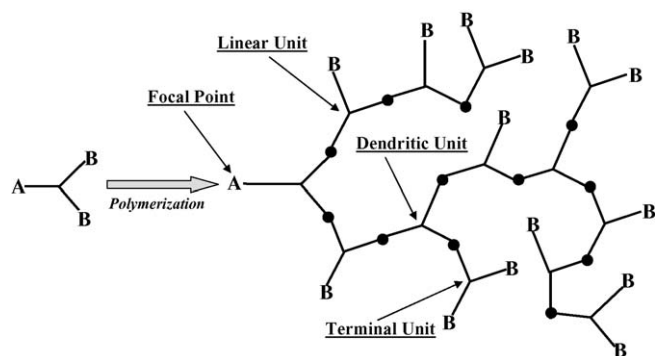


Fig. 6. A Hyperbranched polymer with its different segment types from polymerization of AB_2 monomers.

The degree of branching of a perfect dendrimer equals 1, while a linear polymer has a DB of 0. Two different equations have been suggested for the average DB. The first definition [61], compares the sum of the dendritic and the terminal repeating units to the sum of all repeating units in the structure (Eq. (1))

$$DB(\%) = \frac{D + T}{D + T + L} \times 100 \quad (1)$$

where D , T and L represent the number of dendritic, terminal and linear units per macromolecule. The second definition by Frey and co-workers (see Eq. (2)) does not include the terminal repeating units and is therefore claimed to be more accurate than Eq. (1) at low molar mass [62].

$$DB'(\%) = \frac{2D}{2D + L} \times 100 \quad (2)$$

The fractions of D -, L - and T -repeating units are usually determined by NMR spectroscopy. Eq. (3) has been suggested for the calculation of the molar mass of a hyperbranched polymer using the relative fraction of the respective repeating unit [62].

$$DP_n = \frac{D + L + T}{T - D} \quad (3)$$

2.3. Properties of hyperbranched polymers

2.3.1. Thermal properties

Due to their highly branched structure, dendritic polymers are almost exclusively amorphous materials. Therefore, the glass transition temperature T_g is one of the most important thermal properties. T_g is an important parameter for a dendritic polymer with respect to potential applications in the field of powder coatings or rheology modifiers. Upon heating, amorphous components convert at T_g from a glassy state to a liquid state, i.e., into a melt for low molar mass substances or a rubbery state for high molar mass compounds. In the melt, thermal energy is sufficiently high for long segments of each polymer chain to move in random micro-Brownian motions. In the amorphous solid state, on the other hand, polymer chains assume their unperturbed dimensions as they do in solution under theta-conditions. Below T_g , all long-range segmental motions cease. Rotations around single bonds become very difficult and the only molecular motions that can occur are short-range motions of several

contiguous chain segments and motions of substituent groups [63].

In the case of dendritic polymers the situation is more complex, since segmental motions are also affected by the branching points and the presence of numerous functional groups. The glass transition temperature of a hyperbranched polymer is not only affected by the chain-end composition, but also by the molar mass and the macromolecular composition [64]. According to Schmaljohann et al. it can be understood as a combination of inter- and intramolecular effects. Differences in T_g of hyperbranched polymers with different repeating units but the same end groups demonstrate the intramolecular effect of segmental motion, whereas the change of T_g through variation of the end groups (their polarity in particular) can be assigned to translational motion and an intermolecular effect [6].

For dendritic polymer systems T_g increases with generation number to a limit, above which it remains nearly constant [64]. This increase in T_g with generation number is assumed to reflect a decrease in chain mobility due to branching.

A number of research groups demonstrated that the chemical nature of the large number of terminal groups strongly affects the glass transition temperature (see for instance [2–7,45,64–67]).

By means of DSC measurements Sunder et al. demonstrated that the flexibility, i.e., T_g , of a modified highly polar hyperbranched polymer with large number of hydroxyl end groups is controlled mainly by two factors: (i) hydrogen bonding of the end groups, increasing the rigidity of the molecules and (ii) tendencies of the substituents to form higher ordered phases (mesophases, crystallization) [65]. It is an important information that the degree of alkyl substitution has hardly any effect on T_m , however there is a pronounced effect on T_g [65].

For further information on the thermal properties of hyperbranched polymers see the recent studies of Voit [3], Sunder [65], Schmaljohann et al. [6], Rogunova et al. [66], Magnusson et al. [67] and Behera et al. [157].

2.3.2. Mechanical and rheological properties

Investigations on new applications of a polymer are often closely related to its material and processing properties. Therefore, the mechanical and rheological properties of hyperbranched polymers are of great importance.

Due to the highly branched, globular structure, the configuration of hyperbranched polymers and dendrimers is coined by a lack of chain entanglements. The non-entangled state imposes poor mechanical properties, resulting in brittle dendritic polymers with limited use as thermoplastics [4]. The stress-strain behavior of hyperbranched polymers can be similar to that of ductile metals as observed by Rogunova et al. for hyperbranched polyesters. Like ductile metals, hyperbranched polyesters do not strain harden [66]. This is due to their globular structure, which does not permit the process of chain extension and orientation (the usual mechanisms of strain hardening). However, intermolecular associations, such as hydrogen bonding and possibly intermolecular crystallization of a few linear segments, provide connections between the hyperbranched macromolecules [66].

Apart from the mechanical properties also the viscosity behavior of linear and branched polymers shows remarkable

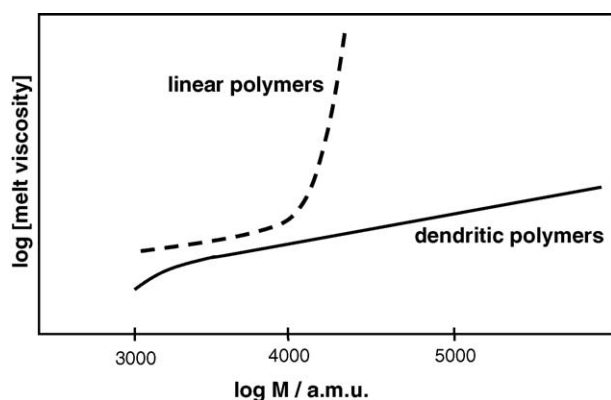


Fig. 7. Melt viscosity vs. molar mass of linear and dendritic polymers [77]: a.m.u., atomic mass unit.

differences. This was already noted by several scientists at the end of the 1960s [69–74]. Fig. 7 illustrates the melt viscosity of linear and dendritic polyethers as a function of the molar mass (given in atomic mass units). For linear polymers, above a critical molar mass, a drastic increase in melt viscosity is observed. However, the line for dendritic polymers shows a continuous slope of 1.1 up to 100,000 a.m.u. with no critical mass limit being observed. This behavior can be explained by the different macromolecular structure of linear and dendritic macromolecules. At low molar mass, linear polymers consist of random coil chains which, as the molar mass increases, start to entangle at a critical molecular size, leading to a sharp increase in melt viscosity. Unlike linear polymers, the globular, highly branched architecture of both dendrimers and hyperbranched polymers prevents chain entanglements, resulting in considerably smaller melt viscosities and a continuous slope of the η -function (see Fig. 7). There are a number of studies confirming the strikingly low melt and solution viscosities of dendritic polymers in comparison to linear polymers [4,7,12,44–46].

2.3.3. Solution properties

A number of excellent research studies have been published focusing on dilute and semi-dilute properties of branched polymer systems [46,75–88].

Hyperbranched polymers have a significantly lower intrinsic viscosity, Mark–Houwink exponent, hydrodynamic volume, and ratio of radius of gyration to hydrodynamic radius in comparison to their linear analogues of the same molar mass. Also the osmotic second virial coefficient A_2 was object of numerous research studies to characterize the effect of branching. As observed for many branched polymer solutions branching decreases the second virial coefficient in ‘good’ solvents. Therefore, for a branched polymer, A_2 is always lower than that for the homologous linear polymer [84,85].

For many potential applications of hyperbranched polymers in the field of chemical engineering (see Section 4) the phase behavior of *concentrated* hyperbranched polymer solutions is of great importance. Therefore, the following section gives an overview of the measured and modelled phase equilibria of concentrated hyperbranched polymer solutions.

3. Phase behavior of hyperbranched polymer solutions

The comprehension of the phase behavior is an essential prerequisite for contemporary polymer science and engineering. Phase separation and segregation often occur during the production and processing of polymers, either due to their necessity or owing to undesirable circumstances such as the incompatibility between polymers or an insufficient solvent power. The impact of high-performance polymer blends on modern material science is significant and continuously growing. Especially improvements in performance characteristics such as rigidity, toughness, abrasion resistance, chemical and flame resistance, heat resistance, and ease of processing are of great importance [89]. Even though in production and processing the equilibrium state is usually not reached, it is nevertheless of great importance to know, what the equilibrium condition of the regarded system would be like, in order to understand the properties of a plastic, to operate a production process optimally, or to modify polymeric materials successfully [90].

The large body of interdisciplinary research on dendritic polymers, i.e., dendrimers, dendrigrafts, and hyperbranched polymers, is a guarantee for emerging applications (see Fig. 4). However, the understanding of essential fundamentals such as the phase behavior of dendritic polymer solutions is still in its infancy. The experimental investigation of the phase behavior of hyperbranched polymer systems is a crucial requirement for a successful introduction of new applications to highly competitive markets. In this context, thermodynamic models, which accurately account for the impact of polymer branching on the phase behavior of polymer systems, play a very important role; they enable the optimization of new applications of hyperbranched polymers without requiring an unjustifiable amount of experimental phase equilibrium data. However, so far, despite the scientific effort of thermodynamicists in this field, almost no g^E -model or equation of state has been developed, which proved its suitability in considering explicitly the influence of the degree of polymer branching on the phase behavior of highly branched polymer systems over a wide temperature and pressure range.

This section summarizes the most important studies on the phase equilibria of hyperbranched and other branched polymer systems that have been investigated so far. In the first section, experimental thermodynamic studies on the miscibility behavior/phase behavior are described, followed by a second section focussing on the modelling of the phase behavior.

3.1. Experimental investigations

Several authors studied the influence of polymer branching on the miscibility behavior of polyolefin–solvent systems [91–96]. Kleintjens et al. investigated the influence of polymer chain branching on liquid–liquid phase equilibria in polymer solutions. For the system polyethylene–diphenyl ether they found that the upper critical solution temperature (UCST)-curve of a branched polyethylene solution may be shifted by more than 10 K compared with that of a linear polyethylene sample of about equal number and mass average molar mass [91].

Charlet and Delmas demonstrated that the lower critical solution temperature (LCST)-curve shifts towards higher temperatures with an increasing degree of polymer branching [92]. This increase in polymer solubility is due to a difference in accessible surface area of the polymer, which, in comparison to a linear polymer of the same molar mass, is larger for branched macromolecules.

Chen et al. investigated the LCST and UCST phase behavior of branchy poly(ethylene-propylene) copolymers in different solvents and the influence of supercritical ethylene on the location of the phase boundaries [94]. The experimental data could be modelled well using the statistical associating fluid theory (SAFT). Further studies were carried out by Chen et al. [95], Whaley et al. [96], De Loos et al. [97,99], and Han et al. [98].

Polyetheramide hyperbranched polymers having alkyl terminated end groups blended with linear low density polyethylenes (LLDPE) were investigated by Sendjarevic et al. [156]. The blends were extruded as thin films so that surface properties and effects of length and concentration of the alkyl groups on the miscibility of the films could be studied. Sendjarevic et al. found that the miscibility of the hyperbranched polymers in LLDPE can be controlled by varying the length of the alkyl terminated end groups [156].

Gitsov and Fréchet demonstrated that hybrid linear-dendritic polyether copolymers are able to form mono- and multimolecular micelles depending on the dendrimer generation and the copolymer concentration of water-methanol solutions [100]. Ishizu et al. showed that alternating maleimide/styrene hyperbranched copolymers exhibit the behavior of nanospheres such as dendrimers with a uniform inner density distribution and an average volume density close to their bulk density [82].

Moorefield and Newkome demonstrated that the solubility of dendrimers can be tailored by introducing appropriate functionalities into a dendrimer's surface groups. By means of hydrophilic functional end groups, hydrophobic dendrimers such as polyethers and polycarbosilanes can become water soluble, and also water-soluble dendrimers can turn into hydrophobic molecules after functionalization with hydrophobic groups [101]. Some dissolved dendritic polymers exhibited considerable variable hydrodynamic radii which predominantly depend on solvent properties such as pH [101].

Regarding dendritic polymers, there are some reports in literature, which discuss the influence of the macromolecular structure as well as the nature and number of chain-end functionalities on the polymer solubility in selected solvents (see for instance [77,101–108]). It was found that hyperbranched polymers and dendrimers are highly soluble in solvents which are capable of solvating the numerous chain ends. For these kinds of solvents, Hawker and Fréchet investigated the solubility of isomeric polyesters. In all cases, the dendrimers were more soluble than their hyperbranched analogues and both proved to be significantly more soluble than the linear polyester [77]. Moreover, the solubility of a polyether dendrimer in tetrahydrofuran (THF) was approximately 50 times higher in comparison to its linear analogue [103].

Seiler and Arlt studied the low- and high-pressure phase behavior of polymer solutions containing commercially avail-

able hyperbranched polymers such as hyperbranched Boltorn[®] polyesters, hyperbranched Hybrane[®] poly(ester amides) and hyperbranched polyglycerols [7,109–116]. At moderate pressures, the investigated vapor-liquid equilibria (VLE) of differently branched polyglycerols and commercially available hyperbranched polymers such as polyesters and poly(ester amides) in ethanol or in water allowed for a discussion on how the degree of polymer branching, the nature and number of polymer functionalities, and the solvent polarity determines the slope of the bubble point curve and the solvent activity. Furthermore, special attention was devoted to the influence of commercially available hydroxyl-functional hyperbranched polymers, dendrimers and linear polymers on the vapor-liquid equilibria of azeotropic systems such as ethanol-water, tetrahydrofuran-water, and 2-propanol-water. The extent of inter- and intramolecular hydrogen bond formation has a dominant impact on the solvent activity and therefore determines partition coefficients and relative volatilities. At large polymer concentrations, hydroxyl-functional hyperbranched polyesters tend to form agglomerates, limiting their polymer solubility and separation efficiency. On the other hand, highly soluble hyperbranched polyglycerols and the hyperbranched poly(ester amide) Hybrane S1200 break the azeotropic system behavior of a variety of aqueous azeotropic mixtures in a remarkable manner making them potential entrainer candidates for the extractive distillation (see Section 4) [7,109–116].

The influence of hyperbranched polymers exhibiting a hydrophobic shell (acetylated polyglycerol, esterified hydroxyl-functional polyester) on the liquid-liquid equilibrium (LLE) of the azeotropic tetrahydrofuran-water system has also been investigated [7]. The system hyperbranched polyester Boltorn H3200-tetrahydrofuran-water shows a remarkably distinct solutropic phenomenon. Moreover, the hyperbranched polyester Boltorn H3200 exhibits a great selectivity and capacity allowing for the breaking of the tetrahydrofuran-water azeotrope by combining single stage extraction with distillation [7,109–115].

Seiler et al. demonstrated that the high-pressure phase behavior of nonaqueous hyperbranched polyester solutions shows the characteristics of a type-IV system according to the classification of van Konynenburg and Scott. In the system hyperbranched polyester Boltorn H20-ethanol-CO₂ the location of the upper solution temperature (UST) curve proved to be dependent on the polymer molar mass and the solvent polarity and independent of the system pressure. However, the lower solution temperature (LST) of the respective system strongly depends on the pressure. An increase in CO₂ concentration leads to a considerable shift of the lower solution temperature curve to lower system temperatures (see Fig. 8). For the system hyperbranched polyester-ethanol-CO₂, the merging of the UST and the LST curve into the hourglass miscibility gap is observed at the CO₂ concentration of 50.5 wt.% [7,109].

Garasmus et al. studied the structure of hyperbranched polyglycerol and amphiphilic poly(glycerol ester)s in aqueous and nonaqueous solution. Similar particles sizes and molar masses of the hyperbranched polyglycerols in D₂O and CD₃OD were observed. The polymers show a compact structure and well-defined entities in both solvents. For the nonpolar solvent

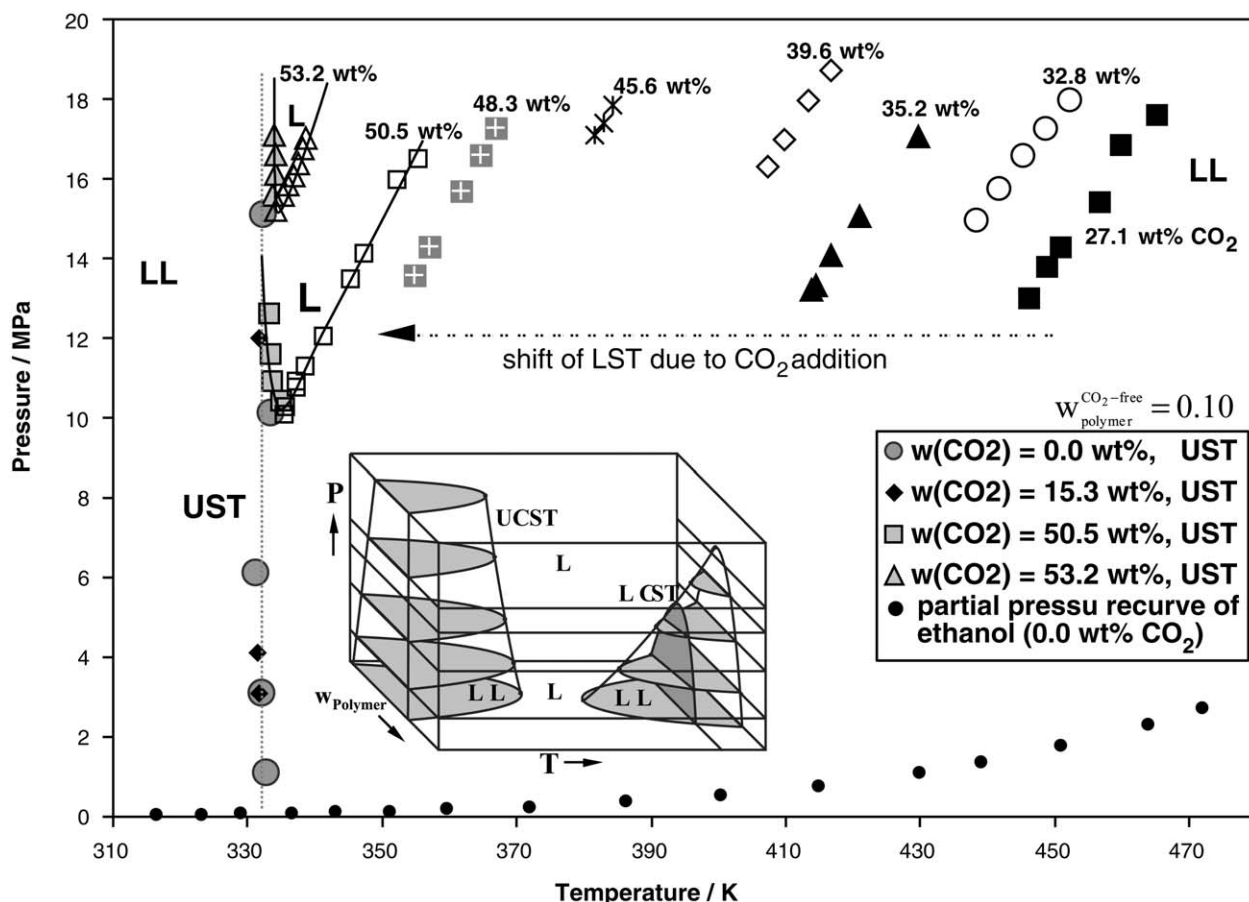


Fig. 8. High-pressure phase behavior of the system hyperbranched polyester (Boltorn H20)–ethanol–CO₂ [109].

C₆D₆ amphiphilic derivatives of the hyperbranched polyglycerols become more compact with increasing degree of esterification [86].

Polese et al. measured infinite-dilution activity coefficients of polar and nonpolar solvents in comb polymers and poly(propylene imine) dendrimers of generation 2–5 [105]. Solvent activity coefficients at infinite dilution change with respect to the dendrimer generation number, reaching a minimum at generation 4 in the temperature range of 333–413 K [105]. Due to the exothermic formation of hydrogen bonding, alcohols form hydrogen bonds with the dendrimer more easily at low temperatures and hence, the solubility decreases with increasing temperature [105]. Since Polese et al. used dendrimers with a basic character, slightly acidic solvents showed better solvent qualities than others (THF, toluene, ethyl acetate).

Boogh et al. demonstrated that hyperbranched polymers represent very effective low viscosity liquid tougheners for epoxy resins requiring no solvent during blending and processing. The multifunctional epoxidised hyperbranched polymers used, phase separate during the curing of the thermosetting resin. The chemical architecture of the shell, i.e., its polarity and reactivity, controls the initial miscibility and the kinetics of the phase separation process [117]. UCST and LCST data are reported for a 5 wt.% modified (solvent-free) epoxy resin using a less polar hyperbranched polymer than the reference modifier.

Pruthikul et al. determined the relative accessibility of internal and terminal carbonyl groups of hyperbranched polyesters from the degree of hydrocarbon bonding measured by FT-IR spectrometry. The results show that in molecules of low-generation number, the terminal groups are about as accessible (e.g. for solvent molecules) as those in linear polymers. However, these functional groups become less accessible as the generation number increases, presumably because the molecule folds back on itself to some degree resulting in a more compact, globular shape [106].

Tian et al. studied a novel amphiphilic biodegradable cationic hyperbranched copolymer with polyethyleneimine (PEI) as backbone and poly(ethylene glycol) (PEG) and poly(γ -benzyl L-glutamate) (PBLG) as hyperbranched arms. The copolymers were found to be self-assembled in water with a critical micelle concentration (CMC) in the range of 0.00368–0.0125 g/l and a high hydrophobic micelle core. With increasing content of the hydrophobic PBLG-block, the CMC value of PEG–PEI–PBLG micelles decreased. It was also shown that protonated environments play a critical role in determining the size and CMC of PEG–PLI–PBLG micells [118].

Hay et al. compared thermal bulk properties and the PvT-behavior of dendrimer melts based on benzyl ether with literature values for monodisperse, linear polystyrenes. Furthermore, property measurements are presented for an exact linear

analogue to the fifth-generation dendrimer [120]. The investigations suggest that, unlike the linear polystyrene, some form of structural transition occurs in the dendrimer bulk at a molar mass near that of the fourth-generation dendrimer. Dendrimers exhibit an increased packing efficiency as evidenced by a decreased specific volume (increased density) when compared with an exact linear analogue of the fifth-generation dendrimer [120]. A crystalline state can be formed by both the lower-generation dendrimer and the linear analogue. This crystalline state is not observed in dendrimers above the third generation [120].

Garamus et al. investigated the solution structure of metal particles prepared in unimolecular reactors of amphiphilic hyperbranched polymers by means of small-angle neutron scattering. They demonstrated that amphiphilic hyperbranched polymers can serve as molecular confined environments for the synthesis and stabilization of inorganic metal particles [86].

Prausnitz and co-workers measured VLE of polyamidoamine (PAMAM) dendrimers and benzyl ether polymers (dendritic and linear) in several polar and nonpolar solvents at 308–343 K [104]. The strongly hydrophilic PAMAM dendrimers show complete miscibility with water, lower alcohols, glycols, ethylenediamine and they are insoluble in nonpolar solvents [104]. The absorption behavior of the latter dendrimers does not depend on the generation number. The linear analogues of the dendrimers absorb less solvent, since, under experimental conditions (303–362 K), they were partially in the crystalline state [104].

Lieu et al. presented VLE data of binary mixtures of arborescent polystyrene and linear polystyrene dissolved in chloroform, toluene or cyclohexane at temperatures between 323 K and 343 K [102]. Only for cyclohexane, a dependence of solvent absorption on polymer generation was found. Unlike chloroform and toluene, cyclohexane is a poor solvent for arborescent polystyrene. Therefore, a significant entropic contribution and a low enthalpic contribution in cyclohexane are believed to be responsible for the absorption behavior, whereas for chloroform and toluene the opposite applies [102].

The experimental results described above represent valuable information to test or develop thermodynamic models for hyperbranched polymer systems. The most important modelling results are summarized in the following section.

3.2. Modelling

van Vliet et al. applied the mesoscopic simulation method *dissipative particle dynamics* to study the dynamics of polymer–solvent liquid–liquid phase separation. It was found that the degree of polymer branching has a pronounced effect on the radius of gyration and the centre of mass diffusion of the polymer [119]. The simulation results show that the difference in chemical potential between the mixed and the demixed state is the main driving force behind the centre of mass diffusion and thus the phase separation, rather than the reduced radius of gyration due to polymer chain collapse [119].

Lue performed Monte Carlo simulations for athermal solutions of dendritic polymers (generation 0–5) and investigated the structural and thermodynamic properties of these systems

from the dilute to the concentrated regimes. At low polymer concentrations, dendritic polymer solutions have a lower system pressure than solutions containing linear polymers of the same molar mass, owing to the more compact dendritic architecture [85]. In the concentrated polymer regime, solutions containing low-generation dendritic polymers behave similarly to linear polymers, while those containing high-generation polymers have a system pressure that increases more rapidly with concentration [85]. Monte Carlo simulations were also used by Timoshenko and Kuznetsov to study conformational structures formed by star and comb hetero-polymers during kinetics of folding from the coil to the globule, as well as the corresponding equilibrium states on going from the good to the poor solution [121].

Apart from Monte Carlo simulations, Steinhäuser also used Molecular Dynamics simulation to investigate the influence of chain branching of various chain topologies on the static properties of polymers. Several important quantities that are suitable for the quantitative characterization of branched polymer structures are discussed. Steinhäuser demonstrated that star polymers in a good solvent are more spherical than in a theta solvent. This effect becomes stronger with increasing arm number. The rheological and thermodynamic properties of dendrimers in solution depend on the location of the terminal groups and the density distribution of the macromolecule [122]. For dendrimers it was found that not all the terminal groups lie near the exterior of the macromolecule. The functional end groups can significantly penetrate the interior of the dissolved dendrimer. Particularly for higher-generation dendrimers ($G \geq 5$) in theta solvents, the terminal groups come very close to the core of the macromolecule. Furthermore, Steinhäuser found that the segments of monomers pertaining to the inner dendrimer generations are more expanded than the ones at the periphery of the polymer. This effect increases with solvent quality and with the total number of dendrimer generations. The stretching of monomer bonds can be understood as a consequence of molecular crowding in the core region. The structure functions of dendrimers exhibit a structure that approaches the one of a solid sphere with increasing generation number [122].

Jang and Bae introduced several modifications of a model based on the lattice cluster theory (LCT) and the Veytsman hydrogen-bonding model to describe liquid–liquid phase behavior of binary hyperbranched polyol–water systems [107,108,123,124]. As the number of polymer end groups increases exponentially with the generation number, the effect of hydrogen bonding between the solvent molecules and the end groups is growing. The solvent–solvent hydrogen bonding dominates the phase behavior of hyperbranched polymer–water systems [107,108,123,124]. In their LCT model, the dendritic structure is characterized by three parameters: (a) the generation number; (b) the separator length, which represents the number of bonds between branching points; and (c) the core segments between zeroth-generation points. The model of Jang and Bae does not account for hydrogen bonding between the solvent molecules and the inner polymer functionalities. The recent version of their model [108] qualitatively accounts for the dependence of pressure, structure and hydrogen bonding

on liquid–liquid equilibria of dendrimer–solvent systems. However, until recently, no comparison was reported underlining the applicability of this model for the description of LCST and coexistence curves of differently branched dendritic polymer–solvent systems. For further information concerning the association behavior of hyperbranched polymers in aqueous solution see [125,126].

Mezzenga et al. developed a new thermodynamic model for the prediction of phase equilibrium behavior of thermoset-reactive modifier polymer blends. The model combines the Flory–Huggins lattice theory with a group contribution theory for the prediction of the free energy of mixing as a function of blend composition, temperature, and degree of polymerization. The model was tested using a diglycidyl ether bisphenol-A epoxy cured with isophorone diamine, blended with epoxy functionalized hyperbranched polymers. After considering the enthalpy and entropy variations of both the thermoset and the modifier, an excellent experimental agreement between the model and the experimental cloud points was obtained. However, the entropy reduction caused by physical polymer–polymer interactions had to be expressed as an addi-

tive term to the enthalpic interaction parameter [127]. Fig. 9 shows some modelling results of the free energy of mixing for a resin-hyperbranched polymer blend at 80 °C as a function of curing time, temperature and composition. Initially, the free energy of mixing is negative at all compositions (see Fig. 9a), so that no two points on the free energy curve have a common tangent and both components are fully compatible. However, at the end of the reaction, the free energy of mixing is positive for all compositions, indicating that the system is in an unstable state [127]. The curves shown in Fig. 9b illustrate the transition from a homogeneous to a heterogeneous system for discrete curing times corresponding to the appearance of inflection points in the curve [127].

The modification of epoxy resins with reactive hyperbranched polymers is of great interest since this class of modifiers allows for easily processable tough thermoset resins and thermoset based composites. The structural build-up during reticulation of thermoset systems containing reactive modifiers can strongly influence the final properties of such blends as shown by Mezzenga et al. in a study of the rheological behavior during cure of an epoxy/amine thermoset system blended

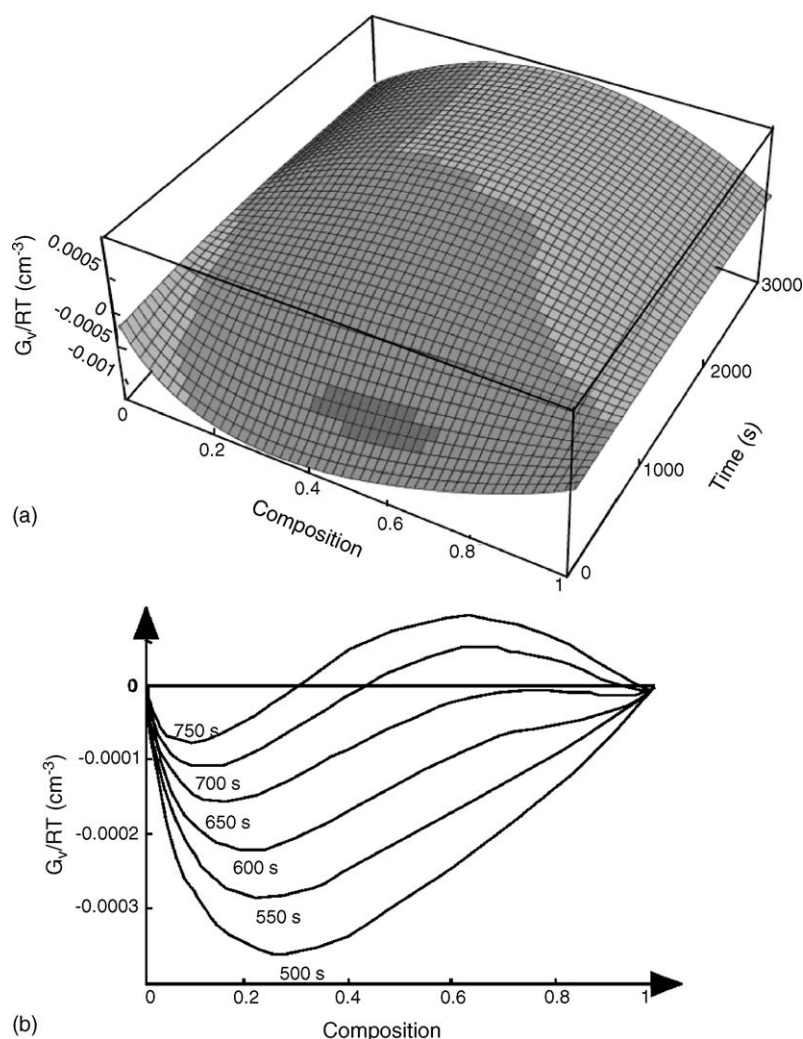


Fig. 9. Resin-hyperbranched polymer blend at 80 °C [127]: (a) 3D plot of free energy as a function of curing time and composition; (b) 2D plot of free energy as a function of composition at discrete times. Composition is expressed in volume fraction of thermoset pseudocomponent.

with reactive hyperbranched polymers. The phase separation and gelation behavior of these epoxy resin/hyperbranched polymer blends was studied as well [127].

Jang et al. also proposed a LCT-based model to describe dendritic vapor–liquid equilibria of dendrimer solutions [124]. By means of three model parameters, the model accounts for the structure of dendrimers, solvent–solvent specific interactions and solvent–end group specific interactions. Jang and Bae examined VLE of polyamidoamine dendrimer–methanol and benzyl dodecyl dendrimer–toluene systems. They demonstrated that the solvent–end group specific interaction dominates VLE of dendrimer solutions, i.e., the nature of end groups has a crucial influence on the VLE of dendrimer solutions [124].

Ko et al. derived a thermodynamic model based on lattice cluster and melting point depression theory to account for the structural effects on the phase behavior of hyperbranched solid polymer electrolyte/salt systems. For these kinds of systems the proposed model accounts for the structural dependence of the free energy of mixing. However, the model does not consider the end-group effect and the specific interaction between the polymer molecules and the salt molecules [128].

Yoon et al. investigated the phase behavior of the nematic liquid crystal 4-ethoxybenzylidene-4'-n-butylaniline in hyperbranched polymers and adopted Freed's lattice cluster theory to describe the structures of the hyperbranched polymers. By introducing an additional parameter, highly oriented interactions between segments could be described resulting in a very good agreement between the calculation and the experiment [129].

Kouskoumvekaki et al. tested the UNIFAC-FV and Entropic-FV models to predict vapor–liquid equilibria of dendrimer solutions [130]. It is shown that both models can predict the solvent activity in dendrimer solutions with acceptable accuracy.

Calculation results by Seiler et al. demonstrated the suitability of the UNIFAC-FV model to describe vapor–liquid equilibria of hyperbranched polymer and dendrimer solutions [113]. A modified approach for a determination of the residual solvent activity was suggested allowing for an indirect consideration of dendritic topologies. This approach is based on the observation that, depending on the solvent polarity and the nature and number of functional polymer groups, only certain kinds of the structural polymer units (linear, dendritic, terminal) dominate the polymer–solvent interactions and thus determine the solvent activity. Hydroxyl-functional hyperbranched polyethers and polyesters dissolved in good, polar solvents such as water and ethanol represent soft globular structures with a comparatively large hydrodynamic volume allowing for penetration of the solvent molecules into the interior of the hyperbranched polymers. Hence, for the latter systems, it seemed appropriate to account for the contribution of the linear, dendritic, and terminal units to the residual solvent activity. This led to a remarkable agreement between experimental and UNIFAC-FV results. However, for other polymer solutions where the hyperbranched polymer, for instance, is dissolved in a bad solvent, the consideration of the terminal group contribution to the residual solvent activity is sufficient [113]. Binary and ternary vapor–liquid equilibria of polymer solutions consisting of an OH-terminated polyamidoamine dendrimer, water and/or ethanol can best be

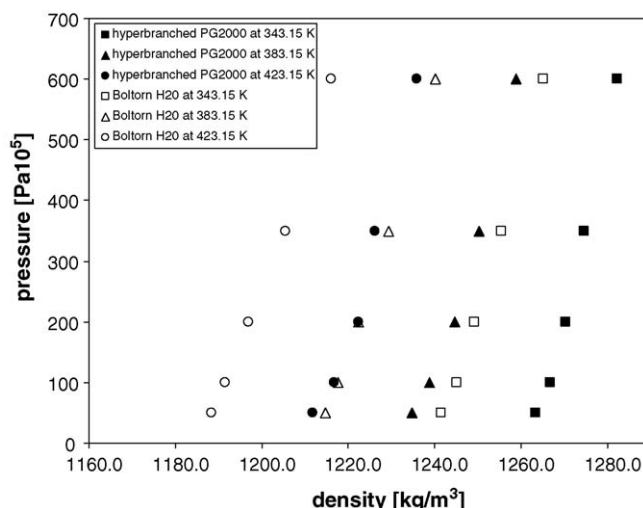


Fig. 10. PVT-data of hyperbranched polymer melts. Filled symbols, hyperbranched polyglycerol PG 2000: $M_n = 2000$ g/mol, $M_w/M_n = 1.5$. Unfilled symbols, hyperbranched polyester Boltorn H2O: $M_w = 2100$ g/mol, $M_w/M_n = 1.3$.

predicted by UNIFAC-FV if one only accounts for the dominant contribution of the terminal groups to the residual solvent activity [7,113].

Further simulation studies on dendritic polymer systems can be found elsewhere [88,131–137].

As already pointed out, thermodynamic models, which accurately account for the influence of polymer branching on the phase behavior of polymer systems, play a very important role; they enable the optimization of new applications of hyperbranched polymers without requiring a large amount of experimental phase equilibrium data. However, many models described above (equations of state, g^E -models) do need the information of experimental PVT-data for the adjustment of parameters. Since these kinds of PVT-data are usually not available in the literature, the author wants to provide new experimental PVT-results [measured at the chair of Prof. G. Sadowski (University of Dortmund) within the scope of M. Seiler's PhD-work which was supervised by Prof. W. Arlt (University of

Table 1
PVT-data of hyperbranched polymer melts

Pressure (Pa $\times 10^5$)	Density at 343.15 K (kg/m ³)	Density at 383.15 K (kg/m ³)	Density at 423.15 K (kg/m ³)
Boltorn H2O			
50	1241.6	1214.7	1188.3
100	1245.1	1217.6	1191.5
200	1249.2	1222.3	1197.0
350	1255.6	1229.4	1205.4
600	1265.2	1240.2	1216.2
PG			
50	1263.5	1234.9	1211.8
100	1266.7	1238.8	1216.8
200	1270.5	1244.7	1222.4
350	1274.7	1250.4	1226.2
600	1282.4	1258.8	1235.9

Hyperbranched polyglycerol PG: $M_n = 2000$ g/mol, $M_w/M_n = 1.5$; Hyperbranched polyester Boltorn H2O: $M_w = 2100$ g/mol, $M_w/M_n = 1.3$.

Erlangen-Nürnberg)] for a hyperbranched polyester and a hyperbranched polyglycerol (see Fig. 10 and Table 1).

4. Applications of hyperbranched polymers in the field of chemical engineering

4.1. Membranes

A wide variety of polymeric materials have been studied to evaluate their potential use as membrane materials for separation processes [139]. However, all the commercially available membrane materials developed so far are limited to linear polymers. During the last years, a number of research groups started focusing on hyperbranched polymer membranes [140–147]. Among these studies, the use of hyperbranched polymers as high-performance gas separation membranes seems particularly promising. Membrane-based gas separations have attracted much attention in the past decade since they offer many advantages over traditional separation processes such as low capital investment cost, low energy consumption, and simple operation [146]. In this context, Fang et al. and Suzuki et al. studied the performance of hyperbranched polyimide membranes [141,143]. In general, polyimide membranes are of considerable interest in gas separation applications due to their high gas selectivity and excellent mechanical and thermal stability. Fang et al. prepared hyperbranched aromatic polyimide membranes by condensation polymerization of a triamine monomer, tris(4-aminophenyl)amine, and a series of commercially available dianhydride monomers [141]. Two types of hyperbranched polyimides, an amine-terminated and an anhydride-terminated sample, were obtained. According to Fig. 11, films of these hyperbranched polyimides were fabricated by crosslinking treat-

ment during film cast. Such a film formation technique is based on the chemical reaction between the terminal functional groups of the hyperbranched polyimide and a difunctional crosslinking agent, which leads to the connection of globular hyperbranched macromolecules via chemical bonds [141]. The resulting films were transparent, tough and suitable for gas permeation measurements.

Crosslinking has a great impact on the gas permeation properties of the hyperbranched polyimide membranes. Lower crosslinking density (i.e., lower concentration of crosslinking agent) results in a higher gas permeability coefficient but similar ideal selectivities [141]. For the same hyperbranched polyimide, the membrane with rigid crosslinking linkages displayed a similar selectivity of CO₂ over N₂ but a much larger CO₂ permeability coefficient than the one with flexible crosslinking linkages. The amine-terminated hyperbranched polyimide membranes showed larger gas permeability coefficients than the anhydride-terminated membranes. Furthermore, most importantly, Fang et al. pointed out that the O₂/N₂ separation performance of terephthaldehyde-crosslinked hyperbranched polyimide membranes is better than that of the linear analogues and many other commercially available linear polymeric membranes and comparable to that of the linear polymeric membranes which have been reported to have the highest separation performance [141].

Suzuki et al. investigated the physical and gas transport properties of hyperbranched polyimide membranes prepared from a triamine, 1,3,5-tris(4-aminophenoxy)benzene (TAPOB), and a dianhydride, 4,4'-(hexafluoroisopropylidene) diphthalic anhydride (6FDA). These 6FDA-TAPOB hyperbranched polyimide membranes exhibited a remarkable thermal stability with a 5% weight-loss temperature of 510 °C. The gas permeability and/or

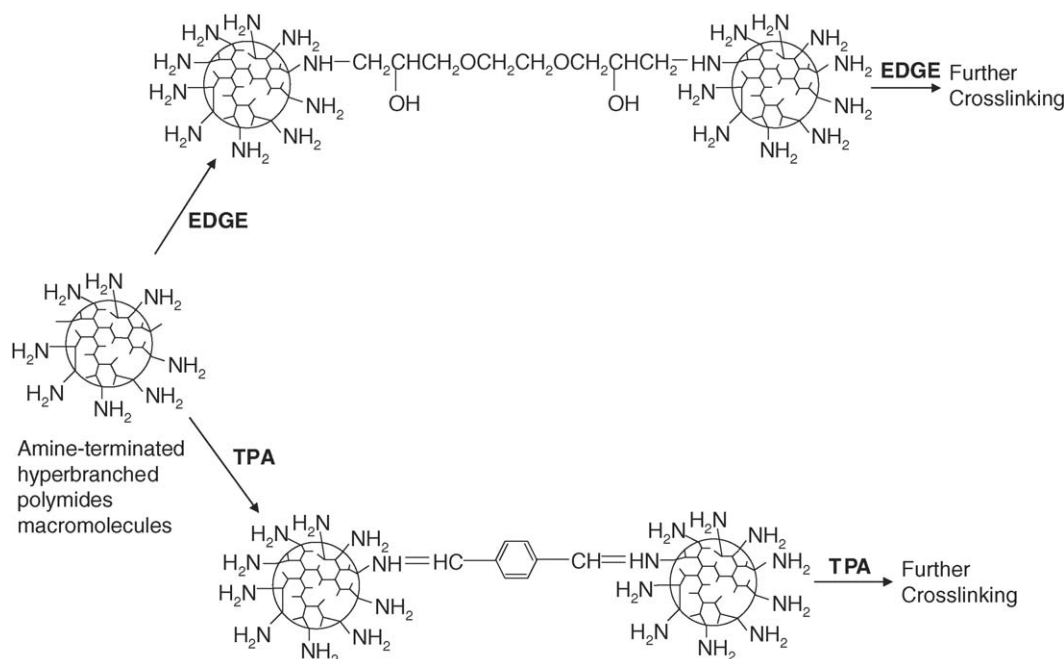


Fig. 11. Crosslinking scheme for amine-terminated hyperbranched polyimides [141]. Crosslinking agents: ethylene glycol diglycidyl ether (EGDE) and terephthaldehyde (TPA).

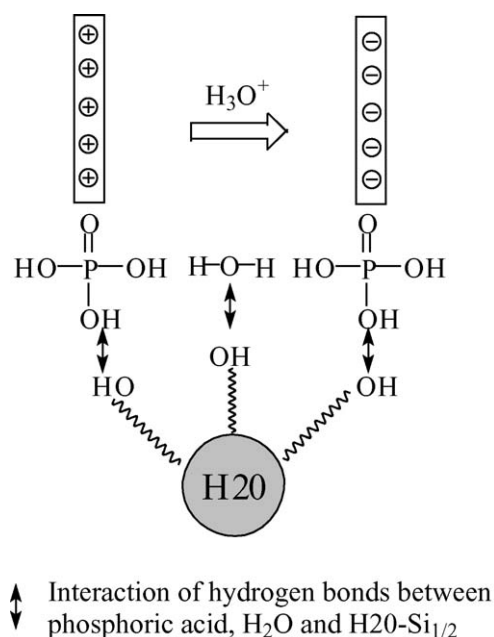


Fig. 12. Sketch map of the structure and proton conductivity mechanism of the hybrid membranes [144].

diffusivity of a polymer depend on the free volume. The fractional free volume value of 6FDA-TAPOB was higher than those of the linear analogues, indicating looser packing of the molecular chains. The hyperbranched membrane exhibits a considerably high gas solubility, and as a result, shows high gas permeability [143]. Therefore, Suzuki et al. suggest that the low segmental mobility and the unique size and distribution of free volume holes arising from the characteristic hyperbranched structure of 6FDA-TAPOB provide an effective O_2/N_2 selectivity. Due to the high permeability and O_2/N_2 selectivity, Suzuki et al. conclude that the 6FDA-TAPOB hyperbranched polyimide meets the requirements of a high-performance gas separation membrane [143].

Shi and co-workers studied the preparation and properties of organic–inorganic hybrid membranes based on phosphoric acid and hyperbranched aliphatic polyesters used as electrolytes for polymer electrolyte membrane fuel cells (PEMFC) operated at a temperature above 100°C [144]. Due to their higher energy transfer efficiency, lower maintenance requirements and lower emission of environmental pollutants such as CO , NO_x , and SO_x compared with that of internal combustion engines, PEMFC are extremely attractive energy conversion systems to be used in many industrial applications including electric vehicles and on-site power plants [144]. Shi and co-workers doped the hyperbranched polyester Boltorn H20 into the hybrid membranes at different levels to provide high hydrophilic and water conservation property. According to Fig. 12, a high proton conductivity was obtained with suitable doping levels of the hyperbranched polyester, and the membrane with the highest proton conductivity remained a conductivity of $5 \times 10^{-4} \text{ S/cm}$ even after holding for 7 h at 130°C under 30% relative humidity. The hybrid membranes prepared via a sol–gel process were stable up to 200°C [144].

4.2. Extractive distillation

In comparison to conventional (low-) volatile entrainers, the use of highly selective nonvolatile hyperbranched polymers showing large separation efficiencies allows for a reduction in the required hot and cold process utilities in extractive distillation [7]. However, apart from the thermodynamic suitability in terms of selectivity and separation efficiency (for VLE and separation factors see [7,111,114]), hyperbranched polymers also meet a number of other important entrainer criteria such as

- a remarkable solubility (because of their large number of functional groups);
- a comparatively low solution viscosity (due to the highly branched topology);
- a remarkable thermal stability (up to 823 K as for hyperbranched polyphenylenes);
- an increasing variety and large-scale availability at low cost (currently $\geq 4 \text{ EUR/kg}$);
- noncorrosive behavior;
- no or tunable reactivity and toxicity;
- adjustable physical and chemical properties.

Furthermore, there is a three-fold advantage of using a non-volatile entrainer:

- the entrainer cannot pollute the distillate;
- no main column separation section and internals are required for the separation of the entrainer from the overhead product;
- a variety of entrainer regeneration options is feasible.

The entrainer recovery in a conventional extractive distillation process is mostly carried out using another countercurrent distillation column. Unlike this conventional process, the regeneration of nonvolatile entrainers such as hyperbranched polymers or the recently suggested ionic liquids [114,116] allows for the use of other unit operations. Conventional distillation for the separation of a binary mixture consisting of a nonvolatile entrainer and a volatile component is not feasible, since the non-volatility of a component would lead to a breakdown of the column's counterflow. A possibility to circumvent this problem is the operation of a stripping column (charge reflux fractionator) without rectifying section and reflux. A (heated) inert gas can be fed into the bottoms of the stripper and guided through the column in countercurrent to the entrainer rich feed, resulting in a concentrated entrainer-bottom product and a solvent rich overhead product (see Fig. 13).

Thin-film evaporators represent another alternative for an effective, thermally gentle and continuous recycling of a non-volatile entrainer. Depending on the viscosity of the solution, falling-film evaporators or, for higher viscosities, rotary thin-film evaporators appear to be suitable. Although the hyperbranched polymer melts show comparatively (to other polymers) low viscosities, it might be advantageous to install a refuse worm at the rotary end of the thin-film evaporator such as those used for the stripping of epoxy resins or the degassing of polyolefins. Hyperbranched polymers can also be recycled by convection

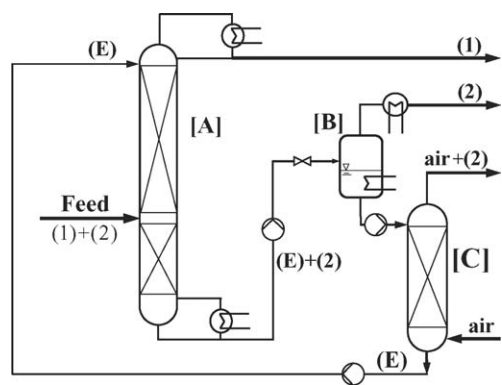


Fig. 13. Separation scheme for an extractive distillation processes using non-volatile entrainers: (1) ethanol; (2) water; (E) hyperbranched polymer of low viscosity; [A] main column; [B] flash drum; [C] stripping column.

drying, using a spray dryer, a thin-film evaporation dryer or a belt dryer.

The recovery options described for a nonvolatile entrainer are competing unit operations, which have to be thoroughly assessed with regard to their investment and operation costs. A comparison with conventional separation processes for azeotropic mixtures shows, that the remarkable separation efficiencies of hyperbranched polymers [111,114] as well as the variety of energetically promising recycling options for the entrainer offer considerable potential for process and economic optimizations.

As an example, Seiler et al. demonstrated the potential use of hyperbranched entrainers by investigating the ethanol–water separation [7,114]. The entrainer used was a hyperbranched polyglycerol ($M_n = 1400$ g/mol, $M_w/M_n = 1.5$, 20 OH-groups per macromolecule). In case of the ethanol–water separation, the entrainer suitability of hyperbranched polyglycerols can be demonstrated by evaluation of the process scheme shown in Fig. 13.

An ethanol–water feed is separated by an extractive distillation main column [A] and an entrainer regeneration, combining a flash drum [B] and an atmospheric stripping column [C]. The flash, operated under vacuum conditions (for process conditions see [114]), allows for a preconcentration of the nonvolatile entrainer. The remaining water fractions are separated from the entrainer using an adiabatic atmospheric stripping column without reboiler and condenser. Dry air is used as the stripping medium. Subsequently, the regenerated entrainer is recycled back to the main column (see Fig. 13).

Energetic process evaluation of the latter process using the hyperbranched polyglycerol and conventional extractive distillation using 1,2-ethanediol as entrainer was carried out by means of Aspen Plus®. For further details see [114]. In comparison to the conventional ethanediol-process, the use of hyperbranched polyglycerol allows a maximum saving in overall heat duty of about 20% [114]. This underlines the potential of hyperbranched polymers for the separation of azeotropic mixtures by extractive distillation. Moreover, in this context, it is worth mentioning that the investigated entrainer (a hyperbranched polyglycerol) represents a chemically non-optimized compound whose properties can be further improved, for instance, by increasing the ratio

number of molecular surface functionalities to molar mass of the hyperbranched polymer. Due to the biocompatibility of many hyperbranched polymers, their use as entrainer or extraction solvents for the separation of flavors, essences, natural substances and food ingredients appears promising as well.

4.3. Extraction

Liquid–liquid extraction is a separation process which is in competition with distillation. Especially with the requirement of low energy consumption, liquid–liquid extraction is gaining importance. It is often applied if the mixture components exhibit low or high boiling points (thus distillation has to be carried out under costly vacuum or low temperature operation), if the mixture is a close boiling or an azeotropic system, if the components to be separated are thermally sensitive or if the mixture comprises a key component of low concentration.

Hyperbranched polymers show many properties which indicate their potential use as extraction solvents. As discussed elsewhere [7,111], there are some hyperbranched polymers commercially available (even with FDA approval) which show high selectivities, remarkable loading capacities for certain key components, no vapor pressure, comparatively low melt and solution viscosities, non-toxic behavior, as well as remarkable thermal and chemical stabilities. Therefore, only recently, a number of studies have been published discussing the separation of components by means of hyperbranched polymers as extractant [7,110,111,114,116,148,149].

Goswami and Singh focused on hyperbranched polyesters and their use as metal ion extractant. They observed pH-dependent extraction efficiencies. The optimum pH range for the maximum extraction of metal ions was found to be 5.0–7.0 for Cu(II) and Pb(II), 4.5–7.0 for Fe(III), 6.0–8.0 for Co(II) and Ni(II), 6.0–7.5 for Cd(II) and 6.5–8.0 for Zn(II) [148]. However, aspects concerning the design and operation of a suitable extraction process have not been discussed.

Arkas et al. investigated the use of alkylated hyperbranched polymers as molecular nanosponges for the purification of water from polycyclic aromatic hydrocarbons. These polymers allow for the extraction of toxic polycyclic aromatic compounds dissolved in water. Due to highly selective hyperbranched nanosponges, the concentration of polycyclic aromatic hydrocarbons in water could be reduced to a few ppb. Structural features such as symmetry of the polymers, flexibility of their branches, intermolecular interactions, and chemical moieties of the nanocavities are the parameters determining the extraction/encapsulation capability [149]. The extracted pollutants can be removed from the hyperbranched nanosponges by treating the saturated hyperbranched extraction medium with organic solvents (regeneration of the hyperbranched polymer).

Seiler and Arlt investigated the separation of the azeotropic tetrahydrofuran–water system. THF is produced by dehydrocyclization of 1,4-butanediol in the presence of an acid catalyst. The key step in purification is the breaking of the THF–water azeotrope [150]. Generally, this is achieved by pressure-swing distillation (low/high pressure) distillation, extractive distillation or azeotropic distillation.

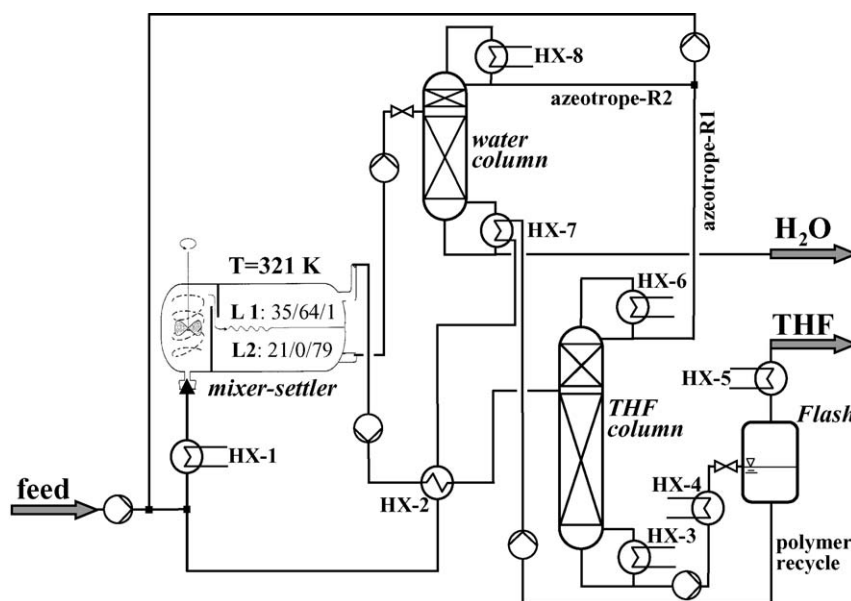


Fig. 14. Separation scheme for the THF–water separation using the hyperbranched polyester Boltorn H3200 as extraction solvent [114]; concentrations in weight percent, THF/polymer/water.

Based on the liquid–liquid equilibrium results discussed recently, different process options for the THF–water separation using hyperbranched polymers as extraction solvents are conceivable [111,114]. Energetic optimizations of the latter process options by means of a pinch analysis (see [114]) and comparison with conventional THF–water separation processes, indicate a noteworthy potential for the separation process illustrated in Fig. 14: A 50 wt.% THF/50 wt.% H₂O mixture of 1000 kg/h is fed into a mixer-settler. A specific amount of the extraction solvent, the hyperbranched polyester Boltorn H3200, is added to the THF–water mixture.² At 321.15 K, the solution splits into the two liquid phases L1 and L2. Due to the large THF-solubility in the polymer-rich phase L1 and its remarkable low density, the polymer-rich phase represents the upper and the water-rich (polymer-free) phase L2 the lower phase (see also Fig. 14). As described elsewhere [7,114], the THF–water ratio of the polymer-rich phase L1 is larger than the azeotropic THF–water concentration ($w_{\text{THF, azeotrope}} = 0.942$ at $P = 105$ Pa). Therefore, when feeding L1 into an atmospheric distillation column (see Fig. 14, THF column), the column's feed composition is located at the right-hand side of the THF–water minimum boiling azeotrope of the corresponding y -, x -diagram. Due to the presence of Boltorn H3200, the azeotropic point shifts to smaller THF concentrations. Thus, the composition of the overhead product of the THF column corresponds to the new location of the shifted minimum boiling azeotrope [7,114]. The bottom product of the THF column contains the remaining THF and the entire polymer. The latter THF–polymer mixture is separated in a flash drum or thin-film evaporator into the THF

product ($x_{\text{THF}} = 0.999$) and a concentrated polymer flow. Due to remaining THF fractions and a temperature far above the melting temperature of Boltorn H3200 ($T_{\text{melt, Boltorn H3200}} \approx 333$ K), the concentrated polymer flow represents still a pumpable mixture of acceptable viscosity, which is recycled to the extraction unit. At 3×10^4 kPa, the water column (see Fig. 14) separates the polymer-free phase L2 within three theoretical stages into water as bottom product and the THF–water minimum boiling azeotrope as overhead product. Both distillation columns do not require a rectifying section.

The process optimization by pinch analysis resulted in a required heat demand of 1705 kJ/kg THF product. The comparison of this result with simulation results for the conventional THF–water separation processes (azeotropic distillation, pressure-swing distillation) indicates a considerable potential for using hyperbranched polymers as extraction solvents [114].

4.4. Absorption, adsorption

In general, the separation of gases via an absorption process using hyperbranched polymers as scrubbing agents appears feasible. However, this field is still in its infancy. The challenge is to find a competitive low-cost hyperbranched polymer having a high selectivity and capacity, a comparatively low molar mass, and a melt/solution viscosity which allows for the operation of an absorber even at ambient temperature or below. Arlt and Rolker (University of Erlangen, Germany) currently evaluate the potential of hyperbranched scrubbing agents for absorption processes [151].

Another interesting idea is the use of hyperbranched polymers as stationary phases for (preparative) chromatography. A number of research groups started focussing on the separation of mixtures by adsorption methods involving dendritic polymers [7,111,116,152–155]. Shou et al. studied non-bonded

² It is worth mentioning, that the choice of the overall mixing point and of the continuous phase is of considerable importance for the viscosity of the coexisting phases and their settling time. The larger the THF fraction of the polymer-rich phase, the smaller its solution viscosity [7].

hyperbranched polymer-coated columns for capillary electrophoresis [152]. Capillary electrophoresis represents a powerful separation tool which is often applied for the analysis of biopolymers such as peptides, proteins, DNA fragments and carbohydrates. However, many biopolymers tend to adsorb to the surface of the capillary column due to hydrophobic or coulomb interactions [152]. Shou et al. synthesized a series of hyperbranched poly(amine esters) and coated them on the inner surface of fused-silica capillaries by physical adsorption. It was found that a hyperbranched poly(amine ester) coating of seventh generation reduced the electroosmotic flow greatly and suppressed protein adsorption effectively. For basic proteins, high separation efficiencies were obtained [152]. Chao and Hanson investigated dendritic poly(aryl ethers) as bonded stationary phases in open tubular capillary electrochromatography. The bonded dendritic polymers tended to reduce the electroosmotic flow and showed promising results in a number of separation experiments including neutral aromatic hydrocarbons and basic proteins [153]. Based on their results, Chao and Hanson conclude that this approach shows promise for the development of new capillary electrochromatography methods for separation science.

5. Conclusions and future work

During the last decade dendritic polymers have attracted considerable attention. To date, dendritic polymers represent a well-established field in polymer science. A remarkable variety of applications for hyperbranched polymers has been investigated and the interdisciplinary research activities are still extremely high. Due to the costly and complex multistep-synthesis of dendrimers and new synthetic developments for hyperbranched polymers, a remarkably increasing driving force towards the replacement of dendrimers by hyperbranched polymers could be observed during the last 3 years. In this context, developments are striving for hyperbranched polymers with higher degrees of branching and for synthetic methodologies that allow for a better control over branching, molar mass distribution and architecture (see for instance [2,3,68,138]).

However, despite the remarkable pace of interdisciplinary research on hyperbranched polymers and the development of new and more complex hyperbranched structures, it is of importance to note that there are still fundamental research areas that have not yet been examined properly. As discussed in this work, one of these areas represents the phase behavior of hyperbranched polymer systems and the development of thermodynamic models, capable of describing the enthalpic and entropic phenomena of highly branched polymer solutions. The challenge is the explicit and adequate consideration of the degree of polymer branching. For this purpose, further experimental investigations focusing on the influence of the degree of polymer branching on the high-pressure phase behavior of polymer systems have to be conducted.

In terms of applications, it has been recognized that the modification of the number and type of functional groups on hyperbranched polymers is essential for the control of their solubility, compatibility, reactivity, thermal stability, adhesion to

various surfaces, self-assembly, chemical recognition, as well as electrochemical and luminescence properties. Thus, these structural modifications provide a powerful tool for designing hyperbranched polymers for specific applications. Low-viscosity hyperbranched polymers represent promising compounds also for the optimization of a variety of separation processes. It has been demonstrated that hyperbranched polymers can show remarkable separation efficiencies, selectivities, and capacities allowing for the elimination of azeotropic system behavior [7,109,111,114]. This enables applications in the field of chemical engineering, for instance, as entrainers in extractive distillation processes, as extraction solvents in liquid–liquid extraction processes or as scrubbing agents in absorption processes. However, the author wants to stress that there are only a few hyperbranched polymers commercially available at present which meet the requirements of an entrainer, an extraction solvent or a scrubbing agent. Especially the combination of (i) a competitive large-scale availability of hyperbranched polymers (<5 EUR/kg); (ii) a low solution viscosity (<100 mPa s at e.g. 70 °C and polymer concentrations in the solution of 70 wt.%); (iii) low glass transition/melting temperatures ($T_g < 20$ °C); (iv) stability against hydrolysis; and (v) appropriate thermodynamic properties such as high selectivities and capacities represent an enormous challenge. To date, the use of hyperbranched polymers as high-performance membranes appears to be one of the most promising applications of hyperbranched polymers in the field of chemical engineering.

However, “smart materials” or “designer polymers” such as the hyperbranched polymers have a bright future. Adjustable polymer properties in combination with a high selectivity and nonvolatility represent a combination of promising features, necessary to develop new processes which are superior to conventional separation processes. Beyond separation processes, future research studies on hyperbranched polymers will be more concerned with the field of polymer science [1–4,138], following the recommendation of John Prausnitz and Paul Flory; namely to demonstrate the properties of hyperbranched polymers, to better understand them and to finally establish a relationship framework for the underlying parameters.

6. Influence of John Prausnitz on my work

John Prausnitz is not only an enthusiastic, warm-hearted teacher of thermodynamics capable of making complex matters easily understandable.

He is a light house, leading ships from different sciences together, guiding them into safe waters and showing them the importance and beauty of thermodynamics along the way.

He is an untiring pathfinder, demonstrating and emphasizing the significance of thermodynamics to academia, industry and politics, and thereby constantly reminding them not to neglect this important area of science.

And last but not least he is a passionate and inspiring researcher, who turned his scientific focus to hyperbranched polymers some years ago, the field that brought us together during my time as a Ph.D. student at the Technical University of Berlin.

Thanks to John's special relationship to Prof. Knapp and Prof. Arlt, he often visited Berlin. During these visits we always discussed new thermodynamic developments, results and challenges in the field of dendritic polymers intensively. His guidance and interest in my work were always an enormous motivation for me, and many solutions to the industrial challenges I currently face would not have been possible without his thermodynamic achievements.

I would like to dedicate this review on hyperbranched polymers to John Prausnitz in gratitude and friendship and in acknowledgement of the tremendous achievements which represent his life's work.

List of symbols

M or MWt	molecular weight (kg/kmol)
P	pressure (Pa)
R	universal gas constant (J/(mol K))
T	temperature (K)
w	weight fraction
x	liquid phase mole fraction
y	vapor phase mole fraction

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