

# Dendrimers vs. Hyperbranched Polymers: Studies of the Polymerization Process Based on Monte Carlo Simulations

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**Abstract:** A simple model was developed for studies of the polymerization process of branched polymers. Monte Carlo simulations were carried out by means of the Dynamic Lattice Liquid algorithm. A living polymerization in bulk of dendrimers and hyperbranched polymers was studied. The mass and structure of both types of macromolecules were investigated. The influence of the functionality of well-defined cores on the structure of the system was also examined. The differences in the kinetics in the formation of both architectures and changes to their structures were discussed. It was shown that both architecture exhibit low dispersity which was found to be higher for hyperbranched macromolecules.

**Key words:** dendrimers, Dynamic Lattice Liquid model, hyperbranched polymers, lattice models, Monte Carlo method

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## I. Introduction

Non-linear polymers may be divided into the following classes: cross-linked, branched and dendritic. The latter class might be further divided into: random hyperbranched polymers, dendrigrafts, dendrons and dendrimers [1]. Dendrimers are macromolecules that are completely and regularly branched. Their dendritic structure is three-dimensional and geometrically perfect [2–3] and therefore they constitute an important model for theoretical considerations [2, 4]. They consist of a central branching point and branched repeating units emanating from it [5–7]. Dendrimers are usually characterized by functionality of branching point (usually 3 or 5), the length of the spacer (the number of mers

between branching points), and the number of generations (the number of shells containing branching points).

Dendrimers are important because of their applications in nanotechnology, drug delivery, catalysis, coatings, biosensors, drug carriers, etc. [2, 7, 8–13]. The polymerization of dendrimers is carried out according to two schemes, divergent and convergent, with increasing and constant reactions per growth step, respectively [7–8]. The properties of dendrimers differ significantly from those of their linear counterparts [14]. Moreover, they vary considerably from regular star-branched polymers [15]. Dendrimers with a small number of generations form an entangled melt, while those with a larger number of generations can be treated as densely packed structures [16]. The number of chain entanglements

is low and their influence on viscoelastic properties is small, but the viscosity of dendrimers appeared to be a nonmonotonic function of molecular weight [17–19].

Theoretical treatment of dendrimers was performed mainly using self-consistent mean field and renormalization group calculations [20–21], Monte Carlo simulations [15, 22–27], and Molecular Dynamics simulations [21–22, 31–37]. The structure and viscoelastic properties of dendrimers studied by computer simulations showed the impact of the functionality, the number of generations, and spacer length on the polymer properties [15, 27, 34–36].

Hyperbranched polymers are synthesized by the polymerization of  $AB_n$  monomers, where  $n \geq 2$  [3, 11, 37–38]. Therefore, the main advantage of hyperbranched polymers over dendrimers is easier synthesis at considerably lower costs, while the main disadvantage is that these macromolecules are irregular and disperse [39–41]. Their structure and dynamic properties also differ from those of dendrimers. The applications of hyperbranched polymers are mainly determined by their relatively low costs, lack of entanglements, and a large number of functional groups [38–40]. The structure of hyperbranched polymers was studied via theories [42–48], Monte Carlo simulations, [45–46, 49–50], and Molecular/Brownian Dynamics simulations [51–56].

These theoretical studies showed main differences between dendrimers and hyperbranched polymers. The size of hyperbranched polymers is greater than that of dendrimers and it decreases with the degree of branching. The scaling of the macromolecule size was found similar for both architectures under consideration and the scaling exponent varied between 0.57 and 0.62, which is close to that for densely packed globules. The shape of hyperbranched polymers appeared to be more prolate when compared to regular dendrimers. Hyperbranched polymers were also shown to exhibit quite different viscoelastic properties compared to linear chains (considerably lower values of viscosity and a maximum of intrinsic viscosity for certain molecular mass) [37–38, 56].

In this paper, the polymerization processes of dendrimers and hyperbranched polymers are compared. An idealized coarse-grained lattice model, the Dynamic Lattice Liquid (DLL), was used. It is classified as the cooperative Monte Carlo simulation method. The main advantages of this model was the possibility of studying polymer systems at high densities and the usage of prefabricated, well-defined cores. Thus, the polymerization process was performed in bulk.

## II. Simulation Method

In order to study large systems consisting of high-mass macromolecules, a coarse-grained representation was used. The second assumption was the limitation of degrees of freedom in the system by the introduction of a lattice approximation. Therefore, all objects in the system were located at the vertices of a face-centered cubic lattice. Each element of the system (monomer and a mer in a growing chain) was allowed to occupy one lattice point only and therefore the size of all these objects was assumed to be identical. The status of monomer could change into a mer as a result of the

polymerization. Each reaction between a pair of neighboring objects, i.e. located in a distance of one lattice constant was irreversible and resulted in formation of an unbreakable bond. The attempt of the reaction and of the modification of chains' conformations takes place simultaneously in each time step. The probability of attaching a monomer to a growing chain was assumed to be 0.02, based on previous findings [15]. The polymerization process was carried out in bulk, which implied a high density of the system. The DLL model dynamics was used to move the elements by self-diffusion. It was shown that this calculational tool provides a proper dynamics for the various soft matter systems [2, 57]. This method was described in detail previously and thus only a short description is given in order to highlight its main features. This model is provided with a dynamics consisting of local vibrations and occasional diffusion steps. In one Monte Carlo step (a pseudo-time unit), a field of unit vectors representing motion attempts is generated at random and then assigned to all objects in the system. Only those attempts are successful which coincide in such a way that the sum of displacements along a closed path (loop) that included more than two molecules is equal to zero (the condition of continuity). In the case of identifying such a loop, each object is then moved to a neighboring lattice site along this loop. All objects that did not contribute to these loops stay in their previous positions. Within a longer time period this kind of dynamics leads to displacements of individual objects along random walk trajectories with steps distributed randomly in time. The most important advantage of this method is that it naturally takes into account the heterogeneity of the system and introduces changes in the local mobility of the system components and steric hindrances resulting from polymerization [15].

The macromolecular system consisted of  $10^6$  elements and the edge of simulation box was  $L = 100$ . The excluded volume was the only interaction potential and periodic boundary conditions were applied in all directions. At the beginning of each simulation run, functional cores (from which the polymerizations of macromolecules start) were randomly distributed in the system. All the remaining lattice sites were filled with monomers and the functionality of each monomer was 4. The studied systems had the following concentrations of functional cores: 0.000125, 0.00025, 0.0005 and 0.0010, which corresponded to 125, 250, 500 and 1000 chains, respectively. In simulations of dendrimers, the spacer was set to 1 while the number of generations was not imposed to the model, and each simulation run lasted until exhaustion of the monomer (up to  $10^6$  Monte Carlo steps). Hyper branched polymers were synthesized in a similar way but contrary to dendrimers the functionality of the attached monomer was chosen at random [50].

## III. Results and Discussion

The kinetics of the polymerization processes for systems containing dendrimers and hyperbranched polymers was studied in terms of the conversion of monomer, i.e., time-dependent polymer mass increase. Fig. 1a shows the conversion of monomers as a function of time for dendrimers

with various numbers of macromolecules in a double logarithmic scale. One can distinguish two clear regimes for all numbers of macromolecules: the increase of the conversion to time near  $10^3$  Monte Carlo simulation steps and a plateau where all monomer molecules become attached to polymers. Fig. 1b presents the derivative of the monomer conversion as a function of time, i.e. the reaction rate. Here, in the first regime, the increase in monomer conversion is linear, which implies that the total reaction rate is almost constant. In the second regime, a rapid linear decline in the reaction rate is visible. These changes take place for the monomer conversion around 0.70–0.80. The location of this point depends very weakly on the number of branches. This point indicates the time for which free-growing dendrimers with no limitation of surrounding monomers begin to compete with other polymers for available monomer molecules. This means that the system was relatively diluted at first, and then became dense (in terms of polymer concentration). The differences in monomer conversion and the reaction rate between all macromolecular systems considered are small, which can be

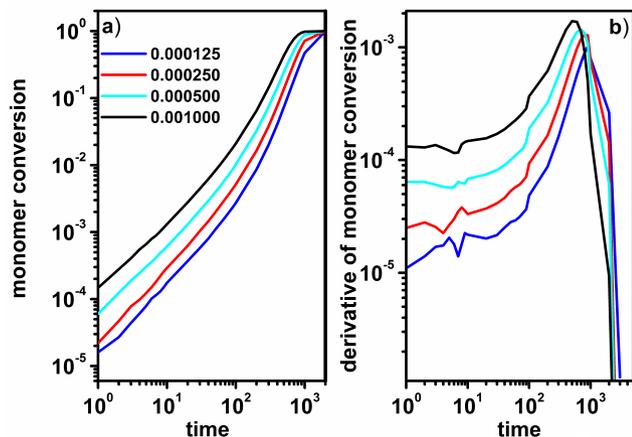


Fig. 1. Conversion of a monomer (a) and its derivative (b) as a function of time during polymerization of dendrimers. The color indicates the concentration of cores

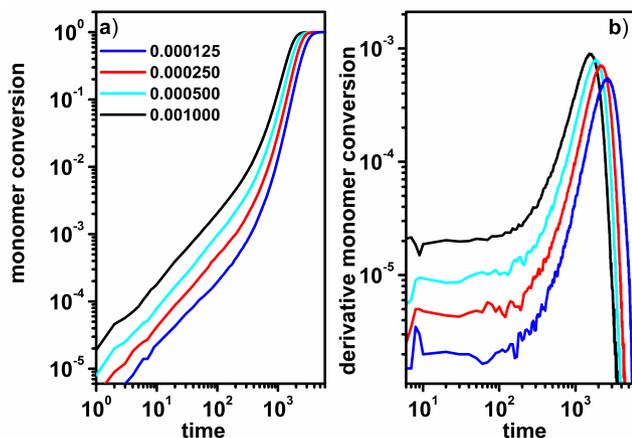


Fig. 2. Conversion of a monomer (a) and its derivative (b) as a function of time during polymerization of hyperbranched polymers. The color indicates the concentration of cores

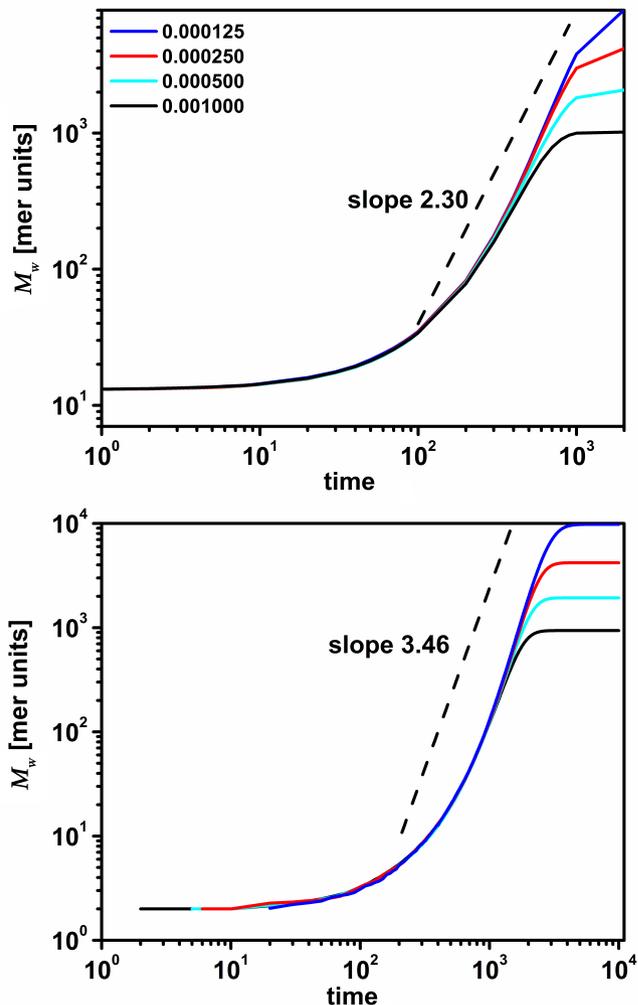


Fig. 3. The average total mass of the dendrimer (upper panel) and hyperbranched polymer (bottom panel) as a function of time. The color indicates the concentration of cores

explained by the fact that the number of growing chains does not change in all dendrimer systems studied.

The dendrimers and hyperbranched polymers cannot be compared directly by means of the number of branches, but they can be compared when systems contain the same number of macromolecules, i.e. the same number of multifunctional cores in the system. Fig. 2 shows the monomer conversion and the reaction rate as functions of time for hyperbranched polymers. One can observe from Fig. 2a that the conversion of monomers is slower than in the case of dendrimers and lasts slightly longer than that confirmed by the values presented in Fig. 2b.

A question arises if the small differences in monomer conversion for both architectures lead to differences in the growth dynamics. Dynamic scaling of a cluster size is usually described using the Smoluchowski coagulation equation which describes the cluster size distribution for dilute systems with binary collisions only [58]. For large clusters at longer time, the number of clusters formed by  $l$  elements

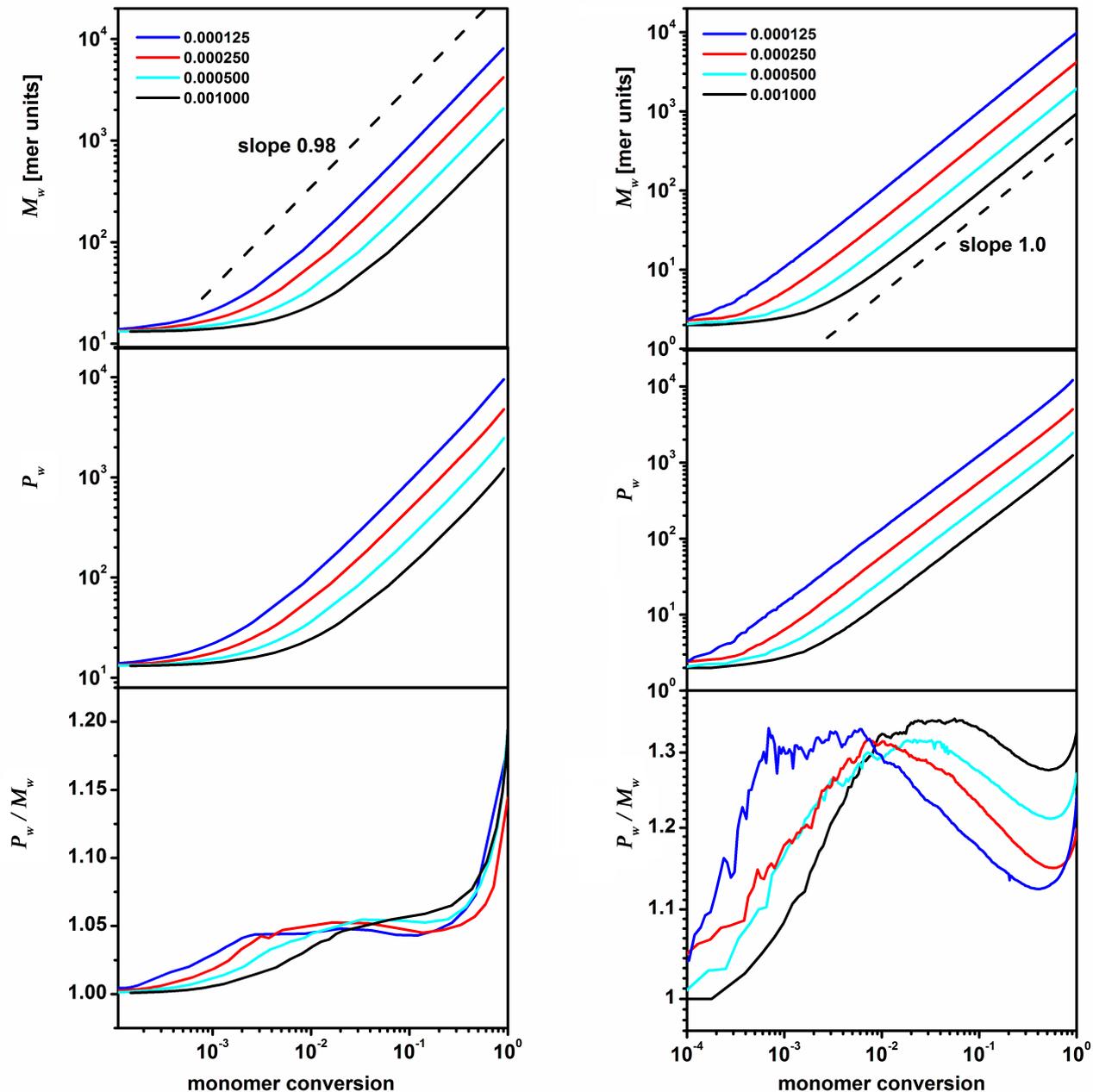


Fig. 4. Number-averaged mass (upper panel), weight-averaged mass (middle panel) and dispersity (bottom panel) as a function of the monomer conversion. The case of dendrimer (left) and hyperbranched polymer (right). The color indicates the concentration of cores

exhibits scaling, and the cluster size distribution should approach the limit form:

$$n_l \approx N^{-2} \Phi(N/l), \quad (1)$$

where  $n_l$  is the cluster size distribution,  $N = N(t)$  is the number-average cluster size, while  $\Phi(N/l)$  is a universally time-independent cluster size distribution, which characterizes the aggregation mechanism [59]. Combining the solution of Eq. (1) with the fractal scaling relationship one obtains the following formula:

$$N(R) = k_0 R^{d_f}, \quad (2)$$

where  $k_0$  is a prefactor,  $R$  is a characteristic size of the cluster,  $d_f$  is the fractal dimension and  $N(R)$  is the number of objects aggregated in the cluster. The mean cluster size given by Eq. (2) can also be obtained as a function of time:

$$N(t) \approx t^z \equiv t^{1/(1-\lambda)}, \quad (3)$$

where  $\lambda$  is the van Dongen and Ernst homogeneity exponent which describes different growth kinetics induced by

the object-object interaction [60–61]. This exponent should take the value 0 and 1 for the diffusion-limited cluster and the reaction-limited cluster aggregations, respectively. In the case of macromolecules studied, the number-averaged mass  $M_w$  (the number of polymer segments) of a dendrimer and a hyperbranched polymer can be treated as  $N(t)$  from Eq. (3). Figs. 3a–b present the average mass  $M_w$  of the both macromolecular architectures studied as a function of time  $t$ . For the case of dendrimers (Fig. 3a), three regimes can be distinguished for all cases (for all number of polymers studied). In the first one the growth of the macromolecule is slow. Then, in the second regime, the mass starts to increase rapidly. In the third, the growth slows down again due to the high density of polymer segments and because of competition between dendrimers in acquiring the remaining monomer molecules. In the latter regimes, the dependence on the number of polymers appears: the greater the number, the slower the process. This increase in  $M_w$  in the second regime can be described by the exponent 2.30, which is considerably stronger than in the case of star-branched polymers, where the exponent was found to be 0.84 [15]. The changes in the mass of hyperbranched polymers with time is presented in Fig. 3b. The behaviour of  $M_w$  is very similar to that of dendrimers. This increase of mass is even stronger with the exponent of 3.46.

The kinetics of polymer growth during the polymerization process is usually described by  $M_w$ , the weight average mass  $P_w$ , and the dispersity  $P_w/M_w$ . Fig. 4 (left) shows the number-averaged mass  $M_w$ , the weight-averaged mass  $P_w$ , and the dispersity  $P_w/M_w$  for dendrimers as functions of the monomer conversion in a log-log plot. Here the monomer conversion plays the role of non-linear time. One can observe that after a short initial period, where the consumption of the monomer is low and stable, the increase of the mass is almost linearly proportional to the monomer conversion in a log-log scale – the scaling exponent was found 0.98. Real experiments showed the same dependence employing ATRP polymerization [62]. Dispersity is definitely low (near

1.05) and increases significantly at the end of the polymerization process. The dispersity almost does not depend on the number of macromolecules and is comparable with that for star-branched polymers (1.07) [15]. Fig. 4 (right) shows the number-averaged mass, the weight-averaged mass and the dispersity for hyperbranched polymers. The changes of  $M_w$  and  $P_w$  are similar to those for dendrimers, as discussed above, and the scaling exponent was determined as 1. The changes of dispersity are considerably higher when compared to those of dendrimers. This parameter was found to be higher than for dendrimers (mainly between 1.2 and 1.3).

In order to obtain insight into details of dispersity values in both discussed cases, total mass distributions must be examined. Fig. 5 presents the distributions of polymer segments (the mass distribution) at the end of the polymerization process for both macromolecular architectures under consideration. One can see that the width of the mass distributions for dendrimers and hyperbranched polymers is comparable, in spite of small differences in dispersity (see Fig. 4). The width of the distribution increases with the number of macromolecules.

The differences between the polymer architectures studied can be seen from the visualization shown in Fig. 6. The increase of the number of cores (macromolecules) does not change the shape of the macromolecule significantly. Hyperbranched polymers have the shape similar to that of dendrimers although they are less compact. The distribution of branching points is uniform in all cases. The distribution of the end groups is important as they usually are made functional.

#### IV. Conclusions

The simulations of an idealized model of dendrimers and hyperbranched polymers were carried out by means of the Monte Carlo method employing the Dynamic Lattice Liquid model. The main focus of this work was the kinetics of the bulk polymerization process of macromolecular architectures. The model system contained well-defined cores and chain growth was carried out by the attachment of multifunctional monomers. The polymerization was carried out in bulk to the exhaustion of monomers with no solvent molecules present.

It was shown that the process of synthesis of both dendrimers and hyperbranched polymers using well-defined cores led to structures with well-defined properties. It was shown that for both macromolecular architectures and for all discussed cases, i.e. the number of cores (macromolecules), the dispersity was found to remain very low during the entire polymerization process although it was higher for hyperbranched polymers. Therefore, this parameter was considerably lower than for systems where cores were formed from initiator and cross-linker molecules simultaneously with the polymerization process. The mass of dendrimers and hyperbranched polymers was found to be comparable at the end of the synthesis. The kinetics of the polymerization was compared for both architectures, showing a faster polymerization of dendrimers because of a higher (and growing) number of points where monomers could be attached.

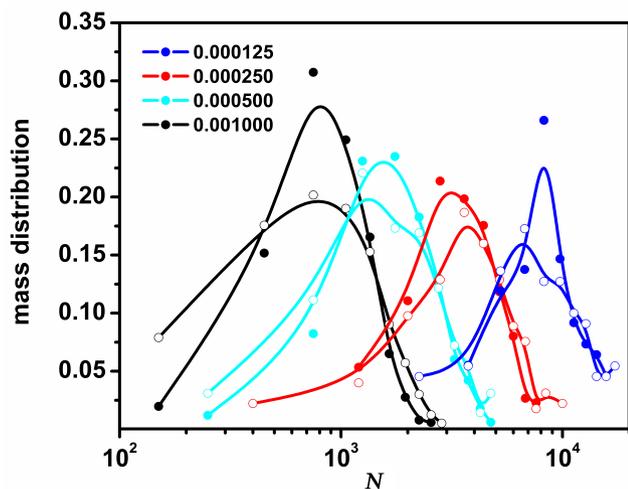


Fig. 5. The mass distribution for dendrimers (solid symbols) and hyperbranched polymers (open symbols). The color indicates the concentration of cores

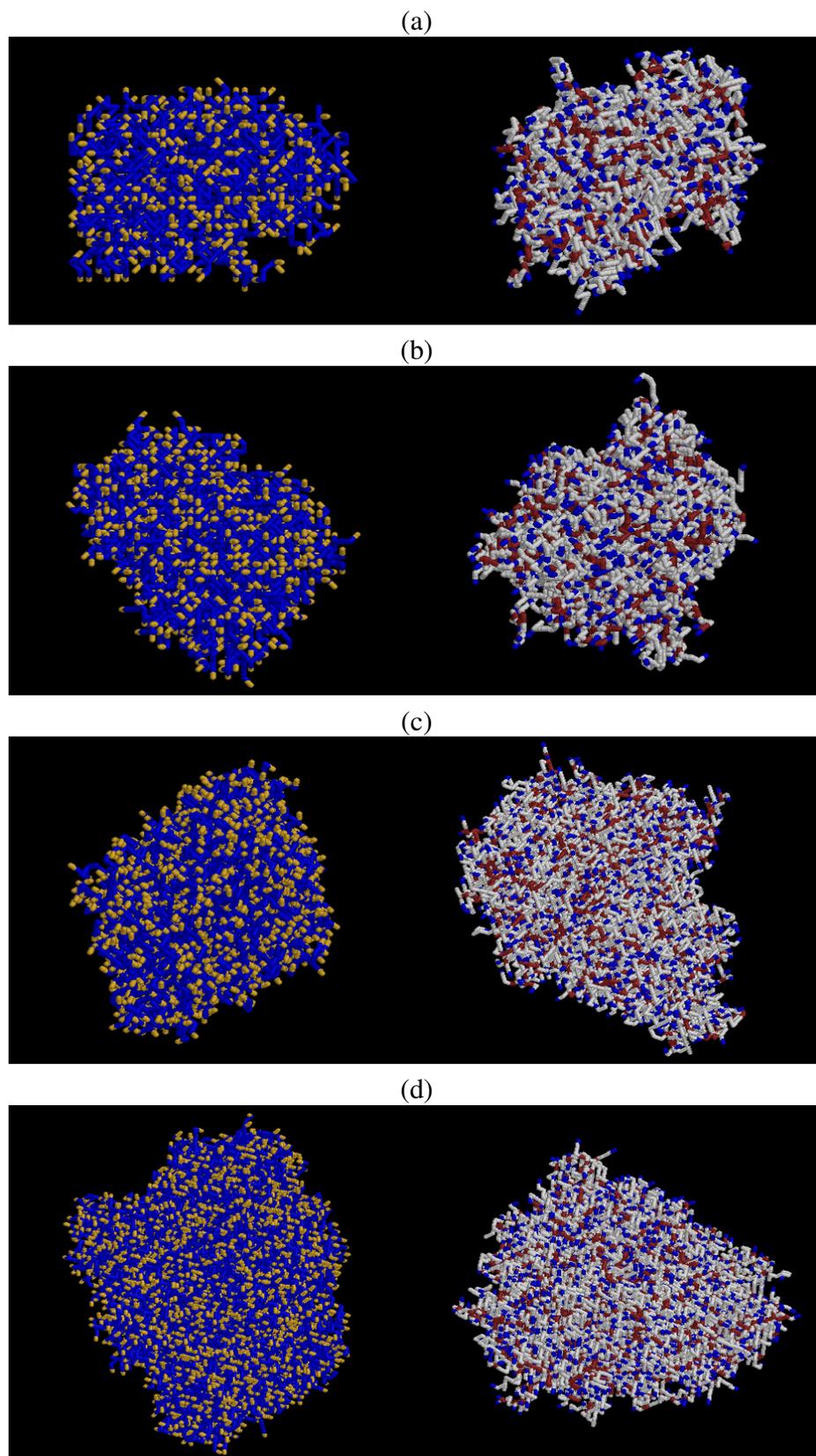


Fig. 6. The snapshots of dendrimers (left) and hyperbranched polymers (right). The case of cores concentration 0.00125 (a), 0.0025 (b), 0.005 (c), and 0.010 (d) is presented. For dendrimers polymer segments are marked in blue and end groups are marked in yellow. For hyperbranched polymers chain segments are marked in white, branching points are marked in red and end groups are marked in blue

## References

- [1] D.A. Tomalia, J.M.J. Frechet, *Discovery of dendrimers and dendritic polymers: A brief historical perspective*, J. Polym. Sci. Part A Polym. Chem. **40**, 2719–2728 (2002).
- [2] D. Astruc, E. Boisselier, C. Ornelas, *Dendrimers designed for functions: From physical, photophysical, and supramolecular properties to applications in sensing, catalysis, molecular electronics, photonics, and nanomedicine*, Chem. Rev. **110**, 1857–1959 (2010).
- [3] C. Gao, D. Yan, *Hyperbranched polymers: from synthesis to applications*, Progress in Polymer Science **29**, 183–275 (2004).
- [4] S.E. Seo, C.J. Hawker, *The beauty of branching in polymer science*, Macromolecules **53**, 3257–3261 (2020).
- [5] D.A. Tomalia, *Birth of a new macromolecular architecture: Dendrimers as quantized building blocks for nanoscale synthetic polymer chemistry*, Prog. Polym. Sci. **30**, 294–324 (2005).
- [6] D.A. Tomalia, *Dendrons/Dendrimers: Quantized, nano-element like building blocks for soft-soft and soft-hard nanocompound synthesis*, Soft Matter **6**, 456–474 (2009).
- [7] D.A. Tomalia, J.B. Christensen, U. Boas, *Dendrimers, Dendrons and Dendritic Polymers: Discovery, Applications, and the Future*, Cambridge University Press: Cambridge, UK (2012).
- [8] C.J. Hawker, J.M.J. Frechet, *Preparation of polymers with controlled molecular architecture: A new convergent approach to dendritic macromolecules*, J. Am. Chem. Soc. **112**, 7638–7647 (1990).
- [9] A.K. Patri, I.J. Majoros, J.R. Baker, *Dendritic polymer macromolecular carriers for drug delivery*, Curr. Opin. Chem. Biol. **6**, 466–471 (2002).
- [10] R. Hourani, A. Kakkar, *Advances in the elegance of chemistry in designing dendrimers*, Macromol. Rapid Commun. **31**, 947–974 (2010).
- [11] K. Inoue, *Functional dendrimers, hyperbranched and stars polymers*, Prog. Polym. Sci. **25**, 453–471 (2000).
- [12] P. Kesharwani, K. Jain, N.K. Jain, *Dendrimer as nanocarrier for drug delivery*, Prog. Polym. Sci. **39**, 268–307 (2014).
- [13] S. Mignani, S. El Kazzouli, M. Bousmina, J.P. Majoral, *Dendrimer space concept for innovative nanomedicine: A futuristic vision for medicinal chemistry*, Prog. Polym. Sci., **38**, 993–1008 (2013).
- [14] P.M. Maiti, T. Çağm, G. Wang, W.A. Goddard, *Structure of PAMAM dendrimers: Generations 1 through 11*, Macromolecules **37**, 6236–6254 (2004).
- [15] P. Polanowski, K. Hatagan, A. Sikorski, *Star Polymers vs. Dendrimers – Studies on the synthesis based on computer simulations*, Polymers **14**, 2522 (2022).
- [16] G.A. Pilkington, J.S. Pedersen, W.H. Briscoe, *Dendrimer nanofluids in the concentrated regime: From polymer melts to soft spheres*, Langmuir **31**, 3333–3342 (2015).
- [17] J.M.J. Frechet, *Functional polymers and dendrimers: Reactivity, molecular architecture, and interfacial energy*, Science **263**, 1710–1715 (1994).
- [18] T.H. Mourey, S.R. Turner, M. Rubinstein, J.M.J. Frechet, C.J. Hawker, K.L. Wooley, *Unique behavior of dendritic macromolecules: Intrinsic viscosity of polyether Dendrimers*, Macromolecules **25**, 2401–2406 (1992).
- [19] A.W. Bosman, H.M. Janssen, E.W. Meijer, *About dendrimers: Structure, physical properties, and applications*, Chem. Rev. **99**, 1665–1688 (1999).
- [20] R. La Ferla, *Conformations and dynamics of dendrimers and cascade macromolecules*, J. Chem. Phys. **106**, 688–700 (1997).
- [21] Y.J. Sheng, S.Y. Jiang, H.K. Tsao, *Radial size of a starburst dendrimer in solvents of varying quality*, Macromolecules **35**, 7865–7868 (2002).
- [22] C.N. Likos, M. Ballauff, *Equilibrium structure of dendrimer: Results and open questions*, Top. Curr. Chem. **245**, 239–252 (2005).
- [23] M. Ballauff, C.N. Likos, *Dendrimers in solution: Insight from theory and simulation*, Angew. Chem. Int. Ed. **43**, 2998–3020 (2004).
- [24] G. Giupponi, D.M.A. Buzza, *Monte Carlo simulation of dendrimers in variable solvent quality*, J. Chem. Phys. **120**, 10290–10298 (2004).
- [25] J.S. Klos, J.U. Sommer, *Properties of dendrimers with flexible spacer-chains: A Monte Carlo study*, Macromolecules **42**, 4878–4886 (2009).
- [26] E. Wawrzyńska, S. Eisenhaber, P. Parzuchowski, A. Sikorski, G. Zifferer, *Simulation of hyperbranched polymers. 1. Properties of regular three generation dendrimers*, Macromol. Theory Simul. **23**, 288–299 (2014).
- [27] E. Wawrzyńska, A. Sikorski, G. Zifferer, *Monte Carlo simulation studies of regular and irregular dendritic polymers*, Macromol. Theory Simul. **24**, 477–489 (2015).
- [28] W.D. Tian, Y.Q. Ma, *Coarse-grained molecular simulation of interacting dendrimers*, Soft Matter **7**, 500–505 (2011).
- [29] S. Kanchi, S. Suresh, U.D. Priyakumar, K.G. Ayappa, P.K. Maiti, *Molecular Dynamics study of the structure, flexibility, and hydrophilicity of PETIM dendrimers: A comparison with PAMAM dendrimers*, J. Phys. Chem. B **119**, 12990–13001 (2015).
- [30] K. Karatasos, D.B. Adolf, G.R. Davies, *Statics and dynamics of model dendrimers as studied by Molecular Dynamics simulations*, J. Chem. Phys. **115**, 5310–5318 (2001).
- [31] A.O. Kurbatov, N.K. Balabaev, M.A. Mazo, E.Y. Kramarenko, *Molecular Dynamics simulations of single siloxane dendrimers: Molecular structure and intramolecular mobility of terminal groups*, J. Chem. Phys. **148**, 014902 (2018).
- [32] D.A. Markelov, A.N. Shishkin, V.V. Matveev, A.V. Penkova, E. Lähderanta, V.I. Chizhik, *Orientalional mobility in dendrimer melts: Molecular Dynamics simulations*, Macromolecules **49**, 9247–9257 (2018).
- [33] F. Khabaz, R. Khare, *Effect of chain architecture on the size, shape, and intrinsic viscosity of chains in polymer solutions: A molecular simulation study*, J. Chem. Phys. **141**, 214904 (2014).
- [34] C. Yu, L. Ma, K. Li, S. Li, Y. Liu, Y. Zhou, D. Yan, *Molecular dynamics simulation studies of hyperbranched polyglycerols and their encapsulation behaviors of small drug molecules*, Phys. Chem. Chem. Phys. **32**, 22446–22457 (2016).
- [35] M.L. Mansfield, L.I. Klushin, *Monte Carlo studies of dendrimer macromolecules*, Macromolecules **26**, 4262–4268 (1993).
- [36] E.G. Timoshenko, Y.A. Kuznetsov, R. Connolly, *Conformations of dendrimers in dilute solution*, J. Chem. Phys. **117**, 9050–9062 (2002).
- [37] C.R. Yates, W. Hayes, *Synthesis and applications of hyperbranched polymers*, Eur. Polym. J. **40**, 1257–1281 (2000).
- [38] M. Seiler, *Hyperbranched polymers: Phase behavior and new applications in the field of chemical engineering*, Fluid Phase Equil. **241**, 155–174 (2006).
- [39] B.I. Voit, *Hyperbranched polymers: a chance and a challenge*, C. R. Chimie **4**, 821–832 (2003).

- [40] I.-Y. Jeon, H.-J. Noh, J.-B. Baek, *Hyperbranched macromolecules: From synthesis to applications*, *Molecules* **23**, 657 (2018).
- [41] T. Higashihara, Y. Segawa, W. Sinananwanich, M. Ueda, *Synthesis of hyperbranched polymers with controlled degree of branching*, *Polym. J.* **44**, 14–29 (2012).
- [42] B.I. Voit, A. Lederer, *Hyperbranched and Highly Branched Polymer Architectures-Synthetic Strategies and Major Characterization Aspects*, *Chem. Rev.* **109**, 5924–5973 (2009).
- [43] A. Kumar, G.J. Rai, P. Biswas, *Conformation and intramolecular relaxation dynamics of semiflexible randomly hyperbranched polymers*, *J. Chem. Phys.* **138**, 104902 (2013).
- [44] L. Li, Y. Lu, L. An, C. Wu, *Experimental and theoretical studies of scaling of sizes and intrinsic viscosity of hyperbranched chains in good solvents*, *J. Chem. Phys.* **138**, 114908 (2013).
- [45] A. Jurjuu, R. Dockhorn, O. Mironova, J.-U. Sommer, *Two universality classes for random hyperbranched polymers*, *Soft Matter* **10**, 4935–4946 (2014).
- [46] D. Konkolewicz, R.G. Gilbert, A. Gray-Weale, *Randomly hyperbranched polymers*, *Phys. Rev. Lett.* **98**, 238301 (2007).
- [47] D. Konkolewicz, O. Thorn-Seshold, A. Gray-Weale, *Models for randomly hyperbranched polymers: Theory and simulation*, *J. Chem. Phys.* **129**, 054901 (2008).
- [48] D. Konkolewicz, A. Gray-Weale, S. Perrier, *Describing the structure of a randomly hyperbranched polymer*, *Macromol. Theory Simul.* **19**, 219–227 (2010).
- [49] D.M.A. Buzza, *Power law polydispersity and fractal structure of hyperbranched polymers*, *Eur. Phys. J. E* **13**, 79–86 (2004).
- [50] E.L. Richards, D. Martin, A. Buzza, G.R. Davies, *Monte Carlo simulation of random branching in hyperbranched polymers*, *Macromolecules* **40**, 2210–2218 (2007).
- [51] P.F. Sheridan, D.B. Adolf, A.V. Lyulin, I. Neelov, G.R. Davis, *Computer simulations of hyperbranched polymers: The influence of the Wiener index on the intrinsic viscosity and radius of gyration*, *J. Chem. Phys.* **117**, 7802–7812 (2002).
- [52] S.V. Lyulin, K. Karatasos, A.A. Darinskii, S. Larin, A. Lyulin, *Structural effects in overcharging in complexes of hyperbranched polymers with linear polyelectrolytes*, *Soft Matter* **4**, 453–457 (2008).
- [53] S.V. Lyulin, E.V. Reshetnikov, A.A. Darinskii, A.V. Lyulin, *Structural behavior of hyperbranched polymers in solvents of various qualities: Brownian Dynamics simulation*, *Polym. Sci. A* **53**, 827–845 (2011).
- [54] T.C. Le, B.D. Todd, P.J. Davis, A. Uhlherr, *The effect of interbranch spacing on structural and rheological properties of hyperbranched polymer melts*, *J. Chem. Phys.* **131**, 164901 (2009).
- [55] I.M. Neelov, D.B. Adolf, *Brownian Dynamics simulation of hyperbranched polymers under elongational flow*, *J. Phys. Chem. B* **108**, 7627–7636 (2004).
- [56] A.V. Lyulin, D.B. Adolf, G.R. Davies, *Computer simulations of hyperbranched polymers in shear flows*, *Macromolecules* **34**, 3783–3789 (2001).
- [57] T. Pakula, *Simulation on the completely occupied lattices*, [In:] *Simulation Methods for Polymers*, Eds. M. Kotelyanskii, D.N. Theodorou, Marcel Dekker, New York, NY, USA, Basel, Switzerland (2004).
- [58] M. von Smoluchowski, *Versuch einer Mathematischen Theorie der Koagulations Kinetik Kolloider Lousungen*, *Phys. Z. Chem.* **92**, 129–168 (1917).
- [59] R. Jullien, R. Botet, *Aggregation and Fractal Aggregate*, World Scientific, Singapore (1987).
- [60] M. Tirado-Miranda, A. Schmitt, J. Callejas-Fernández, A. Frenández-Barbero, *Dynamic scaling and fractal structure of small colloidal clusters*, *Colloid. Surface A* **162**, 67–73 (2000).
- [61] P. Van Dongen, M.H. Ernst, *Dynamic scaling in the kinetics of clustering*, *Phys. Rev. Lett.* **54**, 1396–1399 (1985).
- [62] M. Rubinstein, R.H. Colby, *Polymer Physics*, Oxford University Press, Oxford, UK (2003).



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