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Experimental and theoretical studies of scaling of sizes and intrinsic viscosity of hyperbranched chains in good solvents

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Using a set of hyperbranched polystyrenes with different overall molar masses but a uniform subchain length or a similar overall molar mass but different subchain lengths, we studied their sizes and hydrodynamic behaviors in toluene (a good solvent) at T = 25 °C by combining experimental (laser light scattering (LLS) and viscometry) and theoretical methods based on a partially permeable sphere model. Our results show that both the average radii of gyration ($\langle R_g \rangle$) and hydrodynamic radius ($\langle R_h \rangle$) are scaled to the weight-average molar mass (M_w) as $\langle R_g \rangle \sim \langle R_h \rangle \sim M_w{}^{\gamma} M_{w,s}{}^{\varphi}$, with $\gamma = 0.47 \pm 0.01$ and $\varphi = 0.10 \pm 0.01$; and their intrinsic viscosity ($[\eta]$) quantitatively follow the Mark-Houwink-Sakurada (MHS) equation as $[\eta] = K_\eta M_w{}^{\nu} M_{w,s}{}^{\mu}$ with $K_\eta = 2.26 \times 10^{-5}$, $\nu = 0.39 \pm 0.01$, and $\mu = 0.31 \pm 0.01$, revealing that these model chains with long subchains are indeed fractal objects. Further, our theoretical and experimental results broadly agree with each other besides a slight deviation from the MHS equation for short subchains, similar to dendrimers, presumably due to the multi-body hydrodynamic interaction. Moreover, we also find that the average viscometric radius ($\langle R_\eta \rangle$) determined from intrinsic viscosity is slightly smaller than $\langle R_h \rangle$ measured in dynamic LLS and their ratio ($\langle R_\eta \rangle / \langle R_h \rangle$) roughly remains 0.95 ± 0.05, reflecting that linear polymer chains are more draining with a smaller $\langle R_h \rangle$ than their hyperbranched counterparts for a given intrinsic viscosity. Our current study of the "defect-free" hyperbranched polymer chains offers a standard model for further theoretical investigation of hydrodynamic behaviors of hyperbranched polymers and other complicated architectures, in a remaining unexploited research field of polymer science.
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I. INTRODUCTION

In comparison with regular hyperbranched molecules made of short segments between two neighboring branching points, hyperbranched polymers with long linear subchains often lead to materials with some special mechanical properties, such as a higher level of toughness and stronger impact strength. Therefore, much experimental and theoretical effort has been spent to prepare hyperbranched polymers with different linear subchains to adjust their mechanical properties as well as to investigate their structure-property relationship.[1–4]

Whenever addressing the structure-property relationships of a polymer, its rheological behavior must be one of the first considerations, more specifically, its intrinsic viscosity $[\eta]$, also called the Staudinger index, because it is often used in industry as a quality and process control and in research as a structural characterizing parameter. It has been known that[5]

$$[\eta] = \Phi \left(\frac{R_g^3}{M} \right), \tag{1}$$

where Φ is the Flory hydrodynamic constant, R_g is the root-mean-square radius of gyration, and M is the molar mass of polymer. $[\eta]$ is inversely proportional to the chain density in a given solvent. Φ is roughly related to the chain draining in solution, namely, a higher degree of draining leads to a smaller Φ. Therefore, a linear chain should have a smaller Φ than its hyperbranched counterpart. However, it remains a challenge to properly and quantitatively describe the draining nature of a hyperbranched chain in good solvents. Generally, we know that R_g is scaled to M so that Eq. (1) is written as in the Mark-Houwink-Sakurada (MHS) equation[5]

$$[\eta] = K M^{\alpha}, \tag{2}$$

where K and α are two constants for a given type of polymer solutions. Their values depend on the solvent quality and chain topology. Specifically, for linear chains, $\alpha = 0.7 \sim 1.0$ in good solvents; and $\alpha = 0.5$ under the theta condition.[6–8]

However, Eqs. (1) and (2) completely fail to predict how $[\eta]$ depends on M for dendrimers,[9] partially because of an improper assumption that the hydrodynamic radius (R_h) is proportional to the radius of gyration (R_g); namely, dentritic polymer chains are assumed to be fractal objects. In contrast, a previous theoretical study revealed that, for dendritic chains, such a proportionality between R_h and R_g is invalid and there exists a maximum in the plot of $[\eta]$ versus M, i.e., $[\eta]$ first increases with the number of generation (G) and then decreases after G reaches a certain value.[10] Such an anomalous

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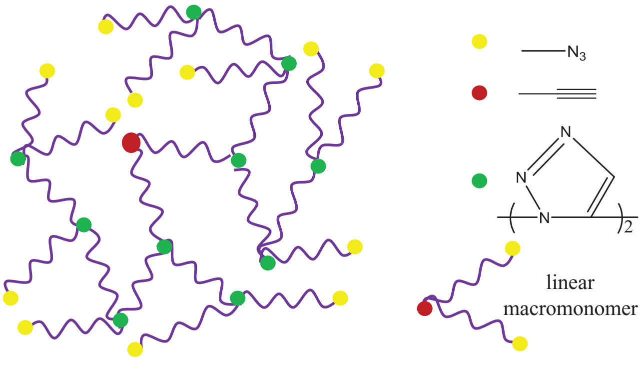
behavior has not been described by the Fox-Flory formula[11] and the existing Zimm or Rouse arguments for a long time. Until recently, An *et al.*[12] developed a *two-zone model* for dendrimers after considering the radial segmental density profile and quantitatively explained those existing experimental results. Further, by combining Debye's theory for free draining polymer chain with Einstein's theory for hard spheres, they presented a general theory for the intrinsic viscosity of polymers with any morphology on the basis of a partially permeable sphere model.[13] Such predictions agree well with the experimental results in the literature, ranging from linear to star and to dendritic chains.

Note that randomly hyperbranched chains are even more complicated than dendrimers. It has not been completely clear (1) whether hyperbranched chains with different subchain lengths follow Eq. (2), i.e., whether they are fractal objects;[14,15] (2) whether those previously reported M-dependent intrinsic viscosities from an on-line combination of the size exclusion chromatograph (SEC) with viscosity and multi-angle laser light scattering (MALLS) detectors actually captured its structure-property relationship;[14,16] and (3) how the subchain length and branching degree of hyperbranched chains affect their intrinsic viscosity ($[\eta]$). To the best of our knowledge, they have not been theoretically or experimentally addressed so far.

In order to answer these questions, one has to first prepare a set of hyperbranched polymer chains with a controllable and adjustable structure, such as a similar overall molar mass but different subchain lengths and an identical subchain length but different overall molar masses, which is rather difficult in polymer synthesis, if not impossible. This explains why literature search shows only few past structure-property studies of non-ideal hyperbranched polymers even though the structure-property relationships are vitally important in their developments and applications. Only very recently, using the "click" chemistry and a specially designed seesaw-type linear macromonomer B∼∼A∼∼B, where A and B denote alkyne and azide groups, respectively; and ∼∼, a polystyrene (PSt) chain, we were able to prepare hyperbranched polystyrenes with long and uniform subchains,[17,18] as schematically shown in Scheme 1.



SCHEME 1. Schematic of structure of a hyperbranched polymer with long and uniform subchains prepared from seesaw-type macromonomers via click chemistry.

Each resultant hyperbranched polymer can be further fractionated into a set of very narrowly distributed chains with different overall molar masses but an identical subchain length that is pre-designed from the macromonomer preparation. It should be stated and noted that this approach is fundamentally different from previously used "A∼∼B$_2$" and "A∼∼A + B$_3$" methods that inevitably result in a broad distribution in subchain lengths due to some unreacted B-groups;[4,7] namely, each unreacted B-group leads to a subchain that is one "∼∼" longer. Such a broad subchain-length distribution in a given hyperbranched polymer makes the correlation between polymer structure and properties difficult and less accurate or even meaningless, depending on how sensitive a property is related to the subchain length.

It should be pointed out that originally we planned to include part of the scaling laws as part of our previous study of the translocation of these hyperbranched chains through a small cylindrical pore (20 nm).[19] However, after completing the intrinsic viscoelastic measurements and the novel theoretical calculation, we found that it is inconsistent and distractive to put those studies of the scaling laws and the ultrafiltration together. This is why we separate them into two papers. In the current study, we have seriously answered those remaining questions and found that the MHS equation is also valid for hyperbranched chains with long subchains; while the deviation from the MHS equation for shorter subchains is presumably attributed to the strong excluded volume effect as well as the multi-body hydrodynamic interaction.

II. EXPERIMENTAL

A. Materials

Scheme 1 schematically shows the structure of our hyperbranched chains with long and uniform subchains prepared from seesaw-type macromonomers via click chemistry. The synthetic detail was described before.[17,18] Using the precipitation fractionation, we obtained four sets of hyperbranched chains with different subchain lengths and overall molar masses. The details of the fractionation was also described before.[17,18] The overall weight-average molar masses and subchain lengths of these hyperbranched polystyrene chains are listed in Table I. Toluene from Acros company (99.8+%, for analysis) was used as solvent in all the experiments described hereafter without further purification.

B. Laser light scattering

A commercial LLS spectrometer (ALV/DLS/SLS-5022F) equipped with a multi-τ digital time correlator (ALV5000) and a cylindrical 22 mW UNIPHASE He-Ne laser (λ_0 = 632.8 nm) as the light source was used. In static LLS,[20,21] the angular dependence of the absolute excess time-average scattering intensity, known as the Rayleigh ratio $R_{VV}(q)$, can lead to the weight-average molar mass (M_w), the root-mean-square gyration radius $\langle R_g^2\rangle_z^{1/2}$ (or simply written as $\langle R_g\rangle$) and the second virial coefficient A_2 by using

$$\frac{KC}{R_{VV}(q)} \cong \frac{1}{M_w}\left(1+\frac{1}{3}\langle R_g^2\rangle_Z q^2\right)+2A_2C, \qquad (3)$$

TABLE I. Molecular parameters of hyperbranched polystyrenes in toluene.

Sample	M_w (g/mol)	μ_2 ($\langle D\rangle^2$)	M_w/M_n	[η] (l/g)	k_h
PSt-73k	1.7×10^7	0.06	1.24	3.6×10^{-1}	0.15
	7.2×10^6	0.10	1.40	2.9×10^{-1}	0.23
	1.6×10^6	0.04	1.16	1.7×10^{-1}	0.17
	8.4×10^5	0.05	1.20	1.2×10^{-1}	0.69
	6.4×10^5	0.03	1.12	1.1×10^{-1}	0.50
	3.9×10^5	0.04	1.16	9.2×10^{-2}	0.43
PSt-21k	3.0×10^7	0.09	1.36	3.0×10^{-1}	0.14
	1.1×10^7	0.06	1.24	2.2×10^{-1}	0.23
	4.5×10^6	0.05	1.20	1.7×10^{-1}	0.62
	2.7×10^6	0.06	1.24	1.3×10^{-1}	0.97
	1.6×10^6	0.03	1.12	1.0×10^{-1}	0.72
	8.7×10^5	0.04	1.16	8.3×10^{-2}	0.60
	6.2×10^5	0.03	1.12	7.1×10^{-2}	0.57
	4.8×10^5	0.03	1.12	5.9×10^{-2}	0.64
	2.6×10^5	0.04	1.16	5.4×10^{-2}	0.54
PSt-8.8k	5.7×10^6	0.02	1.08	1.4×10^{-1}	0.34
	2.8×10^6	0.04	1.16	1.1×10^{-1}	0.35
	1.4×10^6	0.04	1.16	7.9×10^{-2}	0.67
	7.2×10^5	0.03	1.12	5.8×10^{-2}	0.74
	3.0×10^5	0.04	1.16	4.0×10^{-2}	0.89
PSt-3.3k	4.8×10	0.08	1.32	4.3×10^{-2}	…
	1.6×10^5	0.03	1.12	2.9×10^{-2}	…

where $K = 4\pi^2(\mathrm{d}n/\mathrm{d}C)^2/(N_A\lambda_0{}^4)$ and $q = (4\pi/\lambda_0)\sin(\theta/2)$ with C, dn/dC, N_A, and λ_0 being concentration of the polymer solution, the specific refractive index increment, the Avogadro's number, and the wavelength of light in a vacuum, respectively. The extrapolation of $R_{VV}(q)$ to $q \rightarrow 0$ and $C \rightarrow 0$ leads to M_w. The plot of $[KC/R_{VV}(q)]_{C\rightarrow 0}$ vs q^2 and $[KC/R_{VV}(q)]_{q\rightarrow 0}$ vs C leads to $\langle R_g^2\rangle_z$ and A_2, respectively. In a very dilute solution, the term of $2A_2C$ is ignored. For our branched and ultra-large hyperbranched chains, $q\langle R_g\rangle > 1$, so that the Berry plot was used.

In dynamic LLS,[22] the Laplace inversion of each measured intensity-intensity time correlation function $G^{(2)}(q,t)$ in the self-beating mode can lead to a line-width distribution $G(\Gamma)$, where q is the scattering vector. For pure diffusive relaxation, Γ is related to the translational diffusion coefficient D in dilute solutions by $(\Gamma/q^2)_{q\rightarrow 0,C\rightarrow 0} \rightarrow D$, so that $G(\Gamma)$ can be converted into a transitional diffusion coefficient distribution $G(D)$ or further to a hydrodynamic radius distribution $f(R_h)$ via the Stokes–Einstein equation, $R_h = (k_BT/6\pi\eta_0)/D$, where k_B, T, and η_0 are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. In the current study, $G^{(2)}(q,t)$s were analyzed by both the Cumulants and CONTIN analysis.

C. Viscosity measurement

Flow times of polymer solutions were measured using an Ubbelohde capillary viscometer. Relative viscosity (η_r) was obtained from the ratio of the flow times of a solution and the solvent. Before each measurement, a solution in the viscometer was sealed and allowed to equilibrate with a thermostatted water tank for at least 20 min. The temperature fluctuation of the water tank was smaller than 0.1 °C. All samples used for flow time measurements were clarified by filtration through Millipore 0.45 μm polytetrafluoroethylene filters. Each polymer solution was measured for three times so that the relative error was less than 0.2%.

III. RESULTS AND DISCUSSION

In this study, the copper(I)-catalyzed Huisgen [3+2] dipolar cycloaddition "click chemistry" was adopted as a key ingredient to construct our hyperbranched structure due to its merit of quantify, functional group tolerance, and high efficiency.[23–27] Therefore, via "click" chemistry and precipitation fractionation method, we have obtained a series of hyperbranched polystyrenes, and the corresponding molecular parameters of these hyperbranched chains used in the current study are summarized in Table I, where the polydispersity index (M_w/M_n) was roughly estimated from the relative line-width ($\mu_2/\langle D\rangle^2$) measured from dynamic LLS by using $M_w/M_n \approx (1 + 4\mu_2/\langle D\rangle^2)$, where $\mu_2 = \int_0^\infty G(D)(D - \langle D\rangle)^2$ dD and D is the diffusion coefficient. To facilitate discussion hereafter, we denote each hyperbranched polystyrene by its macromonomer's weight-average molar mass, e.g., PSt-8.8k shows that it was made of linear polystyrene macromonomer with a molar mass of $M_w = 8.8$ kg/mol.

First, we measured their molar masses dependent average diffusion coefficients ($\langle D\rangle$) by using a combination of static and dynamic laser light scattering. Figure 1 shows that after normalized by the weight-average molar mass ($M_{w,s}$) of the subchain, the double logarithmical plots of $\langle D\rangle$ versus the weight-average molar mass of the entire hyperbranched chains (M_w) for different hyperbranched chains unquestionably collapse into a single line, which clearly indicates that $\langle D\rangle$ is scaled to both M_w and $M_{w,s}$. Moreover, a much smaller absolute value of the exponent of $M_{w,s}$ (0.1) indicate the diffusion behavior of hyperbranched chains is mainly dominated by the overall molar mass (M_w) but not the subchain length ($M_{w,s}$). To our knowledge, such a scaling has not been well established before even though many people have tried in the past.

Further, Figure 2 shows the average size ($\langle R\rangle$) of the hyperbranched polystyrene chains is scaled to the overall degree of polymerization (N_t), where $N_t = M_w/M_o$ with M_o is the

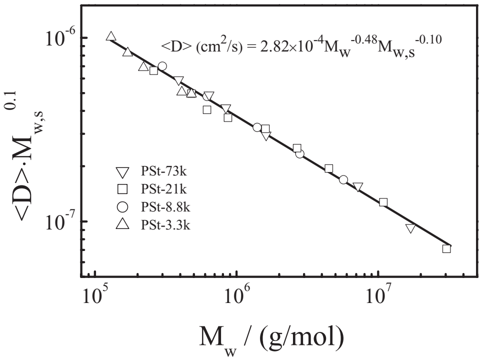


FIG. 1. Weight-average molar mass (M_w) dependence of average translational diffusion coefficient ($\langle D\rangle$) of hyperbranched polystyrenes with different subchain lengths in toluene at T = 25 °C, where $\langle D\rangle$ has a unit of "cm^2/s" and both $M_{w,s}$ and M_w are expressed as "g/mol."

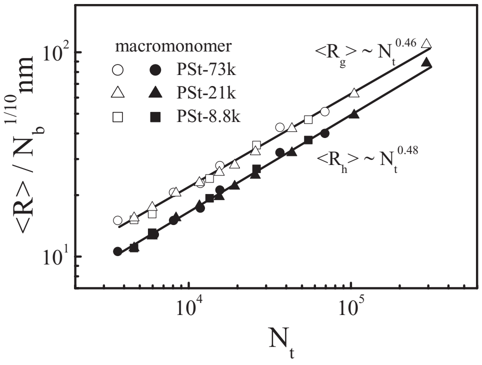


FIG. 2. Overall degrees of polymerization (N_t) dependence of normalized average radius of gyration $\langle R_g \rangle$ and average hydrodynamic radius $\langle R_h \rangle$ of hyperbranched polystyrene chains with different uniform subchain lengths in toluene at T = 25 °C.

molar mass of styrene; $\langle R_h \rangle$ is calculated from $\langle D \rangle$ by using the Stokes–Einstein equation; $\langle R_g \rangle$ is measured using static LLS; and $\langle R \rangle$ is normalized by the polymerization degree of the subchain on the basis of the theoretical prediction;[28–30] namely, $\langle R_g \rangle$ of hyperbranched polymer chains in good solvents is scaled to the polymerization degrees of the overall hyperbranched chain (N_t) and the subchain (N_b) as $\langle R \rangle \sim N_t{}^{\alpha} N_b{}^{\beta}$ with $\alpha = 1/2$ and $\beta = 1/10$. Indeed, the average size of the hyperbranched polystyrenes with different subchain lengths is scaled to the overall polymerization degree but the scaling exponent (α), respectively, for $\langle R_g \rangle$ and $\langle R_h \rangle$, is 0.46 ± 0.01 and 0.48 ± 0.01, smaller than the predicted 1/2. On the other hand, we also attained the scaling exponent β by fixing the overall molar mass of the hyperbranched polystyrenes and plotting $\langle R \rangle$ versus N_b (not shown). We found that β is 0.11 ± 0.01 for $\langle R_g \rangle$ and 0.09 ± 0.01 for $\langle R_h \rangle$, supporting the normalization used. Again, to our knowledge, such scaling laws have not been seriously established before even though much effort has been spent before. These scaling plots indicate that the hyperbranched chains with long subchains are self-similar, which leads us to believe that hyperbranched polymer chains should also obey the MHS equation.

To verify it, we directly measured their concentration dependence of viscosity in toluene at T = 25.0 ± 0.1 °C by a conventional flow viscometer. It should be emphasized that the most used concentrated solution was dilute enough, a region far away from the semi-dilute region, i.e., $C \ll C^*$ (the overlap concentration), to keep the relative viscosity below 1.30. Figure 3 shows typical plots of the concentration dependence of specific viscosity η_{sp}/C of hyperbranched polystyrenes made of one macromonomer, where η_{sp} is defined as $\eta_r - 1$. The intercept and slope of each fitting line, respectively, lead to the intrinsic viscosities ([η]) and the Huggins constant (k_h) of a given hyperbranched polystyrene on the basis of $\eta_{sp}/C = [\eta] + k_h[\eta]^2 C$. The values of [$\eta$] and k_h of all the hyperbranched polystyrenes studied are also summarized in Table I. Note that for some samples we did not have a sufficient quality to make a large number of solutions so that their k_h values were estimated with some uncertainty, which scarcely affects those measured intrinsic viscosity ([η]) because polymer solutions used were sufficiently dilute.

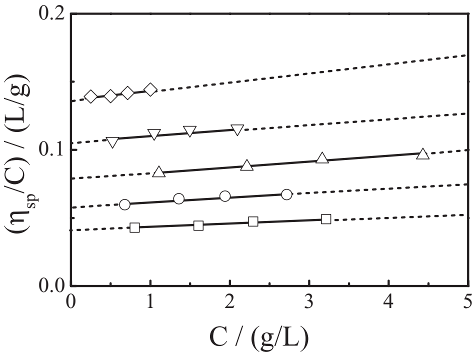


FIG. 3. Typical plots of polymer concentration dependence of reduced specific viscosity (η_{sp}/C) of hyperbranched polystyrenes made of one macromonomer (PSt-8.8k) in toluene at T = 25 °C.

Theoretically, we calculate the intrinsic viscosity of these hyperbranched polystyrene chains using the theory for the intrinsic viscosity of polymers proposed by us recently based on the partially permeable sphere model.[13] By combining Einstein's theory for hard spheres[31] with Debye's theory for free draining polymer chains,[32] our theory, by introducing two phenomenological functions, a drainage function and a drag function, both of which can be determined from the density profile, provides a simple and convenient method that circumvents the explicit treatment of the complex, multi-body hydrodynamic interactions in these systems while capturing their key effects. The parameter choice was detailed before.[13] Figure 4(a) shows our experimental and theoretical results of how [η] depends on both M_w and $M_{w,s}$ for hyperbranched polystyrene chains with different subchain lengths, indicating that hyperbranched chains obey the MHS equation just

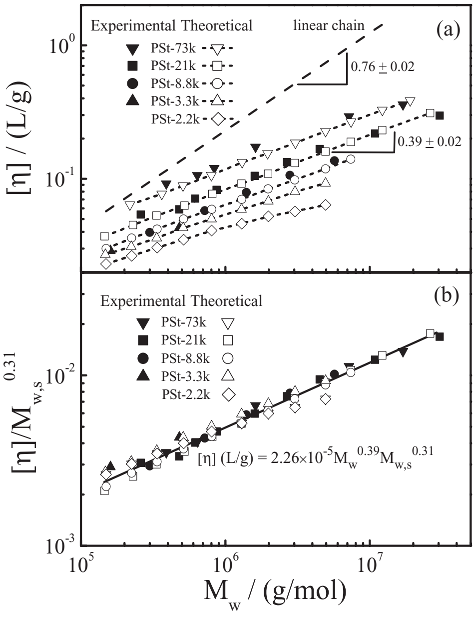


FIG. 4. Weight-average molar mass (M_w) dependence of (a) non-normalized and (b) normalized intrinsic viscosity ([η]) of hyperbranched polystyrenes with different subchain lengths in toluene at T = 25 °C, where the dashed line for linear chains is from the literature.[8] Theoretical results were calculated using our partially permeable sphere model with a density profile accurately calculated from Monte Carlo simulation.

like their linear counterpart, i.e., they are fractal objects. Apparently, the data points spread over a wide range but with a similar slope of 0.39. Also note that a slight deviation from the scaling occurs when $M_{\mathrm{w,s}}$ is less than ∼10^3 g/mol, presumably due to the emergence of a strong effect of the excluded volume.

Furthermore, Figure 4(b) clearly reveals that these scattered data in Figure 4(a) collapse into a single master line when $[\eta]$ is normalized by the corresponding subchain length; namely, $[\eta]$ is scaled to both M_{w} and $M_{\mathrm{w,s}}$ as

$$[\eta] = K_\eta M_{\mathrm{w}}^{\nu} M_{\mathrm{w,s}}^{\mu}, \tag{4}$$

where $\nu = 0.39 \pm 0.01$ and $\mu = 0.31 \pm 0.01$; and $K_\eta = 2.26 \times 10^{-5}$ l/g. Up to now, we have experimentally and theoretically revealed that both Eqs. (1) and (2) are also valid for hyperbranched chains with long and uniform subchains in a good solvent, clearly indicating that these hyperbranched chains are fractal objects; in contrast, a slight deviation from the scalings occurs for hyperbranched chains with a much shorter subchain length, because of the excluded volume effect. It should be emphasized that the fractal behavior of hyperbranched chains have been previously well theoretically discussed via the branching theory[33–35] and further experimentally verified by the scattering experiments finished by Burchard's group;[36–38] however, the subchain lengths in previous studies were extremely short and unchangeable; therefore, their adopted AB_2 monomer is actually different with what we mentioned. It is also interesting to note that the two scaling exponents between $[\eta]$ and both M_{w} and $M_{\mathrm{w,s}}$ are not far away from each other. The literature values of the measured scaling exponent between $[\eta]$ and M_{w} is very widely spread over a range 0.3–0.5 for hyperbranched polymers prepared by conventional methods with a broad distribution of subchain length. With no exception, all of previous experiments used the on-line SEC-viscosity-MALLS to measure both $[\eta]$ and M_{w}.[15,16,39] Unfortunately, it had been repeatedly overlooked that SEC separates polymer chains by their hydrodynamic volumes, not by their molar masses. Namely, for nonlinear polymer chains, each retentive fraction in principle contains polymer chains with a similar hydrodynamic volume but not necessarily with a similar molar mass. Theoretically, Eqs. (1) and (2) require that each fraction contains polymer chains with a similar molar mass, not a similar size. Presumably, it is due to difficulties and limitations in both the sample preparation and experimental methods so that less attention has been paid to this very important point so far.

In contrast, all the hyperbranched polystyrenes used in the current study were fractionated by precipitation, i.e., according to the interaction parameter χM, where M is the overall molar mass of the chain and χ is the Flory-Huggins parameter, a constant, independent on M for a polymer in a given solvent. Therefore, hyperbranched chains in each fraction used here have a similar molar mass. In comparison with our results, some of previous computer simulations[40,41] suggested that the molar mass dependence of intrinsic viscosity of irregular hyperbranched chains deviates from Eq. (2) because the segment density distribution is different from those predicted by de Gennes and Hervet. We will come back to this point later.

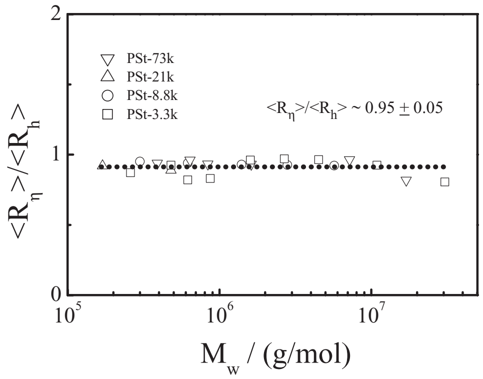


FIG. 5. Weight-average molar mass (M_{w}) dependence of ratio of two hydrodynamics-related radii (average viscometric radius, $\langle R_\eta \rangle$, and average hydrodynamic radius, $\langle R_{\mathrm{h}} \rangle$) of hyperbranched polystyrenes with different subchain lengths in toluene at T = 25 °C.

Previously, we have already used static LLS to reveal that for hyperbranched polystyrene chains with long and uniform subchains,[17] $R_{\mathrm{g}} \sim R_{\mathrm{h}} \sim M_{\mathrm{w}}^{\gamma} M_{\mathrm{w,s}}^{\varphi}$ with $\gamma = 0.47 \pm 0.01$ and $\varphi = 0.10 \pm 0.01$. A combination of Eqs. (1) and (5) leads to

$$[\eta] \sim M_{\mathrm{w}}^{3\gamma - 1} M_{\mathrm{w,s}}^{3\varphi}. \tag{5}$$

A comparison of Eqs. (4) and (5) leads to $\nu = 3\gamma - 1$ and $\mu = 3\varphi$. Inputting our experimentally determined values of γ and φ, we have $\nu = 0.41 \pm 0.01$ and $\mu = 0.30 \pm 0.01$, fairly close to those directly measured values (0.39 ± 0.01 and 0.31 ± 0.01) from the viscosity measurements, which cross-examines and validates our previous LLS data and current viscosity results. It is worth noting that in comparison with LLS, viscosity is more sensitive and much easier to be measured in characterizing the effect of chain topology and conformation, such as the branching degree, because LLS measures the hydrodynamic size, while viscosity detects the hydrodynamic volume that is a cubic of the chain size.

When treating each hyperbranched chain as a suspending hard sphere and taking $\Phi = 2.5$,[42] we can rewrite Eq. (1) as

$$[\eta] = \frac{10\pi}{3} N_{\mathrm{A}} \left(\frac{R_\eta^3}{M_{\mathrm{w}}} \right) \text{ or } R_\eta = \left(\frac{3[\eta] M_{\mathrm{w}}}{10\pi N_{\mathrm{A}}} \right)^{1/3}, \tag{6}$$

where R_η and N_{A} are the average viscometric radius and the Avogadro's number, respectively. Therefore, we can convert each measured intrinsic viscosity $[\eta]$ into a viscometric radius R_η so that we can directly compare two average hydrodynamics-related radii ($\langle R_{\mathrm{h}} \rangle$ and $\langle R_\eta \rangle$), as shown in Figure 5. It reveals that $\langle R_\eta \rangle$ is fairly close to $\langle R_{\mathrm{h}} \rangle$ and their ratio ($\langle R_\eta \rangle / \langle R_{\mathrm{h}} \rangle$) is 0.95 ± 0.05, smaller than ∼1.2 for linear chains in good solvents.[6,43] Such a difference illustrates different structures and solution behaviors of linear and branched chains in good solvents, presumably reflecting that a linear chain is more draining, i.e., its hydrodynamic radius is smaller, than its branch counterpart for a given intrinsic viscosity.

IV. CONCLUSION

The current LLS and viscosity results of a set of hyperbranched chains with different overall molar masses but a uniform subchain length or with a similar overall molar mass but different subchain lengths have revealed that sizes of hyperbranched polystyrenes with long and uniform subchains in a good solvent (toluene, at T = 25 °C) are scaled to the overall weight-average molar masses (M_w) and the subchain molar masses ($M_{w,s}$) as $R_g \sim R_h \sim M_w^{\gamma} M_{w,s}^{\varphi}$ with $\gamma = 0.47 \pm 0.01$ and $\varphi = 0.10 \pm 0.01$; and their intrinsic viscosity *quantitatively* follows the MHS equation, i.e., $[\eta] = K_\eta {M_w}^{\nu} {M_{w,s}}^{\mu}$ with $K_\eta = 2.26 \times 10^{-5}$, $\nu = 0.39 \pm 0.01$, and $\mu = 0.31 \pm 0.01$, indicating that they behave like fractal objects, similar to linear chains, in spite of their different subchain lengths. Our theoretical calculation on the basis of a partially permeable sphere model confirmed these experimental results and the fractal nature of hyperbranched polymers with long and uniform subchains. Our results also reveal a deviation from the MHS equation when the subchain length becomes sufficiently short, presumably due to a stronger effect of the exclude volume and the multi-body hydrodynamic interaction. Moreover, the average viscometric radius $\langle R_\eta \rangle$ determined from intrinsic viscosity is slightly smaller than the average hydrodynamic radius $\langle R_h \rangle$ measured in dynamic LLS with a ratio of $\langle R_\eta \rangle / \langle R_h \rangle = 0.95 \pm 0.05$, smaller than 1.2 for linear chains, reflecting that linear chains are more draining with a smaller $\langle R_h \rangle$ than their hyperbranched counterparts for a given intrinsic viscosity. Our results also point to an overlooked problem; namely, the powerful on-line SEC-viscosity-MALLS method is not suitable to quantitatively study the molar mass dependence of solution behaviors of polymer chains with a nonlinear topology because SEC separates them by their hydrodynamic volumes instead of their molar masses. For serious and quantitative studies, one has no choice but to use better chemistry and a conventional time-consuming precipitation fractionation method. Furthermore, other characterization methods should be used to verify the universality of our findings in the future work. Nevertheless, our current study of the "defect-free" hyperbranched polystyrenes has clarified some of previous questions about thermodynamic and hydrodynamic behaviors of hyperbranched chains in good solvents and also offers a standard model for further theoretical investigation of hydrodynamic behaviors of polymer chains with other more complicated topologies.

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