

Structural Feature and Internal Motion of Hyperbranching Cluster System with Low Polydispersity and Featured Pattern in Dilute Solutions

Si-Qi Huang^{a,b,†}, Mo Zhu^{a,†}, Jin-Xian Yang^a, and Lian-Wei Li^{a*}^a College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen 518060, China^b Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China Electronic Supplementary Information

Abstract This work reports the structural feature and internal motion of one novel hyperbranching cluster system in dilution solution. The cluster system is composed of HB-PS₃₀₀-g-PtBA₄₅ hypergraft copolymer chains with uniform subchain, high molar mass and low polydispersity ($M_w=1.73\times10^6$ g/mol and $\langle M_w/M_n \rangle \approx 1.07$), where HB-PS and PtBA represent hyperbranched polystyrene core and poly(*tert*-butyl polyacrylate) graft, respectively. In the selective solvent of PS blocks (cyclohexane, $T_\theta=34.5$ °C), the aggregation kinetics and structural feature are found to be precisely tunable for assembled clusters by the aggregation temperature (11 °C $<T<17$ °C) and time (0 h $<t<24$ h). An interesting structural evolution kinetics is observed, namely, the fractal dimension (d_f) of clusters is found to first increases and then decreases with t , eventually, it reaches a plateau value of $d_f \approx 3.0$, corresponds to a uniform spherical structure. By using dynamic light scattering (DLS) to monitor the number and strength of relaxation modes in $\Gamma(q)$ with Γ being the decay rate and q being the scattering vector, it is quantitatively revealed that the relaxation, intensity contribution and mode origin of internal motions of clusters are neither similar with previously reported cluster systems with high polydispersity, nor with the classical linear chain systems. In particular, in the broad range of $2.0 < qR_g < 6.0$, we have observed that the reduced first cumulant [$\Gamma^* = \Gamma(q)/(q^3 k_B T/\eta_0)$] does not display an asymptotic behavior. Whereas, a better asymptotic behavior is observed by plotting $\Gamma(q)/q^4$ versus qR_g . For the first time, our observation provides direct evidence supporting that, for hyperbranching cluster system with low polydispersity and high local chain segment density, the hydrodynamic interaction is greatly weakened due to the enhanced hydrodynamic shielding effect.

Keywords Hyperbranching cluster; Structural feature; Internal motion

Citation: Huang, S. Q.; Zhu, M.; Yang, J. X.; Li, L. W. Structural feature and internal motion of hyperbranching cluster system with low polydispersity and featured pattern in dilute solutions. *Chinese J. Polym. Sci.* 2022, 40, 1515–1521.

INTRODUCTION

As one fundamental and important problem, the dynamics of macromolecules in solutions has been extensively studied in the community.^[1–4] Agitated by the thermal energy ($k_B T$), one polymer chain can undergo the Brownian motion in solution, which is called translational motion. Simultaneously, the thermal energy can also induce the motions of individual segments with respect to the center of mass, and such a kind of intramolecular relaxations is called internal motions. Both translational and internal motions are important to dominate the dynamic properties of polymeric materials in practical applications.

Rouse and Zimm (RZ) models are classical theories for de-

scribing the polymer dynamics in normal coordinates, without and with hydrodynamic interactions respectively. Historically, by dynamic light scattering (DLS) technique, a number of classical experiments have been executed to test the theoretical predictions.^[5,6] In related studies, the relaxation time (τ) for the first two order of internal motions, as well as the asymptotic behavior of the reduced first cumulant [$\Gamma^*(q) = \Gamma(q)/(k_B T q^3/\eta_0)$], is the main concern, where k_B is Boltzmann constant, η_0 is the solvent viscosity, Γ is the decay rate and q is the scattering vector. So far, for linear,^[7] comb^[8] and hyperbranched^[9] single chain systems, some qualitative/semi-quantitative agreements have been achieved between experimental and theoretical results.

In contrast, much less attention has been paid to the cluster/assembly systems with much higher segment density and more complex multi-body hydrodynamic interactions. The cluster/assembly systems have been widely studied in various fields such as polymeric catalysts,^[10] photonic materials^[11] and stimuli-responsive materials,^[12] etc. However, due

* Corresponding author, E-mail: lianweili@szu.edu.cn

† These authors contributed equally to this work.

Received July 8, 2022; Accepted September 14, 2022; Published online October 20, 2022

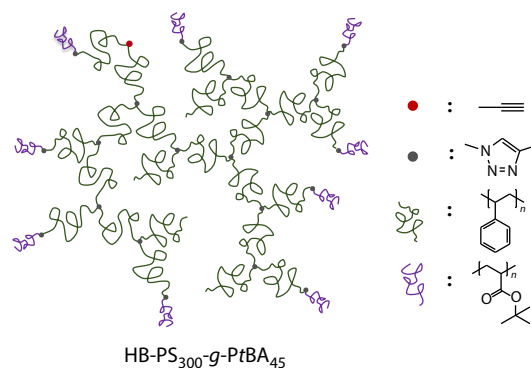
to the difficulty in the construction of qualified cluster systems with well-defined structure feature and low polydispersity, the DLS experimental study cannot provide high-quality data and reliable analysis result, which greatly hinders the deep understanding of the correlation between microscopic dynamic behavior and macroscopic property.

In fact, both the polydispersity in molar mass of unimer precursors (M_w/M_n) and the polydispersity in structure size of assembled clusters (PDI) will significantly influence the observation result in DLS experiments. However, the polydispersity effect has not received enough attention in related studies. There are a few important studies regarding the internal dynamics of clusters worth mentioning. Namely, Wen *et al.* reported the internal dynamics of a polymeric cluster (PDI unreported) in toluene, where the system was composed of poly(2-methoxy-5-(20-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV) diblock chains with high polydispersity ($M_w/M_n \approx 5.0$).^[13] An asymptotic behavior was observed for $f^*(q) = 0.020$ at high q regime. Dahesh *et al.* reported the internal dynamics of Gluten Proteins (GP) cluster system (PDI unreported) composed of high polydispersity GP unimers ($M_w/M_n \approx 3.0$) in aqueous ethanol solution.^[14] Similar to the MEH-PPV cluster system, GP cluster system showed an asymptotic behavior with $f^*(q) = 0.030 \pm 0.004$ at high q regime. Prabhu *et al.* reported the internal dynamics of one polymeric cluster system (PDI unreported) made of high polydispersity P(F-TMC)_m-PEG_n-P(F-TMC)_m triblock chains ($M_w/M_n \approx 1.3$), where F-TMC and PEG represent oligocarbonate-fluorene and poly-(ethylene glycol), respectively. The plateau value of $f^*(q)$ was found to be in the range of 0.035–0.055.^[15] In principle, the conclusions from above studies are not fully convincing due to the polydispersity effect. The high polydispersity in either size or molar mass makes it difficult to interpret the spectral data, this is because the contributions of translational motion from small species are indistinguishable from the contributions of internal motions from large species at high q regime in the scattering spectrum. No doubt, constructing one polymeric cluster system with low polydispersity, well-defined structure and notable equilibrium feature is the prerequisite for DLS study of internal dynamics.

In this work, we report the investigation of internal motions of one model hyperbranching cluster system. As shown in Scheme 1, the cluster system is composed of a number of HB-PS₃₀₀-g-PtBA₄₅ hypergraft copolymer chains with low polydispersity and featured branching pattern, where HB-PS and PtBA represent hyperbranched polystyrene core and poly(*tert*-butyl polyacrylate) graft, respectively. The subchain length between neighboring branching points for HB-PS is strictly controlled to be equal (~5.8 nm), which guarantees a uniform spatial distribution of segments for the clusters. More importantly, in the selective solvent of PS block, the aggregation kinetics and structural feature of HB-PS₃₀₀-g-PtBA₄₅ clusters with low polydispersity in size are found to be precisely tunable by the aggregation temperature (11 °C < T < 17 °C) and aggregation time (0 h < t < 24 h), which greatly facilitates detailed investigation of structural feature and internal dynamics.

EXPERIMENTAL

The synthetic detail, schematic illustration, theoretical



Scheme 1 Schematic illustration of the single chain structure of HB-PS₃₀₀-g-PtBA₄₅.

background, experimental section and complementary data are in the electronic supplementary information (ESI).

RESULTS AND DISCUSSION

Structural Feature of HB-PS₃₀₀-g-PtBA₄₅ Individual Chains in Solutions

The structural parameters of HB-PS₃₀₀-g-PtBA₄₅ individual chains include weight-average molar mass (M_w), apparent radius of gyration ($\langle R_{g,app} \rangle$), apparent hydrodynamic radius ($\langle R_{h,app} \rangle$), polydispersity index ($\langle M_w/M_n \rangle$) and critical overlap concentration (c^*), which can be extracted by static light scattering (SLS) and dynamic light scattering (DLS) measurements. The detail of sample preparation is summarized in ESI (pages S2–S4) and Scheme S1 (in ESI), which can be also found in our recent publish work.^[16] The detail of scattering experiment is also clarified in ESI (pages S6–S10).

For HB-PS₃₀₀-g-PtBA₄₅, the weight fraction (wt%) of PtBA was previously calculated to be 6.0 wt%, and refractive index increment (dn/dc) was calculated to be $dn/dc = 0.179$ mL/g.^[17] Accordingly, M_w and M_w/M_n are determined to be 1.73×10^6 g/mol and 1.07 for HB-PS₃₀₀-g-PtBA₄₅, respectively. Measured at a single concentration at $T = 35$ °C in cyclohexane ($T_\theta = 34.5$ °C for PS) and THF, $\langle R_{g,app} \rangle$ is determined to be 27.3 and 34.6 nm, respectively, indicating the strong contraction of hyperbranched PS core in its selective solvent cyclohexane, in which the excluded volume is close to 0. For c^* , it is estimated to be ~33.7 g/L in cyclohexane, which is ~3400 times higher than the used solution concentration ($c = 0.01$ g/mol), which ensures the individual chains to be extremely far away from each other under experimental conditions.

Temperature-dependent Structural Feature of Hyperbranching Clusters in Cyclohexane

First, we explored the temperature-dependent structural feature of formed hyperbranching clusters. As shown in Fig. 1(a), when T further decreases from 35 °C to 17, 15, 13 and 11 °C, $N_{agg,app}$ increases to 27, 340, 1120 and 1700, respectively, signifying strong interchain aggregation. Note that the SLS measurement was carried out after keeping the solution at the tested temperature for 24 h, this guaranteed that the solution reaches the thermodynamic equilibrium. Clearly, as shown in Fig. 1(b), the Berry plots describe the SLS data well for hyperbranching clusters, and $\langle R_{g,app} \rangle$ increases from 181 nm to 288 nm. As T decreases, the extrapolation to the zero scattering angle leads

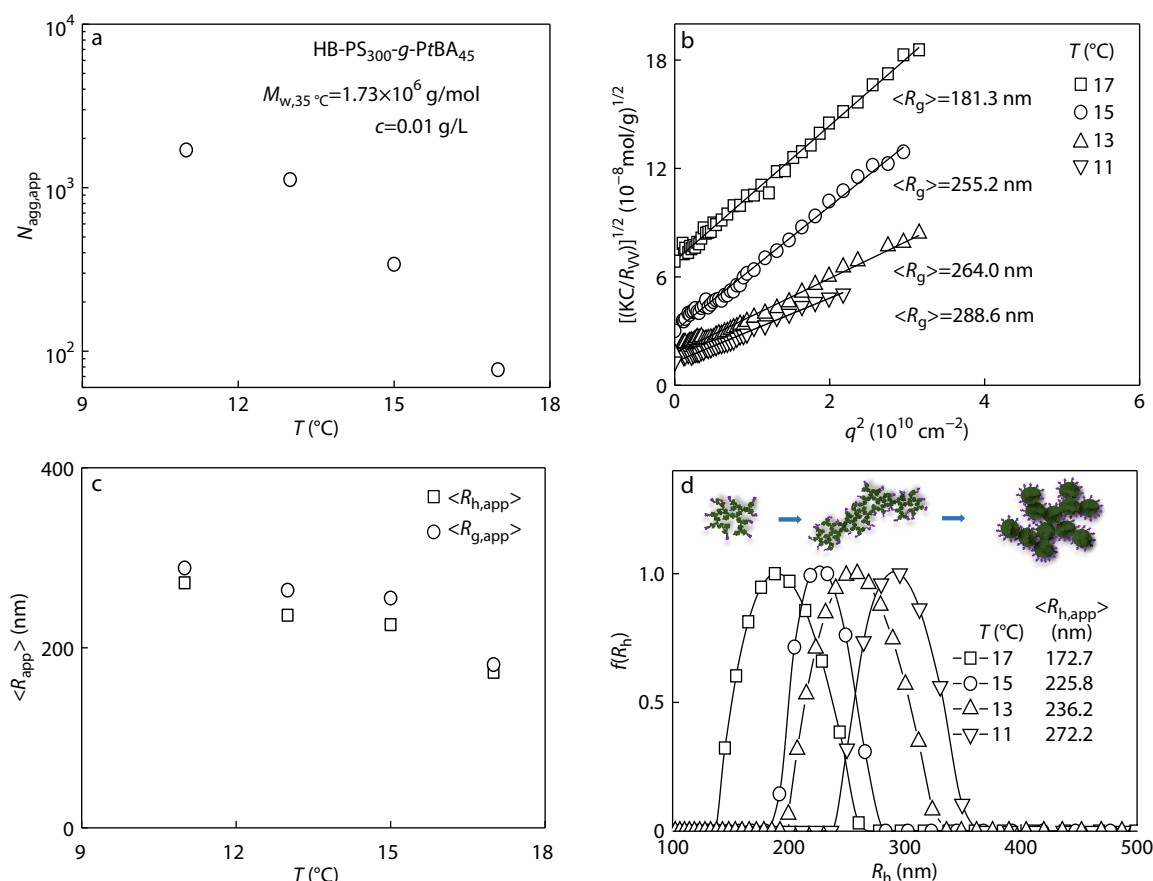


Fig. 1 Temperature dependences of (a) apparent aggregation number ($N_{agg,app}$), (b) Berry plot of SLS data, (c) apparent radius of gyration ($\langle R_{g,app} \rangle$) and hydrodynamic radius ($\langle R_{h,app} \rangle$), and (d) hydrodynamic radius distribution [$f(R_h)$] for HB-PS₃₀₀-g-PtBA₄₅ chains (6 wt%, $M_w=1.73\times 10^6$ g/mol and $\langle R_{g,app} \rangle=34.6$ nm) in cyclohexane at $c=0.01$ g/L, where the measurement was initiated after keeping at a constant temperature for 24 h.

to increased intercepts, quantifying the increase in $N_{agg,app}$. Actually, both $\langle R_{g,app} \rangle$ and $\langle R_{h,app} \rangle$ increase as T decreases (Fig. 1c), agreeing well with the trend of $N_{agg,app}$. Fig. 1(d) further shows that the hydrodynamic radius distribution curve [$f(R_h)$] gradually shifts to the left as T decreases from 17 °C to 11 °C.

More importantly, $f(R_h)$ curve shows a single peak feature at each temperature with the relative variance ($\mu_2/\langle D \rangle^2$) ranging from 0.03 to 0.05. Such an observation unambiguously confirms the low polydispersity of formed clusters. Clearly, above observations show that the solvophilic PtBA grafts can effectively act as an elastic layer to prevent the macroscopic phase separation of HB-PS₃₀₀-g-PtBA₄₅ chains in cyclohexane, and the structural feature and polydispersity index of hyperbranching clusters can be well controlled by adjusting the aggregation temperature.

Further, by plotting the normalized Rayleigh ratio [$R_W(q)/R_W(q=0)$] versus qR_h , the internal structural feature of clusters can be viewed.^[18,19] Theoretically, the negative slope at high q -regime ($qR_h>3.0$) could reflect the ensemble fractal dimension (d_f). In our previous studies of individual hyperbranched chains, d_f is estimated to vary from 2.2 to 2.5, depending on the solvent quality.^[9,20] As shown in Fig. S1a (in ESI), when $T=17$ °C, $d_f\approx 2.29$, indicating that the clusters possess a highly random branching pattern. When T further de-

creases to 15, 13 and 11 °C, d_f is estimated to be 2.78–2.93 (Figs. S1b–S1d in ESI), which are closer to 3.0 for uniform solid sphere, signifying that clusters formed at the three lower temperatures possess more compact fractal structures.

Time-dependent Aggregation Kinetics of Hyperbranching Clusters in Cyclohexane

So far, we are still unclear about the detail of how individual HB-PS₃₀₀-g-PtBA₄₅ chains assemble into large clusters. Monitoring the time-dependence of mass and size information is beneficial for evaluating the structural stability of formed clusters. Fig. S2 (in ESI) shows the aggregation time dependence of $N_{agg,app}$ and $\langle R_{h,app} \rangle$ for clusters measured at different temperatures. Similar trends are observed, namely, both $N_{agg,app}$ and $\langle R_{h,app} \rangle$ initially increase and then reach a plateau as t increases. Specifically, when $0 < t < 3$ h, both $N_{agg,app}$ and $\langle R_{h,app} \rangle$ increase rapidly, indicating a strong interchain aggregation. Importantly, after $t=6$ h, a plateau value is reached. The result also demonstrates that the lower the temperature, the faster the interchain aggregation occurs. Based on the analysis of $f(R_h)$ (Fig. S3 in ESI), only one relaxation mode is observed, indicating that all precursor chains were involved. In addition, $(\mu_2/\langle D \rangle^2)<0.1$ in the whole aggregation process (Fig. S4 in ESI), displaying a low polydispersity.

To clarify the feature of aggregation kinetics, $[R_W(q)/R_W(q=0)]$ can be further plotted versus qR_h to analyze how d_f evolves with the aggregation time for different aggregation temperatures. Namely, Fig. S5 (in ESI) shows the $R_W(q)$ - q plots at high q regime for specific aggregation times and temperatures. When $T=17$ °C, d_f first increases from 1.52 to 3.55, and then slightly decreases to the 2.35 as t increases (Fig. S5a in ESI). When $T=15$, 13 and 11 °C, a similar trend is confirmed (Figs. S5b–S5d in ESI).

A more comprehensive analysis result is shown in Fig. 2(a). An interesting structural evolution kinetics is observed, namely, for a specific T , d_f gradually increases with t and reaches its maximum of $d_f \approx 4.0$ at $t=3$ –6 h, then starts to decrease and eventually reach to a plateau value of $d_f \approx 3.0$ when $t > 12$ h, corresponds to a uniform spherical structure. The lower the temperature, the less time it takes to reach the maximum. In addition, the segmental density (ρ) of clusters is also analyzed, where $\rho = M_w/(N_A(4/3)\pi R_{h,app}^3)$ with N_A being the Avogadro constant. As shown in Fig. 2(b), the cluster structure formed at $T=17$ °C possesses $\rho \approx 0.007$ g/cm³, which is much smaller than the $\rho \approx 0.02$ – 0.06 g/cm³ for lower temperatures, supporting a much looser structure for cluster formed at higher temperature. Above kinetics pro-

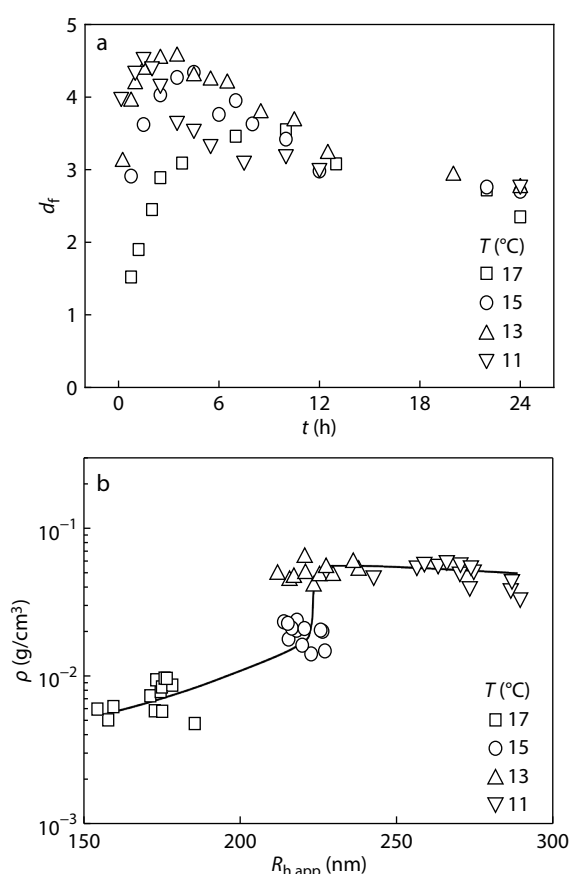


Fig. 2 (a) Aggregation time (t) dependence of fractal dimension (d_f), and (b) apparent average hydrodynamic radius ($\langle R_{h,app} \rangle$) dependence of average segmental density ($\langle \rho \rangle$) for HB-PS₃₀₀-g-PtBA₄₅ chains at different aggregation temperatures ($T=17$, 15, 13 and 11 °C).

cess can be rationalized as follows: at the initial stage, the aggregation of individual chains occurs quickly, and the aggregation rate is significantly larger than the re-construction rate of clusters, which results in loose assembled structure with rough surface feature. As the aggregation proceeds, due to the decreased sticking probability and enhanced viscoelastic property for large clusters, the aggregation rate starts to slow down, and the re-construction of assembled structure eventually results in a more compact structure at equilibrium state.

Number and Line-width of Relaxation Modes of Internal Motions in DLS Spectrum

Based on the clarified structure feature, DLS data are further analyzed to insight into the internal dynamics. Figs. 3(a)–3(d) show the representative $\langle \Gamma \rangle$ -normalized line-width distributions for clusters formed at different temperatures, where $\langle \Gamma \rangle$ represent average line width obtained from cumulant fit. Based on the normalized operation, the relaxation (line-width) related to the pure translational diffusion becomes unity. As shown, when $qR_h \ll 1.0$ at $\theta=13^\circ$, there exists only one single and narrow peak (black curve) for the formed clusters, indicating that the contribution to line-width is solely from the translational motions. When qR_h in the vicinity of 1.0, a second peak related to the internal motions appears in the range of $\Gamma/(Dq^2)=10^0$ – 10^1 . Interestingly, as shown in Figs. 3(a) and 3(b), a third peak located at $\Gamma/(Dq^2)=10^1$ – 10^2 , corresponding to the fastest relaxation, can be observed at some specific values of qR_h for clusters formed at higher aggregation temperatures. While for the lower temperatures (Figs. 3c and 3d), only one fast mode is observed in the whole q -regime. We believe that the observation of third peak may be attributed to the looser and flexible internal structure formed at higher temperatures, which can result in abundant modes of stretching, breathing and rotating internal motions of hyperbranching clusters.

A quantitative evaluation of the intensity contribution from internal motions is shown in Fig. S6 (in ESI), where $A_f/(A_f+A_s)$ denotes the fraction of scattering intensity from the internal motions, where A_s represents the peak area for the slow mode (first peak), and A_f represents the total peak area for the fast modes (second and third peaks). As shown, the internal motions play a significant role when $qR_h > 1$. In general, when $1.0 < qR_h < 4.0$, the contribution of internal motions gradually increases. When $qR_h > 4.0$, only the internal motions can be observed, corresponding to $A_f/(A_f+A_s)=1.0$. This observation is totally different with our previous observations for linear and hyperbranched individual chains with $A_f/(A_f+A_s) \approx 0.05$ and 0.03 at $qR_h=4.0$.^[7,9]

Asymptotic Behavior of Reduced First Cumulant $[\Gamma^* = \Gamma(q)/(q^3 k_B T / \eta_0)]$

The analysis of the reduced first cumulant $\Gamma^* = [\Gamma(q)/(q^3 k_B T / \eta_0)]$ as a function of q has been widely employed to insight into the internal motions of flexible chains in solutions.^[7–9,18–21] Fig. 4(a) shows such an analysis for hyperbranching clusters in cyclohexane. At high q -regime, Γ^* is found to be 0.025–0.045, lower than the values of $\Gamma^* \approx 0.052$ for non-draining linear chains, but much higher than the experimental values for polymer gels of $\Gamma^* \approx 0.013$.^[21]

To our surprise, Γ^* does not display an asymptotic behavior, namely, Γ^* did not reach a plateau value in the regime of

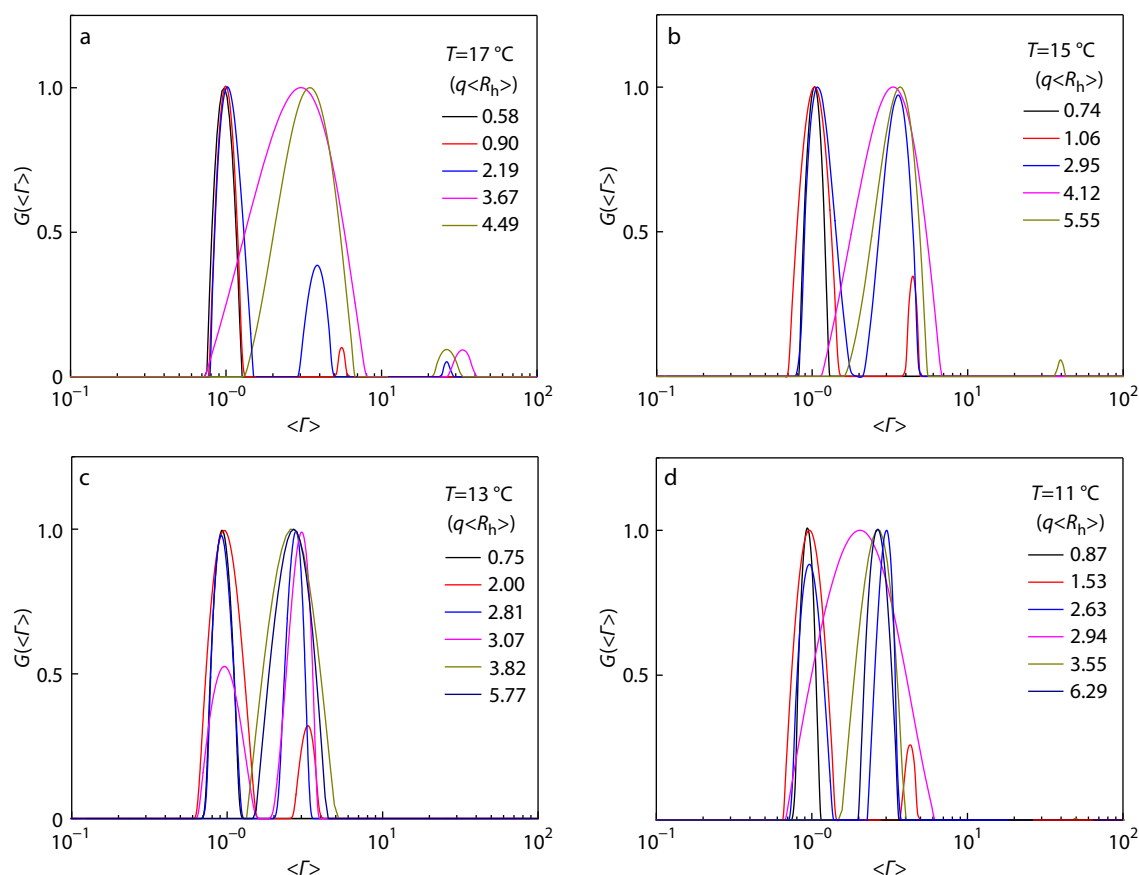


Fig. 3 Representative $\langle \Gamma \rangle$ -scaled line-width distributions $G(\langle \Gamma \rangle)$ for polymeric cluster samples in cyclohexane at the different aggregation temperatures: (a) 17 °C, (b) 15 °C, (c) 13 °C, (d) 11 °C.

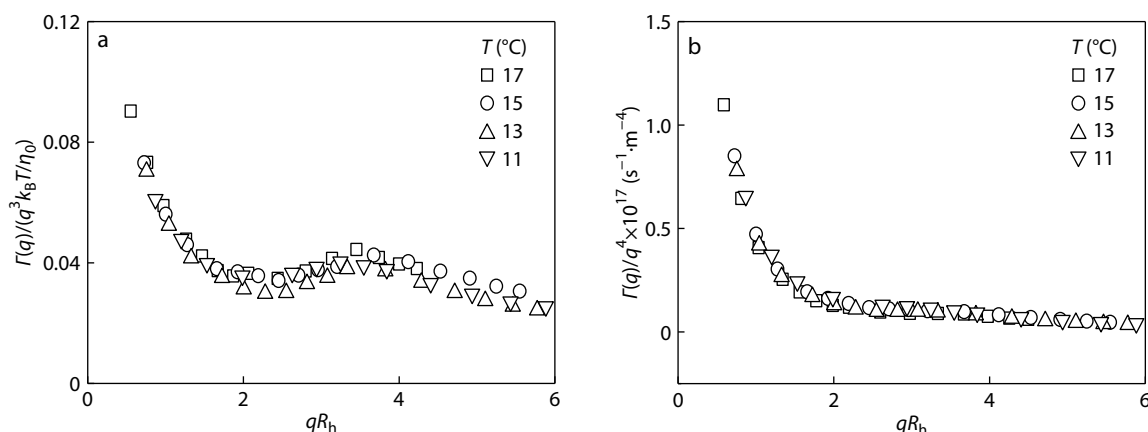
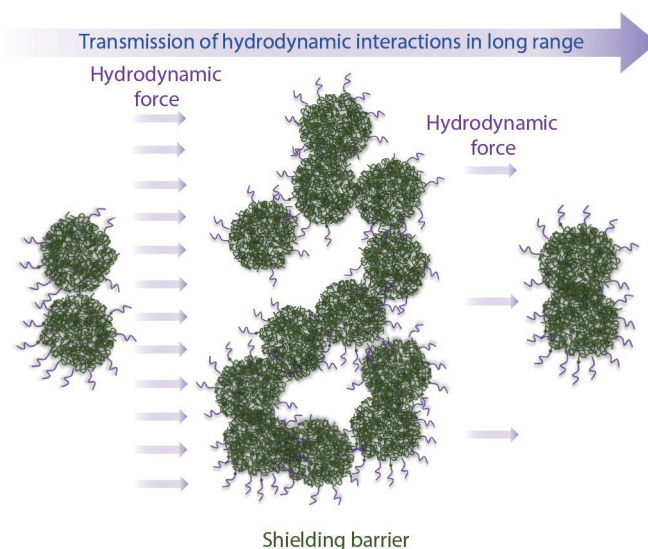


Fig. 4 (a) Normalized observation scale (qR_h) dependence of the reduced first cumulant [$\Gamma^* = \Gamma(q)/(q^3 k_B T/\eta_0)$], and (b) Normalized observation scale (qR_h) dependence of $\Gamma(q)/q^4$ for polymeric clusters in cyclohexane at the different aggregation temperatures ($T=17$, 15, 13 and 11 °C).

$2 < qR_h < 6$, showing that the behavior is neither similar with previously reported cluster systems with high polydispersity,^[13–15,22,23] nor with the classical linear chain systems.^[7,24–27] On the other hand, the trends of Γ^* for clusters formed at different temperatures are similar with each other. Specifically, when $0.5 < qR_h < 2.0$, Γ^* decreases and reaches a minimum value ~ 0.035 ; when $2.0 < qR_h < 3.5$, Γ^* further increases slightly from 0.035 to 0.045; when $3.5 < qR_h < 6$, Γ^* de-

creases again from 0.045 to 0.025.

What is the origin behind our observation? According to the scaling theory of de Gennes,^[28] for linear chains, the line-width due to the internal motions of a chain is predicted to be scaled to qR_g as $\Gamma(q) \sim (qR_g)^z$ when $qR_g \gg 1.0$ with $z=1.0$. For the total line-width Γ , it is predicted to contain the contributions from two items: the translational motions and internal motions, and the product of the two items results in



Scheme 2 Schematic illustration of the shielding of transmission of hydrodynamic interactions in long range in hyperbranching cluster system.

$\Gamma(q) \sim Dq^2(qR_g)^1$, i.e., $z=1.0$ and $\Gamma(q) \sim q^3$ in the intermediate q regime. In the regime, Γ^* is predicted to reach a quasi-plateau value ~ 0.035 . This classical behavior has previously been repeatedly confirmed in a number of studies.^[8,9,27] Whereas for our data, in Fig. S7 (in ESI), by plotting $\Gamma(q)$ against qR_h in the range of $3.5 < qR_h < 6$, it is found that z is close to 2.0 ± 0.2 , i.e., $\Gamma(q) \sim (qR_h)^2$, which is different with the reported results for single chain systems ($z \approx 1.0$)^[8,9] and cluster systems with high polydispersity ($z \approx 1.0$).^[14,15] The analysis indicates a different mode of hydrodynamic interactions in the hyperbranching cluster system.

It is worth mentioning the work from Wen *et al.*, in which the internal motions of MEH-PPV cluster system with high polydispersity was studied.^[13] In their work, they attempted to utilize the free draining Rouse model for the data interpretation. It was pointed out that as contrasted with the Zimm model, when $qR_g \gg 1$, Rouse model predicted that $\Gamma(q)$ is controlled by not only the system temperature and solvent viscosity, but also the chain dimension, i.e., $\Gamma(q) \sim q^4 R_g^2 \sim q^4$ was predicted. Following the idea of Wen *et al.*, $\Gamma(q)$ is further plotted versus q^4 in Fig. 4(b). Indeed, a much better asymptotic behavior is found.

For HB-PS₃₀₀-*g*-PtBA₄₅ hyperbranching clusters, $N_{\text{agg,app}}$ is in the range of 10^2 – 10^3 when $11^\circ\text{C} < T < 17^\circ\text{C}$. If we further count the number of interaction sites (N_{int}) of hyperbranched chains in one cluster, N_{int} will be even much larger $N_{\text{agg,app}}$. Therefore, by considering the large values of N_{int} , $N_{\text{agg,app}}$ and $\langle \rho \rangle$, the hydrodynamic interaction among internal segments is supposed to be greatly weakened due to the enhanced hydrodynamic shielding effect. In other word, our observation provides direct evidence reflecting the change of modes of hydrodynamic shielding effect and hydrodynamic interaction in hyperbranching cluster system with low polydispersity and high local chain segment density. It is not difficult to imagine, in the Rouse model limit, the hydrodynamic interactions between two segment beads will be completely shielded by the intermediate beads when the densities of branching points and chain segments are high enough.

CONCLUSIONS

In summary, by constructing one well-defined hyperbranching cluster system, we have investigated the structural feature and internal motion of clusters in a selective solvent. The result has revealed that unique structural evolution of clusters as a function of aggregation temperature and aggregation time, namely, a transition from loose aggregation structure with rough surface feature to relatively uniform sphere structure has been observed. More importantly, a non-asymptotic behavior of reduced first cumulant has been revealed, which reflects a different behavior from previously reported either individual chain systems with low polydispersity feature, or cluster systems with high polydispersity feature. The origin can be attributed to the enhanced hydrodynamic shielding effect in hyperbranching cluster system (Scheme 2).

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2864-4>.

ACKNOWLEDGMENTS

This work was financially supported by the National Natural Science Foundation of China (No. 21973088) and Shenzhen Science and Technology Program (Nos. RCYX2021070609210 1012 and ZDSYS20210623100800001).

REFERENCES

- 1 Pecora, R. Spectral distribution of light scattered from flexible-

- coil macromolecules. *J. Chem. Phys.* **1968**, 49, 1032.
- 2 Han, C.; Akcasu, A. Z. Dynamic light scattering of dilute polymer solutions in the nonasymptotic q -region. *Macromolecules* **1981**, 14, 1080–1084.
- 3 Chu, B. Light scattering studies of polymer solutions and melts. *Polym. J.* **1985**, 17, 225–238.
- 4 De Gennes, P. G. Quasi-elastic scattering of neutrons by dilute polymer solutions: i. Free-draining limit. *Phys. Phys. Fiz.* **1967**, 3, 37.
- 5 Rouse, P. E. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* **1953**, 21, 1272.
- 6 Zimm, B. H. Dynamics of polymer molecules in dilute solutions: viscoelasticity, flow birefringence and dielectric loss. *J. Chem. Phys.* **1956**, 24, 269.
- 7 Wu, C.; Chan, K.; Xia, K. Experimental study of the spectral distribution of the light scattered from flexible macromolecules in very dilute solution. *Macromolecules* **1995**, 28, 1032–1037.
- 8 Ishaq, M. W.; Hao, N.; Zhu, M.; Li, L. Light scattering study of internal motions of ultralong comb-like chains in dilute solutions under good solvent conditions. *Macromolecules* **2020**, 53, 558–568.
- 9 Hao, N.; Zhu, M.; Li, L. Light scattering study of internal dynamics of hyperbranched polymers with controlled branching patterns and low polydispersities in dilute solutions. *Macromolecules* **2019**, 52, 3794–3804.
- 10 Bhat, S. I.; Ahmadi, Y.; Ahmad, S. Recent advances in structural modifications of hyperbranched polymers and their applications. *Ind. Eng. Chem. Res.* **2018**, 57, 10754–10785.
- 11 Sveinbjörnsson, B. R.; Weitekamp, R. A.; Miyake, G. M.; Xia, Y.; Atwater, H. A.; Grubbs, R. H. Rapid self-assembly of brush block copolymers to photonic crystals. *Proc. Natl. Acad. Sci. U.S.A.* **2012**, 109, 14332–14336.
- 12 Lee, H.; Pietrasik, J.; Sheiko, S. S.; Matyjaszewski, K. Stimuli-responsive molecular brushes. *Prog. Polym. Sci.* **2010**, 35, 24–44.
- 13 Wen, Y.; Lin, P.; Hua, C.; Chen, S. Dynamic structure factor for large aggregate clusters with internal motions: a self-consistent light-scattering study on conjugated polymer solutions. *J. Phys. Chem. B* **2011**, 115, 14369–14380.
- 14 Dahesh, M.; Banc, A.; Duri, A.; Morel, M. H.; Ramos, L. Polymeric assembly of gluten proteins in an aqueous ethanol solvent. *J. Phys. Chem. B* **2014**, 118, 11065–11076.
- 15 Wei, G.; Venkataraman, S.; Yang, Y.; Hedrick, J. L.; Prabhu, V. M. Self-assembly and dynamics driven by oligocarbonate-fluorene end-functionalized poly(ethylene glycol) ABA triblock copolymers. *Macromolecules* **2017**, 50, 1090–1101.
- 16 Huang, S.; Yang, J.; Hao, N.; Ishaq, M. W.; Wang, J.; Jiang, N.; Li, L. Conformational transition and interchain association of hypergraft HB-PS- g -PtBA copolymer chains with varied copolymer compositions and block lengths in a selective solvent. *Macromolecules* **2022**, 55, 3063–3077.
- 17 Calderara, F.; Riess, G. Characterization of polystyrene-block-poly(4-vinyl-pyridine) block copolymer micelles in toluene solution. *Macromol. Chem. Phys.* **1996**, 197, 2115–2132.
- 18 Galinsky, G.; Burchard, W. Starch fractions as examples for nonrandomly branched macromolecules. 4. Angular dependence in dynamic light scattering. *Macromolecules* **1997**, 30, 6966–6973.
- 19 Trappe, V.; Bauer, J.; Weissmüller, M.; Burchard, W. Angular dependence in static and dynamic light scattering from randomly branched systems. *Macromolecules* **1997**, 30, 2365–2372.
- 20 Zhu, M.; Yang, J.; Li, L.; Duan, X.; Li, L. Chain conformation of hyperbranched polymers with uniform branching subchains in dilute solution near the θ point. *Macromolecules* **2020**, 53, 7980–7987.
- 21 Dai, Z.; Wu, C. Internal motions of linear chains and spherical microgels in θ and poor solvents. *Macromolecules* **2010**, 43, 10064–10070.
- 22 Li, X.; Noritomi, T.; Sakai, T.; Gilbert, E. P.; Shibayama, M. Dynamics of critical clusters synthesized by end-coupling of four-armed poly(ethylene glycol)s. *Macromolecules* **2019**, 52, 5086–5094.
- 23 Guo, R.; Hsu, C.; Hua, C.; Chen, S. Colloidal aggregate and gel incubated by amorphous conjugated polymer in hybrid-solvent medium. *J. Phys. Chem. B* **2015**, 119, 3320–3331.
- 24 Tsunashima, Y.; Hirata, M.; Nemoto, N.; Kajiwar, K.; Kurata, M. Dynamic light scattering studies of polymer solutions. 6. polyisoprenes in a θ -solvent, 1,4-dioxane. *Macromolecules* **1987**, 20, 2862–2866.
- 25 Nicolai, T.; Brown, W.; Johnsen, R. The internal modes of polystyrene single coils studied using dynamic light scattering. *Macromolecules* **1989**, 22, 2795–2801.
- 26 Kim, S.; Ramsay, D.; Patterson, G.; Selser, J. Static and dynamic light scattering of poly(α -methyl styrene) in toluene in the dilute region. *J. Polym. Sci., Polym. Phys.* **1990**, 28, 2023–2056.
- 27 Wu, C.; Zhou, S. Internal motions of both poly(N -isopropylacrylamide) linear chains and spherical microgel particles in water. *Macromolecules* **1996**, 29, 1574–1578.
- 28 De Gennes, P. G. *Scaling concepts in polymer physics*. Cornell University Press: **1979**.