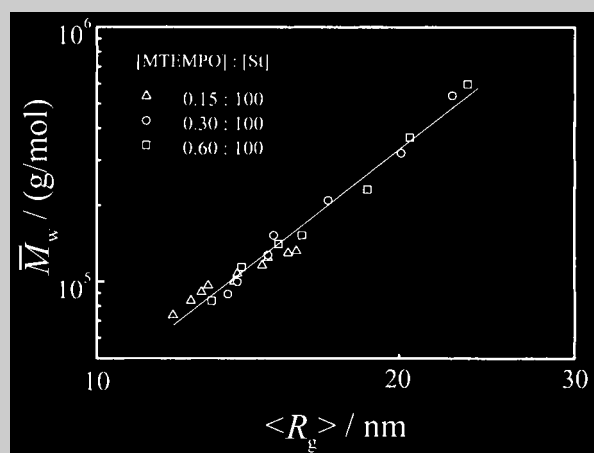


Communication: The thermal decomposition of polystyrene clusters prepared by using 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl as a branching agent was studied. The weight-average molar mass (\bar{M}_w) and the radius of gyration (R_g) of the resultant clusters can be scaled as $\bar{M}_w \propto R_g^{3.0 \pm 0.1}$, revealing that these clusters have a uniform chain density. Moreover, the dynamic properties of such clusters converge unexpectedly faster than the static properties as the molar mass decreases.

Double logarithmic plot of $\langle R_g \rangle$ versus \bar{M}_w for MTEMPO-modified polystyrene clusters in toluene during thermal decomposition at 100 °C.



Novel Polymer Clusters with a Uniform Chain Density

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Introduction

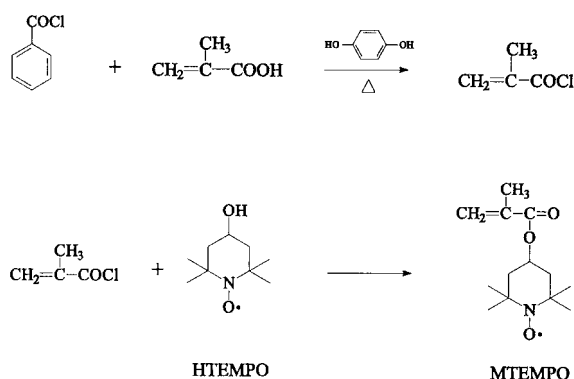
Polymers with special architectures, such as star, block, grafting or hyperbranching structures, often have unusual properties and can be prepared by different modern polymerization methods.^[1,2] A polymer cluster with a hyperbranched structure normally has a non-uniform chain density, decreasing outward from the center, so that its molar mass (\bar{M}) and size (R) can be scaled as $\bar{M} \propto R^a$ with $a < 3$. The formation of such polymer clusters in polymerization often leads to a sol-gel transition; namely the clusters formed in the sol are interconnected to form a gel network wherein each cluster looks like an “island”. This is why it is extremely difficult, if not impossible, to prepare a uniform polymer network. However, the adventure in this field has never stopped because a true uniform polymer network can provide a good model system. On the other hand, the studies of dendritic polymers led to a controversial a values in the range 2.2–5.^[3–5]

Recently, controlled radical polymerization has attracted much attention, wherein a stable radical, such as (2,2,6,6-tetramethylpiperidine-*N*-oxyl), could reversibly

couple with a growing radical.^[6–8] Using this method, a range of polymers with different controlled architectures have been synthesized.^[9–11] In this study, we prepared novel polystyrene clusters using a polymerizable nitroxide, 4-methacryloyloxy-2,2,6,6-tetramethylpiperidine-*N*-oxyl (MTEMPO), as a branching agent.^[12] The MTEMPO branching linkage between two different chains is thermally reversible, leading to potential applications in polymer processing because the breaking of such a branching linkage at higher temperatures can result in a lower viscosity. In this communication, we report a recent discovery that such clusters have a uniform chain density and a rare hydrodynamic property.

Experimental Part

The preparation of the MTEMPO-modified polystyrene clusters involves two steps: (1) the synthesis of stable and polymerizable nitroxyl radical MTEMPO^[13] and (2) the “living” polymerization of styrene in the presence of MTEMPO. The synthesis of MTEMPO is illustrated in Scheme 1. A solution



Scheme 1. Synthesis of stable and polymerizable nitroxyl radical.

of freshly distilled methacrylic acid (20 g, 0.23 mol), freshly distilled benzoyl chloride (0.44 mol) and hydroquinone (1.1 g) was refluxed at 140 °C for half an hour. The distillation of the solution resulted in 18.4 g of methacryloyl chloride. A solution mixture of methacryloyl chloride (7.4 g, 0.07 mol) and dry benzene (29 mL) was added dropwise into a solution of HTEMPO (10 g, 0.058 mol), Et₃N (7.1 g, 0.07 mol) and dry benzene (200 mL), with vigorous stirring at room temperature. Methacryloyl chloride was reacted with HTEMPO in the solution first at room temperature for 1 h and then at 70 °C for 2 h. The precipitate was removed by filtration. The orange crude product obtained by evaporation of the solvent was further purified by recrystallization from cyclohexane. The resultant orange crystal had a melting point in the range 82.2–84.0 °C. The total reaction yield was 7.2 g (51.8%).

In the preparation of the MTEMPO-modified polystyrene clusters, a solution mixture of freshly distilled styrene (41.6 g, 0.4 mol), benzoyl peroxide (0.290 g, 1.2 mmol) as the initiator and MTEMPO (0.288 g, 1.2 mmol) was first subjected to two freezing-thawing cycles in liquid nitrogen and then heated to 120 °C to start the polymerization. After a 28-h reaction under a nitrogen atmosphere, the polymerization was stopped by quenching the reaction mixture into liquid nitrogen. The mixture was dissolved in toluene and precipitated from methanol. The polystyrene precipitate was dried under vacuum at 50 °C. The O–C bond between nitroxide and polystyrene can undergo a reversible dissociation at temperatures higher than 100 °C so each MTEMPO unit can form a thermally reversible branching point.^[14]

In this study, ascorbic acid was added to trap the decomposed MTEMPO free radicals and render the dissociation irreversible. We can therefore study the resultant clusters at each stage of the decomposition. The molar ratio of ascorbic acid to alkoxyamine was 3. The thermal decomposition at

100 °C was monitored by a combination of static and dynamic laser light scattering (LLS). In the static measurement, the \bar{M}_w and the z-average root-mean-square radius of gyration ($\langle R_g^2 \rangle^{1/2}$, written as $\langle R_g \rangle$) were obtained, while in the dynamic measurement, the average translational diffusion coefficient ($\langle D \rangle$) was determined. Details regarding the LLS instrumentation and theory can be found elsewhere.^[15–17]

Results and Discussion

Table 1 summarizes LLS characterization of the three samples prepared with different initial MTEMPO/styrene ratios. Sample 1 has a lower \bar{M}_w than Samples 2 and 3 because less MTEMPO (“branching agent”) was used. The decrease of $\langle R_g \rangle / \langle R_h \rangle$ ($\langle R_h \rangle$ is the average hydrodynamic radius) as the MTEMPO content increases indicates that Sample 1 is less branched. Figure 1 shows that during the thermal decomposition, the \bar{M}_w of the clusters decreases as the decomposition time (t) increases and \bar{M}_w is experimentally scaleable to t by the relationship $\bar{M}_w \propto t^{-\beta}$ with $\beta = 0.74 \pm 0.01$. The exponent β increases with the decomposition temperature, but the decomposition always leads to similar linear polystyrene chains with an average molar mass of $\approx 4 \times 10^4 \text{ g} \cdot \text{mol}^{-1}$. The inset in Figure 1 shows that there is no significant change in the polydispersity index \bar{M}_w / \bar{M}_n of the resultant clusters

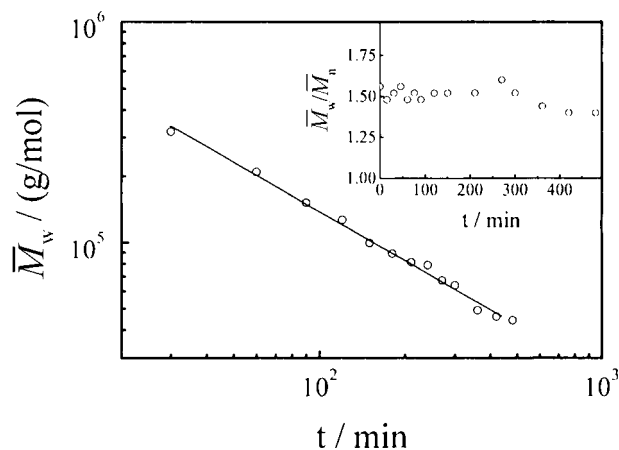


Figure 1. Decomposition time dependence of \bar{M}_w of MTEMPO-modified polystyrene clusters, where the decomposition temperature is 100 °C and [MTEMPO]:[St] is 0.3:100. The inset shows a typical decomposition time dependence of polydispersity index \bar{M}_w / \bar{M}_n .

Table 1. Light-scattering characterization of three MTEMPO-modified polystyrene clusters in toluene at 25 °C.

Sample	MTEMPO/ styrene mol-%	Initiator mol-%	\bar{M}_w $\times 10^{-5} \text{ g} \cdot \text{mol}^{-1}$	$\langle R_g \rangle$ nm	$\langle R_h \rangle$ nm	$\langle R_g \rangle / \langle R_h \rangle$	\bar{M}_w / \bar{M}_n
1	0.15	0.3	1.66 ± 0.02	15.8 ± 0.5	12.6 ± 0.1	1.25	1.52
2	0.3	0.3	5.48 ± 0.02	25.8 ± 0.5	22.1 ± 0.1	1.17	1.56
3	0.6	0.3	4.81 ± 0.02	23.4 ± 0.5	20.2 ± 0.1	1.16	1.60

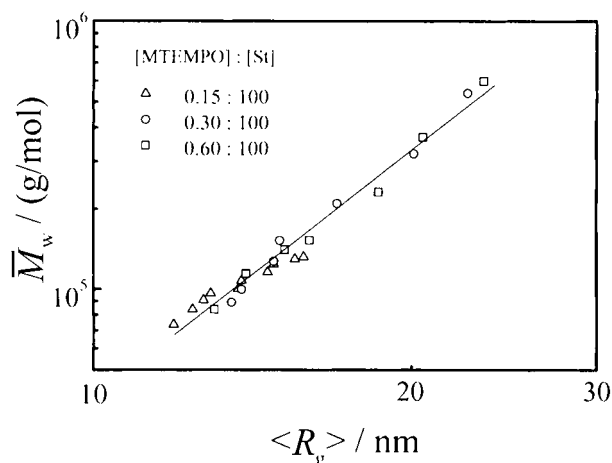


Figure 2. Double logarithmic plot of $\langle R_g \rangle$ versus \bar{M}_w for MTEMPO-modified polystyrene clusters in toluene during thermal decomposition at 100 °C.

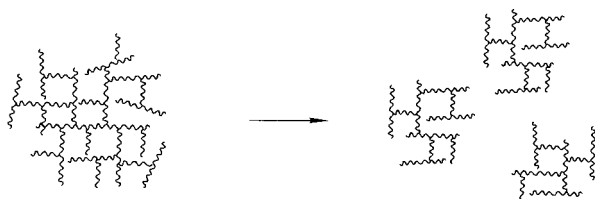


Figure 3. Schematic of cluster-to-cluster thermal decomposition of MTEMPO-modified polystyrene clusters in toluene at temperatures higher than 100 °C.

except a slight decrease near the end of the decomposition ($t > \approx 300$ min), indicating a random decomposition or cleavage of the MTEMPO branching points. The final value of $\bar{M}_w/\bar{M}_n \approx 1.4$ reveals that the polymerization has a “living” nature.

We repeated the decomposition by using three samples with different branching densities. Figure 2 shows that all the results collapse into a single line and \bar{M}_w is scaled to $\langle R_g \rangle$ as $\bar{M}_w \propto \langle R_g \rangle^{3.0 \pm 0.1}$. Since, for a spherical object,

$$M = \int_V \rho(r) dV \sim 4\pi \int_0^R \rho(r) r^2 dr \quad (1)$$

(M , mass; V , volume; $\rho(r)$, density distribution along the radius; R , sphere radius), the scaling of $\bar{M} \sim R^{3.0 \pm 0.1}$ reveals that $\rho(r)$ is independent of r , i.e., the clusters must have a *uniform* chain density. Since the cleavage of the MTEMPO linkages was random, the decomposition could be described by a cluster-to-cluster process, as schematically shown in Figure 3. Near the end of the decomposition, the clusters break into linear chains.

Moreover, we found that in the dynamic measurement of these uniform clusters, the $\langle D \rangle$ could be scaled to \bar{M}_w by $\langle D \rangle \propto \bar{M}_w^{-\alpha_D}$ with $\alpha_D = 0.52 \pm 0.01$, as shown in Figure 4. Note that $\langle D \rangle$ measures the hydrodynamics of the

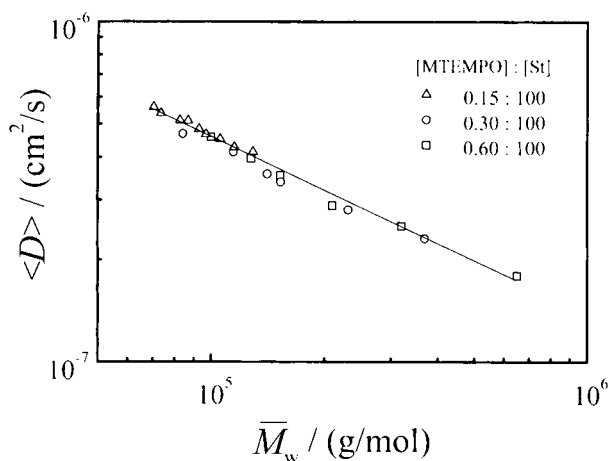


Figure 4. Double logarithmic plot of $\langle D \rangle$ versus \bar{M}_w of uniform MTEMPO-modified polystyrene clusters during thermal decomposition at 100 °C.

clusters in solution and is related to the average hydrodynamic radius ($\langle R_h \rangle$) via the Stokes-Einstein equation $R_h = k_B T / (6\pi\eta D)$ with k_B , η and T the Boltzmann constant, solvent viscosity and the absolute temperature, respectively. A combination of Figure 2 and 4 leads to $\langle R_g \rangle / \langle R_h \rangle \propto \bar{M}_w^{-0.19 \pm 0.01}$, i.e., $\langle R_g \rangle / \langle R_h \rangle$ increases as \bar{M}_w decreases. This due to the fact that as the molar mass increases, the dynamic $\langle R_h \rangle$ increases faster than the static $\langle R_g \rangle$. For a given structure or chain conformation, $\langle R_g \rangle / \langle R_h \rangle$ is normally close to a constant and nearly independent of molar mass, as long as the chain length is not too short. For example, for a uniform non-draining sphere or a linear coiled chain in good solvent, $\langle R_g \rangle / \langle R_h \rangle$ equals $(3/5)^{1/2}$ and 1.504, respectively. For a normal hyperbranched polymer cluster, $\langle R_g \rangle / \langle R_h \rangle \approx 1.0$ –1.3, depending on the degree of branching.^[18–21]

Weill and Cloizeaux^[22] showed that for a long linear chain in a good solvent, as the chain length increases, $\langle R_h \rangle$ increases more slowly than $\langle R_g \rangle$ due to the hydrodynamic draining, so that $\langle R_g \rangle / \langle R_h \rangle \sim M^{0.05}$, i.e., $\langle R_g \rangle / \langle R_h \rangle$ increases as \bar{M}_w increases, which is opposite to what we found in this study for polymer clusters with a uniform density; namely, the increase of dynamic properties with \bar{M}_w is much faster than that of the static properties. Such an unusual behavior can be attributed to the fact that for a uniform polymer cluster swollen in good solvent, its periphery is more hydrodynamically draining than its center, or in other words, solvent molecules in the center are likely to move together with the cluster. As the size of the cluster increases, the relative effect of this draining periphery layer on $\langle R_h \rangle$ decreases so that $\langle R_h \rangle$ increases more quickly than $\langle R_g \rangle$. To our knowledge, this strange hydrodynamic property has been neither predicted nor observed before. Our results should stimulate further theoretical and experimental studies of such uniform polymer clusters.

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