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New Method To Access Hyperbranched Polymers with Uniform Structure via One-Pot Polymerization of Inimer in Microemulsion

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Supporting Information

ABSTRACT: A facile approach is presented for successful synthesis of hyperbranched polymers with high molecular weight and uniform structure by a one-pot polymerization of an inimer in a microemulsion. The segregated space in the microemulsion confined the inimer polymerization and particularly the polymer−polymer reaction within discrete nanoparticles. At the end of polymerization, each nanoparticle contained one hyperbranched polymer that had thousands of inimer units and low polydispersity. The hyperbranched polymers were used as multifunctional macroinitiators for synthesis of "hyper-star" polymers. When a degradable inimer was applied, the hyper-stars showed fast degradation into linear polymer chains with low molecular weight.

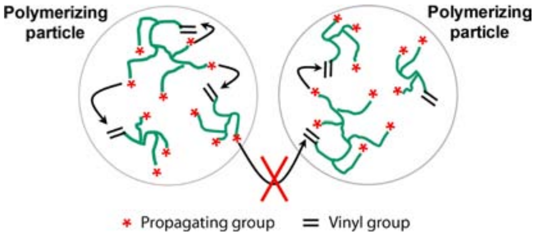
Polymers with highly branched structure, e.g., dendrimers and hyperbranched polymers, show promise in a variety of fields including catalysis, blend additives, cosmetics, and drug delivery.[1] Both have the features of high branching density, three-dimensional shape, and multiple terminal groups, although they have clear differences. Dendrimers possess the most precisely controlled structure, but their widespread utilization is hindered by their less efficient synthesis.[2] In contrast, hyperbranched polymers have a facile synthesis based on a one-pot polymerization reaction; their current challenge is the lack of control over structural uniformity.

Hyperbranched polymers are commonly synthesized in bulk or solution via either step-growth polymerization of AB_f monomer (containing one A group and f (≥ 2) B groups)[1a,d,3] or self-condensing vinyl polymerization (SCVP) of AB* inimer (containing initiator fragment B* and monomer vinyl group A in one molecule).[4] In both cases, the growth of hyperbranched polymers is accompanied by random polymer−polymer reactions in the continuous reaction media and finally results in polymers with extremely broad molecular weight distribution; i.e., the polydispersity equals the number-average degree of polymerization of the product.[4b,5] An effective strategy to decrease the polydispersity of hyperbranched polymer could be the addition of a multifunctional "core" molecule B_f or $(B^*)_f$, with $f \geq 2$.[3,6] However, the AB_f monomers or AB* inimers in these reactions have to be added very slowly to ensure that they only react with the cores or the polymers growing from the cores, but not with each other.[6b,e] It is desirable to develop a new synthetic technique to achieve structural control over hyperbranched polymers using a one-pot, one-batch synthesis.

All the literature so far has reported the polymerization of inimers in bulk or solution. The homogeneous reaction medium causes unconfined polymer−polymer reactions throughout the reactor that lead to polymers with poorly defined structure. On the other hand, polymerization in dispersed media has an intriguing feature: compartmentalization,[7a−d] which refers to the segregation and/or confinement of reactants within discrete polymerizing particles.[7d−f] In the field of radical polymerization, compartmentalization has been studied in various aqueous dispersed systems to show its effect on polymerization kinetics, as well as on the "livingness" and molecular weight of linear polymers.[7c,8] However, its effect on regulating polymer structures, especially its advantage for controlling polymers with complex architectures, has rarely been explored.[9]

Herein, we report for the first time the use of confined space to regulate the synthesis of hyperbranched polymers by conducting one-pot polymerization of AB* inimers in a microemulsion. The segregated space in the microemulsion successfully confined the polymer−polymer reactions within discrete polymerizing nanoparticles (Scheme 1). Consequently, the obtained hyperbranched polymers showed narrow molecular weight distribution and hydrodynamic size similar to that of nanoparticles. This technique has the additional advantage for synthesis of backbone-degradable polymers when the inimer contains a labile linker between the vinyl (A) and initiating (B*) groups.

Scheme 1. Polymerization of Inimers in Microemulsion: An Effective Means To Confine Polymer−Polymer Reactions within Discrete Nanospace



To prove the concept, an inimer **1** (Figure 1A) containing a methacrylate polymerizable group and a 2-bromoisobutyrate initiating group was synthesized to conduct an atom transfer radical polymerization (ATRP) in microemulsion.[10] Beyond

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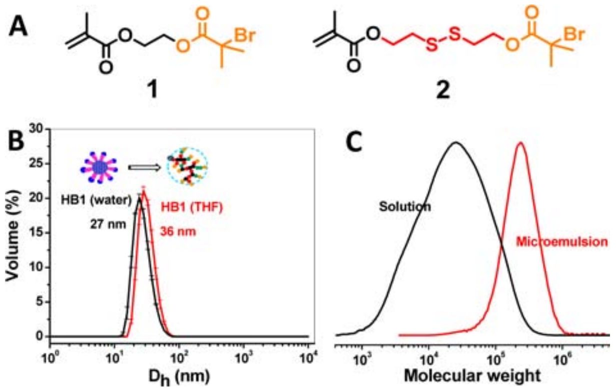


Figure 1. (A) Molecular structure of inimers. (B) Hydrodynamic sizes of **HB1** synthesized by AGET ATRP of inimer **1** in microemulsion before purification in water and after purification in THF. (C) SEC traces of the hyperbranched polymers **HB1s** and **HB1** synthesized via SCVP of **1** in solution and in microemulsion, based on linear PMMA standards in THF.

the general requirement of a microemulsion system, the use of Cu catalyst needs proper selection of surfactant, ligand, and initiation technique in order to obtain a successful ATRP in aqueous dispersed media.[11] In this study, we selected nonionic surfactant Brij98 to achieve the best microemulsion stability and applied bis(2-pyridylmethyl)octadecylamine (BPMODA) as a tridentate hydrophobic ligand to minimize the partition of Cu catalyst in water.[12] Activator generated by electron transfer (AGET)[13] ATRP was used as the initiation technique that started with air-stable Cu(II) catalyst for microemulsion and generated Cu(I) activator when reduced with sodium ascorbate.[10a] To demonstrate the effect of microemulsion on the structural control of hyperbranched polymers, a control experiment of SCVP of inimer **1** by using normal ATRP in concentrated solution was conducted in parallel.

SCVP of **1** in solution (1 g of inimer **1** in 0.3 mL of toluene)[14] produced polymer **HB1s** with poorly defined structure, evidenced by a broad molecular weight distribution (M_w/M_n = 4.72, Table 1) in size exclusion chromatography (SEC, Figure 1C). This result was expected because the unconfined polymer–polymer reaction occurred throughout the solution medium. In contrast, SCVP of **1** carried out in microemulsion produced narrowly distributed nanoparticle **HB1** with hydrodynamic diameter D_h = 27 nm in water before purification. After precipitation in methanol to remove the surfactant, the polymer was dispersed in THF and showed a monomodal peak in dynamic light scattering (DLS) with an increased D_h = 36 nm (Figure 1B). The size increase of **HB1** was probably due to a transition of the polymers from a collapsed state protected by surfactant in water to a well-dissolved state in THF. The hydrodynamic size increase, as well as the monomodal DLS peak in THF, indicates that each latex nanoparticle in the microemulsion contains one polymer molecule at the end of the SCVP reaction. Otherwise, the nanoparticle would break into smaller parts after being redispersed in THF. The polymer from microemulsion was further analyzed by THF SEC. The apparent molecular weight based on linear poly(methyl methacrylate) (PMMA) standards was $M_{n,RI} = 140 \times 10^3$, and M_w/M_n = 1.24. This polydispersity is significantly lower than the result in the control experiment, representing a breakthrough of this new synthetic method. The polymer–polymer reactions were effectively confined within each surfactant-stabilized nanoparticle that produced hyperbranched polymers with narrow distribution. The actual molecular weight of the obtained **HB1** polymer determined by multi-angle laser light scattering (MALLS, d*n*/d*c*(**HB1**) = 0.084[15]) was $M_{n,MALLS} = 1470 \times 10^3$, 10 times higher than the apparent value, indicating a highly branched polymer structure. Based on the absolute molecular weight, each **HB1** hyperbranched polymer contained an average 5270 inimer units.

To determine the degree of branching (DB) of **HB1**, the purified polymer was analyzed by NMR spectroscopy (Figure 2). Without considering radical termination[16] and intramolecular cyclization, two correlated conditions are valid in the system: (1) the number of A* groups in the hyperbranched polymer equals the number of b groups, $N_{A*} = N_b$, and (2) the number of B* groups equals the number of a and A groups, $N_{B*} = N_a + N_A$. These two equations, combined with the integration of NMR peaks (δ = 2.6–2.8, 0.7–1.3, and 0.7–2.2), allowed calculation of $N_{B*}:N_b$ = 0.84:0.16, corresponding to a reactivity ratio $r = k_{A*}/k_{B*}$ = 57 and DB = 0.27 (see SI, section 1, for detailed calculation).[17] $N_{B*}:N_b$ was based on the average of three independent NMR measurements, and the complicated

Table 1. Information on Hyperbranched and Hyper-star Polymers

polymer	medium	inimer	MI[c]	monomer	conv[d] (%)	$M_{n,MALLS}$[e] ($\times 10^{-3}$)	$M_{n,RI}$[f] ($\times 10^{-3}$)	M_w/M_n[f]	D_h[g] (nm)	CV[g]
				Hyperbranched Polymers						
HB1s[a]	solution	**1**			95	38.0	9.72	4.72		
HB1[b]	microemulsion	**1**			99	1470	140	1.24	36.0	0.12
HB2[b]	microemulsion	**2**			97	1510	141	1.25	34.0	0.14
				Hyper-star Polymers						
HS1-P*t*BA	solution		**HB1**	*t*BA	25		175	1.30	96.0	0.09
HS1-PAA									124[h]	0.11[h]
HS1-POEGMA	solution		**HB1**	OEGMA	31		253	1.35	137[i]	0.17[i]
HS2-P*t*BA	solution		**HB2**	*t*BA	27		177	1.37	123	0.13

[a] [Inimer **1**]$_0$:[CuBr]$_0$:[CuBr$_2$]$_0$:[bpy]$_0$ = 70:0.95:0.05:2, 1 g of inimer **1** in 0.3 mL of toluene, [inimer **1**]$_0$ = 2.8 M, 65 °C, 9 h. [b] [Inimer **1**]$_0$:[CuBr$_2$]$_0$:[BPMODA]$_0$:[ascorbate]$_0$ = 70:1:1:0.5, weight ratio of inimer to Brij98 = 1:4, 1 g of Brij98 in 12 g of water, 65 °C, 2 h. [c] Hyperbranched polymer as macroinitiator (MI) with theoretical [R-Br]$_0$:[monomer]$_0$ = 1:140. [d] Conversions of vinyl groups were determined by ^{1}H NMR for inimers and OEGMA and by GC for *t*BA. [e] Number-average molecular weight measured by THF SEC with MALLS detector. [f] Apparent number-average molecular weight and molecular weight distribution measured by SEC with RI detector, calibrated with linear polystyrene (PS) standards for **HS1-P*t*BA** and **HS2-P*t*BA** and linear PMMA standards for the rest. The mobile phase of SEC was THF, except DMF for **HS1-POEGMA**. [g] Hydrodynamic diameter (D_h) and coefficient of variation (CV) determined by DLS in THF (if not stated otherwise). [h] After hydrolysis of P*t*BA arms into poly(acrylic acid)s (PAAs), determined by DLS in pH 7 water. [i] DLS in pH 7 water.

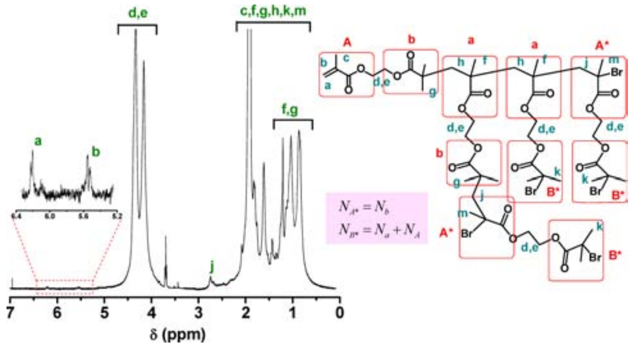
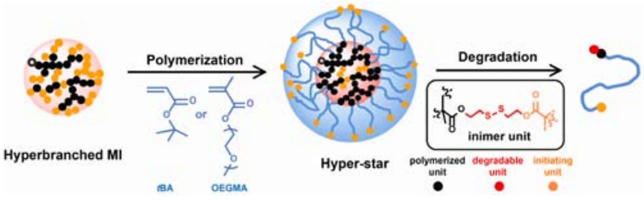


Figure 2. ^{1}H NMR spectrum of the hyperbranched polymer **HB1** synthesized via SCVP of **1** in microemulsion using AGET ATRP.

structure of hyperbranched polymers hindered accurate integration of each NMR peak.[18] The ratio $r = k_{A*}/k_{B*}$ is an apparent value, determined not only by the activation rates of these two species (A*, B*) in ATRP but also by the propagation and deactivation rates of the corresponding radicals, which are significantly affected by experimental conditions.[19] Previous study indicated that the activation rate constant of the A* group was ∼5−10 times higher than that of the B* group under similar conditions.[20] This means that the higher $k_{A*}/k_{B*} = 57$ could also be ascribed to leakage of the Cu(II) deactivator from the polymerizing particle into water.[12] Despite the use of a very hydrophobic ligand, BPMODA, containing a C18 aliphatic tail, the copper complexes, particularly Cu(II)/BPMODA deactivator, still showed partitioning behavior in water.[10a] The exit of deactivator decreased the deactivation rate in polymerizing particles and resulted in more inimers added to propagating chain ends in each activation cycle, i.e., higher N_{B*}:N_b.

The synthesized hyperbranched polymer containing numerous terminal initiating sites (e.g., alkyl bromides) can be used as a multifunctional macroinitiator (MI) for polymerization of another monomer to produce a "hyper-star"[5a,21] polymer (Scheme 2). When *tert*-butyl acrylate (*t*BA, 140 equiv per terminal bromide) was polymerized from the polymer **HB1**, the size of the hyper-star polymer increased from D_h = 36 to 96 nm at 25% *t*BA conversion with narrow size distribution, determined by DLS in THF (**HS1-P*t*BA**, Figure 3A). The apparent molecular weight of the hyper-star polymer was $M_{n,RI} \approx 175 \times 10^3$ based on linear PS standards, although the absolute molecular weight becomes too large to be determined by using a column-based chromatography technique.[22] Hydrolysis of the *tert*-butyl groups produced water-dispersible star polymers with D_h = 124 nm in pH 7 water. The size and surface charge density of the **HS1-PAA** hyper-stars were tunable and sensitive to environmental pH. At basic conditions, e.g., pH > 7, deprotonation of the acid groups allowed the stars to be dispersed in water with zeta potential $\zeta \approx -45$ mV (Figure 3B). Decreasing the pH value below the effective pK_a of the hyper-star polymers quickly diminished the surface charge from negative to neutral.[23] As a result, the star polymers aggregated in water, showing increased size and broader size distribution. When the functional monomer oligo(ethylene glycol) methyl ether methacrylate (OEGMA) was polymerized from **HB1** MI, the obtained hyper-star polymer (**HS1-POEGMA**) was dispersible in water with neutral POEGMA arms, showing D_h = 137 nm in DLS (Table 1).

Scheme 2. Use of Hyperbranched MIs for Synthesis of Degradable "Hyper-star" Polymers



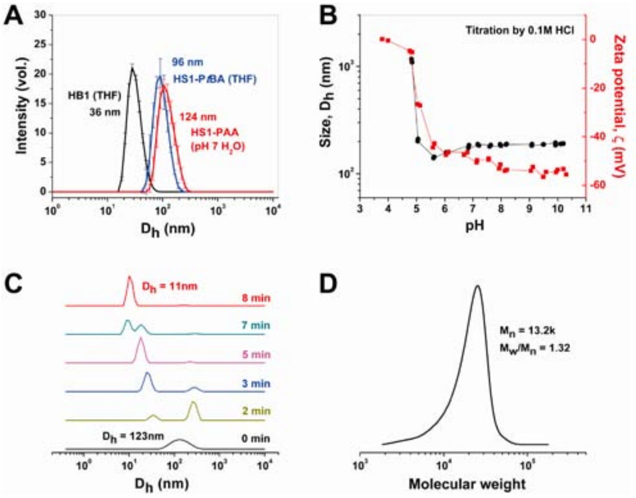


Figure 3. (A) Hydrodynamic diameters (D_h) of **HB1** in THF, the hyper-star **HS1-P*t*BA** in THF, and the hydrolysis product **HS1-PAA** in pH 7 water. (B) Evolution of D_h and zeta potential of **HS1-PAA** as function of pH, 25 °C in water. (C) Size change during the degradation of **HS2-P*t*BA** after adding $(n\text{Bu})_3$P. (D) THF SEC curve of the final degraded product from **HS2-P*t*BA** based on linear PS standards.

It is intriguing that the AB* inimer contains a linker between the vinyl group (A) and initiating group (B*). This provides the possibility to introduce heteroatoms into polymers for labile degradation. For instance, inimer **2** containing a disulfide linker was applied in a microemulsion to synthesize hyperbranched polymer **HB2** similar in molecular weight and hydrodynamic size to **HB1**. When **HB2** was used as MI for polymerization of *t*BA, the obtained hyper-star polymer **HS2-P*t*BA** had D_h = 123 nm in THF (Table 1). Importantly, the hyper-star polymers were degradable under reducing environment.

A typical degradation experiment was carried out at room temperature by using DLS to monitor the change in polymer size as a function of time (Figure 3C). In a glass cuvette, 5 mg of **HS2-P*t*BA** was dispersed in 1 mL of THF, showing a monomodal DLS peak with D_h = 123 nm at 0 min. After adding 5 μL of reducing agent $(n\text{Bu})_3$P into the cuvette, two populations of polymers were observed at 2 min. The polymers with larger size represented hyper-stars with a slightly degraded core, which decreased the core branching and expanded the size of the whole polymers. At the same time, a fraction of polymers appeared with size peak centered at 30 nm, possibly representing some partially degraded fragments. Degradation progressed so quickly that at 5 min there were almost no hyper-stars, and all of them were degraded into parts. The size of the degraded fragments further decreased with time, and the entire degradation reaction finished at 8 min, with $D_h \approx 11$ nm in THF. Further increasing the reaction time and $(n\text{Bu})_3$P amount did not change the polymer size. The final degraded product was analyzed by THF SEC and showed a narrow elution peak with $M_n = 13.2 \times 10^3$ and $M_w/M_n = 1.32$ based on linear PS standards (Figure 3D), indicating a linear P*t*BA chain.

The degradability of hyper-star polymers containing disulfide groups in the core not only is important for their potential application as biomaterials but also provides a method to estimate the number of dangling arms in each hyper-star. Since the absolute molecular weight of **HB2** was $M_{n,MALLS} \approx 1510 \times 10^3$, it contained $\sim$4070 inimer units per polymer molecule. At 27% *t*BA conversion, each dangling arm should have $M_n \approx 4840$[24] if each chain-end bromide had successfully initiated a dangling arm. Since the SEC gave $M_n = 13.2 \times 10^3$ for degraded product (Figure 3D), the initiation efficiency of **HB2** during the polymerization of *t*BA was around $4840/(13.2 \times 10^3) = 37\%$. The incomplete initiation is probably due to the compact environment around the hyperbranched polymer core, which has been reported during the synthesis of miktoarm star polymers by using core cross-linked stars as MIs.[25]

In summary, we developed a new method for synthesis of hyperbranched polymers with both high molecular weight and uniform size by carrying out one-pot polymerization of inimers in microemulsion. The polymer−polymer reactions were successfully confined within discrete nanoparticles in the microemulsion. The obtained hyperbranched polymers containing thousands of inimer units were successfully applied as multifunctional MIs for producing hyper-star polymers. Functional inimers containing labile linker were easily applied for synthesis of degradable hyperbranched polymers that offer potential application as biomedical materials. Microemulsion was demonstrated here as a confined space to introduce the novel concept of utilizing a special environment to control otherwise difficult-to-obtain polymer structures. Other options of confined space with regularly defined pore and channels can also be applied, and this type of research is currently underway in the authors' group.

■ ASSOCIATED CONTENT

Supporting Information

Detailed procedures for preparation and analysis of various kinds of hyperbranched polymers and hyper-star polymers, as well as the degraded products. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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