

Practical Synthesis of Dendritic Hyperbranched Polyacrylates and Their Topological Block Polymers by Organotellurium-Mediated Emulsion Polymerization in Water

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ABSTRACT: The practical synthesis of structurally controlled hyperbranched polymers (HBPs) by organotellurium-mediated radical polymerization (TERP) in emulsions is reported. Copolymerization of vinyltelluride, which induces controlled branch structure and is named evolmer, and acrylates in the presence of TERP chain transfer agent (CTA) in water afforded HBPs having dendron structure. The structure of the HBPs, i.e., molecular weight, dispersity, branch number, and branch length (the number of monomer units between branch points), were controlled by changing the amount of CTA, evolmer, and acrylate monomers, and HB-poly(butyl acrylate)s (HBPBAs) with up to the 8th generation having an average of 255 branches were successfully synthesized. As the monomer conversion reached nearly quantitative and the obtained polymer particles were well dispersed in water, the method is highly suitable for the synthesis of *topological block polymers*, block polymers consisting of different topologies. Thus, linear-*block*-HB, HB-*block*-linear, and HB-*block*-HB-PBAs with the controlled structure were successfully synthesized just by adding the second monomer(s) to the macro-CTA. The intrinsic viscosity of the resulting homo- and topological block PBAs was systematically controlled by the degree of the branch, the branch length, and the topology. Therefore, the method opens the possibility of obtaining various HBPs with diverse branch structures and tuning the polymer properties by the polymer topology.

INTRODUCTION

The topology of polymers, i.e., linear, cyclic, branch, etc., plays a crucial role in their physical properties.¹⁻³ Thus, structurally controlled “topological polymers” could open new doors for nanoscience and nanotechnology. In addition, since different properties can be attained from the same monomer component by changing the topology, their practical synthetic method is expected to be an important technology for the industry. However, practicality and structural control of the synthesis of topological polymers are usually a trade-off, and their practical uses have been a formidable challenge besides linear polymers.

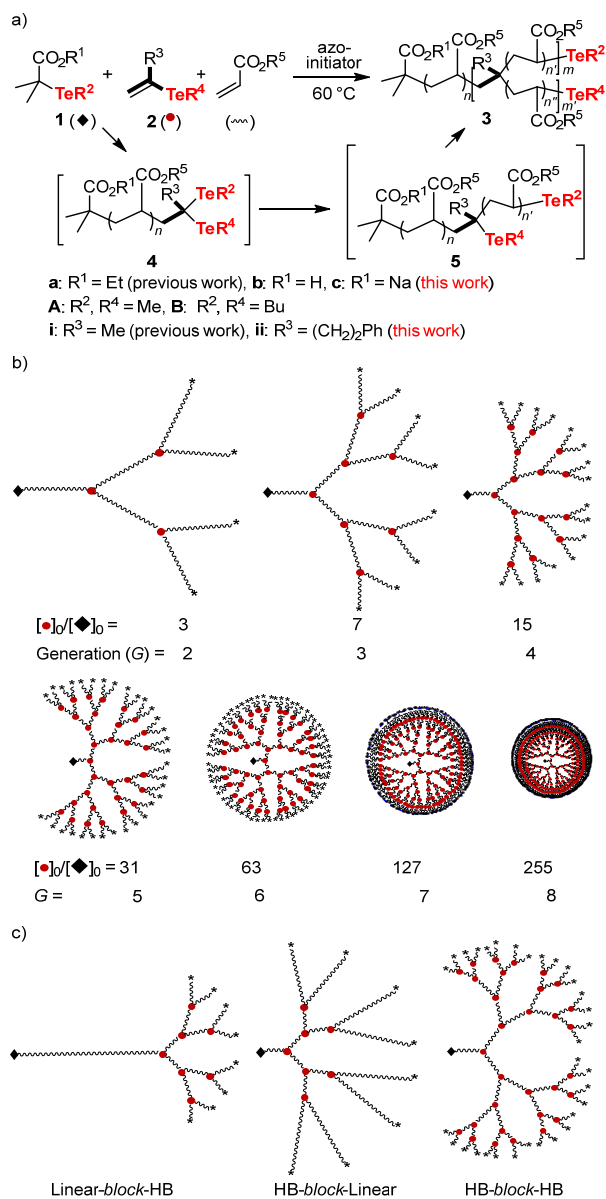
Highly branched polymers, i.e., hyperbranched polymers (HBPs) and dendrimers, are representative topological polymers with various potential applications as functional materials, i.e., viscosity modifiers for lubricants and coating,⁴ vehicles of drug delivery,^{5,6} scaffolds of nanoparticles,⁷ and catalysts.^{8,9} These unique properties lend themselves to their distinctive physical properties, i.e., smaller hydrodynamic volume, lower intrinsic viscosity, and presence of interior, originating from their topology.^{4,10-12} However, the practicality and the structural control of their synthesis have been a trade-off so far. For example, dendrimers and dendrons are the most structurally controlled highly branched polymers but are prepared only by multistep synthesis.¹³ In contrast, HBPs were synthesized in one step by condensation polymerization of AB_x monomers (A and B refer to two functional groups reacting with each other, and x is the number of the B group)^{14,15} and the self-condensing vinyl (co)polymerization [SCV(C)P] using a so-called inimar.¹⁶⁻²⁰ However, structural control cannot be generally achieved. Only

recently, Yokozawa and Gao have independently reported the controlled synthesis of HBPs by condensation polymerization using specially designed AB₂ monomer with defined conditions.^{21,22} However, no general method has been realized so far.

Recently, we have reported a new method of synthesizing structurally controlled HBPs in one step (Scheme 1).²³⁻²⁷ The method relies on the copolymerization of vinyl telluride **2Ai** (R³, R⁴ = Me) and conventional monomers in the presence of chain transfer agent (CTA) **1aA** (R¹ = Et, R² = Me) used in organotellurium-mediated radical polymerization (TERP).²⁸ In sharp contrast to the inimer, **2** does not initiate polymerization by itself but acts as an initiator after reacting as a monomer to form **4**. Then, stepwise activation of both C-Te bonds in **4** leads to the formation of HBP **3** via intermediate **5**. The most remarkable feature of this method is the ability to control the molecular weight, branch number, and branch length (the number of monomer units between branch points) by changing the ratio of **1**, **2**, and a conventional monomer. As the (pseudo) generation (*G*) can be defined as dendrimers, this type of HBPs can be named dendritic HBPs. Hereafter, we will refer to monomer **2** as an “evolmer” because **2** “evolves” its role from a monomer to an initiator by changing the reactivity of the C-Te bond and realizing the structural control in HBP synthesis.

Despite the high control, however, a practical drawback of this method is the high viscosity of the polymer products because the synthesis has been carried out under homogeneous conditions. The viscosity issue becomes more apparent in the synthesis of block copolymers, and a macroinitiator has to

Scheme 1. a) Synthesis of dendritic HB-polyacrylates using organotellurium CTA **1 and evolver **2** and schematic structure of b) homo HBPs with different generations and c) their topologic block polymers.**



dissolve to the second monomer over time. The other practical drawback was the synthesis of evolver **2Ai**. Due to its low boiling point (51–53 °C/33 torr), the isolated yield of **2Ai** was usually moderate (~40 %).

To solve the viscosity issue, we focused on emulsion polymerization,²⁹ which uses a water-soluble initiator in the presence of surfactants. As product polymers are obtained as particles in a heterogeneous mixture, viscosity issues can be avoided. Indeed, we have recently reported that the emulsion TERP of (meth)acrylates and styrenes using a water-soluble TERP CTA **1b** and found that the condition is highly suitable for synthesizing structurally controlled linear homo- and block copolymers.^{30–32}

The potential problem of the application of this method to the HBP synthesis was the diffusion of **2** and the conventional monomer from monomer droplet to polymer particles, where the polymerization takes place.^{33,34} As the current HBP synthesis relies on statistical copolymerization for the control of branch density, the inhomogeneous diffusion of both monomers leads to the loss of the control of branch structure. To clarify this point and further solve the low synthetic efficiency of **2Ai**, we synthesized new evolmers **2Aii** ($R^4 = \text{Me}$, $R^3 = (\text{CH}_2)_2\text{Ph}$), **2Bi** ($R^4 = \text{Bu}$, $R^3 = \text{Me}$), and **2Bii** ($R^4 = \text{Bu}$, $R^3 = (\text{CH}_2)_2\text{Ph}$), which have lower hydrophilicity and higher boiling point than **2Ai** has. These evolmers would also clarify the substituent effect on the Te group in HBP synthesis, as we have already reported that the chain transfer efficiency of the BuTe group is slightly lower than the MeTe group, leading to a decrease in the control of dispersity in linear polymer synthesis.³⁵

Here we report the synthesis of structurally controlled HBPs by emulsion TERP. Due to the high monomer conversion and the formation of well-dispersed polymer particles, the condition is well suited for the synthesis of block copolymers, giving a variety of “topological block polymers” consisting of block segments with different topology, linear and HBP. The most notable feature of the successful synthesis of HBPs and their topological block polymers is the ability to tune physical properties, such as intrinsic viscosity, by the branch structure and topology without changing the composition of the polymers. It is noted that the same synthetic strategy of HBPs based on atom transfer radical polymerization (ATRP) and reversible addition-fragmentation-chain-transfer (RAFT) conditions was also reported by Zhong^{36,37} and Chen³⁸, respectively. However, these methods lack generality due to low monomer conversion rates and difficulty in controlling copolymerization kinetics. Very recently, the application of the ATRP method in water was reported by Matyjaszewski, in which the copolymerization kinetics was improved.³⁹ However, no emulsion conditions have been reported to the best of our knowledge.

RESULTS AND DISCUSSION

Synthesis of New Evolmers. Evolmers **2Aii**, **2Bi**, and **2Bii** were synthesized by the same synthetic procedure used for the synthesis of **2Ai** (See Supporting Information). Thus, the corresponding vinyl bromides were treated with Mg, and the resulting vinyl Grignard reagents were reacted with Te powder generating the tellanyl anion species, which were reacted with methyl or butyl bromide afforded **2**. Purification by vacuum distillation gave **2Aii** and **2Bi** in 61% and 35% yields, respectively. While the reaction conditions were not optimized, the yield of **2Aii** was higher than that of **2Ai**. In contrast, **2Bii** was obtained in 11% yield by preparative gel permeation chromatography. The use of the bromide instead of the iodide gave a higher yield, probably **2** further reacts with alkyl iodide forming telluronium salt.

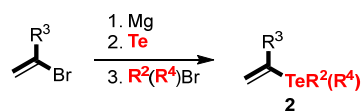


Figure 1. Synthesis of evolver **2**

Optimization of Evolver and Conditions for HBP synthesis. HB-poly(butyl acrylate) (HBPBA) with the 3rd generation ($G = 3$) was synthesized. Thus, carboxylic acid of CTA **1bA** ($R^1 = \text{H}$, $R^2 = \text{Me}$) in water in the presence of polyoxyethylene(20)

oleyl ether (Brij 98) (2.0 wt % to water) was neutralized with an aqueous NaOH solution (1.0 equiv.) forming water-soluble CTA **1cA** ($R^1 = \text{Na}$, $R^2 = \text{Me}$). Then, a solution of the sodium salt of 4,4'-azobis(4-cyanovaleric acid) (ACVA-Na) in deionized water (0.50 equiv.), BA (300 equiv., 20 wt% to water), and **2Aii** (7.0 equiv.) were added, and the resulting heterogeneous mixture was stirred at 65 °C (Table 1, run 1).^{40,41}

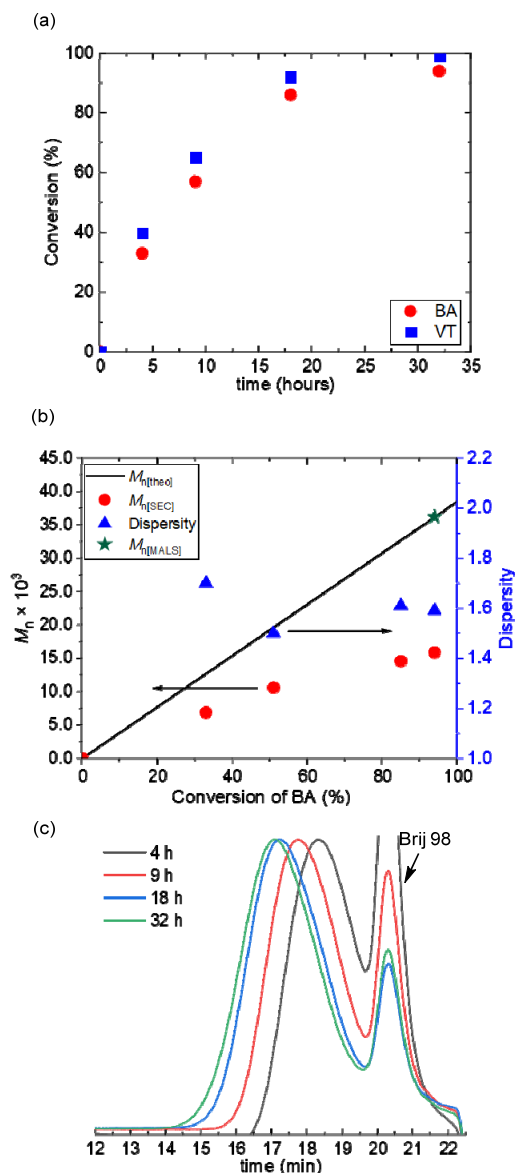


Figure 2. Correlation of molecular weight determined by SEC ($M_n(\text{SEC})$) and MALS ($M_n(\text{MALS})$), and dispersity (D) vs. conversion of BA. The dispersity (D) determined by SEC was 1.59.

Monitoring of the reaction indicated a similar consumption of both monomers, **2Aii** and BA, throughout the polymerization period (Figure 2a). The results suggest the efficient diffusion of both monomers to polymer particles and the statistical incorporation of the branch point in the polymer main chain. The number-average molecular weight determined by SEC ($M_n(\text{SEC})$) became smaller than the theoretical values ($M_n(\text{theo})$) with the increase in monomer conversion (Figure 2b). The results are consistent with the formation of HBPs, which have smaller hydrodynamic volumes than linear polymers. Furthermore, SEC

traces were unimodal and shifted to a high molecular weight region with monomer conversion (Figure 2c). The conversion of **2Aii** and BA reached 99 and 94%, respectively, after 32 h, and the M_n determined by multi-angle laser light scattering (MALS) ($M_n(\text{MALS}) = 36,200$) was very similar to the theoretical value ($M_n(\text{theo}) = 36,100$), while $M_n(\text{SEC})$ (15,900) was significantly smaller than $M_n(\text{theo})$ due to a smaller hydrodynamic volume of branched polymers than linear polymers. The molar fraction of BA and **2Aii** in the final HBPBA estimated from the monomer conversion (BA/**2Aii** = 40.7) was in good agreement with that estimated from the ^1H NMR analysis (BA/**2Aii** = 43.1) of the polymer from the characteristic signal of the phenyl group. The dispersity (D) determined by SEC was 1.59. All these results support the successful synthesis of HBPBA with a controlled structure. The polymer particle determined by dynamic light scattering (DLS) was reasonably controlled with an average diameter (d) of 143 nm and with a polydispersity index (PDI) of 0.14.

The substituent effects of the tellurium group were examined by synthesizing the same HBPBAs using evolmer **2Ai**, **2Bi**, and **2Bii** instead of **2Aii**. TeBu substituted CTA **1cB** ($R^1 = \text{Na}$, $R^2 = \text{Bu}$) was also used instead of **1cA**. Therefore, a total of 5 experiments were carried out by the combination of **1** and **2** (Supporting Information, Table S1, runs 2-6). While **2Ai** was phase-separated on the surface of the reaction mixture and did not diffuse efficiently to the polymer particle, all other evolmers diffused efficiently; the statistical copolymerization took place with a similar consumption of **2** and BA in all cases with 90% conversion (Figure S1), suggesting that the hydrophobicity of **2** did not affect its diffusion. Furthermore, all characteristic features of the control, i.e., the difference of $M_n(\text{MALS})$ and $M_n(\text{SEC})$, unimodality of the SEC traces, and low D of 1.68-2.06, were observed. While the dispersity ($D \sim 2.00$) was slightly larger than that obtained using **2Aii** and **2Bii**, the observed control was still far better than that used SCV(C)P. These results clearly show that **2Bi** and **2Bii** are also excellent evolmer. When comparing the results in detail, however, HBPBAs with narrower dispersities were formed for the CTA and evolmer having TeMe group, **1cA** and **2Aii**, respectively, than those having TeBu group. The results must be due to the higher chain transfer efficiency of the TeMe group than the TeBu group.³⁵ Therefore, we used CTA **1cA** and evolmer **2Aii** in the following experiments. The particle size was also fairly controlled with a PDI of 0.15-0.20.

The effect of surfactant was next examined. Both an anionic surfactant, sodium dodecyl sulfate (SDS), and a cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), were as effective as a non-ionic surfactant, Brij 98, and resulted in virtually identical results for the control of HBP synthesis (Table S1, runs 7-8). However, ionic surfactants tended to give larger particle sizes with broader PDIs. Therefore, Brij 98 was used in the following experiments except for the synthesis of high molecular weight (HMW) polymers (See below).

The concentration of the surfactant and monomer was next optimized using 1 or 4 wt% of Brij 98 and 10 or 40 wt% of BA to water (Table S1, runs 9-12). No apparent concentration effect was observed for the polymerization kinetics and the control of polymer structure, but an increase in particle size and PDI were observed. Therefore, 2 wt% of Brij 98 and 20 wt% of BA to water were used in the following experiments unless otherwise mentioned.

Synthetic Scope of HB-Polyacrylates. The scope of the structural control over molecular weight, dispersity, branch number, and branch length was evaluated by changing the $[\mathbf{1cA}]_0/[\mathbf{2Aii}]_0/[\mathbf{BA}]_0$ ratios. For example, the control of the branch number, in other words, dendritic generation G , and the branch length was successfully achieved for the synthesis of HBPBAs with $G = 2 - 6$ by changing the $[\mathbf{1cA}]_0/[\mathbf{2Aii}]_0$ ratios from 1/3 to 1/63 with keeping $[\mathbf{1cA}]_0/[\mathbf{BA}]_0$ ratio as 1/300 or 1/500 (Table 1, runs 1-5). Furthermore, characteristic features for the formation of structurally controlled HBPBAs were observed in all cases, i.e., unimodal SEC traces with low dispersity ($D < 2$), smaller $M_{n[\text{SEC}]}$ s than $M_{n[\text{theo}]}$ s, and $M_{n[\text{MALS}]}$ s close to $M_{n[\text{theo}]}$ s. All these results demonstrate the successful

synthesis of structurally controlled HBPBAs. The size of polymer particles was almost the same regardless of G . The results may suggest that the particle size is controlled primarily by the molecular weight.

The control over molecular weight and branch length was also successfully achieved. For example, the synthesis of 3rd generation HBPBAs with $M_{n[\text{MALS}]}$ s ranging from 9,700 to 108,000 with low dispersity ($D < 2$) was achieved by changing the $[\mathbf{1cA}]_0/[\mathbf{BA}]_0$ ratio from 1/100 to 1/1000 with keeping $[\mathbf{1cA}]_0/[\mathbf{2Aii}]_0$ of 1/7 (runs 1 and 6-8). The size of polymer particles also increased with the increase of molecular weight with keeping a reasonable size control (PDI ~ 0.15).³⁴

Table 1. Synthesis of HBPBAs by emulsion TERP using 1cA and 2Aii

Run ^a	The ratio of $\mathbf{1cA}/\mathbf{2Aii}/\mathbf{BA}$ (G)	time (h)	Conv. $\mathbf{2}^b$ (%)	Conv. BA ^b (%)	$M_{n[\text{theo}]}$ $\times 10^3$	$M_{n[\text{SEC}]}$ ^c $\times 10^3$	D ^c	$M_{n[\text{MALS}]}$ ^d $\times 10^3$	d^e (nm)	PDI ^e
1	1/7/300 (3)	32	99	94	36.1	15.9	1.59	36.2	142.6	0.14
2	1/3/500(2)	30	99	95	60.8	50.4	1.60	61.2	193.4	0.14
3	1/15/500(4)	44	98	92	59.0	32.3	1.59	54.0	197.5	0.16
4	1/31/500(5)	76	96	90	57.7	25.5	1.88	54.3	205.6	0.15
5	1/63/500(6)	108	96	80	51.3	14.2	1.74	55.5	204.2	0.18
6	1/7/100(3)	30	95	92	11.8	6.90	1.35	9.70	179.5	0.16
7	1/7/500(3)	30	96	90	57.7	35.8	1.69	53.3	204.1	0.14
8	1/7/1000(3)	40	93	90	115	75.0	1.90	108	216.8	0.16
9 ^f	1/63/1000 (6)	120	99	90	115	42.7	1.97	119	265.1	0.27
10 ^f	1/63/2000 (6)	144	96	90	244	78.9	1.88	216	287.2	0.20
11 ^g	1/127/4000 (7)	160	92	85	436	212	2.15	558	259.5	0.29
12 ^g	1/255/4000 (8)	300	98	83	426	50.0	2.60	465	202.6	0.26
13 ^h	1/7/300 (3)	40	99	94	36.1	33.0	1.59	45.2	164.2	0.19
14 ⁱ	1/7/300 (3)	40	99	90	27.0	15.2	1.69	27.7	194.0	0.10
15 ^j	1/7/500 (3)	40	99	71	35.5	16.2	1.60	40.2	136.9	0.10

^aA mixture of **1**, ACVA-Na (0.5 equiv.), a mixture of **2** and monomer (S20 wt% to water), and non-ionic surfactant Brij 98 (2 wt% to water) in water was stirred at 65 °C. ^bDetermined by ¹H NMR. ^cDetermined by SEC calibrated against PMMA standards. When the signal derived from Brij 98 overlapped with that of the product, the peak separation method was employed. ^dCalculated from $M_w[\text{MALS}]/D$, where $M_w[\text{MALS}]$ was weight-average molecular weight determined by MALS and D was dispersity determined by SEC. ^eDetermined by dynamic light scattering (DLS). ^fCationic surfactant CTAB (5 wt% to water) was used instead of Brij 98. ^gCationic surfactant CTAB (10 wt% to water) was used instead of Brij 98. ^htert-butyl acrylate was used instead of BA. ⁱEthyl acrylate was used instead of BA. ^jMethyl acrylate was used instead of BA.

As emulsion polymerization is suitable for the synthesis of HMW polymers,^{33,34} the synthesis of HMW HBPBAs with M_n exceeding 10^5 with $G = 3-8$ was next examined (runs 8-12). As the use of cationic surfactant, CTAB, showed better dispersity control than that of Brij 98 when targeting HMW polymers, probably due to the high particle stability (Table S1, runs 22-25), CTAB was employed as a surfactant for runs 9-12. Statistical copolymerization of **2Aii** and BA took place at nearly

the same consumption ratio with high monomer conversions (Figure S1, runs 24-27), and all HBPBAs synthesized showed characteristic features of the structural control from the SEC-MALS analyses (Figure S2, runs 24-27); the $M_{n[\text{MALS}]}$ close to the $M_{n[\text{theo}]}$ with unimodal SEC trace while the $M_{n[\text{SEC}]}$ significantly smaller than the $M_{n[\text{theo}]}$. Dispersity was below 2 when the targetted M_n was below 2.5×10^5 using 1000 or 2000 equivalents of BA with $G = 3$ or 6 (runs 8-10). Dispersity

increased 2.2 and 2.6 when the targeted M_n increased above 4×10^5 , but the level of control is acceptable considering the branch number, i.e., 127 and 255 corresponding to 7th and 8th generations, respectively. While HBPMA with the 7th generation was already synthesized under homogeneous conditions,²³ this is the first example of synthesizing the 8th generation.

Next, the generality of this method was examined by using other acrylates, i.e., *tert*-butyl acrylate (*t*BA), ethyl acrylate (EA), and methyl acrylate (MA) with targeting $G = 3$ (runs 13-15 in Table 1 and runs 28-30 in Table S1). Statistical copolymerization of each acrylate monomer and **2Aii** took place in all cases, and corresponding structurally controlled HB-polyacrylates were synthesized as judged by the monitoring of the reaction (Figure S1, runs 28-30). As the solubility of MA in water ($S_{MA} = 50 \text{ g L}^{-1}$ at 20 °C) is about 33 times higher than that of BA ($S_{BA} = 1.5 \text{ g L}^{-1}$ at 20 °C)⁴², about 25% of MA was

dissolved in water. Therefore, the conversion of MA became lower than that of BA, *t*BA, and EA. However, the control of the resulting HBPMA was essentially the same as those of HBPBA, HBP*t*BA, and HBPEA, proving the generality of this method.

Synthesis of Topological Block PBAs. We have already shown that the emulsion TERP is highly suitable for synthesizing block copolymers composed of linear segments^{31,32} because the monomer conversion reached nearly quantitative and the obtained polymer particles were well dispersed in water. Therefore, the feasibility of the synthesis of block polymers consisting of HBPBA block with different topologies, i.e., linear-*block*-HB, HB-*block*-linear, and HB-*block*-HB polymers, was tested (Scheme 1c). Since copolymers consisting of two blocks with different stereochemistry are called stereoblock polymers, this type of block polymers can be called topological block polymers.

Table 2. Synthesis of topologic block polymers by emulsion TERP using 1cA/2Aii

Run ^a	First block					Second block				
	2Aii/BA	time (h)	Conv. ^b (%)	M_n [MALS] ^c × 10 ³	\bar{D} ^c	2Aii/BA	time (h)	Conv. ^b (%)	M_n [MALS] ^c × 10 ³	\bar{D} ^c
1	0/500	6	NA ^d /95	60.8	1.30	7/500	70	99/95	144	1.64
2	0/500	6	NA ^d /95	64.8	1.29	15/500	92	99/90	130	1.80
3	0/500	6	NA ^d /96	64.0	1.29	31/500	120	98/90	128	1.79
4	7/500	65	99/95	61.5	1.75	0/500	24	NA ^d /92	143	2.10
5	15/500	80	99/95	60.3	1.89	0/500	24	NA ^d /95	162	2.02
6	31/500	118	99/95	59.9	1.94	0/500	24	NA ^d /92	140	2.21
7	7/500	65	99/93	58.1	1.80	27/500	120	99/92	126	2.29
8	0/1000	6	NA ^d /96	115	1.33	7/1000	65	99/90	204	1.55
9	7/1000	65	99/95	111	1.77	0/1000	40	NA ^d /95	221	2.20
10	7/1000	65	99/95	114	1.69	27/1000	120	99/90	199	2.48

^aThe first block was synthesized by heating a solution of **1cA**, azo-compound (0.5 equiv.), the first monomer (10 wt%), and CTAB (5 wt%). After monomer conversion reached >90%, the second monomer and azo compound (0.5 equiv.) were added, and the resulting mixture was stirred. ^bDetermined by ¹H NMR. ^cCalculated from M_w [MALS]/ \bar{D} , where M_w [MALS] was determined from MALS and \bar{D} was determined from SEC. ^dNot applicable as no **2Aii** was used.

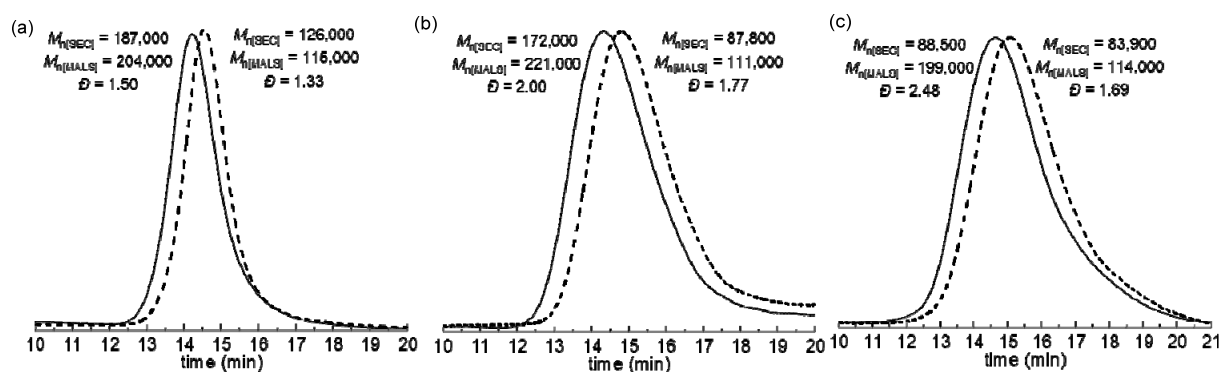


Figure 3. SEC traces of topologic block polymers by emulsion TERP. a) Table 2, run 8, b) run 9, and c) run 10. The dashed and solid lines represent macro-CTAs and block polymers, respectively.

First, linear-*block*-HB-PBA was synthesized. Emulsion TERP of BA (500 equiv.) using **1cA** gave structurally controlled linear PBA (M_n [MALS] = 60,800, $\bar{D} = 1.30$) macro-

CTA after 95% BA conversion. Then, a mixture of evolver **2Aii** (7 equiv) and BA (500 equiv.) was added, and the resulting mixture was heated with stirring for 70 h (Table 2, run 1).

Statistical copolymerization of **2Aii** and BA took place, and the desired linear-*block*-HB-PBA with $G = 3$ for the HB block was obtained ($M_{n[MALS]} = 144,000$, $\mathcal{D} = 1.64$) with high conversion of BA and **2Aii**. The SEC traces shifted to an HMW region with maintaining a unimodal shape, confirming the successful synthesis of the block polymer (Figure S4). Linear-*block*-HB-PBAs having the same molecular weight and linear block but different HB-structures, i.e., $G = 4$ and 5 , were also successfully synthesized by increasing the amount of **2Aii** to 15 and 31 equivalents, respectively (Table 2, runs 2 and 3).

The HB-*block*-linear-PBA having the same M_n was also synthesized by reversing the order of **2Aii** addition. Thus, after HBPBA ($M_{n[MALS]} = 61,500$, $\mathcal{D} = 1.75$) with $G = 3$ was synthesized using **2Aii** (7 equiv.) and BA (500 equiv.), the addition of BA (500 equiv.) afforded the desired block copolymer with the controlled structure ($M_{n[MALS]} = 143,000$, $\mathcal{D} = 2.10$) (run 4, Figure S4). The same topological block copolymers with different HB-structure, i.e., $G = 4$ and 5 , were also successfully synthesized starting from HBPBAs with $G = 4$ and 5 structures, respectively (runs 5 and 6).

Furthermore, HB-*block*-HB-PBA could also be synthesized; the macro-HBPBA-CTA with $G = 3$ ($M_{n[MALS]} = 58,100$, $\mathcal{D} =$

1.80) was synthesized. Then, the block copolymerization of **2Aii** (27 equiv.) and BA (500 equiv.), which targeted $G = 2$, gave the desired block copolymer ($M_{n[MALS]} = 126,000$, $\mathcal{D} = 2.29$) (run 7).

Topological block PBAs having the same topology but different molecular weights targeting the M_n around 2×10^5 were also successfully synthesized (runs 8-10). For the linear-*block*-HB-PBA, the same level of control with low dispersity ($\mathcal{D} = 1.55$) was obtained regardless of the targeted molecular weights (run 1 vs. run 8). While the dispersity control slightly dropped for HB-*block*-linear and HB-*block*-HB PBAs (runs 2 and 3 vs. runs 9 and 10, respectively), SEC analysis showed the apparent shift of SEC traces after the block polymerization to high molecular weight region with keeping unimodal shapes (Figure 3). All these results support the successful synthesis of the desired topological block copolymers.

It is also noting the high conversion of both monomers in all cases. Therefore, the purification of macro-CTAs was unnecessary, and the block copolymerization was started just after the addition of the second monomer(s). These results also add the practical advantages of the current emulsion condition for fabricating functional polymer materials.

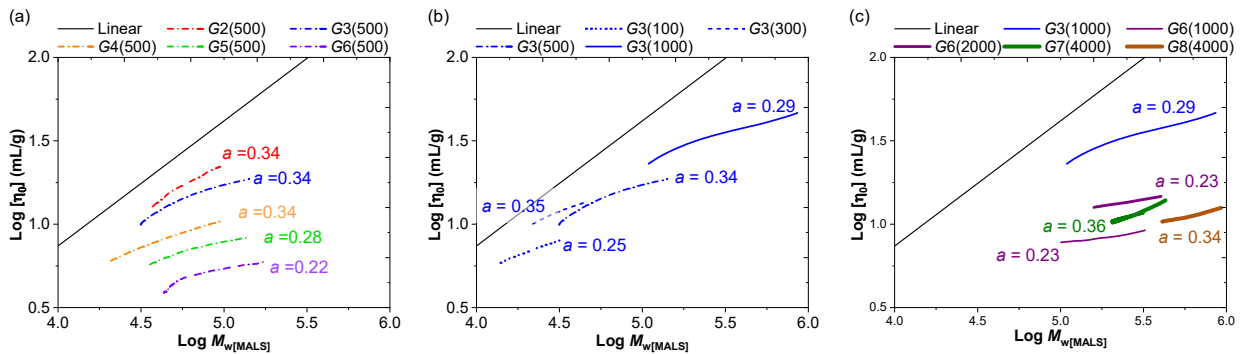


Figure 4. Intrinsic viscosity for HBPBAs for the samples with a) same molecular weight with different generation and branch length (Table 1, runs 1-5); b) same generation with different molecular weight and branch length (Table 1, runs 1 and 6-8); c) high molecular weight with different generation and branch length (Table 1, runs 8-12). The samples are named as $GX(Y)$, in which X and Y are the generation number and the equivalents of BA used for the synthesis, respectively.

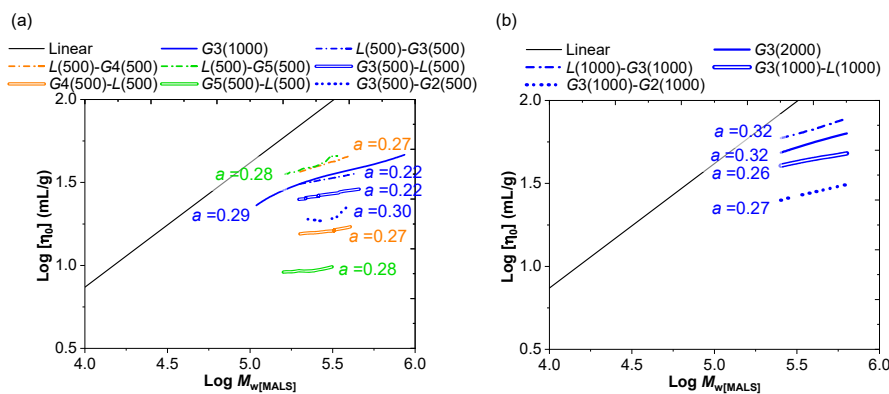


Figure 5. Intrinsic viscosity for HBPBAs for topological block polymers in a) Table 2, runs 1-7; b) Table 2, runs 8-10. The samples are named as $L(Z)-GX(Y)$, $GX(Y)-L(Z)$, and $GX(Y)-GX'(Y')$ for linear-*block*-HB, HB-*block*-linear, and HB-*block*-HB copolymers, respectively, in which $L(Z)$, $X [X']$, and $Y [Y']$ are the equivalents of BA used for linear polymer (L) synthesis, the generation number of block, the equivalents of BA used for HBPBA synthesis, and the equivalents of BA used for linear PBA synthesis, respectively.

Intrinsic viscosity of HBPBAs. The effect of branch and topological structure on intrinsic viscosity ($[\eta_0]$) of HBPBAs and their topological block polymers was studied by the SEC-

MALS-viscometer (Figures 4 and 5). Most importantly, the $[\eta_0]$ of all “homo” and block HBPBAs is lower than that of linear

PBAs with the same M_w and varies systematically with branch structure.

For the homo-HBPBAs samples having the same $M_{w[MALS]}$ but different G , $GX(500)$, synthesized with 500 equivalents of BA with generation number $X = 2-6$ by varying the amount of **2Aii** (Table 1, runs 1-5), the $[\eta_0]$ systematically decreased as the increase of G (Figure 4a). The exponent a in the Mark-Houwink-Sakurada (MHS) equation is 0.22-0.34, which is significantly smaller than that for linear PBA (0.75).⁴³ All these results support the successful synthesis of HBPBAs with a controlled branch structure.

The $[\eta_0]$ of homo-HBPBAs with the same generation ($G3(Y)$) with different $M_{w[MALS]}$ and branch length, synthesized with 7 equivalents of **2Aii** by varying the amount of BA, $Y = 100-1000$ (Table 1, runs 1 and 6-8), shows similar trends for the difference of the $[\eta_0]$ between HBPBAs and linear-PBA with the exponent a in the MHS equation of 0.25-0.35 (Figure 4b). The results are also consistent with the controlled branch structure.

The $[\eta_0]$ of homo-HBPBAs with the high generation, i.e., $G = 6, 7$, and 8 , is remarkably lower than that of linear PBA with the exponent a in the MHS equation of 0.23-0.36 (Table 1, runs 8-12 and Figure 4c). The $[\eta_0]$ of HBPBA $G3(1000)$ is the same as that of linear PBA having about 5 times smaller M_w , and that of $GX(Y)$ with $X = 6, 7$, and 8 and $Y = 1000, 2000$, and 4000 is the same as that of linear PBA with 10 to 100 times smaller M_w . For example, the $[\eta_0]$ of HBPBA $G8(4000)$ having $M_{w[MALS]}$ of about 10^6 is the same as that of linear PBA having M_w of 10^4 . These results clearly demonstrate the effect of controlled branch structure on viscosity and also indicate the potential of the current HBPBs as a highly effective viscosity modifier.

For the topological block PBAs of the same total M_w consisting of about 1000 BA units (Table 2, runs 1-7), a clear topological effect on the $[\eta_0]$ was observed (Figure 5a). Among linear-*block*-HB-PBBAs, $L(500)$ - $GX(500)$, consisting of 500 repeating BA linear units, L , and HB-PBA with $G = 3-5$, the $[\eta_0]$ is very similar but slightly increases as the increase of G . The results appear to contradict the results of the homo-HBPBAs but can be explained by considering that the linear structure is more influential on $[\eta_0]$ than the branch structure. Also, it is interesting to observe that very similar $[\eta_0]$ of block PBA, $L(500)$ - $G3(500)$, and homo PBA, $G3(1000)$. In contrast, the exponent a in the MHS equation (0.22-0.29) is less sensitive to the topology.

In sharp contrast to linear-*block*-HB-PBAs, the $[\eta_0]$ of HB-*block*-linear-PBAs with the same total M_w , $GX(500)$ - $L(500)$ with $X = 3-5$, is significantly affected by the branch structure and decreases as the increase of G (Figure 5a). This result is likely due to the low molecular weight of the linear blocks, preventing the effect of the linear units. Despite the differences of the $[\eta_0]$, the exponent a in the MHS equation (0.22-0.29) is also less sensitive to the length of the linear unit.

For the topological block PBAs of the same total M_w consisting of about 2000 BA units (Table 2, runs 8-10), a similar topological effect on the $[\eta_0]$ was observed (Figure 5b). Among linear-*block*-HB PBA, $L(1000)$ - $G3(1000)$, HB-*block*-linear PBA, $G3(1000)$ - $L(1000)$, and homo PBA, $G3(2000)$ having the same dendritic generation, the HB-*block*-linear PBA is least viscous followed by the homo PBA and the linear-*block*-HB PBA is most viscous. It is also interesting to note that the $[\eta_0]$ of HB-*block*-HB PBA, $G3(1000)$ - $G2(1000)$, is the lowest among the topological block copolymer samples with the same

M_w synthesized in this study and very similar to that of linear PBA with 10 times lower M_w . The exponent a in the MHS equation (0.26-0.32) is also less sensitive to the topology. All these results further support the sufficient control of branch structure synthesized by the current method.

CONCLUSIONS

Structurally well-controlled homo HBPBAs and their topological block copolymers with various molecular weights, branch numbers, and branch lengths were synthesized by emulsion TERP. The advantage of the emulsion condition over the homogeneous conditions includes the access to HBPs with the high generation, such as $G = 8$ having 255 branch number, and the synthesis of topological block polymers. These results open a possibility to finely tune polymer properties by controlling polymer topology. The effects of branch structure on practical polymer materials are now under investigation in our laboratory and will be reported in due course.

ASSOCIATED CONTENT

SUPPORTING INFORMATION.

The following files are available free of charge. Experimental details (Polymerization kinetics, SEC traces, and intrinsic viscosities), NMR spectra of new compounds, and polymerization conditions.

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Notes

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