Macromolecules **2005,** *38,* 5519−5525

$2A_2$ + BB′B″ Approach to Hyperbranched Poly(amino ester)s

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Received November 22, 2004; Revised Manuscript Received April 27, 2005

ABSTRACT: Hyperbranched poly(amino ester)s were synthesized via a novel $2A_2$ + BB′B″ approach, represented by the Michael addition polymerization of a trifunctional amine, 1-(2-aminoethyl)piperazine (AEPZ) (BB′B″-type monomer), with a double molar diacrylate, 1,4-butanediol diacrylate (BDA) (A_2-type monomer). The formation of $B''A_2$-type intermediate via its precursor, B′B″A-type intermediate, was verified by in situ monitoring the polymerizations using NMR and MS (ESI). High molecular weight hyperbranched poly(BDA2-AEPZ1) with vinyl terminal group was obtained from the $B''A_2$-type intermediate when the polymerization was performed in DMSO at 70 °C for ca. 101.0 h. Then the terminal vinyl group was tuned to primary, secondary, and tertiary amine, as verified by NMR. The radius of gyration (R_g) and hydrodynamic radius (R_h) of hyperbranched poly(BDA2-AEPZ1)-MPZ were measured using small-angle X-ray scattering (SAXS) and laser dynamic light scattering (LDLS), respectively, and the ratio of R_g/R_h of ca. 1.0 confirmed the hyperbranched structure. Molecular weights, glass transition temperatures (T_g), and thermal stability (T_d) of hyperbranched poly(amino ester)s were characterized using GPC, DSC, and TGA, respectively.

Introduction

Distinct from linear analogues, hyperbranched polymers have structures and topologies similar to dendrimers albeit with lower degrees of branching. So hyperbranched polymers show properties and functions close to dendrimers rather than their linear analogues and can substitute dendrimers in some applications.[1] Moreover, recent works showed some unique self-assembly of hyperbranched polymers.[2] In comparison with the tedious synthesis procedures for dendrimers, syntheses of hyperbranched polymers are much more straightforward; nevertheless, more cost-effective and novel approaches to hyperbranched polymers are still desirable. AB_m approaches usually start from specific AB_m monomers normally prepared by several steps.[3] Meanwhile, the approaches via the polymerization of multifunctional monomers with equal reactivity, mainly $A_2 + B_m$, must be performed under stringent conditions to avoid gelation, such as very low monomer concentrations, strictly controlled feed molar ratios, slow monomer addition rates, and low monomer conversions.[4−7] However, $A_2 + B_m$ approaches adopting monomers of suitable unequal reactivity have been demonstrated to be practical to preparing hyperbranched polymers from commercially available monomers in one-pot processes.[8−12] The monomers with unequal reactivity can be B_m-type monomers with B of different reactivity[8−10] or CB_m-type monomers.[11,12]

Recently, we found that the reactivity of the three types of amines in some trifunctional amines is different in the Michael addition polymerizations with diacrylates. For these trifunctional amines with less steric hindrance on the 2° amine (original), such as 1-(2-aminoethyl)piperazine (AEPZ) and 4-(aminomethyl)piperidine (AMPD), the reactivity sequence of the amine is 2° amine (original) > 1° amine ≫ 2° amine (formed).[14] On the basis of the results, we exploited a novel $2A_2$ + BB′B″ approach to hyperbranched poly(amino ester)s, where A_2 is diacrylate, BB′B″ is trifunctional amines, and B, B′, B″ represent the 2° amine (original), 1° amine, and 2° amine (formed), respectively. Hyperbranched poly(amino ester)s with terminal vinyl group are expected to be formed via $B''A_2$-type intermediate, which is formed through the reaction of the more reactive B and B′ groups with the double molar A_2. As a demonstration, here hyperbranched poly(amino ester)s were prepared through the Michael addition polymerization of AEPZ with a double molar 1,4-butanediol diacrylate (BDA). The polymerization mechanism was investigated, and hyperbranched poly(amino ester)s with terminal primary, secondary, and tertiary amines were produced through tuning the terminal vinyl group. The hyperbranched structure and properties of the obtained poly(amino ester)s were characterized. Poly(amino ester)s have been demonstrated to be promising materials for safe and efficient delivery of DNA and pH sensitive drug delivery.[15,16] The approach reported here would facilitate further optimization of both chemistries and topologies of poly(amino ester)s for wide applications.

Experimental Section

Characterization. ^1H NMR and ^{13}C NMR studies were performed on a Bruker DRX-400 spectrometer. Gel permeation chromatography (GPC) was implemented on a Waters 2690 apparatus with Waters Styragel HR 1 and 5E columns, a Waters 410 refractive index detector, and a miniDAWN light scattering detector (Wyatt Technology). 0.1 M piperidine/THF was used as eluent and polystyrene as standards. Thermogravimetric analysis (TGA) was conducted by scanning from 50 to 700 °C under nitrogen at a heating rate of 20 °C/min on a Perkin-Elmer TGA7, and T_d was taken as the temperature at which a 5% weight loss happened. Differential scanning calorimetry (DSC) was carried out on a TA modulated DSC 2920 under nitrogen. T_g was obtained in the second scan at a heating rate of 10 °C /min from −150 to 180 °C after samples were heated from 25 to 180 °C followed by quenching to −150

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10.1021/ma047580v CCC: $30.25

°C using liquid nitrogen. MS (ESI) was conducted on a Finnigan TSQ 7000. The spray voltage was 4.5 kV, and the capillary temperature was set at 250 °C.

A Brookhaven BI-9000AT digital autocorrelator was used for dynamic light scattering measurements. The scattering angle was fixed at 90° for measuring hydrodynamic radius (R_h). R_h and polydispersity (PDI), i.e., $\langle \mu_2 \rangle / \Gamma^2$, were obtained using a cumulant analysis. Small-angle X-ray scattering (SAXS) was performed on a SAXS system (Bruker AXS Inc. NanoStar SAXS) with a pinhole collimation configuration and a Cu Kα (λ = 1.5418 Å) radiation source. The SAXS signal was detected using a two-dimensional multiwire proportional HI-STAR area detector corrected for dark current, empty beam, solution cell, and solvent contributions. Samples were scanned at a voltage of 40 kV and a current of 35 mA. Scattering intensity $I(q)$ and corresponding wave vector q were collected for analysis, where $q = 4\pi \sin(\theta/\lambda)$; θ and λ are the scattering angle and the wavelength of X-ray, respectively.

Materials. 1,4-Butanediol diacrylate (BDA, 90%), 1-(2-aminoethyl)piperazine (AEPZ, 99%), deuterium chloroform ($CDCl_3$), deuterium dimethyl sulfoxide (DMSO-d_6), *N*-methylpiperazine (MPZ, 99%), benzyl-1-piperazine carboxylate (ZPZ, 98%), DMSO (99.9%), and palladium on carbon (Pd/C, 10%) were purchased from Aldrich. Piperidine (99%) was from Lancaster; chloroform, DMF, diethyl ether, and acetonitrile were from Tedia. BDA was purified by distillation under vacuum (90 °C/50 Pa) in the presence of a little amount of hydroquinone. DMSO was dried using molecular sieves, and other reagents were used as received.

In Situ Monitoring Polymerization Processes. Typically, a double molar BDA was added into a solution of AEPZ in $CDCl_3$ or DMSO-d_6 in a NMR tube. The monomer concentrations were around 20% (w/v), and the polymerizations were performed at 40 °C in chloroform and at 70 °C in DMSO. ^{13}C NMR spectra were recorded using a power-gated decoupling program (PD). 200 times scan taking around 10 min was enough to get a good ^{13}C NMR spectrum.

Synthesis of Hyperbranched Poly(BDA2-AEPZ1)-Vinyl. A typical process was that BDA (2.26 g, 11.4 mmol) was added into a solution of AEPZ (0.75 g, 5.7 mmol) in DMSO (15 mL). The polymerization was performed at 70 °C under an argon stream. The reaction was stopped after ca. 101.0 h when the ratio of the integral intensities of peaks at ca. 5.6–6.4 ppm (attributed to the protons in the vinyl groups) to those at ca. 4.0 ppm (of α-carbons in the 1,4-butanediol units) was close to 0.375 as monitored by ^1H NMR. The solution was used for tuning terminal groups directly.

Tuning the Terminal Groups of Hyperbranched Poly(amino ester). Poly(BDA2-AEPZ1)-MPZ. MPZ was added into the solution of poly(BDA2-AEPZ1)-vinyl in DMSO with the molar ratio of MPZ to the residual vinyl group being 1.1. The reaction was carried out overnight, and the solution was precipitated into diethyl ether under vigorous stirring. The polymer was collected and purified by precipitation from a chloroform solution into diethyl ether followed by drying under vacuum at room temperature for 3 days.

Poly(BDA2-AEPZ1)-PZ. First its precursor, poly(BDA2-AEPZ1)-ZPZ, was prepared by adding ZPZ into the solution of poly(BDA2-AEPZ1)-vinyl in DMSO. The molar ratio of ZPZ to the residual vinyl group was 1.1. After the reaction was performed at 40 °C for 24 h, the solution was precipitated into diethyl ether under vigorous stirring. The polymer was collected and purified by precipitation from a chloroform solution into diethyl ether followed by drying under vacuum at room temperature for 3 days.

Then the protection group was removed. A flask containing 1.5 g of Pd/C was evacuated and backfilled with hydrogen gas three times. 0.5 g of poly(BDA2-AEPZ1)-ZPZ in 15 mL of DMF was injected into the flask using a syringe. The mixture was stirred at ambient temperature for 24 h under hydrogen gas stream. Pd/C was removed by filtration and washed with 30 mL of DMF. The filtrate was combined and concentrated under vacuum at room temperature. The concentrated solution was precipitated into 300 mL of diethyl ether under vigorous stirring. The polymer was collected and purified by precipitation from a chloroform solution into diethyl ether followed by drying under vacuum at room temperature for 3 days.

Poly(BDA2-AEPZ1)-AEPZ. The solution of poly(BDA2-AEPZ1)-vinyl in DMSO was slowly added dropwise into a DMSO solution of AEPZ. The molar ratio of AEPZ to the residual vinyl group was 5. After the reaction was performed overnight, the solution was precipitated into diethyl ether under vigorous stirring. The polymer was collected and purified by precipitation from a chloroform solution into diethyl ether followed by drying under vacuum at room temperature for 3 days.

Results and Discussion

Mechanism of Polymerization. It is reasonable to speculate that the polymerization of the Michael addition polymerization of 2BDA + AEPZ can be described by Scheme 1 on account of the reactivity sequence of the three types of amines in AEPZ, i.e., 2° amine (original) > 1° amine ≫ 2° amine (formed).[14b] First, the 2° amine (original) would react with BDA, forming $B'B''A$-type intermediate, then the residual BDA should react with the 1° amine, producing $B''A_2$ type intermediate, and finally hyperbranched polymer could be obtained from the polymerization of the in situ formed $B''A_2$-type intermediate. To verify this speculation, ^{13}C NMR was used to in situ monitor the polymerization.

When the polymerization of 2BDA + AEPZ was performed in $CDCl_3$ at 40 °C, only $B'B''A$ intermediate was formed through the reaction of the most reactive 2° amine (original) with BDA at the beginning of the reaction (see Figure S1a in the Supporting Information). Then all the 2° amines (original) in AEPZ were consumed, and further all the 1° amines in the $B'B''A$ intermediate were converted to the 2° amine (formed) (Figures S1b and 1c). But the reactivity of the 2° amine (formed) was so low under this condition that the conversion was ca. 64% even after ca. 840.0 h as evaluated by the integral intensity ratio of peaks a_4 and a_3 (Figure S1d). Such a low reactivity should be due to the significantly increased steric hindrance.

To improve the reaction rate and get high molecular weight hyperbranched poly(amino ester)s, DMSO was used as the solvent, and the polymerization was performed at 70 °C instead. Figure 1 shows the results of in situ monitoring the polymerizations using ^{13}C NMR. The reaction rate was improved so remarkably that it was difficult to detect the formation of only $B'B''A$ intermediate, as indicated in Figure 1a. The peaks of both $B'B''A$ and $B''A_2$ intermediates appeared such as a_2 and a_3 at ca. 39.3 and 46.7 ppm, respectively, and no peaks of AEPZ were detectable in 0.5 h. Figure 1b illustrates that all $B'B''A$ intermediates disappeared in ca. 6.2 h, much shorter than 119.5 h needed for that performed in $CDCl_3$ at 40 °C. Then all the 2° amines (formed) were almost consumed in 101.0 h, as reflected in Figure 1c. The remarkable improvement in the reaction rate should result from a higher reaction temperature. In addition, DMSO probably facilitated the reaction. Moreover, no peaks of AEPZ, $B'B''A$ intermediate, and the 2° amine (formed) were detectable in Figure 1c, indicating that the Michael addition reaction was irreversible under this condition.

To further confirm the polymerization mechanism, a sample was drawn from the solution after the polymerization was performed in DMSO at 70 °C for 6.2 h. After being diluted to 1×10^{-5} g/mL in acetonitrile to avoid the further reaction, the sample was analyzed using MS (ESI). As depicted by Figure 2, a relatively intensive peak of $B''A_2$ intermediate appeared at m/z =

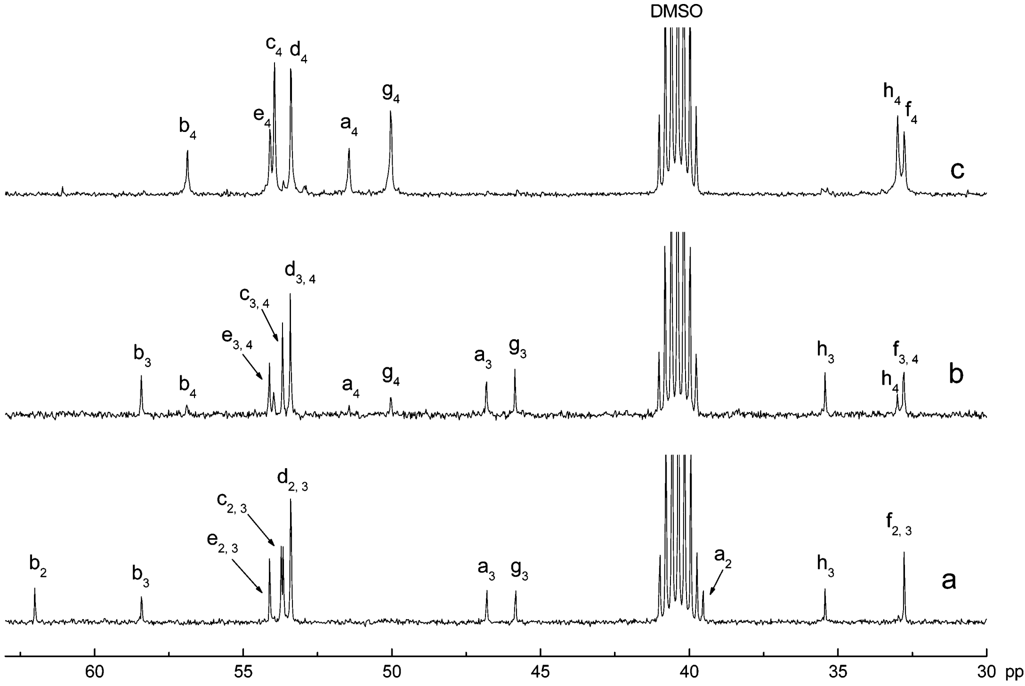
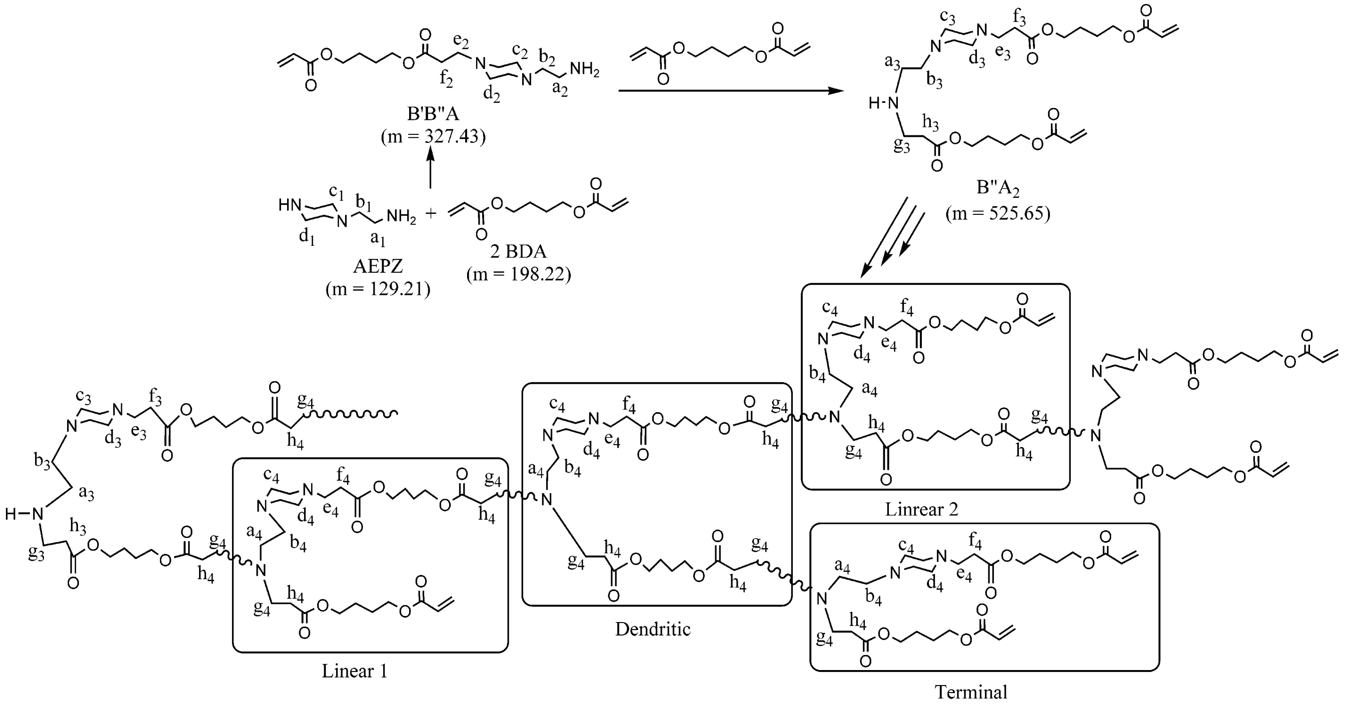


Figure 1. Comparison of the enlarged ^{13}C NMR spectra recorded in situ for the polymerization of BDA + AEPZ with a 2:1 feed molar ratio and a monomer concentration of 20% (w/v) at 70 °C in DMSO-d_6 for (a) 0.5, (b) 6.2, and (c) 101.0 h.

Scheme 1. Mechanism of the Michael Addition Polymerization of 2BDA + AEPZ



Poly(BDA2-AEPZ1)-vinyl

526.3. In addition, there were no peaks ascribed to monomer BDA and AEPZ. At this stage, the result of ^{13}C NMR shown in Figure 1b indicated all the B′B″A intermediate was consumed, and a little amount of the 2° amines (formed) joined in the reaction. Hence, it is reasonable to state that the reaction between B′B″A intermediate and the residual BDA forming B″A_2 intermediate was preferred, as described in Scheme 1.

According to the mechanism described in Scheme 1, the hyperbranched poly(amino ester)s obtained contained focal units as those from normal AB_2-type monomers. The peaks of those carbons adjacent to nitrogen in the focal units were overlapped with those of B″A_2 intermediate due to the negligible effects of the polymerization on the chemistries of these carbons. So, at the final stage of polymerization, the average number of structure units as from B″A_2 intermediate in a hyperbranched poly(amino ester) molecule could be roughly determined by the ratio of the integral intensity of peak a_4 to that of peak a_3. The ratio was ca. 1.8 for the product obtained by the polymerization performed in chloroform at 40 °C even for 840.0 h (Figure S1d).

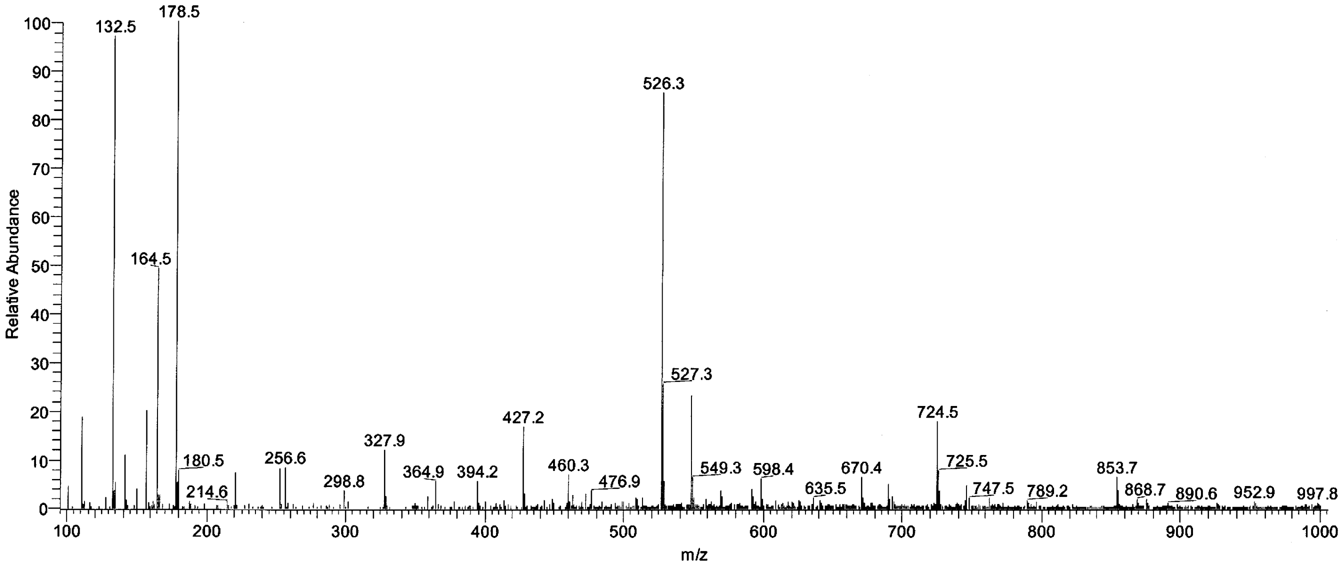
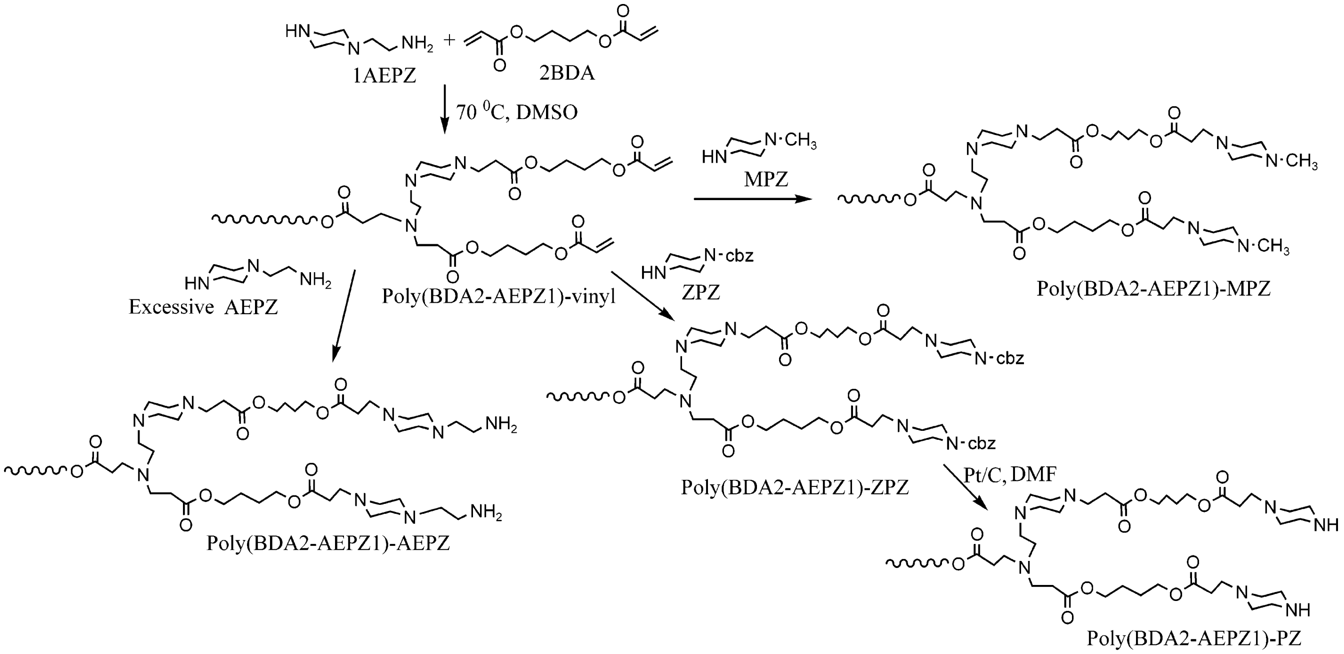


Figure 2. Mass spectrum of the sample drawn from the polymerization solution of 2BDA + AEPZ in DMSO at 70 °C for 6.2 h. The sample was diluted to 1×10^{-5} g/mL in acetonitrile.

Scheme 2. Approaches to Tuning the Terminal Groups of Hyperbranched Poly(BDA2-AEPZ1)-vinyl



So only oligomer containing 2.8 $B''A_2$ units was produced. In contrast, the peaks a_3 almost disappeared in Figure 2c; hence, the polymerization conducted in DMSO at 70 °C for 101 h provided a high molecular weight hyperbranched poly(amino ester).

Synthesis of Hyperbranched Poly(amino ester)s. Hence, hyperbranched poly(amino ester) with vinyl terminal groups, poly(BDA2-AEPZ1)-vinyl, was prepared by performing polymerization of 2BDA + AEPZ in DMSO at 70 °C. No gelation occurred through the polymerization processes. Because of the existence of an amount of reactive terminal vinyl groups, cross-linking occurred easily in the purification processes of poly(BDA2-AEPZ1)-vinyl, so a solid pure poly(BDA2-AEPZ1)-vinyl could not be obtained. Therefore, the terminal vinyl groups were changed into stable terminal groups.

It was interesting to prepare hyperbranched poly(amino ester)s with terminal primary, secondary, and tertiary amines due to different functions of different types of amines for DNA delivery.[17] We adopted the approaches as described in Scheme 2 to convert the terminal vinyl group into primary, secondary, and tertiary amines. The Michael addition reaction of the terminal vinyl group with a slight excess molar MPZ provided tertiary amine. The appearance of peaks k and c′ at ca. 46.4 and 55.4 ppm and the total disappearance of peaks m and n of vinyl groups at 129.3 and 132.2 ppm in Figure 3b indicated a complete conversion. Also, those peaks i_1 and l_1 attributed to the carbons adjacent to the vinyl group disappeared. Secondary amine-terminated hyperbranched poly(amino ester), poly(BDA2-AEPZ1)-PZ, was prepared by the reaction of the terminal vinyl group with ZPZ followed by removing the benzyl carbonate protection group. The appearance of the peaks of ZPZ such as peak k at ca. 67.4 ppm and the disappearance of the peaks of the vinyl group in Figure 4a illustrated the accomplishment of the reaction. The benzyl carbonate protection group could be

Table 1. Properties of the Hyperbranched Poly(amino ester)s with Different Terminal Groups

polymer	$M_n{}^a$	PDI^a	$M_n{}^b$	PDI^b	T_d (°C)^c	T_g (°C)
poly(BDA2-AEPZ1)-MPZ	29 160	3.41	62 520	3.70	238	−28.6
poly(BDA2-AEPZ1)-PZ	28 430	3.50	60 430	3.80	224	−25.8
poly(BDA2-AEPZ1)-AEPZ	38 140	3.70	69 780	3.90	210	−14.4

[a] Molecular weights were determined by GPC using 0.1 M piperidine + THF as the eluent and polystyrene standards. [b] Molecular weights were determined by GPC using 0.1 M piperidine + THF as the eluent and a miniDAWN light scattering detector. [c] Taken as the temperature at which a 5% weight loss happened.

easily removed using hydrogenation catalyzed by Pd/C, which was confirmed by the vanishing of the peaks of benzyl carbonate such as peak k at ca. 67.4 ppm and the appearance of the peaks of terminal piperazine group such as peak c′ at ca. 46.3 ppm in Figure 4b. Primary amine-terminated hyperbranched poly(amino ester), poly(BDA2-AEPZ1)-AEPZ, was prepared by the reaction of the terminal vinyl group with AEPZ on the basis of the lower reactivity of 1° amine than 2° amine (original). To prevent the reaction with the 1° amine, the solution of poly(BDA2-AEPZ1)-vinyl was added dropwise into a solution of an excess molar AEPZ in DMSO. The vanishing of the peaks of the vinyl group and the appearance of the peaks of carbon a′ and b′ at ca. 39.0 and 61.1 ppm in Figure 5 demonstrates that the terminal primary amine was obtained.

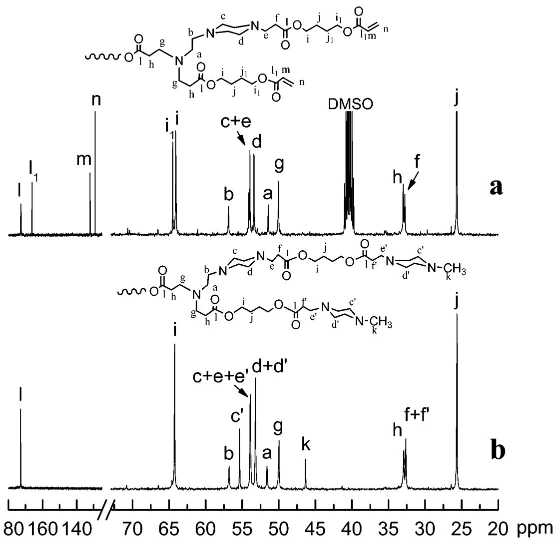


Figure 3. Comparison of the ^{13}C NMR spectrum of (a) poly(BDA2-AEPZ1)-vinyl in DMSO-d_6 with (b) poly(BDA2-AEPZ1)-MPZ in CDCl$_3$.

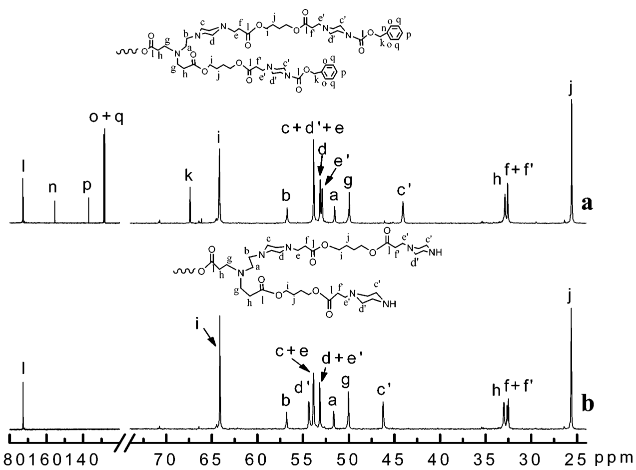


Figure 4. ^{13}C NMR spectra of (a) poly(BDA2-AEPZ1)-ZPZ and (b) poly(BDA2-AEPZ1)-PZ in CDCl$_3$.

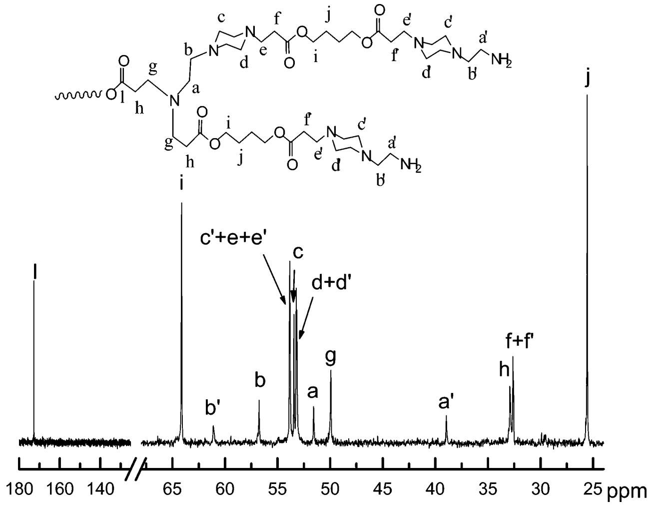


Figure 5. ^{13}C NMR spectrum of poly(BDA2-AEPZ1)-AEPZ in CDCl$_3$.

Hyperbranched Structure. Here DBs of hyperbranched poly(amino ester)s should be assessed by taking the B″A$_2$-type intermediate as a starting monomer. In this way, the terminal, linear, and dendritic units are defined as in Scheme 1. Nevertheless, the structural difference among the terminal, linear, and dendritic unit could not be distinguished in either ^{1}H or ^{13}C NMR, so the DBs according to this definition were difficult to be measured.

The ratio of hydrodynamic radius (R_h) to radius of gyration (R_g) of hyperbranched poly(amino ester) was measured to provide more information on the hyperbranched structures. Hyperbranched poly(BDA2-AEPZ1)-MPZ was adopted for investigation due to a less intermolecular interaction of the terminal tertiary amine. Methanol is a suitable solvent of poly(BDA2-AEPZ1)-MPZ for the measurement of R_h and R_g due to no aggregation in the solution. A 1% (w/w) solution of poly(BDA2-AEPZ1)-MPZ was prepared for the measurements. R_h of poly(BDA2-AEPZ1)-MPZ was measured to be 6.2 nm with a PDI of 0.301 using laser dynamic light scattering (LDLS). However, R_g was too small to be determined using LDLS. SAXS has been used to measure R_g of dendrimers and hyperbranched polymers.[18] Therefore, we also applied SAXS to measure R_g of poly(BDA2-AEPZ1)-MPZ. The method used to fit SAXS results depended on the structures of polymers. For poly(BDA2-AEPZ1)-MPZ, the partial Berry plot as described by eq 1[19] presented a better fitting as compared with other fitting methods such as the Zimm plot and the Guinier plot.[18a]

$$(1/I(q))^{1/2} = C(1 + R_g{}^2q^2/6) \qquad (1)$$

where $I(q)$ is the scattered intensity, q is the scattering wave vector, and C is a constant. R_g was determined to be 6.2 nm. Therefore, the ratio of R_h/R_g for poly(BDA2-

AEPZ1)-MPZ was 1.0. The values of R_g/R_h are around 1.5−1.7 for linear flexible polymers in good solvent, 1.079 for hyperbranched polymers from AB_2-type monomers, and 0.78 for uniform spheres.[20] Hence, the spatial structures of hyperbranched poly(amino ester)s obtained were close to those from AB_2-type monomers, which coincided with the mechanism of polymerization.

Properties of Hyperbranched Polymers. All the primary, secondary, and tertiary amine-terminated hyperbranched poly(BDA2-AEPZ1) had good solubility in methanol, water, chloroform, dichloromethane, acetone, DMSO, DMF, and THF. The molecular weights of these polymers were evaluated using GPC. The relative molecular weights based on polystyrene standards and the absolute values measured by a miniDAWN light scattering detector are listed in Table 1. These relative values were different from the absolute values due to the different hydrodynamic behaviors between hyperbranched poly(amino ester)s and polystyrene standards. For example, the absolute molecular weight of hyperbranched poly(BDA2-AEPZ1)-MPZ obtained was 62 520 higher than the relative value of 29 160. In addition, the high PDI values of polymers obtained were reasonable for the staged polymerizations and polymerizations of AB_2-type monomers.

Hyperbranched polymers have an amount of terminal groups which have effects on their properties. As shown in Table 1, the terminal group of hyperbranched poly(BDA2-AEPZ1) affects the properties apparently as reported for other hyperbranched polymers.[10,21] The three kinds of hyperbranched poly(amino ester)s with different terminal group were prepared from the same precursor, so their core structures were almost the same. With the terminal group being changed from primary to secondary and tertiary amine, T_g decreased probably due to the decreased hydrogen-bonding interaction; meanwhile, T_d increased, indicating an increased thermal stability.

Conclusions

On the basis of the amine reactivity sequence of 2° amine (original) > 1° amine ≫ 2° amine (formed) for AEPZ (BB′B″-type monomer) in the Michael addition polymerization with diacrylate such as BDA (A_2-type monomers), a novel $2A_2 + BB'B''$ approach to hyperbranched poly(amino ester)s was set up. High molecular weight hyperbranched poly(amino ester) with vinyl terminal group, poly(BDA2-AEPZ1)-vinyl, was obtained by the Michael addition polymerization of AEPZ with a double molar BDA via $B''A_2$-type intermediate. The $B''A_2$-type intermediate was formed from B′B″A intermediate. The vinyl terminal group was tuned into primary, secondary, and tertiary amines, and the terminal group had effects on the properties of hyperbranched poly(amino ester)s. The hyperbranched poly(amino ester)s obtained had hyperbranched structures close to those from AB_2-type monomers as reflected by the ratio of R_g/R_h of 1.0, which coincided with the mechanism of polymerization. The properties of these novel poly(amino ester)s with different types of terminal amine for DNA delivery were being investigated.

Acknowledgment. We are grateful to Dr. K. Y. Mya for her help in light scattering measurements.

Supporting Information Available: ^{13}C and ^{1}H NMR spectra for polymerization of BDA + AEPZ, ^{1}H NMR spectra of poly(BDA2-AEPZ1)-AEPZ, poly(BDA2-AEPZ1)-MPZ, poly(BDA2-AEPZ1)-PZ, and poly(BDA2-AEPZ1) in $CDCl_3$, and partial Berry plot of poly(BDA2-AEPZ1)-MPZ in methanol. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Voit, B. I. *C. R. Chimie* **2003**, *6*, 821. (b) Jikei, M.; Kakimoto, M. *Prog. Polym. Sci.* **2001**, *26*, 1233. (c) Jikei, M.; Kakimoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 1293. (d) Haag, R. *Angew. Chem., Int. Ed.* **2004**, *43*, 278. (d) Stiriba, S. E.; Kautz, H.; Frey, H. *J. Am. Chem. Soc.* **2002**, *124*, 9698.

(2) (a) Ornatska, M.; Bergman, K. N.; Rybak, B.; Peleshanko, S.; Tsukruk, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5246. (b) Ornatska, M.; Peleshanko, S.; Genson, K. L.; Rybak, B.; Bergman, K. N.; Tsukruk, V. V. *J. Am. Chem. Soc.* **2004**, *126*, 9675. (c) Yan, D. Y.; Zhou, Y. F.; Hou, J. *Science* **2004**, *303*, 65. (b) Zhou, Y. F.; Yan, D. Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 4896.

(3) See example: (a) Flory, P. J. *J. Am. Chem. Soc.* **1952**, *74*, 2718. (b) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592. (c) Kim, Y. H.; Webster, O. W. *Macromolecules* **1992**, *25*, 5561. (d) Harth, E. M.; Hecht, S.; Helms, B.; Malmstrom, E. E.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2002**, *124*, 3926. (e) Hawker, C. J.; Lee, R.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583.

(4) Fang, J. H.; Kita, H.; Okamoto, K. *Macromolecules* **2000**, *33*, 4639.

(5) Lin, Q.; Long, T. E. *Macromolecules* **2003**, *36*, 9809.

(6) Unal, S.; Yilgor, I.; Yilgor, E.; Sheth, J. P.; Wilkes, G. L.; Long, T. E. *Macromolecules* **2004**, *37*, 7081.

(7) Stumbe, J. F.; Bruchmann, B. *Macromol. Rapid Commun.* **2004**, *25*, 921.

(8) (a) Jikei, M.; Chon, S. H.; Kakimoto, M.; Kawauchi, S.; Imase, T.; Watanebe, J. *Macromolecules* **1999**, *32*, 2061. (b) Jikei, M.; Kakimoto, M. *High Perform. Polym.* **2001**, *13*, S33. (c) Monticelli, O.; Mariani, A.; Voit, B.; Komber, H.; Mendichi, R.; Pitto, V.; Tabuani, D.; Russo, S. *High Perform. Polym.* **2001**, *13*, S45.

(9) (a) Hao J. J.; Jikei, M.; Kakimoto, M. *Macromolecules* **2002**, *35*, 5372. (b) Hao J. J.; Jikei, M.; Kakimoto, M. *Macromolecules* **2003**, *36*, 3519.

(10) Liu, Y.; Chung, T. S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 4563.

(11) (a) Bruchman, B.; Koniger, R.; Renz, H. *Macromol. Symp.* **2002**, *187*, 271. (b) Abdelrehim, M.; Komber, H.; Langenwalter, J.; Voit, B.; Bruchmann, B. *J. Polym. Sci., Part A: Polym. Chem.* **2004**, *42*, 3062. (c) Gao, C.; Yan, D. Y. *Macromolecules* **2003**, *36*, 613.

(12) (a) Li, X. R.; Zhan, J.; Li, Y. S. *Macromolecules* **2004**, *37*, 7584. (b) Benthem, R. A. T. M.; Meijerink, N.; Gelade, E.; Koster, C. G.; Muscat, D.; Froehling, P. E.; Hendriks, P. H. M.; Vermeulen, C. J. A. A.; Zwartkruis, T. J. G. *Macromolecules* **2001**, *34*, 3559.

(13) Chang, Y. T.; Shu, C. F. *Macromolecules* **2003**, *36*, 661.

(14) (a) Liu Y.; Wu, D. C.; Ma, Y. X.; Tang, G. P.; Wang, S.; He, C. B.; Chung, T. S.; Goh, S. H. *Chem. Commun.* **2003**, 2630. (b) Wu, D. C.; Liu Y.; He, C. B.; Chung, T. S.; Goh, S. H. *Macromolecules* **2004**, *37*, 6763.

(15) (a) Lynn, D. M.; Langer, R. *J. Am. Chem. Soc.* **2000**, *122,* 10761. (b) Lynn, D. M.; Anderson, D. G.; Putnam, D.; Langer, R. *J. Am. Chem. Soc.* **2001**, *123*, 8155. (c) Akinc, A.; Lynn, D. M.; Anderson, D. G.; Langer, R. *J. Am. Chem. Soc.* **2003**, *125*, 5316. (d) Anderson, D. G.; Lynn, D. M.; Langer, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 3153. (e) Lim, Y. B.; Kim, S. M.; Lee, Y.; Lee, W. K.; Yang, T. G.; Lee, M. J.; Suh, H.; Park, J. S. *J. Am. Chem. Soc.* **2001**, *123*, 2460.

(16) (a) Lynn, D. M.; Amiji, M. M.; Langer, R. *Angew. Chem., Int. Ed.* **2001**, *40*, 1707. (b) Vazquez, E.; Dewitt, D. M.; Hammond, P. T.; Lynn, D. M. *J. Am. Chem. Soc.* **2002**, *124*, 13992.

(17) (a) Boussif, O.; Lezoualc'h, F.; Zanta, M. A.; Mergny, M. D.; Scherman, D.; Demeneix, B.; Behr, J. P. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 7297. (b) Behr, J. P. *Chimia* **1997**, *1*, 34.

(18) (a) Prosa, T. J.; Bauer, B. J.; Amis, E. J.; Tomalia, D. A.; Scherrenberg, R. *J. Polym. Sci., Part B: Polym. Phys.* **1997**, *35*, 2913. (b) Prosa, T. J.; Bauer, B. J.; Amis, E. J. *Macromolecules* **2001**, *34*, 4897. (c) Ghosh, S. K.; Kawaguchi, S.; Jinbo, Y.; Izumi, Y.; Yamaguchi, K.; Taniguchi, T.; Nagai, K.; Koyama, K. *Macromolecules* **2003**, *36*, 9162.

(19) Berry, G. C. *J. Chem. Phys.* **1966**, *44*, 4550.

(20) (a) Burchard, W. *Adv. Polym. Sci.* **1985**, *48*, 1. (b) Guan, Z. B.; Cotts, P. M.; McCord, E. F.; McLain, S. J. *Science* **1999**,

283, 2059. (c) Scherrenberg, R.; Coussens, B.; Vliet, P. v.; Edouard, G.; Brackman, J.; Brabander, E.; Mortensen, K. *Macromolecules* **1998**, *31*, 456.

(21) (a) Markoski, L. J.; Moore, J. S.; Sendijarevic, I. S.; Lee, A.; McHugh, A. J. *Macromolecules* **2001**, *34*, 2695. (b) Wooley, K. L.; Hawker, C. J.; Pochan, J. M.; Frechet, J. M. J. *Macromolecules* **1993**, *26*, 1514. (c) Stutz, H. *J. Polym. Sci., Part B: Polym. Phys.* **1995**, *33*, 333.

MA047580V