Blue Photoluminescence from Hyperbranched Poly(amino ester)s

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Fluorescence technology has been applied in many areas; especially fluorescence imaging technology plays more and more important roles in biological science.[1−3] Fluorescence can be observed from organic materials typically containing aromatic molecules,[1] and the luminescent property was reported for some inorganic species such as lanthanides,[1] quantum dots, or notable metal nanoclusters.[3] Very recently, it was reported that two popular dendrimers, poly(amidoamines) (PAMAM) and poly(propyleneimine) (PPI), showed strong photoluminescence under suitable conditions, and those dendrimers were expected to function as novel fluorophores.[4,5] Here we report that hyperbranched poly(amino ester)s developed in our lab could also emit blue photoluminescence. These poly(amino ester)s are biodegradable and thus are more biocompatible than PAMAM and PPI. In addition, this phenomenon implied further that similar compacted spatial morphology and abundant terminal groups render hyperbranched polymers some properties similar to dendrimers.[6] However, syntheses of hyperbranched polymers are much more straightforward and economical.

Hyperbranched poly(amino ester)s with terminal monohydroxyl groups (poly(BDA2-AEPZ1)-OH), primary amines (poly(BDA2-AEPZ1)-NH_2), and diol groups (poly(BDA2-AEPZ1)-$(OH)_2$) were obtained from poly(BDA2-AEPZ1)-vinyl, as shown in Scheme 1. Poly(BDA2-AEPZ1)-vinyl could be prepared by the Michael addition polymerization of a trifunctional amine, 1-(2-aminoethyl)piperazine (AEPZ), with a double molar diacrylate, 1,4-butanediol diacrylate (BDA), as described in our previous works.[7] The terminal vinyl group was tuned to the target terminal group through the Michael addition reaction with an excess molar AEPZ,[7] 2-aminoethanol, and 3-amino-1,2-propanediol as verified by ^{13}C NMR (Figure S1 in the Supporting Information). The molecular weights and the degrees of branching of the three kinds of hyperbranched poly(amino ester)s were similar due to the same core. For poly(BDA2-AEPZ1)-NH_2, M_n was ca. 62 520 with a polydispersity index (PDI) of 3.41 measured using GPC with a light scattering detector. R_g and R_h were measured in methanol using laser light scattering and small-angle X-ray scattering, respectively. R_g/R_h of 1.1 was close to the ratio of hyperbranched polymers from AB_2 monomers, indicating a hyperbrached spatial morphology.[8]

0.5 mM (ca. 1% w/w) aqueous solutions of hyperbranched poly(amino ester)s with terminal groups similar to those dendrimers reported[4,5] were prepared for photoluminescence characterization. Figure 1 shows that poly(BDA2-AEPZ1)-OH, poly(BDA2-AEPZ1)-NH_2, and poly(BDA2-AEPZ1)-$(OH)_2$ had emission bands at 473, 469, and 456 nm with the excited bands at 394, 373, and 372 nm, respectively. All the emission intensities increased with increased concentrations similar to that from PAMAM (Figure S2).[5] In addition, those hyperbranched polymers also showed similar fluorescent behavior in THF solutions (Figure S3).

The effects of oxidation through treatment with $(NH_4)_2S_2O_8$ (PS) or just exposure to air and pH on the fluorescence property of hyperbranched poly(amino ester)s were investigated. In these processes, poly(amino ester)s might hydrolyze in aqueous solutions, which may affect the fluorescence properties. The hydrolysis behavior of poly(amino ester)s could be monitored using the decreases in the relative contents of ester bonds measured by ^1H NMR as reported.[9] The results showed that the hydrolysis was much faster in acidic conditions. For poly(BDA2-AEPZ1)-OH, ca. 80% of the ester bonds were hydrolyzed at pH 3 in 450 h; however, almost no hydrolysis was detectable at pH 7 or under PS treatment (Figure S4).

At pH 7, both PS treatment and exposure to air improved the fluorescence intensities of all the three hyperbranched poly(amino ester)s. Figure 2a shows that the fluorescence intensities of poly(BDA2-AEPZ1)-OH increased by 4.7 times in ca. 50 h after PS treatment and by 3.0 times in ca. 360 h after exposure to air and then faded. Similarly, Figure 2b depicts that the maximum fluorescence intensities of poly(BDA2-AEPZ1)-NH_2 were obtained in ca. 52 and 488 h with ca. 4.3 and 2.0 times increases by PS treatment and exposure to air, respectively. In comparison, Figure 2c reflects that the fluorescence intensity of poly(BDA2-AEPZ1)-$(OH)_2$ increased much slower and leveled off after ca. 500 h, and the increscent degrees were less than 2.0 times for both oxidation methods. Note that exposure to air led to slower increases in the fluorescence intensities than PS treatment, but the fluorescence intensities obtained were comparable or even higher. NH_4PF_6 treatment produced similar results.

All the three hyperbranched poly(amino ester)s showed pH-dependent photoluminescence emission similar to PAMAM.[5] Adjusting pH from 11.7 to 6.0 led to no significant changes in fluorescence intensities, but further reducing pH from 6.0 to 2.0 led to higher fluorescence intensities. Maximum fluorescence intensities appeared at around pH 3.0 with a 4.0 times increase in the fluorescence intensity of poly(BDA2-AEPZ1)-OH, but less than 2 times increases for poly(BDA2-AEPZ1)-NH_2 and poly(BDA2-AEPZ1)-$(OH)_2$ (Figure S5). In addition, Figure 2 indicates that exposure to air at pH 3 led to faster increases in fluorescence intensities for all the three hyperbranched poly(amino ester)s. This may resulted from that all the tertiary amines were protonated at pH 3, and the compacted spatial morphologies became very open.[10] But the fluorescence intensity of poly(BDA2-AEPZ1)-OH decreased with time significantly at pH 3 as depicted in Figure 2a, which should be due to the faster hydrolysis. In contrast, the

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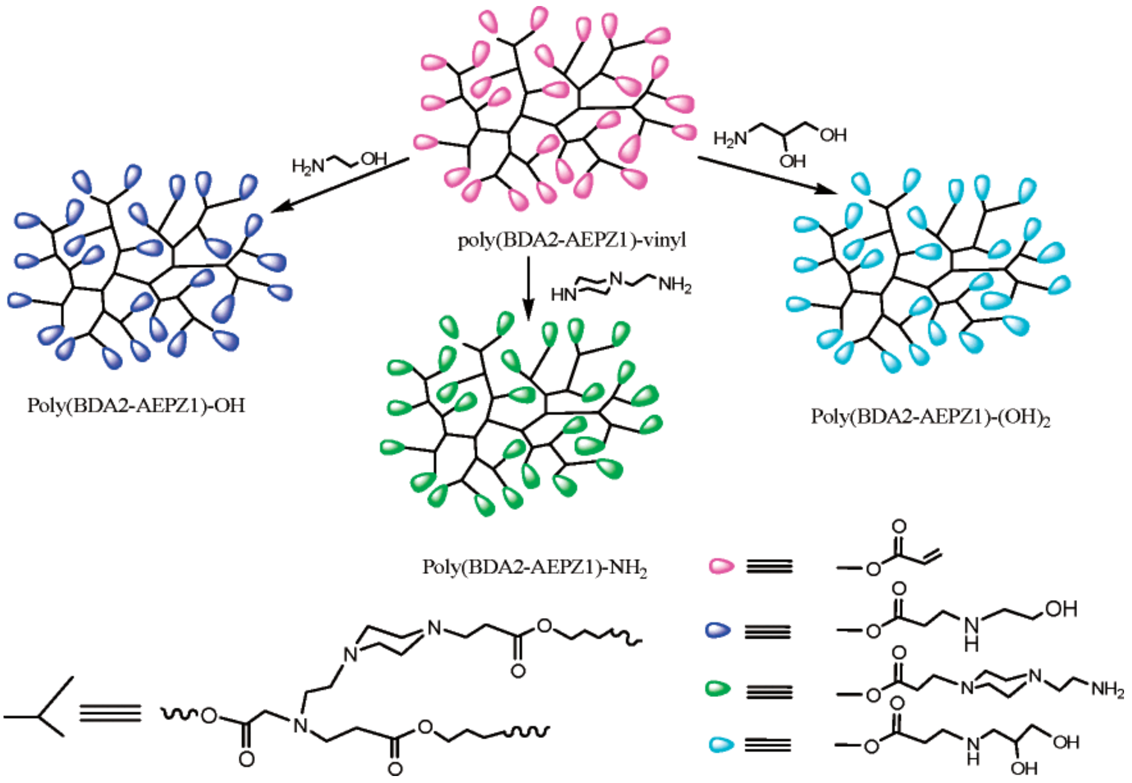
Scheme 1. Reaction Scheme for Preparing Hyperbranched Poly(amino ester)s with Different Terminal Groups



fluorescent intensities of poly(BDA2-AEPZ1)-NH_2 and poly(BDA2-AEPZ1)-$(OH)_2$ were almost constant. The difference should result from the strongest original fluorescent intensity of poly(BAD2-AEPZ1)-OH, as illustrated in Figure 2. Poly(BDA2-AEPZ1)-OH also emitted the strongest fluorescence under PS treatment or exposure to air at pH 7, similar to the results of Lee et al.[4] The quantum yield of poly(BDA2-AEPZ1)-OH after PS treatment for 48 h at pH 7 was 3.5%.

The fluorescence from PAMAM was attributable to the formation of some kinds of fluorescent chemical species with the structures still unidentified.[4,5] Similarly, some kinds of fluorescent chemical species should be formed in the solutions of poly(amino ester)s reported here. For example, a new absorption band at 394 nm appeared in the differential UV spectrum of the aqueous solution of poly(BDA2-AEPZ1)-OH after exposure to air for 6 days, as shown in Figure 3, but meanwhile no convincing changes in the chemical structures could be detected by ^1H and ^{13}C NMR. Hyperbranched poly(amino ester)s have several structural features similar to PAMAM, i.e., the abundant terminal groups, dendritic morphology albeit with lower degrees of branching, and a coexistence of tertiary amines and carbonyl groups in the core (esters groups for poly(amino ester)s and amide groups for PAMAM). In contrast, no photoluminescence was observed from 0.5 mM aqueous solutions of model polymers, i.e., linear poly(amino ester), poly(BDA-PZ), containing ester groups and tertiary amines in the backbones prepared via the polymerization of BDA and piperazine (PZ) (M_n = 10 970, M_w/M_n = 1.94)[11] or a commercially available hyperbranched polyethylenimine (PEI) (M_n = 25 000) containing primary amines in the periphery and secondary and tertiary amines in the core (Figure S6). Hence, a coexistence of tertiary amines/carbonyl groups in the core and compacted dendritic architecture with abundant suitable terminal groups was indispensable to showing blue fluorescence. Neither the coexistence of tertiary amines and carbonyl groups as in the linear poly(BDA-PZ) nor the combination of the hyperbranched structures and the amines as in PEI could produce photoluminescence, although G5 PPI was reported to show photoluminescence.[5]

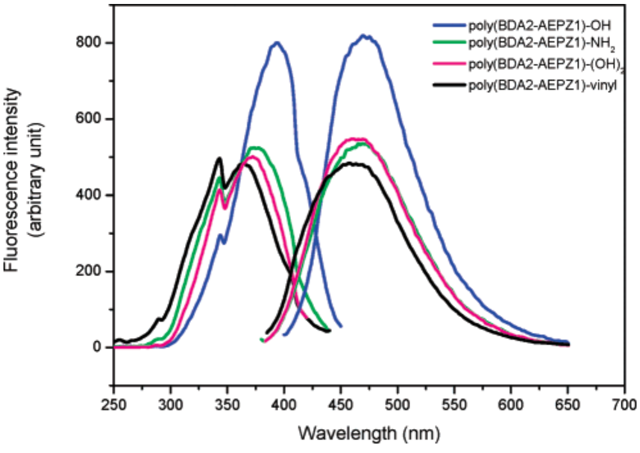


Figure 1. Emission and excitation spectra of 0.5 mM aqueous solutions of poly(BDA2-AEPZ1)-OH, poly(BDA2-AEPZ1)-NH_2, poly(BDA2-AEPZ1)-$(OH)_2$ at pH 7 with exposure to air, and 0.5 mM solution of poly(BDA2-AEPZ1)-vinyl in DMSO without exposure to air.

Oxidation via PS treatment or just exposure to air favored the formation of stronger fluorescence as indicated by the above results and those reported.[4] But it is interesting to investigate whether oxidation treatment is indispensable to the fluorescence of dendritic polymers, which will facilitate a further understanding of the mechanism. Experimentally, it is difficult to prevent air exposure across the whole synthesis and purification processes of these hyperbranched poly-

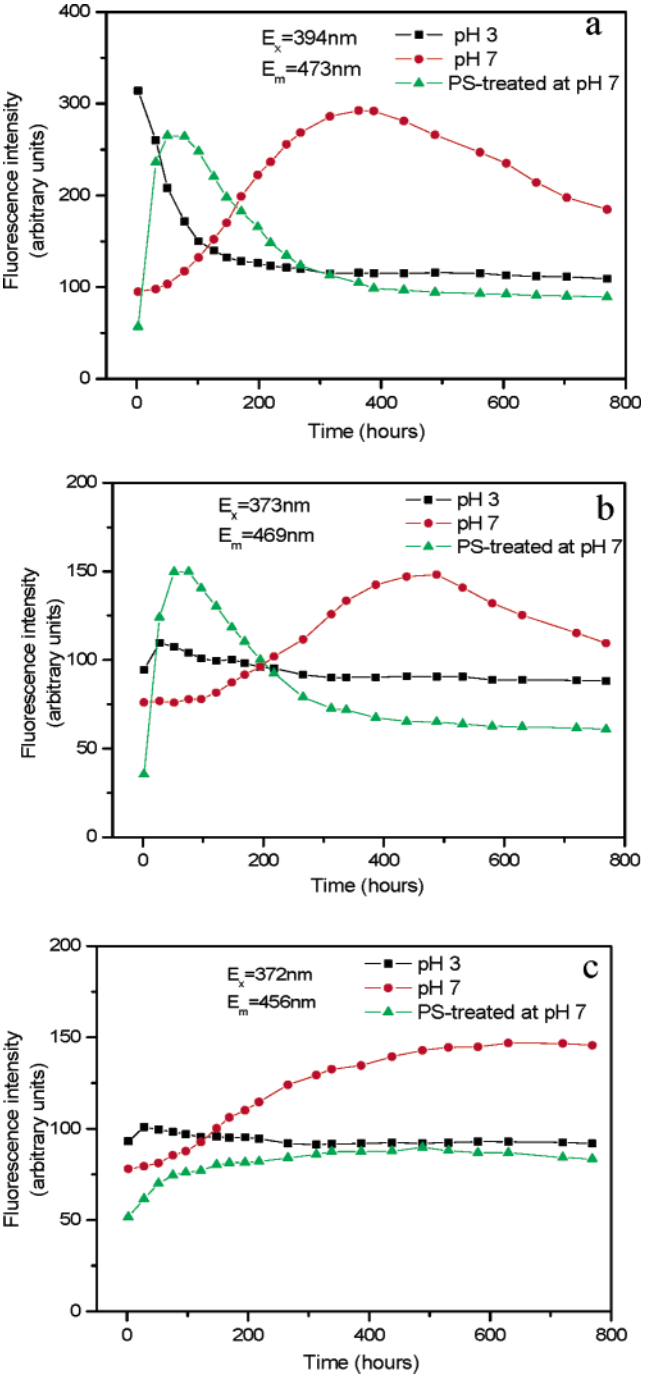


Figure 2. Time course of fluorescence intensity of (a) poly(BDA2-AEPZ1)-OH, (b) poly(BDA2-AEPZ1)-NH_2, and (c) poly(BDA2-AEPZ1)-$(OH)_2$ at pH 3 and 7 or treated by PS at pH 7, respectively.

(BDA2-AEPZ1)-OH, poly(BDA2-AEPZ1)-NH_2, and poly(BDA2-AEPZ1)-$(OH)_2$, but a solution of poly(BDA2-AEPZ1)-vinyl in DMSO without air exposure could be obtained feasibly by freeze vacuuming−thaw purging with argon of the monomer solutions to remove dissolved air followed by performing the polymerization under argon flow to avoid exposure to air. After polymerization for 101.0 h at 70 °C, the obtained solution of poly(BDA2-AEPZ1)-vinyl in DMSO was cooled and used directly for fluorescence measurement under argon protection. Fluorescence was observed for the solution of hyperbranched poly(BDA2-AEPZ1)-vinyl solution without exposure to air. The emission and excitation spectra of the solution of poly(BDA2-AEPZ)-vinyl in DMSO without exposure to air are shown in Figure 1. In contrast, no fluorescence was observed from the solution of BDA and AEPZ in DMSO, respectively, and a weak fluorescence from that of 2BDA + AEPZ in DMSO (just after mixing the two monomers together at ambient temperature) (see Figure S7). Hence, this indicates that fluorescence is an inherent property of hyperbranched poly(amino ester)s instead of caused by oxidation treatment although suitable oxidation treatment can enhance the luminescence. In addition, all the three polymers had two similar discrete fluorescence lifetimes, i.e., ca. 11.4 and 26.0 ns for poly(BDA2-AEPZ1)-OH, ca. 8.7 and 25.0 ns for poly(BDA2-AEPZ1)-NH_2, and ca. 8.7 and 24.3 ns for poly(BDA2-AEPZ)-$(OH)_2$. This may imply that the fluorescent species in these three hyperbranched poly(amino ester)s with different terminal groups are similar. Furthermore, no quenching of fluorescence was observed for KI treatment as observed for those fluorescent aromatic species.

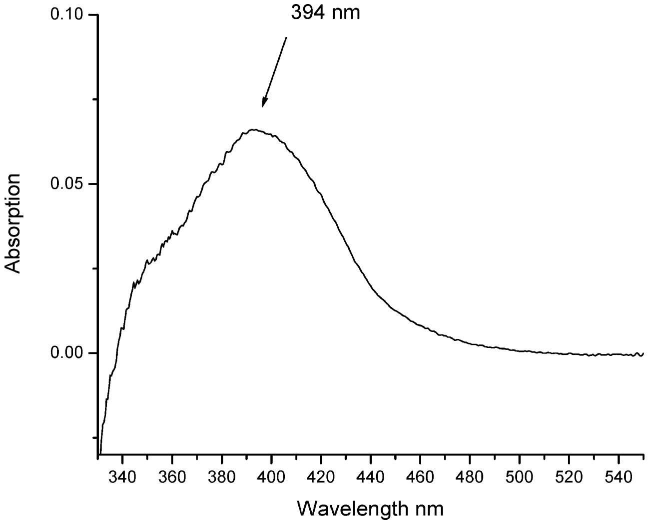


Figure 3. Differential UV−vis absorption spectrum of 0.5 mM aqueous solution poly(BDA2-AEPZ1)-OH exposed to air for 6 days obtained by subtraction of that of the original solution at pH 7.

In conclusion, blue photoluminescence was observed from the aqueous solution of hyperbranched poly(amino ester)s. A coexistence of tertiary amines/carbonyl groups in the core and compacted dendritic structures with suitable terminal groups of hyperbranched polymers was the key structural factor for showing fluorescence, and the monohydroxyl terminal group resulted in the strongest fluorescence. Fluorescence is an inherent property of hyperbranched poly(amino ester)s rather than caused by oxidation treatment, but oxidation through treatment with PS or exposure to air rendered stronger fluorescence. These hyperbranched poly(amino ester)s are promising novel fluorophores, especially applicable for those applications requiring good biodegradability. The effects of the core and periphery chemical structure on the fluorescent properties, the mechanisms of fluorescence formation, and the applications of these novel fluorescent poly(amino ester)s will be investigated further.

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Supporting Information Available: Synthesis, characterization, and hydrolysis profile of polymers, effects of concentration and pH on the fluorescence intensity, emission spectra in THF, and illusion photographs. This material is available free of charge via the Internet at http://pubs.acs.org.

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