Effect of Core Structure on the Fluorescence Properties of Hyperbranched Poly(phenylene sulfide)

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ABSTRACT: We functionalize the focal group of hyperbranched poly(phenylene sulfide) (HPPS) with benzyl, phenyl, and naphthyl group, respectively. DSC analysis shows that T_g of HPPS is increased from 55 to 93°C by functionalization of the focal group with a conjugated naphthyl group. The fluorescence properties of the three core-functionalized HPPS' are studied under the comparison with the original HPPS. Functionalization by a nonconjugated benzyl group has no effects on the fluorescence properties of HPPS at all. Both the phenyl-cored and the naphthyl-cored HPPS' give rise to a new highly polarized fluorescent peak around 500 nm due to the formation of intermolecular excimers with encumbered molecular rotation. Differing from the often reported significant increase in core fluorescence due to the so-called ''antenna effect,'' the fluorescence of HPPS backbones is drastically enhanced after functionalization of the cores with naphthyl groups that is 10- to 18-fold higher than the original HPPS' depending on the molecular weights of HPPS'. The phenyl-cored HPPS does not show a notable increase in fluorescence intensities compared with the original HPPS. The clear comparison results are rationalized by the restriction of intramolecular rotations of the naphthyl cores against the HPPS periphery. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 1857–1864, 2008

Key words: hyperbranched; conjugated polymers; fluorescence

INTRODUCTION

Generally, highly branched polymers including dendrimers and hyperbranched polymers have core-initiated branches-upon-branches structures that somewhat resemble an exaggerating process from the core to the rim or a concentrating process from the rim to the core. Such structures are attractive to those researchers who are looking for materials with high efficiency of energy-transfer, for example, light-harvesting materials or fluorescence materials. Dendrimers are good model compounds for academic research, however, the facile and versatile production methods make hyperbranched polymers better candidates for industrial applications.

Much attention has been paid to the effects of the focal groups on photophysical properties of highly branched polymers for the purpose of increasing the efficiency of energy-transfer or fluorescence. Hyperbranched conjugated polymers with triphenylamine as the core exhibit strong two-photon absorption properties.[1] The energy harvested by the dendritic periphery (energy donor) can be efficiently transferred to the conjugated core (energy acceptor), resulting in a significant increase in core emission on excitation of the peripheral chromophores, and in many cases, the fluorescence of dendritic backbones is efficiently quenched by the incorporated core,[2–7] as has happened, for instance, in1,1′-bi-2-naphthol cored dendrimers.[8–10] Some dye moieties attached to the focal groups of highly branched polymers perform with a high fluorescence efficiency with little quenching because that the aggregation tendency of the dyes to form a self-quenching charge-transferred complex is suppressed by the highly branched-protection.[11,12]

Above all, most researchers studying the effects of cores on photophysical properties of highly branched polymers concern, actually, the increase of the fluorescence efficiency of the core moieties by the use of highly branched structures, not the increase of the fluorescence efficiency of the highly branched backbones by the modification of the core groups. The latter can be useful in the quest for effective fluorescent dyes for use in dye-laser technology, fluorescence analysis, and for new materials for light-emitting devices, especially those made from thin films of dendritic polymers synthesized by

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surface-initiated polymerization. According to the law of energy conservation, it never happens that the energy absorbed at the core will result in totally augmented energy irradiation from peripheral chromophores if just energy transfer from the core to the rim takes place. Core-induced enhancement of fluorescence of dendritic backbones is affirmatively related to the increment of fluorescence quantum yields due to the change of molecular structures or conformations. It is widely accepted that a rigid planar molecule tends to have larger fluorescence efficiency than a non-rigid one.[13,14] Thus study on the effects of core moieties on the fluorescence properties of hyperbranched conjugated polymers will enrich the knowledge of highly branched polymeric conjugated structures.

The hyperbranched polymer we are interested in, in this work is hyperbranched poly(phenylene sulfide) (HPPS).[15,16] Poly(phenylene sulfide) (PPS) is a special macromolecule with sulfur atoms connecting the conjugated systems of consecutive phenyl rings. Sulfur atoms play an important role in connecting the conjugated systems and accounts for doped conductivity of PPS.[17] Compared with other conjugated polymers, PPS is a promising material due to its high thermal stability and high affinity to metals and carbon materials.[18–21] HPPS is a blue light-emitting material. In this work, we functionalize the core of HPPS with benzyl, phenyl, and naphthyl group, respectively, and investigate the effects of the core structures on the fluorescence properties of HPPS, aiming at enhancement of fluorescence of HPPS backbones. Differing from dendrimers, functionalizing the core is a better way for the study of core effects on the properties of a hyperbranched polymer than functional core-initiated synthesizing of a hyperbranched polymer, because the number of fluorophores is kept the same for parallel comparison.

EXPERIMENTAL

Materials

All reagents and solvents of analytical grade are purchased from commercial suppliers and used without further purification unless stated otherwise. Potassium carbonate is dried 24 h in an oven at 200°C before use.

Instrumentation

FTIR spectra are recorded in an Eouinox55 Model Fourier transform infrared spectrometer. Three hundred megahertz ^{1}H NMR is performed on an AVANCE 300 spectrometer. The molecular masses of polymers are analyzed by size-exclusion chromatography on a Waters 1515 equipped with three Waters Styragel columns and a differential refractometer detector. Chromatograms are run using inhibitor-free THF at a flow rate of 1.0 mL/min and an injection volume of 50 μL with a sample concentration of 3.0 mg/mL. All samples are degassed and filtered through a 0.45-μm filter before injection. Column temperature is maintained at 30°C for all sample runs. Polystyrene standards are used for calibration. Differential scanning calorimetry (DSC) is performed with Perkin Elmer Diamond Differential Scanning Calorimeter in nitrogen atmosphere at a heating rate of 10°C/min.

UV–vis absorption spectra are acquired with Perkin Elmer λ40 spectrophotometer. Steady-state fluorescence spectra at room temperature are measured with a RF-5301PC fluorescence spectrophotometer. Photoluminescent decay curves and fluorescence lifetimes are measured on a Fluorolog-3-TAU steady-state/lifetime spectrofluorimeter (Spex, Edison, NJ). Fluorescence polarization measurements are performed on Fluorolog-3-TAU spectrofluorometer equipped with FL-1044L dual polarizers. The quantum yield of all compounds is determined according to eq. (1)[22,23]

$$\Phi = \left(\frac{F_{\text{sample}}}{F_{\text{ref}}}\right)\left(\frac{A_{\text{ref}}}{A_{\text{sample}}}\right)\Phi_{\text{ref}}\left(\frac{n^2_{\text{sample}}}{n^2_{\text{ref}}}\right) \quad (1)$$

where F_{sample} and F_{ref} are the measured fluorescence (area under the fluorescence spectra) of the sample and the reference respectively, A is the absorbance at the same excitation wavelength, Φ_{ref} is the quantum yield of the reference, and n is the refractive index. Rhodamine B in THF is used as a reference ($\Phi = 0.88$) in these measurements.

Synthesis of hyperbranched poly(1,3,5-phenylene sulfide)

HPPS and HPPS with a naphthyl core (HPPS-Np) are prepared according to our previous work on the synthesis of hyperbranched poly(1,2,4-phenylene sulfide).[16]

HPPS with no core

3,5-Dichlorobenzenethiol (20 g; 112 mmol) is added to K_2CO_3 (26.8 g, 192 mmol) in *N*-methylpyrrolidone (NMP; 160 mL), and the reaction is heated to 150°C and maintained for the required time (7 h for sample H1 and 16 h for sample H2). The reaction systems are then cooled and diluted with an equal volume of water and carefully poured into 6*M* HCl (300 mL). The resulting precipitates are vigorously stirred for 10 h and then filtered. After having been carefully washed with water, the precipitates are dried thoroughly under vacuum and then are dissolved under vigorous stirring in a minimal amount of THF. The THF solution is added dropwise to hexanes (at least

TABLE I
Fluorescent Quantum Yields, Molecular Masses, and Glass Transition Temperatures of HPPS

			H1-Np		H2-Np	
Sample	H1	H2	Apparent	Pure	Apparent	Pure
Φ	0.03	0.025	0.17	0.36	0.19	0.46
M_n	1900	4500	2100		4900	
PDI	1.4	1.2	1.3		1.1	
T_g (°C)	55	–	93		–	

five times the volume of the THF solution) with vigorous stirring over a period of 2 h. The dissolving/precipitating cycles are repeated for three times. This precipitate is then filtered, washed with hexanes, and dried thoroughly under vacuum. The products are pale powders. FTIR (KBr): 3053, 1545, 1402, 843, 794, 667 cm^{-1}. Three hundred megahertz ^1H NMR ($CDCl_3$): 7.16, 7.11 ppm (all broad).

HPPS with a naphthyl core

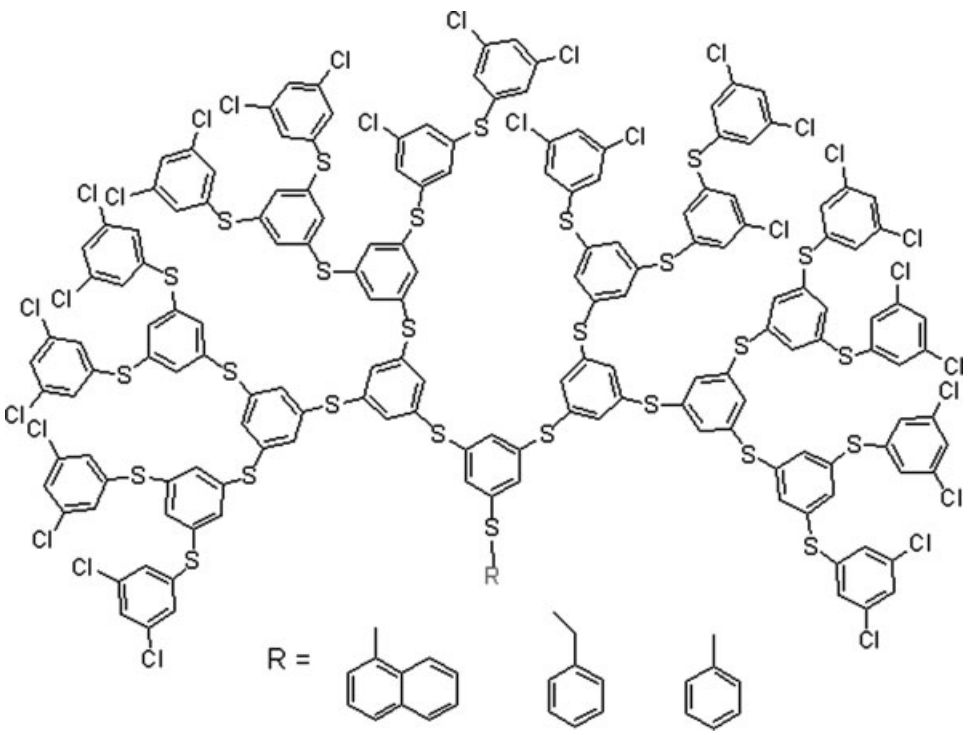
Dithiothreitol (DTT) is used to activate –SH group in HPPS.[24,25] HPPS (sample H1 or H2; 1 g) and DTT (0.05 g) are dissolved in NMP (20 mL). After the solution has been stirred at 70°C for 3 h, α-bromo-naphthalene (1 mL) and K_2CO_3(1 g) are added into the solution. The solution is then stirred at 150°C for 15 h. NMP is removed by vacuum distilling. The reaction mixture is precipitated in acetone and washed with acetone and distilled water several times to remove solvents and salts. After removal of the solvent, the raw product is purified by column chromatography on silica gel (gradient eluents: hexane to THF) to give tan solids. FTIR (KBr): 3059, 1549, 1402, 845, 798, 671 cm^{-1}. Three hundred megahertz ^1H NMR ($CDCl_3$): weak peaks from the naphthyl group: 8.26, 7.84, 7.64; and 7.11 (broad), 7.16 ppm (broad).

By the same process, HPPS with a core of benzyl group (HPPS-Bz) and HPPS with a phenyl group (HPPS-Ph) are synthesized by the reaction of HPPS with bromo-methyl benzene and bromo-benzene, respective.

RESULT AND DISCUSSION

Synthesis and structures of HPPS and HPPS-cores

According to our previous work and other groups' work,[15,16] the polymerization of 2,4-dichloro-benzenethiol produced hyperbranched poly(1,2,4-phenylene sulfide) with high polydispersity indices (PDIs), due to the different reactivities of 2,4-dichloro groups. In contrast, the polymerization of 3,5-dichloro-benzenethiol with better symmetry can easily produce hyperbranched polymers with very narrow PDIs. We synthesize two hyperbranched poly(*1,3,5*-phenylene sulfide)s with number average molecular mass (M_n) of 1900 (sample H1 obtained in polymerization of 7 h) and 4500 (sample H2 obtained in polymerization of 16 h), and PDI of 1.36 and 1.16, respectively (Table I). Under the same reaction conditions, three different molecules are attached to the central –SH group (Scheme 1). The prod-



Scheme 1 Schematic structure of core-functionalized hyperbranched poly(phenylene sulfide).

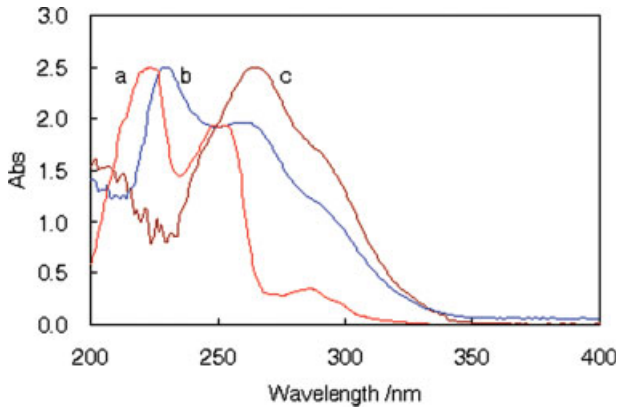


Figure 1 UV–vis spectra of (a) 3,5-dichloro-benzenethiol, (b) H1/H1-Np, (c) H2/H2-Np. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

ucts are purified by passing through a plug of silica gel. Because of the very close retention factors of core-functionalized HPPS (HPPS-cores) and the original HPPS, however, it is unable to separate pure functionalized HPPS from the original HPPS by column chromatography. The apparent products are mixtures of HPPS and pure core-functionalized HPPS, with a yield of 0.46 for H1 and 0.41 for H2, measured by ^{1}H NMR. Low conversion is perhaps because of the bad miscibility between HPPS and core molecules or the bad reachability of the focal place. A possible ''closed loop'' reaction between one of the chloro groups on a branch and the core –SH groups can also result in low yields of HPPS-Np.[26] The total core functionalization of highly branched polymers seems a challenging work.[27] A failure in full substitution of cores of dendrons is also reported.[28] Thus, investigation of the properties of apparent core-functionalized HPPS is based on an assumption that the contribution of unreacted HPPS to the measured results of the core-functionalized HPPS samples is in a linear proportion to its molar parts when using unreacted HPPS as a reference. Nonlinear changes in the apparent HPPS-core mixture samples are regarded as results from the pure core-functionalized HPPS samples. The assumption is reasonable because the highly branched structures of HPPS and core-functionalized HPPS are the same.

DSC analysis shows that the glass transition temperature (T_g) of the apparent HPPS-Np is much higher than that of the original HPPS, 93°C in H1-Np, however, 55°C in H1. Branches in HPPS-Np become more rigid than those in HPPS. No significant change in T_g is found in HPPS-Bz or HPPS-Ph.

UV–vis absorption and steady state photo-fluorescence

Figure 1 illustrates the UV–vis absorption spectra of the monomer 3,5-dichloro-benzenethiol, HPPS, and HPPS-cores in THF solutions. The core-functionalized HPPS samples do not show any change in normalized UV–vis spectra compared with those of the original H1 and H2. Thus, UV–vis spectra of HPPS-cores are omitted from Figure 1. The monomer shows three red-shifted absorption bands of benzene rings due to the auxochromic thiol and chloride groups, the E1 band at 220 nm, the E2 band at 250 nm, and the B band at 286 nm. A notable red-shifting of both the E1 and E2 bands is clearly seen in HPPS, and the E1 band is more bathochromic with the increase of the molecular weight, changing from 231 nm in H1/H1-cores to 240 nm in H2/H2-cores. This indicates that sample H2/H2-Np with higher molecular weight has longer conjugated structures than that of H1/H1-Np.

Photo-fluorescence analysis of HPPS and HPPS-cores is performed. Figure 2 illustrates the fluorescence spectra of the H1-Np and H2-Np excited at 370 nm, a maximum excitation peak of HPPS, under the comparison with the spectra of the original H1, H2 and a mixture of H1 and naphthalene at the same composition of H1-Np. Figure 3 shows the spectra of H1-Bz and H1-Ph under the comparison with H1.

The fluorescence spectra of HPPS and HPPS-cores show a large Stokes-shifted emission with a Stokes-shift of above 180 nm between the B band of absorption and the maximum fluorescence peak, which indicates that the excited-state relaxes radiatively. The large Stokes-shifted fluorescence has an attractive character of unusual emission at longer wavelength and, therefore, is not self-absorbed even in a high concentration of chromophores. However, the efficiency of the large Stokes-shifted fluorescence is

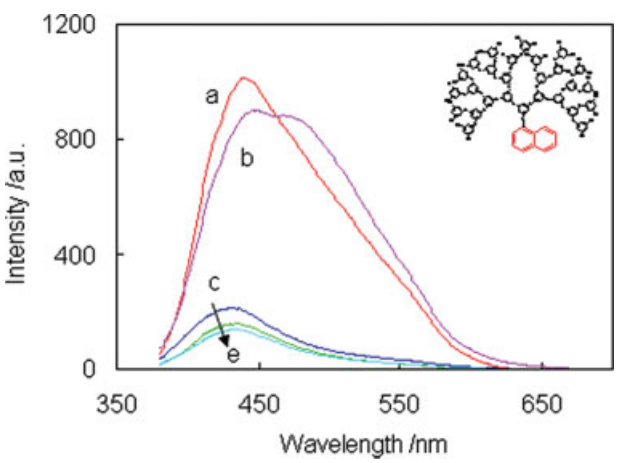


Figure 2 Fluorescence spectra excited at 370 nm in THF solutions with a concentration of 0.5 mg/mL. (a) H1-Np; (b) H2-Np; (c) H1; (d) a mixture of H1 and naphthalene with the same composition of H1-Np; (e) H2. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

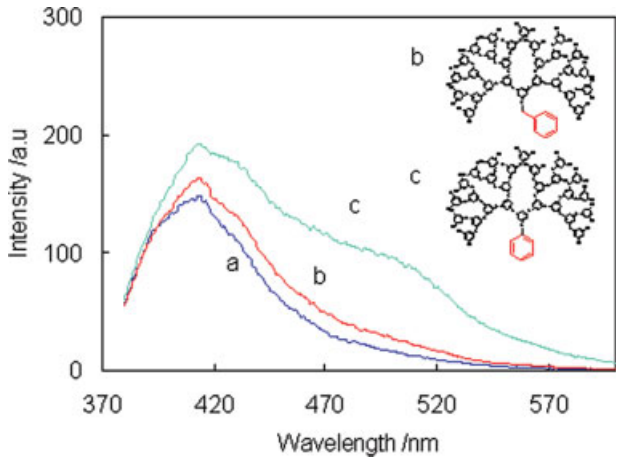


Figure 3 Fluorescence spectra excited at 370 nm in THF solutions with a concentration of 0.5 mg/mL. (a) H1; (b) H1-Bz; (c) H1-Ph. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

generally low due to the deactivation by isomerization from the excited-state tautomer or radiative relaxing processes. Ohshima et al. succeeded in the suppression of the isomerization efficiency by a dendritic structure to increase the efficiency of the large Stokes-shifted fluorescence.[29]

According to the fluorescence spectra illustrated in Figure 2, the fluorescent intensities of HPPS-Nps are significantly increased compared with the original HPPS at the same concentrations. The fluorescence intensities of HPPS-Nps are 5 to 10-fold higher than those of original HPPS. Neither HPPS-Bz nor HPPS-Ph shows notable fluorescence enhancement. The fluorescence spectra clearly manifest that conjugated core structures have important effects on the fluorescence intensities. The mixtures of H1 and naphthalene at different compositions do not show any fluorescence enhancements.

Considering the fact that the apparent HPPS-Nps are mixtures of HPPS and pure HPPS-Np, we compare the fluorescence of HPPS and the apparent HPPS-Np at different concentrations, which indicates that fluorescence intensities of HPPS in THF solutions show linear relations to the concentrations of apparent HPPS-Np [Fig. 4(a)] and the concentrations of pure HPPS-Np [Fig. 4(b)]. Figure 4 endorses the applicability of our assumption that the contribution of unreacted HPPS to the measured results of the core-functionalized HPPS samples is in a linear proportion to its molar parts when using unreacted HPPS as a reference. Thus, we can estimate the fluorescent quantum yields of pure HPPS-Nps by extrapolation. The quantum yields of fluorescence (Φ) in HPPS-Np are measured by comparison with the quantum yield of 0.88 of Rhodamine B excited at 370 nm according to a comparative method (Table I).[22,23] According to extrapolation results, Φ of pure H1-Np is 0.36, 10-fold higher than 0.03 of H1, and 0.46 of pure H2-Np is 18-fold higher than 0.025 of H2.

HPPS-Bz without a conjugated core structure does not show any differences in the fluorescence spectrum from that of HPPS, whereas new peaks around 500 nm appear in the spectra of HPPS-Ph and HPPS-Np with conjugated cores. The fluorescence spectra of H1-Np can be well fitted by a superposition of two peaks. Peak b at 434 nm does not change its position when changing concentrations, whereas peak a is red-shifted with the increase of concentrations up to about 0.1 mg/mL (Fig. 5), which indicates that the formation of the so-called excimers gives rise to the peaks around 500 nm in HPPS-Np. Upon the curve-fitting, the integral intensities of both peaks a and b increase with the increase of concentrations, however, the area ratios of peak a to peak b reach a constant value at concentrations above 0.1 mg/mL (Fig. 6). The structure of the excimer perhaps adopts a stable conformation at high

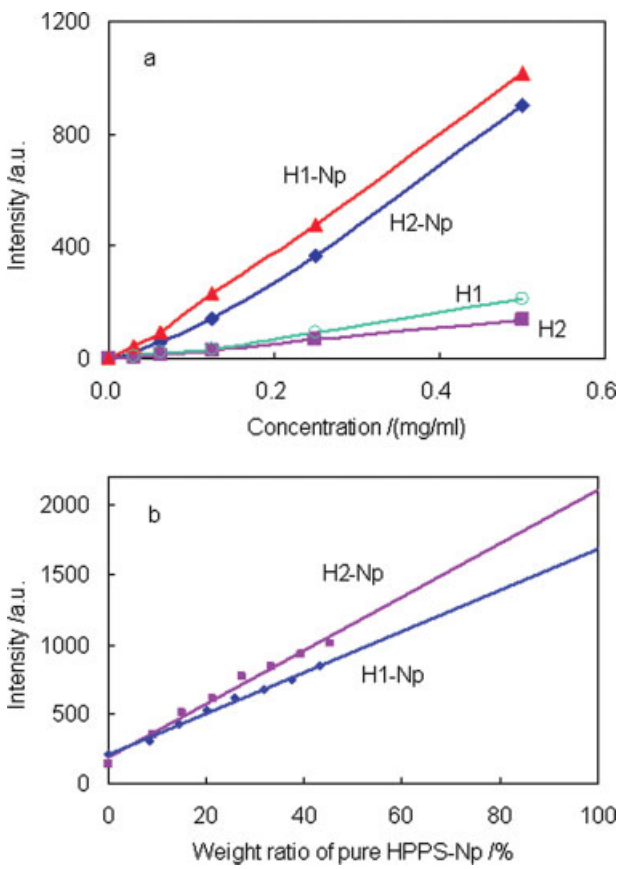


Figure 4 Fluorescence intensities of HPPS in THF solutions excited at 370 nm versus concentrations of apparent HPPS-Np (a) and concentrations of pure HPPS-Np (b). The total concentrations were 0.5 mg/mL. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

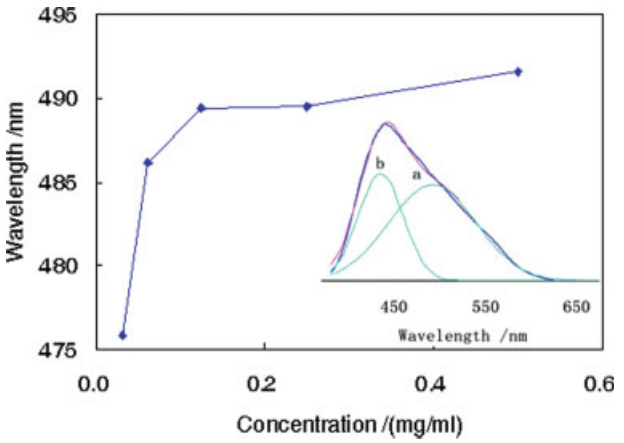


Figure 5 Shifting of the fitting peak ''a'' of H1-Np upon the change of the concentration of H1-Np. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

concentrations. Peak-shifting upon concentration implies the formation of intermolecular excimers. The excited chromophore can interact with the unexcited chromophore in other hyperbranched macromolecule when they form a ''face to face'' association structure.[30] A rigid planar structure will facilitate the formation of such kinds of excimers. The fluorescence analysis results of HPPS-Np and the comparison between HPPS-Bz and HPPS-Ph indicate that the core structures conjugated with the hyperbranched backbones may have important effects in structural rigidity of the hyperbranched backbones. The naphthyl-cored HPPS shows enhanced fluorescence spectra compared with the original HPPS, whereas the benzyl- and phenyl-cored HPPS do not. This is perhaps caused by different restriction of intramolecular rotations (RIR) of the cores against the HPPS periphery.[31] The naphthyl core is more restricted in its intramolecular rotations than the phenyl core.

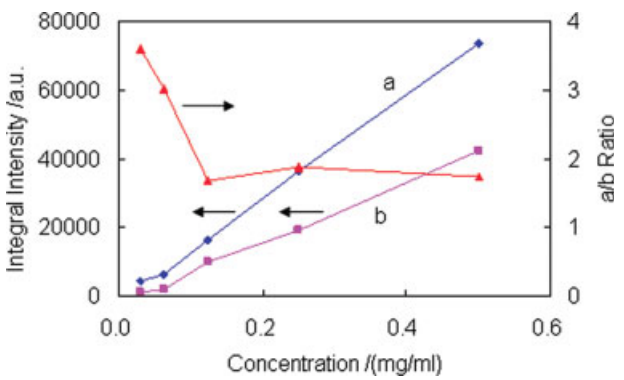


Figure 6 Relation of integral intensities of fitting peak ''a'' and ''b'' of H1-Np to the concentration of H1-Np. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Energy-donor effects of the cores

Viewing from the point of fluorescence resonance energy transfer, the core structures studied in this work are energy donors to the HPPS periphery. Figure 7 illustrates the absorption, excitation, and emission spectra of naphthalene and H1/H1-Np. The emission peak of naphthalene at about 330 nm partially overlaps with the two excitation peaks of HPPS. When excited at 280 nm that is the maximum excitation peak of naphthalene, the fluorescence spectra of HPPS-Nps show typical but very weak emission peaks of HPPS-Nps. However, the fluorescence peaks at 500 nm are of higher intensities than peaks at 434 nm, which differs from the fluorescence spectra excited from the hyperbranched structures (Fig. 8). Figure 8 clearly demonstrates that the formation of the excimers is closely related to the conjugated cores. HPPS and the mixture of HPPS and naphthalene do not show their typical fluorescence spectra that are obtained by excitation from the hyperbranched structures. The results indicate that energy transfer from the naphthyl core to hyperbranched branches can indeed occur, however, energy transfer from the core to the peripheral can not account for the drastic fluorescence enhancement of HPPS-Np.

Fluorescence lifetime and fluorescence polarization

The fluorescence lifetime is determined with phase-modulation techniques. The average fluorescence life-time (T_f) obtained from frequency-domain time-resolved fluorescence analysis is 3.99 ns for H1 and 3.30 ns for H1-Np. The average fluorescence life-

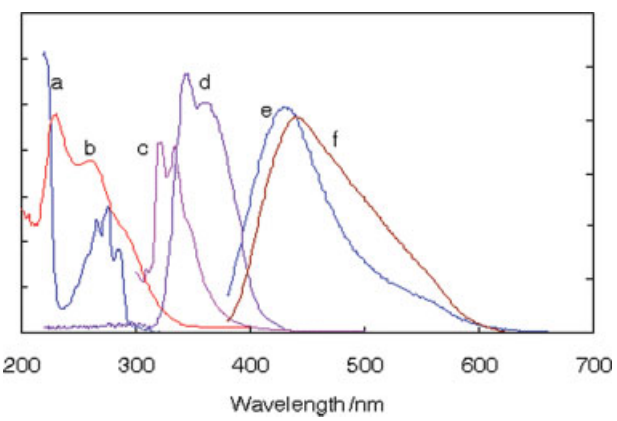


Figure 7 Absorption, fluorescence excitation and emission spectra of naphthalene, H1, and H1-Np. (a) Absorption of naphthalene, (b) absorption of H1, (c) emission of naphthalene, (d) excitation of H1 monitored at 440 nm, (e) emission of H1 excited at 370 nm, (f) emission of H1-Np excited at 370 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

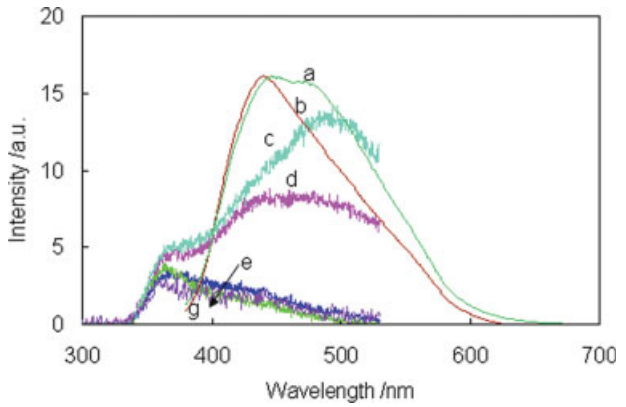


Figure 8 Fluorescence spectra of HPPS in THF solutions with a concentration of 0.5 mg/mL. (a, b) H2-Np and H1-Np excited at 370 nm. (c–g) H2-Np, H1-Np, H1, H2, and a mixture of H1 and naphthalene excited at 280 nm, respectively. (a) and (b) are scaled to fit the height of the figure. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

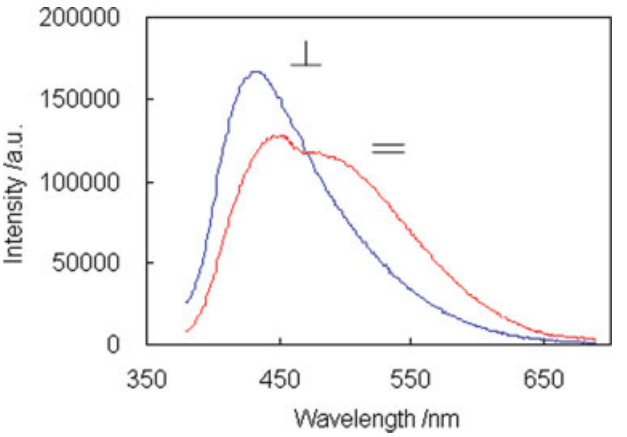


Figure 9 Vertical and parallel polarized fluorescence spectra of H1-Np in THF solution. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

time of H2 is about 3.05 ns, whereas the fluorescence lifetime of H2-Np is too short to be measured on the instrument used in this work. This significant decrease in the fluorescence lifetime usually indicates an increase in the local dynamics.[32] It is hardly imaged that H2-Np with bigger molecular weight has more flexible segmental motion than H1-Np or H2. The most reasonable interpretation of shorter fluorescence lifetime of H2-Np is that the H2-Np assumes a compact or highly symmetric structure in solution which is rotating faster.

The fluorescence polarization of HPPS samples is investigated. Figure 9 illustrates the polarized fluorescence spectra of H1-Np in a THF solution excited at 370 nm. Sharp difference is between the vertical and parallel polarized spectra. In the parallel polarized spectrum, the peak at 500 nm is strongly shown, which nearly disappears in the vertical polarized spectrum. Molecular packing will result in high degree of fluorescence polarization. The intermolecular ''face-to-face'' packing structures of the excimers baffle the molecular rotation.

A direct means to investigate the rotational motion of excited states is provided by fluorescence polarization measurements.[33] The concept of molecular movement and rotation is the basis of fluorescence polarization. Fluorescence polarization is defined by[34]

$$p = \frac{F_p - F_c}{F_p + F_c} \tag{2}$$

where F_p and F_c refer to the emission intensity measured with parallel and crossed polarizers, respectively. The theoretical upper limit for p is 0.5. Figure 10 illustrates the fluorescence polarization of H1 and H1-Np in THF solutions excited at 370 nm. According to Figure 10, H1-Np actually contains two components: polarization component with fluorescence peaked at 500 nm and depolarization component peaked at 440 nm. The profound polarization in H1-Np was 0.45, whereas the highest polarization for H1 was about 0.09 perhaps caused by light scattering.

The degree of polarization is related to the rotational relaxation time T_R. The Perrin equation [eq. (3)], which was first described in 1926, describes the relation between the observed fluorescence polarization, the limiting polarization ($p_0 = 0.5$), the fluorescence lifetime of the fluorophore (T_f), and its rotational relaxation time (T_R):[34]

$$T_R = 6T_f[(1/p_0 - 1/3)/(1/p - 1/p_0)] \tag{3}$$

We can compare the rotational relaxation time in H1 and H1-Np by substituting T_f with 3.99 ns for

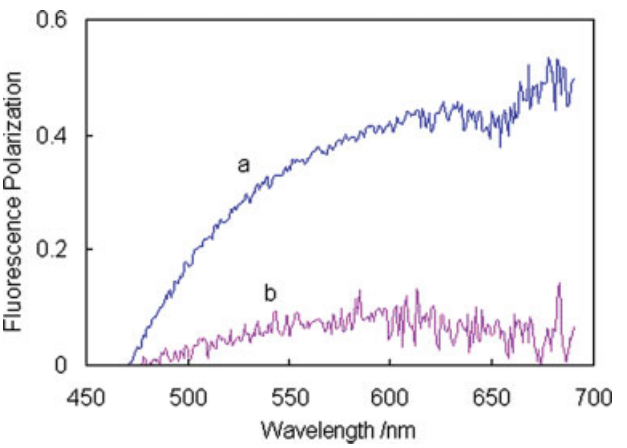


Figure 10 Fluorescence polarization of H1 (b) and H1-Np (a) excited at 370 nm. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

H1, and 3.30 ns for H2-Np, and substituting p with 0.45 for H1-Np and 0.09 for H2. Thus, $T_{R(\mathrm{H1-Np})}/T_{R(\mathrm{H2})} = 33.9$. This indicates that the rate of rotation of the excimers in H1-Np corresponding to the emission at 500 nm is much slower than that of H1-Np in the THF solution. The intermolecular ''face-to-face'' packing structures of excimers baffle the molecular rotation.

CONCLUSIONS

We study the effects of three core structures (benzyl, phenyl, and naphthyl groups) on the fluorescence properties of HPPS with the comparison of the original HPPS. Phenyl and naphthyl groups can form conjugated structures with the HPPS backbones through sulfide bridges, whereas benzyl group can not. Benzyl group has nearly no effects on the fluorescence properties of HPPS at all. Both the phenyl-cored and the naphthyl-cored HPPS give rise to the peak at about 500 nm due to the formation of excimers. The excimers are formed by intermolecular packing which results in a high degree of fluorescence polarization due to encumbered molecular rotation. For a three-dimensional highly branched conjugated structure, the strengthened intermolecular packing implies a strengthened planar rigidity. DSC result shows that HPPS-Np has higher glass transition temperature than HPPS which means a more rigid structure in HPPS-Np.

The naphthyl-cored HPPS' show drastic fluorescence enhancement that is 10- to 18-fold higher than the original HPPS depending on the molecular weight of HPPS.' The phenyl-cored HPPS does not show a notable increase in fluorescence intensities, compared with the original HPPS. The clear comparison results may be rationalized by the restriction of intramolecular rotationsof the naphthyl cores against the HPPS periphery. The small phenyl core can easily rotate.

It is inferred from this work that the focal group may have important effects on the total electronic structure of a highly branched conjugated polymer. Decoration of the core by a suitable group may be an efficient way for functions of a hyperbranched polymer. Electrodes modified by surface-initiated dendritic polymers may have special properties, especially when electrons move from dendritic peripheral to the core.

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