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A Modified Strategy for the Synthesis of Hyperbranched Poly(*p*-phenylenevinylene): Achieving Extended π-Conjugation with Growing Molecular Weight

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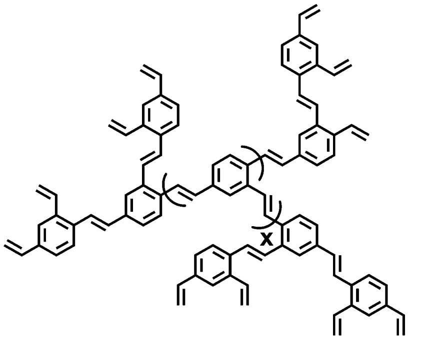
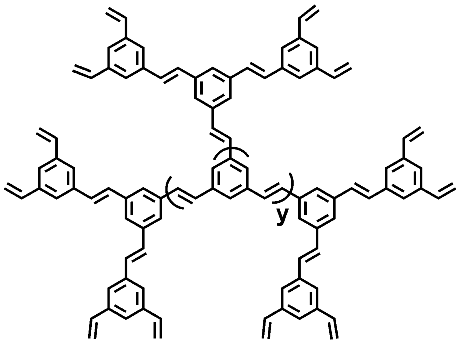
Aiming at the realization of high-performance polymeric electroluminescence (EL) devices, various kinds of poly(*p*-phenylenevinylene) derivatives (PPVs) have been synthesized and investigated with emphasis on their processability, color tunability, and stability.[1−4] To improve a poor processability of the original PPV, incorporation of solubilizing functional groups or the use of precursor routes has been extensively employed for EL application.[2,3] As an alternative approach, dendritically structured PPVs are gaining significant attention, very recently, due to their excellent solubility, film quality, and improved luminescence efficiency.[5−8] It is well-known that the dendritic molecules, i.e., dendrimers and hyperbranched polymers, are provided with the favorably reduced intramolecular and intermolecular interactions due to their characteristic branch structures, which in turn render them more soluble and highly fluorescent in the solid state.[9−12] It must be critically noted, however, that all the dendritic PPVs reported so far[5−8] comprise 1,3,5-connectivity (two *meta*-linkages) in the branch units which strictly restricts the extension of π-conjugation length within the branch points (see the π-conjugation resonance structure of 1,3,5-dendritic PPV in Figure 1). Because of this limited π-conjugation, the optical properties of the 1,3,5-dendritic PPV must be independent of their molecular weights (vide infra for the data). However, increased π-conjugation length with growing molecular weight is a fundamental property of the conjugated PPVs. In this communication, we demonstrate a modified strategy for obtaining a proper dendritic PPV which shows increasing π-conjugation length with growing molecular weight. To this end, we employed a simple but novel strategy of adopting 1,2,4-linking (*ortho*- and *para*-connecting) AB_2 monomer for the dendritically conjugated PPV synthesis because 1,4-connectivity as well as 1,2-connectivity (lesser extent) contributes to the extension of π-conjugation lengths (see the structure in Figure 1).

Two different types of AB_2 monomers, 4-bromo-1,3-divinylbenzene and 5-bromo-1,3-divinylbenzene, for obtaining 1,2,4-dendritic PPV and 1,3,5-dendritic PPV (as the control sample), respectively, were synthesized according to the reaction routes shown in Scheme 1, and their structures were fully characterized by ^1H NMR, ^{13}C NMR, FT-IR, and mass spectroscopy analysis (see Supporting Information for the synthesis and structural identification data).



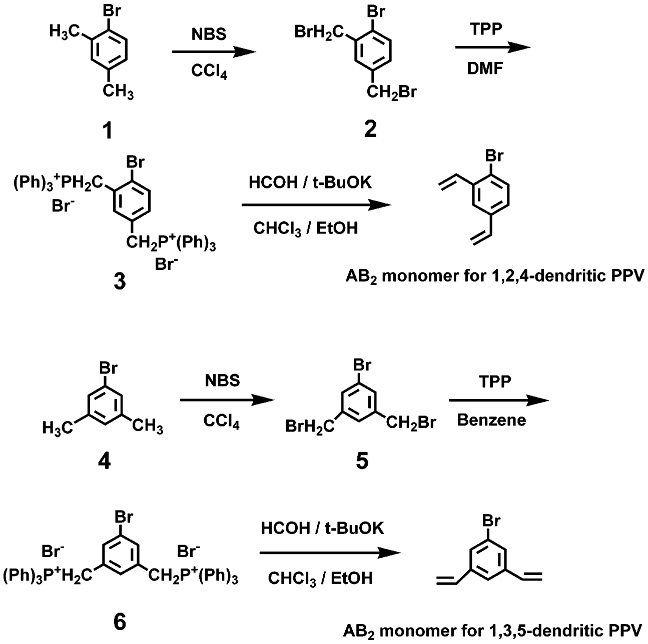
1,2,4-dendritic PPV



1,3,5-dendritic PPV

Figure 1. Chemical structures of two different types of dendritic hyperbranched PPVs.

Scheme 1. Synthetic Routes to the AB_2 Monomers for 1,2,4-Dendritic PPV and 1,3,5-Dendritic PPV



These two different types of AB_2 monomers were successfully polymerized via Heck coupling reactions,[13,14] and the synthesized polymers were purified by the repeated reprecipitation from chloroform solution to methanol to remove the residual metal catalyst, monomers, and low molecular weight oligomers. The product yields of 1,2,4-dendritic PPV and 1,3,5-dendritic

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Table 1. Molecular Weights and Photophysical Properties of Dendritic PPVs as a Function of Polymerization Time

polymer		polymerization time^{a} (h)	M_n	M_w	PDI	$\lambda^{\mathrm{ab}}_{\mathrm{max\ sol}}$ ^{b}	$\lambda^{\mathrm{em}}_{\mathrm{max\ sol}}$ ^{b,c}	$\lambda^{\mathrm{em}}_{\mathrm{max\ film}}$ ^{c}	Φ_F $^{b-d}$
1,2,4-dendritic PPV	a	1	1900	2800	1.5	354	494	524	0.51
	b	3	2200	3800	1.7	360	497	540	0.66
	c	5	2500	4600	1.8	366	505	550	0.67
	d	24	4700	20500	4.4	370	511	564	0.61
1,3,5-dendritic PPV	a	1	1700	2600	1.5	318	414	444	0.35
	b	3	3300	9000	2.7	318	405, 423	442	0.38

[a] Polymerization was carried out with 4 mol % of palladium(II) acetate, 8 mol % of tri-*o*-tolylphosphine, and 2.5 equiv of triethylamine at 95 °C in *N,N*-dimethylformamide (DMF) under N_2. [b] Measured in chloroform ($CHCl_3$) solution. [c] Obtained from the PL spectra excited at 315 nm. [d] Fluorescence quantum yields (Φ_F) were relatively calculated using 9,10-diphenylanthracene (DPA) in benzene as a standard reference (1×10^{-4} M, $\Phi_F = 0.83$).[17]

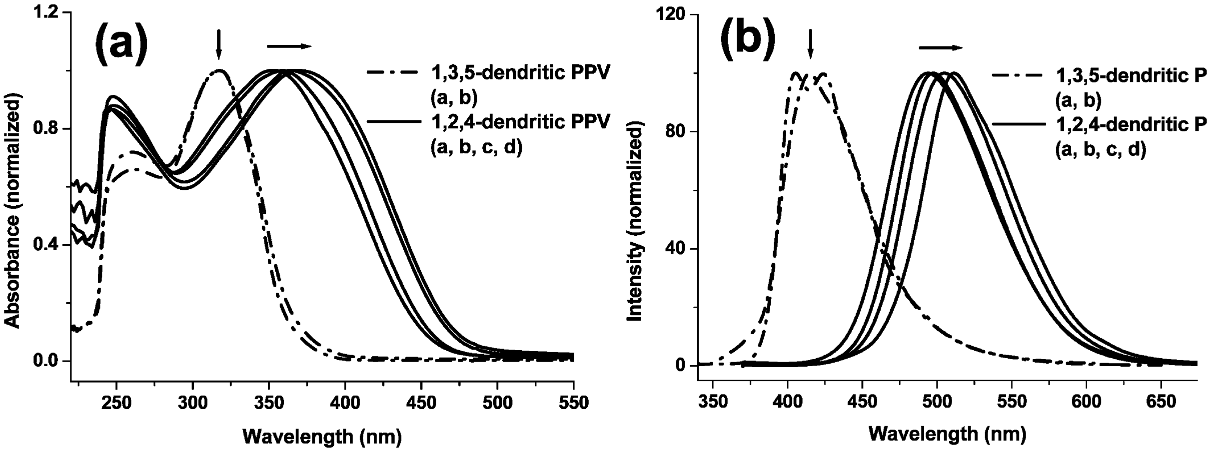

Figure 2. UV−vis absorption (a) and photoluminescence (PL) spectra excited at 315 nm (b) of the polymer solutions in chloroform.

PPV were as high as 80% and 50%, respectively, and depended on the reaction time. The structures of the dendritic polymers were fully characterized by ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy analysis, through which it was specifically indicated that the terminal vinylene chromospheres of the dendritic polymers were very stable under the Heck polymerization condition because the ^{1}H NMR spectra of the polymers showed only the styrene end-group protons without any alkyl protons (see Supporting Information for the structural characterization data). The number-average molecular weights (M_n) and the values of M_w/M_n (PDI) of the 1,2,4-dendritic PPV and 1,3,5-dendritic PPV were determined as a function of polymerization time by the gel permeation chromatography (GPC) analysis, as shown in Table 1. Both dendritic polymers regardless of their molecular weight were highly soluble in common organic solvents such as chloroform, tetrahydrofuran (THF), tetrachloroethane, dimethylformamide (DMF), etc., from which optically transparent and highly fluorescent polymer films were readily and conveniently spin-coated. It is considered that the good solubility of 1,2,4-dendritic PPV and 1,3,5-dendritic PPV is attributed to the weak intermolecular interactions and low solvation energy induced by the large steric hindrance of branch structures, which is consistent with many other hyperbranched polymers.[6]

The chemical structures of the novel hyperbranched conjugated PPVs, 1,2,4-dendritic PPV and its control sample, 1,3,5-dendritic PPV, are compared in Figure 1. The *trans*-stilbene units of 1,2,4-dendritic PPV are linked by 1,4-connectivity (*para*-linkage) as the more extended backbone units as well as 1,2-connectivity (*ortho*-linkage) as the lesser extended branch units, allowing their effective π-conjugation lengths to be controlled by the molecular weight, whereas those of 1,3,5-dendritic PPV are linked only by 1,3-connectivity and 1,5-connectivity (two *meta*-linkages) with limited π-conjugation between the branch points like other hyperbranched PPVs reported so far.

Figure 2a shows the UV−vis absorption spectra of 1,2,4-dendritic PPV and 1,3,5-dendritic PPV solutions. The absorption spectra of 1,2,4-dendritic PPV are 35−50 nm red-shifted (depending on the M_w) compared to those of 1,3,5-dendritic PPV certainly due to their extended π-conjugation and comprise unique broad absorption bands in UV and visible regions including those of 1,3,5-dendritic PPV. It is particularly noted that the absorption maxima of 1,2,4-dendritic PPV are gradually red-shifted from 354 to 370 nm with growing molecular weights, whereas the absorption maxima of 1,3,5-dendritic PPV are fixed at 318 nm independent of their molecular weights. It is most likely considered that the 1,4-linking (*para*-connecting) stilbene backbones with longer π-conjugation lengths are responsible for the 354−370 nm molecular-weight-dependent absorption while a large number of 1,2-linking (*ortho*-connecting) stilbene branches with shorter π-conjugation lengths are responsible for the unique broad absorption bands in the UV regions. Such a unique structural feature of the 1,2,4-dendritic PPV specifically indicates that an energy gradient from the outside 1,2-linking stilbene branches with higher energy band gaps to the 1,4-linking stilbene backbones with lower energy band gaps is inherent in this 1,2,4-dendritic PPV, as shown in the previous report studying an efficient energy funneling effect in the π-conjugated dendrimer based on *meta*- and *para*-linked phenylacetylenes.[15]

Increased π-conjugation length with M_w in the 1,2,4-dendritic PPV is also revealed in the photoluminescence (PL) spectra, as shown in Figure 2b. The emission maxima of 1,2,4-dendritic PPV are 80−100 nm red-shifted depending on their M_w compared to those of 1,3,5-dendritic PPV fixed at 414 nm independent of their molecular weights. Because of the efficient energy funneling effect, moreover, the PL spectra of 1,2,4-dendritic PPV (illuminated with 315 nm source to excite the shorter 1,2-linking stilbene branches) totally lacks the emissions of the isolated stilbene units (∼410 nm) but exclusively shows the red-shifted emissions of the longer 1,4-linking stilbene backbones (>490 nm). This experimental result certainly indicates an efficient energy transfer and funneling process from the higher band-gap 1,2-linking branches to the lower band-gap 1,4-linking backbones. More evidently, the fluorescence quantum yields (Φ_F)[16,17] of 1,2,4-dendritic PPV (>0.51) are much higher than those of 1,3,5-dendritic PPV (<0.38) (see Table 1) presumably due to the efficient energy funneling effect, which is an additional advantage to the extended π-conjugation length with growing molecular weight of the 1,2,4-dendritic PPV. In addition, intermolecular cross-linking reactions could be effectively induced when the 1,2,4-dendritic PPV as well as the 1,3,5-dendritic PPV films were irradiated with a high-intensity 254 nm UV light because the dendritic polymers have a large number of active vinylene chromospheres as the terminal groups allowing the attachment of a variety of structural units.

In conclusion, we synthesized a π-conjugated and hyperbranched 1,2,4-dendritic PPV which showed extended π-conjugation with growing molecular weight. Energy funneling and enhanced fluorescence efficiency were also observed in this π-conjugated hyperbranched polymer.

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Supporting Information Available: Synthetic details and structural identification data of intermediates, monomers, and polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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