High Molecular Weight Dendronized Poly(fluorene)s with Peripheral Carbazole Groups: Synthesis, Characterization, and Properties

Yaqin Fu, Yi Li, Jing Li, Shouke Yan, and Zhishan Bo*

State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received February 26, 2004; Revised Manuscript Received June 16, 2004

ABSTRACT: Novel kinds of dendronized polymers with both functional core and periphery were synthesized by Suzuki polycondensation (SPC) of carbazole-functionalized 2,7-dibromofluorene macromonomers with 9,9-dioctylfluorene-2,7-diboronic ester. The polymers obtained are of high molecular weight and good thermal stabilities. Photoluminescent studies showed that these kinds of dendronized polymers were promising blue light-emitting materials, which exhibited high quantum efficient yields in solution and films (mainly for second generation).

Introduction

Dendronized polymers are dendrimers with a central linear polymeric core and have attracted considerable scientific attention in recent years due to their unique structures and properties.[1] They attain a rodlike, cylindrical shape with the polymer backbone encapsulated into the dendritic envelope. High generation dendronized polymers with an appreciable degree of polymerization (DP) could be considered as "nanoobjects" because they attain cylindrical shape in both solution and solid state.[1,2] The synthetic routes leading to dendronized polymers can be divided into three main categories, namely, macromonomer route, "attach to" route, and divergent route. Particular attention was paid to the macromonomer route because it can accomplish dendronized polymers carrying structurally perfect dendrons. The syntheses of many kinds of dendronized polymers have been well documented by Schlüter et al. in two recent reviews.[1] Dendronized polymers with a conjugated polymer backbone are of special interest due to their potential applications as "nanowires" and light-emitting materials. The "site isolation" effect of the dendritic wedges can prevent the conjugated backbone from doing cross-talk. Conjugated backbones available now include poly(*p*-phenylene)s,[2] poly(*p*-phenylene−vinylene)s,[3] poly(*p*-phenylene−ethynylene)s,[4] poly(triacetylene)s,[5] poly(acetylene)s,[6] and poly(fluorene)s.[7] Additionally, the synthesis of high generation dendronized polymers with considerable molecular weight was still a challenging goal in this field.[1,8]

Highly soluble poly(2,7-(9,9-dialkyl)fluorene)s (PFs) and their copolymers are considered as very promising blue light-emitting materials.[9] Problems encountered with these rodlike PFs and their copolymers are their color stability. A low-energy green emission band is generated during operation or annealing in air. In the literature, two kinds of popular points of view on the origin of green emission band have been proposed.[10,11] Many studies have been done to understand the origin of this green band emission and to search for the effective ways to suppress it.[12] Recent studies have proposed that the origin of the green emission band is rather from fluorenone defects than aggregation or formation of excimers.[11] However, very recent results have demonstrated that the green emission band is related to not only fluorenone defects but also the microscopic morphology of the films.[13] They found that organized structures (dense interchain packing) lead to significant long wavelength emission in the green while nonorganized structures retain pure blue emission.[13]

The encapsulation of polyfluorene backbones into dendritic envelopes[7] and the blends of polyfluorenes with low molecular weight hole-transporting molecules[10b,14] have been proposed to achieve pure blue color emission. However, the dendritic wedges used in the literature are poor hole- or electron-transporting materials that are detrimental for electroluminescent applications, and the use of low molecular weight dopants can arise several problems, such as diffusion and recrystallization.

We report here the synthesis of a family of high molecular weight, dendronized poly(fluorene)s carrying peripheral carbazole functional groups. Such molecular structural design should overcome the drawbacks mentioned above and may give better performance. The dendritic wedges play the role of not only site isolation but also hole-transporting. This kind of dendronized polymer should be considered as an ambipolar carrier transporting material because the polyfluorene core is an electron-transporting material and the carbazole-functionalized periphery is a hole-transporting material. Suzuki polycondensation of the dendronized macromonomers with appropriate diboronic ester afforded considerably high molecular weight materials. To the best of our knowledge, this is the first report on dendronized polymers with both functional core and periphery.

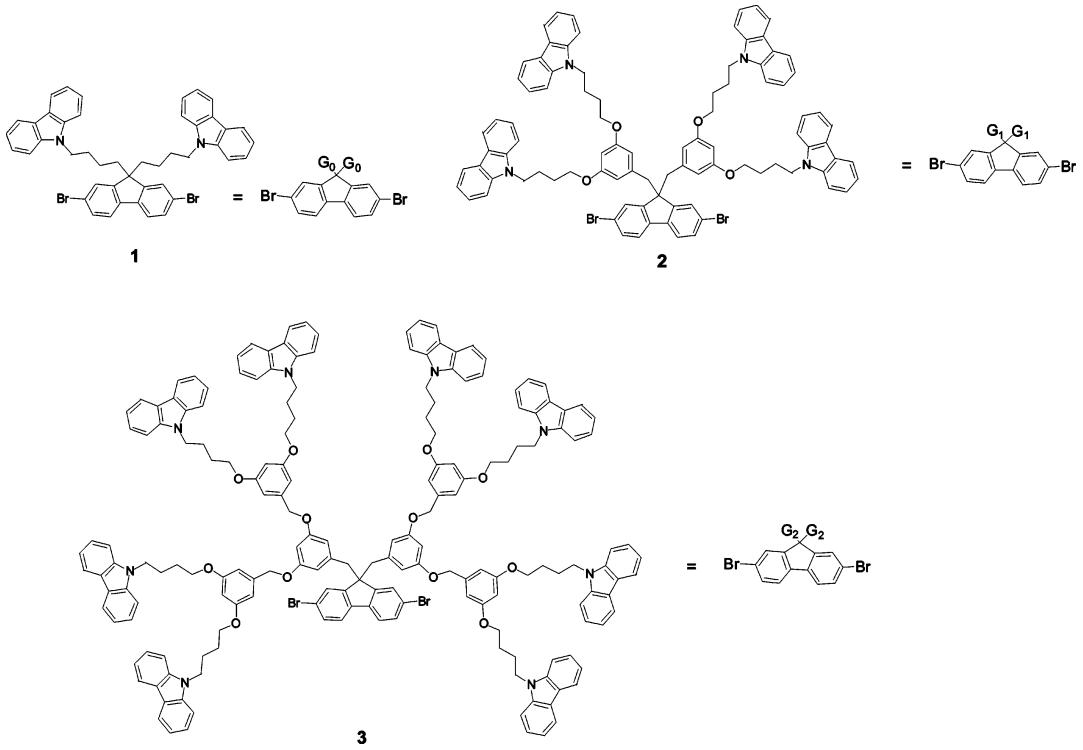
Results and Discussion

Synthesis of Monomers and Polymers. The chemical structures of dendronized monomers **1**−**3** are shown in Chart 1. Monomer **1**, which carries two carbazole groups, was synthesized according to the literature procedure.[15] The synthetic routes leading to **2** and **3** are shown in Scheme 1. Start from **4a**,[16] reduction of the ester group with $LiAlH_4$ afforded the corresponding benzyl alcohol **4b** in a yield of 98%. Appel bromination

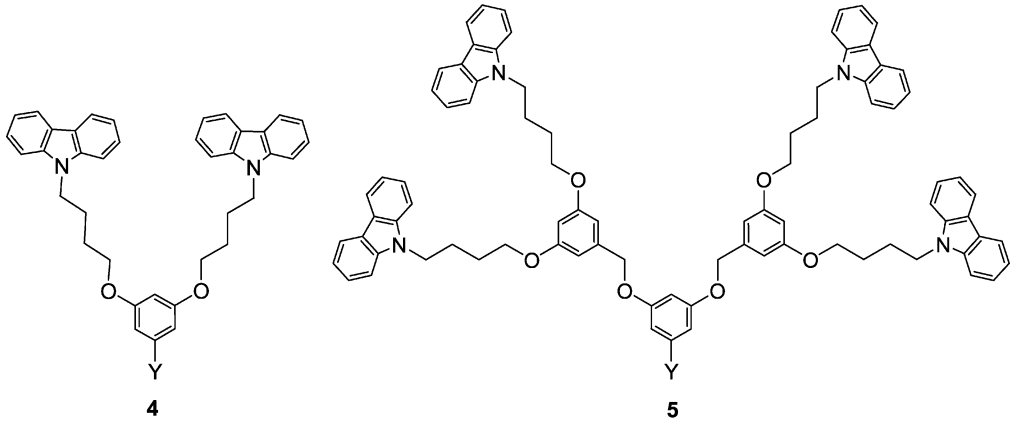
* To whom correspondence should be addressed: e-mail zsbo@iccas.ac.cn.

10.1021/ma049613c CCC: $27.50
Published on Web 07/23/2004

Chart 1



Scheme 1



4a: Y = CO_2CH_3 → **4b**: Y = CH_2OH ($LiAlH_4$/THF)

4b: Y = CH_2OH → **4c**: Y = CH_2Br (CBr_4/PPh_3/THF)

4c: Y = CH_2Br → **5b**: Y = CH_2OH (3,5-dihydroxybenzyl alcohol, K_2CO_3/acetone)

5b: Y = CH_2OH → **5c**: Y = CH_2Br (CBr_4/PPh_3/THF)

4c + **6** → **2** (DMSO/NaOH, TEBAB)

5c + **6** → **3** (DMSO/NaOH, TEBAB)

of **4b** with CBr_4/PPh_3 in THF furnished **4c** in a 91% yield. Reaction of **4c** with 3,5-dihydroxybenzyl alcohol under Williamson etherification conditions (K_2CO_3/acetone) gave **5b** in a yield of 87%, which was brominated with CBr_4/PPh_3 to give the second generation dendritic bromide **5c**. The yield is 94%. The final

Scheme 2

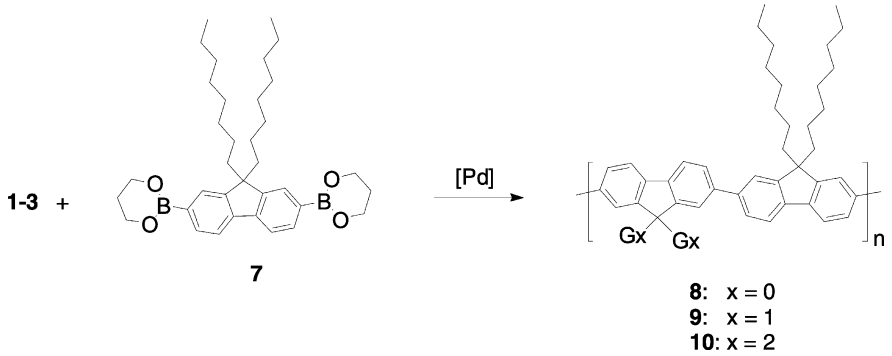


Table 1. Molecular Weights, Thermal Properties, and the Fluorescence Quantum Yield of the Dendronized Polymers in THF and as Films

							Φ_F	
polymer	M_n	P_n	M_w	P_w	M_w/M_n	T_g	in solution	films
8	46 700	47	104 000	104	2.21	103	0.93	0.29
9	131 000	78	157 000	93	1.20	73	0.96	0.55
10	143 000	47	171 000	60	1.19	73	0.86	0.64

attachment of **4c** or **5c** to 2,7-dibromofluorene (**6**) was done following a literature procedure[7b,17] with DMSO as a solvent, aqueous NaOH as a base, and triethylbenzylammonium bromide (TEBAB) as a phase transfer catalyst (PTC). Pure macromonomers **2** and **3** were obtained by normal silica gel column chromatography in yields of 82% and 55%, respectively. Their high purities (>98%) were confirmed by ^{1}H and ^{13}C NMR spectroscopy, gel permeation chromatography (monomodal distribution, M_w/M_n < 1.01), and combustion analysis.

Suzuki polycondensations (SPC) with 2,7-bis(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (**7**)[18] were done in a biphasic system (THF/aqueous $NaHCO_3$) with freshly prepared $Pd(PPh_3)_4$ as a catalyst precursor (Scheme 2). The reactions were kept stirring at reflux for 24 h. During the reaction, all dendronized polymers **8**−**10** started to precipitate from the reaction mixture in about 10 h. All the precipitated polymers could be fully redissolved in common organic solvent, such as methylene chloride, chloroform, and THF. Standard workup afforded the dendronized polymers **8**−**10** as amorphous, slightly yellow materials. The crude polymers were redissolved in certain amount of THF, to which methanol was added dropwise to precipitate the high molar mass polymers. The fractioned high molar mass dendronized polymers were separated by filtration, taken into benzene, and freeze-dried in high-vacuum line. As shown in Figure 1, the GPC elution curves of **8**−**10** are narrow and monomodal distribution. The molecular weights determined by GPC against polystyrene standard are summarized in Table 1. These data show that considerable molecular weights were achieved. The weight-average molecular weights (M_w) for **9** and **10** were found up to 157 and 171 kg/mol, respectively. The results are amazing for dendronized polymers prepared by SPC. For the well-known reason, the molecular weights determined by GPC calibrated with polystyrene standard should be treated with carefulness. GPC method is known to underestimate the actual molecular weight of dendronized polymers.[1,19] The polymers were unambiguously characterized with ^{1}H and ^{13}C NMR spectroscopy as well as elemental analysis.

The thermal properties of the dendronized polymers **8**−**10** were investigated using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). All these polymers **8**−**10** exhibit good thermal stabilities. They show less than 5% decomposition up to 400 °C under nitrogen but lose about 50% of their weights at about 450−480 °C (Figure 2). As shown in Figure 3, in the DSC trace of second heating (10 °C/min) polymer **8** showed a glass transition at about 103 °C, a crystallization peak at about 156 °C, and a melting peak at about 277 °C. Polymers **9** and **10** exhibited only a distinct glass transition at about 77 °C; no crystallization and melting peaks were observed.

Optical Properties. All polymers **8**−**10** were readily dissolved in common organic solvents such as methylene chloride, toluene, and THF and exhibited bright blue fluorescence in solution. The absorption and photoluminescent (PL) spectra of **8**−**10** in dilute THF solution are shown in Figure 4. The absorption maxima are blue-shifted with increasing the generation of the side dendrons. This indicates that the large dendrons can twist the polyfluorene backbone and decrease the effective conjugation in some extent. The two peaks at around 332 and 347 nm, whose intensities increased with the generation, were due to the absorption of the peripheral carbazole groups. Polymers **8** and **9** in dilute THF solution exhibit two emission peaks at 420 and 444

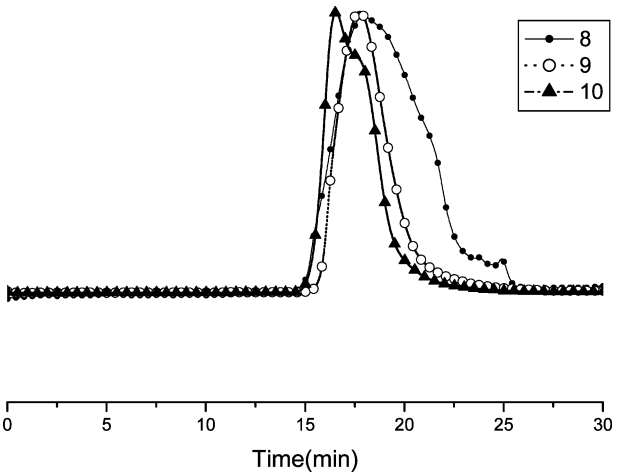


Figure 1. GPC elution traces of dendronized polymers **8**, **9**, and **10.**

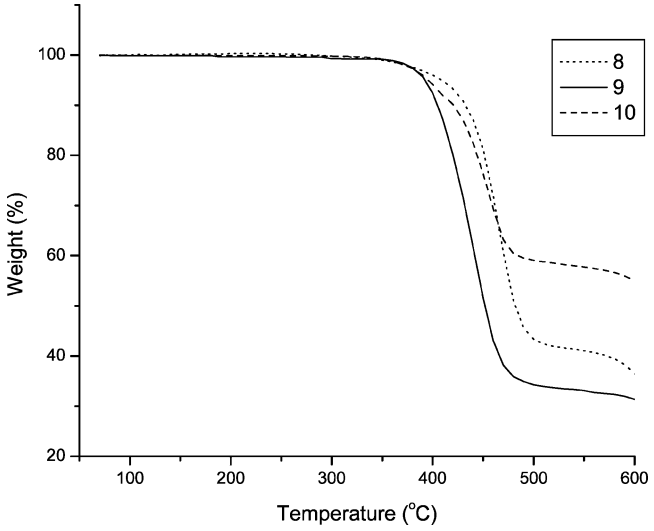


Figure 2. TGA traces of dendronized polymers **8**, **9**, and **10**.

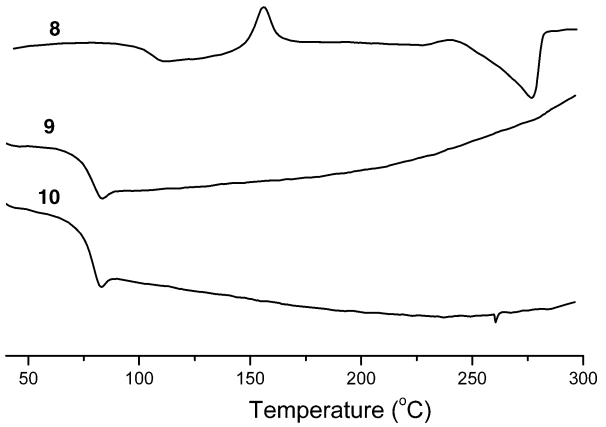


Figure 3. DSC traces of dendronized polymers **8**, **9**, and **10**.

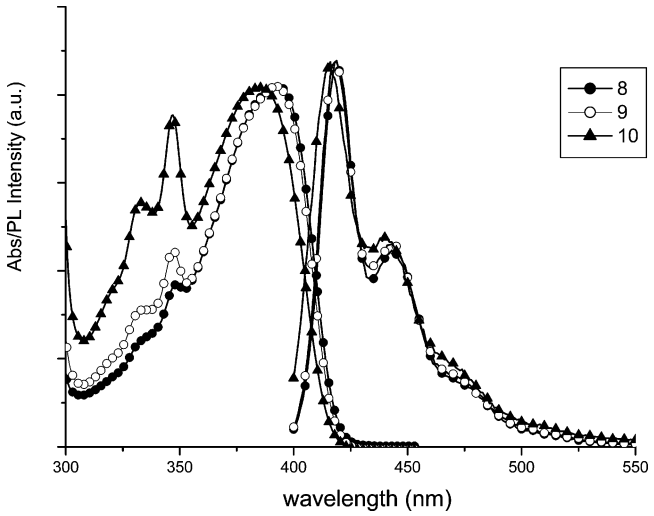


Figure 4. UV−vis absorption and PL spectra (excited at 388 nm) of dendronized polymers **8**, **9**, and **10** in THF.

nm, which resemble poly(2,7-(9,9-dioctyl)fluorene)s in dilute THF solution. For the reason of backbone twisting, the emission peaks of second generation dendronized polymer **10** were blue-shifted to 415 and 440 nm. The PL quantum yields (Φ_F) of polymers **8**−**10** in toluene solution were measured with 9,10-diphenylanthracene as a reference standard (toluene, $\Phi_F = 0.9$)[20] and listed in Table 1. The highest quantum efficient yield (relative) reaches 0.96. The fluorescence quantum yields of the dendronized polymers as films were estimated by comparing the fluorescence intensity of the dendronized polymers with that of a sample of poly(2,7-(9,9-dioctyl)fluorene) (POF) excited at 384 nm (Φ_f = 0.55).[7b,10d] The results are listed in Table 1. This relative method can only give an estimation of the fluorescence quantum yields of the polymers. However, these data still indicated that the fluorescence quantum yields of the polymers films depend on the size of the attached dendrons. The second generation dendronized polymer **10** in film shows the highest quantum yield, which attributed to the minimization of the self-quenching by attaching the bulky dendrons on the polymer backbone.

In conclusion, a novel kind of dendronized 2,7-dibromofluorene macromonomers carrying peripheral carbazole groups were designed and synthesized. Suzuki polycondensation with 9,9-dioctylfluorene-2,7-diboronic ester afforded high molecular weight dendronized polymers. Primary studies showed that this kind of dendronized polymer is a good blue light-emitting material, which exhibited high PL quantum yields (Φ_F) in solution and films (mainly for second generation). Further experiments on electroluminescent properties and detailed in situ investigation on their aggregation behaviors with AFM technology are in progress.

Experimental Section

Materials. 2,7-Dibromo-9,9-dioctylfluorene (**6**),[12h] methyl 3,5-bis[4-(9-carbazoly)butoxy]benzoate (**4a**),[16] 9-(4-bromobutyl)-carbazole,[15] 9,9-bis(4-carbazol-9-ylbutyl)-2,7-dibromofluorene (**1**),[15] and 2,7-bis(1,3,2-dioxaborinan-2-yl)-9,9-dioctylfluorene (**7**)[18] were synthesized according to the literature procedures. All the chemicals were purchased from Acros and used as received.

Characterization. The ^{1}H and ^{13}C NMR spectra were recorded on an AV400 spectrometer in $CDCl_3$. The gel permeation chromatography (GPC) measurements were performed on Waters 410 system against polystyrene standards with THF as an eluent. Electronic absorption spectra were obtained on a Shimadzu UV−vis spectrometer model UV-1601PC. Florescence emission spectra were recorded in THF at 293 K with a Hitachi F4500 fluorescence spectrophotometer. Fluorescence quantum yields (Φ_F) of the samples in toluene were measured by using 9,10-diphenylanthracene (Φ_F = 0.9 in toluene)[20] as standard. The films on quartz used for PL measurements were prepared by spin-coating with 1% toluene solution at 2000 rpm. TGA (TA2100) and DSC (TA2910) measurements were performed under a nitrogen atmosphere at a heating rate of 10 °C/min to record the differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA), respectively.

First Generation Benzyl Alcohol (4b). To a suspension of $LiAlH_4$ (0.50 g, 13 mmol) in THF (100 mL) was added a solution of **4a** (4.67 g, 7.65 mmol) in THF, and the reaction mixture was stirred for 24 h under nitrogen. Aqueous HCl solution was added, the mixture was extracted with CH_2Cl_2 (×3), and the combined organic phase was dried over $MgSO_4$ and evaporated to dryness. The residue was dissolved in CH_2Cl_2 and passed through a short pad of silica gel to afford **4b** as a white solid (4.36 g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, 4H), 7.48−7.41 (m, 8H), 7.37 (s, 1H), 7.26−7.21 (m, 4H), 6.45 (s, 2H), 6.29 (s, 1H), 4.59 (s, 2H), 4.40 (t, 4H), 3.90 (t, 4H), 2.07 (m, 4H), 1.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.26, 143.33, 140.39, 128.39, 125.69, 122.89, 120.43, 118.87, 108.68, 105.19, 100.56, 67.56, 65.33, 42.74, 27.01, 25.90. Anal. Calcd for $C_{39}H_{38}N_2O_3$: C, 80.38; H, 6.57; N, 4.81. Found: C, 80.82; H, 6.66; N, 4.76.

Second Generation Benzyl Alcohol (5b). A mixture of **4c** (1.00 g, 1.55 mmol), 3,5-dihydroxybenzyl alcohol (0.10 g, 0.72 mmol), dry acetone (150 mL), K_2CO_3 (0.50 g, 3.6 mmol), and 18-crown-6 (10 mg) was heated to reflux and stirred under

nitrogen for 24 h. The mixture was evaporated to dryness under reduced pressure, the residue was partitioned between water and CH_2Cl_2, the aqueous layer was extracted with CH_2Cl_2 (×3), and the combined organic layers dried over Na_2SO_4 and evaporated to dryness. Chromatography on silica gel eluting with CH_2Cl_2/hexane (4:1, v/v) afforded **5b** as a white solid (0.80 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, 8H), 7.44 (m, 16H), 7.28−7.22 (m, 9H), 6.60 (s, 2H), 6.52 (s, 4H), 6.33 (s, 3H), 4.93 (s, 4H), 4.61 (s, 2H), 4.39 (t, 8H), 3.91 (t, 8H), 2.08 (m, 8H), 1.83 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.25, 160.09, 143.39, 140.37, 139.19, 125.68, 122.87, 120.40, 118.85, 108.65, 105.83, 105.71, 101.32, 100.80, 69.97, 67.56, 65.29, 42.71, 26.96, 25.88. Anal. Calcd for $C_{85}H_{80}N_4O_7$: C, 80.41; H, 6.35; N, 4.41. Found: C, 80.28; H, 6.54; N, 4.37.

General Procedure for Appel Bromination. To a mixture of the appropriate dendritic benzyl alcohol (1.00 equiv) and CBr_4 in THF was added a solution of PPh_3 in THF under nitrogen, and the reaction mixture was stirred under nitrogen for 30 min. A larger excess of CBr_4 and PPh_3 (2.0 equiv for G1-Br and 5.0 equiv for G2-Br) were required to force the reaction of completion. Water was added, and the aqueous layer was extracted with CH_2Cl_2 (×3). After drying of the organic layer and removal of the solvent under reduced pressure, the crude product was purified as outlined in the following text.

First Generation Benzyl Bromide (4c). 4b (3.06 g, 5.25 mmol), CBr_4 (3.48 g, 10.5 mmol), and PPh_3 (2.75 g, 10.5 mmol) were used. The crude product was purified by a short column eluting with CH_2Cl_2/hexane (1:1, v/v) and precipitated into toluene to give **4c** as a white solid (3.08 g, 91%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, 4H), 7.50−7.43 (m, 8H), 7.28−7.23 (m, 4H), 6.49 (s, 2H), 6.31 (s, 1H), 4.44−4.39 (m, 6H), 3.93 (t, 4H), 2.10 (m, 4H), 1.85 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.17, 140.40, 139.75, 125.71, 122.91, 120.44, 118.90, 108.67, 107.59, 101.44, 67.63, 42.73, 33.63, 26.97, 25.88. Anal. Calcd for $C_{39}H_{37}BrN_2O_2$: C, 72.55; H, 5.78; N, 4.34. Found: C, 72.02; H, 5.81; N, 4.22.

Second Generation Benzyl Bromide (5c). 5b (0.63 g, 0.50 mmol), CBr_4 (0.82 g, 2.5 mmol), and PPh_3 (0.65 g, 2.5 mmol) were used. The crude product was purified by a short column eluting with CH_2Cl_2/hexane (1:1, v/v) and precipitated into methanol to give **5c** as a white solid (0.63 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (d, 8H), 7.50−7.42 (m, 16H), 7.27−7.23 (t, 8H), 6.63 (s.2H), 6.52 (s, 5H), 6.34 (s, 2H), 4.93 (s, 4H), 4.41 (t, 8H), 3.93 (t, 8H), 3.54 (s, 2H), 2.10 (m, 8H), 1.84 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.27, 159.99, 140.38, 139.79, 138.95, 125.69, 122.88, 120.42, 118.87, 108.67, 108.16, 105.87, 102.20, 100.89, 70.06, 67.58, 42.72, 33.64, 26.97, 25.89. Anal. Calcd for $C_{85}H_{79}BrN_4O_6$: C, 76.62; H, 5.98; N, 4.20. Found: C, 76.77; H, 5.99; N, 4.26.

General Procedure for the Synthesis of Dendronized Macromonomers (2, 3). A mixture of **6** and TEBAB in DMSO was degassed three times; a 50 wt % aqueous NaOH solution was added and stirred for 10 min under N_2. To this mixture was added the solution of **4c** or **5c** in degassed DMSO under nitrogen; the reaction mixture was stirred under nitrogen for 10 h, water was added, and the aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic phases were dried over $MgSO_4$. After removal the solvent, the residue was purified by column chromatography with CH_2H_2/hexane (4:1, v/v).

First Generation Dendronized Macromonomer (2). 6 (0.13 g, 0.39 mmol), TEBAB (3.0 mg, 0.01 mmol), DMSO (140 mL), aqueous NaOH solution (2 mL, 50 wt %), and **4c** (0.53 g, 0.82 mmol) were used. **2** was obtained as a colorless solid (0.47 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, 8H), 7.50 (s, 2H), 7.44 (t, 8H), 7.36 (t, 8H), 7.23 (t, 8H), 7.10 (d, 2H), 6.94 (d, 2H), 6.07 (s, 2H), 5.77 (s, 4H), 4.32 (t, 8H), 3.64 (t, 8H), 3.20 (s, 4H), 1.98 (m, 8H), 1.75 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.98, 150.36, 140.36, 138.85, 138.12, 130.27, 127.95, 125.67, 122.87, 121.40, 120.41, 118.84, 108.70, 100.67, 67.43, 57.14, 45.29, 42.67, 26.85, 25.78. Anal. Calcd for $C_{91}H_{80}Br_2N_4O_4$: C, 75.20; H, 5.55; N, 3.85. Found: C, 74.85; H, 5.63; N, 3.70.

Second Generation Dendronized Macromonomer 3. 2,7-Dibromofluorene (0.04 g, 0.1 mmol), TEBAB (0.6 mg), DMSO (90 mL), aqueous NaOH solution (2 mL, 50 wt %), and **5c** (0.32 g, 0.24 mmol) were used. **3** was obtained as a white solid (0.17 g, 55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, 16H), 8.60−7.36 (m, 34H), 7.24−7.18 (m, 18H), 7.09 (d, 2H), 6.43 (s, 8H), 6.27 (s, 6H), 5.86 (s, 4H), 4.61 (s, 8H), 4.33 (t, 16H), 3.84 (t, 16H), 3.10 (s, 4H), 2.02 (m, 16H), 1.77 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.19, 158.81, 140.36, 139.31, 138.22, 130.34, 128.35, 128.02, 125.67, 122.87, 121.42, 120.38, 118.85, 109.22, 108.64, 105.66, 100.71, 69.74, 67.53, 42.68, 29.72, 26.95, 25.86, 0.011. Anal. Calcd for $C_{183}H_{164}Br_2N_8O_{12}$: C, 77.75; H, 5.85; N, 3.96. Found: C, 76.98; H, 5.95; N, 3.76.

General Procedure for the Synthesis of Dendronized Polymers 8−10. A mixture of the respective dendritic monomers **1**−**3**, **7**, $NaHCO_3$, THF, and H_2O was degassed, and $Pd(PPh_3)_4$ was added under a nitrogen atmosphere. The reaction mixture was heated at reflux and stirred under nitrogen for 24 h. CH_2Cl_2 (200 mL) was added to dissolve the precipitate; the organic layer washed with water for three times and dried over Na_2SO_4. After removal of most of the solvent, the residue was precipitated in methanol. The crude polymers were purified by precipitation from THF into methanol again and dried under vacuum to give dendronized polymers **8**−**10**.

Dendronized Polymer 8. Dendronized monomer **1** (0.54 g, 0.70 mmol), **7** (0.39 g, 0.70 mmol), $NaHCO_3$ (1 g), $Pd(PPh_3)_4$ (8.00 mg), THF (25 mL), and H_2O (10 mL) were used. **8** was obtained as a slightly yellow solid (0.59 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (broad, 4H), 7.93−7.86 (broad, 4H), 7.76−7.66 (broad, 8H), 7.40 (broad, 4H), 7.36 (s, 4H), 7.20 (broad, 4H), 4.11 (broad, 4H), 2.31−2.04 (broad, 8H), 1.72 (broad, 4H), 1.34−1.29 (broad, 4H), 1.16 (broad, 20H), 1.03−0.89 (broad, 4H), 0.80 (broad, 6H). ^{13}C NMR (100 MHz, CDCl3): δ 151.91, 150.85, 140.71, 140.20, 126.65, 126.31, 125.51, 122.80, 121.31, 120.29, 118.70, 108.52, 55.45, 55.22, 42.84, 40.44, 40.01, 31.82, 30.12, 29.70, 29.28, 24.04, 22.61, 22.02, 14.06. Anal. Calcd for $[C_{74}H_{78}N_2]_n$: C, 89.29; H, 7.90; N, 2.81. Found: C, 86.87; H, 7.84; N, 3.10.

Dendronized Polymer 9. Dendronized monomer **2** (0.71 g, 0.49 mmol), **7** (0.27 g, 0.49 mmol), $NaHCO_3$ (1 g), $Pd(PPh_3)_4$ (5.60 mg), THF (25 mL), and H_2O (10 mL) were used. **9** was obtained as a slightly yellow solid (0.74 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (broad, 8H), 7.98−7.00 (broad, 36H), 6.17 (broad, 2H), 6.02 (broad, 4H), 4.18 (broad, 8H), 3.60 (broad, 8H), 3.43 (broad, 4H), 1.93−1.86 (broad, 12H), 1.61 (broad, 8H), 1.43−1.26 (broad, 4H), 1.10−0.89 (broad, 20H), 0.73 (broad, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.02, 140.28, 125.60, 122.83, 120.33, 118.78, 108.55, 67.33, 42.52, 31.74, 29.30, 26.75, 25.72, 22.56, 14.02. Anal. Calcd for $[C_{120}H_{120}N_4O_4]_n$: C, 85.68; H, 7.19; N, 3.33. Found: C, 84.86; H, 7.15; N, 3.33.

Dendronized Polymer 10. Dendronized monomer **3** (0.37 g, 0.13 mmol), **7** (0.07 g, 0.1 mmol), $NaHCO_3$ (1 g), $Pd(PPh_3)_4$ (2.40 mg), THF (25 mL), and H_2O (8 mL) were used. **10** was obtained as a slightly yellow solid (0.28 g, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (broad, 16H), 7.87−7.00 (broad, 60H), 6.35 (broad, 2H), 6.27 (broad, 8H), 6.16 (broad, 4H), 6.05 (broad, 4H), 4.55 (broad, 8H), 4.14 (broad, 16H), 3.59 (broad, 20H), 2.15 (broad, 16H), 1.84 (broad, 20H), 1.26 (broad, 4H), 0.89−0.85 (broad, 20H), 0.63 (broad, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.14, 158.86, 140.29, 139.30, 128.32, 125.61, 122.80, 120.31, 118.81, 108.59, 105.47, 100.67, 69.71, 67.34, 42.53, 31.69, 29.95, 29.20, 26.84, 25.73, 22.54, 14.03. Anal. Calcd for $[C_{212}H_{204}N_8O_{12}]_n$: C, 83.32; H, 6.73; N, 3.67; Found: C, 82.03; H, 6.67; N, 3.67.

Acknowledgment. Financial support from The Chinese Academy of Sciences (Hundred Talents Program), the National Natural Science Foundation of China (the Outstanding Youth Fund No. 20225415), and the Major State Basic Research Development Program (No. 2002CB613401) is greatly acknowledged.

References and Notes

(1) (a) Zhang, A. F.; Shu, L. J.; Bo, Z. S.; Schlüter, A. D. *Macromol. Chem. Phys.* **2003**, *204*, 328. (b) Schlüter, A. D.; Rabe, J. P. *Angew. Chem., Int. Ed.* **2000**, *39*, 864.

(2) (a) Karakaya, B.; Claussen, W.; Gessler, K.; Saenger, W.; Schlüter, A. D. *J. Am. Chem. Soc.* **1997**, *119*, 3296. (b) Stocker, W.; Karakaya, B.; Schürmann, B. L.; Rabe, J. P.; Schlüter, A. D. *J. Am. Chem. Soc.* **1998**, *120*, 7691. (c) Bo, Z. S.; Schlüter, A. D. *Macromol. Rapid Commun.* **1999**, *20*, 21. (d) Bo, Z. S.; Rabe, J. P.; Schlüter, A. D. *Angew. Chem., Int. Ed.* **1999**, *38*, 2370. (e) Bo, Z. S.; Schlüter, A. D. *Chem.—Eur. J.* **2000**, *6*, 3235. (f) Bo, Z. S.; Zhang, C. M.; Severin, N.; Rabe, J. P.; Schlüter, A. D. *Macromolecules* **2000**, *33*, 2688.

(3) Bao, Z. N.; Amundson, K. R.; Lovinger, A. J. *Macromolecules* **1998**, *31*, 8647.

(4) Sato, T.; Jiang, D. L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10658.

(5) Schenning, A. P. H. J.; Martin, R. E.; Ito, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J. P.; Gross, M. *Chem. Commun.* **1998**, 1013.

(6) Kaneko, T.; Horie, T.; Asano, M.; Aoki, T.; Oikawa, E. *Macromolecules* **1997**, *30*, 3118.

(7) (a) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. *J. Am. Chem. Soc.* **2001**, *123*, 946. (b) Marsitzky, D.; Vestberg, R.; Blainey, P.; Tang, B. T.; Hawker, C. J.; Carter, K. R. *J. Am. Chem. Soc.* **2001**, *123*, 6965. (c) Chou, C. H.; Shu, C. F. *Macromolecules* **2002**, *35*, 9673.

(8) Grayson, S. M.; Fréchet, J. M. J. *Macromolecules* **2001**, *34*, 6542.

(9) (a) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416. (b) Neher, D. *Macromol. Rapid Commun.* **2001**, *22*, 1365. (c) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477. (d) Leclerc, M. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2867.

(10) (a) Prieto, I.; Teetsov, J.; Fox, M. A.; van den Bout, D. A.; Bard, A. J. *J. Phys. Chem. A* **2001**, *105*, 520. (b) Sainova, D.; Miteva, T.; Nothofer, H. G.; Scherf, U.; Glowacki, I.; Ulanski, J.; Fujikawa, H.; Neher, D. *Appl. Phys. Lett.* **2000**, *76*, 1810. (c) Weinfertner, K.-H.; Fujikawa, H.; Tokito, S.; Taga, Y. *Appl. Phys. Lett.* **2000**, *76*, 2502. (d) Grice, A. W.; Bradley, D. D. C.; Bernius, M. T.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Appl. Phys. Lett.* **1998**, *73*, 629. (e) Lee, J.-I.; Klaerner, G.; Miller, R. D. *Synth. Met.* **1999**, *101*, 126. (f) Teetsov, J. A.; Vanden Bout, D. A. *J. Am. Chem. Soc.* **2001**, *123*, 3605. (g) Zeng, G.; Yu, W. L.; Chua, S. J.; Huang, W. *Macromolecules* **2002**, *35*, 6907.

(11) (a) Craig, M. R.; de Kok, M. M.; Hofstraat, J. W.; Schenning, A. P. H. J.; Meijer, E. W. *J. Mater. Chem.* **2003**, *13*, 2861. (b) Lupton, J. M.; Craig, M. R.; Meijer, E. W. *Appl. Phys. Lett.* **2002**, *80*, 4489. (c) List, E. J. W.; Günther, R.; Scandiucci de Frietas, P.; Scherf, U. *Adv. Mater.* **2002**, *14*, 374. (d) Gaal, M.; List, E. J. W.; Scherf, U. *Macromolecules* **2003**, *36*, 4236. (e) Romaner, L.; Pogantsch, A.; Scandiucci de Freitas, P. Scherf, U. *Adv. Funct. Mater.* **2003**, *13*, 597. (f) Zojer, E.; Pogantsch, A.; Hennebicq, E.; Beljonne, D.; Brédas, J.-L.; Scandiucci de Frietas, P.; Scherf, U.; List, E. J. W. *J. Chem. Phys.* **2002**, *117*, 6794.

(12) (a) Teetsov, J.; Fox, M. A. *J. Mater. Chem.* **1999**, *9*, 2117. (b) Shu, C. F.; Dodda, R.; Wu, F. I.; Liu, M. S.; Jen, A. K. Y. *Macromolecules* **2003**, *36*, 6698. (c) Ego, C.; Grimsdale, A. C.; Uckert, F.; Yu, G.; Srdanov, G.; Müllen, K. *Adv. Mater.* **2002**, *14*, 809. (d) Marsitzky, D.; Scott, J. C.; Chen, J. P.; Lee, V. Y.; Miller, R. D.; Setayesh, S.; Müllen, K. *Adv. Mater.* **2001**, *13*, 1096. (e) Jiang, X. Z.; Liu, S.; Ma, H.; Jen, A. K. Y. *Appl. Phys. Lett.* **2000**, *76*, 1813. (f) Yu, W. L.; Pei, J.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828. (g) Zhan, X. W.; Wang, S.; Liu, Y. Q.; Wu, X.; Zhu, D. B. *Chem. Mater.* **2003**, *15*, 1963. (h) Xia, C. J.; Advincula, R. C. *Macromolecules* **2001**, *34*, 5854. (i) Kreyenschmidt, M.; Klaerner, G.; Fuhrer, T.; Ashenhurst, J.; Karg, S.; Chen, W. D.; Lee, V. Y.; Scott, J. C.; Miller, R. D. *Macromolecules* **1998**, *31*, 1099. (j) Redecker, M.; Bradley, D. D. C.; Inbasekaran, M.; Wu, W. W.; Woo, E. P. *Adv. Mater.* **1999**, *11*, 241. (k) Klärner, G.; Miller, R. D.; Hawker, C. J. *Polym. Prepr.* **1998**, 1047. (l) Miteva, T.; Meisel, A.; Knoll, W.; Nothofer, H. G.; Scherf, U.; Müller, D. C.; Meerholz, K.; Yasuda, A.; Neher, D. *Adv. Mater.* **2001**, *13*, 565. (m) Lee, J. L.; Hwang, D. H.; Park, H.; Do, L. M.; Chu, H. Y.; Zyung, T.; Miller, R. D. *Synth. Met.* **2000**, *111*, 195. (n) Klärner, G.; Lee, J. I.; Lee, V. Y.; Chan, E.; Chen, J. P.; Nelson, A.; Markiewicz, D.; Siemens, R.; Scott, J. C.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1800. (o) Chen, J. P.; Klaerner, G.; Lee, J. I.; Markiewicz, D.; Lee, V. Y.; Miller, R. D.; Scott, J. C. *Synth. Met.* **1999**, *107*, 129. (p) Cho, H. J.; Jung, B. J.; Cho, N. S.; Lee, J.; Shim, H. K. *Macromolecules* **2003**, *36*, 6704.

(13) Surin, M.; Hennebicq, E.; Ego, C.; Marsitzky, D.; Grimsdale, A. C.; Müllen, K.; Brédas, J.-L.; Lazzaroni, R.; Leclère, P. *Chem. Mater.* **2004**, *16*, 994.

(14) Suh, M. C.; Chin, B. D.; Kim, M. H.; Kang, T. M.; Lee, S. T. *Adv. Mater.* **2003**, *15*, 1254.

(15) Xia, C. J.; Advincula, R. C. *Chem. Mater.* **2001**,*13*, 1682.

(16) Bo, Z. S.; Zhang, W.; Zhang, X.; Zhang, C. M.; Shen, J. C. *Macromol. Chem. Phys.* **1998**, *199*, 1323.

(17) Woo, E. P.; Inbasekaran, M.; Shiang, W.; Roof, G. R. International Patent, WO 97/05184, 1997.

(18) Chen, H.; He, M. Y.; Pei, J.; Liu, B. *Anal. Chem.* **2002**, *74*, 6252.

(19) (a) Percec, V.; Ahn, C. H.; Barboiu, B. *J. Am. Chem. Soc.* **1997**, *119*, 12978. (b) Förster, S.; Neubert, I.; Schlüter, A. D.; Linder, P. *Macromolecules* **1999**, *32*, 4043.

(20) Hamai, S.; Hirayama, F. *J. Phys. Chem.* **1983**, *87*, 83.

MA049613C