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Effects of Methyl Substitution of Poly(9-alkyl-9*H*-carbazole-2,7-diyl)s at the 3,6-Positions on Their Physical Properties

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The preparation and characterization of poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-2,7-diyl)s **P1** and poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-*alt*-9-alkyl-9*H*-carbazole-2,7 -diyl)s alternating copolymers **P2** are presented. The polymers were prepared via Suzuki cross-coupling reactions, and two different alkyl substituents were used for both classes of polymers to investigate the effects of their different steric bulks on the properties of the resulting materials. Both classes of materials provided wide-band-gap polymers that emit in the blue part of the electromagnetic spectrum. Cyclic voltammetry studies on the two classes of polymers indicate greater electrolytic stability of these new polymers as compared to poly(9-alkyl-9*H*-carbazole-2,7-diyl)s as a result of a full or partial methyl functionalization of the 3,6-positions on carbazole repeat units on the polymer chains. The new polymers are also thermally stable up to 350 °C.

Introduction

Currently, there is a considerable drive to develop highly fluorescent blue-light-emitting polymers. Such polymers not only are required for efficient emission in the blue part of the electromagnetic spectrum, but could also serve as energy-transfer donors when used in conjunction with added lower-band-gap fluorophores.[1] They could also be used as hosts for phosphorescent dyes in an effort to enable the use of both singlet and triplet excitons in the radiative decay process.[2]

Carbazole-based polymers such as poly(vinylcarbazole) (PVK) are used extensively in this area of research, chiefly as hole-transporting materials,[3] but also as wide-band-gap hosts to lower-band-gap fluorophores.[4] Poly(9-alkyl-9*H*-carbazole-3,6-diyl)s constitute another class of carbazole-based polymers that has also been targeted in the literature.[5] This class of carbazole polymers differs from PVK, as these are main-chain carbazole polymers rather than linear polymers with pendant carbazole units. However, in view of their structural makeup and 3,6-linkage between consecutive carbazole repeat units, electronic conjugation in poly(9-alkyl-9*H*-carbazole-3,6-diyl)s is limited to about two carbazole units; in addition, their quantum yields of fluorescence are fairly low.

Polyfluorenes and poly(*p*-phenylene)s have attracted much interest in this area, and great advances have been achieved with these materials. Recently, much effort has been directed toward developing alternative polymers to these two classes of materials, and special interest has focused on 2,7-linked carbazole polymers.[6] We have recently shown that poly(9-alkyl-9*H*-carbazole-2,7-diyl)s[7] offer many advantageous properties such as high photoluminescence efficiencies and lower oxidation potentials than their polyfluorene analogues. These polymers also emit in the blue part of the electromagnetic spectrum; however, cyclic voltammetry studies on this class of polymers have revealed that they do oxidize irreversibly under electrolytic conditions. We and others[8] have explained this instability as arising from the high reactivity of their unprotected 3,6-positions. A review on this class of materials has recently been published. In this study, we present our results on the preparation of a range of 2,7-linked 9-alkylcarbazole homopolymers and copolymers where the 3,6-positions are fully and partly functionalized, respectively, with methyl substituents and examine their electrolytic stability and physical properties.

Experimental Section

Materials. 2,7-Dibromo-9*H*-carbazole was obtained according to literature procedures.[9] The sodium hydroxide was quickly ground

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just before use when employed in the alkylation reactions of 2,7-dibromo-9*H*-carbazole or 2,7-dibromo-3,6-dimethyl-9*H*-carbazole. Tetrahydrofuran (THF) was distilled over sodium benzophenone under inert nitrogen atmosphere. Toluene was dried and distilled over sodium under an inert argon atmosphere. Acetonitrile (HPLC grade) was dried and distilled over phosphorus pentoxide under an inert argon atmosphere and was then stored over molecular sieves 3A. 2,5-Dibromo-4-nitrotoluene was prepared according to literature procedures,[10] as were 2,7-dibromo-9*H*-carbazole[9] and 2,7-dibromo-9-(2-hexyldecyl)-9*H*-carbazole (**6a**).[7]

Measurements. NMR spectra were recorded on Bruker 250 MHz, AMX400 400 MHz, or DRX500 500 MHz NMR spectrometers at 22 °C in chloroform-d_1 or acetone-d_6 solution with TMS as the internal standard. IR absorption spectra were recorded on the Nicolet model 205 FT-IR spectrometer. Liquid samples were analyzed neat using the NaCl-plate method, and solid samples were analyzed using the diamond ATR attachment for solid samples. Melting points were obtained using a Gallenkamp melting point apparatus. GC-MS spectra were recorded on a Perkin-Elmer Turbomass mass spectrometer equipped with a Perkin-Elmer PE-5MS capillary column. Mass spectra were obtained by the electron impact method (EI) or the chemical ionization method (CI). GPC curves were recorded on equipment consisting of a Waters Model 515 HPLC pump, a Gilson model 234 autoinjector, a Millipore Waters Lambda-Max model 481 LC spectrometer, an Erma ERC-7512 refractive index (RI) detector, a PLgel 5-m 500A column, and a PLgel 10-m MIXED-B column using THF as the eluent at a rate of 1 cm^3 min^{-1}. Polymer solutions in THF (2.5 mg cm^{-3}) were used as samples for GPC analysis. The GPC curves were obtained by the RI detection method, calibrated with a series of narrow polystyrene standards (Polymer Laboratories). Elemental analyses were carried out with a Perkin-Elmer 2400 CHN elemental analyzer for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. UV−visible absorption spectra were measured with a Hitachi U-2010 double-beam UV−visible spectrophotometer. The absorbance of monomers and polymers was measured in a solution of dichloromethane (HPLC grade) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm) purchased from Sigma-Aldrich. Samples of pristine polymer thin films for UV−visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm^{-3} polymer solutions in dichloromethane (HPLC grade), and the measurements were carried out at ambient temperature. Photoluminescence spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer equipped with a Hamamatsu Photonics R928F photomultiplier tube (PMT). PL solution measurements were carried out using a quartz fluorescence cuvette (light path length = 10 mm) purchased from Sigma-Aldrich. Photoluminescence spectra measurements of harmine and quinine sulfate dihydrate solutions were carried out in 0.05 and 0.5 mol dm^{-3} sulfuric acid, respectively, at 25 °C in air, as both harmine and quinine sulfate dihydrate exhibit no oxygen quenching effect.

Photoluminescence spectra measurements of the polymer solutions were carried out in dichloromethane (HPLC grade) at 25 °C. The oxygen quenching effects of polymers **P1** and **P2** were examined by comparing the photoluminescence spectra of their solutions in air with those under an argon atmosphere. Because the solutions exhibited no oxygen quenching effect, photoluminescence spectra measurements of their solutions were carried out in air. Samples of pristine polymer thin films for PL spectra measurements were prepared by dip coating quartz plates into 0.1 mg cm^{-3} polymer solutions in dichloromethane (HPLC grade), and the measurements were carried out at ambient temperature in air.

The absorbances of the sample solutions at the excitation wavelengths used were kept below 0.05 to obtain inner-filter-effect-free photoluminescence spectra. All photoluminescence spectra were corrected. The correction factors were obtained by excitation spectra measurements of the quantum counter (rhodamine B standard solution) for the excitation side and by a synchronous wavelength scan using a light diffuser for the emission side. The light diffuser (part no. 650-1576) was provided with the spectrophotometer as an accessory. The correction factors obtained were stored in the memory of the spectrophotometer. As a result, the spectrophotometer automatically gave corrected excitation and emission spectra when measurements were carried out.

Harmine and quinine sulfate dihydrate in sulfuric acid (0.05 and 0.5 mol dm^{-3}, respectively) were employed as fluorescence standards. The quantum yields in dilute solutions were obtained by comparison with a fluorescence standard of a known quantum yield using the equation

$$\Phi_x = \Phi_s(S_s/A_s)^{-1}(S_x/A_x)(n_x^2/n_s^2)$$

where the subscripts s and x refer to the standard and the unknown sample solutions, respectively; Φ is the quantum yield; *A* is the absorbance at the excitation wavelength used; *S* is the integral intensity of the corrected photoluminescence spectra; and *n* is the refractive index of the solvent. The fluorescence standard solution and the unknown sample solution were excited at the same wavelength. Quinine sulfate dihydrate solution in 0.5 mol dm^{-3} sulfuric acid ($\Phi_s = 0.546$) was employed as the fluorescence standard solution. With regard to the refractive indexes of the solvents, values of 1.339, 1.334, and 1.424 were employed for 0.5 mol dm^{-3} sulfuric acid, 0.05 mol dm^{-3} sulfuric acid, and dichloromethane, respectively. *S*/*A* values for each sample in solution could simply be obtained by dividing the integral intensities of the spectra by the absorbances at the excitation wavelengths employed using a sample solution of a certain concentration. To minimize experimental error, the final *S*/*A* values used in the calculations for each sample were obtained from plots of the integral intensities of the spectra vs the absorbances at the excitation wavelengths employed using sample solutions of various concentrations. The reliability of our measurements was confirmed upon measurement of the quantum yield of harmine using quinine sulfate dihydrate as the standard. The experimental value obtained was identical to that reported in the literature ($\Phi_s = 0.45$).[11]

TGA curves were obtained on a Perkin-Elmer Pyris 1 thermogravimetric analyzer at a scan rate of 20 °C min^{-1} under an inert nitrogen atmosphere. Platinum pans were used as sample pans. The weights of the samples were ca. 5 mg. Cyclic voltammograms were recorded with equipment consisting of a Princeton Applied Research model 263A potentiostat/galvanostat. Measurements were carried out under argon at 25 ± 2 °C. Tetrabutylammonium perchlorate ($TBAClO_4$) solution in acetonitrile (0.1 mol dm^{-3}, 10 cm^3) was used as the electrolyte solution. A three-electrode system was used. The three electrodes consisted of a Ag/Ag^+ reference electrode (silver wire in 0.01 mol dm^{-3} silver nitrate solution in the electrolyte solution), a platinum working electrode (2-mm-diameter smooth platinum disk, area = 3.14×10^{-2} cm^2), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop-casting 1.0 mm^3 of polymer solution in dichloromethane (HPLC grade) (1 mg cm^{-3}) onto the working electrode and then drying in air.

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Ferrocene was employed as the reference redox system according to IUPAC's recommendation[12] Polymer thin films were formed by drop-casting 1.0 mm^3 of polymer solution in dichloromethane (analytical reagent) (1 mg cm^{-3}) onto the working electrode and then drying in air.

Preparation of the Monomers. All reactions were carried out under inert nitrogen atmosphere.

*4,4′-Dibromo-5,5′-dimethyl-2,2′-dinitrobiphenyl (**1**).* A mixture of 2,5-dibromo-4-nitrotoluene (25.70 g, 87.12 mmol) and copper powder (−150 mesh) (13.29 g, 209.08 mmol) in DMF (230 cm^3) was heated at 120 °C with stirring for 2 h. The reaction mixture was cooled to ambient temperature, and then toluene (350 cm^3) was added. Unreacted copper powder and insoluble materials were filtered off. The filtrate was washed with a saturated NaCl solution (350 $cm^3 \times 6$) and dried over $MgSO_4$, and then the solvent was removed in vacuo. The obtained residue was further dried in vacuo to give 4,4′-dibromo-5,5′-dimethyl-2,2′-dinitrobiphenyl (**1**) as a yellow powder (16.01 g, 85.4% yield). mp: 246.0−247.9 °C (lit.[13] 228−230 °C). The product gave a single peak on GC (retention time = 11.04 min). IR (solid state): 3106, 2961, 1596, 1562, 1513, 1434, 1382, 1338, 1283, 1260, 1117, 1095, 1057, 1034, 1012, 913, 894, 881, 840, 798, 761, 738, 699, 684, 658, 630, 620, 569, 545 cm^{-1}. ^1H NMR ($CDCl_3$) δ_H (ppm): 2.49 (6H, s), 7.11 (2H, s), 8.41 (2H, s). ^{13}C NMR ($CDCl_3$), δ_C (ppm): 23.0 (2C), 124.8 (2C), 128.8 (2C), 132.3 (2C), 132.5 (2C), 145.0 (2C), 145.1 (2C). Anal. Calcd for $C_{14}H_{10}N_2O_2Br_2$: C, 39.10; H, 2.34; N, 6.51; Br, 37.16. Found: C, 39.20; H, 2.79; N, 5.60; Br, 36.67.

*4,4′-Dibromo-5,5′-dimethylbiphenyl-2,2′-diamine (**2**).* To a mixture of 4,4′-dibromo-5,5′-dimethyl-2,2′-dinitrobiphenyl (**1**) (15.60 g, 36.27 mmol), ethanol (HPLC grade) (200 cm^3), and 37 wt % hydrochloric acid (80 cm^3) was added tin powder (−325 mesh) (17.22 g, 145.08 mmol). The reaction mixture was then refluxed for 1.5 h, and an additional portion of tin powder (−325 mesh) (17.22 g, 145.08 mmol) was added. The reaction mixture was then refluxed for an additional period of 1.5 h. The reaction mixture was cooled to ambient temperature, and the unreacted tin powder was filtered off. The filtrate was poured onto a mixture of ice and 10 wt % NaOH aqueous solution (600 cm^3) and then extracted with diethyl ether (450 $cm^3 \times 4$). The diethyl ether layer was then washed with distilled water (300 $cm^3 \times 3$) and dried over $MgSO_4$, and then the solvent was removed in vacuo. The obtained residue was further dried in vacuo to give 4,4′-dibromo-5,5′-dimethylbiphenyl-2,2′-diamine (**2**) as a pale yellow powder (11.26 g, 84% yield). The product gave a single peak on GC (retention time = 12.86 min). mp: 122.1−123.9 °C. IR (solid state): 3402, 3294, 3092, 3015, 2960, 2869, 2017, 1967, 1918, 1848, 1789, 1715, 1615, 1584, 1525, 1474, 1438, 1349, 1324, 1291, 1268, 1194, 1135, 1102, 1074, 1002, 976, 925, 904, 880, 862, 823, 779, 718, 665, 652, 611, 594, 563, 534, 510 cm^{-1}. MS (EI) (*m*/*z*): 368, 370, 372 ($M^{\bullet+}$). ^1H NMR ($CDCl_3$) δ_H (ppm): 2.22 (6H, s), 3.34 (4H, s), 6.85 (2H, s), 6.91 (2H, s). ^{13}C NMR ($CDCl_3$) δ_C (ppm): 21.68 (2C), 118.88 (2C), 119.04 (2C), 123.12 (2C), 127.70 (2C), 132.64 (2C), 142.98 (2C). Anal. Calcd for $C_{14}H_{14}N_2Br_2$: C, 45.44; H, 3.81; N, 7.57; Br, 43.18. Found: C, 45.39; H, 3.84; N, 6.99; Br, 46.47.

*2,7-Dibromo-3,6-dimethyl-9H-carbazole (**3**).* A mixture of 4,4′-dibromo-5,5′-dimethylbiphenyl-2,2′-diamine (**2**) (11.10 g, 29.99 mmol) and 4-dodecylbenzenesulfonic acid (19.60 g, 60.03 mmol) in 5-*tert*-butyl-*m*-xylene (180 cm^3) was refluxed for 24 h. The solution was evaporated to dryness upon distillation of the solvent in vacuo. The residue was purified by column chromatography on silica gel 60 with toluene/hexane (3/7, v/v) as the eluent to give 2,7-dibromo-3,6-dimethyl-9*H*-carbazole (**3**) as a white powder (7.62 g, 72.0% yield). mp: 242.2−243.4 °C. The product gave a single peak on GC (retention time = 11.34 min). IR (solid state): 3416, 2921, 2360, 1707, 1601, 1479, 1450, 1377, 1324, 1303, 1276, 1241, 1210, 1053, 1038, 995, 972, 903, 874, 856, 809, 777, 724, 669, 620, 598, 579, 570 cm^{-1}. MS (EI) (*m*/*z*): 351, 353, 355 ($M^{\bullet+}$). ^1H NMR (acetone-d_6) δ_H (ppm): 2.50 (6H, s), 7.71 (2H, s), 8.02 (2H, s), 10.46 (1H, s). ^{13}C NMR (acetone-d_6) δ_C (ppm): 23.0 (2C), 115.3 (2C), 122.4 (2C), 122.7 (2C), 123.1 (2C), 128.4 (2C), 140.7 (2C). Anal. Calcd for $C_{14}H_{11}NBr_2$: C, 47.63; H, 3.14; N, 3.97; Br, 45.26. Found: C, 47.93; H, 3.30; N, 3.98; Br, 44.91.

*2,7-Dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole (**4a**).* A mixture of 2,7-dibromo-3,6-dimethyl-9*H*-carbazole (**3**) (7.40 g, 20.96 mmol), 7-bromomethylpentadecane (9.72 g, 31.83 mmol), tetrabutylammonium hydrogensulfate (0.30 g, 0.88 mmol), and NaOH (1.27 g, 31.75 mmol) in acetone (HPLC grade) (60 cm^3) was refluxed for 16 h. After the reaction was completed, the acetone was removed in vacuo, and the residue was extracted with toluene (500 cm^3). The toluene solution was washed with a saturated NaCl aqueous solution (350 $cm^3 \times 3$), dried over $MgSO_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel 60 with hexane as the eluent to give 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (**4a**) as an oil that turns to a white powder over time (11.72 g, 96.8% yield). mp: 58.5−59.3 °C. The product gave a single peak on GC (retention time = 16.83 min). IR (solid state): 2935, 2918, 2852, 1601, 1556, 1478, 1466,1450, 1378, 1342, 1300, 1290, 1245, 1235, 1182, 1158, 1040, 996, 946, 922, 869, 844, 803, 781, 754, 722, 696, 672, 652, 627, 602, 576, 566, 544, 525, 517 cm^{-1}. MS (EI) (*m*/*z*): 575, 577, 579 ($M^{\bullet+}$). ^1H NMR ($CDCl_3$) δ_H (ppm): 0.78−0.91 (6H, m), 1.14−1.40 (24H, m), 2.04 (1H, septet, $J = 6$ Hz), 2.54 (6H, s), 3.92 (2H, d, $J = 8$ Hz), 7.48 (2H, s), 7.81 (2H, s). ^{13}C NMR ($CDCl_3$) δ_C (ppm): 14.10 (1C), 14.13 (1C), 22.67 (1C), 22.70 (1C), 23.01 (2C), 26.38 (1C), 26.41 (1C), 29.08 (1C), 29.29 (1C), 29.52 (1C), 29.61 (1C), 29.92 (1C), 31.65 (1C), 31.81 (1C), 31.89 (1C), 37.54 (1C), 47.81 (1C), 112.62 (2C), 121.33 (2C), 121.59 (2C), 122.35 (2C), 127.74 (2C), 140.37 (2C). Anal. Calcd for $C_{30}H_{43}NBr_2$: C, 62.40; H, 7.51; N, 2.43; Br, 27.67. Found: C, 62.69; H, 7.74; N, 2.35; Br, 27.57.

*2,7-Dibromo-3,6-dimethyl-9-(2-butyloctyl)-9H-carbazole (**4b**).* 2,7-Dibromo-3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole (**4b**) was prepared according to the method used for 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (**4a**), except that 2.50 g (7.08 mmol) of 2,7-dibromo-3,6-dimethyl-9*H*-carbazole (**3**), 2.65 g (10.63 mmol) of 5-bromomethylundecane, 0.20 g (0.59 mmol) of tetrabutylammonium hydrogensulfate, and 0.70 g (17.50 mmol) of NaOH were used in 50 cm^3 of acetone (HPLC grade). 2,7-Dibromo-3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole (**4b**) was isolated as a colorless oil (1.70 g, 46.0% yield). The product gave a single peak on GC (retention time = 14.76 min). IR (solid state): 2939, 2926, 2856, 1603, 1560, 1477, 1459, 1379, 1343, 1301, 1285, 1240, 1182, 1041, 997, 948, 931, 866, 836, 780, 725, 699, 672, 603, 568, 508, 495 cm^{-1}. MS (EI) (*m*/*z*): 519, 521, 523 ($M^{\bullet+}$). ^1H NMR ($CDCl_3$) δ_H (ppm): 0.79−0.92 (6H, m), 1.11−1.41 (16H, m), 2.04 (1H, septet), 2.54 (6H, s), 3.94 (2H, d, $J = 7.5$ Hz), 7.48 (2H, s), 7.82 (2H, s). ^{13}C NMR ($CDCl_3$) δ_C (ppm): 14.00 (1C), 14.05 (1C), 22.61 (1C), 22.98 (2C), 26.33 (1C), 28.59 (1C), 29.58 (1C), 29.70 (1C), 31.37 (1C), 31.60 (1C), 31.77 (1C), 37.61 (1C), 47.87 (1C), 112.65 (2C), 121.35 (2C), 121.61 (2C), 122.37 (2C), 127.78 (2C), 140.43 (2C). Anal. Calcd for $C_{26}H_{35}NBr_2$: C, 59.90; H, 6.77; N, 2.69; Br, 30.65. Found: C, 60.09; H, 6.75; N, 2.46; Br, 30.49.

*2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole (**5a**).* *t*-Butyllithium (30.6 cm^3, 52.02 mmol, 1.7 M in pentane) was added dropwise to a solution

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of 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (**4a**) (10.0 g, 17.32 mmol) in THF (500 cm^3) at -78 °C. The reaction mixture was stirred at -78 °C for 4 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (32.3 g, 17.36 mmol) was then added dropwise to the solution at -78 °C, and the reaction mixture was stirred at -78 °C for an additional 2 h. The reaction mixture was then allowed to warm to ambient temperature and stirred for another 36 h. The reaction mixture was then poured onto water (600 cm^3) and extracted with diethyl ether. The organic extracts were combined, washed with water (400 cm^3 × 3), and dried over MgSO$_4$, and the solvent was removed in vacuo. The residue was purified by flash vacuum chromatography eluting first with hexane to remove starting material and then with dichloromethane to obtain the product. The dichloromethane solution was dried over MgSO$_4$ and concentrated in vacuo to obtain **5a** as a pale orange oil that turns to a pale orange solid over time (10.60 g, 91.1% yield). mp: 67.6$-$68.4 °C. The product gave a single peak on GC (retention time = 21.55 min). IR (solid state): 2943, 2924, 2852, 1551, 1458, 1437, 1370, 1326, 1285, 1271, 1246, 1212, 1145, 1109, 1068, 1010, 967, 858, 792, 738, 720, 701, 690, 676, 659, 594, 578 cm^{-1}. MS (EI) (*m*/*z*): 671, 672, 673 (M$^{\bullet+}$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.73$-$0.86 (6H, m), 1.09$-$1.30 (24H, m), 1.37 (24H, s), 2.12 (1H, m), 2.62 (6H, s), 4.12 (2H, d, J = 7 Hz), 7.74 (2H, s), 7.77 (2H, s). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 14.11 (2C), 22.31 (1C), 22.61-(2C), 22.66 (1C), 24.91 (8C), 26.42 (1C), 26.46 (1C), 29.30 (1C), 29.58 (1C), 29.61 (1C), 29.69 (1C), 29.93 (1C), 31.74 (1C), 31.84 (1C), 31.90 (1C), 37.92 (1C), 47.16 (1C), 83.30 (4C), 116.56 (2C), 121.16 (4C), 124.42 (2C), 133.92 (2C), 139.40 (2C). Anal. Calcd for C$_{42}$H$_{67}$B$_2$NO$_4$: C, 75.11; H, 10.06; N, 2.09. Found: C, 73.92; H, 10.04; N, 1.97.

*2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-butyloct yl)-9H-carbazole (**5b**).* 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-butyloc tyl)-9*H*-carbazole (**5b**) was prepared according to the method used for **5a**, except that 4.0 cm^3 (6.80 mmol, 1.7 M in pentane) of *tert*-butyllithium was added dropwise to a solution of 1.17 g (2.24 mmol) of 2,7-dibromo-3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole (**4b**) in 90 cm^3 of THF at -78 °C. After this solution had been stirred for 4 h, 4.2 g (22.57 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was then added dropwise at -78 °C. **5b** was isolated as a white solid (1.21 g, 87.6% yield). mp: 117.2$-$118.9 °C. The product gave a single peak on GC (retention time = 18.47 min). IR (solid state): 2945, 2923, 2854, 1554, 1438, 1387, 1370, 1329, 1287, 1273, 1245, 1214, 1142, 1112, 1070, 1009, 969, 859, 837, 791, 738, 720, 700, 676, 659, 594, 582 cm^{-1}. MS (EI) (*m*/*z*): 615, 616, 617 (M$\bullet^+$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.74$-$0.90 (6H, m), 1.10$-$1.29 (16H, m), 1.31 (24H, s), 2.07 (1H, m), 2.63 (6H, s), 4.12 (2H, d, J = 7 Hz), 7.75 (2H, s), 7.78 (2H, s). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 14.12 (1C), 14.21 (1C), 22.33 (2C), 22.64(1C), 23.00 (1C), 24.93 (8C), 26.46 (1C), 28.60 (1C), 29.63 (1C), 31.37 (1C), 31.74 (1C), 31.86 (1C), 37.89 (1C), 47.06 (1C), 83.34 (4C), 116.58 (2C), 121.18 (4C), 124.45 (2C), 133.96 (2C), 139.44 (2C). Anal. Calcd for C$_{38}$H$_{59}$B$_2$NO$_4$: C, 74.15; H, 9.66; N, 2.28. Found: C, 74.84; H, 9.98; N, 2.23.

*2,7-Dibromo-9-(2-butyloctyl)-9H-carbazole (**6b**).* 2,7-Dibromo-9-(2-butyloctyl)-9*H*-carbazole (**6b**) was prepared according to the literature procedure for 2,7-dibromo-9-(2-hexyldecyl)-9*H*-carbazole (**6a**),[7] except that 1.50 g (4.62 mmol) of 2,7-dibromo-9*H*-carbazole, 1.73 g (6.94 mmol) of 2-butyl-1-bromooctane, 0.2 g (0.59 mmol) of tetrabutylammonium hydrogensulfate, 0.28 g (7.00 mmol) of NaOH, and 40 cm^3 of acetone (HPLC grade) were used. 2,7-Dibromo-9-(2-butyloctyl)-9*H*-carbazole (**6b**) was obtained as a colorless oil (2.20 g, 96.6% yield). The product gave a single peak on GC (retention time = 13.63 min). IR (solid state): 2938, 2926, 2856, 1867, 1621, 1587, 1524, 1484, 1451, 1426, 1378, 1327, 1315, 1268, 1245, 1224, 1204, 1133, 1056, 1019, 999, 952, 928, 900, 867, 839, 793, 741, 667, 594, 558 cm^{-1}. MS (EI) (*m*/*z*): 491, 493, 495 (M$^{\bullet+}$). ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.76$-$0.94 (6H, m), 1.08$-$1.44 (16H, m), 2.06 (1H, m), 4.01 (2H, d, J = 7.5 Hz), 7.32 (2H, dd, J = 2 Hz, 8 Hz), 7.47 (2H, d, J = 2 Hz), 7.85 (2H, d, J = 2 Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 14.05 (1C), 14.13 (1C), 22.66 (1C), 23.04 (1C), 26.36 (1C), 28.61 (1C), 29.61 (1C), 31.38 (1C), 31.60 (1C), 31.80 (1C), 37.62 (1C), 47.81 (1C), 112.28 (2C), 119.64 (2C), 121.20 (2C), 121.39 (2C), 122.49 (2C), 141.80 (2C). Anal. Calcd for C$_{24}$H$_{31}$NBr$_2$: C, 58.43; H, 6.33; N, 2.84; Br, 32.39. Found: C, 58.64; H, 6.26; N, 2.77; Br, 32.37.

Preparation of the Polymers. All polymerizations were carried out under an inert argon atmosphere. All polymers obtained were stored in the dark.

*Poly(3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole-2,7-diyl) (**P1a**).* A solution of palladium(II) acetate (2.0 mg, 8.9 μmol) and triphenylphosphine (9.4 mg, 0.036 mmol) in toluene (3 cm^3) was stirred at 50 °C for 15 min in a sealable tube. After this mixture had cooled to ambient temperature, a solution of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (**5a**) (0.4541 g, 0.676 mmol) and 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (**4a**) (0.3807 g, 0.659 mmol) in toluene (7 cm^3) was added to the sealable tube and stirred at ambient temperature for 10 min. Then, 20 wt % tetraethylammonium hydroxide (4 cm^3, 5.43 mmol) was added, the glass tube was sealed, and the mixture was heated at 120 °C with stirring for 72 h. The mixture was allowed to cool to ambient temperature, then bromobenzene (0.1 cm^3, 0.950 mmol) was added, and the mixture was stirred for an additional 1 h at 120 °C. The mixture was again allowed to cool to ambient temperature, after which phenylboronic acid (0.12 g, 0.984 mmol) was added, and the mixture was stirred for an additional 1 h at 120 °C. After cooling to ambient temperature, the mixture was poured onto methanol (500 cm^3). The precipitates were filtered off and dissolved in chloroform (200 cm^3). The insoluble materials in the chloroform solution were filtered off, and then the filtrate was concentrated in vacuo. The concentrated chloroform solution (~20 cm^3) was poured onto methanol (500 cm^3), and the precipitates were filtered off and dried in vacuo to give poly(3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole-2,7-diyl) (**P1a**) as a white powder (0.47 g, 84.2% yield). GPC: M_w = 9200, M_n = 4400, M_w/M_n = 2.1.

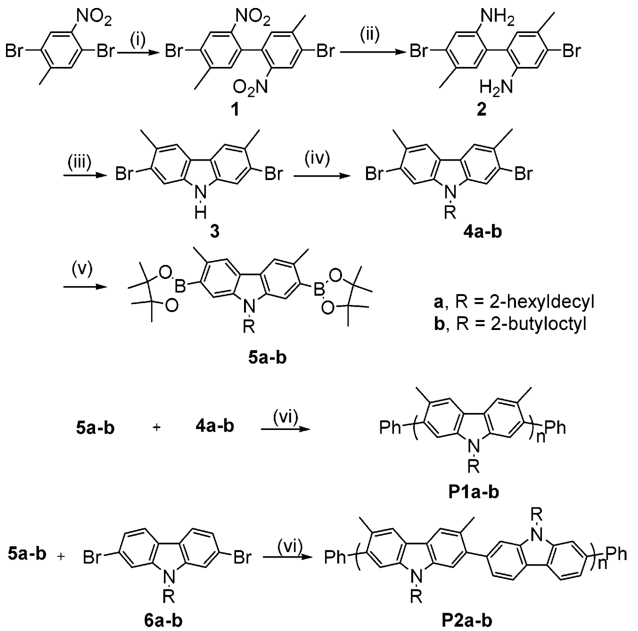
Polymer **P1a** was also made under similar conditions using palladium(II) acetate and tri-*p*-tolylphosphine in a ratio of 1/3 and was obtained as a white powder in 86.8% yield. GPC: M_w = 13 500, M_n = 6500, M_w/M_n = 2.1. IR (solid state): 2932, 2921, 2853, 1867, 1609, 1465, 1376, 1348, 1289, 1236, 1224, 992, 868, 846, 780, 722, 667, 618, 588, 567, 557, 523, 492 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.69$-$0.93 (6H, m), 1.01$-$1.49 (24H, m), 2.03$-$2.22 (1H, m), 2.25 (6H, s), 4.00$-$4.26 (2H, m), 7.28 (2H, s), 8.04 (2H, s). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 14.03 (1C), 14.11 (1C), 20.18 (1C), 22.61 (1C), 22.64 (2C), 26.40 (2C), 29.27 (1C), 29.49 (1C), 29.66 (1C), 30.00 (1C), 30.09 (1C), 31.70 (1C), 31.88 (2C), 37.90 (1C), 47.97 (1C), 109.74 (2C), 120.69 (2C), 121.31 (2C), 126.44 (2C), 139.82 (2C), 140.45 (2C). Anal. Calcd for (C$_{30}$H$_{43}$N)$_n$: C, 86.27; H, 10.38; N, 3.35. Found: C, 86.27; H, 10.80; N, 3.30.

*Poly(3,6-dimethyl-9-(2-butyloctyl)-9H-carbazole-2,7-diyl) (**P1b**).* Poly(3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole-2,7-diyl) (**P1b**) was prepared according to the method used for **P1a**, except that 9.4 mg (0.036 mmol) of triphenylphosphine, 0.3626 g (0.5891 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole (**5b**), 0.2843 g (0.5453 mmol) of 2,7-dibromo-3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole (**4b**), and 4 cm^3 (5.43 mmol) of tetraethylammonium hydroxide were used. Poly(3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole-2,7-diyl) (**P1b**) was obtained as a white powder (0.26 g, 63.4% yield). GPC: $M_w = 25\,100$, $M_n = 12\,100$, $M_w/M_n = 2.1$. IR (solid state): 2934, 2921, 2855, 2360, 1610, 1467, 1376, 1353, 1287, 1238, 1202, 1176, 1036, 991, 922, 868, 839, 780, 725, 701, 668, 636, 585, 546, 526, 516, 498 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.69−0.90 (6H, m), 1.04−1.45 (16H, m), 1.99−2.23 (1H, m), 2.26 (6H, s), 3.97−4.31 (2H, m), 7.27 (2H, s), 8.04 (2H, s). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 13.98 (1C), 14.02 (1C), 20.14 (1C), 22.60 (1C), 23.06 (2C), 26.43 (1C), 28.57 (1C), 29.67 (2C), 31.49 (1C), 31.70 (1C), 31.93 (1C), 37.91 (1C), 48.03 (1C), 109.76 (2C), 120.69 (2C), 121.79 (2C), 126.49 (2C), 139.85 (2C), 140.49 (2C). Anal. Calcd for $(C_{26}H_{35}N)_n$: C, 86.37; H, 9.76; N, 3.87. Found: C, 85.14; H, 9.56; N, 3.65.

*Poly(3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole-alt-9-(2-hexyldecyl)-9H-carb azole-2,7-diyl) (**P2a**).* Poly(3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole-*alt*-9-(2-hexyldecyl)-9*H*-carb azole-2,7-diyl) (**P2a**) was prepared according to the method used for **P1a**, except that 0.6701 g (0.998 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole (**5a**) and 0.5348 g (0.973 mmol) of 2,7-dibromo-9-(2-hexyldecyl)-9*H*-carbazole (**6a**) were used. Poly(3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole-*alt*-9-(2-hexyldecyl)-9*H*-carbaz ole-2,7-diyl) (**P2a**) was obtained as a white powder (0.64 g, 80.4% yield). GPC: $M_w = 31\,200$, $M_n = 13\,900$, $M_w/M_n = 2.2$. IR (solid state): 2931, 2922, 2853, 1602, 1560, 1454, 1374, 1323, 1285, 1239, 1209, 1136, 1068, 1031, 1001, 868, 852, 811, 782, 722, 694, 630, 589, 560, 548, 533, 499 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.66−0.94 (6H, m), 1.02−1.52 (24H, m), 2.11−2.34 (1H, m), 2.54 (6H, s), 4.00−4.42 (2H, m), 7.34 (2H, s), 7.38 (2H, d, $J = 7$ Hz), 7.49 (2H, s) 8.05 (2H, s), 8.22 (2H, d, $J = 7$ Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 14.06 (2C), 14.10 (2C), 21.05 (2C), 22.64 (C), 26.41 (2C), 26.67 (2C), 29.30 (2C), 29.33 (C), 29.53 (2C), 29.57 (1C), 29.70 (2C), 29.75 (1C), 30.06 (1C), 31.74 (2C), 31.79 (1C), 31.87 (2C), 31.90 (1C), 32.11 (2C), 37.87 (1C), 38.21 (1C), 47.84 (1C), 47.99 (1C), 110.10 (2C), 110.35 (2C), 119.67 (2C), 120.88 (2C), 121.39 (4C), 121.75 (2C), 125.95 (2C), 140.3 (2C), 140.68 (2C), 140.79 (2C), 141.24 (2C). Anal. Calcd for $(C_{58}H_{82}N_2)_n$: C, 86.29; H, 10.24; N, 3.47. Found: C, 86.15; H, 10.27; N, 3.38.

*Poly(3,6-dimethyl-9-(2-butyloctyl)-9H-carbazole-alt-9-(2-butyloctyl)-9H-carbazole-2,7-diyl) (**P2b**).* Poly(3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole-*alt*-9-(2-butyloctyl)-9*H*-carba zole-2,7-diyl) (**P2b**) was prepared according to the method used for **P1a**, except that 0.4374 g (0.711 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole (**5b**) and 0.3418 g (0.693 mmol) of 2,7-dibromo-9-(2-butyloctyl)-9*H*-carbazole (**6b**) were used. Poly(3,6-dimethyl-9-(2-butyloctyl)-9*H*-carbazole-*alt*-9-(2-butyloctyl)-9*H*-carbazol e-2,7-diyl) (**P2b**) was obtained as a white powder (0.30 g, 61.5% yield). GPC: $M_w = 27\,700$, $M_n = 10\,100$, $M_w/M_n = 2.7$. IR (solid state): 2935, 2923, 2853, 1601, 1560, 1453, 1373, 1322, 1285, 1240, 1199, 1134, 1062, 1036, 1001, 917, 851, 810, 781, 724, 691, 672, 623, 588, 566, 530, 520, 503, 498 cm^{-1}. ^{1}H NMR (CDCl$_3$) δ_H (ppm): 0.55−0.91 (12H, m), 0.95−1.46 (32H, m), 1.97−2.26 (2H, m), 2.45 (6H, s), 3.89−4.34 (4H, m), 7.27 (2H, s), 7.31 (2H, d, $J = 7$ Hz), 7.42 (2H, s), 7.98 (2H, s), 8.14 (2H, d, $J = 7$ Hz). ^{13}C NMR (CDCl$_3$) δ_C (ppm): 13.59 (2C), 13.99 (1C), 14.04 (1C), 21.03 (2C), 22.60 (1C), 22.63 (1C), 23.08 (2C), 26.41 (1C), 26.48 (1C), 26.66 (2C), 28.60 (1C), 28.69 (1C), 29.70 (1C), 29.75 (1C), 30.92 (1C), 31.73 (1C), 31.79 (1C), 32.10 (1C), 37.90 (1C), 38.19 (1C), 47.89 (1C), 48.05 (1C), 110.09 (2C), 110.36 (2C), 119.67 (2C), 120.90 (2C), 121.32 (2C), 121.39 (2C), 121.77 (2C), 125.99 (2C), 140.14 (2C), 140.72 (2C), 140.82 (2C), 141.26 (2C). Anal. Calcd for $(C_{50}H_{66}N_2)_n$: C, 86.40; H, 9.57; N, 4.03. Found: C, 86.23; H, 9.58; N, 3.90.

Scheme 1^a



^{a} Conditions: (i) Cu, DMF. (ii) (a) Sn, HCl, EtOH; (b) NaOH. (iii) $C_{12}H_{25}(C_6H_4)SO_3H$, 5-*tert*-butyl-*m*-xylene. (iv) RBr, NaOH, $(n\text{-}C_4H_9)_4N(HSO_4)$, acetone. (v) (a) *t*-BuLi; (b) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, THF. (vi) (a) [Pd], NEt$_4$OH, toluene; (b) PhB(OH)$_2$; (c) PhBr.

Results and Discussion

Synthesis and Characterization of the Polymers. The preparation of polymers **P1** and **P2** was initiated by the synthesis of monomers **4** and **5** as depicted in Scheme 1. Ullmann coupling of the known 2,5-dibromo-4-nitrotoluene[10] afforded 4,4′-dibromo-5,5′-dimethyl-2,2′-dinitrobiphenyl (**1**) in 85% yield. This was then followed by reduction of **1** in a second step to afford 4,4′-dibromo-5,5′-dimethylbiphenyl-2,2′-diamine (**2**) in 84% yield. Reaction of 4-dodecylbenzenesulfonic acid with **2** in refluxing 5-*tert*-butyl-*m*-xylene afforded 2,7-dibromo-3,6-dimethyl-9*H*-carbazole (**3**) in 72% yield. 9-Alkyl-2,7-dibromo-3,6-dimethyl-9*H*-carbazole derivatives (**4**) were prepared in quantitative yields, upon alkylation of **3** in the presence of a phase-transfer catalyst following a modified literature procedure for the alkylation of carbazoles.[14] Two branched alkyl substituents of different steric requirements were used in this study to probe the effects of their steric bulk on the physical properties of the new polymers. The 9-alkyl-3,6-dimethyl-2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-car bazole derivatives (**5**) were also obtained in quantitative yields upon lithium−halogen exchange of derivatives **4** upon reaction with *tert*-butyllithium at low temperature, followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Polymers **P1** and **P2** were prepared using a Suzuki-type cross-coupling condensation polymerization reaction (Scheme 1). The polymerization reactions were carried out using palladium acetate and triphenylphosphine as precursor catalysts in a ratio of 1 to 4 for all polymers and tetra-*n*-butylammonium hydroxide as a base in toluene in sealable autoclaves at 120 °C.

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(14) Beginn, C.; Gražulevičius, J. V.; Strohriegl, P.; Simmerer, J.; Haarer, D. *Macromol. Chem. Phys.* **1994**, *195*, 2353.

Table 1. Molecular Weight Distributions of Polymers P1 and P2

polymer	M_n	M_w	polydispersity	DP[a]
P1a	4400	9200	2.1	11
P1a[b]	6500	13 500	2.1	16
P1b	12 100	25 100	2.1	33
P2a	13 900	31 200	2.2	34
P2b	10 100	27 700	2.7	29

[a] Degree of polymerization. [b] Palladium acetate/tri-*p*-tolylphosphine (1/3 ratio) used as the catalyst.

Gel permeation chromatography results from these polymerization reactions are reported in Table 1. Under these polymerization conditions, the degree of polymerization (DP) of polymer **P1b** is much higher than that of polymer **P1a** (33 vs 11). Preparation of homopolymer **P1a** under similar conditions using palladium acetate and tri-*p*-tolylphosphine as precursor catalysts in a ratio of 1 to 3 gave a polymer with a slightly higher degree of polymerization (DP = 16), which was still lower than that of polymer **P1b**. These results indicate that sterically demanding substituents on the carbazole ring have a negative effect on the polymerization reaction in the preparation of homopolymers **P1**. These effects are, however, not observed in the preparation of copolymers **P2**, as both copolymers **P2a** and **P2b** have similar degrees of polymerization (DP ≈ 30), regardless of the bulk of the alkyl chains (2-hexyldecyl or 2-butyloctyl). These results suggest that the presence of methyl substituents on alternate carbazole rings at the ortho positions of the coupling sites do not affect the polymerization, even if bulky alkyl substituents are attached to the carbazole ring, as opposed to polymerization reactions where both coupling partners have methyl substituents, as is the case for polymers **P1**.

NMR Spectroscopy. NMR studies were conducted in chloroform on the resulting carbazole polymers. ^{1}H NMR studies on poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-2,7-diyl)s (**P1**) reveal, in the aromatic region, two broad peaks with equal integral intensities, centered around 8.04 and 7.28 ppm, corresponding to the two chemical environments of hydrogens at the 1,8- and 4,5-positions, respectively, of the carbazole rings. In addition, broad multiplets centered around 4.13 ppm, corresponding to hydrogens of the methylene groups directly attached to the 9-position of the carbazole rings, were observed for polymers **P1a** and **P1b**. Peaks corresponding to the hydrogen atoms of methyl substituents at the 3,6-positions of the carbazole repeat units appear around 2.26 ppm.

^{13}C NMR studies on polymers **P1** reveal six chemical environments with signals at around 140.4, 139.8, 126.4, 121.7, 120.7, and 109.7 ppm, corresponding to carbons at the 8a,9a-, 3,6-, 2,7-, 4,5-, 4a,4b-, and 1,8-positions, respectively, of the carbazole rings. These NMR results indicate a homogeneous structure for the poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-2,7-diyl)s (**P1**) prepared in this study with exclusive 2,7-linkage of the carbazole repeat units on the polymer chains.

^{1}H NMR studies on alternating copolymers poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-*alt*-9-alkyl-9*H*-carbazole-2,7-diyl)s (**P2**) reveal, in the aromatic region, a broad doublet, a broad singlet, and another broad doublet, centered around 8.22, 7.49, and 7.34 ppm, respectively, corresponding to the three chemical environments of hydrogens at the 4,5-, 1,8-, and 3,6-positions, respectively, of the carbazole repeat units with no methyl substituents. In addition, in the aromatic region, there are two broad peaks centered around 8.05 and 7.38 ppm, corresponding to the two chemical environments of hydrogens at the 1,8- and 4,5-positions, respectively, of the carbazole repeat units with methyl substituents at the 3,6-positions. In addition, broad peaks centered around 4.20 ppm, corresponding to hydrogens of the methylene groups directly attached to the 9-position of the carbazole rings, were observed for polymers **P2**. Peaks corresponding to the hydrogen atoms of the methyl substituents at the 3,6-positions on alternate carbazole repeat units appear around 2.50 ppm. ^{13}C NMR studies on polymers **P2** reveal, in the aromatic region, 12 peaks corresponding to the different chemical environments of the two different carbazole repeat units. These NMR results indicate a homogeneous structure of the alternating copolymers **P2** prepared in this study with exclusive 2,7-linkage of the carbazole repeat units on the polymer chains.

Solution and Solid-State Electronic Spectra. The extent of π-orbital overlap between neighboring repeat units on polymers **P1** and **P2** can be directly assessed from their electronic spectra. Table 2lists the absorption maxima values, for the different carbazole polymers both in solution and in the solid state (films). Polymers **P1** display maximum absorptions in solution (dichloromethane) at a λ_{max} value of 317 nm (Table 2). In addition, absorption shoulder peaks at 346 and 360 nm are also clearly evident in these spectra (Figure 1). These could be explained by the existence of segments of more extended electronic conjugation along the polymer chains, on the basis of the fact that the relative intensities of these shoulder peaks increase with increasing molecular weights of the polymers. The electronic spectra of these polymers in the solid state display features similar to those recorded in solution with very close absorption maxima values (λ_{max} = 318 nm), as well as shoulder peaks at 343 and 360 nm for P1a and at 345 and 359 nm for **P1b**. The presence of methyl substituents at the 3,6-positions on consecutive carbazole repeat units in these polymers clearly reduces the planarity of the polymer backbones and leading to high band gap materials with $E_g \approx 3.2$ eV as determined from the onset position of their absorption bands.

Polymers **P2** display maximum absorptions in solution (dichloromethane) at a λ_{max} value of around 342 nm (Table 2). The electronic spectra of these polymers in the solid state display a small red shift with a λ_{max} value of 350 nm, indicating slightly more electronic conjugation in the solid state (Figure 2). The band gap of polymers P2 as determined from the onset position of their absorption bands, E_g, is around 2.95 eV. It is clear from these data that the electronic conjugation in polymers **P2** is more extended than that in polymers **P1** as a result of the absence of methyl groups on alternate carbazole repeat units in the former polymers.

Solution and Solid-State Fluorescence Spectra. Fluorescence studies on polymers **P1** and **P2** were performed both in solution (dichloromethane) and in the solid state. The results of these studies are reported in Table 2. Fluorescence

Table 2. UV−Vis and Fluorescence Data for Polymers P1 and P2

	absorption, $\lambda_{max}{}^{a}$ (nm)		emission, $\lambda_{max}{}^{a}$ (nm)				
polymer	CH_2Cl_2	film	CH_2Cl_2	film	Φ^{β} (CH_2Cl_2)	Stokes shift (nm)	band gap^{c} (eV)
P1a	317 (346, 360)	318 (343, 360)	393	397 (453, 468, 495)	0.16	79	3.21
P1b	317 (346, 360)	318 (345, 359)	392	396 (441, 468, 496)	0.25	78	3.21
P2a	342	350	397	400 (450, 470, 495)	0.64	50	2.95
P2b	341	350	397	403 (450, 460, 495)	0.51	53	2.95

[a] Numbers in parentheses correspond to shoulder absorption and emission peaks. [b] Measured using quinine sulfate dihydrate as the standard. [c] Determined from the onset position of the absorption band.

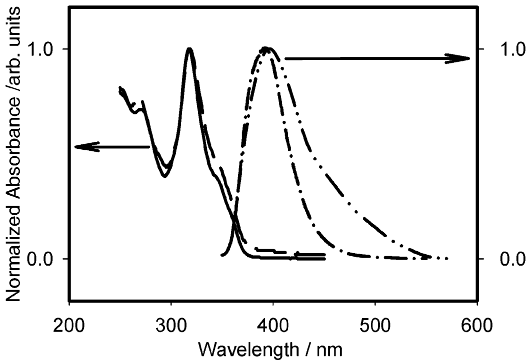

Figure 1. Normalized absorption spectra of **P1a** in dichloromethane (solid line) and as a thin film (long dashed line) and normalized emission spectra of **P1a** in dichloromethane (dash-dotted line) and as a thin film (dash-dot-dotted line).

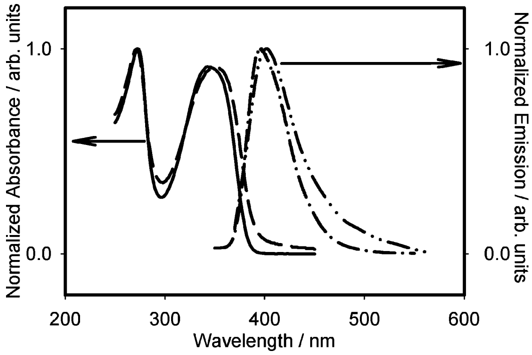

Figure 2. Normalized absorption spectra of **P2a** in dichloromethane (solid line) and as a thin film (long dashed line) and normalized emission spectra of **P2a** in dichloromethane (dash-dotted line) and as a thin film (dash-dot-dotted line).

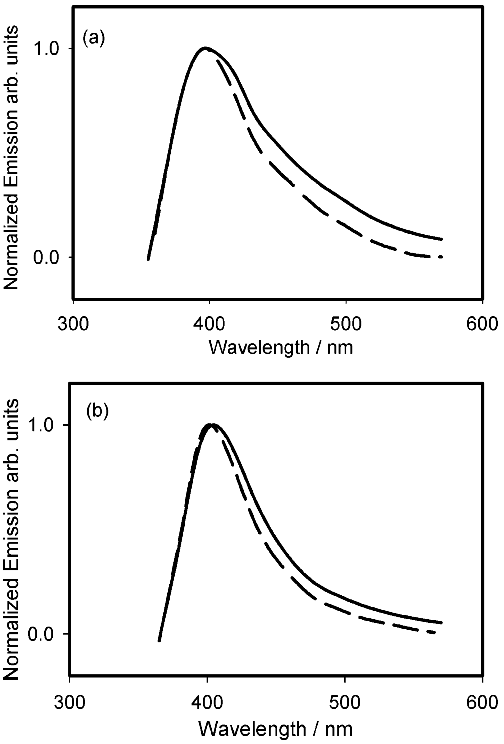

Figure 3. Comparison of normalized emission spectra of thin films of (a) **P1a** (long dashed line) and **P1b** (solid line) and (b) **P2a** (long dashed line) and **P2b** (solid line).

spectra of polymers **P1** in solution showed emission bands centered on λ_{max} values between 392 and 393 nm. The fluorescence spectra of these polymers in the solid state showed emission bands between 396 and 397 nm with shoulder peaks between 441 and 496 nm (Figure 1). These polymers display large Stokes shifts (about 80 nm), which points to large structural differences between the ground and excited states in these materials, both in solution and in the solid state. Fluorescence spectra of polymers **P2** in solution showed emission bands centered on a λ_{max} value of 397 nm. The fluorescence spectra of these polymers in the solid state showed emission bands between 400 and 403 nm with shoulder peaks between 450 and 495 nm (Figure 2). These polymers display smaller Stokes shifts (~50 nm) than homopolymers **P1**, which points to smaller structural differences between the ground and excited states in these materials, both in solution and in the solid state, when compared to polymers **P1**.

Comparison of the fluorescence spectra of thin films of homopolymers **P1** and copolymers **P2** (Figure 3) indicates broader emission spectra and larger full width at half-maximum (fwhm) values in the two respective classes for polymers with shorter alkyl chains (**P1b** and **P2b**) when compared to those with longer alkyl chains (**P1a** and **P2a**). This could be explained as arising from a propensity for less aggregation in the polymers with bulkier alkyl chains; however, further work involving lifetime measurements is required to confirm this assumption.

The fluorescence quantum yields of the polymers in dichloromethane solution were also determined. These were determined upon excitation of the polymers at their λ_{max} values and by comparison with the solution emission of quinine sulfate dihydrate ($\Phi_{fl} = 0.546$) used as the standard. The fluorescence quantum yields of these polymers are listed in Table 2. Homopolymers **P1** displayed quantum yields ranging from 0.16 to 0.25. These values are higher than those obtained in previous studies for poly(9-alkyl-9*H*-carbazole-3,6-diyl)s,[5a] which were found to be between 0.04 and 0.06. Copolymers **P2** were found to be highly fluorescent, with quantum yields Φ ranging from 0.51 to 0.64, indicating their great potential for application in light-emitting diodes.

Electrochemical Studies. Investigations of the electrochemical properties of polymers **P1** and **P2** were also undertaken in this study. Cyclic voltammetry measurements

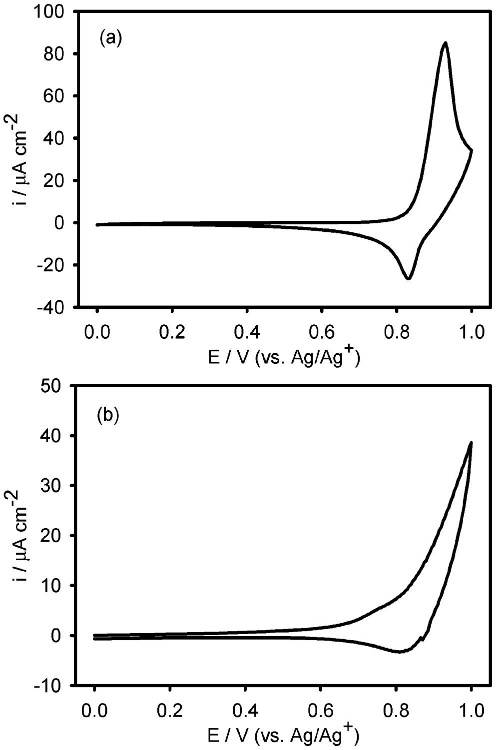

Figure 4. CV curves (second scan) of thin films of (a) **P1b** and (b) **P2b** on a platinum disk electrode (area 0.031 cm^2) at a scan rate of 100 mV s^{-1} in acetonitrile/tetrabutylammonium perchlorate (0.1 mol dm^{-3}).

Table 3. Redox Potentials of P1 and P2 in 0.1 M $TBAClO_4/CH_3CN$ on Pt Working Electrode at 100 mV s^{-1} Using Ag/Ag$^+$ Reference Electrode

polymer	E_{pa} (V)	E_{pc} (V)	I_P^{a} (eV)
P1a	0.93	0.87	5.5
P1b	0.93	0.83	5.5
P2a	0.70 0.95^b	0.81	5.2
P2b	0.77 0.95^b	0.81	5.2

^{a} Ionization potential (vs vacuum) determined from onset of oxidation. ^{b} Second oxidation peak not clearly defined.

on drop-cast polymer films were conducted in acetonitrile with tetrabutylammonium perchlorate as the electrolyte. The cyclic voltammograms of polymers **P1b** and **P2b** are shown in Figure 4 as representative examples of the two classes of polymers. The redox potentials of the various polymers as well as their respective ionization potentials (vs vacuum) are reported in Table 3.

The redox behavior of polymers **P1** indicates a reversible redox wave with an oxidation wave at the potential E_{pa} = 0.93 V and an associated reduction wave at potentials E_{pc} between 0.83 and 0.87 V. The oxidative reversibility of these polymers is to be contrasted with that of poly(9-alkyl-9*H*-carbazole-2,7-diyl)s[7] and indicates the stabilizing effect of introducing methyl substituents at the 3,6-positions in this new class of materials on the electrolytic stability of the resulting materials. Indeed, the electrolytic instability of the poly(9-alkyl-9*H*-carbazole-2,7-diyl)s was attributed to the formation of new species as a result of the creation of new linkages between the 3,6-positions of adjacent polymer chains within the films.[7,8] The redox behavior of polymers **P2** differs from that of polymers **P1**. The cyclic voltammograms of **P2** show a first oxidation wave at E_{pa} potentials of around 0.7 V, as well as a less distinct second oxidation wave at E_{pa} potentials of around 0.95 V. A reduction wave at the potential E_{pc} = 0.81 V is observed for both **P2a** and **P2b**. This class of materials has methyl substituents at the 3,6-positions on alternate carbazole repeat units, and although it is conceivable that some side reactions involving the formation of new species might be occurring as a result of the creation of new linkages between the 3,6-positions of adjacent polymer chains within the films from the carbazole repeat units with no methyl substituents on the copolymer chains, it must be noted that the electroactivity of these polymers is preserved after several cycles at a scan rate of 100 mV s^{-1} as opposed to the electroactivity of poly(9-alkyl-9*H*-carbazole-2,7-diyl)s,[7] which is lost at the first few cycles under similar conditions.

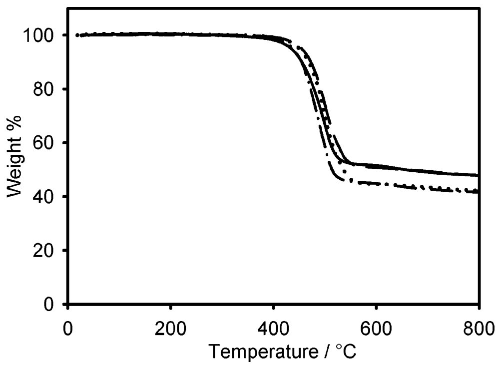

Figure 5. TGA results for **P1b** (solid line), **P2b** (long dashed line), **P1a** (dash-dotted line), and **P2a** (dotted line).

The ionization potentials (vs vacuum) of polymers **P1** and **P2** were estimated from the onset of their oxidation in cyclic voltammetry responses at 5.5 and 5.2 eV, respectively (on the basis that ferrocene/ferrrocenium is 4.8 eV below the vacuum level[15]). The lower ionization potential of polymers **P2** could originate from the fact that they have a higher electronic conjugation than polymers **P1**. It must also be noted that the ionization potentials of polymers **P1** and **P2** are 0.3 to 0.6 eV lower, respectively, than those of poly(9,9-dioctyl-fluorene-2,7-diyl).[16] The ionization potentials of polymers **P1** and **P2** are also lower than that of poly(vinylcarbazole) reported as ranging from 5.85 to 6.0 eV.[17] This could suggest an easier hole injection into films from indium tin oxide (ITO) electrodes in device applications such as light-emitting diodes.

Thermal Gravimetric Analysis. Thermal gravimetric analysis (TGA) studies were also conducted on polymers **P1** and **P2** and revealed a good stability of these materials up to 350 °C. The subsequent degradation and weight loss in these materials beyond ~560 °C was proportional to the mass of their alkyl substituents, as shown in Figure 5. This indicates a degradation path affecting the alkyl substituents in a first instance. The polymers did not show any further weight loss up to a temperature of 800 °C.

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Conclusion

The development of preparation routes of two new classes of 2,7-linked poly(9-alkyl-9*H*-carbazole-2,7-diyl)s with methyl substituents at the 3,6-positions on all repeat units of the polymer chains or on alternate repeat units of the polymer chains has been realized. The effects of the methyl substituents at the 3,6-positions on the polymerization reaction together with the effects of the bulk of 9-alkyl substituents on the carbazole repeat units have been discussed. Homopolymers with methyl substituents at the 3,6-positions on all carbazole repeat units, poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-2,7-diyl)s, displayed large band gaps (3.21 eV), were found to be stable under electrolytic conditions, and displayed good redox reversibility. Copolymers with methyl substituents at the 3,6-positions on alternate carbazole repeat units, poly(3,6-dimethyl-9-alkyl-9*H*-carbazole-*alt*-9-alkyl-9*H*-carbazole-2,7-diyl)s, also displayed wide band gaps, although lower than those of the homopolymers (2.95 eV). Homopolymers **P1** displayed moderate fluorescence quantum yields in solution (between 0.16 and 0.25), whereas copolymers **P2** displayed higher fluorescence quantum yields in solution (between 0.51 and 0.64). The copolymers have different electrochemical properties than the homopolymers. They also exhibit good stability to reversible oxidation under electrolytic conditions, although they have lower ionization potentials than the homopolymers (5.2 vs 5.5 eV for the homopolymers). Both classes of polymers emit in the blue part of the electromagnetic spectrum and are thermally stable up to 350 °C. The electrolytic stability of these new classes of materials compared to that of 2,7-linked 9-alkylcarbazole polymers with no methyl substituents at their 3,6-positions should enable their effective use as stable blue-light-emitting materials in display devices.

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