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Preparation and Properties of 2,7-Linked *N*-Alkyl-9*H*-carbazole Main-Chain Polymers

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Preparation of poly(9-alkyl-9*H*-carbazole)-2,7-diyls using palladium-catalyzed cross-coupling reactions involving 2-bromo-7-bromomagnesio-9-alkyl-9*H*-carbazole derivatives is described. Monomers with a range of alkyl group substituents with different steric requirements were investigated, and their effects on the polymerization reaction were studied using gel-permeation chromatography. Polymers with different degrees of polymerization were obtained; dependent on the size and branching of alkyl group substituents on the carbazole repeat units. Structural analyses of the polymers revealed exclusive 2,7-linkage between consecutive carbazole repeat units on the polymer chains. The new polymers are thermally stable up to 450 °C. Electrochemical studies as well as absorption and fluorescence studies on the new polymers are presented together with a determination of their quantum yield of fluorescence in solution.

Introduction

Research in the area of conjugated polymers has attracted significant interest recently in view of their exciting prospects for application in a range of electronic devices. An important area, which has seen major advances, is concerned with development of materials for optoelectronic uses, and the past decade has seen the development of a range of conjugated polymers with great promise for application in polymer-based light-emitting diodes[1] (PLEDs) and solar cells.[2]

Among the physical properties sought in new materials, especially for application in PLEDs, is their quantum yield of fluorescence. Currently there is a range of polymers that fulfill these requirements, such as poly(*p*-phenylenevinylene)s (PPVs), poly(*p*-phenylene)s (PPPs), and polyfluorenes.

Carbazole-based polymers such as poly(vinylcarbazole) (PVK) have been widely used in this area of research chiefly as hole-transporting materials,[3] but also as wide band gap energy transfer donors.[4] Poly(9-alkyl-9*H*-carbazole)-3,6-diyls, another class of carbazole-based polymers in which the carbazole repeat units are linked together through their 3- and 6-positions, have 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 pendent 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-diyls is limited to about two carbazole units; in addition, their quantum yields of fluorescence are fairly low.

Main-chain conjugated carbazole polymers in which the carbazole repeat units are linked together through their 2- and 7-positions have recently been described in the literature[6] (poly(9-alkyl-9*H*-carbazole)-2,7-diyls). These are truly conjugated polymers that structurally resemble polyfluorenes and where electronic conjugation is extended further than in the case of poly(9-alkyl-9*H*-carbazole)-3,6-diyls. We have being researching the development of new synthetic strategies to these polymers, as a major drive to develop highly fluorescent blue-emitting materials for use in optoelectronic applications. In this article we present our findings on the preparation and characterization of a range of these new carbazole-based conjugated polymers, together with studies of their thermal stability and determination of their quantum yields of fluorescence.

Experimental Section

Materials. 2,7-Dibromo-9*H*-carbazole was obtained according to literature procedures.[7] The sodium hydroxide was quickly ground just before use when used for the alkylation reactions of 2,7-dibromo-9*H*-carbazole. The magnesium (turn-

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ings) was activated before use (on washing successively with dilute hydrochloric acid, ethanol, and diethyl ether and drying under high vacuum, followed by crashing upon vigorous stirring under inert atmosphere) when used for polymerizations. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under inert nitrogen atmosphere. Methanol was dried and distilled over magnesium (turnings) under inert nitrogen atmosphere before use when used for the reprecipitations of polymers. Other solvents were used as received.

Measurements. IR absorption spectra were recorded on a Nicolet model 205 FT-IR spectrometer or Perkin-Elmer Paragon FT-IR spectrometer by the KBr-pellet method for solids, NaCl-plate method for liquid films, or KBr-plate method for polymer thin films, which were formed by drop-casting the polymer solutions in dichloromethane onto the KBr plates. NMR spectra were recorded on a JEOL GSX400 400 MHz NMR spectrometer or a Bruker AMX400 400 MHz NMR spectrometer with TMS as the internal standard. Melting points were obtained with a Gallenkamp melting point apparatus. GC-MS spectra were recorded on a Perkin-Elmer Turbomass spectrometer equipped with a Perkin-Elmer PE-5MS capillary column. Mass spectra were obtained by the electron impact (EI) or the chemical ionization (CI) methods. Direct injection mass spectra were recorded on a Hitachi M-80B GC double-focusing mass spectrometer. Mass spectra were obtained by the electron impact (EI) method. HPLC analyses were carried out by Gilson HPLC analysis equipment consisting of model 303 and 305 HPLC Pumps, model 113 UV-visible detector, model 811B mixer, model 806 monometric module, and a VarianODS 150-mm silica gel column using 65% THF solution in water as the eluate at the flow rate of 1 cm^3 min^{-1}. The HPLC curves were obtained by the UV-detection method at 254 nm. 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 RI detector, a PLgel 5-m 500A column, and a PLgel 10-m MXDED-B column using THF as the eluate at the flow rate of 1 cm^3 min^{-1}. The molecular weights of the polymers were calibrated with a series of polystyrene narrow standards. TGA curves were obtained by a Perkin-Elmer TGA-7 thermogravimetric analyzer at the scan rate of 20 °C min^{-1} under inert nitrogen atmosphere. Platinum pans were used as sample pans. UV−visible absorption spectra were measured by a Hitachi U-2010 double beam UV/visible spectrophotometer equipped with a Haake DC30/K20 liquid-flow type temperature controller.

Photoluminescence spectra were obtained using a Hitachi F-4500 fluorescence spectrophotometer equipped with a Hamamatsu Photonics R928F photomultiplier tube (PMT) and a Haake D3/G liquid-flow type temperature controller. Photoluminescence spectra measurements of harmine and quinine sulfate dihydrate solutions were carried out in, respectively, 0.05 mol dm^{-3} and 0.5 mol dm^{-3} sulfuric acid at 25 °C in the air because both harmine and quinine sulfate dihydrate exhibit no oxygen quenching effect.

Photoluminescence spectra measurements of the polymer solutions were carried out in dichloromethane (analytical reagent) at 25 °C. The oxygen quenching effects on poly(9-alkyl-9*H*-carbazole)-2,7-diyls were examined by comparing the photoluminescence spectra of their solution in the air with those under a nitrogen atmosphere. Because the solutions exhibited no oxygen quenching effect, photoluminescence spectra measurements of their solutions were carried out in the air.

Absorbances at employed excitation wavelengths of the sample solutions 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 measurement of the quantum counter (Rhodamine B standard solution) for the excitation side; and by synchronous wavelength scan using a light diffuser for the emission side. The light diffuser (parts 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 0.05 and 0.5 mol dm^{-3} sulfuric acid, respectively, were employed as fluorescence standards. The quantum yields in diluted solutions were obtained by comparison with a fluorescence standard of a known quantum yield using the following equation:

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

where the subscripts s and x refer to the standard and the unknown sample solutions, Φ is the quantum yield, A is the absorbance at used excitation wavelength, 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, 1.339, 1.334, and 1.424 were employed for, respectively, 0.5 mol dm^{-3} sulfuric acid, 0.05 mol dm^{-3} sulfuric acid, and dichloromethane. (S/A) values of each sample in solution could be obtained by simply dividing the integral intensities of the spectra by the absorbances at used excitation wavelengths 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 the plots of the integral intensities of the spectra vs the absorbances at used excitation wavelengths using sample solutions of various concentrations. Reliability of our measurements was confirmed upon measurement of the quantum yield of harmine using quinine sulfate dihydrate as a standard. The experimental value obtained was identical to that reported in the literature[8] ($\Phi_s = 0.45$).

Cyclic voltammograms were recorded with a Princeton Applied Research model 263A potentiostat/galvanostat. Measurements were carried out under argon at 25 ± 2 °C. Tetrabutylammonium tetrafluoroborate ($TBABF_4$, 10 cm^3) solution in acetonitrile (0.1 mol dm^{-3}) was used as the electrolyte solution. A three-electrode system was used. The three electrodes consisted of an 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 diam smooth platinum disk, area $= 3.14 \times 10^{-2}$ cm^2), and a platinum counter electrode (platinum wire).

Ferrocene was employed as a reference redox system according to IUPAC's recommendation.[9] Fresh reference electrodes were made before each series of measurements and calibrated against Fc/Fc^+. Polymer thin films were formed by drop-casting 1.0 mm^3 of polymer solutions in dichloromethane (analytical reagent, 1 mg cm^{-3}) onto the working electrode, and then dried in the air.

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

*2,7-Dibromo-9-(2-ethylhexyl)-9H-carbazole (**1a**).* A mixture of 2,7-dibromo-9*H*-carbazole (4.56 g, 14.0 mmol), 3-bromomethylheptane (2.97 g, 15.4 mmol), tetrabutylammonium hydrogensulfate (0.14 g, 0.41 mmol), and NaOH (0.84 g, 21 mmol) in acetone (HPLC grade, 30 cm^3) was refluxed for 9 h. After the reaction, the acetone was removed in vacuo, and the residue was extracted with toluene (300 cm^3). The toluene solution was washed with a saturated NaCl aqueous solution three times (200 cm^3 × 3), dried with $MgSO_4$, and evaporated to dryness in vacuo. The residue was purified by column chromatography on silica gel 60/hexane. Then the obtained residue was dried in vacuo to give 9-(2-ethylhexyl)-2,7-dibromo-9*H*-carbazole **1a** as a colorless powder (5.49 g, 90% yield); mp 99−100 °C. The product gave a single peak on GC (RT = 15.92 min). Mass (EI) (m/z): 435, 437, 439 (M^+). IR (KBr): 3202, 3079, 2962, 2930, 2859, 1885, 1857, 1681, 1619, 1587, 1483,

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1453, 1426, 1381, 1365, 1328, 1311, 1272, 1250, 1226, 1213, 1146, 1057, 999, 967, 947, 904, 879, 848, 823, 799, 728, 666, 600, 558, 437 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.82−0.94 (6H, m); 1.16−1.46 (8H, m); 1.98 (1H, septet, $J = 6$ Hz); 3.96 (1H, dd, $J = 7$ Hz, 15 Hz); 4.00 (1H, dd, $J = 7$ Hz, 15 Hz); 7.31 (2H, dd, $J = 2$ Hz, 8 Hz); 7.46 (2H, d, $J = 2$ Hz); 7.83 (2H, d, $J = 8$ Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 10.88 (1C); 14.02 (1C); 23.03 (1C); 24.32 (1C); 28.54 (1C); 30.77 (1C); 39.13 (1C); 47.63 (1C); 112.34 (2C); 119.74 (2C); 121.31 (2C); 121.48 (2C); 122.61 (2C); 141.92 (2C). Anal. Calcd. for $C_{20}H_{23}NBr_2$: C, 54.94; H, 5.30; N, 3.20; Br, 36.55. Found: C, 55.14; H, 5.52; N,3.00; Br, 36.48.

*2,7-Dibromo-9-(2-hexyldecyl)-9H-carbazole (**1b**).* 2,7-Dibromo-9-(2-hexyldecyl)-9*H*-carbazole **1b** was prepared according to the preparation of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole **1a** except that 7.80 g (24.0 mmol) of 2,7-dibromo-9*H*-carbazole, 10.99 g (35.99 mmol) of 7-bromomethylpentadecane, 0.49 g (1.4 mmol) of tetrabutylammonium hydrogensulfate, and 1.92 g (48.0 mmol) of NaOH were used, and that the reaction time was 5 h. 2,7-Dibromo-9-(2-hexyldecyl)-9*H*-carbazole **1b** was obtained as a pale yellow oil (12.42 g, 94% yield). The product gave a single peak on GC (RT = 17.92 min). Mass (EI) (*m*/*z*): 547, 549, 551 (M$^+$). IR (NaCl): 3088, 2962, 2933, 2859, 2732, 2670, 1865, 1625, 1590, 1487, 1453, 1430, 1382, 1330, 1315, 1272, 1250, 1230, 1136, 1055, 1026, 1003, 943, 902, 875, 842, 822, 794, 725, 667, 600, 563, 510 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.80−0.93 (6H, m); 1.10−1.42 (24H, m); 2.04 (1H, septet, $J = 6$ Hz); 3.97 (2H, d, $J = 8$ Hz); 7.31 (2H, dd, $J = 2$ Hz, 8 Hz); 7.46 (2H, d, $J = 2$ Hz); 7.83 (2H, d, $J = 8$ Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 14.11 (1C); 14.15 (1C); 22.66 (1C); 22.70 (1C); 26.39 (1C); 26.41 (1C); 29.31 (1C); 29.54 (1C); 29.62 (1C); 29.94 (1C); 31.65 (1C); 31.68 (1C); 31.82 (1C); 31.91 (1C); 37.59 (1C); 47.84 (1C); 112.38 (2C); 119.76 (2C); 121.32 (2C); 121.49 (2C); 122.61 (2C); 141.94 (2C). Anal. Calcd. for $C_{28}H_{39}NBr_2$: C, 61.21; H, 7.15; N, 2.55; Br, 29.09. Found: C, 61.45; H, 7.27; N, 2.40; Br, 29.03.

*2,7-Dibromo-9-dodecyl-9H-carbazole (**1c**).* 2,7-Dibromo-9-dodecyl-9*H*-carbazole **1c** was prepared according to the preparation of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole **1a** except that 7.80 g (24.0 mmol) of 2,7-dibromo-9*H*-carbazole, 8.97 g (36.0 mmol) of 1-bromododecane, 0.49 g (1.4 mmol) of tetrabutylammonium hydrogensulfate, and 1.92 g (48.0 mmol) of NaOH were used, and that the reaction time was 5 h. 2,7-Dibromo-9-dodecyl-9*H*-carbazole **1c** was obtained as a colorless powder (10.28 g, 87% yield); mp 78−79 °C. The product gave a single peak on GC (RT = 17.68 min). Mass (EI) (*m*/*z*): 491, 493, 495 (M$^+$). IR (KBr): 3081, 2955, 2923, 2853, 1880, 1866, 1660, 1622, 1590, 1487, 1467, 1449, 1426, 1370, 1343, 1330, 1315, 1273, 1243, 1226, 1131, 1058, 1001, 950, 915, 882, 839, 822, 799, 760, 733, 677, 659, 600, 567, 434 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.87 (3H, t, $J = 7$ Hz); 1.18−1.42 (18H, m); 1.80 (2H, quintet, $J = 7$ Hz); 4.13 (2H, t, $J = 7$ Hz); 7.31 (2H, dd, $J = 2$ Hz, 8 Hz); 7.49 (2H, d, $J = 2$ Hz); 7.83 (2H, d, $J = 8$ Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 14.15 (1C); 22.72 (1C); 27.18 (1C); 28.77 (1C); 29.35 (2C); 29.51 (1C); 29.58 (1C); 29.63 (2C); 31.94 (1C); 43.34 (1C); 112.08 (2C); 119.79 (2C); 121.36 (2C); 121.56 (2C); 122.60 (2C); 141.46 (2C). Anal. Calcd. for $C_{24}H_{31}NBr_2$: C, 58.43; H, 6.33; N, 2.84; Br, 32.39. Found: C, 58.50; H, 6.56; N, 2.69; Br, 32.51.

*2,7-Dibromo-9-hexadecyl-9H-carbazole (**1d**).* 2,7-Dibromo-9-hexadecyl-9*H*-carbazole **1d** was prepared according to the preparation of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole **1a** except that 7.80 g (24.0 mmol) of 2,7-dibromo-9*H*-carbazole, 10.99 g (35.99 mmol) of 1-bromohexadecane, 0.49 g (1.4 mmol) of tetrabutylammonium hydrogensulfate, and 1.92 g (48.0 mmol) of NaOH were used, and that the reaction time was 5 h. 2,7-Dibromo-9-hexadecyl-9*H*-carbazole **1d** was obtained as a colorless powder (11.32 g, 86% yield); mp 85−86 °C. The product gave a single peak on GC (RT = 19.53 min). Mass (EI) (*m*/*z*): 547, 549, 551 (M$^+$). IR (KBr): 3090, 2965, 2923, 2853, 1880, 1866, 1625, 1592, 1487, 1469, 1454, 1429, 1373, 1346, 1333, 1323, 1280, 1253, 1204, 1139, 1062, 1007, 952, 926, 899, 866, 841, 826, 800, 733, 677, 656, 601, 568, 431 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.87 (3H, t, $J = 7$ Hz); 1.17−1.42 (26H, m); 1.79 (2H, quintet, $J = 7$ Hz); 4.12 (2H, t, $J = 7$ Hz); 7.31 (2H, $J = 2$ Hz, 8 Hz); 7.49 (2H, d, $J = 2$ Hz); 7.83 (2H, d, $J = 8$ Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 14.14 (1C); 22.73 (1C); 27.18 (1C); 28.78 (1C); 29.34 (1C); 29.41 (1C); 29.52 (1C); 29.60 (1C); 29.64 (1C); 29.68, (1C); 29.70 (2C); 29.73 (2C); 31.96 (1C); 43.34 (1C); 112.07 (2C); 119.79 (2C); 121.36 (2C); 121.56 (2C); 122.61 (2C); 141.46 (2C). Anal. Calcd. for $C_{28}H_{39}NBr_2$: C, 61.21; H, 7.15; N, 2.55; Br, 29.09. Found: C, 61.48; H, 7.29; N, 2.33; Br, 28.86.

Preparation of the Polymers. All polymerizations were carried out under inert nitrogen atmosphere.

Typical Polymerization Reactions. Polymerization reactions were performed in THF in sealed vessels at 120 °C. A typical protocol for these reactions is outlined below.

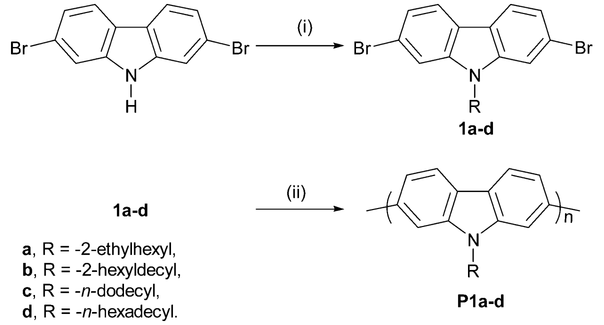
*Poly(9-(2-ethylhexyl)-9H-carbazole)-2,7-diyl (**P1a**).* A mixture of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole **1a** (1.57 g, 3.59 mmol), magnesium (turnings) (96.3 mg, 3.96 mmol), (2,2′-bipyridine)dichloro palladium(II) (24.0 mg, 0.0720 mmol), and THF (15 cm^3) was placed in a sealed glass tube and heated at 120 °C with stirring for 72 h. Upon cooling of the reaction mixture, it was poured into methanol (1000 cm^3) under an inert nitrogen atmosphere. The precipitates were filtered off and then dissolved in chloroform (300 cm^3). The insoluble materials in the chloroform solution were filtered off, and then the filtrate was concentrated in vacuo. The concentrated chloroform solution was poured into methanol (1000 cm^3) under inert nitrogen atmosphere, and the precipitate was filtered off. The precipitate was reprecipitated from chloroform into methanol under inert nitrogen atmosphere two more times. The precipitate was dried in vacuo to give poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a** as a dull yellow powder (0.47 g, 47% yield). GPC: Mw = 4800; Mn = 2500; Mw/Mn = 1.9. IR (KBr): 3062, 3030, 2965, 2933, 2882, 2864, 2743, 2675, 1883, 1625, 1605, 1560, 1502, 1457, 1434, 1381, 1325, 1247, 1217, 1201, 1158, 1134, 1059, 1081, 997, 943, 921, 848, 802, 769, 744, 728, 685, 669, 643, 592, 563, 448, 439, 409 cm^{-1}. Anal. Calcd. for $(C_{20}H_{23}N)_n$: C, 86.59; H, 8.36; N, 5.05. Found: C, 84.35; H, 8.37; N, 4.83; Br, 2.25. In this preparation, 0.48 g of an olive-green powder, a mixture of high-molecular-weight poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a** and a trace amount of unreacted magnesium, was also obtained as an insoluble material in chloroform (Insoluble fraction **P1a** IR (KBr): 3062, 3030, 2965, 2933, 2882, 2864, 2743, 2675, 1883, 1713, 1625, 1605, 1560, 1502, 1457, 1434, 1381, 1325, 1247, 1217, 1201, 1134, 1059, 997, 943, 848, 826, 799, 769, 744, 728, 685, 669, 625, 591, 561, 472, 439, 409 cm^{-1}. A 275.0-mg aliquot of the soluble fraction of **P1a** was fractionated by Soxhlet extraction with hexane for 24 h under inert nitrogen atmosphere. The insoluble fraction in the hot hexane was dissolved in a small amount of chloroform. Then the chloroform solution was poured into methanol (1000 cm^3) under inert nitrogen atmosphere, and the precipitate was filtered off. The precipitate was dried in vacuo to give the polymer **P1a** as a dark gray-brown powder (242.7 mg, 88 wt %). GPC: Mw = 4900; Mn = 3000; Mw/Mn = 1.6. IR (KBr): 3062, 3030, 2965, 2933, 2882, 2864, 2743, 2675, 1883, 1625, 1605, 1560, 1502, 1457, 1434, 1381, 1325, 1247, 1217, 1201, 1158, 1134, 1059, 997, 943, 848, 802, 769, 744, 728, 685, 669, 593, 561, 467, 437, 409 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.78−1.08 (6H, m); 1.18−1.72 (8H, m); 2.06−2.36 (1H, m); 4.14−4.52 (2H, m); 7.66 (2H, d, $J = 8$ Hz); 7.76 (2H, s); 8.25 (2H, d, $J = 8$ Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 11.05 (1C); 14.11 (1C); 23.19 (1C); 24.52 (1C); 28.95 (1C); 31.20 (1C); 39.60 (1C); 47.54 (1C); 108.09 (2C); 119.32 (2C); 120.71 (2C); 122.00 (2C); 140.32 (2C); 142.33 (2C). Anal. Calcd. for $(C_{20}H_{23}N)_n$: C, 86.59; H, 8.36; N, 5.05. Found: C, 83.92; H, 8.16; N, 4.92; Br, 2.42.

*Poly(9-(2-hexyldecyl)-9H-carbazole)-2,7-diyl (**P1b**).* Preparation was carried out according to the preparation of poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a** except that 1.43 g (2.60 mmol) of 2,7-dibromo-9-(2-hexyldecyl)-9*H*-carbazole, 69.5 mg (2.86 mmol) of magnesium (turnings), and 17.3 mg (0.0519 mmol) of (2,2′-bipyridine)dichloropalladium(II) were used. Poly(9-(2-hexyldecyl)-9*H*-carbazole)-2,7-diyl **P1b** was obtained as a yellow powder (0.94 g, 93% yield). GPC: Mw = 19 500; Mn = 5100; Mw/Mn = 3.8. IR (KBr): 3074, 3033, 2962, 2937, 2864, 2739, 2698, 2595, 1872, 1625, 1608, 1560, 1455, 1431, 1377, 1331, 1251, 1233, 1205, 1137, 1063, 989, 939, 889, 855, 848, 801, 769, 747, 726, 687, 670, 646, 617, 594, 561, 447, 431, 409 cm^{-1}. A 757.1-mg aliquot of the obtained polymer **P1b** was fractionated according to the fractionation procedure of poly-(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a**. **P1b** was obtained as a deep yellow-brown powder (543.6 mg, 72 wt %). GPC: Mw = 28 400; Mn = 15 100; Mw/Mn = 1.9. IR (KBr): 3074, 3033, 2962, 2937, 2864, 2748, 2677, 2598, 1872, 1744, 1714, 1625, 1608, 1560, 1455, 1431, 1377, 1331, 1251, 1233, 1205, 1137, 1063, 1034, 999, 939, 889, 855, 848, 801, 769, 747, 726, 687, 670, 646, 617, 594, 561, 442, 419 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.75−0.94 (6H, m); 0.96−1.70 (24H, m); 2.15−2.43 (1H, m); 3.80−4.80 (2H, m); 7.66 (2H, d, J = 8 Hz); 7.75 (2H, s); 8.23 (2H, d, J = 8 Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 14.12 (2C); 22.70 (2C); 26.77 (2C); 29.40 (1C); 29.71 (1C); 29.84 (1C); 30.19 (1C); 31.93 (1C); 31.95 (1C); 32.13 (2C); 38.19 (1C); 47.84 (1C); 108.10 (2C); 119.28 (2C); 120.64 (2C); 121.99 (2C); 140.30 (2C); 142.32 (2C). Anal. Calcd. for $(C_{28}H_{39}N)_n$: C, 86.32; H, 10.09; N, 3.59. Found: C, 85.84; H, 10.02; N, 3.71; Br, 0.64.

*Poly(9-dodecyl-9H-carbazole)-2,7-diyl (**P1c**).* Preparation was carried out according to the preparation of poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a** except that 1.48 g (3.00 mmol) of 2,7-dibromo-9-dodecyl-9*H*-carbazole, 80.2 mg (3.30 mmol) of magnesium (turnings), and 20.0 mg (0.0600 mmol) of (2,2′-bipyridine)dichloropalladium(II) were used. Poly(9-dodecyl-9*H*-carbazole)-2,7-diyl **P1c** was obtained as a strong yellow-green powder (0.81 g, 81% yield). GPC: Mw = 6600; Mn = 2300; Mw/Mn = 2.9. IR (KBr): 3074, 3031, 2960, 2935, 2861, 2732, 2677, 2593, 1878, 1625, 1602, 1560, 1456, 1432, 1327, 1241, 1207, 1135, 1057, 1000, 943, 862, 847, 805, 770, 743, 724, 670, 629, 592, 563, 438, 406 cm^{-1}. In this preparation, a trace amount of insoluble polymer in chloroform was obtained. A 650.4-mg aliquot of the soluble fraction of **P1c** was fractionated by Soxhlet extraction with hexane according to the fractionation procedure of poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a**. **P1c** was obtained as a gray-olive powder (471.0 mg, 72 wt %). GPC: Mw = 8600; Mn = 6300; Mw/Mn = 1.4. IR (KBr): 3074, 3031, 2960, 2935, 2861, 2732, 2677, 2593, 1893, 1873, 1625, 1602, 1560, 1456, 1432, 1377, 1365, 1327, 1241, 1207, 1181, 1135, 1088, 1057, 1000, 943, 862, 847, 818, 805, 770, 743, 724, 683, 658, 626, 592, 556, 470, 440, 421 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.85 (3H, m); 1.00−1.76 (18H, m); 1.85−2.18 (2H, m); 4.20−4.70 (2H, m); 7.67 (2H, d, J = 8 Hz); 7.77 (2H, s); 8.26 (2H, d, J = 8 Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 14.15 (1C); 22.71 (1C); 27.51 (1C); 29.19 (1C); 29.38 (2C); 29.57 (1C); 29.67 (1C); 29.71 (2C); 31.94 (1C); 43.25 (1C); 107.91 (2C); 119.41 (2C); 120.75 (2C); 122.03 (2C); 140.43 (2C); 141.80 (2C). Anal. Calcd. for $(C_{24}H_{31}N)_n$: C, 86.43; H, 9.37; N, 4.20. Found: C, 80.96; H, 9.17; N, 4.00; Br, 1.43.

*Poly(9-hexadecyl-9H-carbazole)-2,7-diyl (**P1d**).* Preparation was carried out according to the preparation of poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a** except that 1.43 g (2.60 mmol) of 2,7-dibromo-9-hexadecyl-9*H*-carbazole, 69.5 mg (2.86 mmol) of magnesium (turnings), and 17.3 mg (0.0519 mmol) of (2,2′-bipyridine)dichloropalladium(II) were used; and that the reaction time was 504 h. Poly(9-hexadecyl-9*H*-carbazole)-2,7-diyl **P1d** was obtained as a light yellow-green powder (0.84 g, 83% yield). GPC: Mw = 8300; Mn = 2800; Mw/Mn = 3.0. IR (KBr): 3072, 3029, 2935, 2859, 2732, 2677, 2593, 1881, 1626, 1603, 1557, 1469, 1454, 1432, 1327, 1241, 1226, 1203, 1138, 1062, 1026, 998, 885, 862, 848, 817, 801, 769, 744, 726, 665, 629, 592, 558, 441, 413 cm $^{-1}$. In this preparation, a trace amount of insoluble polymer in chloroform was obtained. A 745.0-mg aliquot of the soluble fraction of **P1d** was fractionated by Soxhlet extraction with hexane according to the fractionation procedure of poly(9-(2-ethylhexyl)-9*H*-carbazole)-2,7-diyl **P1a**. **P1d** was obtained as an olive powder (625.4 mg, 84 wt %). GPC: Mw = 10 700; Mn = 6800; Mw/Mn = 1.6. IR (KBr): 3072, 3029, 2935, 2859, 2732, 2687, 2595, 1898, 1881, 1626, 1603, 1557, 1469, 1454, 1432, 1377, 1365, 1327, 1241, 1226, 1203, 1138, 1062, 1026, 998, 946, 885, 862, 848, 817, 801, 769, 744, 726, 665, 629, 592, 558, 514, 473, 441, 413 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 0.86 (3H, m); 0.98−1.74 (26H, m); 1.88−2.12 (2H, m); 4.20−4.70 (2H, m); 7.67 (2H, d, J = 8 Hz); 7.77 (2H, s); 8.25 (2H, d, J = 8 Hz). ^{13}C NMR (CDCl$_3$, TMS) δ_C/ppm: 14.15 (1C); 22.72 (1C); 27.52 (1C); 29.19 (1C); 29.41 (1C); 29.58 (1C); 29.75 (8C); 31.97 (1C); 43.25 (1C); 107.90 (2C); 119.42 (2C); 120.75 (2C); 122.04 (2C); 140.44 (2C); 141.82 (2C). Anal. Calcd. for $(C_{28}H_{39}N)_n$: C, 86.32; H, 10.09; N, 3.59. Found: C, 84.33; H, 9.93; N, 3.59; Br, 1.47.

Scheme 1



(i) RBr, NaOH, (Bu^n)$_4$NHSO$_4$, acetone; (ii) Mg, PdCl$_2$(bpy), THF.

Results and Discussions

Poly(9-alkyl-9*H*-carbazole)-2,7-diyls were prepared via a palladium-catalyzed cross-coupling reaction involving 2-bromo-7-bromomagnesio-9-alkyl-9*H*-carbazole derivatives, generated in situ, from their corresponding 9-alkyl-2,7-dibromo-9*H*-carbazole derivatives. Polymerizations of monomers **1** were undertaken upon their reaction with 1.1 mol equiv of magnesium in the presence of catalytic amounts (2 mol equiv percent) of (2,2′-bipyridine)dichloropalladium (II) according to Scheme 1.

The use of 10% molar excess of magnesium is necessary in these reactions because there was always about that amount of unreacted magnesium and magnesium oxide left after each polymerization reaction. These conditions were also found to afford polymers in the highest yields and average molecular weights. This polymerization method was very effective in the preparation of poly(*p*-phenylene)s as described by Yamamoto et al.[10]

9-Alkyl-2,7-dibromo-9*H*-carbazole derivatives **1** were prepared on alkylation of 2,7-dibromo-9*H*-carbazole in the presence of a phase-transfer catalyst following a modified literature procedure for the alkylation of carbazoles. A range of alkyl substituents of different steric requirements was used in this study to probe the effects of their steric bulk on the physical properties of the new polymers.

Gel permeation chromatography results from these polymerization reactions on crude products isolated on repeated precipitation from methanol are shown in Table 1. Polymerizations were performed in tetrahydrofuran (THF) for varying time periods, either at reflux temperature (66 °C) or in sealed tubes at 120 °C. Polymerization of 2,7-dibromo-9-(2-ethylhexyl)-9*H*-carbazole **1a**, (Table 1, entries 1 and 2) led to polymers that are only partially soluble in chloroform and THF (about half of the polymer produced was insoluble). This reduced solubility of polymer **P1a** can be explained by the fact that poly(9-alkyl-9*H*-carbazole)-2,7-diyls form rigid rodlike polymer backbones with extended electronic conjugation, and that the 2-ethylhexyl-substitu-

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[10] Yamamoto, T.; Hayashi, Y.; Yamamoto, A. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2091.

Table 1. Comparison of Molecular Weight Distributions of Crude Poly(9-alkyl-9*H*-carbazole)-2,7-diyls Prepared at Different Temperatures and Varying Time Periods

entry	polymer	reaction conditions	M_N[a]	M_W[a]	yield %
1	**P1a**[b]	66 °C/24 h	2200[c]	4400[c]	45
2	**P1a**[b]	120 °C/72 h	2500[c]	4800[c]	47
3	**P1b**	120 °C/72 h	5100	19500	93
4	**P1c**	120 °C/72 h	2300	6600	81
5	**P1d**	120 °C/504 h	2800	8300	83

[a] Results on crude products isolated on repeated precipitation from methanol. [b] ~50% of the polymer produced was insoluble in chloroform and THF. [c] Values representing the soluble fractions of polymer.

Table 2. Molecular Weight Distributions and UV–Vis and Fluorescence Data of Poly(9-alkyl-9*H*-carbazole)-2,7-diyls Isolated after Soxhlet Extraction with Hexane

polymer	M_N	M_W	absorption λ_{max} /nm ($CHCl_3$)	emission λ_{max}[b]/nm (CH_2Cl_2)	Φ[c] (CH_2Cl_2)	Stokes shift /nm
P1a	3000[a]	4900[a]	377	418 (441)	0.76	41
P1b	15100	28400	388	419 (442)	0.59	31
P1c	6300[a]	8600[a]	378	418 (441)	0.66	40
P1d	6800[a]	10700[a]	380	418 (441)	0.68	38

[a] A small fraction of the polymer was not soluble in THF upon running the GPC analysis. [b] Numbers in parentheses correspond to shoulder emission peaks. [c] Measured using quinine sulfate dihydrate as a standard.

ents are unable to impart a good solubility to the resulting polymers. It must also be noted that the GPC results presented for **P1a** only account for fractions that are at the limit of their solubility in chloroform.

On using 9-alkyl-2,7-dibromo-9*H*-carbazole monomers with larger alkyl chains such as the 2-hexyldecyl, *n*-dodecyl, and *n*-hexadecyl groups, the solubility of the resulting poly(9-alkyl-9*H*-carbazole)-2,7-diyls is greatly improved with only trace amounts of insoluble materials produced. Results in Table 1 also indicate that poly(9-alkyl-9*H*-carbazole)-2,7-diyls are produced with higher average molecular weights than those reported[5a] for the corresponding poly(9-alkyl-9*H*-carbazole)-3,6-diyls made in similar reaction conditions. The enhanced degrees of polymerization are explained by the fact that there is less end group cleavage during polymerization reactions involving 9-alkyl-2,7-dibromo-9*H*-carbazoles monomers than there is in the case of 9-alkyl-3,6-dihalo-9*H*-carbazole monomers.

Polymerizations of monomers **1** are greatly affected by the size of the alkyl groups attached to the carbazole rings. Although **1c** gave polymers with reasonable molecular weights after 72 h at 120 °C (Table 1, entry 4), monomer **1d** barely showed any reaction at the same conditions (little magnesium was consumed) and required three weeks at 120 °C to produce **P1d** with reasonable average molecular weights (Table 1, entry 5).

Comparison of the average molecular weights of polymers made in the same experimental conditions from **1b** and **1c** shows a greater degree of polymerization for **1b** than **1c** (Table 1, entries 3 and 4). This result could be explained by steric factors, considering the *n*-dodecyl substituent on **1c** sterically interferes more with the 2,7-positions of the carbazole rings in **1c** during the reaction, than does the 2-hexyldecyl substituent in **1b**, despite the branching of the substituent.

The *n*-dodecyl and *n*-hexadecyl substituents on **P1c** and **P1d**, respectively, impart a greater solubility to the resulting poly(9-alkyl-9*H*-carbazole)-2,7-diyls than the 2-ethylhexyl substituents (**P1a**). However, **P1b** was found to have the greatest solubility of all the polymers in this series, as a result of both the size and branching of its 2-hexyldecyl substituents.

Fractionation of the polymers upon Soxhlet extraction with hexane afforded polymers with higher average molecular weights. The GPC results of the fractionated polymers together with their absorption maxima in solution and in the solid state (films) and their fluorescence data are presented in Table 2.

The GPC results indicate that the degrees of polymerization of the fractionated polymers in the poly(9-alkyl-9*H*-carbazole)-2,7-diyls series range from 11 for **P1a** to about 40 for **P1b**. It should be noted that the low degrees of polymerization measured for **P1a** are a consequence of its low solubility and only account for soluble fractions of low average molecular weights.

NMR Spectroscopy. NMR studies conducted in chloroform on poly(9-alkyl-9*H*-carbazole)-2,7-diyls polymers confirmed their assigned structure and linkage of the carbazole repeat units at the 2,7-positions. ^1H NMR studies reveal in the aromatic region a broad doublet, a broad singlet, and another broad doublet with equal integral intensities, centered around 8.25, 7.76, and 7.66 ppm, corresponding to the three chemical environments of hydrogens at, respectively, the 4- and 5-positions, 1- and 8-positions, and 3- and 6-positions of carbazole rings. In addition broad peaks centered around 4.36 ppm, corresponding to hydrogens of the methylene groups directly attached to the 9-position of carbazole rings, were observed for polymers with branched alkyl-substituents (**P1a** and **P1b**). Additional shoulder peaks next to these peaks at 4.27 ppm were also observed for polymers with low average molecular weights. These were attributed to hydrogens with similar chemical environments from carbazole repeat units at the end of polymer chains. Hydrogens belonging to the methylene groups directly attached to the 9-position of carbazole rings in polymers with linear chains (**P1c** and **P1d**) revealed broad peaks centered around 4.45 ppm. Additional shoulder peaks next to these peaks at 4.36 ppm were also observed for polymers with low average molecular weights. ^{13}C NMR studies on polymers in the poly(9-alkyl-9*H*-carbazole)-2,7-diyl series reveal six chemical environments at around 142, 140, 122, 121, 119, and 108 ppm, corresponding, respectively, to carbons at the 8a- and 9a-positions, 2- and 7-positions, 4- and 5-positions, 3- and 6-positions, 4a- and 4b-positions, and 1- and 8-positions of carbazole rings. It is worth noting that no peaks could be observed around 133 ppm (signals attributed to carbons at the 3,6-positions in poly(9-alkyl-9*H*-carbazole)-3,6-diyls) in the ^{13}C NMR spectra for all polymers in this series, indicating the absence of any 3,6-linkage defects, and demonstrating exclusive 2,7-linkage of carbazole repeat units on polymer chains.

The thermal stability of the poly(9-alkyl-9*H*-carbazole)-2,7-diyls derivatives was investigated in this study. Thermal gravimetric analysis (TGA) measurements revealed the remarkable stability of these materials up to 450 °C. The subsequent degradation and weight loss in these materials beyond 450 °C was proportional to the mass of their alkyl-substituents as shown in Figure 1. This is indicative of a degradation pathway affecting

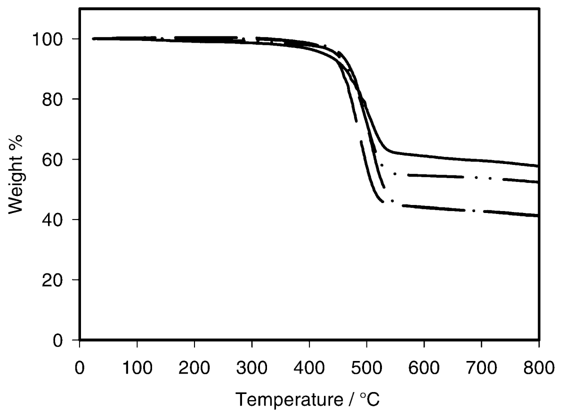

Figure 1. TGA analysis of poly(9-alkyl-9*H*-carbazole)-2,7-diyls: **P1a** (——); **P1b** (— —); **P1c** (— · ·); **P1d** (— ·).

Table 3. UV−Vis and Fluorescence Data of Fractionated Poly(9-alkyl-9*H*-carbazole)-2,7-diyls in the Solid State (Films)

polymer	absorption λ_{max} /nm	emission λ_{max} /nm	Eg[a]/eV
P1a	385	441, 465	2.89
P1b	398	430, 457	2.88
P1c	390	433, 459	2.90
P1d	388	434, 460	2.90

[a] Band gap estimated from the onset position of the absorption band.

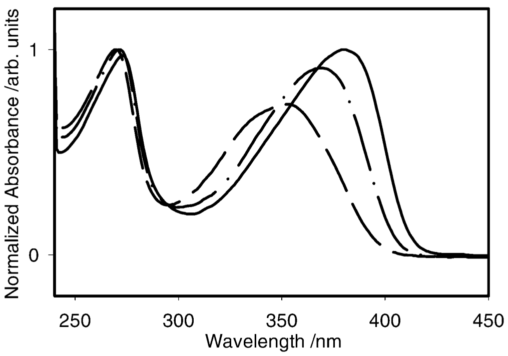

Figure 2. Normalized absorption spectra of different fractions of **P1c** in dichloromethane (——) fraction of **P1c** insoluble in hot hexane; (— ·) fraction of **P1c** soluble in hot hexane but precipitates upon cooling; (— —) fraction of **P1c** soluble in cold hexane.

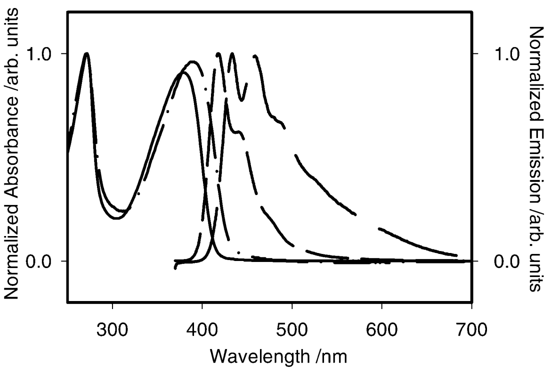

Figure 3. Normalized absorption spectra of **P1c** in dichloromethane (——) and as a thin film (—•) and normalized emission spectra of **P1c** in dichloromethane (- -) and as a thin film (— —).

the alkyl-substituents in a first instance. No further degradation and weight loss was observed for these polymers up to a temperature of 800 °C.

Solution and Solid-State Electronic Spectra. The extent of π orbital overlap between neighboring repeat units on conjugated polymers can be directly assessed from their electronic spectra. The extent of electronic conjugation directly affects the observed energy of the $\pi-\pi^*$ transition, which appears as the maximum absorption in these materials. Absorption spectra on poly(9-alkyl-9*H*-carbazole)-2,7-diyls were run in solution as well as in the solid-state (films). Tables 2 and 3 show the absorption maxima values for the carbazole polymers.

Measurements of maximum absorptions in solution (dichloromethane) of the various poly(9-alkyl-9*H*-carbazole)-2,7-diyls derivatives, reveal λ_{max} values between 377 and 388 nm (Table 2). The values of absorption maxima of the different polymers are closely linked to their average molecular weights. **P1b** has the highest degree of polymerization (~40) and shows the highest absorption maxima, while **P1a** has the lowest degree of polymerization (~11) and shows the lowest absorption maxima. This is also clearly shown in the absorption spectra of different fractions of **P1d** (Figure 2), isolated on fractionation of the crude polymer upon its Soxhlet extraction with hexane. The first fraction with the highest average molecular weight (degree of polymerization DP ~ 17) has an absorption maximum $\lambda_{max} =$ 380 nm. The second fraction was a precipitate that formed in the hexane Soxhlet extracts upon cooling, and represents a polymer with an intermediate average molecular weight (DP ~ 7) and has an absorption maximum $\lambda_{max} =$ 369 nm. The third fraction, which is mainly constituted of smaller oligomers (DP ~ 4), isolated upon evaporation of the hexane filtrate from the Soxhlet extracts once the second fraction was removed, has an absorption maximum $\lambda_{max} =$ 353 nm. These results clearly demonstrate an extended electronic delocalization on polymer backbones in the poly(9-alkyl-9*H*-carbazole)-2,7-diyl series as opposed to polymers in the poly(9-alkyl-9*H*-carbazole)-3,6-diyl series[5] in which electronic delocalization did not exceed two carbazole repeat units in view of its 3,6-linkage pattern.

Measurements of maximum absorptions in the solid-state (films) for the poly(9-alkyl-9*H*-carbazole)-2,7-diyls derivatives (Table 3) reveal a slight red shift in their absorption peaks (~10 nm) as compared to their solution spectra and indicate a little difference between the arrangement of consecutive repeat units on polymer chains in solution and those in the solid state. The band gaps of these materials were also established from these measurements and revealed Eg values between 2.88 and 2.90 eV, indicating the potential use of these polymers as blue-emitting materials.

Solution and Solid-State Fluorescence Spectra. Fluorescence studies on poly(9-alkyl-9*H*-carbazole)-2,7-diyls were performed both in solution (dichloromethane) and in the solid state. Results of the studies undertaken in solution are shown in Table 2. All polymers showed similar emission bands centered around λ_{max} values between 418 and 419 nm with shoulder peaks around 441 nm. Figure 3 shows typical absorption and emission spectra from these polymers and displays small Stokes shifts especially in solution (31 to 41 nm). This points to small structural differences between the ground and excited states in these materials in solution.

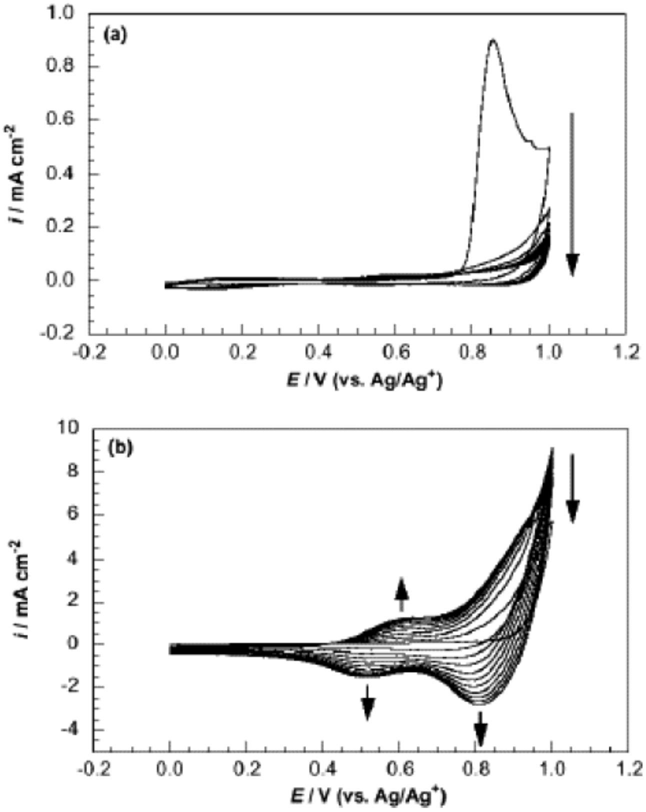

Figure 4. CV curves of thin films of poly(9-(2-hexyldecyl)-9H-carbazole)-2,7-diyl **P1b** upon repeated cycling at different scan rates: (a) scan rate = 20 mV s $^{-1}$, (b) scan rate 2 V s^{-1}.

The polymers were stable for storage in the air, away from light, at room temperature and showed no changes in their spectral properties for extended time periods.

The fluorescence quantum yields of the polymers were also determined in dichloromethane solutions. These were determined on excitation of polymers at their λ_{max} and comparison with the solution emission of quinine sulfate dihydrate ($\Phi_{fl} = 0.546$) used as a standard. The quantum yields of fluorescence for these polymers are shown in Table 2. All polymers were found to be highly fluorescent with quantum yield Φ ranging from = 0.59 to 0.76 indicating their great potential for application in light-emitting diodes.

Fluorescence measurements on the polymers in the solid state (films) reveal a red shift in their emission spectra as compared to solution spectra. These measurements also show a vibronic structure to their emission bands with two main peaks at 441 and 465 nm for **P1a** and around 432 and 459 nm for the other polymer derivatives (**P1b**−**d**).

Electrochemical Studies. Investigations of the electrochemical properties of poly(9-alkyl-9*H*-carbazole)-2,7-diyls **P1** were also undertaken in this study. Cyclic voltammetry measurements on drop-cast polymer films were conducted in acetonitrile with tetrabutylammonium tetrafluoroborate as an electrolyte. The cyclic voltammograms of these materials were found to depend to a great extent on the scan rates used as shown in Figure 4.

Table 4. Redox Potentials of Poly(9-alkyl-9*H*-carbazole)-2,7-diyls in 0.1 M TBABF$_4$/CH$_3$CN on Pt Working Electrode at 2 Vs^{-1} Using Ag/Ag$^+$ Reference Electrode

polymer	E$_{pa}$/V	E$_{pc}$/V	I $_P$^{b}/eV
P1a	0.60	0.47	5.4
	[a]	0.74	
P1b	0.60	0.51	5.5
	[a]	0.81	
P1c	0.57	0.50	5.4
	[a]	0.79	
P1d	0.60	0.52	5.4
	[a]	0.81	

[a] Second oxidation peak not clearly defined. [b] Ionization potential (vs vacuum) determined from onset of oxidation from scans before formation of new redox waves (see text).

At low scan rates (20 mVs^{-1}) and on repeated cycling (between 0 and 1.0 V vs Ag/Ag$^+$), significant decays of the anodic peaks and no counter-cathodic peaks were observed (Figure 4a). At faster scan rates (2 Vs^{-1}), a less pronounced decay in the anodic peaks was observed at the same time counter-cathodic peaks with increasing intensities were observed. It is also worth noting that, at faster scan rates, new reversible redox waves are observed at lower potentials and the intensities of these increased with repeated cycling (Figure 4b). Such peaks could be attributed to the formation of new species as a result of creation of new linkages between the 3,6-positions of adjacent polymer chains within the films. A similar explanation was reported by Zotti et al.[6c] for poly(9-octyl-9*H*-carbazole)-2,7-diyl.

Table 4 shows the redox potentials of the various polymers. It also shows their respective ionization potentials (vs vacuum). These were determined upon running CV scans at a scan rate of 20 mVs^{-1} between 0 and 0.7−0.8 V (vs. Ag/Ag$^+$) rather than between 0 and 1.0 V (vs. Ag/Ag$^+$), to minimize over-oxidation (cross-linking) of polymers.

The ionization potentials were estimated from the onset of oxidation of the various polymer films on electrodes and ranged from 5.4 to 5.5 eV (on the basis that ferrocene/ferrrocenium is 4.8 eV below the vacuum level[11]). These ionization potentials are 0.3 to 0.4 eV lower than those of poly(9,9-dioctyl-fluorene-2,7-diyl).[12]

Conclusion

Development of a new palladium-catalyzed cross-coupling polymerization route to new main-chain 9-alkylcarbazole polymers in which the carbazole repeat units are linked exclusively through their 2,7-positions was optimized. The reaction is sensitive to the size of alkyl group substituents on the carbazole monomers and proceeds faster with shorter alkyl group substituents. Thermal gravimetric analysis measurements revealed the remarkable stability of these materials up to 450 °C. Electronic delocalization in this class of main-chain carbazole polymers was demonstrated as their absorption maxima varied with their chain length. Preliminary electrochemical investigations have revealed that these materials are unstable under electrolytic conditions. However, fluorescence measurements have shown that this class of wide band gap polymers could have a great potential for use as blue-emitting materials in polymer-based light-emitting diodes in view of their high quantum yields of fluorescence.

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