Polymer 49 (2008) 4494–4501

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Synthesis and properties of polyacetylenes having pendent phenylethynylcarbazolyl groups

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ARTICLE INFO

Article history:
Received 21 April 2008
Received in revised form 29 July 2008
Accepted 11 August 2008
Available online 20 August 2008

Keywords:
Phenylethynylcarbazole
Photoluminescence
Polyacetylene

ABSTRACT

Novel acetylene monomers substituted with phenylethynylcarbazolyl groups, 3-[(4-octylphenyl)ethynyl]-9-propargylcarbazole (**1**), 3,6-bis[(4-octylphenyl)ethynyl]-9-propargylcarbazole (**2**), 9-(4-ethynylphenyl)-3-[(4-octylphenyl)ethynyl]carbazole (**3**), and 9-(4-ethynylphenyl)-3,6-bis[(4-octylphenyl)ethynyl]carbazole (**4**) were synthesized, and polymerized with $Rh^+(nbd)[\eta^6–C_6H_5B^-(C_6H_5)_3]$ and WCl_6–*n*-Bu_4Sn catalysts. The corresponding polyacetylenes with number-average molecular weights ranging from 9200 to 94 000 were obtained in 20–98% yields. The IR spectra of the polymers revealed that acetylene polymerization took place at the terminal ethynyl group, while the ethynylene group remained intact. The UV–vis absorption band edge wavelengths of W-based poly(**3**) and poly(**4**) were longer than those of the other polymers. W-Based poly(**4**) emitted fluorescence with the highest quantum yield (41%). Poly(**1**) exhibited excimer-based fluorescence in dilute solution.

1. Introduction

Carbazole is a well-known conjugated unit featuring a wide band gap originated from the bridging nitrogen atom and biphenyl unit. Carbazole derivatives exhibit interesting optoelectronic properties such as photoconductivity, photorefractivity, and electroluminescence, and used as hole transport and blue emission materials for photoelectronic devices [1]. Much effort has been done to synthesize polymers carrying carbazole in the main and side chains, e.g., poly(carbazole) consisting of carbazolylene main chains exhibit properties largely different from each other according to the position of linkage. Namely, 3,6-linked poly(carbazole) undergoes redox reaction via stable cation radical species [2]. 2,7-Linked poly(carbazole) emits blue light in the film state based on the long conjugation length like poly(*p*-phenylene) [3]. The photo luminescent property of poly(carbazolyleneethynylenearylene)s are controllable by choosing arylene units and linkage positions [4]. Poly(*N*-vinylcarbazole), a typical polymer carrying pendent carbazole at the side chains undergoes photo-induced electron transfer to show high photoconductivity [5].

Meanwhile, polyacetylene derivatives exhibit unique characteristics based on the alternating double bonds and rigid structure, which include semiconductivity, nonlinear optical properties, high gas permeability, and helix formation [6]. It is expected that incorporation of carbazole moieties into polyacetylene leads to development of novel functional polymers on the basis of synergistic actions of carbazole and main chain conjugation. We have synthesized several poly(acetylene) derivatives carrying carbazole moieties in the side chains that show photoconductivity, photo- and electroluminescence [7]. We may tune the optical and electrical properties by extending the conjugation of carbazole moiety at the side chain. In this paper, we report the synthesis and polymerization of novel acetylene monomers, *N*-propargyl and *N*-(4-ethynyl)phenylcarbazoles substituted with 4-octylphenylethynyl group at 3- and 3,6-position, and examination of the properties of the obtained polymers (Scheme 1).

2. Experimental section

2.1. Measurements

^1H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded on a JEOL EX-400 spectrometer using tetramethylsilane as an internal standard. IR, UV–vis and fluorescence spectra were measured on JASCO FT/IR-4100, V-550 and FP-750 spectrophotometers, respectively. Melting points (Mp) were measured on a Yanaco micro-melting point apparatus. Elemental analysis was carried out at the Microanalytical Center of Kyoto University. Number- and weight-average molecular weights (M_n and M_w) of polymers were

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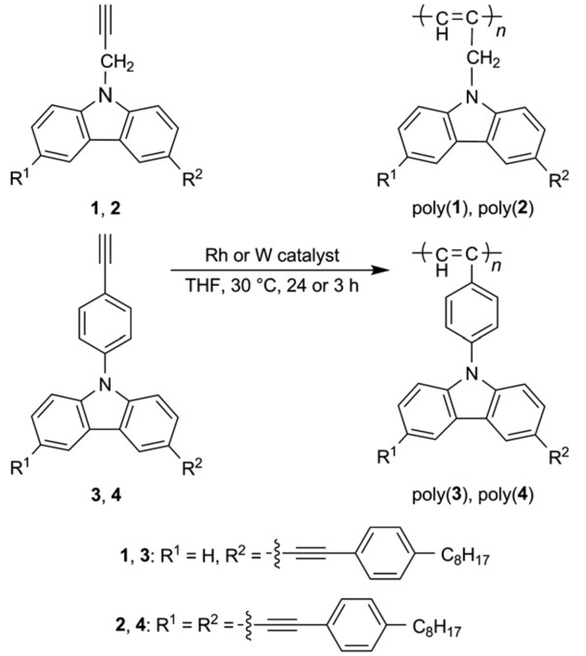
doi:10.1016/j.polymer.2008.08.028



Scheme 1. Polymerization of **1**–**4**.

determined by gel permeation chromatography (GPC) on a JASCO GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns KF-805L), using THF as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C.

2.2. Materials

Unless otherwise stated, reagents were commercially obtained, and used without further purification. 3-Iodocarbazole [8], 3,6-diiodocarbazole [9], $Rh^+(nbd)[\eta^6\text{-}C_6H_5B^-(C_6H_5)_3]$ [10] were synthesized according to the literature. Solvents used for polymerization were purified before use by the standard methods.

2.3. Monomer synthesis

2.3.1. 3-(4-Octylphenyl)ethynylcarbazole

4-Octylphenylacetylene (2.60 mL, 11.5 mmol) was added to a mixture of 3-iodocarbazole (2.95 g, 10.0 mmol), $PdCl_2(PPh_3)_2$ (71.9 mg, 0.10 mmol), PPh_3 (80.5 mg, 0.30 mmol), CuI (77.3 mg, 0.40 mmol) and Et_3N (70 mL) under hydrogen, and the resulting mixture was stirred at room temperature overnight. Then, solvent-insoluble salt precipitated was filtered off, and Et_3N was removed from the mixture by evaporation. The residue was extracted with $CHCl_3$, and the combined organic layer was washed with 1 M HCl, sat. $NaHCO_3$ aq. and water. The organic layer was dried with anhydrous $MgSO_4$, and concentrated by evaporation to give brown solid. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate to obtain the product as white solid. Yield 2.31 g (7.14 mmol, 71%).^{1}H NMR (400 MHz, *δ* in ppm, DMSO-d_6): 0.85 (t, *J* = 7.2 Hz, 3H, $-CH_2CH_3$), 1.24–1.27 (br, 10H, $-CH_2-$), 1.56 (br, 2H, $-CH_2-$), 2.61 (t, *J* = 7.6 Hz, 2H, $-CH_2-$), 7.18 (vt, *J* = 7.8 Hz, 1H, Ar), 7.23 (d, *J* = 8.0 Hz, 2H, Ar), 7.41 (vt, *J* = 7.8 Hz, 1H, Ar), 7.45 (d, *J* = 7.6 Hz, 2H, Ar), 7.49–7.54 (m, 3H, Ar), 8.17 (d, *J* = 7.8 Hz, 1H, Ar), 8.35 (s, 1H, Ar), 11.48 (s, 1H, NH); ^{13}C NMR (100 MHz, *δ* in ppm, DMSO-d_6): 14.1, 22.2, 28.7, 28.8, 28.9, 30.8, 31.4, 35.1, 87.4 (–*C*≡*C*–), 90.6 (–*C*≡*C*–), 111.3, 111.4, 112.1, 119.2, 120.4, 120.7, 122.0, 123.7, 126.2, 128.7, 128.9, 131.1, 139.6, 140.2, 142.8.

2.3.2. 3-[(4-Octylphenyl)ethynyl]-9-propargylcarbazole (**1**)

Sodium hydride (0.16 g, 6.80 mol, 60% in paraffin) was fed to a flask, and the paraffin was removed by washing with hexane. A benzene (40 mL) solution of 3-(4-octylphenyl)ethynylcarbazole (1.30 g, 3.43 mmol), and then dimethylsulfoxide (DMSO, 2.0 mL) were fed into the flask, and the resulting mixture was stirred at room temperature for 30 min. Then, propargyl bromide (1.50 mL, 13.5 mmol) was gradually added to the mixture, and it was stirred at 60 °C for 3 h. Water (60 mL) was added to the reaction mixture, and the organic layer was washed with water and separated. The organic layer was dried with anhydrous $MgSO_4$, and concentrated on a rotary evaporator to give brown solid. It was purified by preparative HPLC (eluent $CHCl_3$) to obtain **1** as white solid. Yield 0.40 g (0.95 mmol, 28%). Mp 70.2–71.6 °C. ^{1}H NMR (400 MHz, *δ* in ppm, DMSO-d_6): 0.85 (t, *J* = 7.2 Hz, 3H, $-CH_2CH_3$), 1.24–1.26 (br, 10H, $-CH_2-$), 1.56 (br, 2H, $-CH_2-$), 2.60 (t, *J* = 7.6 Hz, 2H, $-CH_2-$), 3.29 (s, 1H, –C≡CH), 5.34 (s, 2H, $-CH_2$C≡), 7.24 (d, *J* = 8.0 Hz, 2H, Ar), 7.28 (d, *J* = 7.6 Hz, 1H, Ar), 7.47 (d, *J* = 7.6 Hz, 2H, Ar), 7.52 (vt, *J* = 7.8 Hz, 1H, Ar), 7.63 (d, *J* = 8.8 Hz, 1H, Ar), 7.70 (d, *J* = 8.0 Hz, 1H, Ar), 7.71 (vt, *J* = 8.0 Hz, 1H, Ar), 8.24 (d, *J* = 7.6 Hz, 1H, Ar), 8.41 (s, 1H, Ar). ^{13}C NMR (100 MHz, *δ* in ppm, DMSO-d_6): 14.0, 22.1, 28.6, 28.7, 28.8, 30.7, 31.3, 32.0 (–*C*H$_2$C≡), 35.0, 74.7 (–C≡*C*H), 78.9 (–*C*≡CH), 87.8 (–*C*≡*C*–), 90.1 (–*C*≡*C*–), 109.8, 110.0, 113.1, 120.0, 120.1, 120.8, 122.0, 122.7, 123.8, 126.5, 128.7, 129.1, 131.1, 139.3, 140.0, 142.9. IR (cm^{-1}, KBr): 3278 (H–C≡), 3054, 2915, 2850, 2210 (C≡C), 2117 (HC≡C), 1596, 1508, 1461, 1369, 1334 (N–Ar), 1265, 1203, 1141, 1056, 1022, 925, 890, 802, 736, 682, 651, 609. Anal. Calcd for $C_{31}H_{31}N$: C 89.16; H 7.48; N 3.35. Found: C 88.87; H 7.50; N 3.34.

2.3.3. 3,6-Bis[(4-octylphenyl)ethynyl]carbazole

This compound was synthesized from 3,6-diiodocarbazole and 4-octylphenylacetylene in a manner similar to 3-(4-octylphenyl)-ethynylcarbazole. Yield 55% (white solid). ^{1}H NMR (400 MHz, *δ* in ppm, DMSO-d_6): 0.84 (t, *J* = 7.2 Hz, 6H, $-CH_2CH_3$), 1.23–1.26 (br, 20H, $-CH_2-$), 1.56 (br, 4H, $-CH_2-$), 2.59 (t, *J* = 7.6 Hz, 4H, $-CH_2-$), 7.23 (d, *J* = 8.0 Hz, 4H, Ar), 7.45 (d, *J* = 8.0 Hz, 4H, Ar), 7.51–7.57 (m, 4H, Ar), 8.41 (s, 2H, Ar), 11.74 (s, 1H, NH); ^{13}C NMR (100 MHz, *δ* in ppm, DMSO-d_6): 13.6, 21.7, 28.3, 28.3, 28.5, 30.3, 30.9, 34.7, 87.3 (–*C*≡*C*–), 90.0 (–*C*≡*C*–), 111.3, 112.6, 120.0, 121.9, 123.7, 128.3, 130.8, 139.6, 142.5.

2.3.4. 3,6-Bis[(4-octylphenyl)ethynyl]-9-propargylcarbazole (**2**)

This compound was synthesized from 3,6-bis[(4-octylphenyl)-ethynyl]carbazole and propargyl bromide in a manner similar to **1**, and purified by silica gel column chromatography eluted with hexane/ethyl acetate. Yield 33% (pale brown solid). Mp 97.8–99.2 °C. ^{1}H NMR (400 MHz, *δ* in ppm, $CDCl_3$): 0.88 (t, *J* = 7.2 Hz, 6H, $-CH_2CH_3$), 1.28–1.31 (br, 20H, $-CH_2-$), 1.62 (br, 4H, $-CH_2-$), 2.30 (s, 1H, –C≡CH), 2.62 (t, *J* = 7.6 Hz, 4H, $-CH_2-$), 5.02 (s, 2H, $-CH_2$C≡), 7.18 (d, *J* = 8.0 Hz, 4H, Ar), 7.44 (d, *J* = 8.8 Hz, 2H, Ar), 7.49 (d, *J* = 8.0 Hz, 4H, Ar), 7.67 (d, *J* = 8.4 Hz, 2H, Ar), 8.25 (s, 2H, Ar). ^{13}C NMR (100 MHz, *δ* in ppm, $CDCl_3$): 14.1, 22.7, 29.2, 29.3, 29.5, 31.3, 31.9, 35.0 (–*C*H$_2$C≡), 35.9, 72.9 (–C≡*C*H), 77.3 (–*C*≡CH), 88.2 (–*C*≡*C*–), 89.6 (–*C*≡*C*–), 109.0, 115.0, 120.7, 122.9, 124.1, 128.5, 129.9, 131.4, 139.7, 143.1. IR (cm^{-1}, KBr): 3027 (H–C≡), 2923, 2850, 2206 (C≡C), 2121 (HC≡C), 1901, 1600, 1508, 1376 (N–Ar), 1338, 1284, 1211, 1141, 879, 802, 740. Anal. Calcd for $C_{47}H_{51}N$: C 89.62; H 8.16; N 2.22. Found: C 89.45; H 8.15; N 2.23.

2.3.5. 9-(4-Iodophenyl)-3-[(4-octylphenyl)ethynyl]carbazole

A mixture of 3-(4-octylphenyl)ethynylcarbazole (0.57 g, 1.50 mmol), 1,4-diiodobenzene (1.48 g, 4.50 mmol), CuI (14.2 mg, 0.075 mmol), 1,10-phenanthroline (54.0 mg, 0.30 mmol), K_3PO_4

(0.64 g, 3.00 mmol), and toluene (15 mL) was stirred at 120 °C for 24 h. After cooling, the residue was extracted with CH_2Cl_2, and the organic layer was combined and washed with water. The organic layer was dried with anhydrous $MgSO_4$, and concentrated on a rotary evaporator to give gray solid. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate to obtain the product as pale yellow solid. Yield 0.57 g (0.97 mmol, 65%). ^1H NMR (400 MHz, δ in ppm, $CDCl_3$):0.88 (t, J = 7.2 Hz, 3H, -CH_2CH_3), 1.27–1.30 (br, 10H, –CH_2–), 1.61 (br, 2H, –CH_2–), 2.61 (t, J = 7.6 Hz, 2H, –CH_2–), 7.16 (d, J = 8.0 Hz, 2H, Ar), 7.29–7.45 (m, 6H, Ar), 7.48 (d, J = 8.0 Hz, 2H, Ar), 7.56 (d, J = 7.8 Hz, 1H, Ar), 7.92 (d, J = 8.0 Hz, 2H, Ar), 8.11 (d, J = 7.8 Hz, 1H, Ar), 8.30 (s, 1H, Ar); ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 14.1, 22.7, 29.2, 29.3, 29.4, 31.2, 31.9, 35.9, 88.2 (–*C*≡*C*–), 89.7 (–*C*≡*C*–), 92.4, 109.6, 109.8, 115.1, 120.5, 120.7, 120.8, 123.1, 123.5, 123.9, 126.5, 128.4, 128.8, 129.6, 131.3, 137.0, 140.0, 140.9, 143.1.

2.3.6. 9-(4-Ethynylphenyl)-3-[(4-octylphenyl)ethynyl]carbazole (3)

Trimethylsilylacetylene (0.42 mL, 3.0 mmol) was added to a mixture of 9-(4-iodophenyl)-3-[(4-octylphenyl)ethynyl]carbazole (567 mg, 0.97 mmol), $PdCl_2(PPh_3)_2$ (6.8 mg, 0.0097 mmol), PPh_3 (7.7 mg, 0.030 mmol), CuI (7.4 mg, 0.039 mmol), and Et_3N (15 mL) and the resulting mixture was stirred under hydrogen at room temperature overnight. Then, Et_3N was removed from the mixture by evaporation. Ether was added to the resulting mass, and insoluble solid was filtered off. The filtrate was washed with 1 M HCl, sat. $NaHCO_3$ aq. and water. The organic layer was dried with anhydrous $MgSO_4$, and concentrated to provide crude 9-(4-trimethylsilylethynylphenyl)-3-[(4-octylphenyl)ethynyl]carbazole. It was dissolved in THF (10 mL), and 1 M NaOH aq. (10 mL) was added to the solution. The resulting mixture was stirred at room temperature overnight. After that, THF was removed by evaporation, and the residue was extracted with ether. The organic layer was washed with 1 M HCl and water subsequently, dried over anhydrous $MgSO_4$, and concentrated on a rotary evaporator to give pale yellow solid. It was purified by silica gel column chromatography eluted with hexane/ethyl acetate to obtain **3** as pale yellow solid. Yield 0.39 g (0.87 mmol, 90%). Mp 78.2–79.6 °C. ^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.88 (t, J = 7.2 Hz, 3H, –CH_2CH_3), 1.22–1.30 (br, 10H, –CH_2–), 1.61 (br, 2H, –CH_2–), 2.61 (t, J = 7.6 Hz, 2H, –CH_2–), 3.17 (s, 1H, –C≡CH), 7.16 (d, J = 8.0 Hz, 2H, Ar), 7.29–7.45 (m, 4H, Ar), 7.47–7.58 (m, 6H, Ar), 7.72 (d, J = 8.0 Hz, 2H, Ar), 8.12 (d, J = 7.6 Hz, 1H, Ar), 8.31 (s, 1H, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 14.0, 22.7, 29.2, 29.3, 29.4, 31.3, 31.9, 35.9, 78.3 (–C≡*C*H), 82.8 (–*C*≡CH), 88.1 (–*C*≡*C*–), 89.7 (–*C*≡*C*–), 109.7, 109.9, 115.1, 120.5, 120.7, 120.8, 121.4, 123.1, 123.6, 123.9, 126.5, 126.7, 128.4, 129.7, 131.4, 133.7, 137.7, 140.0, 140.9, 143.0. IR (cm^{-1}, KBr): 3322, 3305 (H–C≡), 2917, 2850, 2214 (C≡C), 2113 (HC≡C), 1601, 1509, 1475, 1455, 1364, 1329 (N–Ar), 1265, 1226, 1132, 838, 814, 765, 746, 726, 635, 606, 592. Anal. Calcd for $C_{36}H_{33}N$: C90.15; H 6.93; N 2.92. Found: C 89.54; H 6.97; N 2.89. High-resolution mass. Calcd for $C_{36}H_{33}N$: 479.2613. Found: 479.2613.

2.3.7. 9-(4-Iodophenyl)-3,6-bis[(4-octylphenyl)ethynyl]carbazole

This compound was synthesized from 3,6-bis[(4-octylphenyl)-ethynyl]carbazole and *p*-diiodobenzene in a manner similar to 9-(4-iodophenyl)-3-[(4-octylphenyl)ethynyl]carbazole. Yield 77% (brown solid). ^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.88 (t, J = 7.2 Hz, 6H, –CH_2CH_3), 1.27–1.31 (br, 20H, –CH_2–), 1.62 (br, 4H, –CH_2–), 2.62 (t, J = 7.6 Hz, 4H, –CH_2–), 7.17 (d, J = 8.0 Hz, 4H, Ar), 7.28–7.31 (m, 4H, Ar), 7.48 (d, J = 8.0 Hz,, 4H, Ar), 7.57 (d, J = 8.4 Hz, 2H, Ar), 7.93 (d, J = 8.4 Hz, 2H, Ar), 8.28 (s, 2H, Ar); ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 14.1, 22.7, 29.2, 29.3, 29.5, 31.3, 31.9, 35.9, 88.7, 88.4(–*C*≡*C*–), 89.5 (–C≡C–), 92.7, 109.8, 115.6, 120.7, 123.1, 124.0, 128.5, 128.7, 130.0, 131.4, 136.6, 139.2, 140.3, 143.1.

2.3.8. 9-(4-Ethynylphenyl)-3,6-bis[(4-octylphenyl)-ethynyl]carbazole (4)

This compound was synthesized from 9-(4-iodophenyl)-3,6-bis[(4-octylphenyl)ethynyl]carbazole and trimethylsilylacetylene in a manner similar to **3**. Yield 73% (brown solid). Mp 97.4–99.2 °C. ^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.88 (t, J = 7.2 Hz, 6H, –CH_2CH_3), 1.27–1.31 (br, 20H, –CH_2–), 1.62 (br, 4H, –CH_2–), 2.62 (t, J = 7.6 Hz, 4H, –CH_2–), 3.14 (s, 1H, –C≡CH), 7.16 (d, J = 7.6 Hz, 4H, Ar), 7.32 (d, J = 8.8 Hz, 2H, Ar), 7.49 (m, 6H, Ar), 7.57 (d, J = 8.4 Hz, 2H, Ar), 7.72 (d, J = 8.4 Hz, 2H, Ar), 8.28 (s, 2H, Ar). ^{13}C NMR (100 MHz, δ in ppm, $CDCl_3$): 14.1, 22.7, 29.2, 29.3, 29.5, 31.3, 31.9, 35.9, 78.4 (–C≡CH), 82.7 (–C≡CH), 88.4 (–C≡*C*–), 89.5 (–C≡C–), 109.0, 115.6, 120.7, 121.6, 123.1, 124.0, 126.7, 128.5, 130.0, 131.4, 133.7, 137.2, 140.3, 143.1; IR (cm^{-1}, KBr): 3292 (*H*–C≡), 2922, 2851, 2205 (C≡C), 2110 (HC≡C), 1903, 1600, 1509, 1473, 1455, 1363 (N–Ar), 1332, 1278, 1226, 1183, 1167, 841, 813, 656, 589. Anal. Calcd for $C_{52}H_{53}N$: C 90.26; H 7.72; N 2.02. Found: C 90.38; H 7.92; N 1.74.

2.4. Polymerization

All the polymerizations were carried out in a glass tube equipped with a three-way stopcock under nitrogen. A monomer solution was added to a catalyst solution under dry nitrogen, and the resulting solution was kept at 30 °C for a set time. The polymerization mixture was poured into a large amount of methanol to precipitate a polymer. It was separated from the supernatant by filtration and dried under reduced pressure.

2.5. Spectroscopic data of the polymers

2.5.1. Poly(1)-Rh

^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.8–1.0 (br, 3H, –CH_2CH_3), 1.2–1.4 (br, 10H, –CH_2–), 1.5–1.7 (br, 2H, –CH_2–), 2.4–2.7 (br, 2H, –CH_2–), 5.1 (br, 2H, –CH_2C=), 6.1 (br, 1H, –C = CH–), 6.6–7.8 (br, 11H, Ar). IR (cm^{-1}, KBr): 2923, 2854, 2210 (C≡C), 1623, 1600, 1511, 1465, 1334 (N–Ar), 1265, 1211, 1149, 1095, 1022, 883, 806, 744.

2.5.2. Poly(1)-W

^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.7–1.0 (br, 3H, –CH_2CH_3), 1.2–1.4 (br, 10H, –CH_2–), 1.5–1.7 (br, 2H, –CH_2-), 2.4–2.7 (br, 2H, –CH_2-), 5.1 (br, 2H, –CH_2C=), 6.4–7.8 (br, 12H, –C = CH–, Ar). IR (cm^{-1}, KBr): 2923, 2850, 2210 (C≡C), 1600, 1508, 1461, 1334 (N–Ar), 1265, 1211, 1149, 806, 744.

2.5.3. Poly(2)-Rh

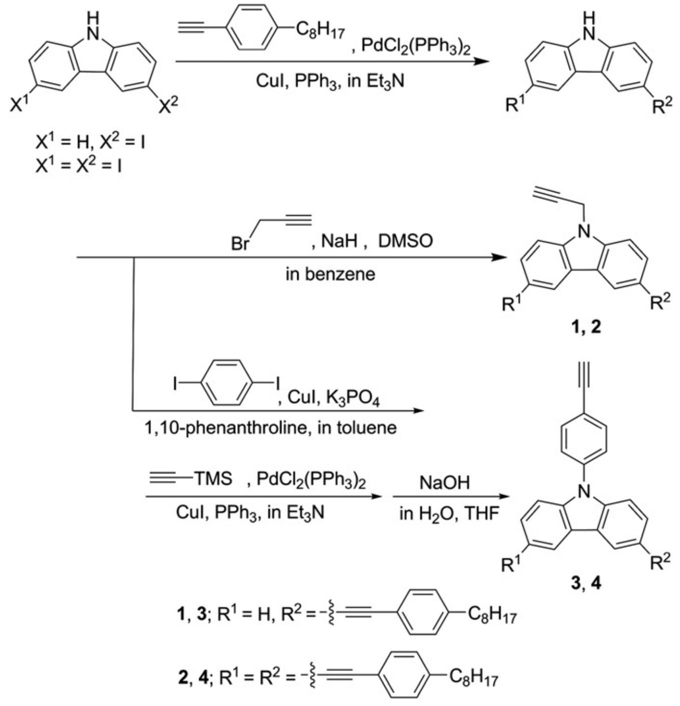
^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.7–1.0 (br, 6H, –CH_2CH_3), 1.0–1.4 (br, 20H, –CH_2–), 1.5–1.7 (br, 4H, –CH_2–), 2.2–2.7 (br, 4H, –CH_2–), 5.1 (br, 2H, –CH_2C=), 6.1 (br, 1H, –C = CH–), 6.6–7.7 (br, 12H, Ar) 8.3 (br, 2H, Ar). IR (cm^{-1}, KBr): 2923, 2850, 2206 (C≡C), 1600, 1511, 1477, 1373 (N–Ar), 1311, 1284, 1261, 1211, 1141, 1091, 1022, 879, 806.

2.5.4. Poly(2)-W

^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.7–1.0 (br, 6H, –CH_2CH_3), 1.0–1.4 (br, 20H, –CH_2–), 1.5–1.7 (br, 4H, –CH_2–), 2.2–2.7 (br, 4H, –CH_2–), 5.0 (br, 2H, –CH_2C=), 6.2–7.7 (br, 13H, –C = CH–, Ar) 8.3 (br, 2H, Ar). IR (cm^{-1}, KBr): 2923, 2854, 2206 (C≡C), 1600, 1511, 1481, 1373 (N–Ar), 1311, 1284, 1211, 1145, 883, 806.

2.5.5. Poly(3)-Rh

^1H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.8–1.0 (br, 3H, –CH_2CH_3), 1.1–1.4 (br, 10H, –CH_2–), 1.6–1.8 (br, 2H, –CH_2–), 2.4–2.7 (br, 2H, –CH_2–), 5.7 (br, 1H, –C = CH–), 6.6–8.2 (br, 15H, Ar). IR (cm^{-1}, KBr): 2922, 2852, 2214 (C≡C), 1599, 1509, 1475, 1455, 1361 (N–Ar), 1325, 1263, 1226, 1101, 1017, 806, 742, 726.



Scheme 2. Synthetic routes of **1**–**4**.

2.5.6. Poly(**3**)-W

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.8–1.0 (br, 3H, $-CH_2CH_3$), 1.1–1.4 (br, 10H, $-CH_2-$), 1.6–1.8 (br, 2H, $-CH_2-$), 2.4–2.7 (br, 2H, $-CH_2-$), 6.2–7.8 (br, 16H, $-C=CH-$, Ar). IR (cm^{-1}, KBr): 2923, 2852, 2213 (C≡C), 1599, 1509, 1475, 1455, 1361 (N–Ar), 1325, 1227, 807, 743, 726.

2.5.7. Poly(**4**)-Rh

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.8–1.0 (br, 6H, $-CH_2CH_3$), 1.1–1.4 (br, 20H, $-CH_2-$), 1.6–1.8 (br, 4H, $-CH_2-$), 2.3–2.7 (br, 4H, $-CH_2-$), 5.7 (br, 1H, $-C=CH-$), 6.5–7.8 (br, 18H, Ar). IR (cm^{-1}, KBr): 2952, 2923, 2852, 2206 (C≡C), 1599, 1510, 1473, 1455, 1363 (N–Ar), 1334, 1279, 1225, 1170, 1018, 879, 809.

2.5.8. Poly(**4**)-W

^{1}H NMR (400 MHz, δ in ppm, $CDCl_3$): 0.8–1.0 (br, 6H, $-CH_2CH_3$), 1.1–1.4 (br, 20H, $-CH_2-$), 1.6–1.8 (br, 4H, $-CH_2-$), 2.4–2.7 (br, 4H, $-CH_2-$), 6.7–7.8 (br, 17H, $-C=CH-$, Ar) 8.3 (br, 2H, Ar). IR (cm^{-1}, KBr): 2952, 2922, 2852, 2205 (C≡C), 1600, 1510, 1470, 1455, 1362 (N–Ar), 1279, 1226, 1018, 809.

2.6. Calculation of atomic charge

The calculation was carried out with the semi-empirical molecular orbital method using the AM1 hamiltonian on Wave Function Inc. Spartan ’06 for Windows.

3. Results and discussions

3.1. Monomer synthesis

Scheme 2 illustrates the synthetic routes for carbazole-containing novel acetylene monomers **1**–**4**. Monomers **1** and **2** were synthesized by *N*-propargylation of 3-[(4-octylphenyl)ethynyl]- and 3,6-bis[(4-octylphenyl)ethynyl]carbazoles, which were prepared by the Sonogashira coupling of 4-octylphenylacetylene with 3-iodo- and 3,6-diiodocarbazoles, respectively. Monomers **3** and **4** were synthesized by the Ullmann type coupling of 3-[(4-octylphenyl)ethynyl]- and 3,6-bis[(4-octylphenyl)ethynyl]carbazoles with 1,4-diiodobenzene, followed by the Sonogashira coupling with trimethylsilylacetylene and desilylation using NaOH. The structures of the monomers were confirmed by ^{1}H, ^{13}C NMR, and IR spectroscopies besides elemental analysis.

3.2. Polymerization

Table 1 summarizes the conditions and results of polymerization of carbazole-derived novel acetylene monomers **1**–**4** catalyzed with $Rh^+(nbd)[\eta^6-C_6H_5B^-(C_6H_5)_3]$ and WCl_6–*n*-Bu_4Sn in THF and toluene at 30 °C for 3 and 24 h. Polymers with M_n ranging from 9200 to 94 000 were obtained in 20–98% yields. With the rhodium catalyst, monomers **1**, **3**, and **4** gave polymers in good yields (81–98%), while **2** did not, presumably due to the presence of bulky two 4-octylphenyl groups close to the propargyl group. In addition, **2** had the lowest electronic density of terminal carbon atom of the ethynyl group among the monomers; the net atomic charges of **1**, **2**, **3**, and **4** were −0.170 e, −0.168 e, −0.189 e, and −0.187 e, respectively, which were calculated by the semi-empirical molecular orbital method using the AM1 hamiltonian. It seems less favorable for **2** to coordinate the rhodium complex at the ethynyl group compared to the other three monomers. Thus, it is conceivable that the polymerization of **2** was the most unsuccessful due to both steric and electronic factors. Monomers **3** and **4** have net atomic charges at the terminal carbon atoms of the ethynyl groups almost the same to each other. Monomer **4** has two (4-octylphenyl)ethynyl groups, while **3** has one. The bulky structure of **4** possibly causes some side reactions such as chain transfer, resulting in the decrease of polymer molecular weight.

With the tungsten–tin catalyst, monomers **1** and **2** gave polymers in 82 and 68% yields, which were higher than monomers **3**

Table 1
Polymerization of **1**–**4**[a]

Monomer	Catalyst	Solvent	Time (h)	Polymer		
				Yield[b] (%)	M_n[c]	M_w/M_n[c]
1	$Rh^+(nbd)[\eta^6-C_6H_5B^-(C_6H_5)_3]$	THF	24	98	22 000	2.1
1	WCl_6–*n*-Bu_4Sn[d]	Toluene	3	82	94 000	2.2
2	$Rh^+(nbd)[\eta^6-C_6H_5B^-(C_6H_5)_3]$	THF	24	36	9 200	1.7
2	WCl_6–*n*-Bu_4Sn[d]	Toluene	24	68	30 000	1.7
3	$Rh^+(nbd)[\eta^6-C_6H_5B^-(C_6H_5)_3]$[e]	THF	24	81	73 800	3.1
3	WCl_6–*n*-Bu_4Sn[d]	Toluene	24	26	38 800	3.2
4	$Rh^+(nbd)[\eta^6-C_6H_5B^-(C_6H_5)_3]$[e]	THF	24	82	14 700	1.5
4	WCl_6–*n*-Bu_4Sn[d]	Toluene	24	20	32 500	1.9

[a] Conditions; $[M]_0 = 0.10$ M, $[M]_0/[Rh] = 100$ at 30 °C.
[b] Methanol-insoluble part.
[c] Determined by GPC (THF, polystyrene calibration).
[d] $[M]_0/[W] = 20$, $[n\text{-}Bu_4Sn]/[W] = 1$.
[e] $[M]_0/[Rh] = 50$.

and **4** did (26 and 20%). The difference of the nature between methylene and phenylene spacers seems to affect the polymer yield larger than steric factor as previously reported in the polymerization of 1-propyne and phenylacetylene [6b]. W-Based poly(**3**) and poly(**4**) were reddish, while the other polymers were yellowish. It is likely that the color difference is brought about by the difference of *cis–trans* ratio of the polyacetylene main chain of the polymers according to the catalysts used, together with the conjugation between the polyacetylene main chain and side chains. The polymers were soluble in THF, $CHCl_3$ and toluene.

3.3. *Polymer structure*

The polymer structures were examined by ^1H NMR and IR spectroscopies. Rhodium catalysts commonly afford *cis*-stereoregular polyacetylenes, while tungsten catalysts afford non-stereoregular polyacetylenes [11]. In the present study, the ^1H NMR signals of the polymers appeared very broadly, and the signal assignable to the olefinic proton in the polyacetylene main chain coalesced with aromatic proton signals. Consequently, it is impossible to determine the *cis/trans* ratio of the main chain by ^1H NMR spectroscopy. On the other hand, the IR spectra gave important information on the polymer structure. As shown in Fig. 1, monomer **1** showed absorption peaks at 2117 and 2210 cm^{-1} assignable to $\nu_{C\equiv C}$ of ethynyl and ethynylene groups, respectively, and a peak at 3278 cm^{-1} assignable to $\nu_{\equiv C\text{–}H}$ of ethynyl group. On the other hand, poly(**1**) obtained by the polymerization with rhodium catalyst [poly(**1**)-Rh] showed only one absorption peak of $\nu_{C\equiv C}$ of ethynylene group at 2210 cm^{-1} among the peaks described above. It was therefore concluded that the ethynyl group was completely consumed to give a polyacetylene as illustrated in Scheme 1. The ethynylene group seems to remain intact causing no crosslinking, judging from the good solubility of the polymer. In fact, rhodium catalysts cannot polymerize disubstituted acetylenes [6b]. Poly(**1**) obtained by the polymerization with tungsten catalyst [poly(**1**)-W] showed almost the same IR spectroscopic pattern as that of poly(**1**)-

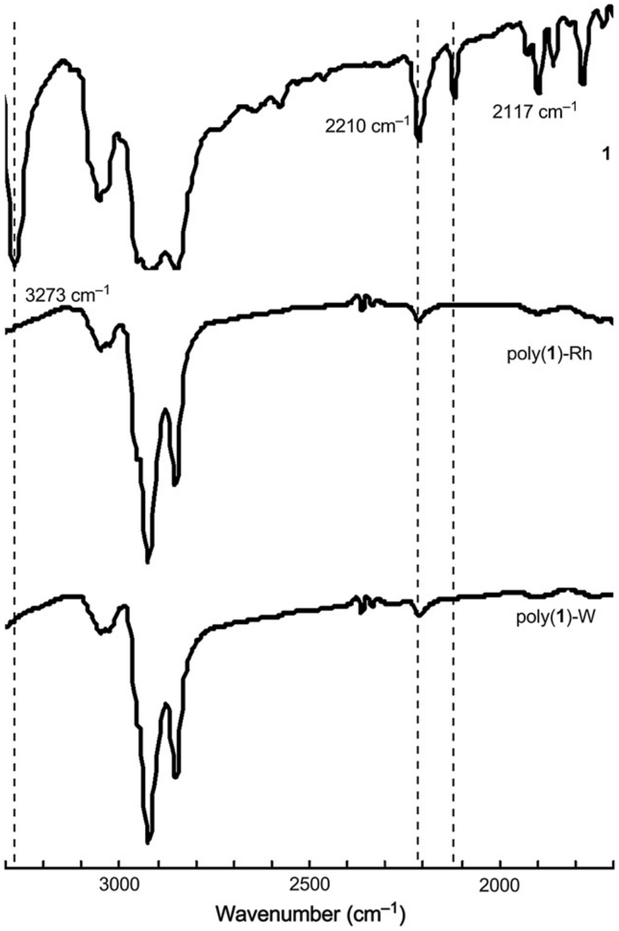


Fig. 1. Partial IR spectra of **1** and the polymers obtained by the polymerization with rhodium catalyst [poly(**1**)-Rh] and tungsten catalyst [poly(**1**)-W].

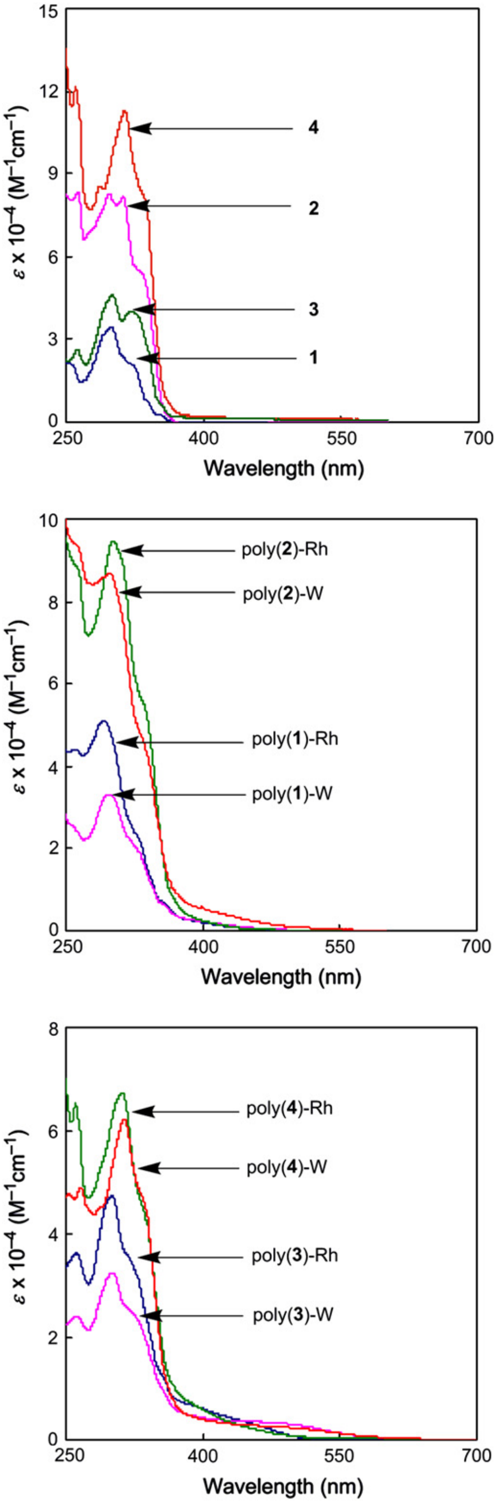


Fig. 2. UV–vis spectra of **1**–**4** and poly(**1**)–poly(**4**) measured in THF ($c = 3.18$–28.0×10^{-6} M). Rh and W represent the catalysts used in the polymerization.

Rh. It is considered that the ethynyl group selectively underwent polymerization keeping the ethynylene group intact as well, because poly(**1**)-W was also soluble in organic solvents. The other polymers exhibited the same results as that of poly(**1**).

3.4. Optical properties

Fig. 2 shows the UV–vis spectra of the polymers and the monomers, wherein the absorption peaks based on the phenylethynylcarbazolyl moiety were observed around 300 nm. The UV–vis spectroscopic patterns of the polymers were almost the same as those of the monomers, but the absorption band edges of the former were positioned at a longer wavelength region than those of the latter presumably due to the main chain absorption.

The Rh-based polymers absorbed light stronger than the W-based ones in all cases. Poly(**3**) and poly(**4**) exhibited another absorption peak at 260 nm assignable to the phenylene unit at 9-position. Poly(**3**)-W and poly(**4**)-W also exhibited a shoulder absorption peak around 500 nm based on the main chain chromophore. The band edge at a longer wavelength region indicates that the main chain conjugation is longer than the others. This is presumably due to the *trans*-rich structure of the W-based polymers compared to the Rh-based ones. The color of the W-based polymers was red accordingly.

Fig. 3 shows the fluorescence spectra of the polymers. Poly(**1**) emitted fluorescence at 364, 380, and 531 nm [12]. The last peak is assignable to emission from excimers formed at the side chains. The relative intensity of the excimer-based fluorescence to the other ones of poly(**1**)-Rh was higher than that of poly(**1**)-W. The quantum yields (φ) of the fluorescence were 1.1 and 1.6%, respectively (Table 2). The partial overlap of absorption and fluorescence emission, along with intramolecular quenching is probably the reason for the low φ values. On the other hand, poly(**2**) emitted no excimer-based fluorescence around 530 nm but fluorescence at 392 nm. It is assumed that the overlap between the side chains is suppressed by the presence of two 4-octylphenylethynyl groups per monomer unit, resulting in no excimer formation. Poly(**2**)-Rh and poly(**2**)-W exhibited almost the same fluorescence spectroscopic pattern as depicted in Fig. 3, indicating that the carbazole moieties in the side chains emit fluorescence predominantly and independently from the polyacetylene backbone.

The φ values of Rh- and W-based poly(**2**)s were 7.8 and 11%, respectively, which were higher than those of poly(**1**)s, presumably due to the smaller overlap between the side chains. Poly (*N*-ethynylphenylcarbazole) derivatives, poly(**3**) and poly(**4**)

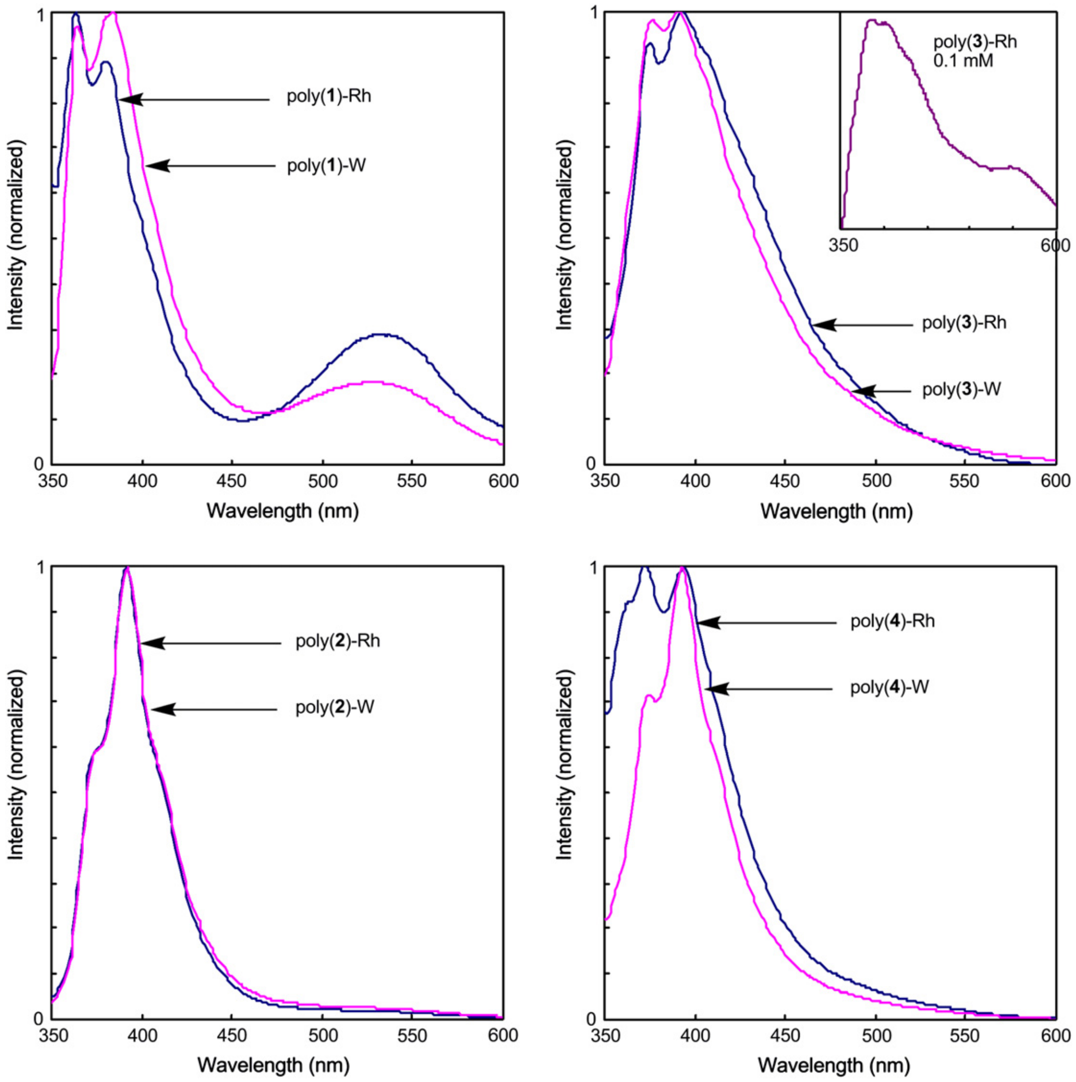


Fig. 3. Fluorescence spectra of poly(**1**) ($c = 3.98 \times 10^{-6}$ M, excited at 331 nm), poly(**2**) ($c = 1.14 \times 10^{-6}$ M, excited at 340 nm), poly(**3**) ($c = 2.08 \times 10^{-6}$ M, excited at 338 nm), and poly(**4**) ($c = 2.08 \times 10^{-6}$ M, excited at 338 nm) measured in THF. Rh and W represent the catalysts used in the polymerization.

Table 2
UV–vis absorption and fluorescence spectroscopic data of the polymers[a]

Polymer[b]	λ_{max} (nm)	λ_{emi} (nm)	φ[c]
poly(**1**)-Rh	292	364, 380, 531	0.011
poly(**1**)-W	296	365, 383, 531	0.016
poly(**2**)-Rh	302	392	0.078
poly(**2**)-W	298	392	0.11
poly(**3**)-Rh	261, 300	375, 393	0.072
poly(**3**)-W	262, 301	376, 392	0.11
poly(**4**)-Rh	261, 312	373, 394	0.21
poly(**4**)-W	261, 314	375, 393	0.41

[a] Measured in THF.
[b] Rh and W represent the catalysts used in the polymerization.
[c] Determined using carbazole as a standard.

emitted fluorescence more strongly than the poly(*N*-propargylcarbazole) counterparts, poly(**1**) and poly(**2**). The conjugation between the polyacetylene main chain and carbazole side chain through phenylene group seems to be effective to enhance the φ values. The W-based polymers showed φ values higher than the Rh-based ones in all cases.

As shown in Fig. 3, poly(**3**) did not emit excimer-based fluorescence under dilute condition ($c = 2.08 \times 10^{-6}$ M), but did it at 550 nm, when the sample solution was prepared with a 50 times higher polymer concentration ($c = 1.04 \times 10^{-4}$ M), presumably due to the occurrence of intermolecular interaction between the carbazole moieties.

3.5. Thermal properties

Fig. 4 shows the TGA curves and Table 3 summarizes the TGA data of the polymers. The temperatures for 5% weight loss of the polymers ranged from 292 to 371 °C under air. The Rh-based polymers were thermally more stable than the W-based ones similar to the other polyacetylenes substituted with carbazole moieties reported so far [7b]. It is considered that the main chain fission takes place more rapidly due to the larger steric repulsion between the polymer side chains in the case of W-based *trans*-rich polymers. We also performed DSC of the polymers, but observed no peaks assignable to glass transition and melting temperatures in the range of 30–250 °C.

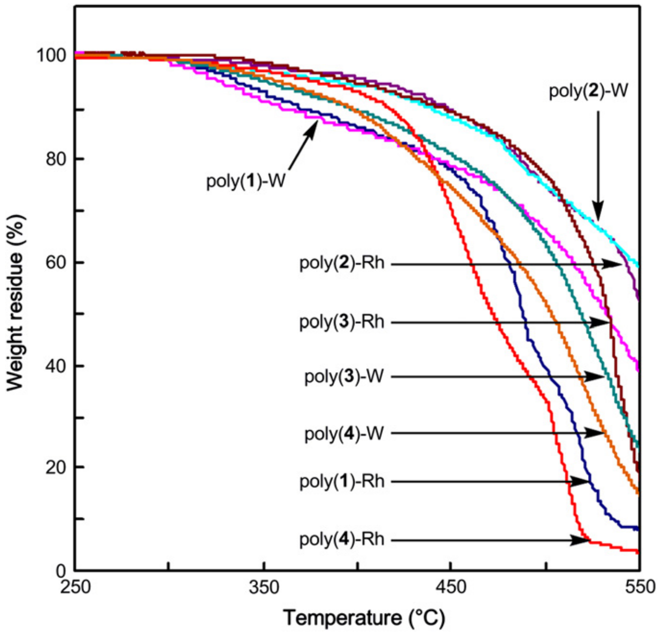


Fig. 4. TGA traces of poly(**1**)–poly(**4**) measured at a heating rate of 10 °C/min in air.

Table 3
Thermogravimetric analysis of the polymers

Polymer[a]	T_0[b] (°C)	Polymer[a]	T_0[b] (°C)
poly(**1**)-Rh	313	poly(**3**)-Rh	338
poly(**1**)-W	292	poly(**3**)-W	321
poly(**2**)-Rh	371	poly(**4**)-Rh	341
poly(**2**)-W	333	poly(**4**)-W	325

[a] Rh and W represent the catalysts used in the polymerization.
[b] 5% weight loss temperature measured at a heating rate of 10 °C/min in air.

4. Conclusions

In this article, we have demonstrated the synthesis and polymerization of novel *N*-propargyl and *N*-(4-ethylnyl)phenylcarbazoles **1**–**4** substituted with 4-octylphenylethynyl group at 3- and 3,6-positions by using rhodium and tungsten catalysts, and examined the optical and thermal properties of the obtained polymers [poly(**1**)–poly(**4**)]. The polymerization of ethynyl group selectively proceeded keeping ethynylene group intact. The polymers exhibited UV–vis absorption peaks based on the phenylethynylcarbazolyl moiety around 300 nm. W-Based poly(**3**) and poly(**4**) also absorbed light around 500 nm, indicating the presence of efficient conjugation between the polyacetylene backbone and the side chains via phenylene spacer. Among them, W-based poly(**4**) emitted fluorescence with the highest quantum yield (41%). It was considered that disubstitution of phenylethynyl groups at 3,6-position enhanced the fluorescence emission. At dilute conditions, only poly(**1**) exhibited excimer-based fluorescence, suggesting the occurrence of intramolecular overlapping between the less bulky side chains. The Rh-based polymers were thermally stable than the W-based counterparts, presumably due to the small steric repulsion of the *cis*-stereoregular structure.

Acknowledgment

This research was partly supported by a Grant-in-Aid for Science Research in a Priority Area "Super-Hierarchical Structures (No. 446)" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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