

Synthesis of polymers having arylene-vinylene units by palladium-catalyzed hydroarylation polymerization of diethynylbenzene derivatives

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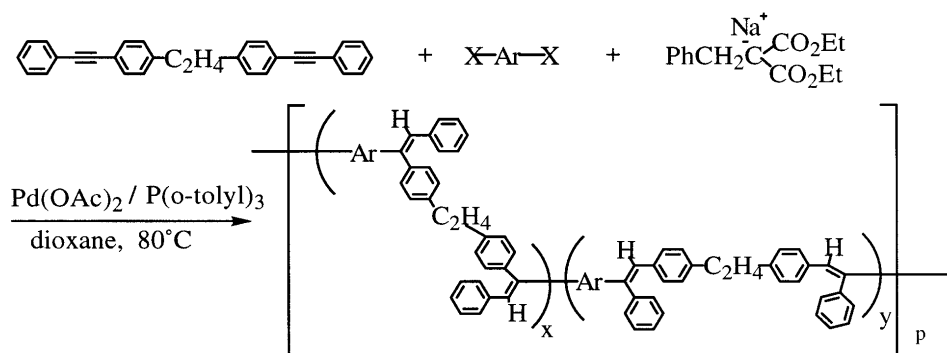
Summary

Arylene-vinylene-containing polymers with fully aromatic backbone structures were prepared by the palladium-catalyzed hydroarylation polymerization of diethynylbenzene derivatives with diiodobenzene and alkylmalonate anions as a hydride source. For instance, the polymerization of 1,4-bis(4'-dodecyloxy)phenylethynebenzene, diiodobenzene, and sodium diethyl benzylmalonate was carried out at 80 °C for 2 days in 1,4-dioxane in the presence of Pd(OAc)₂ / tri-*o*-tolylphosphine (7 equiv. to Pd) to produce a polymer ($M_n = 6,390$, $M_w/M_n = 1.53$) in high yield (86 %). Using various diethynylbenzene derivatives, polymers having arylene-vinylene units were also obtained in high yields.

Introduction

Because of practical and theoretical interest in π -conjugated polymers such as poly(arylene-vinylene)s (1-3), various approaches have been made to prepare these polymers by, for example, the Heck reaction (4), the Wittig reaction (5), the McMurray condensation (6), the Knoevenagel reaction (7), precursor routes (8) and so on. We reported the three-component polycondensations using bisallenes to prepare poly(arylene-vinylene) derivatives possessing repeating units originated from three monomers (9). We also reported the unique palladium-catalyzed three-component coupling polymerization of bisacetylene, aryl dihalides, and sodium diethyl benzylmalonate, where the anion of the benzylmalonate serves as a hydride source and polymers having olefin moieties were obtained through the formal hydroarylation process (Scheme 1) (10).

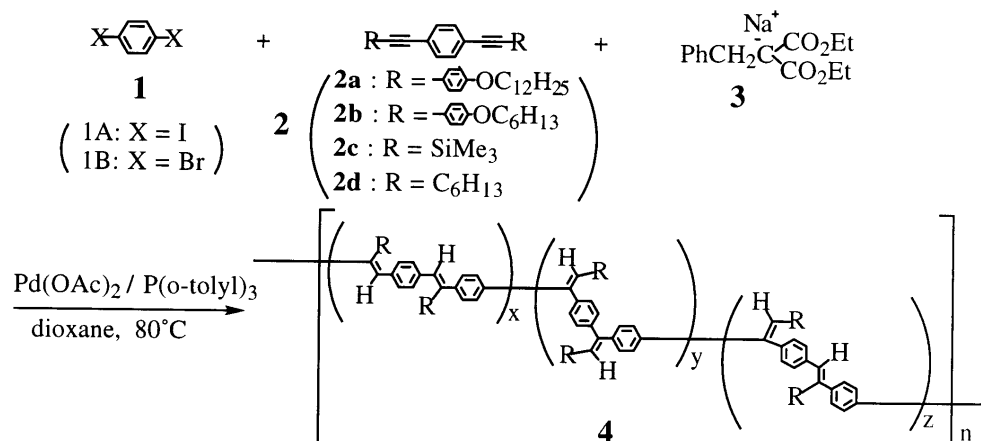
Scheme 1



On the basis of this hydroarylation process, polymers having arylene vinylene backbones might be produced by using appropriate monomers, although the hydroarylation of asymmetrically substituted acetylene derivatives gives two regioisomeric trisubstituted ethylene moieties. Accordingly, we report herein the hydroarylation polymerization of diethynylbenzene derivatives as a new synthetic route for substituted poly(arylene-vinylene)s (Scheme 2).

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Scheme 2



Experimental

Instruments. IR spectra were obtained on a JASCO FT/IR-5300 spectrophotometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded in CDCl_3 on a JEOL JNM-GX400 instrument (400 MHz and 100 Mhz, respectively). Gel permeation chromatographic (GPC) analyses were carried out on a Tosoh HLC-8020 (TSK gel G2500HXL and G3000HXL tandem columns, standard polystyrene samples, tetrahydrofuran as an eluent). Thermogravimetric analyses (TGA) were made on a Shimadzu TGA-50 instrument under nitrogen stream (at a heating rate of $10^\circ\text{C} / \text{min}$). UV-vis spectra were recorded on a Shimadzu UV-2100 spectrometer in CHCl_3 . Fluorecence spectra were recorded on a Shimadzu RF-5300PC spectrometer in CHCl_3 .

Materials. Sodium diethyl benzylmalonate (**3**) was prepared from sodium hydride and diethyl benzylmalonate and then purified by washing successively with *n*-hexane. 1,4-Diethynylbenzene was prepared by the coupling reaction of 1,4-diiodobenzene and trimethylsilylacetylene followed by desilylation step, as reported previously (11). 4-Dodecyloxyiodobenzene and 4-hexyloxyiodobenzene were prepared by the reaction of 4-iodophenol with 1-bromododecane and 1-bromo-hexane, respectively and then purified by SiO_2 column chromatography (*n*-hexane). 1,4-Diiodobenzene (**1A**), 1,4-dibromobenzene (**1B**), and tri-*o*-tolylphosphine were purified by recrystallization from *n*-hexane. 1,4-Dioxane was dried over sodium and distilled under nitrogen. Other reagents were used as received.

Synthesis of Monomer. (Typical procedure for 1,4-bis(4'-dodecyloxyphenylethynyl)benzene (**2a**)). In a 100 mL two-necked flask equipped with a magnetic stirrer bar, were added 1,4-diethynylbenzene (0.63 g, 5.00 mmol), 4-dodecyloxyiodobenzene (3.88 g, 10.0 mmol), CuI (0.08 g, 0.40 mmol), $\text{Pd(PPh}_3)_4$ (0.23 g, 0.20 mmol), Et_2NH (20 mL), and toluene (20 mL) under nitrogen. The mixture was stirred at room temperature for 4 h, and then at 50°C for 8h. After the reaction mixture was cooled to room temperature, the precipitate was collected by filtration and washed by deionized water. The collected crude product was recrystallized from THF to give 2.69 g (4.15 mmol, 83 % yield) of 1,4-bis(4'-dodecyloxyphenylethynyl)benzene. $^1\text{H-NMR}$ (δ , ppm) 0.88 ($-\text{CH}_3$, t, $J = 6.4$ Hz, 6H), 1.27-1.79 ($-(\text{CH}_2)_{10}-$, m, 40H), 3.96 ($-\text{OCH}_2-$, t, $J = 6.4$ Hz, 4H), 6.85 (C_6H_4 , d, $J = 8.8$ Hz, 4H), 7.43 (C_6H_4 , d, $J = 8.8$ Hz, 8H); $^{13}\text{C-NMR}$ (δ , ppm) 14.0, 22.6, 26.0, 29.2, 29.6, 31.9, 68.2, 87.9, 91.3, 114.7, 115.1, 123.2, 131.3, 133.0, 159.5, IR (KBr) 3030, 2955, 2920, 2874, 2851, 2218, 2025, 1923, 1903, 1736, 1685, 1655, 1604, 1568, 1520, 1473, 1394, 1286, 1249, 1174, 1149, 1130, 1109, 1022, 831, 723, 532 cm^{-1} .

1,4-Bis(4'-hexyloxyphenylethynyl)benzene (**2b**): from 1,4-diethynylbenzene (0.63g, 5.00 mmol) and 4-hexyloxyiodobenzene (2.88 g, 10.0 mmol); Yield 86 % (1.92 g, 0.43

mmol); $^1\text{H-NMR}$ (δ , ppm) 0.89 ($-\text{CH}_3$, t, $J = 6.4$ Hz, 6H), 1.33-1.77 ($-(\text{CH}_2)_4$ -,m, 16H), 3.95 ($-\text{OCH}_2$ -, t, $J = 6.4$ Hz, 4H), 6.86 (C_6H_4 , d, $J = 8.8$ Hz, 4H), 7.45 (C_6H_4 , d, $J = 8.8$ Hz, 8H); $^{13}\text{C-NMR}$ (δ , ppm) 14.0, 22.6, 25.7, 29.1, 31.5, 68.1, 87.8, 91.2, 114.5, 114.8, 123.1, 131.3, 133.0, 159.3; IR (KBr) 2955, 2930, 2872, 2218, 1923, 1774, 1736, 1685, 1655, 1604, 1566, 1543, 1518, 1471, 1394, 1284, 1246, 1176, 1147, 1109, 1028, 935, 839, 723, 534 cm^{-1} . Anal. calcd for $\text{C}_{34}\text{H}_{38}\text{O}_2$: C, 85.31; H, 8.01; O, 6.69, Found: C, 85.40; H, 8.14. 1,4-Bis(trimethylsilylethynyl)benzene (**2c**): from 1,4-diiodobenzene (3.30g, 10.0 mmol) and (trimethylsilyl)acetylene (2.16 g, 22.0 mmol); Yield 96 % (2.58 g, 9.60 mmol): $^1\text{H-NMR}$ (δ , ppm) 0.22 ($-\text{CH}_3$, s, 18H), 7.36 (C_6H_4 , 4H); $^{13}\text{C-NMR}$ (δ , ppm) -0.1, 96.3, 104.5, 123.1, 131.7; IR (KBr) 2957, 2899, 2156, 1944, 1907, 1751, 1718, 1701, 1685, 1655, 1560, 1543, 1504, 1493, 1458, 1404, 1327, 1246, 1215, 1159, 1103, 1047, 1016, 848, 760, 698, 628, 551 cm^{-1} . Anal. calcd for $\text{C}_{16}\text{H}_{28}\text{Si}_2$: C, 71.04; H, 8.20; Si, 20.76, Found: C, 70.62; H, 8.18.

1,4-Bis(hexylethynyl)benzene (**2d**): from 1,4-diiodobenzene (1.65g, 5.00 mmol) and 1-octyne (1.21 g, 11.0 mmol); Yield 58 % (0.85 g, 2.90 mmol); $^1\text{H-NMR}$ (δ , ppm) 0.91 ($-\text{CH}_3$, t, $J = 6.8$ Hz, 6H), 1.33-1.62 ($-(\text{CH}_2)_4$ -,m, 16H), 2.40 ($-\text{CH}_2$ -, t, $J = 6.4$ Hz, 4H), 7.30 (C_6H_4 , s, 4H); $^{13}\text{C-NMR}$ (δ , ppm) 14.3, 19.7, 22.8, 28.9, 31.6, 80.6, 92.2, 123.4, 131.6; IR (neat) 3038, 2957, 2930, 2858, 2227, 1909, 1664, 1508, 1466, 1429, 1402, 1377, 1329, 1101, 1008, 887, 837, 725 cm^{-1} .

Polymerization. (Typical procedure for 1,4-diiodobenzene (**1A**), 1,4-bis(4'-dodecyloxy)phenylethynylbenzene (**2a**), and sodium diethyl benzylmalonate (**3**)). To a test tube equipped with a magnetic stirrer bar, were added **1A** (0.08 g, 0.25 mmol), **2a** (0.16 g, 0.25 mmol), **3** (0.27 g, 1.00 mmol), and 1,4-dioxane (2 mL). To the resulting mixture, a dioxane solution (1 mL) of tri-*o*-tolylphosphine (0.03 g, 0.09 mmol) and palladium acetate (2.80 mg, 12.5 μmol) was added and the tube was sealed under reduced pressure. After the reaction at 80 $^\circ\text{C}$ for 2 days, the solvent was evaporated under reduced pressure, dissolved in THF (3 mL), and precipitated with methanol (50 mL).

4Aa: 86 % yield (17.2 mg, 0.22 mmol); $^1\text{H-NMR}$ (see, also Figure 1. δ , ppm) 0.89 ($-\text{CH}_3$, 6H), 1.29-1.78 ($-(\text{CH}_2)_{10}$ -, 40H), 3.97 ($-\text{OCH}_2$ -, 4H), 6.7-7.4 ($-\text{C}=\text{CH}$ -, $-\text{C}_6\text{H}_4$ -, 18H); $^{13}\text{C-NMR}$ (δ , ppm) 14.0, 22.6, 26.1, 29.1, 29.6, 31.9, 67.9, 113.8, 115.0, 115.1, 128.0, 129.1, 129.5, 130.8, 132.1, 132.9, 137.1, 157.9, 158.7, 159.1; IR (KBr) 3030, 2924, 2852, 1736, 1604, 1510, 1467, 1388, 1286, 1246, 1174, 1109, 1020, 831, 723, 532 cm^{-1} .

4Ba: from **1B** (59.0 mg, 0.25 mmol), **2a** (162 mg, 0.25 mmol), and **3** (274 mg, 1.00 mmol); 65 % yield (132 mg, 163 μmol); $^1\text{H-NMR}$ (δ , ppm) 0.89 ($-\text{CH}_3$, 6H), 1.29-1.78 ($(\text{CH}_2)_{10}$ -, 40H), 3.97 ($-\text{OCH}_2$ -, 4H), 6.7-7.4 ($-\text{C}=\text{CH}$ -, $-\text{C}_6\text{H}_4$ -, 18H); $^{13}\text{C-NMR}$ (δ , ppm) 14.0, 22.6, 26.1, 29.1, 29.6, 31.9, 67.9, 113.8, 115.0, 115.1, 128.0, 129.1, 129.5, 130.8, 132.1, 132.9, 137.1, 157.9, 158.7, 159.1; IR (KBr) 3030, 2924, 2852, 1736, 1604, 1510, 1467, 1388, 1286, 1246, 1174, 1109, 1020, 831, 723, 532 cm^{-1} .

4Ab: from **1A** (165 mg, 0.50 mmol), **2b** (215 mg, 0.50 mmol), and **3** (548 mg, 2.00 mmol); Yield 79 % (0.22 g, 395 μmol); $^1\text{H-NMR}$ (δ , ppm) 0.91 ($-\text{CH}_3$, 6H), 1.27-1.77 ($(\text{CH}_2)_4$ -, 16H), 3.95 ($-\text{OCH}_2$ -, 4H), 6.67-7.3 ($-\text{C}=\text{CH}$ - and $-\text{C}_6\text{H}_4$ -, 18H); $^{13}\text{C-NMR}$ (δ , ppm) 14.3, 22.9, 26.0, 29.5, 31.9, 68.2, 114.2, 114.8, 128.0, 129.4, 130.1, 131.1, 131.8, 133.2, 158.6, 158.8; IR (KBr) 3028, 2930, 2858, 1736, 1604, 1510, 1467, 1379, 1286, 1246, 1174, 1111, 1018, 939, 831, 698, 615, 532 cm^{-1} .

4Ac: from **1A** (82.5 mg, 0.25 mmol), **2c** (67.6 mg, 0.25 mmol), and **3** (274 mg, 1.00 mmol); Yield 72 % (62.7 mg, 0.18 mmol); $^1\text{H-NMR}$ (δ , ppm) 0.24 ($-\text{Si}(\text{CH}_3)_3$, 18H),

6.33-7.44 (-C=CH-, -C₆H₄-, 10H); ¹³C-NMR (δ, ppm) 0.2, 127.6, 129.6, 131.6, 137.3; IR (KBr) 3030, 2955, 2897, 2156, 1913, 1736, 1574, 1506, 1440, 1404, 1248, 1105, 1018, 962, 912, 839, 760, 694, 630, 542 cm⁻¹.

4Ad: from **1A** (82.5 mg, 0.25 mmol), **2d** (73.5 mg, 0.25 mmol), and **3** (274 mg, 1.00 mmol); Yield 75 % (69.5 mg, 186 μmol); ¹H-NMR (δ, ppm) 0.90 (-CH₃, 6H), 1.25-1.60 (-CH₂)₁₀-, 16H), 2.41 (-CH₂-, 4H), 6.7-7.4 (-C=CH- and -C₆H₄-, 12H); ¹³C-NMR (δ, ppm) 14.3, 19.7, 22.8, 28.9, 30.0, 32.3, 67.9, 113.8, 115.0, 115.1, 128.3, 129.6, 132.7; IR (KBr) 2955, 2928, 2856, 1736, 1685, 1655, 1560, 1545, 1508, 1460, 1377, 1269, 1180, 1107, 1005, 833, 723, 700, 424 cm⁻¹.

Results and Discussion

Polymerizations. The hydroarylation polymerization of diiodobenzene (**1A**), 1,4-bis(4'-dodecyloxyphenylethynyl)benzene (**2a**), and sodium diethyl benzylmalonate (**3**) was carried out at 80 °C for 2 days in 1,4-dioxane in the presence of Pd(OAc)₂ (5 mol %) / tri-*o*-tolylphosphine (7 equiv. to Pd). As a result, a red powdery polymer (**4Aa**) was obtained in 86 % yield by precipitation with methanol. The obtained polymer is soluble in organic solvents whose number-average molecular weight (*M_n*) was estimated to be 6,390 by GPC measurement. As shown in Figure 1, the ¹H-NMR spectrum supported the structure of the obtained polymer (**4Aa**). That is, protons of the alkoxy and the arylene-vinylene moieties were observed at 3.9 ppm and 6.9 - 7.4 ppm, respectively. From our previous experiment using a model reaction, the polymer should consist of a specific *cis*-hydroarylated unit (10). The ratio of the geometrical isomeric structure (i.e., 1,2- and 2,1-addition units) in **4Aa** should be comparable and the polymer (**4Aa**) was supposed to have three regioisomeric units as shown in Scheme 2, although they could not be distinguished by NMR technique.

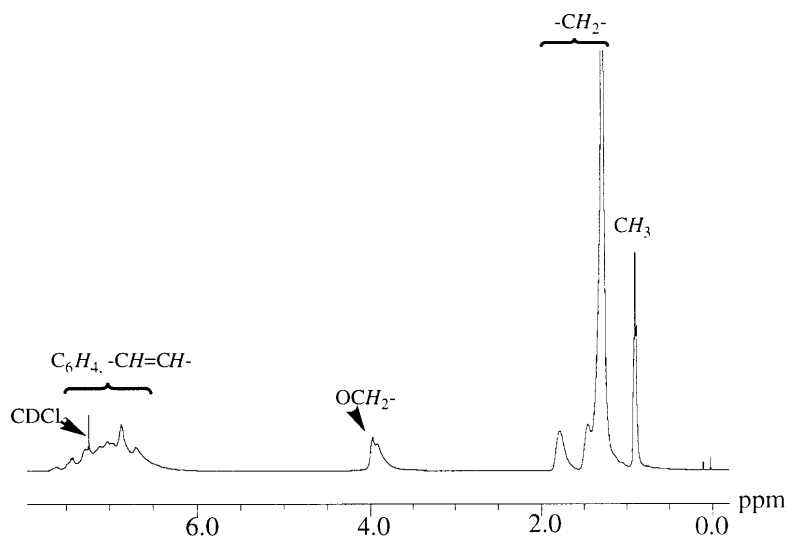


Figure 1. ¹H-NMR spectrum of **4Aa**.

The polymerization of diethynylbenzenes (**2a-2d**) with aryl dihalides (**1A-1B**) and **3** also gave the corresponding polymers possessing arylene-vinylene moieties (Table 1). The polymers thus obtained are soluble in organic solvents owing to the substituents introduced into the diyne monomers.

Table 1. Polymerization of Diethynylbenzene Derivatives (**2a- 2d**) with Aryl Dihalides (**1A-1B**) and **3**.^{a)}

Run	Aryl Halides	Diyynes	Yield(%) ^{b)}	$M_n(M_w/M_n)$ ^{c)}
1	1A	2a	86	6,390 (1.53)
2	1B	2a	65	4,100 (1.18)
3	1A	2b	79	5,230 (1.60)
4	1A	2c	72	3,310 (1.51)
5	1A	2d	75	3,680 (1.66)

a) Runs 1-5 : Polymerization was carried out at 80°C for 2 days. Run 6 : Polymerization was carried out at 80°C for 2hrs.

b) Precipitated with CH₃OH. c) GPC (THF, PSt Std).

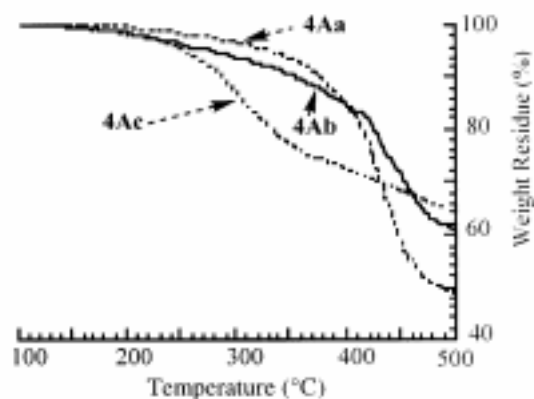


Figure 2. Thermogravimetric Analyses of **4Aa-4Ac** (under Nitrogen)

Properties of the polymers. Thermal stability of the polymers was estimated by thermogravimetric analyses (TGA) under nitrogen, from which 10 % weight loss temperatures (T_{10}) of **4Aa**, **4Ab**, and **4Ac** were observed at 376 °C, 361 °C, and 288 °C, respectively (Figure 2).

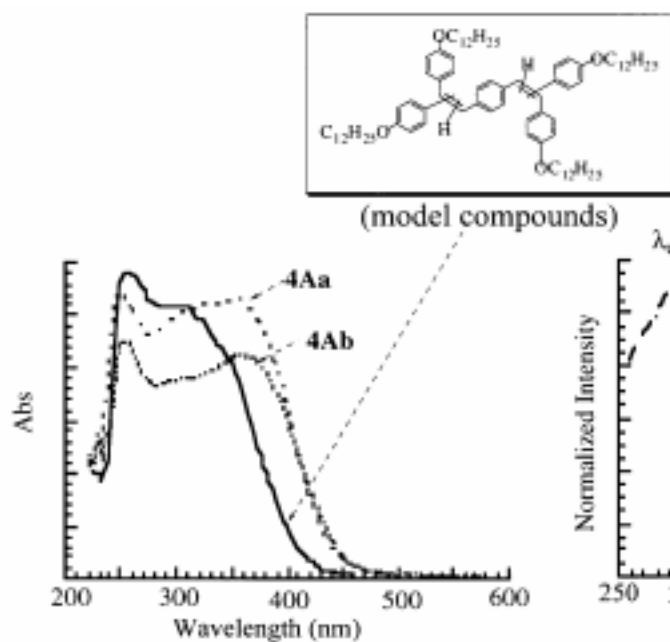


Figure 3. UV spectra of model compounds, **4Aa**, and **4Ab**.

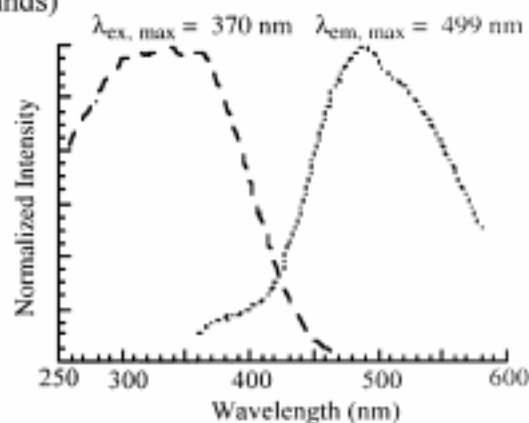


Figure 4. Emission (...) and excitation (- -) spectra of **4Aa**.

The UV spectra of the obtained polymers (**4Aa**, **4Ab**, **4Ac**, and **4Ad**) and model compounds prepared from **2a**, 4-dodecyloxyiodobenzene, and **3** are shown in Figure 3. The absorption spectra of the polymers (**4Aa** and **4Ab**) displayed a clear red-shift and their λ_{max} and the shoulder reached ca. 360 and ca. 450 nm, respectively. These polymers had the absorption

maxima in shorter wavelength in comparison with that reported for the substituted poly(*p*-phenylene-vinylene)s ($\lambda_{\text{max}} = 460 \text{ nm}$) (4), most probably due to the coexistence of three regioisomeric units and the sterically hindered structure of the repeating unit.

Emission and excitation spectra of **4Aa** were acquired on a dilute chloroform solution with optical absorption maxima of 0.1, from which their maxima were observed at 370 and 499 nm, respectively (Figure 4), although the photoluminescence quantum yield was rather low (0.027).

In summary, the hydroarylation polymerization of diethynylbenzene derivatives successfully gave soluble poly(arylene-vinylene)s with disordered repeating units. The degree of π -conjugation was supposed to be shorter than those with regular structures reported previously, which, however, might be applicable to functional materials with unique electronic properties.

References

1. (a) Skotheim T A Ed. Handbook of Conducting Polymers: Marcel Dekker: New York 1986: Vol 1 (b) Skotheim T A, Elsenbaumer R L, Reynolds J R Eds. Handbook of Conducting Polymers 2nd ed: Marcel Dekker: New York 1997
2. (a) Lenz R B, Han C C, Lux M (1989) Polymer 30: 1041 (b) Burroughes J H, Bradley D D, Brown A R, Marks R N, Mackay K, Friend R H, Burns P L, Holmes A B (1990) Nature 340: 539
3. For the review, see: (a) Feast W J, Friend R H (1990) J Mat Sci 25: 3796 (b) Kraft A, Grimsdale A C, Holmes A B (1998) Angew Chem Int Engl 37: 402
4. (a) Greiner A, Heitz W (1988) Makromol Chem Rapid Commun 9: 581 (b) Heitz W (1988) Makromol 189: 119 (c) Greiner A, Martelock H, Noll A, Siegfried N, Heitz W (1991) Polymer 32: 1857 (d) Bao Z, Chen Y, Cai R, Yu L (1993) Macromolecules 26: 5281
5. (a) Mcdonal R N, Campbell T W (1960) J Am Chem Soc 82: 4669 (b) Feld W A, Ganesan A, Nymberg D D (1983) ACS Polym Prepr 24 (1): 143 (c) Kossmehl G, Samandari M, (1985) Makromol Chem 186: 1565 (d) Memeger Jr W, Yu L (1989) Macromolecules 22: 1577
6. (a) Feast W J, Millichamp I S (1983) Polym Commun 24: 102 (b) Rehahn M, Schluter A.-D (1990) Makromol Chem Rapid Commun 11: 375 (c) Cooke A W, Wagener K B (1991) Macromolecules 24: 1404
7. (a) Greenham N C, Moratti S C, Bradley D D C, Brown A R, Friend R H, Holmes R W (1993) Nature 365: 628 (b) Staring E G J, Demandt R C J E, Braun D, Rikken G L J, Kessener Y A R R, Venhuizen A H J, van Knippenberg M M F, Bouwmans M (1995) Synth Metals 71: 2179 (c) Dottinger S E, Hohloch M, Hohnholz D, Segura J L, Steinhuber E, Hanack M (1997) Synth Metals 84: 267
8. (a) Horhold H H, Helbig M (1987) Makromol Chem Macromol Symp 12: 229 (b) Swatos W J, Gordon III B (1990) ACS Polym Prepr 31 (1): 505 (c) Zhang C, von Seggern H, Pakbaz K, Kraabel B, Schmidt H-W, Heeger A J (1994) Synth Metals 62: 35
9. Miyaki N, Tomita I, Endo T (1997) Macromolecules 30: 4504
10. Miyaki N, Tomita I, Endo T (1997) Polym Bull 39: 677
11. Takashi S, Kuroyama Y, Sonogashira K, Hagihara N (1980) Synthesis 627