# Synthesis and Properties of Carbazole-Containing Poly(aryleneethynylenes) and Poly(aryleneimines)

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ABSTRACT: Novel poly(aryleneethynylenes) and poly(aryleneimines) containing carbazole units in the main chain were synthesized by polycondensation of diethynylcarbazoles with dihaloarenes, or diformyl-carbazole with phenylenediamines, and their general properties were studied. The polymers with  $M_w = 2700-33700$  were obtained in 60–100% yields. Compared to carbazole, the UV–vis absorption of the polymers was red-shifted, which indicates the extension of conjugation length. Excited at the absorption maxima, the polymers containing ethynylene moieties showed blue or green emission with high fluorescence quantum yields (6–86%) in the solution state, while in the film state, they exhibited fluorescence at longer wavelength, which suggests the formation of excimers. On the contrary, the polymers having imine moieties showed emission with low fluorescence quantum yields (<1%).

## Introduction

Carbazole is a conjugated unit that has interesting optical and electronic properties such as photoconductivity and photorefractivity.<sup>1</sup> In the field of electroluminescence, carbazole derivatives are often used as the materials for hole-transporting layers, utilizing the high charge mobility. Moreover, carbazole derivatives are used as light-emitting layers because they are thermally stable and show blue photo- and electroluminescence due to the large band gap of the biphenyl unit and planarity improved by the bridging nitrogen atom.<sup>2</sup> Meanwhile, poly(aryleneethynylenes) (PAEs) are known as typical conjugated polymers, which possess conductivity, nonlinear optical properties, fluorescence, and so on.<sup>3</sup> Especially with respect to luminescence, the rigid structure reduces nonradiative decay, leading to high fluorescence quantum yields. In fact, some PAEs show almost quantitative fluorescence quantum yields.<sup>4</sup> Although PAEs containing carbazole units in the main chain are expected as light-emitting polymers, the reports concerning them<sup>5</sup> are fewer than those of poly(arylenevinylenes).<sup>6</sup> This paper deals with the synthesis of carbazole-containing PAEs and characterization of their basic properties, where the arylene units are para- and meta-linked phenylene, biphenylene, anthracenylene, thiazolylene, phenazinylene, and ferrocenylene (Scheme 1). We also describe the synthesis and characterization of polymers whose carbazole is linked by an imine group.<sup>7</sup>

### **Experimental Section**

**Measurements.** <sup>1</sup>H and <sup>13</sup>C 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 Shimadzu FTIR-8100, JASCO V-550, and JASCO FP750 spectrophotometers, respectively. Melting points were measured by a Yanaco micro-melting point apparatus. Elemental analysis was carried out at the Kyoto University Elemental Analysis Center. The sensitivity and detecting limit

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of the elemental analysis is 0.3%. High-resolution mass spectra were recorded on a JEOL JMS-HX110A or a JMS-SX102A spectrometer. The number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) of polymers were determined by gel permeation chromatography on a JASCO GULLIVER system (PU-980, CO-965, RI-930, and UV-1570) equipped with polystyrene gel columns (Shodex columns K804, K805, and J806), using CHCl<sub>3</sub> as an eluent at a flow rate of 1.0 mL/min, calibrated by polystyrene standards at 40 °C. MALDI-TOF mass spectrometry was performed on a PerSeptive Biosystems Voyager DE-STR equipped with a 337 nm nitrogen laser. Thermal gravimetric analysis was carried out with a Perkin-Elmer Pyris 1 TGA.

**Materials.** Unless otherwise stated, reagents were purchased and used as received. The solvents used for polymerization were purified by standard methods. *N*-Dodecyl-3,6-diformylcarbazole,<sup>8</sup> 1,4-dibutyl-2,5-diiodobenzene,<sup>9</sup> 1,4,6,9-tetrahexyl-2,7-diiodophenazine,<sup>10</sup> and 1,1'-diiodoferrocene<sup>11</sup> were synthesized according to the literature.

**N-Octyl-3,6-diethynylcarbazole.** The title compound was synthesized according to the modified method referring to the literature.<sup>12</sup> 3,6-Dibromocarbazole (7.0 g, 42 mmol) and 1-bromooctane (8.1 g, 22 mmol) were dissolved in tetrahydrofuran (THF)/N,N-dimethylformamide (DMF) (80 mL, 3:1, volume ratio) at room temperature. After washed with hexane, NaH (1.0 g, 42 mol) was slowly added to the solution. The resulting mixture was stirred at room temperature for 1 day, and then methanol (30 mL) was added to the mixture to quench the reaction. The solvents were removed under reduced pressure, CH<sub>2</sub>Cl<sub>2</sub> was added to the residue, and then the mixture was washed with 2 M HCl twice and water, dried over MgSO<sub>4</sub>, and filtered. The obtained solution was concentrated by rotary evaporation and poured into a large amount of methanol to precipitate N-octyl-3,6-dibromocarbazole as a white solid. It was collected by filtration and used in the next step without further purification.

A mixture of *N*-octyl-3,6-dibromocarbazole (6.6 g, 15 mmol), CuI (98 mg, 1.1 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (365 mg, 0.5 mmol), PPh<sub>3</sub> (179 mg, 0.7 mmol), trimethylsilylacethylene (8.0 mL, 58 mmol), and *i*-Pr<sub>2</sub>NH (220 mL) was stirred with refluxing for 24 h. The solvent was distilled off by rotary evaporation, and the residue was extracted with Et<sub>2</sub>O. The solution was dried over MgSO<sub>4</sub>, filtered, and concentrated. The resulting solution was subjected to silica gel column chromatography (eluent: hexane/CH<sub>2</sub>Cl<sub>2</sub> = 8/1, volume ratio). From the third band, *N*-octyl-3,6-bis(trimethylsilylethynyl)carbazole was obtained as oil, which was used in the next step as it was.

A solution of N-octyl-3,6-bis(trimethylsilylethynyl)carbazole (2.0 g, 4.1 mmol) in THF/methanol (24 mL, 3:1, volume ratio) was added to a 1 M tetrabutylammonium fluoride solution (12 mL) at room temperature. The resulting solution was stirred overnight, and water was added to the solution. It was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was concentrated and purified by silica gel column chromatography (eluent: hexane/ $CH_2Cl_2 = 5/1$ , volume ratio) to obtain the title compound, which solidified in 1 day. Yield 1.0 g (3.0 mmol); mp 69-70 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 060–0.80 (m, 15H) 3.06 (s, 2H), 4.05 (t, J = 7.6 Hz, 2H), 7.17 (d, J = 8.8 Hz 2H), 7.51 (d, J = 6.8 Hz, 2H), 8.11 (s, 2H). IR (neat): 3308, 2955, 2105, 1597, 808 cm<sup>-1</sup>. <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 14.6, 23.1, 27.7, 29.4, 29.6, 29.8, 32.3, 43.8, 75.9, 85.2, 109.4, 113.1, 122.7, 125.2, 130.6, 141.1. Mass (m/z): Calcd for C24H25N: 327.1987. Found: 327.1989 [M<sup>+</sup>]

**N-Dodecyl-3,6-diethynylcarbazole.** It was synthesized in a manner similar to the product mentioned above, starting from 1-bromododecane instead of 1-bromooctane. Mp: 51–53 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.80–1.90 (m, 23H), 3.08 (s, 2H), 4.27 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 26.4 Hz, 2H), 7.60 (d, J = 8.8 Hz, 2H), 8.22 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 14.1, 22.7, 27.2, 28.8 29.3, 29.5, 29.5, 29.6, 31.9, 43.2, 75.4, 84.7, 108.9, 112.6, 122.1, 124.7, 130.0, 140.5. IR (KBr): 3274, 2923, 2105, 1597, 1483, 806 cm<sup>-1</sup>. Anal. Calcd for C<sub>28</sub>H<sub>33</sub>N: C, 87.68; H, 8.67; N, 3.65. Found: C, 87.71; H, 8.74; N, 3.50.

**N-Octadecyl-3,6-diethynylcarbazole.** It was synthesized in a manner similar to the product mentioned above, starting from 1-bromooctadecane instead of 1-bromooctane. Mp: 53– 54 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.80–1.90 (m, 35H), 3.11 (s, 2H), 4.29 (t, J = 6.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 7.62 (d, J =8.0 Hz, 2H), 8.21 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>,  $\delta$ ): 13.8, 22.4, 26.9, 28.6, 29.0, 29.0, 29.1, 29.2, 29.3, 29.3, 29.4, 31.6, 43.0, 75.1, 84.4, 108.6, 112.3, 121.8, 124.4, 129.7, 140.2. IR (KBr): 3312, 2924, 2853, 2106, 1597, 1482, 806 cm<sup>-1</sup>. Mass (m/z): Calcd for C<sub>34</sub>H<sub>45</sub>N: 467.3552. Found: 467.3551 [M<sup>+</sup>].

**Polycondensation (Typical Procedure).** The polycondensation of diethynylcarbazoles with dihaloarenes was conducted in a two-necked 50 mL glass flask under nitrogen.<sup>13</sup>

 Table 1. Polycondensation of N-Alkyldiethynylcarbazoles

 with Dihaloarenes<sup>a</sup>

	monomer		polymer					
run	1	2	3	yield <sup>b</sup> (%)	$M_{\rm w}^{c}$	$M_{\rm w}/M_{\rm n}^c$		
1	1A	2a	3a	60	9200 <sup>e</sup>	$1.5^{e}$		
$2^d$	1B	2b	3b	100	$3100^{e}$	$2.8^{e}$		
$3^d$	1B	2c	<b>3c</b>	74	$6500^{e}$	$1.8^{e}$		
$4^d$	1B	2d	3d	83	33700 <sup>f</sup>	$3.4^{f}$		
$5^d$	1B	2e	3e	81	4500	1.3		
$6^d$	1B	<b>2f</b>	<b>3f</b>	97	5800	1.6		
7	1A	2g	3g	100	7800 <sup>e</sup>	$1.4^{e}$		
8	1A	2h	3ĥ	86	$5600^{e}$	$1.7^{e}$		
9	1C	2h	<b>3h</b> ′	100	g	g		

<sup>*a*</sup>  $[1]_0 = [2]_0 = 50$  mM,  $[CuI] = [Pd(PPh_3)_4] = 2$  mM, at 80 °C, 72 h in *i*-Pr<sub>2</sub>NH. <sup>*b*</sup> MeOH-insoluble part. <sup>*c*</sup> Determined by GPC (CHCl<sub>3</sub>, PSt). <sup>*d*</sup> In *i*-Pr<sub>2</sub>NH/THF (1:2, volume ratio). <sup>*e*</sup> The polymer was partly insoluble in CHCl<sub>3</sub>. The GPC data of the CHCl<sub>3</sub>-soluble part are shown here. <sup>*f*</sup> Bimodal. <sup>*g*</sup> Could not be determined.

 Table 2. Polycondensation of

 N-Dodecyl-3,6-diformylcarbazole with

 Phenylenediamines<sup>a</sup>

	monomer		polymer					
run	1	2	3	yield <sup>b</sup> (%)	$M_{ m w}{}^c$	$M_{\rm w}/M_{\rm n}^{c}$		
1 2	1D 1D	2i 2j	3i 3j	82 79	2700 6600	1.8 2.1		

<sup>*a*</sup>  $[1]_0 = [2]_0 = 0.24$  M, [LiCl] = 0.5 M, at rt, 24 h in NMP/HMPA (4:1). <sup>*b*</sup> MeOH-insoluble part. <sup>*c*</sup> Estimated by GPC (CHCl<sub>3</sub>, PSt).

N-Octadecyl-3,6-diethynylcarbazole (117 mg, 0.25 mmol), 1,4diiodobenzene (83 mg, 0.25 mmol), CuI (2.2 mg, 0.01 mmol), and Pd(PPh<sub>3</sub>)<sub>4</sub> (13.3 mg, 0.01 mmol) were added to *i*-Pr<sub>2</sub>NH (5 mL), and the resulting mixture was stirred at 80 °C for 72 h. i-Pr2NH was removed from the mixture by evaporation, and then the obtained material was washed with water, dissolved in a small amount of CHCl<sub>3</sub>, and poured into a large amount of methanol to precipitate a polymer. It was filtered and dried under reduced pressure. Yield 60%. Runs 2–9 in Table 1 were conducted in a similar manner. The polycondensation of diformylcarbazole with phenylenediamines was conducted as follows.<sup>14</sup> N-Dodecyl-3,6-diformylcarbazole (180 mg, 0.45 mmol), para-phenylenediamine (49 mg, 0.45 mmol), and LiCl (40 mg, 0.95 mmol) were added to *N*-methylpyrrolidinone (NMP) hexamethylphosphoramide (HMPA) (2 mL, 4:1, volume ratio) in a two-necked 50 mL glass flask under nitrogen, and the resulting mixture was stirred at room temperature for 24 h. A small amount of CHCl<sub>3</sub> was added to the mixture, and it was poured into a large amount of methanol/water (1:1, volume ratio) to precipitate a polymer. It was filtered and dried under reduced pressure. Yield 82%. Run 2 in Table 2 was conducted in a similar manner.

Spectroscopic Data of the Polymers. 3a <sup>1</sup>H NMR  $(CDCl_3, \delta): 0.87 \text{ (t, } J = 8.0 \text{ Hz, } 3\text{H}), 1.01-2.41 \text{ (m, } 32\text{H}), 4.28$ (s, 2H), 7.09-8.30 (m, 10H). IR (neat): 2924, 2853, 1597, 1510, 1485, 1286, 804 cm<sup>-1</sup>. **3b** <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.77-1.90 (m, 23H) 4.30 (s, 2H), 6.85-8.37 (m, 14H). IR (KBr): 2920, 2849, 2105, 1593, 1480, 1283, 804 cm<sup>-1</sup>. **3c** <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.65-1.97 (m, 23H), 3.82-4.35 (m, 2H), 6.65-8.86 (m, 14H). IR (KBr): 2924, 2853, 2191, 1597, 1489, 804 cm<sup>-1</sup>. 3d <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.80-2.30 (m, 37H), 3.06 (s, 2H), 4.35 (m, 2H), 7.17-8.60 (m, 8H. IR (neat): 2955, 2926, 2855, 1597, 1497, 1482, 804 cm<sup>-1</sup>. **3e** <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.80–1.90 (m, 23H), 4.05 (m, 2H), 7.03-8.22 (m, 10H). IR (neat): 2924, 2853, 2208, 2105, 1859, 1489,<br/>1215, 884, 806 cm^-ı. **3f** <code>^1H</code> NMR (CDCl\_3, <br/>  $\delta$ ): 0.74-2.55 (m, 23H), 4.02-4.51 (m, 2H), 7.21-8.45 (m, 7H). IR (KBr): 2924, 2853, 2205, 1595, 1483, 1287, 806 cm<sup>-1</sup>. 3g <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.80–1.90 (m, 69H), 3.20–3.65 (m, 8H), 4.30 (s, 2H), 7.18-8.19 (m, 8H). IR (KBr): 2955, 2924, 2853, 2201, 1595, 804 cm<sup>-1</sup>. **3h** <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ): 0.51-2.62 (m, 35H), 3.15-4.95 (m, 10H), 6.61-8.70 (m, 6H). IR (KBr): 2924, 2853, 806 cm<sup>-1</sup>. 3h' IR (KBr): 2205, 1595, 804 cm<sup>-1</sup>. 3i <sup>1</sup>H NMR (CDCl<sub>3</sub>, *δ*): 0.80-1.92 (m, 23H), 4.35 (m, 2H), 6.50-8.74



Figure 1. MALDI-TOF mass spectrum of 3d.

(m, 11H). IR (KBr): 2923, 2851, 1612, 1595, 810 cm<sup>-1</sup>. **3j** <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 0.80–1.92 (m, 23H), 4.35 (m, 2H), 6.50–8.74 (m, 11H). IR (KBr): 2924, 2853, 1612, 1593, 810 cm<sup>-1</sup>.

## **Results and Discussion**

**Polycondensation.** Table 1 summarizes the results of the polycondensation of N-alkyldiethynylcarbazoles with dihaloarenes catalyzed by a mixture of CuI and Pd(PPh<sub>3</sub>)<sub>4.</sub> The proceeding of the Sonogashira coupling was confirmed by disappearance of the signal at 3.1 ppm in the <sup>1</sup>H NMR spectrum and the peak at 3273 cm<sup>-1</sup> in the IR spectrum due to monosubstituted alkyne observed in the corresponding monomers. Polymers with  $M_{\rm w} = 3100 - 33700$  were obtained in good yields.<sup>15</sup> The molecular weight of the polymer in run 9 could not be measured because it was insoluble in common organic solvents. Polymer 3d exhibited a bimodal GPC trace, whose peak top molecular weights were 30 000 and 3000 (run 4 in Table 1). We measured the MALDI-TOF mass spectrum of 3d to reveal the component of the lowmolecular-weight peak as shown in Figure 1. The signals at 1708.41, 2277.94, 2846.78, and 3415.51 m/z can be assigned to cyclic trimer, tetramer, pentamer, and hexamer, respectively, judging from the agreement between the theoretical and observed values.<sup>16</sup> The signals at 1521.00, 2090.81, 2660.58, and 3228.46 m/z can be assigned to linear oligomers, which have carbazole units in both ends. The halogen content of polymer determined by elemental analysis was negligible, which supports the formation of cyclic oligomers and linear polymers with carbazole terminals.

Table 2 summarizes the results of the polycondensation of *N*-dodecyl-3,6-diformylcarbazole **1D** with *para*and *meta*-phenylenediamines **2i** and **2j** using lithium chloride as a dehydration agent. Polymers with  $M_w$  = 2700 and 6600 were obtained in 82 and 79% yields, respectively.

**Polymer Properties.** Polymer **3h**' having an *N*-octyl group was insoluble in common organic solvents, in contrast to **3h** having an *N*-octadecyl group, which was partly soluble in THF, toluene,  $CH_2Cl_2$ , and  $CHCl_3$ 

Table 3. Solubility of the Polymers<sup>a</sup>

	solvent <sup>b</sup>						
polymer	acetone	MeOH	THF	$CH_2Cl_2 \\$	CHCl <sub>3</sub>	toluene	hexane
3a	_	_	+	+	+	+	_
3b	_	_	+	+	+	+	-
3c	-	-	+	+	+	+	-
3d	-	-	++	++	++	++	-
3e	-	-	++	++	++	++	-
3f	-	-	++	++	++	++	-
3g	-	-	+	+	+	+	-
3ĥ	-	-	+	+	+	+	-
3h′	-	-	_	-	_	-	-
3i	-	-	++	++	++	++	-
3j	-	-	++	++	++	++	-
_		-				-	

<sup>*a*</sup> Polymer 1 mg in solvent 1 mL. <sup>*b*</sup> Symbols: ++, soluble; +, partly soluble; -, insoluble.

 
 Table 4. Optical Properties of the Polymers Measured in CHCl<sub>3</sub>

polymer	$\lambda_{\rm Abs}$ (nm)	$\lambda_{\mathrm{E,max}}^{a}$ (nm)	Ф (%)
3a	320, 359	403 <sup>b</sup>	86
3b	320, 357	409 <sup>c</sup>	73
3c	461	522	28
3d	362	403	45
3e	313, 344	$398^d$	10
3f	319, 365, 382	466 <sup>e</sup>	45
3g	310	522	5.8
3 <b>h</b>	308	f	f
3i	388	409	0.8
3j	351	433	1.0

 $^a$  Excited at the absorption maxima.  $^b$  Excited at 320 nm.  $^c$  Excited at 357 nm.  $^d$  Excited at 313 nm.  $^e$  Excited at 365 nm.  $^f$  Not determined.

(Table 3). This fact shows that the length of *N*-alkyl group is important for solubility of the polymers. Incorporation of butyl group on the phenylene moiety was also effective in enhancing the solubility (**3a** vs **3d**). The polymers with *para*-arylene structures, **3a**, **3b**, and **3c**, were only partly soluble, while the polymers with *meta*-arylene and thiazole structures, **3e** and **3f**, were completely soluble. It seems that polymers with twisted main chains are more soluble than those with straight ones.

Table 4 summarizes the optical properties of the polymers, and Figure 2 shows the UV–vis spectra of ethynylene-type polymers **3a**–**h** measured in CHCl<sub>3</sub> solution. All the polymers exhibited absorption peaks at 310–320 nm, which originate from the carbazole units and are red-shifted compared to **1A** ( $\lambda = 290$  nm). This fact suggests the extension of conjugation length of the polymers. The absorption at 461 nm of **3c** is attributable to the anthracene moiety.<sup>17</sup> We can say that **3a** with *para*-structure is more conjugated than **3e** with *meta*-structure judging from the UV–vis absorption wavelength.

Figure 3 depicts the fluorescence spectra of ethynylene-type polymers (3a-g) excited at the absorption maxima. The concentrations of the sample solutions were set so that the absorbance at the excited wavelength stayed in the range from 0.05 to 0.1. Strong emission was observed at the blue-green region. In particular, *para*-phenylene polymer **3a** and biphenylene polymer **3b** showed very high fluorescence quantum yields (86 and 73%, respectively). On the contrary, the quantum yield of phenazinylene polymer **3g** was as low as 6%, like other phenazine-containing polymers.<sup>10</sup> The emission at 522 nm of **3c** seems to be based on the anthracene unit.<sup>17</sup> On the contrary to *para*-phenylene



**Figure 2.** UV-vis spectra of ethynylene-type polymers measured in CHCl<sub>3</sub> ( $c = 8.0 \times 10^{-7}$ -1.7 × 10<sup>-5</sup> M). (a) **3a**-e, (b) **3f**-h.



Figure 3. PL spectra of ethynylene-type polymers 3a-g measured in CHCl<sub>3</sub> ( $c = 8.0 \times 10^{-7}-2.1 \times 10^{-6}$  M).

polymer **3a**, the quantum yield of *meta*-phenylene polymer **3e** was as low as 10%. It is likely that the *meta*linked polymer **3e** is less rigid than the *para*-linked **3a**, resulting in the low quantum yield due to nonradiative decay.

We paid attention to **3d** because it showed two kinds of fluorescence peaks: a sharp one at 403 nm and a broad one at longer wavelength region. First, its excitation spectra for the emissions at 403 and 485 nm were measured in order to confirm whether the broad emission is due to a different fluorophore or not as shown in Figure 4. Since both spectra were similar to each other, we can conclude that the broad emission band is based on carbazole. We next checked the dependence of the



Figure 4. Excitation spectra of 3d monitored at 403 and 485 nm, measured in CHCl<sub>3</sub>.



**Figure 5.** UV–vis (a) and PL (b) spectra of **3d** measured as film and CHCl<sub>3</sub> solutions.

spectroscopic pattern on the sample concentration and state. The relative intensity of the emission at longer wavelength became larger with the sample concentration and especially obvious in the film state. There was little difference in the absorption spectra between the solution and film ones, which suggests the ground states are almost the same (Figure 5). These findings lead to the idea that the emission of longer wavelength is due to the formation of excimers.<sup>18</sup>

The fluorescence spectra of other polymers **3b**, **3e**, and **3f** were also measured in the film state (Figure 6). The relative intensities of the peaks at 500-600 nm to those at shorter wavelength were larger in film than in solution like the case of **3d**. It is assumed that these polymers also form excimers in the solid state.



Figure 6. PL spectra of ethynylene-type polymers 3b, 3e, and 3f measured as film.



**Figure 7.** UV–vis spectra of **1D** and imine-type polymers **3i** and **3j** measured in CHCl<sub>3</sub> ( $c = 2.2 \times 10^{-7}$ –7.8 × 10<sup>-7</sup> M).

The optical properties of the imine-type polymers were also investigated. As shown in Figure 7, the absorption peak measured in CHCl<sub>3</sub> was red-shifted compared to **1D**. The conjugation of *para*-linked polymer **3i** seems to be longer than *meta*-linked polymer **3j** because the degree of red shift of **3i** is larger than that of **3j**. The fluorescence spectra of **3i** and **3j** were measured, but the fluorescence quantum yields of them and **1D** were all less than 1%. The very low quantum yield of **1D** should be due to the  $n-\pi^*$  transition of the carbonyl group. In a similar fashion, the  $n-\pi^*$  transition of the imine group of the polymers may be responsible for the low quantum yields.

The stability of the polymers was examined by TGA in air. None of the polymers decomposed up to 300 °C (Figure 8). The weight loss of polymer **3h** stopped at 460 °C, and 13% of the original weight remained even at 800 °C, presumably due to  $Fe_2O_3$ , which agreed well with the theoretical value (12%).

## **Summary**

In the present study, we have demonstrated the synthesis and properties of ethynylene- and imine-type conjugated polymers containing carbazole units in the main chain. Introduction of long *N*-alkyl groups and *meta*-structure was effective in enhancing the solubility of the polymers. The obtained polymers were thermally stable ( $T_d$  = ca. 300 °C) in air. It was confirmed by TOF mass spectrometry that **3d** contained cyclic 3–6mers. It was suggested that the polymers with *para*-structure have conjugation length longer than those with *meta*-



**Figure 8.** TGA curves of the polymers measured in air (heating rate is 10 °C/min). (a) **3a**–**e**, (b) **3f**–**j**.

structure. The ethynylene-type polymers emitted bluegreen light in  $CHCl_3$  in good fluorescence quantum yields. In the film state, photoluminescence originating from excimer was observed. The imine-type polymers exhibited low quantum yields, presumably because of their imine groups.

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Poly(aryleneethynylenes) and Poly(aryleneimines) 7583

3. The formed polymers may partly precipitate during the polycondensation process, but this point is not clear because the reaction mixture is dark. Another possible reason is formation of cyclic oligomers as confirmed by the MALDI–TOF mass measurement.

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