Nitrogen-linked Aromatic Poly(2,7-carbazole)s: Partially Annulated Poly(*m*-aniline)s

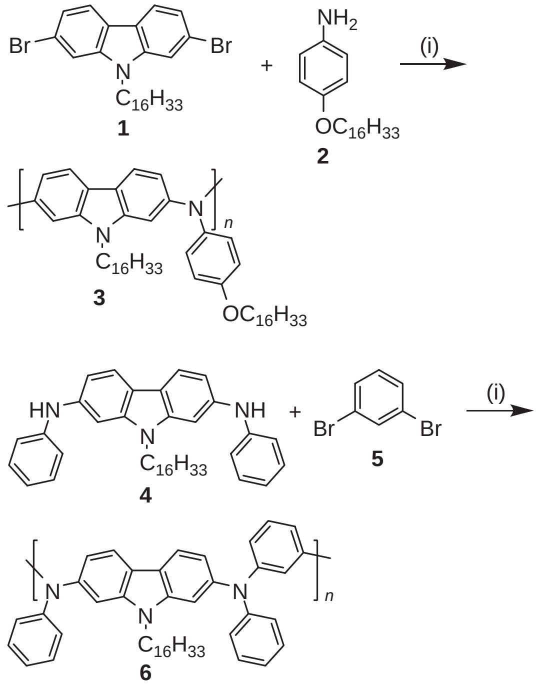
Tsuyoshi Michinobu,*[1] Hiroe Kumazawa,[2] and Kiyotaka Shigehara*[1,2]
[1]*Institute of Symbiotic Science and Technology, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588*
[2]*Graduate School of Engineering, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184-8588*

(Received February 13, 2007; CL-070166; E-mail: tmichi@cc.tuat.ac.jp, jun@cc.tuat.ac.jp)

Nitrogen-linked aromatic carbazole polymers were prepared by palladium-catalyzed amination reactions. They are classified as a partially annulated poly(*m*-aniline), and show a bathochromic shift of absorption maxima as well as reversible redox responses in solutions.

Carbazole polymers have been extensively investigated as photoconductors and hole-transporting materials for electro-optic applications.[1] Recent trend is directed to 2,7-linked aromatic carbazole polymers, since efficient synthetic routes of some 2,7-substituted carbazole monomers have been established.[2] As compared to conventional 3,6-linked carbazole polymers, they have smaller band gaps because of the linear conjugation of 2,7-positions.[3] Further fine-tuning of the electronic properties such as HOMO elevation is expected if electron-donating substituents are introduced between the carbazole units. In this context, we planned to synthesize nitrogen-linked poly(2,7-carbazole)s, which are expected to show high hole mobilities. Herein, we report the rational design of monomer structures for high molecular weight polymers when the polymerization is performed by palladium-catalyzed reactions as well as the electronic properties of the polymers determined by UV–vis spectra and electrochemistry.

We have tried two monomer combinations of bifunctional amines (containing two NH reactive sites) and dibromides for the polycondensation. When 2,7-dibromocarbazole derivative **1** and 4-hexadecyloxyaniline (**2**) were reacted in toluene at 100 °C for 24 h with $Pd_2(dba)_3$ and $P(t\text{-Bu})_3$ as the catalysts, the number-average molecular weight (M_n) and polydispersity (M_w/M_n) of the resulting polymer **3**, measured by GPC (THF eluent, calibrated by polystyrene standards), were 2600 and 1.3, respectively (Scheme 1). The MALDI-TOF mass spectrum of **3** indicated the presence of hydrodehalogenated oligomers (see Supporting Information[10]). Since carbazoles and amino-substituted carbazoles are considerable electron-rich substrates, oxidative addition of such aryl bromides to the Pd catalyst is supposed to be slow and the generated intermediates become relatively unstable, leading to the hydrodehalogenation or other side reactions.[4,5] On the other hand, when diaminocarbazole **4** and 1,3-dibromobenzene (**5**) were reacted under the same conditions, the molecular weight of the resulting polymer **6** was improved ($M_n = 6500$ and $M_w/M_n = 1.6$). These results suggest that the monomer design is one of the most important factors in producing high-molecular weight polymers by transition metal-catalyzed reactions.



Scheme 1. Synthesis of poly(2,7-carbazole)s by palladium-catalyzed amination reaction. (i) 1.3% $Pd_2(dba)_3$, 4.0% $P(t\text{-Bu})_3$, NaO*t*-Bu (1.5 equiv.), toluene, 110 °C, 24 h.

The IR and NMR spectra substantiated the polymer structures. The IR peak intensities at 3406 cm^{-1} of **2** and 3378 cm^{-1} of **4**, ascribed to the NH stretching vibration, reasonably decreased for the corresponding polymers (see Supporting Information[10]). The ^1H NMR spectra were consistent with the IR spectra. Differential scanning calorimetry revealed the relatively high glass-transition temperatures (T_g), e.g., 138 °C for **6**. Thermogravimetric analysis showed that 5% weight loss occurred at 360 °C for **3** and >500 °C for **6**, indicating the high thermal stability of the polymers.

Very interestingly, these polymers can be considered as a partially annulated form of poly(*m*-aniline)s. Previously, some poly(*m*-aniline)s were also prepared by the palladium-catalyzed amination reactions.[6] As compared to the reported poly(*m*-aniline) derivatives, the carbazole polymers **3** and **6** display absorption maxima (λ_{max}) in CH_2Cl_2 in the longer wavelength region such as ca. 400 (sh) and 380 nm, respectively (Table 1 and Figure 1a). In thin film states, **6** exhibited almost the same λ_{max} of 382 nm, but **3** showed a distinct bathochromic shift to ca. 420 nm (sh). This difference is attributed to the different conformations in the solid states, probably caused by the intermolecular interaction of the long alkyl chains. Both polymers show very weak emission in CH_2Cl_2 with the quantum yield of 8–15%, but do not fluorescent in the thin film states. A small Stokes shift of ca. 1700 cm^{-1} observed in CH_2Cl_2 indicates a small transition dipole moment of these polymers.

Table 1. Optical properties of the polymers

Polymer	Solution λ_{max} /nm[a]			Thin film λ_{max} /nm[b]
	abs	emi	Φ_f[c]	abs
3	363, 400[d]	439[e]	0.08	373, 420[d]
6	380	406[f]	0.15	382

[a]Absorption and emission spectra measured in CH_2Cl_2 at 10^{-5} and 5×10^{-7} M/repeat unit, respectively. [b]Cast film from a CH_2Cl_2 solution. [c]Fluorescence quantum yields (Φ_f) were determined in CH_2Cl_2 against quinine sulfate in 0.5 M aqueous H_2SO_4 ($\Phi_f = 0.546$) as a standard. [d]Shoulder. [e]Excited at 363 nm. [f]Excited at 380 nm.

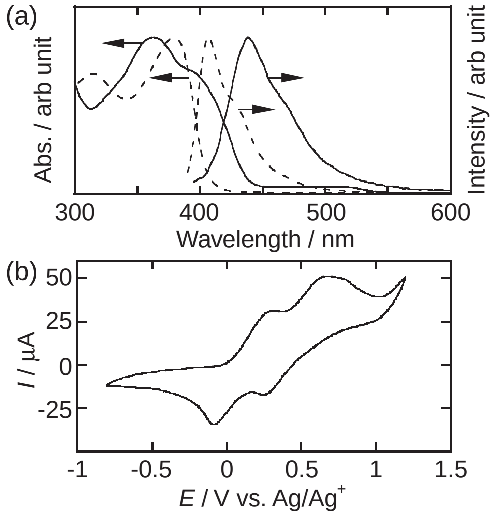


Figure 1. (a) UV–vis absorption and fluorescence spectra of **3** (solid line) and **6** (dotted line) in CH_2Cl_2. (b) Cyclic voltammogram of **3** in CH_2Cl_2 (4 mM/repeat unit) with 0.1 M $(n\text{-}C_4H_9)_4NClO_4$ at room temperature, at a scan rate of 0.1 V s^{-1}. $Fc/Fc^+ = 0.07$ V (vs Ag/Ag^+).

Cyclic voltammograms (CVs) of the polymers **3** and **6** were measured in CH_2Cl_2 (+0.1 M $(n\text{-}C_4H_9)_4NClO_4$) at room temperature. Both polymers displayed two well-resolved, reversible oxidation steps at 0.11 and 0.46 V (vs Ag/Ag^+) for **3** and 0.32 and 0.75 V for **6**, indicating that the generated radical cations are stable on CV timescale (Figure 1b and Supporting Information[10]). This result is in sharp contrast to the poly(*m*-aniline)s, which show only the irreversible oxidation peaks in solutions.[6c] The separation of the first and second oxidation potentials originates from the cation–cation repulsion through the cross-conjugated or linear linkage.[7] Thus, **6** possessing an additional cross-conjugated *m*-phenylene spacer shows a greater potential difference than **3**. The potentials were also explained by the electron-donating effect of the alkoxy substituent.

Electrochemical behaviors in the thin film states were also investigated to get insights into the light-emitting diodes (LEDs) applications. The first oxidation potentials, recorded for the polymer cast films on a glassy carbon electrode in CH_3CN (+0.1 M $(n\text{-}C_4H_9)_4NClO_4$) at room temperature, were quasi-reversible. The HOMO levels of **3** and **6** were estimated to be −5.16 and −5.12 eV, respectively. These HOMO levels are as high as those of low-molecular weight hole-transporting materials and triarylamine polymers.[8] However, the second oxidation potentials were irreversible, indicating that intra- and/or intermolecular coupling reactions occurred. The intramolecular reaction would lead to further annulation of the current carbazole polymers.[9]

In conclusion, we have prepared, by elegant monomer design, nitrogen-linked poly(2,7-carbazole)s, of which electronic properties were investigated by optical and electrochemical measurements. Their HOMO levels are relatively high (ca. −5.1 eV), which is promising as hole-transporting materials in LED devices that are currently pursued.

We thank Prof. T. Watanabe (Tokyo University of Agriculture and Technology) for the use of electrochemical setup and Prof. H. Nishide (Waseda University) for GPC measurements.

References and Notes

1 a) X.-T. Tao, Y.-D. Zhang, T. Wada, H. Sasabe, H. Suzuki, T. Watanabe, S. Miyata, *Adv. Mater.* **1998**, *10*, 226. b) J. V. Grazulevicius, P. Strohriegl, J. Pielichowski, K. Pielichowski, *Prog. Polym. Sci.* **2003**, *28*, 1297. c) F. Sanda, T. Nakai, N. Kobayashi, T. Masuda, *Macromolecules* **2004**, *37*, 2703. d) A. Kimoto, J.-S. Cho, M. Higuchi, K. Yamamoto, *Macromolecules* **2004**, *37*, 5531.

2 a) J.-F. Morin, M. Leclerc, *Macromolecules* **2001**, *34*, 4680. b) F. Dierschke, A. C. Grimsdale, K. Müllen, *Synthesis* **2003**, 2470. c) A. W. Freeman, M. Urvoy, M. E. Criswell, *J. Org. Chem.* **2005**, *70*, 5014.

3 a) J.-F. Morin, P.-L. Boudreault, M. Leclerc, *Macromol. Rapid Commun.* **2002**, *23*, 1032. b) J.-F. Morin, M. Leclerc, *Macromolecules* **2002**, *35*, 8413. c) J.-F. Morin, S. Beaupré, M. Leclerc, I. Lévesque, M. D'Iorio, *Appl. Phys. Lett.* **2002**, *80*, 341. d) J. Bouchard, M. Belletête, G. Durocher, M. Leclerc, *Macromolecules* **2003**, *36*, 4624. e) S. Tirapattur, M. Belletête, N. Drolet, M. Leclerc, G. Durocher, *Chem. Phys. Lett.* **2003**, *370*, 799. f) A. Iraqi, I. Wataru, *Chem. Mater.* **2004**, *16*, 442. g) S. W. Thomas, III, T. M. Swager, *Macromolecules* **2005**, *38*, 2716. h) Y. Fu, Z. Bo, *Macromol. Rapid Commun.* **2005**, *26*, 1704. i) M. Kijima, R. Koguchi, S. Abe, *Chem. Lett.* **2005**, *34*, 900. j) A. Iraqi, T. G. Simmance, H. Yi, M. Stevenson, D. G. Lidzey, *Chem. Mater.* **2006**, *18*, 5789. k) N. Kobayashi, R. Koguchi, M. Kijima, *Macromolecules* **2006**, *39*, 9102. l) J. Li, F. Dierschke, J. Wu, A. C. Grimsdale, K. Müllen, *J. Mater. Chem.* **2006**, *16*, 96. m) N. Zhang, A. Hayer, M. K. Al-Suti, R. A. Al-Belushi, M. S. Khan, A. Köhler, *J. Chem. Phys.* **2006**, *124*, 244701.

4 a) J. P. Wolfe, S. Wagaw, J.-F. Marcoux, S. L. Buchwald, *Acc. Chem. Res.* **1998**, *31*, 805. b) J. F. Hartwig, *Angew. Chem., Int. Ed.* **1998**, *37*, 2046.

5 Z.-B. Zhang, M. Fujiki, H.-Z. Tang, M. Motonaga, K. Torimitsu, *Macromolecules* **2002**, *35*, 1988.

6 a) T. Kanbara, K. Izumi, Y. Nakadani, T. Narise, K. Hasegawa, *Chem. Lett.* **1997**, 1185. b) J. Louie, J. F. Hartwig, *Macromolecules* **1998**, *31*, 6737. c) F. E. Goodson, S. I. Hauck, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 7527.

7 a) T. Michinobu, M. Takahashi, E. Tsuchida, H. Nishide, *Chem. Mater.* **1999**, *11*, 1969. b) T. Michinobu, E. Tsuchida, H. Nishide, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 1021. c) T. Michinobu, E. Tsuchida, H. Nishide, *Polyhedron* **2001**, *20*, 1147. d) T. Michinobu, J. Inui, H. Nishide, *Org. Lett.* **2003**, *5*, 2165.

8 a) Y. Shirota, *J. Mater. Chem.* **2000**, *10*, 1. b) Y.-J. Pu, M. Soma, J. Kido, H. Nishide, *Chem. Mater.* **2001**, *13*, 3817.

9 See some fused carbazole oligomers and polymers: a) J. Bouchard, S. Wakim, M. Leclerc, *J. Org. Chem.* **2004**, *69*, 5705. b) F. Dierschke, A. C. Grimsdale, K. Müllen, *Macromol. Chem. Phys.* **2004**, *205*, 1147. c) A. K. Mishra, M. Graf, F. Grasse, J. Jacob, E. J. W. List, K. Müllen, *Chem. Mater.* **2006**, *18*, 2879. d) Y. Li, Y. Wu, B. S. Ong, *Macromolecules* **2006**, *39*, 6521.

10 Supporting information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) April 7, 2007; doi:10.1246/cl.2007.620