Efficient Thermal Conversion of Poly(pyridinediylbutadiynylene)s to Nitrogen-containing Microporous Carbon

Masashi Kijima,* Takayuki Oda, Takahisa Yamazaki, Yasunori Tazaki, and Junji Nakamura
Institute of Materials Science, Graduate School of Pure and Applied Science, University of Tsukuba,
1-1-1 Tennodai, Tsukuba 305-8573

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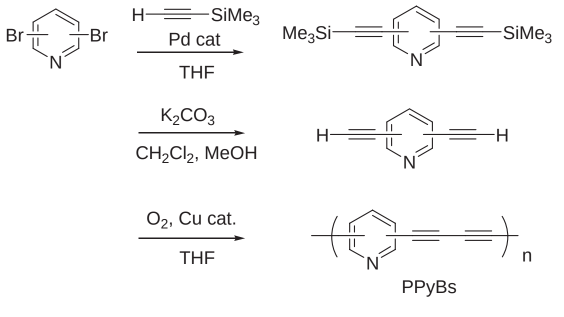
Poly(pyridinediylbutadiynylene)s, a conjugated polymer alternatively consisted of the pyridine and butadiyne units, were synthesized by oxidative polycondensation of diethynylpyridine with the Hay catalyst. They converted to microporous carbons in high yields with a high efficiency of fixation of nitrogen by heating up from room temperature to 900 °C under flowing of argon.

Incorporation of electron-donating nitrogen into porous carbons has attracted attention to change the physical and chemical properties of carbon materials especially on the surface.[1] One possible application would be the electrode of electric double-layer capacitors (EDLC).[2] The achievement need of the electrode made from the nitrogen-enriched carbon is basically having a large surface area with low resistivity. However, the reactivity of nitrogen-containing pre-carbon materials makes difficult to prepare porous carbons in high yield with high content of nitrogen by the usual carbonization and activation methods. We have recently reported that the pyrolytic carbonization of conjugated polymers having carbon–carbon triple bonds such as poly(phenylenebutadiynylene)s under an argon flow could afford microporous carbons in high yields above 80%.[3] It is thought that if the phenylene portion of the polymer is substituted by a thermal-stable N-containing aromatic portion, this pyrolytic method would be simple, efficient and alternative to the ingenious methods reported so far for preparation of the nitrogen-enriched porous carbons. Thus, in this paper, we attempted to synthesize poly(pyridinediylbutadiynylene)s (PPyBs) and investigated their carbonization behavior, and characterized the carbonized products.

According to the reaction course shown in Scheme 1, the monomer, diethynylpyridine, was synthesized by Sonogashira coupling of 2,5-, 2,6-, or 3,5-dibromopyridine with trimethylsilylacetylene, and the successive elimination of trimethylsilyl by the alkaline treatment.[4] The monomer underwent oxidative polycondensation in tetrahydrofuran under O_2 in the presence of Hay catalyst, giving $P_{25}PyB$, $P_{26}PyB$, and $P_{35}PyB$, respectively.[5]



Scheme 1. Synthesis of PPyBs with 2,5-, 2,6-, and 3,5-linkage.

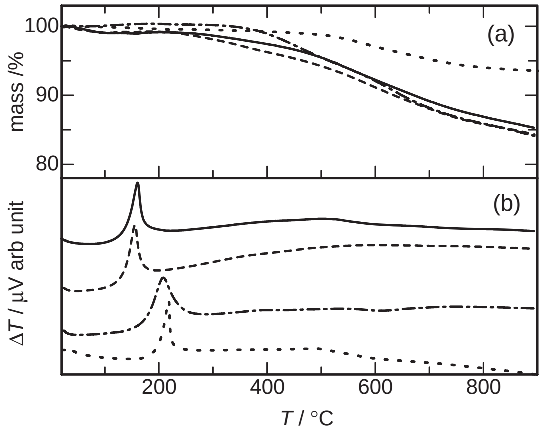


Figure 1. TG/DTA curves of $P_{25}PyB$ (—), $P_{26}PyB$ (----), $P_{35}PyB$ (–-–), and P*m*PB (······).

The results of thermogravimetric and differential thermal analysis (TG/DTA) for PPyBs were compared with that of poly(*m*-phenylenebutadiynylene) P*m*PB. In all cases, the carbonization yields at 900 °C were about 85%. In the DTA curves (Figure 1b), PPyBs showed an exothermic peak around 200 °C accompanying no mass loss, which suggested that the cross-linking reaction occurred at the butadiyne portion during the exothermal process as well as P*m*PB.[3] In the case of P*m*PB, most of mass loss in the range from 500 to 700 °C was due to dehydrogenation from the phenylene portion, while the TG curves of PPyBs (Figure 1a) suggested that nitrogen-containing fragments would continuously eliminate in the temperature region above 300 °C in addition to the dehydrogenation process.

The polymer in a form of pellet ($\phi = 13$ mm) was carbonized in a quartz tube by heating up from room temperature to 300 °C at a rate of 0.5 °C/min and successively from 300 to 900 °C at a rate of 10 °C/min under flowing argon in a furnace. After carbonization, the sample was allowed to cool to room temperature and stored in a desiccator. The carbonization results and some analytical data of the carbonized samples are summarized in Table 1.

The carbonization yields of the disk-pellet samples of PPyBs are comparable to the TG results. The contraction of volume was about 30%. The bulk density of the carbonized pellet was about 1.2 g/cm^3. The electrical conductivity was about 5 S/cm. The N_2 adsorption isotherm shown in Figure 2 is of Type I, suggesting the microporous nature of carbon. The specific surface area (S_{BET}) of the carbonized PPyBs was in the range of 300–400 m^2/g. The N elimination during the carbonization affected increasing meso- and macroporosities of the carbon (V_{micro}/V_{total}) compared to P*m*PB. The subtracting pore effect

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Table 1. Carbonization results of PPyBs

Polymer	Yield[a]	S_{BET}[b]	V_{micro}[c]	V_{micro}/	EA[d]/%		D_{fix}[e]
	/%	/$m^2\ g^{-1}$	/$cm^3\ g^{-1}$	V_{total}	C	N	
P_{25}PyB	81	306	0.12	0.46	73.97	6.25	0.59
P_{26}PyB	85	305	0.12	0.48	84.93	6.26	0.57
P_{35}PyB	85	416	0.18	0.62	88.51	5.05	0.46
P*m*PB	94	471	0.20	0.71	94.37	—	—

[a]Carbonization yield at 900 °C. [b]Surface area was estimated by Brunauer–Emmett–Teller method. [c]Micropore volume was estimated by α_s method. [d]Elemental analysis data (wt %) of the carbonized polymers. [e]Degree of N-fixation at 900 °C defined as the N content (wt %) ratio of the carbonized PPyB to the untreated PPyB.

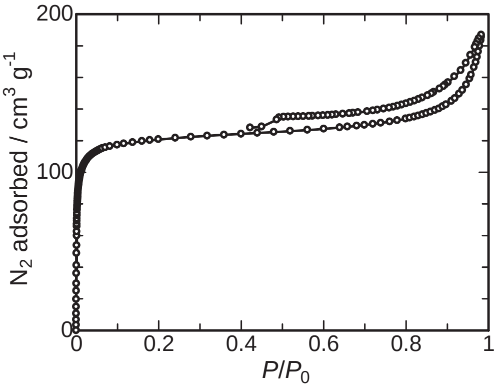

Figure 2. N_2 adsorption–desorption isotherm of the carbonized P_{35}PyB at −196 °C.

analysis[6] of the α_s plots of the carbonized PPyBs gave results of a surface area larger than S_{BET} and an average pore width in the range of 0.71–0.77 nm.

From elemental analysis, the carbonized PPyBs retain about 6 mass % of N with a high efficiency of N-fixation (D_{fix}). However, the total mass % of C, H, and N was always below 95% in all cases, which suggested that considerable amount of O is present on the surface. The results of X-ray photoelectron spectroscopy (XPS) for the carbonized P_{35}PyB in the region of O_{1s}, N_{1s}, and C_{1s} are shown in Figure 3. The peak value of main Gaussian component of O_{1s} (532.5 eV) falls in a range between phenolic compounds. The fitting of the peaks in the region of N_{1s} shows three contributions at binding energies of 398.1, 400.5, and 402.6 eV. These peaks suggest the presence of N-bonding states of pyridine (398.5), pyridone (2-hydroxypyridine) (400.5), and oxidized nitrogen (402.9) rather than the usually considered quaternary N (401.2).[1] In the C_{1s} region, three peaks at 284.5, 285.2, and 287.7 eV fall in a region of graphite, carbons with N, and carbons with O, respectively. These results suggest that the surface of the carbonized PPyBs is easily oxidized and sufficiently polar to adsorb moisture, which is appropriate to the observation of abundance of O (21 mass %) by XPS. The EDLC capacitance of the disk pellet of the carbonized P_{35}PyB measured by a constant current method (0.02 A/g) using a three-electrode cell was quite high (452 F/g) in 1 mol/dm^3 H_2SO_4, which might be affected by abundance of the pyridine-like carbons on the surface.

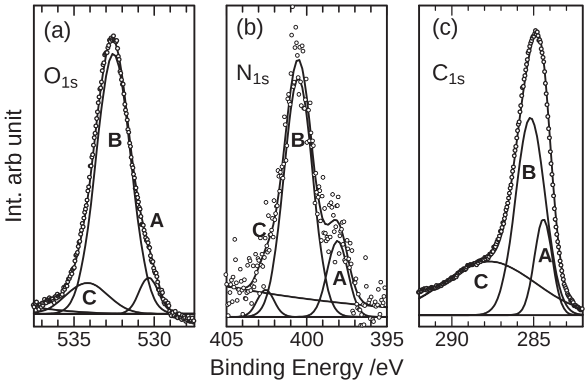

Figure 3. XPS spectra of the carbonized P_{35}PyB and the fitting results with Gaussian.

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References and Notes

1 J. Lahaye, G. Nansé, A. Bagreev, V. Strelko, *Carbon* **1999**, *37*, 585; C.-M. Yang, K. Kaneko, *Carbon* **2001**, *39*, 1075; E. Raymundo-Piñero, D. Cazorla-amorós, A. Linares-Solano, J. Find, U. Wild, R. Schlögl, *Carbon* **2002**, *40*, 597; W. J. Gammon, O. Kraft, A. C. Reilly, B. C. Holloway, *Carbon* **2003**, *41*, 1917; T. Matsuoka, H. Hatori, M. Kodama, J. Yamashita, N. Miyajima, *Carbon* **2004**, *42*, 2329; P.-X. Hou, H. Origasa, T. Yamazaki, K. Matsuoka, A. Tomita, N. Setoyama, Y. Fukushima, T. Kyotani, *Chem. Mater.* **2005**, *17*, 5187; A. Garsuch, R. R. Sattler, S. Witt, O. Klepel, *Microporous Mesoporous Mater.* **2006**, *89*, 164.

2 K. Jurewicz, K. Babel, A. Źiólkowski, H. Wachowska, *Electrochim. Acta* **2003**, *48*, 1491; D. Hulicova, J. Yamashita, Y. Soneda, H. Hatori, M. Kodama, *Chem. Mater.* **2005**, *17*, 1241.

3 M. Kijima, H. Tanimoto, H. Shirakawa, A. Oya, T.-T. Liang, Y. Yamada, *Carbon* **2001**, *39*, 297; M. Kijima, D. Fujiya, T. Oda, M. Ito, *J. Therm. Anal. Calorim.* **2005**, *81*, 549.

4 S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, *Synthesis* **1980**, 627; J. Cheng, Y. Sun, F. Wang, M. Guo, J.-H. Xu, Y. Pan, Z. Zhang, *J. Org. Chem.* **2004**, *69*, 5428.

5 General procedure of polymerization: To the catalyst solution prepared by mixing CuCl (2 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (2 mmol) in THF (50 mL) for 15 min with bubbling of O_2 was added corresponding diethynylpyridine (8 mmol) in THF (35 mL), which was further stirred for 48 h at room temperature under O_2. After evaporation of the solvent, the insoluble precipitated product was washed with stirring in MeOH (300 mL) containing concd HCl (3 mL). The product collected by filtration was sequentially washed with 7.5% aq NH_3, H_2O, MeOH, and acetone. A powdery brown polymer was obtained over 85% yield after drying under vacuum in each case.

6 K. Kaneko, C. Ishii, H. Kanoh, Y. Hanzawa, N. Setoyama, T. Suzuki, *Adv. Colloid Interface Sci.* **1998**, *76–77*, 295.

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