Chem. Mater. **2001,** *13,* 2933−2939

Preparation of Porous Carbon by Defluorination of Poly(tetrafluoroethylene) and the Effect of γ-Irradiation on the Polymer

Tien-Tzu Liang,[†] Yoshio Yamada,*,[†] Noriko Yoshizawa,[†] Soshi Shiraishi,[‡] and Asao Oya[‡]

*National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa,
Tsukuba, Ibaraki 305-8569, Japan, and Gunma University, 1-5-1 Tenjin-cho,
Kiryu, Gunma 376-8515, Japan*

Received February 28, 2001. Revised Manuscript Received June 18, 2001

Porous carbon materials were prepared by direct reduction of poly(tetrafluoroethylene) (PTFE) powder with potassium vapor. After the reaction, the black powder product under vacuum showed a Raman peak at around 1950 cm^{-1}, which was assigned to the C≡C bond in a polyyne-type structure. After the byproduct, potassium fluoride, was removed, by using hydrogen fluoride, the powder was heat-treated up to 2800 °C in an argon atmosphere. The structural changes of the powder with heat treatment were analyzed by Raman spectroscopy. The changes in the pore structure were examined by N_2 adsorption. It was found that the product contains a high amount of mesopores as well as micropores. For example, the meso- and micropore volumes for the carbon heat-treated at 1000 °C were 669−844 and 200−233 mm^3/g, respectively. The same experiments were performed by using γ-irradiated PTFE powder. The product gave a more porous structure, i.e., a higher total surface area of 1385−1516 m^2/g and mesopore area of 877−1126 m^2/g, while the carbon derived from the nonirradiated polymer showed 1041 and 620 m^2/g, respectively. The formation mechanism of the porous carbons is discussed on the basis of the polymer aggregation, and the effects of defluorination and γ-irradiation on the polymer.

Introduction

Activated carbons are useful for gas and water purification, solvent recovery, gas storage adsorbents, electrodes for an electric double-layer capacitor (EDLC), and so on.[1−5] The conventional porous carbons are generally prepared by pyrolysis of organic precursors and then by thermal activation with oxidative gas or chemicals.[6] The products thus obtained contain a wide range of pore size distributions, and it is difficult to control the pore structure in the carbons because thermal decomposition and nonselective polycondensation occur simultaneously in these processes.[7]

Recently Hatori et al. have prepared carbon films with a mesoporous structure by a polymer blend method without activation.[8] Tamai et al. reported the formation of mesoporous carbons[9] or carbon fiber[10] using 0.3 wt % $Y(acac)_3$ in a pitch, and the resultant carbons are suitable for removal of large molecular impurities from water. Also they might be a promising material for electrodes in EDLC because the pores on the carbon surface must be large enough to contain electrolyte or solvated ions.[11] Kavan et al. have synthesized carbon materials by electrochemical reaction of halogenated polymers and studied various properties of the carbons so-derived.[12] However, they did not pursue the pore changes of the carbons with heat treatment. We have attempted to synthesize carbynes, one-dimensional linear carbons with sp-hybrid orbitals, through reduction of a poly(tetrafluoroethylene) (PTFE) film by potassium metal (K).[13] In this case the carbon materials can be generated at low temperature by defluorination of PTFE. At the same time the reaction is accompanied

---

* To whom correspondence should be addressed. E-mail: y-yamada@aist.go.jp.

[†] National Institute of Advanced Industrial Science and Technology.

[‡] Gunma University.

(1) Derbyshire, F.; Jagtoyen, M.; Thwaites, M. In *Porosity in Carbon*; Patrick, J. W., Ed.; Edward Arnold: London, 1995; Chapter 9.

(2) Parkyns, N. D.; Quinn, D. F. In *Porosity in Carbon*; Patrick, J. W., Ed.; Edward Arnold: London, 1995; Chapter 11.

(3) Shi, H. *Electrochim. Acta* **1996**, *41*, 1633.

(4) Cook, T. L.; Komodromos, C.; Quinn, D. F.; Ragan, S. In *Carbon Materials for Advanced Technologies*; Burchell, T. D., Ed.; Pergamon: Oxford, 1999; Chapter 9.

(5) Shiraishi, S.; Kurihara, H.; Tsdubota, H.; Oya, A.; Soneda, S.; Yamada, Y. *Electrochem. Solid-State Lett.* **2001**, *4*, A5.

(6) Smisek, M.; Cerny, S. *Active Carbon Manufacture, Properties and Applications*; Elsevier: New York, 1970.

(7) Fitzer, E.; Mueller, K.; Schaefer, W. In *Chemistry and Physics of Carbon*; Walker, P. L., Jr., Ed.; Marcel Dekker: New York, 1971; Vol. 7.

(8) Hatori, H.; Kobayashi, T.; Hanzawa, Y.; Yamada, Y.; Iimura, T.; Kimura, T.; Shiraishi, M. *J. Appl. Polym. Sci.* **2001**, *79*, 836−841.

(9) Tamai, H.; Kakii, T.; Hirota, Y.; Kumamoto, T.; Yasuda, H. *Chem. Mater.* **1996**, *8*, 454.

(10) Tamai, H.; Ikeuchi, M.; Kojima, S.; Yasuda, H. *Adv. Mater.* **1997**, *9*, 55.

(11) Sakata, Y.; Muto, A.; Uddin, M. A.; Yamada, N.; Marumo, C.; Ibabaki, S.; Kojima, K. *Eletrochem. Solid-State Lett.* **2000**, *3*, 1.

(12) Kavan, L. *Chem. Rev.* **1997**, *97*, 3061.

(13) Soneda, Y.; Maruoka, K.; Nakano, M.; Akuzawa, N.; Yamada Y. *Proc. ADC/FCT ‘99* **1999**, 571.

10.1021/cm010184w CCC: \$20.00

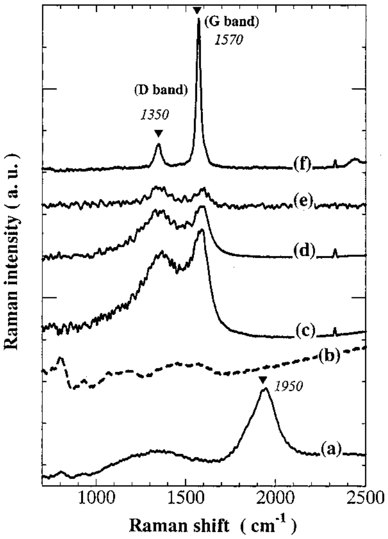

Figure 1. Raman spectra of the as-reacted PTFE powder treated at 200 °C (a) (or 500 °C (b)) under vacuum, then washed with HF (c), and treated at 1000 (d), 1500 (e), and 2800 (f) °C under argon.

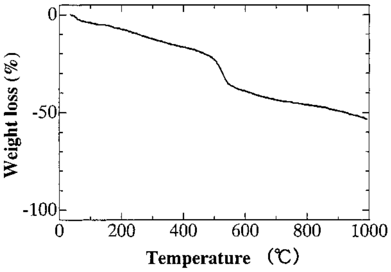

Figure 2. TGA curve of the carbyne-like material treated at 200 °C under vacuum and washed with HF solution.

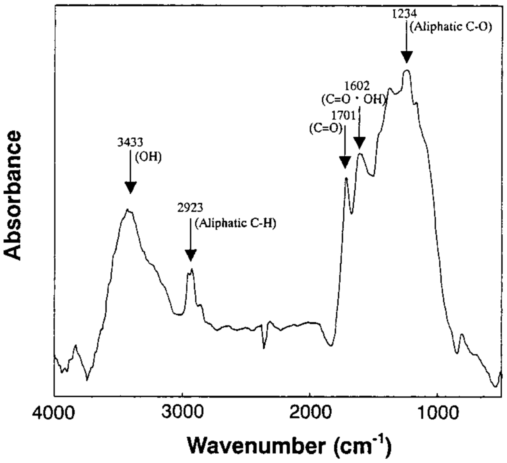

Figure 3. FT-IR spectrum of the as-reacted PTFE powder treated at 200 °C under vacuum and then washed with HF.

by the formation of potassium fluoride (KF), which inhibits cross-linking between linear carbon chains.[13] Thus, the elimination of KF from the as-reacted product is expected to leave spaces which may lead to the formation of pores in the carbon matrix.

The purpose of this study was to elucidate the pore structure of the carbons obtained by direct reduction of the PTFE with K and to examine the structural changes with heat treatment temperature. In addition the original PTFE was γ-irradiated, resulting in the lowering of the molecular weight of the PTFE, and the irradiation effect on the pore structure was studied in relation to aggregation of the original polymer.

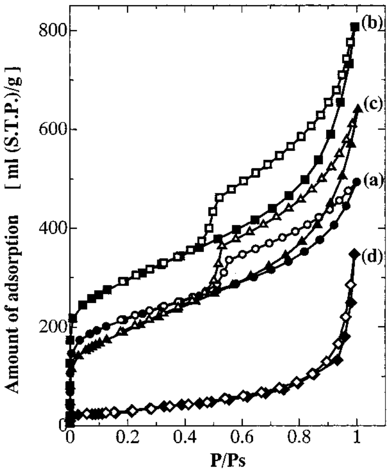

Figure 4. Adsorption isotherm curves (N_2 at 77 K) of the as-reacted PTFE powder treated at 200 °C under vacuum, then washed with HF (a), and treated at 1000 (b), 1500 (c), and 2800 (d) °C under argon.

Experimental Section

Sample. PTFE employed is a commercially available powder product with a polymerization degree of ca. 10^6 (MP1500-J) which was supplied by Dupont-Mitsui Fluorochemicals Co. Ltd. The powder has an average diameter of 20 μm and a specific surface area of 8−12 m^2/g.

Preparation Procedure. The reaction of PTFE with K[14] was performed in a glass tube in the absence of air by contacting the powder directly to potassium vapor through a breakable seal; after the seal was ruptured by a hammer under vacuum, the whole tube was kept at 200 °C for 12 h in an oven to expose the powder to an adequate vapor of the purified K. As the reaction proceeded, the sample changed from a gray to a black color. The as-reacted powder was treated again at 200 or 500 °C for 1 h under vacuum, and the residual K was removed under vacuum and sealed off from the reaction tube. The treated sample was then taken out of the sealed tube, washed with hydrogen fluoride (HF[15]) to remove KF, and dried at 110 °C. The product was then heated at 1000−2800 °C under argon.

Raman Spectroscopy, Transmission Electron Microscopy (TEM), and N_2 Adsorption. Raman spectra for the sample treated at 200 or 500 °C under vacuum and for those heat-treated at higher temperatures in argon gas were measured in the sealed tube and in air, respectively, by using an Ar^+ laser (ν =514 nm) in a Jovin Yvon Ramanor S320C apparatus. Observation with TEM using a Philips CM30 was conducted at an accelerating voltage at 200 kV for the ground sample dispersed on a grid. The pore structure of the sample was characterized with N_2 adsorption isotherms at 77 K by using a Nihon Bell BELSORP 28SA instrument.

γ-Ray Irradiation. The PTFE powder stored in a sealed tube without air was γ-irradiated at room temperature for various hours at a dose rate of 3.9 × 10^2 C/(kg·h) with a ^{60}Co γ-source of the Japan Atomic Energy Research Institute, Tokai. The total dose was 3.12 × 10^3, 1.56 × 10^4, and 3.12 × 10^4 C/kg, abbreviated to γ, 5γ, and 10γ, respectively, in the text below.

---

(14) K is highly reactive to humidity, so the handling of the metal was carried out in a glovebox filled with nitrogen gas. Also, after use, the metal was allowed to stand for a long time in contact with moisture until the metal was completely converted into potassium hydroxide compounds.

(15) The HF solution is a toxic material. One must be careful in its handling. The used solution was neutralized with Na_2CO_3 solution to give NaF, which is an inert and nontoxic material.

Table 1. Porosity Characteristics of PTFE Reacted with K at 200 °C and Treated at 200 or 500 °C under Vacuum, Then Washed with HF, and Treated at Different Temperatures[a]

	BET method	DH method: adsorption branch			
sample	A_{BET} (m^2/g)	A_{meso} (m^2/g)	V_{meso} (mm^3(liq)/g)	R_p (nm)	A_{meso}/A_{BET} (%)
(1) as-reacted carbyne-like material treated at 200 °C under vacuum and					
(a) washed with HF	762	444	517	0.84	58.3
(b) treated at 1000 °C	1036	620	844	0.84	59.8
(c) treated at 1500 °C	658	561	721	0.84	85.3
(d) treated at 2800 °C	103	112	287	1.21	
(2) as-reacted carbyne-like material treated at 500 °C under vacuum and					
(a) washed with HF	820	487	624	0.84	59.4
(b) treated at 1000 °C	1053	567	669	0.84	53.8
(c) treated at 2800 °C	91	92	155	1.35	

[a] These parameters were obtained by the BET and DH methods.

Table 2. Pore Characteristic of PTFE Reacted with K at 200 °C and Treated at 200 or 500 °C under Vacuum, Then Washed with HF, and Treated at Different Temperatures[a]

	α_s method				
sample	a_{total} (m^2/g)	a_{micro} (m^2/g)	a_{meso} (m^2/g)	V_{micro} (mm^3/g)	a_{meso}/a_{total} (%)
(1) 200 °C					
(a) HF	776	392	384	162	49
(b) HF/1000 °C	1060	499	561	200	53
(c) HF/1500 °C	668	170	498	76	75
(2) 500 °C					
(a) HF	842	398	444	160	53
(b) HF/1000 °C	1098	592	506	233	46

[a] These parameters were obtained by the α_s method.

Results and Discussion

Structural Changes with Heat Treatment. A Raman spectrum of the product treated at 200 °C under vacuum is shown in Figure 1a. It has a broad peak at around 1950 cm^{-1}, which was assigned to the $-C{\equiv}C-$ stretching mode in a carbyne structure of the polyyne type.[12,13,16] The average length of the conjugated bond was calculated as $(-C{\equiv}C-)_{10}$ from the peak position by using an equation of Kaster et al.[17] When the product was treated at 500 °C instead of 200 °C or exposed to air, this peak disappeared completely (Figure 1b). Hence, it suggests that the carbyne-like structure formed by the reaction is very unstable even at low temperatures such as 500 °C or to air exposure.[13,16] Kavan et al. reported that the carbyne-type linear chains generated by defluorination of PTFE with alkali-metal amalgam are easily transformed into a graphene-like two-dimensional network structure owing to migration of alkali-metal fluoride compounds which inhibit the cross-linking between the linear chains.[16] We also obtained the same result from the analysis of the Raman spectra and X-ray photoelectron spectroscopy as reported in an earlier paper.[13] The treatment with HF gave a conventional carbon which exhibits two typical Raman bands, i.e., a disorder-induced band at 1350 cm^{-1} (D band) and an intrinsic graphite band at 1580 cm^{-1} (G band).[18] The result indicates that the carbyne-like material with sp-hybrid orbitals is converted to a carbonaceous material composed of sp^2 bonding only with HF treatment.

It was found from thermogravimetric analysis of the sample treated with HF that heating to 1000 °C in an inert gas is accompanied by ca. 15% weight loss around 500 °C, which gradually decreases (Figure 2). The elemental analysis of the sample treated with HF solution gave hydrogen and oxygen contents of 1.7 and 22.0 wt %, respectively. The presence of these atoms in the sample is considered to arise from reactions occurring on exposure to air and then on contact with the solution. When the reaction product was treated with the HF solution, most of these atoms occurred in chemical species such as C—H, C—OH, C═O, or COOH, the presence of which was confirmed by FT-IR spectroscopy. The spectrum is shown in Figure 3, together with peaks identified with these functional groups. Thus, the weight loss until 1000 °C (ca. 50%) may be predominantly caused by thermal decomposition of these species and nonaromatic carbon species. The reason why a rapid weight loss took place at around 500 °C (Figure 2) is not clear. The mechanism might be elucidated by the analysis of evolved gases during the heat treatment.

The Raman spectra shown in Figure 1d−f were observed when the sample without KF was heated at 1000, 1500, and 2800 °C in argon atmosphere. The intensity of the G band for the sample treated at 2800 °C became stronger although a weak D band still remained.

Pore Characteristics. The N_2 adsorption and desorption isotherm curves of the sample, in which the as-reacted powder was treated at 200 °C under vacuum and then treated to removed KF, are shown in Figure 4, together with those for the products heated at 1000, 1500, and 2800 °C. Also, when the as-reacted sample was treated at 500 °C in the presence of KF, the samples treated at the same temperature gave curves analogous to those in Figure 4. Each sample except for that treated at 2800 °C belongs to a type IV isotherm according to the original IUPAC classification, having a hysteresis loop which is a feature common to mesoporous carbon with slit-shaped pores.[19] It is noted from the adsorption

---

(16) Kavan, L.; Hlvaty, J.; Kastner, J.; Kuzmany, H. *Carbon* **1995**, *33*, 1321.

(17) Kastner, J.; Kuzmany, H.; Kavan, L.; Dousek, F. P.; Kûrti, J. *J. Macromol.* **1995**, *28*, 344.

(18) Vidan, R.; Fischbach, D. B. *J. Am. Ceram. Soc.* **1978**, *61*, 13.

(19) Sing, K. S. W.; Everett, D. H. W.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem.* **1985**, *57*, 603.

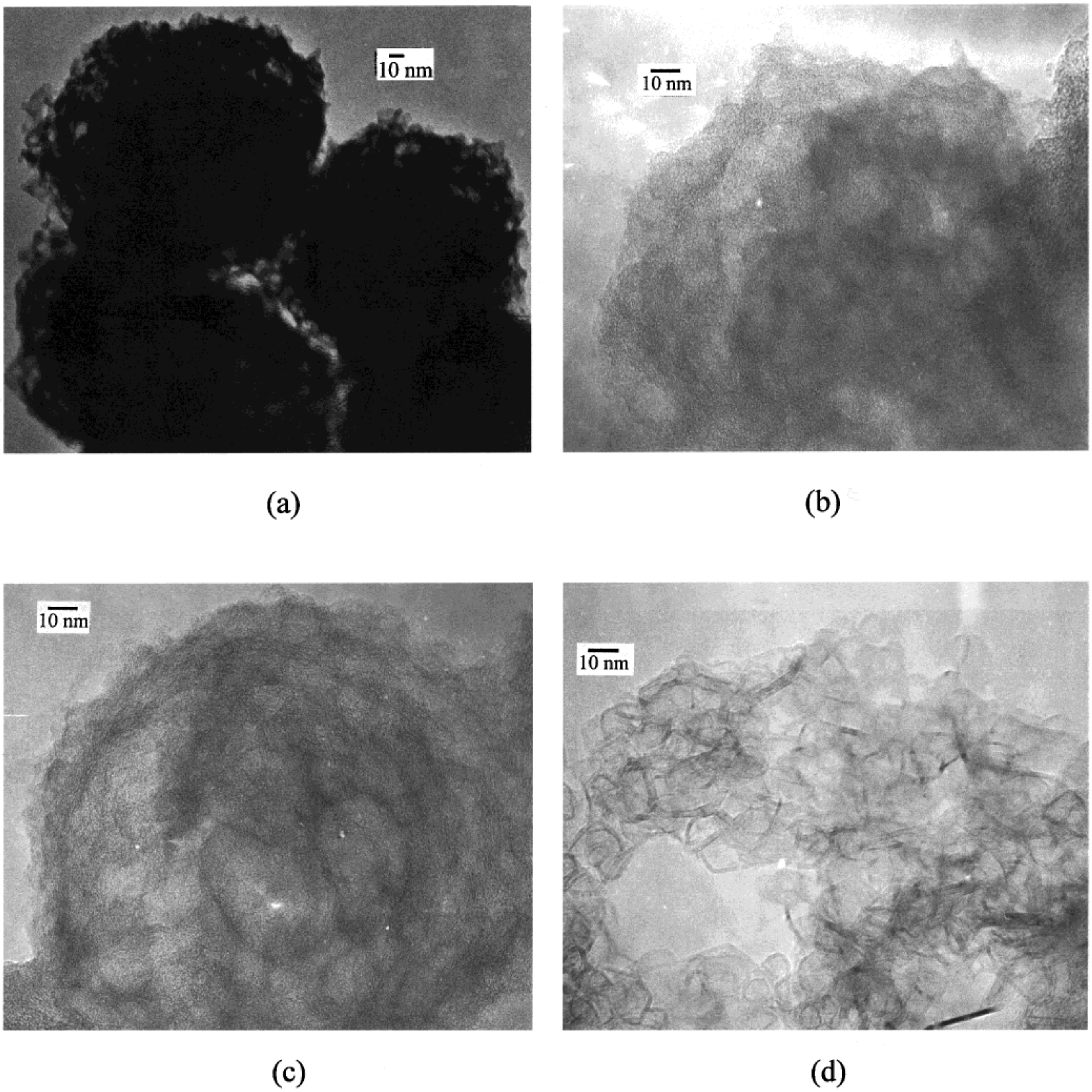

Figure 5. TEM images of the as-reacted PTFE powder treated at 200 °C under vacuum (a), washed with HF (b), and then treated at 1000 (c) and 2800 (d) °C under argon.

curves for the samples heated to 1500 °C that a considerable amount of mesopores are present in the products as well as micropores. The difference in the shape of the isotherm curves was hardly discernible between two samples which were treated at 200 and 500 °C in the presence of KF. This fact means that the difference in KF crystal size with heat treatment between 200 and 500 °C does greatly influence the size of the pores, which may be generated by removal of volatile byproducts.

The pore characteristics of the products are summarized in Table 1. The surface area, A_{BET}, calculated by the BET method,[20] corresponds to the total area of the porous carbon. The data on the characteristics of mesopores, surface area (A_{meso}), pore volume (V_{meso}), and pore radius (R_{p}), which were calculated by the Dollimore−Heal (DH) method[21,22] on the basis of the adsorption branch, are listed in Table 1 along with another parameter, $A_{\mathrm{meso}}/A_{\mathrm{BET}}$, which is defined to evaluate the extent of mesoporosity. In addition, the results for the pore parameters as calculated by the α_s method[23] are indicated in Table 2 for reference. It is worth noting that the sample washed only with HF solution gives a very porous carbon with micro- and

---

(20) Gregg, J. S.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: London, 1982.

(21) Dollimore, D.; Heal, G. R. *J. Appl. Chem.* **1964**, *14*, 109.

(22) Dollimore, D.; Heal, G. R. *J. Colloid Interface Sci.* **1970**, *33*, 508.

(23) Sing, K. S. W. In *Surface Area Determination*; Everett, D. H., Ottewill, D. H., Eds.; Butterworths: Markham, Canada, 1970; p 25.

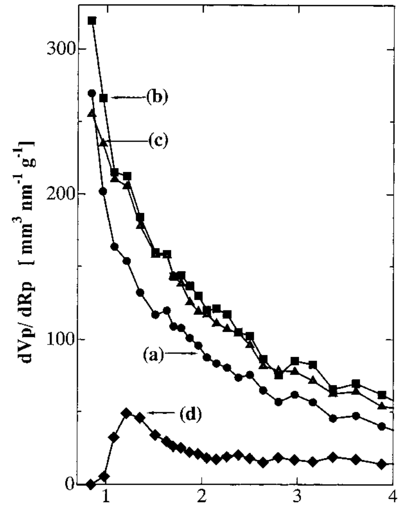

Figure 6. Pore size distribution curves (DH method) from the adsorption branch. The samples were washed with HF (a) and then treated at 1000 (b), 1500 (c), and 2800 (d) °C under argon.

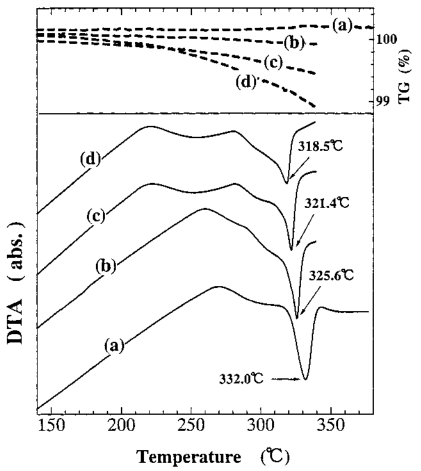

Figure 7. DTA and TGA of as-received PTFE (a) and PTFE irradiated with γ (total dose 3.12×10^3 C/kg) (b), 5γ (total dose 1.56×10^4 C/kg) (c), and 10γ (total dose 3.12×10^4 C/kg) (d).

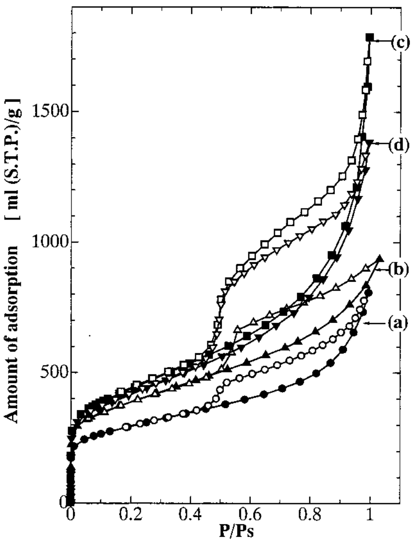

Figure 8. Adsorption isotherm curves (N_2 at 77 K) of porous carbon prepared from as-received PTFE (a) and PTFE irradiated with γ (total dose 3.12×10^3 C/kg) (b), 5γ (total dose 1.56×10^4 C/kg) (c), and 10γ (total dose 3.12×10^4 C/kg) (d). The samples were treated at 1000 °C under argon.

mesopores. At the same time the agreement between the pore parameters obtained from the DH method and the α_s method is remarkably close. The results suggest that the characterization of these pores by the methods employed is reasonable. The defluorination and the removal of KF rather than the treatment at higher temperatures contribute mainly to the pore formation. The amount of N_2 adsorption for these samples increases with heat treatment up to 1000 °C, but then decreases at higher temperatures. In particular the amount of not only the micropores but also the mesopores decreases drastically when the sample is treated at 2800 °C. The shrinkage of the sample during the heat treatment may induce pore closure. This phenomenon is also supported by TEM observations. Figure 5 shows the morphological changes of the samples with heat treatment temperature. The original PTFE powder consists of spheres of around 200−300 nm. The particle size held almost constant after the powder was reacted with K, as can be seen in Figure 5a. The presence of mesopores with a few nanometers in size can be seen in the large aggregates of Figure 5b,c. Such a morphology was maintained during treatment up to 1000 °C. When the sample was treated at 2800 °C, however, these spheres were converted to clusters of spider-like cages with a few nanometers in diameter. A large number of shells covered with a few bundles of graphite ribbons are dispersed in the sample (Figure 5d). These cages look like hard and closed pores. At the same time many micropores located between loosely stacked layers in the untreated sample are considered to disappear with the development of a layer stacking structure although it is impossible to observe these pores by TEM.

It is generally accepted that the pore size distribution can be obtained from the desorption branch by the DH method.[21,22] In the case of mesoporous carbons showing a big hysteresis behavior due to capillary condensation between adsorption and desorption isotherms, however, it is unreasonable to employ the desorption curve for the calculation of the distribution. Thus, the distribution for these samples was obtained from the adsorption branch (Figure 6). Each sample gives the analogous, continuously decreasing pattern, except for the samples treated at 2800 °C. This suggests that the size of the micropores is almost constant for the samples treated up to 1500 °C. In addition, Tables 1 and 2 indicate that the mesoporosity parameter, $A_{\mathrm{meso}}/A_{\mathrm{BET}}$, is increased with the treatment temperature. This result may be interpreted in terms of the disappearance of micropores, caused by development of the stacking structure and by shrinkage of the sample.

γ-Ray Irradiation Effect on PTFE. As is clear from the results described above, it is more important to change the morphology of the initial PTFE powder before defluorination to enhance the mesoporosity of the products. Hence, the original PTFE powder was γ-irradiated to decrease the degree of polymerization. The differential thermal and thermogravimetric analyses (DTA and TGA) for the samples irradiated with various doses were carried out as estimations for the degree of polymerization. The results are shown in Figure 7 in comparison with those of the nonirradiated polymer. The melting point of the polymer decreases, and a very

Table 3. Pore Characteristics of Porous Carbons Prepared from PTFE γ-Irradiated with Various Doses[a] These parameters were obtained by the BET and DH Methods

	BET method	DH method: adsorption branch			
sample	A_{BET} (m^2/g)	A_{meso} (m^2/g)	V_{meso} (mm^3 (liq)/g)	R_p (nm)	A_{meso}/A_{BET} (%)
(a) non	1041	620	844	0.84	59
(b) γ^a	1385	877	972	0.84	63
(c) 5γ	1516	1126	1662	0.84	74
(d) 10γ	1444	1077	1571	0.84	74

[a] These parameters were obtained by the BET and DH Methods. [b] Exposure dose $\gamma = 3.12 \times 10^3$ C/kg.

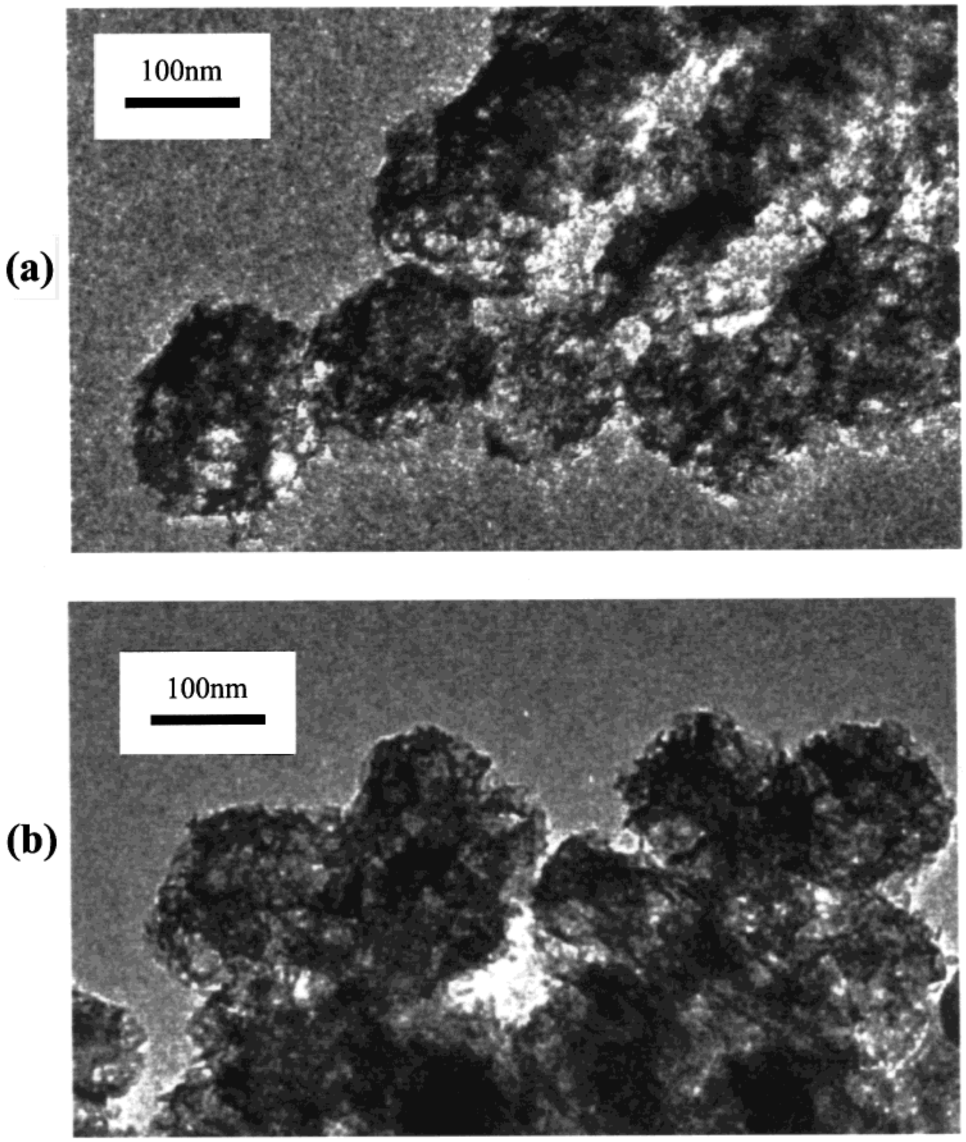

Figure 9. TEM images of porous carbon prepared from PTFE γ-irradiated with γ (total dose 3.12×10^3 C/kg) (a) and 5γ (total dose 1.56×10^4 C/kg) (b).

broad glass transition band near 280 °C splits into two parts with higher irradiation dose, accompanied by a few percent of weight loss. These results demonstrate that the depolymerization proceeds homogeneously with higher irradiation of the PTFE polymer. Figure 8 shows the adsorption and desorption isotherms of the porous carbons from the PTFE polymer irradiated at different doses. All of the samples treated in the same manner as the nonirradiated one were heated at 1000 °C. The micropores increased a little with the irradiation, but the amount does not depend on the magnitude of the dose. On the other hand, the amount of mesopores and/or macropores increased until a total dose of 5γ, but then decreased at 10γ. Table 3 lists the data for the pore parameters analyzed from the isotherm curves. It is obvious that γ-irradiation enhances only the meso- and/or macroporosity in the carbons obtained but the excess irradiation does not contribute to the further development of these pores very much. The TEM images of these porous carbons are shown in Figure 9. It may be recognized that the size of the aggregates in the sample from the γ-irradiated polymer is roughly 100−150 nm, smaller than that from the nonirradiated one, and that the morphology became more porous and coarse, as shown in Figure 9, although the existence of microporosity cannot be detected by TEM observation. Hence, it seems reasonable to conclude that the γ-irradiation of the polymer-induced morphological changes which result in carbons with more meso- and macroporous structure.

Conclusion

The carbonaceous materials prepared by direct reduction of PTFE powder with potassium vapor showed a feature in the pore structure; the carbons heat-treated up to 1000 °C gave a total surface area of 1385−1516 m^2/g and a mesopore area of 877−1126 m^2/g. Also micro- and mesopore volumes of the carbons were 669−844 and 200−233 mm^3/g, respectively. It is considered that these pores are mainly caused by defluorination and the removal of the byproduct, KF. When the carbons were treated at higher temperatures such as 2800 °C, however, these pores in the product were almost closed due to the shrinkage of the sample and to the development of stacking structures. The γ-irradiation of the starting polymer enhanced only the meso- and macroporosity in the carbons prepared. The result was explained in terms of the morphological changes of the polymer due to the irradiation.

Acknowledgment. Part of this work is supported by a grant-in aid for the “Research for the Future” Program from the Japan Society for the Promotion of Science (JSPS). We thank JSPS for financial assistance of this work. We also thank Prof. M. Kijima of the University of Tsukuba for measurement of the TGA and DTA.

CM010184W