

Full paper/Mémoire

Macro- and microporous carbon monoliths with high surface areas pyrolyzed from poly(divinylbenzene) networks

Joji Hasegawa, Kazuyoshi Kanamori*, Kazuki Nakanishi, Teiichi Hanada

Department of Chemistry, Graduate School of Science, Kyoto University, Kitashirakawa, Sakyo-ku, Kyoto 606-8502, Japan

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Abstract

Carbon monoliths with well-defined macropores and high surface areas were prepared by carbonization of macroporous poly(divinylbenzene) (PDVB) monoliths. The carbonization reactions of PDVB networks are studied by thermal analysis and FT-IR measurements. According to the measurement results, the PDVB networks are mostly pyrolyzed at 430 °C and their structures dynamically change to graphite-like structure between 600 and 700 °C. The macropore structure retained while the mesopores disappeared after carbonization. In addition, the surface area of the obtained carbons dramatically increased over 900 °C. The typical carbon monolith carbonized at 1000 °C for 2 h had a surface area of 1500 m² g⁻¹ and uniform macropores with a diameter of 1 μm. **To cite this article:** J. Hasegawa *et al.*, *C. R. Chimie* 13 (2010).

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1. Introduction

Porous carbons are attractive materials for a wide range of applications including adsorbents, filters, catalysts, hydrogen storage and electrodes for electrochemical devices [1–6]. Recently, macroporous carbon monoliths have been prepared by various methods [7–10]. In particular, macroporous carbon materials are prepared either by direct carbonization of precursor polymer gels such as resorcinol-formaldehyde gels (RF gels) [11,12] or the sacrificial templating method in a monolithic silica molds [13,14]. These macroporous carbons are promising materials because fluids such as gas and liquid in the pores are smoothly transported through macropores and the available surface area is

relatively large due to their inherent micropores. Moreover, carbon monoliths with narrow size distribution of pores are more desirable for attaining more homogeneous flow, which enables better access toward their interiors, and for applications requiring size-selectivity. The control of the pore properties of pores, however, is relatively difficult because of the lack of controllability of precursor porous polymer materials. Also, the templating method requires a lot of elaborate steps including etching of the silica mold with hydrofluoric acid.

We have previously reported that macroporous poly(divinylbenzene) (PDVB) monoliths with well-defined bicontinuous structure can be obtained by organotellurium-mediated living radical polymerization (TERP) [15] accompanied by polymerization-induced spinodal decomposition [16]. Whereas the conventional free radical polymerization tends to form the heterogeneous networks composed of aggregated-

* Corresponding author.

E-mail address: kanamori@kuchem.kyoto-u.ac.jp (K. Kanamori).

microgels due to an abrupt increase in the local degree of polymerization (DP), living radical polymerization enables to form the homogeneous networks owing to the gradual increase of DP with time. In the homogeneous networks derived from TERP, macropores are formed as a result of isotropic spinodal decomposition under the coexistence of a nonreactive polymer which induces instability in the network. It was found that the pore size and pore volume can be easily and independently controlled by varying starting compositions.

In this work, such macroporous PDVB monoliths were heat-treated in an inert atmosphere at various temperatures to directly carbonize, and the pore properties of the obtained carbons were examined by mercury porosimetry and nitrogen sorption measurements. Furthermore, the carbonization process of PDVB was investigated by thermal analysis and FT-IR.

2. Experiment

Divinylbenzene (DVB) (80% mixture of isomers) was purchased from Sigma-Aldrich Co. (USA). The solvent 1,3,5-trimethylbenzene (TMB) was purchased from Kishida Chemical Co., Ltd. (Japan). Polydimethylsiloxane (PDMS) (trimethylsiloxy-terminated, molecular weight $M_w = 9,000$ – $10,000$ and 2,2'-azobisisobutyronitrile (AIBN) were purchased from Gelest, Inc. (USA) and Tokyo Chemical Industry Co., Ltd. (Japan), respectively. Ethyl-2-methyl-2-butyltellanyl propionate (BTEE) was kindly supplied from Otsuka Chemical Co., Ltd. (Japan). All chemicals were used as received.

Macroporous PDVB gels as carbon precursors in this study were prepared according to the procedure reported previously [16]. In a typical synthesis, 0.7 g of PDMS was dissolved in a solution containing 5 mL of DVB and 8 mL of TMB. The mixture was stirred at room temperature for 3 min to be homogenized followed by degassing by ultrasonication for 3 min. Then, 0.029 g of AIBN was added to the resultant homogeneous solution and purged with nitrogen supplied using a stainless-steel needle through a silicone resin septum for 10 min. Subsequently, 0.08 mL of BTEE, a promoter of living radical polymerization, was injected followed by stirring until AIBN was dissolved. The resultant yellow transparent solution was transferred to an ampule and kept at 80 °C for 24 h. The obtained wet gels were washed with tetrahydrofuran (THF) and dried at 60 °C for 24 h.

The PDVB gels described above were heat-treated at different conditions under nitrogen flow with at a rate of 1 L min⁻¹. The samples for FT-IR measurement were

heat-treated at 300–800 °C for 6 h with a heating rate of 300 °C h⁻¹ while the samples for preparing carbon monoliths were carbonized at 250 °C for 2 h and then 600–1000 °C for 2 h.

The thermogravimetry (TG) and differential thermal analysis (DTA) measurements of PDVB gels were performed by TG–DTA (Thermo plus TG 8120, Rigaku Corp., Japan) at a rate of 5 °C min⁻¹ while continuously supplying N₂ at a rate of 100 mL min⁻¹. The FT-IR spectra were recorded on an FT-IR spectrometer (FT-IR-8300, Shimadzu, Japan) using ground samples that were mixed with KBr to give a 1 wt.% sample. A total of 100 scans were recorded with a resolution of 4 cm⁻¹. The microstructures of the fractured surfaces of the samples were observed by SEM (JSM-6060S, JEOL, Japan) and FE-SEM (JSM-6700F, JEOL, Japan). A mercury porosimeter (Pore Master 60-GT, Quantachrome Instruments, USA) was used to characterize the macropores of the carbon monoliths, while nitrogen adsorption–desorption (Belsorp mini II, Bel Japan, Inc, Japan) was employed to characterize the meso- and micropores of the carbons. For mercury porosimetry, the pore size was characterized using the Washburn equation assuming a cylindrical shape for the pores. For nitrogen adsorption-desorption, the surface area was calculated by the *t*-plot method. The crystal structure was confirmed by X-ray diffraction (Ultima III, Rigaku Corp., Japan) using CuK_α ($\lambda = 0.154$ nm) as the X-ray source.

3. Results & discussions

The TG–DTA curves for the PDVB gel and the FT-IR spectra of the heat-treated PDVB are shown in Figs. 1 and 2, respectively. It is found that the weight of the gel dramatically decreases around 430 °C in Fig. 1. The FT-IR spectrum of PDVB gel in Fig. 2 shows the adsorption

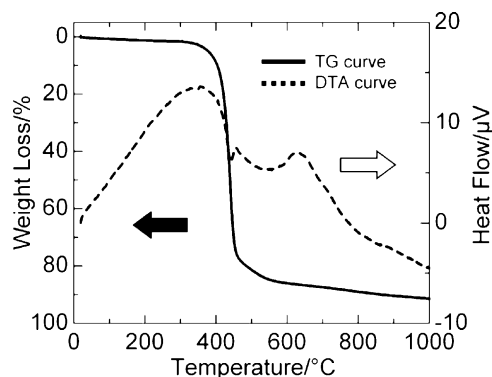


Fig. 1. TG and DTA curves obtained for the precursor PDVB gel with increasing temperature at a rate of 5 °C min⁻¹ in N₂ atmosphere.

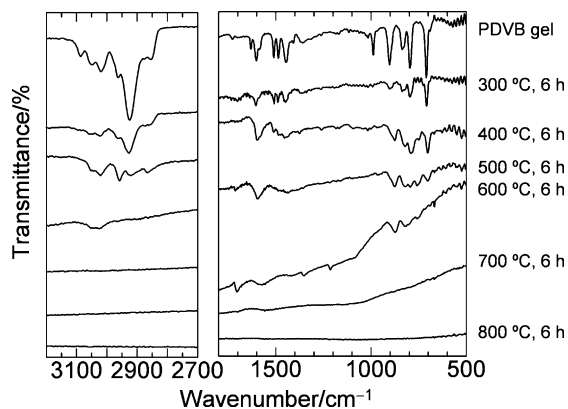


Fig. 2. FT-IR spectra of the PDVB samples heat-treated at different temperatures in the 3200–2700 cm^{-1} (left) and 1800–500 cm^{-1} regions (right).

bands at 2990–3100 cm^{-1} (Ar C—H), 2810–2990 cm^{-1} (CH_2), 1600 cm^{-1} , 1510 cm^{-1} (Ar C=C), 1450 cm^{-1} (CH_2), 900 cm^{-1} (Ar C—H), 700 cm^{-1} (Ar C—H). [17] According to the FT-IR spectra of the samples after heat-treatment, the most prominent structural change is the disappearance of the adsorption bands in the range of 2800–3100 cm^{-1} and 1450–1550 cm^{-1} , attributed to aromatic C—H and CH_2 , respectively, with increasing heat treatment temperature from 400 to 500 °C. This is because of the pyrolysis of the PDVB network [18] which can also be confirmed by TG–DTA curves. The adsorption band at 700–1000 cm^{-1} , which is assigned to the out-of-plane deformation mode of aromatic C—H, decreases in FT-IR spectrum of the sample treated at 500 °C. This means that dehydrogenation occurs not only in aliphatic moieties but also in aromatic ones at around 430 °C. Since the wave numbers of adsorption bands in this region somewhat vary with increasing temperature, the reaction of forming polyaromatic rings is considered to start simultaneously. Moreover, there is no adsorption in the FT-IR spectra of the samples treated at 700 and 800 °C. This implies that the chemical structure changes to graphite-like structure, which hardly exhibits any adsorption by a conventional FT-IR measurement [19,20]. The broad exothermic peak of DTA curve between 600 and 700 °C in Fig. 1 supports the enhanced formation of graphite-like polyaromatic rings at that temperature. The XRD patterns of prepared porous carbons in Fig. 3 shows that two broad diffraction peaks were observed for the samples heat-treated at 800 and 1000 °C while those peaks in the sample treated at 600 °C are relatively small. Since the broad peaks centered at 23° and 43° correspond to the diffractions from (0 0 2) and (1 0 0) planes of

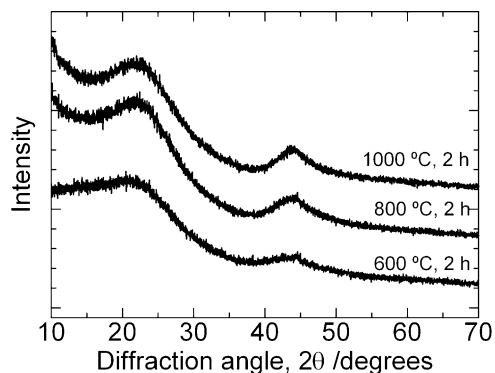


Fig. 3. XRD patterns of carbons carbonized at different temperatures.

disordered turbostratic graphite structure, respectively [10], the formation of turbostratic structure is mainly occurred between 600 and 800 °C.

Fig. 4 shows the macropore and mesopore structures of PDVB gel and carbon monolith observed by SEM and FE-SEM, respectively. It is found that the co-continuous structure with well-defined macropores is retained even after carbonized at 1000 °C as shown in part (b) and it is attributed to the shrinkage due to the partial pyrolysis during carbonization as described above. Fig. 5 shows the pore size and pore volume of the samples measured by Hg porosimetry and indicates that both of the pore size and pore volume decrease as the carbonization temperature increases. This is mainly because the shrinkage of the sample becomes larger with higher temperature. Although the sample weight decreases with increasing carbonization temperature and pore volume per unit weight is affected by the sample weight, it has only a little influence on the specific pore volume. Whereas the macropores are retained in the carbonized sample, the mesopore structure of carbon is different from that of PDVB gel as presented in Fig. 4 (c) and (d). The PDVB networks possessed various sizes of pores in the skeletons of the PDVB gel (part (c)), while no mesopore can be found in the carbonized skeletons (part (d)). Fig. 6 displays the N_2 adsorption–desorption isotherms of the PDVB gel and porous carbons. The N_2 isotherm patterns of the prepared carbons are classified as type-I according to the IUPAC nomenclature classification, [21] which indicates the existence of micropores. Fig. 6 also indicates that the mesopores in the PDVB gels thoroughly collapsed during the carbonization due to the shrinkage. On the other hand, micropores dramatically increase when heat-treated above 900 °C. This is because of the partial pyrolysis of the carbonized networks. In Fig. 7, it is shown that the amounts pyrolyzed during each heat-treatment temperature. The

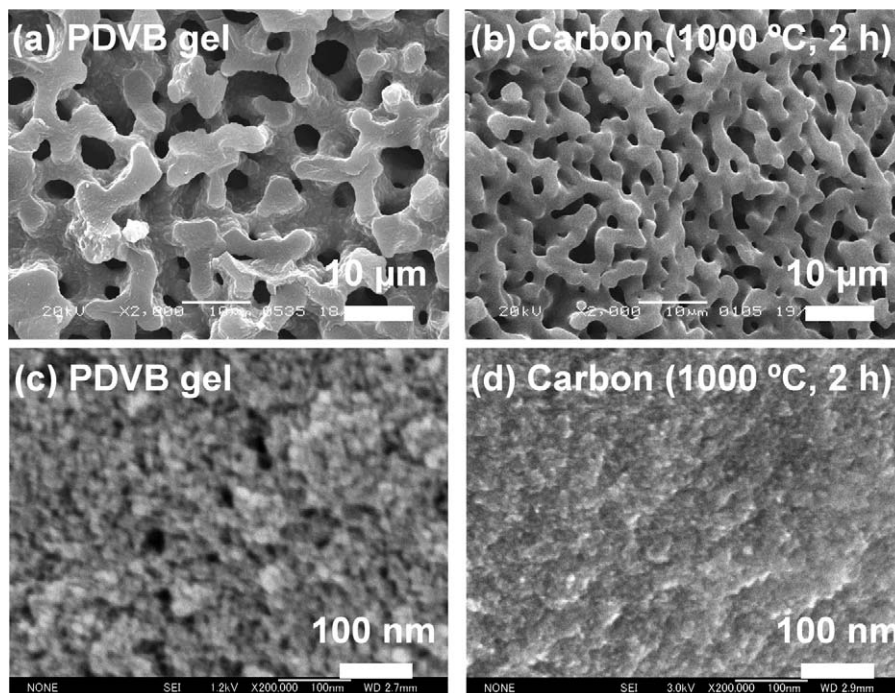


Fig. 4. SEM and FE-SEM images of the PDVB gel and the carbon carbonized sample at 1000 °C for 2 h. (a, b) Macropores of the precursor PDVB and the carbonized sample, respectively, and (c, d) mesopores of the precursor PDVB and the carbonized sample, respectively.

relations among the heat-treatment temperature, surface area and yield indicate that 20 wt.% of carbon can be obtained when carbonized at 800 °C, while only 15 wt.% and 13 wt.% of carbons can be obtained when carbonized at 900 and 1000 °C, respectively. The surface areas of pyrolyzed carbons become larger with increasing temperature, showing that the partial pyrolysis increases the amount of micropores because

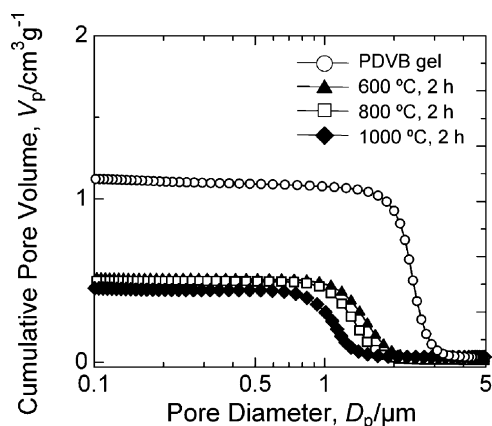


Fig. 5. Comparison of the cumulative pore volume of the PDVB gel and the carbon samples carbonized at 600, 800 and 1000 °C by Hg porosimetry.

a certain amount of carbon atoms are removed to generate microscopic interstices or pores. This process is similar to the more enhanced micropore formation during the activation process using carbon dioxide or steam etc. The porous carbon carbonized at 1000 °C has a surface area of about 1500 m² g⁻¹ as shown in Fig. 7.

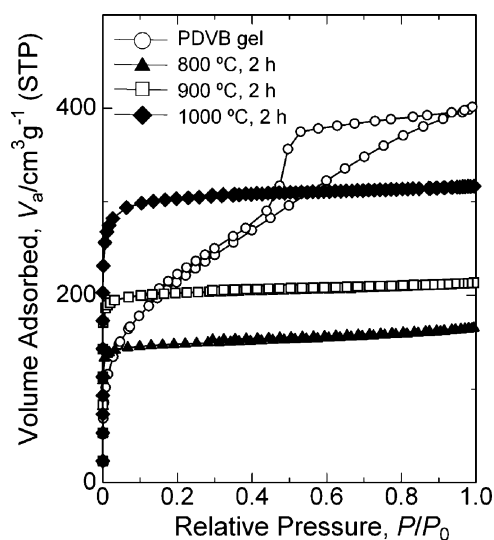


Fig. 6. Nitrogen adsorption–desorption isotherms of the PDVB gel and the carbon samples carbonized at 800, 900 and 1000 °C.

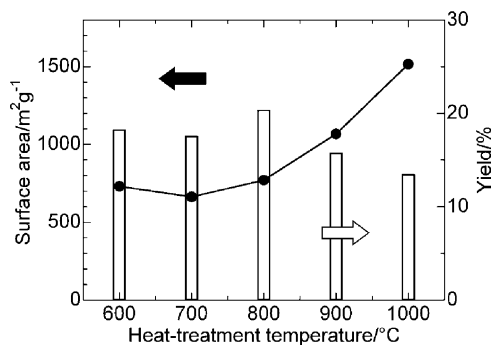


Fig. 7. Comparison of the surface areas and the yields of the carbons carbonized at different temperatures.

4. Conclusions

Macroporous carbon monoliths with sharp macropore size distributions are obtained by carbonization of macroporous PDVB monoliths. According to the TG–DTA measurement, PDVB network mostly pyrolyzes at around 430 °C. The FT-IR spectra indicate that the aromatic rings of PDVB network as well as the aliphatic moieties pyrolyze at that temperature. In addition, the change of the chemical structure to a graphite-like structure occurs between 600 and 700 °C.

The macropore structure is retained even after carbonized at 1000 °C for 2 h while the macropore size of the resultant carbon decreases as carbonization temperature increases. On the other hand, the mesopore structure of PDVB networks changes dramatically after carbonization, i.e. the mesopores in the skeletons of PDVB disappear due to the shrinkage of the network. Micropores of the carbon dramatically increase over 900 °C due to the partial pyrolysis of the carbonized network. The obtained carbon monolith carbonized at 1000 °C has uniform macropores with a diameter of 1 μm and a surface area of 1500 m² g⁻¹ owing to a lot of micropores.

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