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

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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 m<sup>2</sup> g<sup>-1</sup> 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-

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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<sup>-1</sup>. The samples for FT-IR measurement were

heat-treated at 300–800 °C for 6 h with a heating rate of 300 °C h<sup>-1</sup> 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<sup>-1</sup> while continuously supplying N<sub>2</sub> at a rate of 100 mL min<sup>-1</sup>. 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<sup>-1</sup>. 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<sub>α</sub> ( $\lambda = 0.154$  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

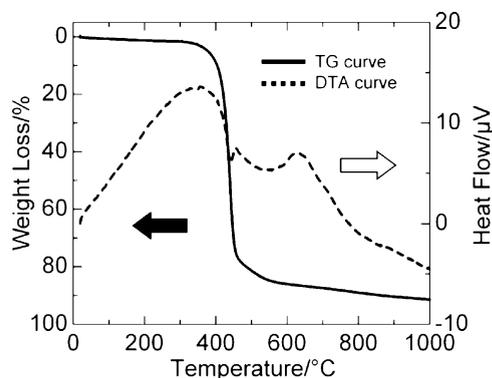


Fig. 1. TG and DTA curves obtained for the precursor PDVB gel with increasing temperature at a rate of 5 °C min<sup>-1</sup> in N<sub>2</sub> atmosphere.

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