Pyrolytic Conversion of Structured Polymeric Materials to Porous Carbons

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Preparation of porous materials that have specific porosity such as micropore, mesopore, and macropore have received considerable attention in recent years to be used in each purpose such as gas adsorbents, gas separation, catalyst supports, electrodes and active materials for electrical double-layer capacitors and batteries. Among them, porous carbon has merits of inherent thermal and chemical stability, electrical and thermal conductivity, low specific gravity, and so on, compared to various porous materials from inorganic, organic, and metal components. The activation method is the most popular to prepare high-porous carbons from carbonized or carbon-rich materials, but is difficult to control the porosity. Recently, porous carbons that have a regular porosity have been developed using templates of porous inorganic silicates [1]. However, this method requires a process of elimination of the template, and mass production is generally difficult. On the other hand, pyrolysis of pre-carbon materials under an inert gas atmosphere can afford molecular sieve carbons [2]. If the pyrolytic method can be applied in preparing porous materials that have a regular porosity, the mass production will be easier than the template method.

When microporous carbon is produced from materials by pyrolysis, in general, it is thought that their carbon precursors might have a rigid network to retain their fine structures during the carbonization process [3, 4]. In line with this thinking, several porous carbon materials were attempted to be prepared by pyrolytic conversion of polymeric materials under an inert atmosphere without activation process. The starting materials used here are conjugated polymers having carbon-carbon triple bonds, biopolymers from woody materials, organic (or metal-organic) frameworks, whose thermal degradation behaviors are investigated by thermal gravimetry / differential thermal analysis, in advance. The polymeric materials are structured as micelle particles, thin films, or hiper-branched polymer gel to increase their effective surface area and to produce microporosity on the carbonization in addition to inherent meso to macroporosity. The surface area and porosity of the carbonized materials are attempted to be controlled by these structurations of the starting polymeric materials under heating conditions with examining the starting and final materials by SEM and N_2 adsorption methods.

Chemical structures of polymers used in this study are summarized in Figure 1, and alkaline lignin (L) and cellulose were purchased from Tokyo Kasei and Aldrich, respectively. Water soluble cellulose (C) was prepared by partial etherification with benzyl bromide Poly(*m*-phenylenebutadiynylene) **P*m*PB**, which is carbonized in high yield around 90% to produce microporous carbon [3], is a reference sample to compare results obtained

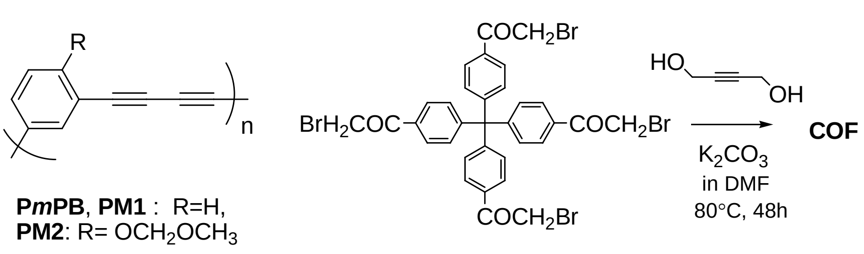

Figure 1. Chemical structures of **P*m*PB** derivatives and **COF**

from the structured polymers. **PM1** is a particle sample of **P*m*PB** prepared by emulsion polymerization of *m*-diethynylbenzene in water using sodium dodecylbenzenesulfonate (SDBS) as the surfactant. **PM2** is a particle sample prepared by precipitation of an emulsified P*m*PB derivative (in $CHCl_3$-H_2O with SDBS) from MeOH followed by H_2SO_4 treatment. **LCM** is a composite particle prepared by precipitation of an L-C (2:1) emulsion (in $CHCl_3$-H_2O with SDBS) from acetone. **LCF** is a cast film of L-C composite prepared from L and C (8:1) solution (H_2O). **COF** is a covalent organic framework, which is formed by condensation of a tetraphenylmethane derivative and 2-butyne-1,4-diol. All the polymers were heated from room temperature to 900°C at a constant heating rate under flowing of argon to obtain carbonized samples.

Table 1. Carbonization yields and surface parameters of the carbonized materials.

Carbonized Polymer	C-yield %	S_{BET} m^2/g	$S_{\alpha s}$ m^2/g	V_{micro} ml/g	V_{meso} ml/g	V_{total} ml/g
C-P*m*PB	89	471	540	0.20	0.03	0.28
C-PM1	47	638	727	0.14	0.45	0.81
C-PM2	51	781	1067	0.26	0.34	0.72
C-LCM$_W$	(38)	1760	1757	0.52	0.38	1.28
C-LCF	42	1069	1112	0.36	0.10	0.60
C-COF	55	782	1070	0.29	0.15	0.50

The carbonization yields and N_2 adsorption results of the carbonized samples were summarized in Table 1. Typical N_2 adsorption isotherms of the carbonized polymers are shown in Figure 2. Although carbonization yields of the structured polymers as particles (**PM1**, **PM2**, **LCMw**) went low to about 50% in comparison with that of **P*m*PB**, the surface areas of the carbonized samples apparently increased. This suggests that effective surface of the carbonized samples is provided by the structurations. In the case of **C-PM2**, a narrow distribution of mesopores is specifically recognized, which is probably due to void space of aggregated rigid fine particles. The highest surface area was observed for **C-LCMw** that was a washed sample with water after the carbonization to rinse a separated alkaline metal and salts. The thin film of the L-C composite thermally converted to a microporous carbon film with high surface area. Rigid **COF** was also effective to produce microporous carbon.

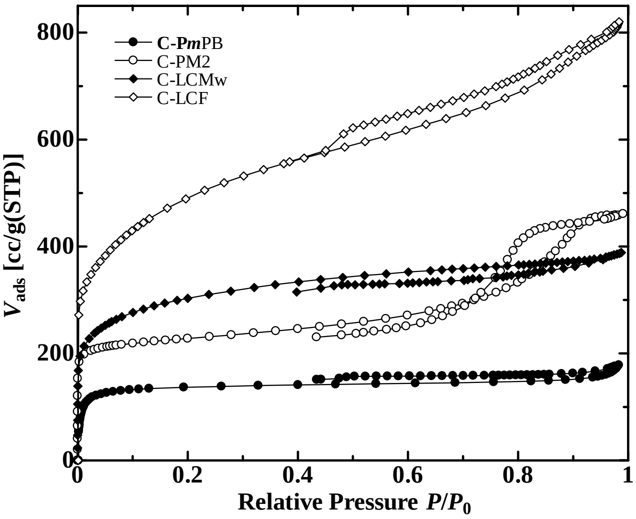

Figure 2. N_2 adsorption isotherms of the carbonized polymers at 77K

References
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