

# Preparation of Macroporous Carbons from Phase-Inversion Membranes

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## SYNOPSIS

Preparation of porous carbons from phase-inversion membranes was investigated as a control method of pore structure in carbon materials. The structure in carbon films was estimated by means of electron microscopy, mercury porosimetry, and gas-adsorption methods. When phase-inversion membranes of Kapton-type polyimide were carbonized, they maintained the film form and gave macroporous carbon films having high porosity. However, micro- and mesopore structures in the carbon films were not influenced by phase inversion in the polymer stage, and, thus, the macroporous carbons had a molecular sieve property similar to that of carbons prepared from nonporous polyimide films. A macroporous structure in cellulose membranes was similarly maintained through the carbonization step, but some of these were fractured or deformed owing to the large shrinkage. Polymer membranes have a capability as porous carbon precursors if they satisfy two requirements: solid-state carbonization and relatively high carbon yield. A composite membrane of a macroporous carbon with a dense carbon having an impervious ability was readily produced by shaping at the precursor stage. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

The pore structure in carbon materials is an important factor which influences their characteristics when used as electrodes, adsorbents, or carriers of catalysts. Micro- and mesopores in carbon materials provide a large area of the surface which chemical species can contact. Activation by use of steam, carbon dioxide, or some oxidation reagents is a popular method to prepare micro- and mesoporous carbons having a large surface area. Macropores influence the diffusion of chemical species into the inner surface of carbon materials. For example, application of carbon electrodes in fuel cells requires a macroporous structure that allows easy transport of fuel gases in the electrode.<sup>1</sup> The moldings of fibrous carbon, a macroporous carbon plate in which the pores are present among fibers, are employed for the cell.<sup>2</sup>

Structural control of polymeric materials is easier than it is for carbons. The pore size within surface-active layers of phase-inversion membranes, used

for various separation processes, e.g., hyperfiltration, ultrafiltration, and reverse osmosis, can be controlled to the order of a few or a few tens of nanometers.<sup>3</sup> If a polymer is carbonized, maintaining the shape and pore structures, the phase-inversion method is applicable to the design of carbon materials with various pore structures.

Aromatic polyimide films have become of interest as carbon precursors in recent years. Many workers have studied the graphitization behavior of these films because one of the polyimide films, commercially available "Kapton" film, is transformed into a highly oriented graphite film by high-temperature heat treatment.<sup>4,5</sup> We have already elucidated that the graphitizability of Kapton-type polyimide (PI) largely depends on molecular orientation in the film.<sup>6,7</sup> Another important characteristic of the films is that they are carbonized in the film form without fracture or deformation.<sup>8</sup> We have found that the resultant carbon films show molecular sieve properties comparable to zeolite 4A or 5A.<sup>9</sup> In addition, the carbon molecular sieve (CMS) films had high permselectivity for gases. In a short communication, we briefly reported on macroporous carbon films prepared from PI,<sup>10</sup> related to the application of the

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CMS films for gas-separation processes. In the present article, preparation of porous carbons from phase-inversion membranes was investigated in more detail as a method for controlling pore structures in carbon materials.

## EXPERIMENTAL

### Preparation

A solution of poly(4,4'-oxydiphenylene pyromellitic acid) (PAA) in *N,N*-dimethylacetamide (DMAc) was prepared according to the procedure by Dine-Hart and Wright.<sup>11</sup> The porous structure in PI film was formed by the phase-inversion method. The solution of PAA was cast onto a glass substrate and immediately immersed in nonsolvents for PAA polymer. Porous PAA gel prepared by this method was dried at 60°C *in vacuo* and subsequently imidized at 200°C. The nonsolvents used for phase inversion were benzene, toluene, xylene, and mixtures of DMAc and H<sub>2</sub>O. When DMAc/H<sub>2</sub>O mixtures were used, the cast film was successively immersed in 7/3, 6/4, 5/5, and 0/10 mixtures. The porous PI films thus obtained are indicated by the abbreviations for nonsolvents: BEN, TOL, XYL, and DMAc/H<sub>2</sub>O. Membranes of cellulose (CEL) and its derivatives used here are commercially available products (Fuji Photo Film Co.) usually employed for filtration. The published size of pores in CEL is 0.2 μm. A combination of a porous PI membrane with a nonporous one was achieved as follows: The PAA solution was cast onto a nonporous PI film prepared in advance and the macroporous structure was formed by phase inversion in DMAc/H<sub>2</sub>O mixtures.

The polymer membranes, sandwiched between polished graphite plates, were carbonized at 800°C for 1 h in flowing argon. The heating rate up to 800°C was at 3°C/min.

### Characterization of Porous Structure

Pores with sizes of more than 0.1 μm were observed by scanning electron microscopy (SEM). Pore-size distributions of film samples without grinding having pore diameters from 7.5 μm to 15 nm were measured by mercury porosimetry (Porosimeter 2000, Carlo Erba). Distributions of micropore size were evaluated by adsorption (25°C) of three gases having different molecular sizes, CO<sub>2</sub>, butane, and isobutane,<sup>12</sup> the sizes of which are 0.33, 0.43, and 0.50 nm, respectively. Mesopores with diameters of about

2–30 nm were estimated by means of adsorption isotherms of nitrogen at 77 K. The isotherms were analyzed by the  $\alpha_s$  method<sup>13,14</sup> using a standard isotherm of Carrott et al.<sup>15</sup> A commercial automatic apparatus (Sorptomatic 1800, Carlo Erba) was used for the adsorption measurements.

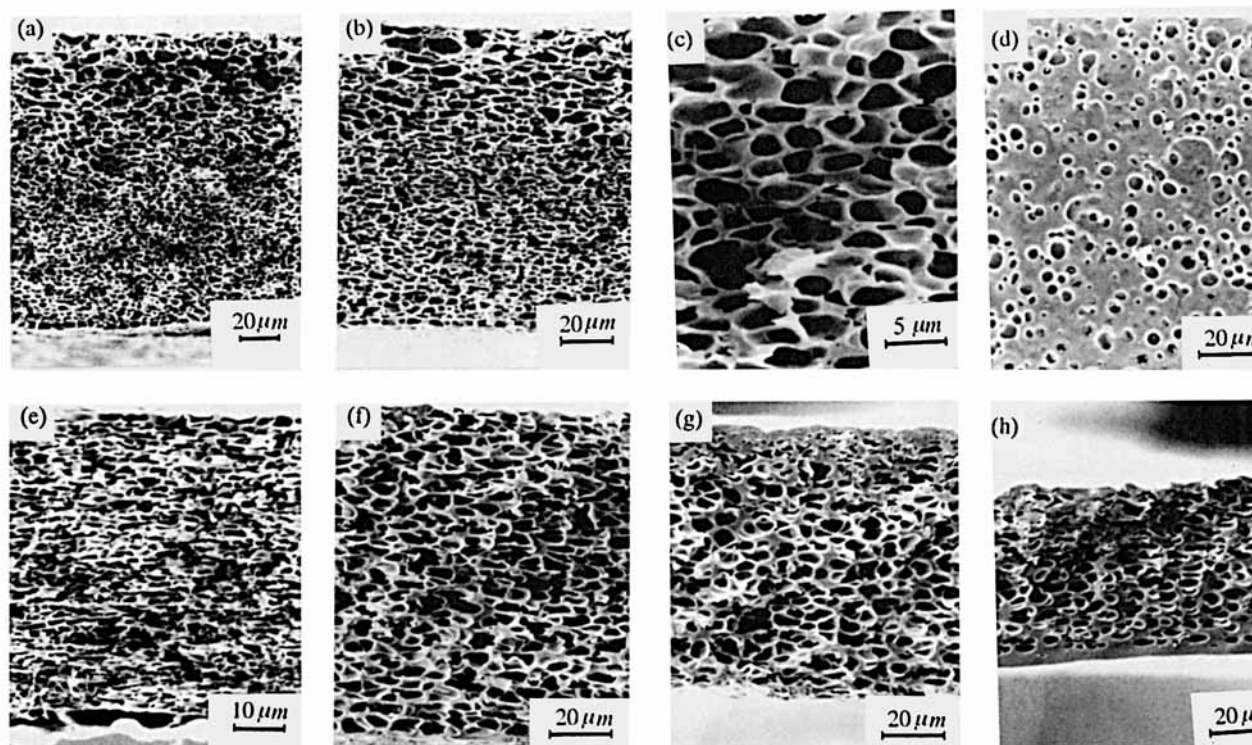
## RESULTS AND DISCUSSION

### Macroporous Carbons Prepared from Polyimide Membranes

Macroporous features in a cross section of DMAc/H<sub>2</sub>O membrane are shown in Figure 1(a). The pores are approximately uniform, although the size of the pores near each surface of the membrane is somewhat different. Such an asymmetric structure is considered to be due to differences of solvent extraction conditions in the phase-inversion process between the glass substrate side and the opposite side.

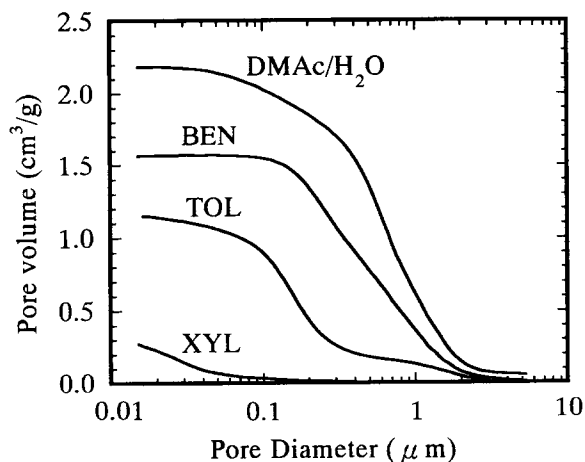
Film shrinkage of about 20% was observed during carbonization up to 800°C, but the porous structure was unchanged except for the size [Fig. 1(b)]. The degree of shrinkage and the carbon yield (53%) were almost the same as those of nonporous PI films providing CMS.<sup>9</sup> The carbonization mechanism of the PI polymer was extensively reported elsewhere.<sup>6,16</sup> The pores shown in a cross section are connected to each other through holes with sizes under about 1 μm on the pore walls [Fig. 1(c)]. Holes of 1–5 μm diameter are observed on a surface [Fig. 1(d)]. It was proved that an organic liquid such as benzene dropped on a surface easily passes through the film to the other side. The porous structure was maintained after further heat treatment up to 2800°C [Fig. 1(e)]. The structures in PI membranes formed by the phase inversion largely depended on the kind of nonsolvents, but all of them were carbonized, maintaining the forms of the precursors. When a series of organic nonsolvents such as benzene, toluene, and xylene were employed for cast solutions having the same thickness, the porosity of porous carbons is different, as is suggested by the features in sections [Fig. 1(f)–(h)], i.e., film thickness is decreased in that order and the pore walls seem to become thick.

Accumulative curves of pore volume from 7.5 μm to 15 nm are shown for macroporous films in Figure 2. The pore volume in DMAc/H<sub>2</sub>O carbon goes up to over 2 cm<sup>3</sup>/g, corresponding to about 70–80% of the film volume. The result of mercury porosimetry indicates that most of the pores in DMAc/H<sub>2</sub>O car-



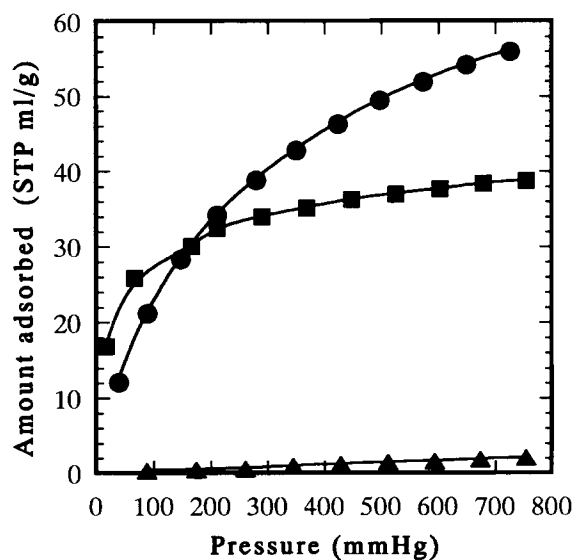
**Figure 1** SEM micrographs of porous films. These are cross sections except for (d) showing a surface morphology: (a) DMAC/H<sub>2</sub>O; (b–d) DMAC/H<sub>2</sub>O carbon; (e) DMAC/H<sub>2</sub>O treated at 2800°C; (f–h) carbons prepared from BEN, TOL, and XYL, respectively.

bon have sizes of 2–0.2  $\mu\text{m}$ . This is because mercury permeates into the film through such sizes of holes connecting the large pores [Fig. 1(c)]. The total pore volumes in BEN, TOL, and XYL carbons decreased in that order, as is expected from the result of SEM observations [Fig. 1(f)–(h)].

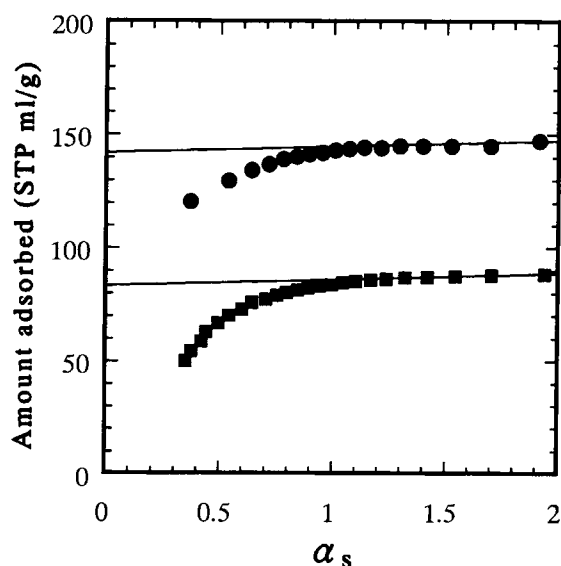


**Figure 2** Accumulative curves of pore volume in the porous films carbonized at 800°C.

Micro- and mesopores in the macroporous films were estimated by gas-adsorption methods. Non-porous PI film treated at 800°C gives a CMS having



**Figure 3** Adsorption isotherms (25°C) of gases having different molecular sizes on BEN carbon: (●) CO<sub>2</sub>; (■) butane; (▲) isobutane.



**Figure 4**  $\alpha_s$  plots of nitrogen for BEN (●) and nonporous PI (■) films treated at 800°C.

micropores with sizes below 0.50 nm.<sup>9</sup> The macroporous carbon films showed the same CMS properties; carbon dioxide and butane were adsorbed on BEN carbon but isobutane was hardly adsorbed (Fig. 3), indicating that the micropore size is below 0.50 nm. The sieve effect is comparable to that of zeolite 5A.<sup>12</sup>

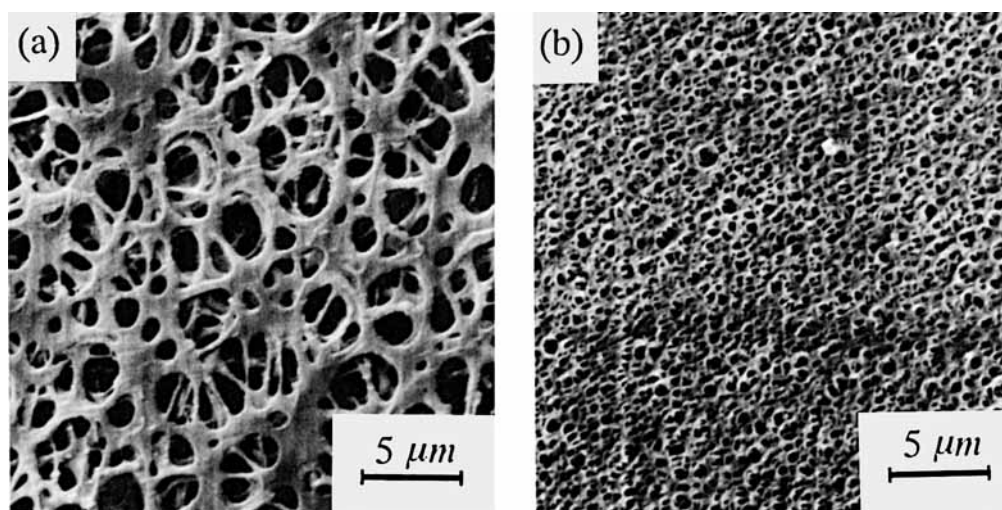
Micropore volumes determined by  $\alpha_s$  plots (Fig. 4) using adsorption isotherms of  $N_2$  at 77 K were 0.13 and 0.22  $\text{cm}^3/\text{g}$  for carbon films prepared from nonporous PI and BEN, respectively. On the other hand, the external surface areas are 9–10  $\text{m}^2/\text{g}$  for

both films. The results suggest that both carbon films have microporous structures with few mesopores. The difference of micropore volumes between the two types of films may be due to the low diffusivity of nitrogen into micropores which are located on inner positions of the carbon film derived from nonporous PI. Actually, estimation of micropore volume in microporous carbon by nitrogen adsorption at low temperature has been known to be difficult.<sup>17</sup> In conclusion, the phase-inversion method has little influence upon the micro- and mesopore structure in PI carbons.

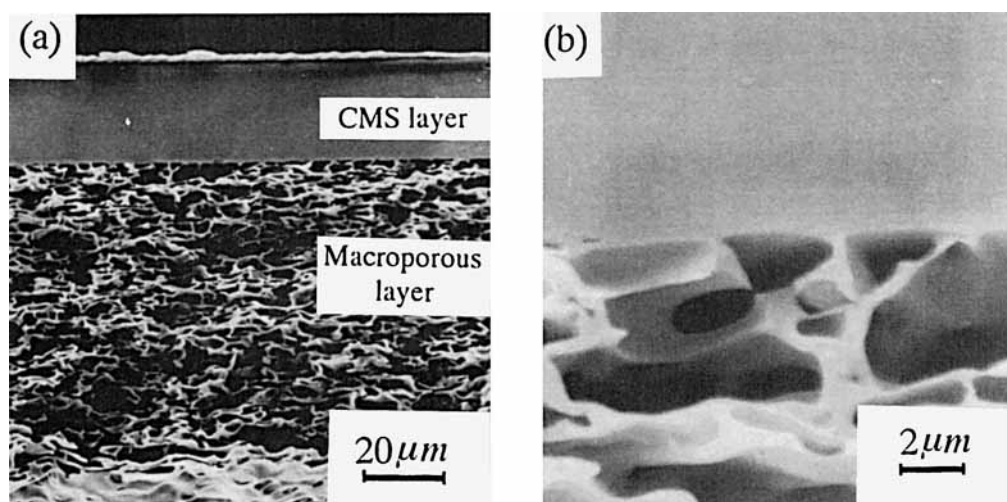
### Macroporous Carbons Prepared from Cellulose Membranes

Phase-inversion membranes prepared from cellulose and its derivatives are widely used for separation processes. The membranes with various pore structures are commercially produced. Films of cellulose derivatives such as cellulose acetate or the nitrate lost their form on carbonization. On the other hand, CEL membranes gave porous carbons, though some of them were fractured or deformed owing to the low carbon yield (ca. 10%) and the large shrinkage of film size (50% of the pristine film). An asymmetric structure in CEL membranes was maintained through the carbonization (Fig. 5), and pores with the size of a few thousands nanometers remained on the outlet side as well.

The polymer precursors have to satisfy two requirements in the carbonization step to yield porous carbons by the present method. The first and ab-



**Figure 5** Surface morphology on both sides of a CEL carbon film: (a) inlet and (b) outlet of filtrate when used as a filter membrane.



**Figure 6** (a) A cross section of the composite carbon film and (b) enlargement of the boundary between CMS and macroporous layers.

solute condition is that the carbonization proceeds in the solid state without melting. The second is to give a high carbon yield, minimizing the size change, because large shrinkage causes deformation or destruction such as with some CEL membranes. However, various polymer membranes have a potential as porous carbon precursors, because the stabilization method applied for production of carbon fibers realizes the solid-state carbonization and enhancement of carbon yield.

### Fabrication of Porous Carbons

Asymmetric and hollow-tube structure enhances the efficiency of separation processes. A combination of a thin active layer with porous supports is also effective. In the case of electrochemical applications of porous carbon, a similar procedure is employed in order to assemble a cell. For instance, a porous carbon plate is incorporated with a gas-shielding material in fuel cells. The control of product shape suited to practical applications is needed for porous materials.

Fabrication in a polymer stage is much easier than that of carbon. Hollow fiber and asymmetric membrane, if prepared by a single polymer which satisfies the requirements above mentioned, is expected to be carbonized, maintaining forms. On the other hand, composite membranes have the greatest problem in maintaining the shape after carbonization. The combination of plural materials showing different carbonization behaviors or thermal properties may cause deformation during heat treatment. The PI used, however, gives two types of carbons,

i.e., CMS film having permselectivity and the macroporous one prepared by the present method. The CMS film prepared from the nonporous PI precursor is applicable to gas separation, whereas the impermeous ability is close to that of glasslike carbons used as a shielding material.<sup>9</sup> Actually, a composite membrane of PI was carbonized without any deformation, and adherence between the two carbon layers was excellent (Fig. 6). The shape of porous carbon films can be variously modified in the precursor stage. The porous carbon films prepared by the present method are expected to be used as electrodes or separation membranes possessing heat resistance and corrosion resistance.

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