Morphology-Retaining Carbonization of Honeycomb-Patterned Hyperbranched Poly(phenylene vinylene) Film

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ABSTRACT: Ordered porous materials are of great technological interest for use as separation, catalysis, adsorbents, and electronic devices. We report here a fabrication of honeycomb-patterned porous films from fluorescent hyperbranched poly(phenylene vinylene) (hypPPV) by breath figure method and the thermal conversion of this film to macroporous carbon. This hexagonal porous film is very thermally stable and retained its structure at up to >600 °C. After the heating, carbonization of hypPPV occurred, and black porous carbon film was obtained. Additionally, because π-conjugated hypPPV has many vinylene moieties at its terminus, the photo-cross-linking reaction easily proceeds without the collapse of the honeycomb structures. This cross-linking reaction rendered the honeycomb films completely insoluble in organic solvents. Because of the provided high thermal and chemical stability, the honeycomb films are a new class of microstructured materials that is promising for many applications such as durable electroluminescence devices, bandgap materials, adsorbents, electrodes, and solvent-resistant porous membranes.

Porous carbons are important materials used in a wide field of applications including catalysis and adsorption and as materials for electrochemical devices.[1,2] Because the pore structures strongly influence the properties of porous carbons, a wide variety of synthetic methods of carbon architectures with controlled size and arrangement of pores is critically needed. To achieve this goal, the synthesis of porous carbons using defined solid templates has been extensively studied.[1,2] Structural features of the voids of templates are transferred to carbon materials by filling the templates with the carbon precursor, followed by carbonization. Zeolite,[3] mesoporous silicas,[4] and colloidal crystals[5] have been widely used as templates. However, these templates have to be removed selectively by elaborate procedures such as strong acid or base treatment. Here, we show a solid-template-free synthesis of well-ordered macroporous carbon. The key to our method is the use of hyperbranched poly(phenylene vinylene) (hypPPV, Figure 1a) as an efficient carbonizable precursor. We fabricate a microstructured hypPPV film and directly convert it to carbonaceous film retaining its structure. We also demonstrate that the photo-cross-linking under UV irradiation readily renders the microstructured hypPPV film solvent resistant.

We used water-droplet templating method[6−9] (often referred to as breath figure method) as a microfabrication process. When polymers are cast from appropriate solvents that are immiscible with water on solid substrates under humid conditions, films with hexagonally packed pores (so-called honeycomb films) can be obtained. Shimomura and coworkers clearly showed that condensated water droplets on the surface of the organic solvents packed into hexagonal arrays and worked as a template.[6,10] Honeycomb films fabricated in this way are useful for separation membranes, picoliter beakers,[11] precursors for porous ceramic materials,[12] photovoltaic applications,[13] templates for cell growth,[14] microarrays of nanoparticles,[15] and the fabrication of microlens arrays.[16]

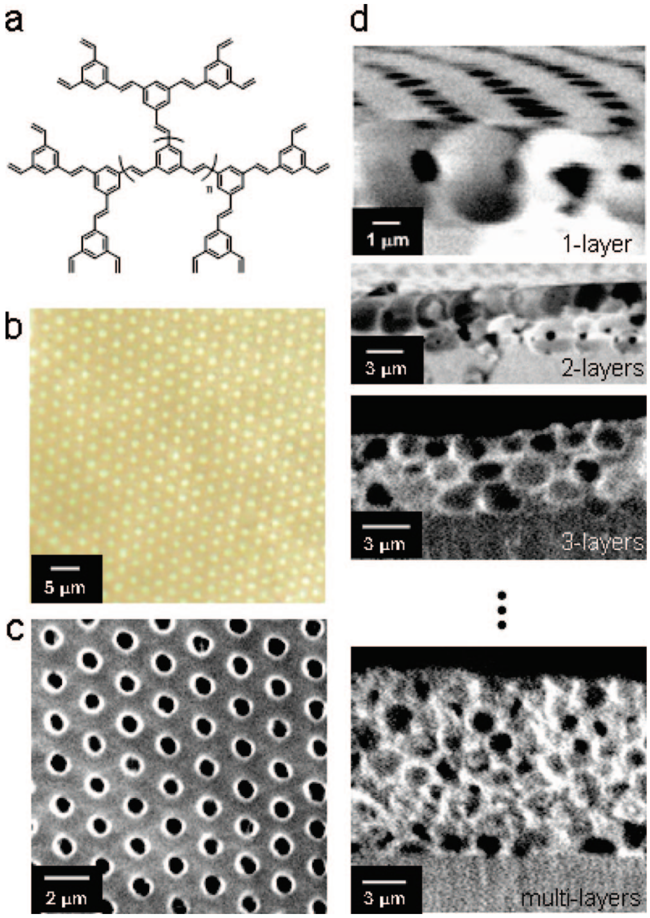

Figure 1. Honeycomb films of hyperbranched poly(phenylene vinylene) (hypPPV) made via breath figure method. (a) Chemical structure of hypPPV. (b) An optical microscope (OM) image in large area. (c,d) Scanning electron microscope (SEM) images. (c) Top view. (d) Cross sections prepared by simple freeze fracturing.

PPV is one of the most important promising conjugated polymers for optoelectronic devices.[17] Linear PPV without any

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side chains is also known to be an efficient carbon precursor arising from its high carbon content.[18,19] However, it is difficult to fabricate intact linear PPV in solution process because of its insolubility. Recently, hyperbranched PPV[20,21] was found to have good solubility in common organic solvents without any solubilizing side chains because of the weak intermolecular interactions induced by the large steric hindrance between the branches.[21]

To confirm whether hypPPV can be fabricated by breath figure method, we synthesized hypPPV according to a previous report.[20] The weight-averaged molecular weight and polydispersity index of hypPPV, determined by gel permeation chromatography, were 1700 and 1.2, respectively. By a simple casting from $CHCl_3$ or CS_2 under the flow of humid air, we could obtain honeycomb films. Figure 1b,c shows typical optical microscope (OM) and scanning electron microscope (SEM) images of the honeycomb film, respectively. These pictures clearly display highly arranged, hexagonally close-packed air holes. The area of well-ordered single hexagonal lattice without grain boundaries reaches more than thousands of squared micrometers (Figure 1b). As reported elsewhere,[8,22−24] the decrease in the concentration of the polymer solution resulted in an increase in the pore size. From SEM observations, the average diameter of the pores of the honeycomb films, which were obtained from 8, 5, and 3 mg/mL solution in CS_2, were 0.47 ± 0.09, 0.86 ± 0.12, and 4.8 ± 1.1 μm (mean ± S.D.), respectively. The films were fractured open, and the cross sections were observed under SEM (Figure 1d). Films with mono- and multilayers of the pores were formed depending on its thickness. This is probably because water droplets can sink into the organic solvents by convective flow during the formation of the honeycomb film.[8] The regularity of the pores in the vertical direction decreases with increasing film thickness. The neighboring pores are connected to each other by small pores on the wall.

Under UV excitation, this honeycomb film emitted blue light (Figure 2a). Figure 2b shows the fluorescence spectrum of the hypPPV film, which presents the fluorescence maxima located at 444 nm. By irradiating the high-energy UV light, hypPPV could be easily cross-linked, and the honeycomb structure of the film was fixed. Figure 2c shows the change in the UV−vis absorption spectra of the hypPPV film by UV-irradiation. The absorption peak with $\lambda_{max} = 318$ nm arising from stilbene units[25] was slightly shifted to a lower wavelength in the course of the photoreaction, which indicated a reduction in the conjugated length. Additionally, the absorption markedly decreased with increasing UV irradiation time, which indicated the loss of conjugated double bonds. From FTIR spectra, the consumption of the double bonds is confirmed by the nearly complete disappearance of the peak at 959 cm^{-1} (*trans*-vinylene). Under high-energy UV irradiation, the vinyl groups are known to be involved in complicated reactions including dimerization ([2 + 2] cycloaddition), oxidation, and radical reaction to form a 3D network.[26,27] The extent of the photoreaction degree, estimated by the absorption at $\lambda = 318$ nm (Abs at initial state is 0% and at zero absorption is 100%), is plotted against UV irradiation time (Figure 2d). This plot shows that irradiation for 3 min is enough to accomplish 50% progress of the photoreaction. Because hypPPV has a large number of reactive vinylene moieties at its outer part, the intermolecular cross-linking reaction effectively occurred.[20,26,27]

The cross-links given by the irradiation of UV light make the honeycomb film solvent-resistant. The films irradiated for 1 and 2 min were still soluble and partially soluble, respectively. However, after ≥5 min of UV irradiation, the honeycomb structure became completely insoluble in any organic solvent such as $CHCl_3$, CS_2, THF, and DMF, which had been good solvents for the original un-cross-linked hypPPV. Thus, we have successfully imparted resistance to organic solvents to the honeycomb films prepared via breath figure method. This cross-linked honeycomb film can be a good porous membrane for applications that require organic solvent resistance.

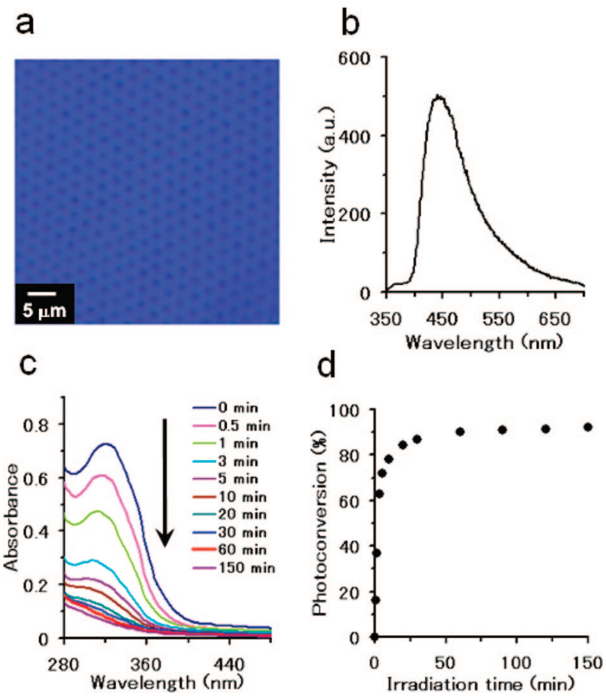

Figure 2. Photo-cross-linking of honeycomb hypPPV films. (a) OM image of a blue-light-emitting honeycomb film of hypPPV under UV irradiation at wavelength of 365 nm. (b) Fluorescence spectrum of hypPPV film. (c) UV−vis absorption spectra of hypPPV film after UV irradiation for the indicated times. (d) Time course of the photoconversion degree estimated by UV absorption at 318 nm.

Recently, it was reported that a honeycomb film made from four-armed star shaped poly(D,L-lactide) (PDLLA) functionalized with photoreactive methacrylate end groups was photo-cross-linkable when photoinitiator was added.[23] However, during the irradiation of UV light, the honeycomb structure is apt to soften and collapse. In contrast, in our hypPPV film, no morphological deformation occurred by UV irradiation (Figure S1 in the Supporting Information).

To obtain carbonaceous honeycomb films, the hypPPV honeycomb films were placed on a hot stage and were heated to 600 °C at a rate of 10 °C/min under a N_2 atmosphere. During the thermal treatment, originally yellow honeycomb films turned orange, red, and finally black (Figure 3a,b) because of the carbonization of hypPPV. Significantly, the microfabricated honeycomb morphology of hypPPV was carbonized without deformation (Figure 3a). Thus, microfabricated hypPPV is an effective precursor to microstructured carbon. The film shrinkage was 20% of hyp PPV's length. From the thermogravimetric analysis (TGA) of hypPPV (Figure S2 in the Supporting Information), the carbonization yield was 60%. The layered bubble 3D structures of the precursor were also maintained (Figure S3a in the Supporting Information). Cell-like structures were still connected by small pores on walls (before carbonization, Figure 1d; after carbonization, Figure S3b (arrow) in the Supporting Information). SEM observations of the carbonized films (Figure 3c) revealed that the average pore diameter was also reduced ca. 20% when compared with that before heat treatment.

There have already been a few attempts to obtain semiconducting honeycomb films from PPV.[28−30] In these studies, however, copolymers of PPV or PPV with alkyl side chains

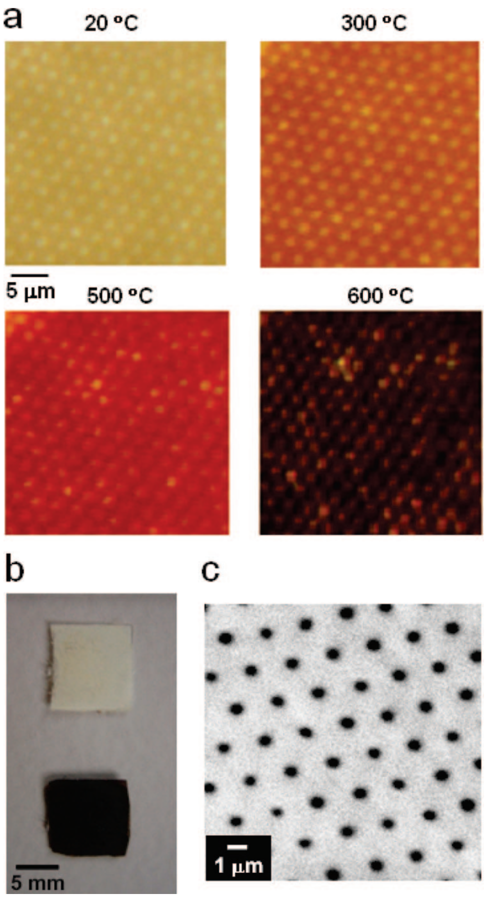

Figure 3. Carbonization of honeycomb hypPPV films. (a) OM images of a hypPPV film in the process of heating to 600 °C. (b) Photograph of hypPPV films before (upper) and after carbonization at 600 °C (bottom). (c) SEM image of the carbonized honeycomb film.

were used as soluble PPV analogues. These PPV analogues are unsuitable for use as precursors of carbon because the comonomers and the side chains would cause a significant decrease in the carbonization yield. Hence, the use of soluble dendritic hypPPV without any side groups is the key to accomplishing the morphology-retaining carbonization of polymeric honeycomb films. Govor and coworkers showed that a hexagonal carbon network can be obtained by heating honeycomb nitrocellulose films.[31−33] In this case, only the monolayer structure was obtained, and the walls of the honeycomb structure were very thin. In contrast, ours is porous carbon rather than a carbon network, and it consists of mono- to multilayers and has thick walls (Figures 3c and S3 in the Supporting Information), as we mentioned above.

In summary, the long-range ordered hexagonal packing of pores in films of hypPPV was attained by utilizing the standard breath figure method. The hypPPV honeycomb films exhibit exceptionally high thermal and chemical stability when compared with previous reports.[23,34,35] Furthermore, simple thermal treatment converts the honeycomb hypPPV film to the carbonaceous film with the same porous structure. Our concept of obtaining porous carbons, that is, patterning the precursor polymer films, followed by direct carbonization without deformation, does not require the removal of solid templates by cumbersome procedures. Therefore, it is envisaged that this approach can be a simple and facile fabrication method for well-ordered porous carbon. Detailed characterization of the carbonized honeycomb film is currently under way.

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Supporting Information Available: Experimental details, SEM image of a photo-cross-linked honeycomb film, TGA analysis curve of hypPPV, and SEM images of the carbonized honeycomb films. This material is available free of charge via the Internet at http://pubs.acs.org.

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