Preparation of Porous Conjugated Polymers Using Amphiphilic Triblock Copolymers PEO–PPO–PEO as Structure-directing Agents

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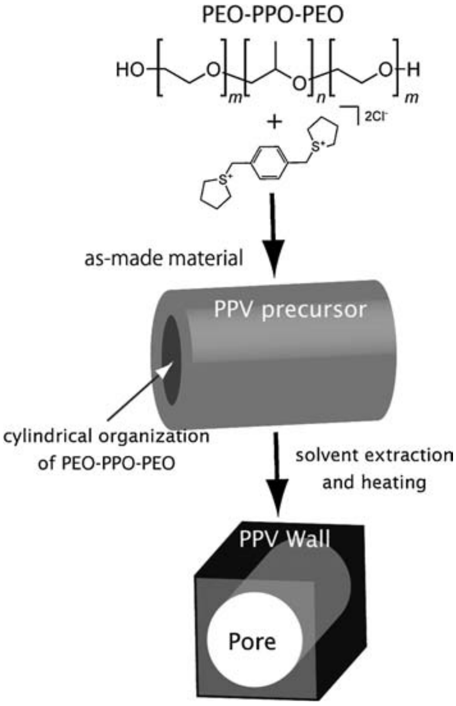
Use of amphiphilic triblock copolymers PEO–PPO–PEO to direct the organization of polymerizing organic monomers has resulted in the preparation of porous poly(*p*-phenylene vinylene) with an uniform pore size of 3.8 nm. The fluorescence was significantly quenched by the immersion in the solution of vitamin K_3.

Mesoporous materials containing pores with diameters between 2 and 50 nm have attracted special attention because of their enormous potential for many applications, such as catalysis, separation, sorption, gas sensing, optics, and drug delivery.[1] In this context, mesoporous inorganic oxides have been synthesized using amphiphilic organic surfactants based on liquid-crystal template sol–gel polymerization.[2] Recently, Zhao et al. reported the preparation of highly ordered mesoporous organic materials using amphiphilic triblock copolymers as a template.[3] Polymerization of phenol around supramolecular organizations made of triblock copolymers resulted in the formation of highly ordered hexagonal and cubic organic mesostructures. This process can be applicable to construct mesostructured organic materials using other organic monomers having unique or superior functionalities.[4] In this study, we report a synthesis of porous conjugated polymers having nanometer-scale channels by the amphiphilic surfactant-templating approach. We chose poly(*p*-phenylene vinylene) (PPV) as a polymer matrix of mesostructured organic material. While the enhancement of optoelectronic properties of PPVs incorporated into the organic and inorganic channels has been widely investigated,[5] the channels were fully occupied with guest PPV. The large surface area and channels within the porous conjugated polymers may provide a unique microenvironment for molecular recognition and transduction.

To produce the material, water-soluble monomer, *p*-xylylene bis(tetrahydrothiophenium chloride) (0.6 g), was added to an aqueous solution (7.0 mL) of amphiphilic triblock copolymer (PEO–PPO–PEO, $M_n = 5800$ g/mol, EO:PO:EO = 20:70:20) (0.17 g) containing sodium hydroxide (8.4 mg), and kept for 24 h (Scheme 1). In the absence of PEO–PPO–PEO, the monomer is polymerized to give a homogeneous aqueous solution of the PPV precursor, poly(*p*-xylylenedimethylsulfonium chloride).[6] On the other hand, polymerization in the presence of PEO–PPO–PEO formed a pale-yellow precipitation, suggesting the generation of composites between PEO–PPO–PEO and PPV precursor. The composite was obtained by collecting the precipitate **1** (as-made materials) and removing PEO–PPO–PEO by solvent extraction with methanol and acetone.[7] The product was heated at 220 °C in vacuo to give an orange solid **2**.[6] The FT-IR spectrum of **1** is the sum of PEO–PPO–PEO and PPV precursor. After the solvent extraction, the intensities of two IR absorption peaks at 1100 and 2980 cm^{-1} attributed to the C–O–C and C–H groups belonging to PEO–PPO–PEO decreased, indicating the release of PEO–PPO–PEO from the composites. Furthermore, **2** after the thermal treatment exhibited new two peaks around 1600 and 935 cm^{-1} corresponding to the vibrational mode of C=C and the C–H out-of-plane bending of *trans*-vinylene, respectively.[8] The appearance of new peaks reveals the conversion of the PPV precursor to the conjugated PPV within the solid. The thermogravimetric curve of **2** in air showed that weight loss of about 18% occurred at 250 °C. The weight loss at 250 °C can be assignable to the decomposition of PEO–PPO–PEO,[2] indicating that PEO–PPO–PEO partially remains within the composites after the solvent extraction and the heating process.



Scheme 1. Schemeatic representation of the procedure used to prepare porous PPVs.

Transmission electron microscopy (TEM) images of **2** show the presence of pores of average 4.1 nm diameter and 3.8 nm wall thickness with one-dimensional channels (Figure 1). The dark contrast in TEM images ascribed to the accumulation of aromatic PPVs, and the observed diameter of pores almost agree with that of mesoporous silica SBA-15.[2] The nanoscale structure observed in TEM images is evidence of the domain-selective polymerization of organic monomer for PPV in the PEO do-

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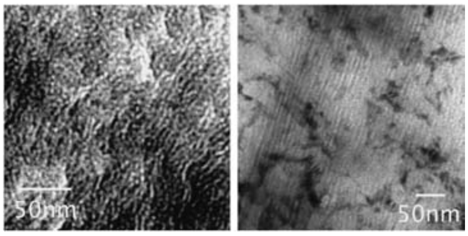

Figure 1. TEM images of **2** viewed from the different directions.

mains of the cylindrical organizations. However, the ordering of pores observed in the TEM image is poor compared to SBA-15. The XRD pattern of **2** showed a broad peak at *d* spacing around 4.0 nm, also indicating the poor ordering of channels. The ordering of cylindrical organization of PEO–PPO–PEO may be disarranged because of the swelling of PPV wall during the solvent extraction and heating processes. Nitrogen adsorption–desorption isotherms of **2** yielded a type-IV curve with a sharp capillary condensation step at $P/P_0 = 0.45$–0.70, characteristic in mesoporous materials with cylindrical channels. The adsorption data indicate a high Brunauer–Emmett–Teller (BET) surface area of $155\,m^2\,g^{-1}$ and pore volume of $0.17\,cm^2\,g^{-1}$. The observed BET surface area was large compared to that of the pure PPV prepared in the absence of PEO–PPO–PEO (BET surface area was less than $2\,m^2\,g^{-1}$). The pore size distribution calculated by the Barrett–Joynes–Halenda (BJH) method from the adsorption curve is narrow, indicating a uniform pore structure with a pore diameter of 3.8 nm. This pore diameter is in agreement with that observed in TEM. Our results show the successful syntheses of porous PPVs having large surface area and cylindrical mesoporous channels by using the amphiphilic PEO–PPO–PEO as a structure-directing agent.

When excited at 375 nm, the porous PPV **2** exhibited an emission band with a maximum at 534 nm (Figure 2). The position of emission band is almost in agreement with that of the pure PPV,[6] indicating that the walls of porous materials are composed of conjugated PPVs. The fluorescence changes can be used as an output signals for molecular recognition events.[9] A fluorescence quenching study was carried out by dispersing powdered **2** (1.0 mg) in degassed DMF solution of vitamin K_3 (2-methyl-1,4-naphthoquinone 6.0 μM) as a quencher.[10] While the pure PPV lacking pores showed no fluorescence quenching in the solution of vitamin K_3, the fluorescence of **2** was significantly quenched by 90%. The fluorescence quenching is caused by an electron or energy transfer between conjugated PPV wall and vitamin K_3. This result suggests the effective penetration of small quencher molecules within the channels in **2**.

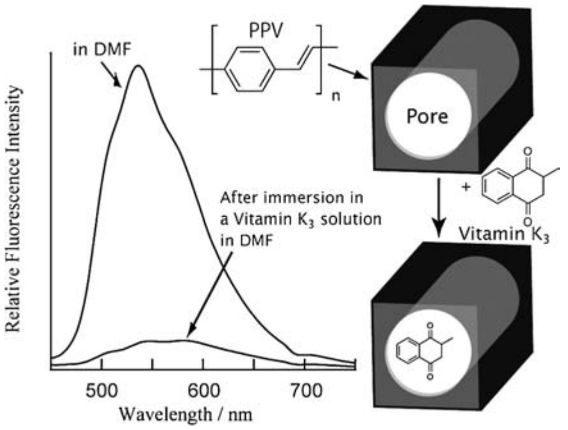

Figure 2. Fluorescence spectra of **2** in DMF and DMF solution containing quencher at room temperature. Excitation was at 375 nm.

In conclusion, the present paper demonstrates the creation of porous conjugated polymers by using amphiphilic PEO–PPO–PEO as a structure-directing agent. The TEM and BET analyses support the claim of the creation of porous PPVs having almost uniform pore size. The channels within porous conjugated polymers enhanced the efficiency of fluorescence quenching. Porous conjugated polymers will open a new possibility for the fabrication of size- or shape-selective chemosensors by tuning the mesostructures.[11]

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References and Notes

1 J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem., Int. Ed.* **1999**, *38*, 56; F. Schüth, W. Schmidt, *Adv. Mater.* **2002**, *14*, 629; F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem., Int. Ed.* **2006**, *45*, 3216.

2 D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548.

3 Y. Meng, D. Gu, F. Zhang, Y. Shi, H. Yang, Z. Li, C. Yu, B. Tu, D. Zhao, *Angew. Chem., Int. Ed.* **2005**, *44*, 7053; Y. Huang, H. Cai, T. Yu, F. Zhang, F. Zhang, Y. Meng, D. Gu, Y. Wan, X. Sun, B. Tu, D. Zhao, *Angew. Chem., Int. Ed.* **2007**, *46*, 1089; C. Liang, Z. Li, S. Dai, *Angew. Chem., Int. Ed.* **2008**, *47*, 3696.

4 P. M. Lipic, F. S. Bates, M. A. Hillmyer, *J. Am. Chem. Soc.* **1998**, *120*, 8963.

5 R. C. Smith, W. M. Fischer, D. L. Gin, *J. Am. Chem. Soc.* **1997**, *119*, 4092; J. Wu, A. F. Gross, S. H. Tolbert, *J. Phys. Chem. B* **1999**, *103*, 2374; T.-Q. Nguyen, J. Wu, V. Doan, B. J. Schwartz, S. H. Tolbert, *Science* **2000**, *288*, 652; G. C. Claudio, E. R. Bittner, *J. Phys. Chem. A* **2003**, *107*, 7092; S. Madhugiri, A. Dalton, J. Gutierrez, J. P. Ferraris, K. J. Balkus, Jr., *J. Am. Chem. Soc.* **2003**, *125*, 14531; W. C. Molenkamp, M. Watanabe, H. Miyata, S. H. Tolbert, *J. Am. Chem. Soc.* **2004**, *126*, 4476.

6 R. W. Lenz, C.-C. Han, M. Lux, *Polymer* **1989**, *30*, 1041.

7 During the treatment with methanol, the PPV precursor may be converted to the precursor with a methoxy-leaving group.

8 D. D. C. Bradley, R. H. Friend, H. Lindenberger, S. Roth, *Polymer* **1986**, *27*, 1709; B. Tian, G. Zerbi, K. Mullen, *J. Chem. Phys.* **1991**, *95*, 3198.

9 D. T. McQuade, A. E. Pullen, T. M. Swager, *Chem. Rev.* **2000**, *100*, 2537; M. Kimura, T. Horai, K. Hanabusa, H. Shirai, *Adv. Mater.* **1998**, *10*, 459; K. Tajima, L. Li, S. I. Stupp, *J. Am. Chem. Soc.* **2006**, *128*, 5488.

10 R.-H. Jin, T. Aida, S. Inoue, *J. Chem. Soc., Chem. Commun.* **1993**, 1260.

11 Q. Zhang, K. Ariga, A. Okabe, T. Aida, *J. Am. Chem. Soc.* **2004**, *126*, 988; K. Ariga, A. Vinu, Q. Ji, O. Ohmori, J. P. Hill, S. Acharya, J. Koike, S. Shiratori, *Angew. Chem., Int. Ed.* **2008**, *47*, 7254.

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