

Fabrication of mesoporous polymer using soft template method

Jyongsik Jang* and Joonwon Bae

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Mesoporous polymer materials were fabricated from micelle/polymer precursors prepared by the micelle template method in reverse microemulsion systems and the pore size could be tuned by varying the type and concentration of surfactant.

The diverse applicability of mesoporous polymer materials such as adsorption of large molecules, purification, energy storage, and batteries has motivated the development of various fabrication methods of tailored mesoporous polymers with a tunable pore size.¹ Most synthetic strategies of mesoporous polymers are related to the hard template technique such as silica or block copolymers, and it is unavoidable to use toxic chemicals such as hydrofluoric acid to generate well-ordered mesopores by removing the templates.² Therefore, there has been significant effort for the facile fabrication of mesoporous polymer materials. The concept of "micelle templating" with self assembled surfactants, provided a simple and reliable synthetic tool to tailor mesoporous materials such as MCM-41 and SBA-15.³ Although several researches on the fabrication of mesoporous carbon using micelle templating have been reported,⁴ the preparation of mesoporous polymer materials from micelle embedded polymer precursors is still a challenging task, because the self-assembled micelle structures in polymer networks were destroyed after polymerization due to phase separation between the surfactant and monomer in the organic medium.⁵ Herein, we report on the novel fabrication of micelle polymer (polyacrylonitrile, PAN) precursors in reverse micro-emulsion systems and mesoporous polymers derived from micelle/polymer precursors using self-assembled spherical micelles as porogens.

The typical synthetic procedure for the mesoporous polymer is illustrated in Fig. 1. Nonionic surfactants, PPO₁₉-PEO₃₃PPO₁₉ (Pluronic 25R4) or PPO₁₄-PEO₂₃-PPO₁₄ (Pluronic 17R4) were used to control the micelle size in the polymer matrix. Pluronic 25R4 and 17R4 are typical block copolymers which have different spacer lengths of poly(propylene oxide)-poly(ethylene oxide)-poly(propylene oxide) (PPO-PEO-PPO) sequence. These nonionic

surfactants are composed of a hydrophilic poly(ethylene oxide) terminated with two hydrophobic groups and form micelles in the organic phase.⁶ In addition, it was expected that more bulky PPO groups might provide improvement of stability of the resulting micelles during polymerization. Subsequently, acrylonitrile (AN) monomer was mixed with nonionic surfactant and dissolved in *N*-methyl-2-pyrrolidone (NMP) solvent in order to form well-dispersed micelles in mixed organic solution medium. NMP was used as a reaction medium for dissolving monomer and surfactant, as well as facilitating heat transfer during polymerization. In addition, azobisisobutyronitrile (AIBN, 0.01 g), as an initiator, was added to the AN/surfactant/NMP mixed solution. The final mixed solution was achromatous and transparent (Fig. 1(a)).

AN monomer was located at the exterior of the micelles and the pale yellow micelle/PAN precursor was synthesized by radical polymerization at 70 °C for 2 h (Fig. 1(b)).⁷ The fabrication of the micelle/PAN precursor was strongly dependent on the surfactant/AN weight ratio. It was revealed that homogeneous micelle/PAN precursor was fabricated within the range of 15–40 wt% of Pluronic 25R4 surfactant. Meanwhile, the polymer precursor can be prepared in the range of 20–45 wt% for Pluronic 17R4.⁷ Below these ranges, micelle/PAN was not fabricated due to the deficient number of surfactant molecules required to form the micelles. The AN/surfactant/NMP mixed solution was too viscous for the reverse microemulsion system to form a micelle/PAN precursor above these ranges. Subsequently, the surfactant embedded in the synthesized micelle/PAN precursor was removed by reflux with hot water at 110 °C for 24 h. FTIR spectroscopy showed a PAN C≡N stretching band at 2250 cm⁻¹ and C≡N asymmetric stretching peak at 1510 cm⁻¹. The bands of C–O–C bending from the surfactant were observed at 1440 and 1290 cm⁻¹. The peak at 1620 cm⁻¹ resulted from the C=C stretching mode in the acrylonitrile monomers and this band completely disappeared after radical polymerization. The FTIR analysis demonstrated the fabrication of micelle/PAN precursor as well as the successful polymerization of AN monomer.

Fig. 1(c) displays the transmission electron microscopy (TEM) image of the mesoporous PAN prepared with 3.0 mL of AN, 1.5 g

*jsjang@plaza.snu.ac.kr

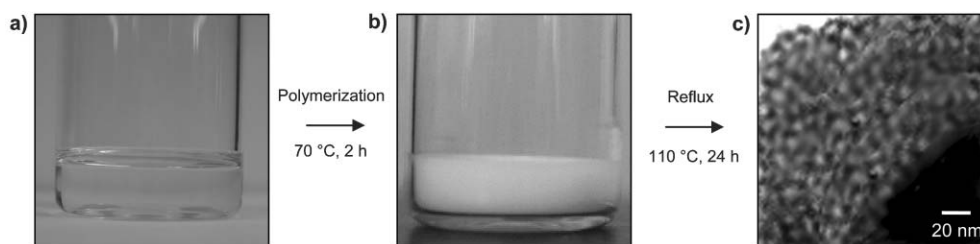


Fig. 1 (a) Photograph of homogeneous Pluronic 25R4 surfactant/AN monomer/NMP solution; (b) photograph of micelle/PAN precursor produced using 1.5 g of Pluronic 25R4, 3 mL of AN and 1 mL of NMP; (c) TEM image of microtomed mesoporous PAN.

of Pluronic 25R4 and 1 mL of NMP. For the TEM analysis, the mesoporous PAN was microtomed under liquid nitrogen and the sample thickness was *ca.* 80 nm. Although it was generally accepted that embedded micelles were deformed during the polymerization process, the image indicated that the self-assembled micelle structures in the PAN matrix were kept intact after radical polymerization and reflux (surfactant removal) process. The micelles from Pluronic 25R4 generated spherical micelles within the range of 15–40 wt%.⁸ It was also reported that the micelle diameter of Pluronic 25R4 was in the range of 7–10 nm.⁷ This value was consistent with the average pore size of mesoporous PAN. Elemental analysis showed that the surfactants in the polymer matrix were completely removed by reflux because the atomic ratio of C/N is in good agreement with the theoretical atomic ratio of PAN (*ca.* 3.3).⁹ To verify that these mesopores were generated from the micelles, a blank system containing AN monomer and initiator was examined without the surfactant; no mesopores were observed from bulk PAN.

The nitrogen adsorption/desorption behavior of the mesoporous PAN exhibited type IV behavior, illustrating the presence of mesopores (Fig. 2). The pore size distribution (PSD) curve was derived by the Barret–Joyner–Halenda (BJH) method and revealed uniform pores with the PSD centered at *ca.* 6.7 nm. The presence of micropores with average size of less than 2 nm was observed in the PSD curve. These windows reflected the paths of extracted surfactant molecules during reflux. The typical surface area of mesoporous PAN prepared with 3.0 mL of AN, 1.5 g of Pluronic 25R4, and 1 mL of NMP was *ca.* 502 m² g⁻¹. The nitrogen adsorption isotherm represented an increasing tendency between the relative pressure of 0.05–0.8, while there was a conspicuous increment from the relative pressure of 0.8. These results indicated the presence of mesopores within as-prepared PAN.

Average pore size and surface area of mesoporous PAN were also studied as a function of surfactant/monomer weight ratio and type of surfactant (Table 1). In the control of average pore diameter of mesoporous polymers, we selected two nonionic surfactants having different spacer lengths. To investigate the effect of surfactant composition, surfactant/monomer weight ratio and

Table 1 Average pore diameter and surface area of various mesoporous PANs

AN/g	NMP/ml	Pluronic surfactant (wt/g)	Average pore diameter/nm	Surface area/m ² g ⁻¹
3.0	1.0	25R4 (1.5)	6.7	502
		17R4 (1.50)	8.7	396
		17R4 (2.25)	10.6	337

solvent concentration were fixed under this experimental condition. Compared with mesoporous PAN prepared with 1.5 g of Pluronic 25R4 (6.7 nm), the average pore diameter of mesoporous PAN fabricated with 1.5 g of Pluronic 17R4 was 8.7 nm. In this case, the micelles generated from surfactant with shorter spacer length must have more free volume to reduce hydrophobic repulsion between relatively bulky adjacent PPO spacer groups, although the number of surfactant molecules required to form individual micelles increased as the molecular weight of surfactant increased.¹⁰ The pore diameter could be also tuned by varying the weight ratio of surfactant/monomer. As the surfactant/monomer weight ratio increased, the pore size of mesoporous PAN increased gradually. A pore diameter of *ca.* 10.6 nm was obtained with 2.25 g of Pluronic 17R4. It was clear that the surface area decreased as the average pore diameter of mesoporous PAN increased. Judging from these data, it can be concluded that surface area and average pore size of mesoporous polymer could be controlled by surfactant/monomer weight ratio and kind of surfactant.

In this communication, our novel methodology describes the first demonstration of the fabrication of mesoporous polymers from micelle/polymer precursors. The resulting mesoporous PANs have nearly monodisperse closed pores and the average pore diameter of the mesoporous PAN can be tuned by varying the type and concentration of surfactants. The micelle mediated polymerization technique illustrates the elegant and facile approach to synthesize mesoporous polymer materials, which may find useful applications in versatile areas including high surface area catalyst supports, double-layer capacitors, nanoreactors, adsorbents, optical devices, and supercapacitors. Furthermore, this concept of “micelle as a nanoporogen” could be expanded to the fabrication of mesoporous organic and inorganic materials.

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Jyongsik Jang* and Joonwon Bae

Hyperstructured Organic Materials Research Center, School of Chemical Engineering, Seoul National University, Shinlimdong 56-1, Seoul, Korea 151-742. E-mail: jsjang@plaza.snu.ac.kr; Fax: +82 2 888 7295; Tel: +82 2 880 7069

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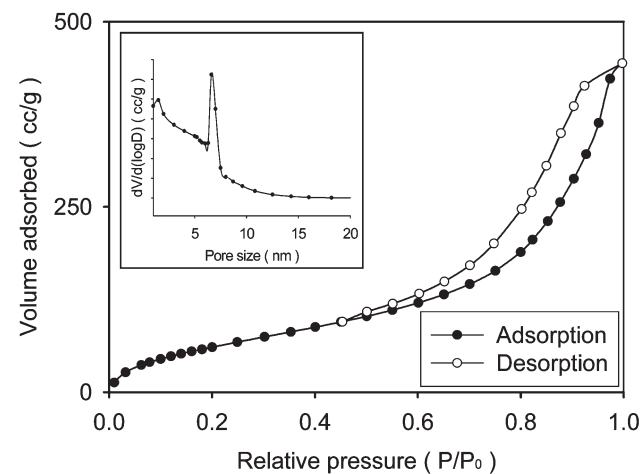


Fig. 2 Nitrogen adsorption/desorption isotherm and corresponding pore size distribution of mesoporous PAN prepared with 1.5 g of Pluronic 25R4, 3 mL of AN and 1 mL of NMP.

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